Opportunities for **Neutron Scattering** at the ILL in the **third millennium**
The two-day “Millennium Symposium and European Users Meeting” was organized as an integral part of the spring 2001 session of the Scientific Council. The objective of the Symposium was to indicate directions shaping the future of science at ILL. In particular, the ambitious Millennium Programme, launched on 1st January 2000 with the aim of renewing almost all of ILL’s instruments and infrastructure will receive input and backing not only from ILL staff, but from the whole of the Institute's user community.

The Symposium was held at the Alpexpo centre in Grenoble. More than 300 registered participants from 14 different countries delivered 170 scientific presentations. In addition, two panel sessions were held, one on Future Science at ILL and one on its organization. A closed meeting was also organized between the Institute’s Industrial Liaison Group and representatives from industry. ILL Management will carefully consider all information obtained during this meeting.

Accompanying these Proceedings you will find several other brochures: the “ILL Millennium Programme” containing proposals for the renewal programme assembled by C. Carlile, “Neutrons and Life”, a review of biological research at ILL, and the “Annual Report 2000”, both produced by C. Vettier and G. Cicognani, and, finally, the “ILL Roadmap”, a long-term strategy document and distillation of the many suggestions, observations, criticisms and ideas we have received from a wealth of sources.

I wish to thank all the many individuals who have contributed to the success of this Symposium. I would mention in particular the speakers, contributors and panel members for their lively presentations, the audience for their active participation, the members of the International Advisory Committee for their good advice, the Steering Committee for suggesting and the Scientific Council for accompanying this event. I also thank Grenoble City, the Departement of Isère and the Rhône-Alpes Region for their sponsorship, and, last but not least, my colleagues at ILL and the local committees, including in particular the Conference Secretary, Barbara Standke, who organized with great enthusiasm and professionalism, at very short notice, such a wonderful event.

Dirk Dubbers
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Plenary talks
The Development of Instrumentation at the ILL

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The ILL’s pre-eminent position, which it still enjoys today, was founded upon the implementation of high quality novel instrumentation ranging from the first full scale use of neutron guides to backscattering spectroscopy and small angle scattering. Equally well a constant element in the life of the ILL has been the development of new techniques for future improvement of instruments. Supermirrors, focussing monochromators and position sensitive detectors are highlights of this process. The reactor itself was totally renewed in 1994 and will operate for at least the next 20 years. In 1995 a programme of instrument renewal including the new reflectometer D17 and the liquids diffractometer D4 was started, which is now bearing fruit. In 1999 the opportunity arose to implement a more ambitious programme of instrument upgrades which would bring the performance of the Institut’s instruments back to the cutting edge of neutron technology, in many cases using techniques developed at the ILL, such as the use of polarised 3He. In January 2000 the Millennium Programme was formally launched with funding from within the Institut’s own budget for five instrument projects including a new image plate diffractometer VIVALDI. This programme was received with enthusiasm by the user community and by our funding authorities and, encouraged by this support, other projects have been included for 2001 and individual capital bids have been made, driven by groups of users. Furthermore the Institut’s infrastructure, such as the ageing neutron guides, was also the subject of re-examination. The aim behind the Millennium Programme is to set in place a continuous programme of instrument renewal. Analysis shows that the major cost of an instrument is its operation and therefore maintaining every instrument at the highest standard is extremely cost effective. In parallel a broader strategic study of opportunities available to the Institut has been published in the ILL’s Road Map which gives directions for the future evolution of the Millennium Programme.

1. Introduction

The ILL has always had a strong tradition of both instrument development and of neutron technique development. Indeed the imaginative application of innovative technology in the 1970s, notably neutron guides, was the determining reason why the centre of gravity of neutron scattering shifted to Europe from the United States, where it has remained ever since. The Brookhaven reactor, built a few years earlier, was conservatively instrumented and remained an inward-looking facility, in direct contrast to the ILL, and it is fair to say that it has not had the overall scientific impact of the ILL. Amongst these innovations one can point to: small angle scattering; microelectronvolt spectroscopy; the production and use of ultra cold neutrons; tanzboden triple-axis spectrometers; the use of extended detector arrays and 1-D and 2-D position sensitive detectors; variable temperature cryostats and dilution fridges; the implementation of focusing monochromators and analysers; neutron spin-echo; polarising devices including supermirrors and helium-3; and the ability to handle a wide range of samples from bacteria and viruses to transuranic compounds. One should not forget either the pioneering work in neutron physics – the half-life of the neutron, the search for the electric dipole moment of the neutron, neutron interferometry and fission spectroscopy – which has brought great distinction to the Institut, nor the Theory Group which has, at one time or another, welcomed virtually all the top-class condensed matter theoreticians in the world.
The Institut is centred around a high flux research reactor operating at 58MW. Its single-element highly compact core makes it the most intense neutron source in existence. The reactor, furnished with two cold sources and one hot source, supplies neutrons to ~40 instruments, 25 of which are fully scheduled for the user programme, 8 CRG instruments partially scheduled for users and a number of special instruments and test beams. These instruments are available to scientists from the ILL’s nine partner countries for their research. The reactor operates for 225 days each year providing over 6000 instrument-days for science. The ILL welcomes ~1200 individual researchers each year, who carry out 750 experiments and publish over 500 papers. In a survey of papers published in the top journals (Phys. Rev. Letters, Phys. Rev. & Nature) the ILL’s output in neutron scattering accounts for almost 40% of world output.

The Institut was set up as a purpose-built user facility – the first of its kind – and provides today a complete infrastructural backup (scientific local contacts, sample environment facilities, sample preparation laboratories, data manipulation and visualisation, a 160-bedroom guesthouse, restaurant and library etc.) for users to derive the most from their hard-won beam-time. On a site shared by the European Synchrotron Radiation Facility and the European Molecular Biology Laboratory, the three International Institutes constitute an unparalleled world centre for condensed matter studies. With the rebuild and upgrade to the reactor completed in 1994, the ILL put all its energies into re-launching the user programme. At the same time a limited programme of instrument renewal was set in place which is now bearing fruit. During 2000 we welcomed the integration into the user programme of:

- the new IN4 chopper spectrometer with 7x increase in intensity and its low angle detector, a collaboration with INFM Italy.
- the IN15 time-of-flight spin-echo spectrometer, a collaboration with FZ Juelich. (B. Farago, p. 81).
- the Mark-II version of the D20 diffractometer with its upgraded microstrip detector continuously covering 160° of scattering angle. (P. Convert, p. 276). The new instrument is shown in Figure 3.

In addition, for 2001, we shall bring back into service the IN5 spectrometer with its new primary spectrometer, offering an 8x increase in intensity for the same resolution. The new incident beam layout and one of the aluminium disc choppers is shown in Figure 4. The totally rebuilt IN8 triple-axis spectrometer, a collaboration with CSIC Spain, is well underway. Its three-sided monochromator is shown in Figure 5. (M. Jimenez-Ruiz, p. 300).

The D17 reflectometer, able to be operated as a time of flight machine or a monochromatic beam instrument with polarised and non-polarised beam options. (R. Cubitt, p. 279). A time of flight pattern from a ruled diffraction grating is shown in Figure 1.

- the rebuilt D4 liquids diffractometer with 5x increase in luminosity and 5x improvement in detector stability. (B. Guérard, p. 271). The instrument layout and the improvement in detector stability is shown in Figure 2.

- the new IN4 chopper spectrometer with 7x increase in intensity and its low angle detector, a collaboration with INFM Italy.
- the IN15 time-of-flight spin-echo spectrometer, a collaboration with FZ Juelich. (B. Farago, p. 81).
- the Mark-II version of the D20 diffractometer with its upgraded microstrip detector continuously covering 160° of scattering angle. (P. Convert, p. 276). The new instrument is shown in Figure 3.
Towards the end of the last decade however, it became clear that the rebuild of the reactor, a very positive event in itself, had delayed the maintenance of ILL’s instruments and infrastructure at the cutting edge of neutron technology, much of which, like super-mirrors and polarised helium-3, had been developed at ILL but never fully implemented on its own instruments.

Accordingly the ILL formally launched its Millennium Programme on 1st January 2000 after wide consultation with the User Community. The Millennium Programme is intended to be a continuous and accelerated programme of investment in instrumentation and infrastructure so as to improve the overall output of the instrument suite by between a factor of 10 to 20 on average. At the end of 1999 the Associates of the ILL gave the go-ahead for the start of five instrument projects from within economies in the ILL’s own budget with the intention to add two further projects each year thereafter. All five projects are now well advanced:

- The rebuild of the single crystal diffractometer D3 as a spherical polarimeter is moving ahead quickly. It is conceptually and technologically complex and will come on line gradually over a three year period of development and commissioning. Decpol, a spin sensitive detector for the new instrument, comprising polarised He³ plus a He⁰ detector within its magnetic shield, has already been commissioned on the instrument, and a new version of Cryopad, see Figure 6, which controls the spin of the neutron as it interacts with the sample, is under manufacture. (E. Bourgeat-Lami, p. 198).

Fig. 4: For spectroscopy in the 10 to 20 microelectron volt resolution range, IN5 has been the instrument of choice for 25 years. A rebuild of the primary spectrometer – the guide and the chopper system – will bring an increase in data rate of a factor 8.

Fig. 5: The monochromator for IN8 is a three-faced doubly focussing monochromator built in Spain, and furnished with monochromators – copper, germanium and graphite - from the ILL’s Optics Group.
An order of magnitude increase in polarised neutron flux to $8.8 \times 10^7$ n cm$^{-2}$s$^{-1}$ on the sample at a neutron energy of 50 meV has been obtained by the remodelling of the IN20 primary spectrometer. A larger diameter beam tube using a source diameter of 170 mm together with apertures which constitute a virtual source was installed in January 2001 and a new large area (230 mm x 140 mm) doubly focussing Heusler monochromator, grown in-house, was put in place in April 2001. The analyser and the new instrument in its spin-echo option is shown in Figure 7. A rebuild of the analysers will follow thereafter, making IN20 the finest polarisation analysis triple axis in existence. Present indications are that what was achieved in a complete cycle in 1998 could be done in a single day. The opportunities are manifold. (J. Kulda, p. 206).

- **2MHz detector for SANS.** We have commissioned five prototype linear position sensitive gas detectors, of only 7 mm active diameter and 1 m active length. The aim of achieving a position resolution of 7 mm along the length of the detector by an appropriate balance of absorber and quench gases and anode voltage has been exceeded in recent tests – 3 mm can be achieved. An array of 140 such detectors are to be ordered which will deliver the appropriate pixel resolution (7 mm x 7 mm) for the D22 and, shortly thereafter we hope, the D11 small-angle scattering instruments at an overall count rate exceeding the original 2 MHz specifications. Commissioning tests indicate that a rate of 5 MHz can be achieved. Currently these instruments are limited to around 50 kHz and must use beam attenuators, a serious misuse of the potent cold neutron flux, in order to avoid data corruption, even with the detectors at large distances from the sample. A one-hundred-fold increase in data rate will now allow complex & demanding experiments, previously only dreamed of, to be tackled. (P. van Esch, p. 313).

- **The Strain Imager** is a joint project with the University of Manchester. Beam line design is now complete, integrating D1A, D1B, the Strain Imager and VIVALDI along the same upgraded neutron guide. The foundations for the instrument have already been prepared in order to support the 1 tonne capacity, 10 µm precision hexapod orientation device which will sit on the granite sample table. A CAD drawing laid onto the construction site is shown in Figure 8. This purpose-built engineering instrument will be a welcome addition to the ILL’s instrument suite, adding further breadth to the programme. (T. Pirling, p. 254).

- **VIVALDI, the Very Intense, Vertical Axis, Laue Diffractometer** with its 50 µm resolution image plate detector has completed its manufacturing phase. Delivery of the complete instrument took place at the end of May 2001 and it will be installed...
on its guide position in June. It is shown in Figure 9. Experience on the LADI diffractometer allowed important improvements in efficiency to be made, for example neutron illumination and laser read-out from the same side of the image-plate. Tests with a prototype version gave remarkably good quality data with low background. Weak superlattice reflections in magnetic materials were clearly seen. E F Schumacher’s catch phrase *Small is Beautiful* appears to apply here. Certainly speed of manufacture, relative cheapness and small sample size, are all qualities in favour of such instruments. (G. McIntyre, p. 298).

In response to the launch of the Millennium Programme there followed a number of other significant events:

- the increase in the UK contribution to the ILL, rising progressively from 25% in 2000 to 30% in 2003,
- a recognition by the ILL Associates that the infrastructure of the Institut has to be systematically renewed,
- the setting of the Millennium Programme into a more wide-ranging strategy – the ILL Road Map.
- a willingness to accept that user-driven bids for funds to upgrade instruments be incorporated into the ILL’s culture.

In 2001, the second year of the Millennium Programme, four further instrument projects have been started, along with a number of infrastructural improvements:

- **Super D2b**, the high resolution powder diffractometer will be totally rebuilt with a cold focussing monochromator and a continuous position-sensitive detector and associated collimators. A sum of 0.5MFF has been given by the French Ministry of Research and a team of users, led by Dr Paul Attfield, Cambridge, has submitted a capital grant proposal to EPSRC for 50% funding of this instrument. (E. Suard, p. 175).
- **The D19 fibre and large unit cell single crystal diffractometer** has pioneered structural biology work with neutrons but has suffered from a limited luminosity. This will now be rectified by the refurbishment of the secondary spectrometer and the addition of a large area detector increasing data rate by nearly 20 times. A prototype detector, a microstrip device, is shown in Figure 10. The complementarity between synchrotron radiation will be enhanced by this initiative which is the subject of a capital grant proposal to EPSRC by a user group led by Professor Judith Howard from Durham. (S.A. Mason, p. 332).
- **The Microball neutron dripline detector**. There are three big questions in science, one of which is “What is the origin of the Universe?” The experimentally observed distribution of the isotopes, shown in Figure 11, is currently inexplicable. Whilst knowing that elements heavier than 56 amu can only have been generated in supernova explosions, the pathways to these elements are only dimly glimpsed. Particularly important is information on the so-called waiting-point nuclei at the extreme edge of the neutron dripline, which are relatively long-lived and beyond the time scales of other methods. The installation of gamma coincidence detectors – Microball – on the Lohengrin beamline promises a hundred fold increase in sensitivity at one hundredth the cost of other methods proposed, for isotopes in the decay spectrum from fission ringed in the figure. (G.S. Simpson, p. 244).
- **The D7 polarisation analysis diffuse scattering instrument** was a tour de force when it was built, but in spite of this only demonstration experiments showing the opportunities made possible with such measurements were feasible. A total upgrade of the instrument with a heavy investment in supermirror polariser technology will transform...
the applicability of the instrument thanks to an increase in data rate exceeding a factor of 20. (J.R. Stewart, p. 158).

- The 40 metre long collimation mechanism for the D11 small angle instrument is now 30 years old. It is currently being replaced, together with its equally ancient neutron guide, thereby delivering better reliability and higher intensity. A spare neutron velocity selector will be bought which allows the beam-line design to be simplified. (P. Lindner, p. 293).

- The neutron guide for D1A, D1B, the Strain Imager and Vivaldi is to be renewed. Monte Carlo simulations show that gains averaging a factor of four can be achieved by the application of supermirror technology and much improved surface quality and construction techniques than were available three decades ago.

Two other support laboratories are to be built:

- A bacteriological deuteration laboratory, jointly with EMBL, which is the subject of grant applications to the UK from Professor Watson Fuller, Keele and to the EU by Dr Dean Myles (EMBL) & Dr Trevor Forsyth (ILL). The latter has recently succeeded in obtaining 1M€ funding from the EU. This laboratory will form part of a larger initiative – a Centre for Structural Biology – launched by ESRF, ILL & EMBL. (V.T. Forsyth, p. 47).

- A facility for materials engineering, FaME, jointly with ESRF, headed by Professor Peter Webster, Salford which will key in well with the new Strain Imager and the engineering instruments at the ESRF, which are to be upgraded. (P.J. Webster, p. 256).

In coming years the Millennium Programme will continue as a vehicle to upgrade instruments and to build new ones – the IN16 backscattering instrument, (M.A. González, p. 284), the Brillouin scattering instrument BRISP, the LADI diffractometer on a significantly enhanced cold beam, the complete Microball neutron dripline detector, a horizontal surface reflectometer, a rebuild of the original IN11 spin-echo spectrometer, (G. Ehlers, p. 321), the PASTIS thermal TOF polarisation analysis instrument amongst other projects. We encourage collaborative ventures with our user community and our funding bodies in order to push forward into existence the many ideas which are now coming forward.

2. Outlook

A sustained effort has been devoted over the last eighteen months into establishing a solid foundation for the regeneration of the Institute’s instruments and infrastructure through the launching of the ILL’s Millennium Programme. Perhaps it is more than symbolic that ILL is an integral part of the word millennium. Such an ambitious programme requires a concurrence of three essential ingredients – motivated and well-qualified manpower, adequate sources of finance, and inspired ideas. It also requires good luck and a willingness to take risks. As the second year of the Millennium Pro-
gramme draws to a close, there are strong signs that all these elements are in place. Building upon the newly rebuilt reactor, the momentum generated by instrument projects already in place, the increasingly youthful staff and the guidance of our users, our funding bodies have all the evidence which they can possibly need to respond positively and unequivocally to our appeal for the investment necessary to fulfil the vision which is illustrated in the ILL's long-term strategy document – the Road Map.

Therefore, as we look ahead to the next 20 years and beyond, we envisage a bright future for researchers using the ILL in a renewed partnership with the Institut to fully realise the value of the 1.5 BEuro capital invested and to optimise the scientific output to all partners. Whilst the present output is unquestionably second to none, quantity, quality and reliability can be even further enhanced in a cost-effective manner by a relatively modest investment in instrumentation.

Acknowledgements
We wish to thank heartily all those ILL staff who have contributed so energetically to the launch of the Millennium Programme, and to the encouragement we have received from our users and representatives of our partner countries.

References
All references in the text refer to the present proceedings. A full set of proposals for the Millennium Programme is described in: “The ILL Milenium Programme” (April 2001), ILL Report 01CA01T, available on the web at:
http://www.ill.fr/pages/menu_g/docs/millennium_programme.pdf
The Road Map is available at:
http://www.ill.fr/pages/menu_g/docs/newroadmap.pdf
Neutrons in biology at the beginning of the millennium

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The state of the art and perspectives of biological applications of neutron scattering are reviewed. It is shown that because of the neutron’s particular properties, it is possible to obtain information on biomolecular structures, dynamics and interactions that is not accessible to other methodologies. Neutron scattering experiments are essential and their use is imperative if we hope to achieve a reasonable understanding of biology at the molecular level.

1. Early days: development of the methodology

The original methods of neutron scattering in biology were developed in the 1970’s and 1980’s, essentially at the Brookhaven National Laboratory (BNL) High Flux Beam Reactor, in the USA, and at the Institut Laue Langevin (ILL) High Flux Reactor, in Grenoble. This is not a coincidence. Because of relatively weak signal to noise ratios, intense beams from high flux reactors are in practice imperative for such experiments. This is easily illustrated by the example of protein contrast variation in small angle neutron scattering (SANS) from solution. A full data set requires data from heavy water (D₂O) solutions. The fundamental studies of enzymes involved in protein synthesis and of their interactions with transfer RNA remain a prime example of how neutron scattering can provide structural parameters for an interacting polydisperse system in solution [1, 2]. Currently, in a scientific context where structural results on a biological system must be obtained relatively quickly, and in which access to any neutron scattering facility is severely limited, such experiments can only be performed at a high flux reactor.

This is not to say that work at medium flux reactors such as Dido or Pluto in Harwell, the reactor at the Bhabha Atomic Research Centre near Bombay (BARC), Orphée at the Laboratoire Léon Brillouin (LLB) in Saclay, the Berlin reactor at the Hahn Meitner Institute (HMI), or the JAERI reactor in Japan has not been or does not continue to be useful. The first crystallographic experiments on molecules of biological interest were performed in Harwell and at BARC. An important landmark experiment on nucleosome structure was performed in Harwell, over a relatively long time on a diffractometer dedicated to biological studies [3]. Even though SANS results from the LLB appear to have been limited to high signal to noise D₂O solutions by the medium flux incident intensity, important work on the conformation of denatured protein has been published following experiments performed in deuterated solvent only [4]. A dedicated diffractometer at JAERI is providing high quality crystallography data on protein crystals [5]. The full range of neutrons in biology methods, however, can at present be exploited only at the ILL high flux reactor with the appropriate instrumentation.

Biological applications of neutron scattering are based on the fact that important questions in structural molecular biology can be addressed because of the special properties of the interaction between thermal or cold neutrons and matter. The most important of these properties are the weak absorption for most elements, the large isotope effect for hydrogen and deuterium, and the energy-wavelength relation that is unique for studies of molecular dynamics. The questions deal with various levels of spatial and temporal resolution – from the location of H atoms in enzymatic mechanisms at Å resolution to the structural relationships between nucleic acid and protein in chromatin or between specific lipids and proteins in natural membranes at lower resolution – from the picosecond vibrational modes of proteins to slower nanosecond conformational fluctuations.

Even in the pre-synchrotron days of the 1970’s, it was clear that X-ray beams of similar wavelength to thermal neutrons would remain the radiation of choice for structural work in molecular biology, because of their much higher intensity. Neutron experiments, then as now, could never be competitive for a standard structural study. They constitute the exception, the way to address a well-put question for a selected system that cannot be addressed in any other way. This author believes that time has shown that neutron scattering experiments are essential and that their use is imperative if we hope to achieve a reasonable understanding of biological interactions at the molecular level.

In the early days of neutron scattering in biology, quasielastic neutron scattering had already characterised motions in liquid water [6] and neutron crystallography had already established itself in chemistry to solve for hydrogen and other light atom positions. Amino acid structures were being solved at BNL and at the BARC [7, 8]. Data collection on vitamin B12 crystals and membranes of biological interest started in Harwell [9, 10]. At BNL, diffractometers dedicated to biological systems were planned [11], and data collection started on myoglobin crystals [12] and model membranes [13]. The ILL SANS camera, D11, which had by far the highest incident neutron flux then available promised exciting biological applications. On the methodological front, contrast variation by using H₂O:D₂O solvent exchange was put on a firm quantitative basis [14], paving the way for important studies such as on the nucleosome, showing that DNA is wrapped
around the histone core [3], or on spherical viruses, describing the internal distribution of nucleic acid and protein components [15], or on retinal rod outer segment membranes showing the distribution of rhodopsin in the lipid bilayer [16], or on the kinetic interactions between transfer RNA and enzymes involved in translation [1, 2]. More general “contrast variation” approaches combining X-ray, neutron and light scattering were also developed [17]. The method of “triangulation” of complex structures by using specific labelling of components was invented [18, 19]; the biggest triumph of this method was to achieve the description of all protein positions in the small ribosomal subunit of Escherichia coli [20, 21] more than a decade before the crystal structure was solved by X-ray diffraction. New “contrast variation” techniques based on specific deuterium labelling and neutron scattering continued to be developed, such as the triple isomorphous substitution method [22].

2. Why low resolution neutron studies have (almost) never been proven wrong

It is notorious that conclusions from medium resolution structural studies by X-ray crystallography have often been proven wrong when higher resolution data became available. The ultimate test of an X-ray structure is provided by its chemistry. This is straightforward with sufficiently high resolution data and when the electron density shows continuity with known features or is otherwise recognisable, as for the configuration of a large amino-acid side chain, for example. When groups are disordered, however, or “free standing” as in the case of water molecules or ions, electron density assignment is problematic. Assignment of structural features in a complex structure is even more difficult at very low resolution, because the average electron density values for protein and nucleic acid, for example, are quite close, as are those for detergent and water in membrane protein complexes, so that they cannot be distinguished. Contrast variation by $H_2O:D_2O$ exchange and/or specific deuterium labelling in neutron scattering experiments enhance structural features enormously, especially at low resolution. The neutron scattering length density difference between protein and solvent (the contrast) varies from zero (in 40% $D_2O$ solvent) to more than $3.10^9$ cm$^{-3}$ in 100% $D_2O$. In 40% $D_2O$, nucleic acid contrast is larger than $1.10^9$ cm$^{-3}$ making it perfectly “visible”. Protein contrast is larger than $1.10^9$ cm$^{-3}$ in 70% $D_2O$ where nucleic acid contrast is zero. Furthermore, specific deuterium labelling can now be measured by mass spectrometry to verify whether or not the structural feature identified in the structural study corresponds to the correct labelling intensity, as was done in the study locating glycolipids in purple membranes [23].

Access to neutron scattering facilities being as difficult as it is, the question arises: why bother with a low resolution neutron study at all? Why not put the effort into obtaining good X-ray quality crystals of the system diffractioning to very high resolution, where the information can be checked by the chemistry? Glossing over the difficulties of crystallisation, the answer is simply that low resolution neutron experiments are imperative because functionally important groups in biologically molecules are often not ordered to high resolution—water molecules in enzymes, glycolipids in membranes, or the nucleic acid component in viruses, being striking examples of this—and will remain “invisible” in highly ordered crystal structures even if these were obtained.

3. Experiments before the 1990s: four broad methodological fields

Neutrons in biology studies fall into four broad methodological fields, each requiring specific sets of instrumentation and sample preparation methods: single molecule crystallography to a resolution of a few Å, lower resolution crystallography and diffraction from partially ordered systems and fibres, SANS, and neutron spectroscopy at various values of energy resolution (time of flight spectroscopy, back-scattering spectroscopy, spin-echo spectroscopy). The four fields also require different conceptual approaches. For example, crystallography results are best tackled in a chemical context, whereas spectrometry provides information on dynamics best tackled in the context of condensed matter physics.

Neutron single crystal crystallography localised functionally important H atoms and water molecules and provided indirect dynamics information from H-D exchange between proteins and solvent [24-26].

In the partially ordered structures field, neutron diffraction provided unique information on the conformation of lipid molecules and their interactions in lipid bilayers [10, 27, 28], on membrane protein-lipid-water structures and membrane protein structure in a natural membrane [29, 30]. Neutron fibre diffraction was developed and applied to study hydration networks in DNA [31]. Low resolution neutron crystallography using $H_2O:D_2O$ contrast variation was developed to show the distribution of detergent in membrane protein crystals [32], and of nucleic acid and protein in nucleosome core particles, for example [33].

In SANS, contrast variation applications to protein-nucleic acid complexes provided essential structural information on the organisation of complexes such as ribosomes, chromatin, viruses [15] and on kinetic interactions between transfer RNA, enzymes [1, 2] and elongation factors involved in translation [34], as well as large molecular machines like DNA polymerase [35]. Triangulation experiments, placing all the proteins in the small ribosomal subunit, represented a major feat, both in its biochemical and scattering analysis aspects [20, 21]. Interestingly, $H_2O:D_2O$ exchange also allowed to enhance the contrast between the hydration shell of biological macromolecules and bulk solvent, opening up new perspectives in the study of molecular interactions [36, 37]. Salt binding to the hydration shell and its role in protein stabilisation were characterised in enzymes from extreme halophiles (organisms that live in hypersaline conditions like the Dead Sea) [38]. In the dynamics field, the capability of the neutron methodology to measure macromolecular and water dynamics of biological significance was demonstrated [39, 40]. The dynamical transition
at about 200K was characterised in myoglobin hydrated powders [41] and later in purple membranes [42], setting the stage for a quantitative exploration of the dynamics-function relation in molecular biology.

Figure 1, which is based on a slide from the early 1990s, depicts the wide range of biomolecular interactions for which neutron scattering made important contributions at the time, as shown by the number of publications in very high and high impact journals, such as Nature, Science, Proc. Natl. Acad. Sci. (USA), J. Mol. Biol., Biochemistry, Biophys. J.

4. The structural biology explosion and the neutron hiatus in the 1990s

The 1990’s saw an explosion in structural biology associated with the opportunities for macromolecular crystallography opened up by synchrotron radiation. Structural biology underwent a profound transformation. Gone were the days when structural studies were limited to a few well chosen problems and took years. The gap between neutron and X-ray studies widened. Neutrons remained tools for careful slow experiments in crystallography or requiring large amounts of highly characterised biochemical material for SANS or spectroscopy. X-ray crystallography, however, was providing wonderfully detailed structures even of large complexes, when sufficient effort had been invested in crystallisation. The qualitative gap became a quantitative one. Thousands of structures were solved by X-rays. The biomedical potential of these structures stimulated large investment in the field. Young scientists were attracted to its challenges. Neutrons were neglected. The source troubles at BNL and ILL, in that period, threatened to completely destroy neutron applications in biology. But it was not so. A few groups in various places in the world, convinced that even a huge number of crystal structures in data banks would not answer all the important questions in structural biology, continued to develop neutron methods and to provide results.

5. Complementarity and cross-fertilisation: no one method in structural biology provides all the information required on a system

The strong complementarity between the X-ray and neutron results became apparent. Early neutron SANS experiments that had been done because crystals were not available, turned out to provide even richer information on interactions or solvent effects when crystal structures were already known. It appeared that many of these early experiments were performed “before the time was ripe”. An example of this is provided by the work on aminoacyl tRNA synthetases [1, 2], which would have been even more striking if the modelling of the SANS results on interactions were done on the basis of the crystal structures that became available in the following decades. In fact, the large number of high resolution structures resulting from Synchrotron Radiation crystallography now emphasises even more that such knowledge is a starting point in understanding a biological system and not an end in itself. The special advantages of neutrons combined with the progress in biochemistry and molecular biology are powerful reasons to stimulate a rebirth of neutron scattering experiments in biology in this context.

When the structures of the components of a system are known, the questions are: how do they interact with each other? what is the role of the environment, through hydration and ion binding? what is the dynamics underlying the structures? how do they move? All questions that can be addressed by neutron scattering. In the dynamics field in particular, neutrons are unique in being able to provide simultaneously the amplitudes and frequencies of molecular thermal motions—motions that have already been shown to be involved in biological function and activity.

The crystal structure of a biological macromolecule or complex is a beautifully detailed time averaged picture. Neutrons provide unique information that contributes to making such a structure “come alive”, by defining H-atom positions, interactions and dynamics.

6. Neutrons in biology at the beginning of the millenium

The four fields discussed remain a good basis for the discussion of the current perspectives of Neutrons in Biology.

6.1 Single crystal studies

Hydrogen and water are involved in all the molecular processes of biology. Information on these aspects, however, is severely
lacking. Research in this area has concentrated on a few studies of hydration and hydrogen location in enzyme mechanisms. Since many enzyme reactions involve hydrogen there is great potential for wide application. The role of water in molecular recognition is essential and poorly understood, and its definition by X-ray crystallography is very sensitive to disorder. Neutrons have big advantages in this area. Examples of recent work at ILL [43] and on a dedicated diffractometer for protein crystallography in Japan have shown the high quality of the results that can be expected [5]. The incorporation of bound water knowledge can radically alter the modeling of proteins, for drug design applications, for example. Neutron capabilities in protein crystallography could have a major impact, if significant improvements were made in instrumentation and sample preparation to increase the data collection rate and range of proteins that can be studied. The broad wavelength band LADI diffractometer at ILL has already demonstrated the vast improvements that can be expected from instrumental developments [43-45]; now every effort should be made to obtain maximum gains from the high flux reactor, for example, by moving the instrument to a high intensity beam position. A LADI type instrument also stands to gain greatly from a time-structured beam, such as will be available at the future European Spallation Source (ESS). The pro-active approach to improving sample preparation aspects by setting up a deuterium facility on the ILL site is an extremely positive development that should be complemented by consequent efforts in crystal growth.

6.2 Membranes and fibres

Neutron diffraction studies of purple membranes of *Halobacterium salinarum*, started a quarter of a century ago with work to describe hydration [29], have evolved with other knowledge on the system and continue to provide unique information on this natural light-sensitive membrane; e.g. to describe important glycolipid-protein interactions by specific in vivo deuterium labelling [23] or by the study of mutants and intermediate functional states [46]. The D16 diffractometer at ILL and V1 diffractometer at HMI are especially adapted to these studies. The sample, however, is a special case in that it occurs naturally as highly ordered two-dimensional arrays, in large amounts suitable for diffraction work. The information that can be obtained from neutron diffraction on such samples justifies a major effort to build on work already being done in electron microscopy to develop methods for two dimensional crystallisation of membrane proteins.

Beyond work on particular membrane proteins, membrane biophysics on the molecular scale has been developed in model systems for the understanding of phenomena such as transport, molecular recognition on surfaces and cell adhesion. New preparation techniques now allow native membranes to be deposited onto solid substrates while maintaining their functional integrity. The relatively new technique of neutron reflectometry promises exciting results for studies on (single!) membrane samples, with an important recent development constituted by the possibility to study an essentially free floating lipid bilayer [47].

Fibre diffraction work to study H-atom and water positions has profited from important upgrades in instrumentation. It is continuing on DNA [48], and has been extended to other systems such as cellulose [49].

6.3 SANS

SANS continues to provide unique possibilities to study the structure, hydration and interactions of biological macromolecules in solution, primarily because of contrast variation by H2O:D2O exchange and deuterium labelling [e.g. 50-54]. It is interesting to note that with the advent of the D22 camera at ILL, these studies can be considered as no longer being flux-limited. Results provided by neutron scattering have been used in conjunction with data from other techniques, such as small angle X-ray scattering, and crystallography [50, 51, 53, 54], analytical ultra-centrifugation [49] or electron microscopy [53, 54]—the unique information provided by the neutron experiments often resolving conflicting situations. After years of controversy, for example, the local density in the hydration layer of proteins has been characterised experimentally to be higher than that of bulk water [50]. In particular, it is to be expected that SANS, because of the power of H-D labelling and the possibility to study different conformational states by adjusting solution conditions, will play an important role in the understanding of cellular molecular machines such as chaperons or proteasomes [53, 54].

6.4 Dynamics

From the Greek *Δυναμις* (Strength) dynamics pertains to forces. Macromolecular structures are created and maintained by forces. Atoms are held in specific positions by a balance of known forces (H-bonds, van der Waals, “hydrophobic”, electrostatic ...). Thermal motions are constituted by atoms moving about these positions or between positions. Motions are described by two parameters: amplitude and frequency in a space-time window spanning the 1 Å-10 Å, picosecond to nanosecond range. This space-time window exactly matches the wavelength frequency relation in thermal and cold neutron beams. Following on the groundwork laid in the late 1980’s [41, 42] neutron experiments on purple membranes [e.g. 55, reviewed in 56] and on soluble proteins [e.g. 57-62] have established that macromolecular thermal motions are themselves involved in protein activity and stability. Despite its acknowledged importance for biological function and activity, the dynamics dimension in molecular structural biology remains difficult to characterise and poorly understood. It is now evident, for example, that structural information alone is not sufficient to account for specific drug binding effects in that the dynamics dimension should be involved in drug design efforts. We recall that chemical dynamics provides a much more stringent test of a model than structure. Practically no information is available at present on the dynamics of complexes or organised systems. In an original approach bridging molecular and cell biology, neutron experiments have provided data on the dynamics of proteins, in vivo, within their cellular environment.
[Zaccai, private communication]. Neutron scattering in fact provides unique opportunities to probe the natural cellular environment, which because of its molecular crowding properties, is very different from the usual conditions of laboratory biochemistry. Such exploratory studies became possible because of the IN13 French-Italian Collaborating Research Group instrument at ILL, which is dedicated to studies of biological molecular dynamics. The field of neutron applications to study biological molecular dynamics is wide open, with hydrogen-deuterium labelling allowing to focus on the dynamics of amino acid groups within a protein as was done in purple membranes [63], or on protein domains within large complex structures or molecular machines. Simulations and molecular dynamics approaches in the same space-time window providing a strong basis for interpretation of experimental results [64]. In an attempt to describe the neutron scattering dynamics results by parameters that are more familiar to molecular biologists, an interpretation in terms of effective force constants defining protein resilience was introduced in a recent review [65], and developed in an analytical biophysical model [66].
Introducing the complexity of structural biology

Structural biology aims to enhance understanding of the functioning of biological systems by relating them to the atomic and molecular structure, dynamics and interactions of the participating biological macromolecules. Given the evident complexity of biological systems this is an ambitious and challenging task. The example of DNA, the cell's genetic material, shows the scope of the challenge (Fig. 1). One of the most significant scientific discoveries of the last century was to show how hydrogen bonds between complimentary pairs of nucleotides in the DNA double helix could explain the chemical basis of heredity. This is structural biology at its most fundamental chemical level. But in the living cell genomic DNA is found in a hierarchical series of higher order structures which permit meter lengths of DNA to be packaged, first in nucleosomes and then in fibres in micron sized chromosomes. This is only possible through the interactions of DNA with proteins (histones), which not only package DNA into higher order structures but also can replicate it (DNA polymerase), transcribe messenger RNA from it to make proteins (RNA polymerase), cut it at precisely defined places (restriction enzymes), supercoil it (topoisomerases), repair it from UV damage (repair enzymes), unwind the two strands (helicases), recognise specific sequences of DNA (transcription factors) etc. All these aspects of the biology of DNA are within the scope of structural biology and range from the chemical level of hydrogen bonds and van-der Waals packing complementarity in macromolecular recognition to the macroscopic ultrastructural level of chromatin structure. Correspondingly a spectrum of structural methods, from X-ray or neutron diffraction via electron microscopy to light microscopy are required to tackle such problems as DNA packaging. Not to speak of the fact that DNA structure at all levels is dynamic and a variety of molecular machines and motors actively manipulate DNA structure for instance during the cell cycle, when the whole DNA is replicated and then physically separated into two sets of chromosomes destined for each of the daughter cells.

From ‘chemical’ structural biology to the structural biology of cellular processes

Faced with this complexity and constrained by the difficulty of obtaining sufficient amounts of pure material for structural studies, structural biologists for a long time worked on relatively simple proteins such as myoglobin (an oxygen storage protein in muscle) and lysozyme (an anti-bacterial enzyme which degrades oligosaccharides) which function relatively independently of other cellular components. Even after decades of study on such systems, with ever-increasingly sophisticated experimental methods, fundamental aspects of enzyme mechanisms or kinetics of ligand binding and release are not yet resolved. A relevant example of the ongoing interest in these problems concerns the detailed catalytic mechanism of the aspartic proteases, a very important family of proteolytic enzymes. A recent neutron crystallographic analysis at 1.95Å resolution (performed on the EMBL-ILL instrument, LADI) of the aspartic protease, endothiapepsin, complexed with a transition state analogue, has for the first time directly revealed the position of the key catalytic hydrogen positions at the active site (Coates et al., 2001). Despite endless unresolved problems at the ‘chemical’ end of structural biology, many structural biologists are now more concerned with studying the structural basis of cellular processes which only
make sense in the context of the living cell. This has become more feasible since the recombinant DNA technology driven revolution of the 80-90s which provided very powerful new tools both to molecular biologists trying to understand cell function and to structural biologists who could now produce large amounts of rare cellular proteins in bacterial hosts, and then the genomics and bioinformatics revolution of the 90s, continuing now, where knowledge of complete genome sequences allows rapid identification of functionally related groups of proteins.

**Intracellular traffic**

The cellular process I would like to focus on is intracellular traffic (Fig. 2). Cells of higher organisms (eukaryotic cells) are compartmentalised into various membrane bound organelles (nucleus, mitochondria, lysosome, Golgi complex etc) each with their own special complement of proteins necessary for carrying out their particular cellular functions. On the other hand, essentially all proteins are synthesised by the same ribosome based machinery associated with the endoplasmic reticulum in the cytoplasm. The question is: how are the right proteins targeted and transported to their correct destination? The necessary elements of such a directed transport system are an identity tag attached to the ‘cargo’ and a recyclable system that recognises the identity tag and couples it to the machinery that transports it (often by translocation through a membrane) into the correct organelle. The cell has evolved several such systems, completely different in detail but conforming to these principals. For instance, identity tags are now known for proteins that have to be transported into the nucleus (nuclear localisation signal, NLS), out of the nucleus (nuclear export signal, NES), into the mitochondria (mitochondrial import signal) or into the endoplasmic reticulum (the signal sequence). These tags are short consensus peptide sequences, with a distinct character (e.g. positively charged for the NLS, leucine-rich for the NES or hydrophobic for the signal sequence), often near the beginning of the protein and they are sometimes cut off when the protein has reached its destination.

**Nucleo-cytoplasmic transport**

The case of nucleo-cytoplasmic transport is particularly central to the fundamental functioning of the cell, since the nucleus is where the genomic DNA is stored, replicated and transcribed, yet the cytoplasm is where all proteins are made and where most metabolic processes go on (Fig. 3). Separating the two is the nuclear envelope, a double membrane bilayer. Heavy traffic continually goes both ways from nucleus to cytoplasm and vice versa through complex proteinaceous structures embedded in the nuclear envelope called nuclear pore complexes, which are very much glorified holes (see below). How does all this work in the usual, amazing, essentially error free way, of living cells? Molecular biologists and biochemists now have a pretty good idea of...
the complex mechanisms involved and structural biologists are providing atomic resolution pictures of several of the components and the key inter-molecular recognition events involved. Excellent recent reviews on nucleocytoplasmic transport are to be found by Nakielny and Dreyfuss (1999), Chook et al. (1999) and Conti and Izaurralde (2001).

The key concept required to understand nucleocytoplasmic transport is the role of a small protein called RAN, which acts like a molecular switch and defines the directionality of transport. RAN can be in two distinct structural states depending on whether it has guanosine diphosphate (GDP) or guanosine triphosphate (GTP) bound (Fig. 4). The conformational difference between the two states of RAN is dependent on the absence or presence of the gamma-phosphate of GTP (Scheffzek et al., 1995, Vetter et al., 1999a) and determines whether or not RAN can bind tightly to other molecules involved in nuclear transport. Things are arranged such that in the nucleus it is quickly converted into the GTP bound form (RAN:GTP) by means of an exclusively nuclear localised guanosine exchange factor (GEF) which exchanges GTP for GDP in the active site of RAN (Fig. 5). In contrast, on the cytoplasmic side, all RAN is quickly converted into the GDP bound form (RAN-GDP) by a cytoplasmic GTPase activating protein (GAP) which helps RAN hydrolyse GTP bound in its active site to GDP.

The other key components in nucleocytoplasmic transport are so-called nuclear transport receptors. These are proteins with three properties: they bind either directly or indirectly to the cargoes to be transported; they bind to the nuclear pore complex and can be transported (with their cargo) through it; and they bind RAN, but only in the GTP bound form.

**Getting proteins into the nucleus**

To illustrate how this works we first consider the case of nuclear import of proteins (Fig. 6). As mentioned above, proteins to be imported into the nucleus from the cytosol carry a positively charged NLS peptide (non-unique but always rich in arginine and lysine) embedded in their sequence. The NLS is specifically recognised and tightly bound by a protein called alpha-importin and crystallographic studies have now given a very detailed view of how alpha-importin can recognise different NLS sequences (Conti et al., 1998). Alpha-importin itself has a special N-terminal sequence (called the IBB) which is specifically recognised by the nuclear import receptor which is known as beta-importin. Alpha-importin
is thus an adaptor molecule linking the cargo to the import receptor. The ternary complex of cargo protein, alpha-importin and beta-importin (Fig. 7) is thus able to interact with and pass through the nuclear pore into the nucleoplasm. Once in the nucleus the complex encounters a high concentration of RAN:GTP which can bind tightly to beta-importin. However this is incompatible with beta-importin binding the alpha-importin-cargo complex which then dissociates, releasing the cargo. Crystal structures of beta-importin either with the IBB bound, as in the import complex (Cingolani et al., 1999), or with RAN:GTP bound (Vetter et al., 1999b) show that the binding sites of the two substrates are overlapping and explain this incompatibility. Finally to make the whole system efficient, beta-importin and alpha-importin are recycled back through the nuclear pore into the cytoplasm.

**The nuclear pore complex**

The nuclear pore complex itself is a structural biologist’s challenge of still a greater magnitude (Fig. 8). In mammals it is an enormous complex of about 125 MDaltons molecular weight and comprising 80–100 distinct proteins (called nucleoporins or NUPS). While we are a long way from an atomic resolution structure of the entire nuclear pore, low resolution information is available from various sources. Electron microscopy reveals that the nuclear pore complex has 8-fold symmetry about an axis perpendicular to the membrane and distinct cytoplasmic and nucleoplasmic faces. Using very up to date methods of proteomics (systematic analysis of proteins by two-dimensional electrophoresis and mass spectroscopy, coupled with genomic information) the location of the various different nucleoporins in the sub-structures of the yeast nuclear pore complex has recently been determined (Rout et al., 2000). About half of nucleoporins so far characterised contain multiple repeats of a tetrapeptide FxFG (F: phenylalanine, G: glycine, X any amino acid). These are thought to be the transient binding sites for nuclear transport receptors such as beta-importin and exportin as they move through the pore with their cargo, a process which in itself does not require energy. A recent crystallographic structure sheds light on this idea by showing how FxFG repeats bind to beta-importin (Bayliss et al., 2000).

**The challenge of transient and flexible, multi-component complexes: combining high and low resolution structural techniques.**

Nuclear export works in a related by cleverly different way to import. Nuclear export receptors (e.g. exportin) belong to the same family of proteins as beta-importin but have the distinctive property that they only bind cargo simultaneously with RAN:GTP i.e. the RAN:GTP and cargo binding sites on the export receptors are non-overlapping. Thus in the nucleus, a protein carrying a leucine-rich nuclear export sequence (NES) binds to exportin which also binds RAN:GTP (the nuclear form of RAN). This ternary complex can then pass through the nuclear pore into the cytoplasm. Here, as described above, RAN:GTP is rapidly converted to RAN:GDP which has a low affinity for exportin leading to the dissociation of the export complex and release of the cargo. Unlike the case of nuclear import, no crystal structures have yet been determined of an export complex. This is a more challenging problem since the minimal complex involves three proteins (cargo, export receptor and RAN:GTP) and in the case of particular cargoes can be even more complex. For instance, the nuclear export of a class of small RNA molecules (called snRNA) requires two adapter proteins (one of which itself comprises two proteins) to link the RNA to the export receptor. The complete export complex thus comprises five proteins plus the snRNA cargo. Structural studies on such a system typify the challenges that will more and more face structural biologists in the future. The snRNA export complex, although it is stable, only exists transiently in cells and hence cannot be purified from them in any useful amount. In order to reconstitute the complex from recombinant material, five proteins have to be produced (expressed), purified and mixed together with the snRNA. This is a lot of work and may not be straightforward as not all eukaryotic proteins express well in bacteria. There is then no guarantee at all that the complex will crys-
tallise and give a high resolution structure, particularly if it is too flexible. Therefore one may have to turn to more low resolution structural methods to give shape information or an envelope into which high resolution X-ray or NMR structures of parts of the complex can be fitted. Single particle 3-D reconstruction by cryo-electron microscopy is now a very successful method for studying medium to large complexes (see for instance Stark et al., 2001 for EM studies on a medium sized protein-RNA complex), but the method needs to be extended to smaller complexes (a few hundred kilodaltons) such as the export complex we have been talking about.

The other currently available low resolution structural method is small angle X-ray and neutron solution scattering. Here again advances in data analysis are demonstrating that these techniques will also play a very important role in structural studies of complexes in the future (Gabashvili et al., 2000, Svergun et al., 2001).

Acknowledgements
The author wishes to thank Gino Cingolani, Elena Conti, Iain Mattaj, Catherine Mazza, Christoph Müller and Carlo Petosa for educating me in nuclear transport and providing figures.

References
Nuclear and particle physics with slow neutrons

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Nuclear and particle physics with slow neutrons cover a very broad field of investigation. The radiative neutron capture reaction in nuclei provides very detailed information on the excitation modes of nuclear matter at low energy. Neutron induced fission shows several new aspects. Recent symmetry measurements in binary and ternary fission give new inside into the fission process itself. Modern multidetector systems allow the measurement of rare fission fragments yielding an access to very neutron rich nuclei. They are of special interest in astrophysics and nuclear matter physics. The neutron as an elementary particle is an ideal probe to study the weak force and fundamental symmetries in nature, with links to high energy particle physics and astrophysics. New generation of experiments are in progress due to modern developments in detector technology, neutron beams and UCN sources. The review gives a personal outlook with relevance to the possibilities at the ILL.

1. Introduction

The neutron is an important probe in nuclear and particle physics. In nuclear physics the strong and weak interaction in nuclear matter can be investigated including reaction symmetries. The neutron capture reaction deposites typically 7 MeV of excitation energy in the nucleus due to the binding energy of the captured neutron. The following radiation or fission can be investigated including reaction symmetries. The neutron scattering at nuclei lays more in the application to condensed matter physics although the base for this application is the understanding of the nuclear scattering process. Symmetries in scattering of polarized neutrons are also used to answer nuclear and particle questions. As an elementary particle the neutron is of high interest by itself. In the quark picture it is composed of the quark structure udd. As an elementary particle the neutron is of high interest by itself. In the quark picture it is composed of the quark structure udd. The neutron allows very fundamental experiments on weak interaction in the first generation of elementary particles. Particle properties, the decay of the neutron by weak interaction to a proton, electron and electron antineutrino are subject of outstanding studies. Experiments on the symmetries in the free neutron system can be performed with high sensitivity due to the neutral charge of the neutron and the easy handling of the polarization of neutron beams. Furthermore the possibility to store ultra cold neutrons (UCN) in traps yields long observation times and hence precise energy determination of the neutron state. These data combined with results from high energy measurements at accelerators, astrophysical observations and high precision experiments on other particles provide a detailed base for theories. The study of matter wave covers also a very broad field and is just mentioned here (see contributions to this symposium by H. Rauch and V.V. Nesvizhevsky).

2. Nuclear physics with slow neutrons

2.1 Radiative neutron capture: A(n,γA+1 process

The studies with the (n,γ) reaction have developed in the recent years towards very detailed investigations performing high precision experiments. Important topics are:

- excitation modes in the (A+1) nucleus at low energy and relatively low angular momentum
- very detailed properties on nuclear levels, completeness in levels and transitions
- coherence and collectivity in nuclear matter
- structure and chaos in nuclear matter
- phase transition in a mesoscopic quantum system
- symmetries in nuclear level structure versus geometrical pictures

The many particle system of a nucleus shows astonishing structures which for predictable cases can be described by algebraic formulas with only scaling parameters. This findings are of importance also for other mesoscopic systems. An example is the X(5) scheme of 149Sm which was presented in this symposium by R. Casten for phase transitions in nuclear matter. Important information for low energy nuclear levels was provided all over the years by the gamma ray crystal spectrometers GAMS at the ILL. With the improvement of resolution at GAMS close to the theoretical limit of diffraction, the Doppler broadening of MeV gamma rays due to the emission from recoiling nuclei (GRID) became visible and is used widely for the life time of nuclear levels and thus absolute gamma ray transition probabilities [1]. In turn this effect is used to check atomic potentials in collisions in the few 10 eV range (see contribution to this symposium by M. Jentschel et al).

A further application of the ultra high resolution gamma ray spectroscopy is the determination of mass standards. In the n+p reaction the gamma ray was determined with an absolute precision of 0.4 eV corresponding to 2.10^{-7}. For this purpose the Bragg angle of the GAMS 4 crystals was determined as 0.083202194(14) degree. Including mass spectroscopy measurements for the proton and the deuteron mass, the neutron mass is determined to a precision of 10^{-8} [2,3].

The experiments at the GAMS spectrometers will further develop and an important gain in efficiency is expected from the bent two

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crystal spectrometer GAMS 5. On the other hand the investigation of the \((n,\gamma)\) reaction by multi detector arrangements which covers a large solid angle is almost unexplored.

### 2.2 Neutron induced fission: \((n,f)\) reaction

Neutron induced fission is a classical field of nuclear physics with many modern trends and problems:
- Is the fission process understood?
- Is there a complete enough data set for neutron induced fission (cross sections, fission product yields) (*)
- spectroscopy of fission products
  - direct sources (example: Lohengrin PN1 at the ILL)
  - moderated: in-pile ion source (PIAFE, MAFF project FRM 2)
  - neutron halos
  - shell structure for very neutron rich nuclei
- astrophysical path of element breeding (super nova, red giants)
- fusion of neutron rich nuclei to superheavies
- incineration of nuclear waste (*)

The points marked with (*) are very relevant for the question about the long term use of nuclear power. At the ILL, experiments are running for these important questions. The Lohengrin (PN1) spectrometer at the ILL is ideally suited for the detailed fission product spectroscopy also for rare fissile isotopes. With the Mini Inca project the incineration is studied by samples placed close to the ILL reactor core (see contribution by G. Fioni et al to this symposium).

For the spectroscopy of very neutron rich fission products, many studies have to be done. The direct source PN1 transports in a few microseconds all the fission products to the detector site. Ion sources are more limited in fission products and transport times but yield higher intensities. Thus the two methods are complementary. To really be competitive PN1 has to use modern multi detector arrangements. Many sensitive experiments can be already done with the proposed set of 7 high resolution HPGe detectors. For rare fission products the full solid angle should be covered by particle detectors and set-ups such as “Miniball” should be placed at the focal plane of Lohengrin.

The present world wide activity towards intense radioactive beams (RIB) such as fission product beams will lead to a deeper understanding of exotic nuclei. The breeding of elements in the so-called r process in a supernova goes along a chain of very neutron rich nuclei and will be better understood.

### 2.3 Search for the weak interaction in nuclear reactions with neutrons

In the interaction of hadrons (matter with quarks) the strength of the weak force is about \(10^{-7}\) of the strong force. The weak force violates parity symmetry while parity is conserved for the strong force. Thus a signature for the weak force is the spatial asym-
metry between $\psi(r,1)$ and $\psi(-r,1)$. In general an asymmetry is defined by $(N\cdot N)/(N+ \cdot N)$, were $N$ and $N$ denote the event counting rate for the two opposite spin directions of the neutron.

In reactions of neutrons with heavier nuclei an enhancement of the weak interaction part may occur by the mixing of close lying nuclear levels with the same spin but opposite parity. For favorable cases the asymmetry can reach the percent level. A famous example is $^{139}$La. Using a $^3$He spin filter [4] and neutrons from the hot source of the ILL the dichroism and the neutron spin rotation for polarized neutrons passing a sample of $^{139}$La were observed (Fig.1). Asymmetry of the fission fragment emission relative to the neutron spin direction were also observed at a rather high level of several $10^{-3}$. Here the polarized neutron is captured leading to a polarized exited state which in turn undergoes fission. It is suggested that the parity effect is due to level mixing in the compound state prior to fission [5].

For reactions of neutrons with few nucleon systems, in particular with the proton, the fundamental weak pion exchange (or $Z$ boson exchange) can be studied. The gamma asymmetry $A_\gamma$ in the reaction with transversely polarized neutrons $n(p,p')d$ is related to the weak pion-nucleon coupling constant $H_\pi$ by $A_\gamma = -0.045(\Delta H_\pi^t)$. For this experiment an asymmetry measurement of the gamma in and opposed to the neutron spin direction at the level better than $10^{-4}$ is necessary. At present the best precision was obtained by J.Alberi et al [6] with $A_\gamma = (1.5 \pm 4.7) \times 10^{-4}$. A recent proposal by W. M. Snow et al [7] aims at a precision of better than $5 \times 10^{-5}$. Furthermore the spin rotation of polarized neutrons in hydrogen would be also a very valuable experiment for this type of physics, but was not yet tried, as well as the dichroism in hydrogen. They are in the range of feasibility although difficult.

A surprising effect was found in ternary fission. The triple correlation between the neutron spin, the light fission product and the ternary particle were detected rectangular to each other (analog to the D coefficient in the beta decay). Inversion of the motion of the reaction corresponds to change in the spin direction of the compound state (defined by the polarized neutron capture). The coincidence counting rate between the light fission fragment and the ternary particle (mostly alpha particle) changed by several $10^{-3}$, when the neutron spin (and hence the direction of polarization of the compound state) was inverted. This looks like a violation of the time reversal symmetry, but is more likely a final state interaction between the angular momenta of the outgoing particles [8].

The final state effects are not present in neutron scattering and similar experiment like the dichroism measurement (but with a polarized target) are suggested by several groups in view of a sensitive test of time reversal symmetry.

### 3. Particle property of the free neutron

A comprehensive survey of the present activities in this field can be found in the proceedings of the workshop on ‘Particle Physics with Slow Neutrons’, held at the ILL [9]. Also topics of weak interaction in nuclei and neutron matter waves are included.

#### 3.1 Static properties of the neutron

Precise data on the properties of the neutron such as mass, magnetic dipole moment, charge, charge distribution and also on the neutron scattering length on n,e,p were obtained in many years of experiments. An outstanding value and experimental challenge is the search for an electric dipole moment (EDM) of the neutron. A neutron with a magnetic $\mu_n$ and a non-zero electric $d_e$ dipole moment would violate time reversal symmetry, a violation which is observed till now only in the kaon system. Time reversal would mean reversal of the motion, changing only the magnetic dipole moment in direction. The time reversed system would be distinguished by the original system by different relative directions of the two dipole momenta (Fig.2).

![Fig. 2: Visualization of time reversal and parity operation for a neutron with magnetic and electric dipole moment. Such a system violates both time reversal and parity symmetry since the individual operation $T$ or $P$ brings the system to a different relative orientation of the dipoles.](image)

The concept of the experiments consists in the measurement of the potential $\Delta E$ of the neutron in a magnetic and electric field: $\Delta E = \mu_n B + d_e E$. The energy difference is measured by the Lamor precession frequency using the Ramsey magnetic resonance method. This Lamor frequency should change for a non-zero $d_e$, when the electric field is inverted. The most precise experiment runs at the ILL by the Sussex/RAL/ILL collaboration and at present a limit of $d_e < 6 \times 10^{-28} \text{ e cm}$ is obtained [10]. Ultracold neutrons in a material trap are used for this experiment since the observation time increases the precision in energy determination in analogy to the uncertainty principle.

A future EDM experiment is in preparation at the ILL and uses superfluid Helium in the UCN trap as an inner converter to UCN. A sensitivity for $d_e$ as high as $10^{-26} \text{ e cm}$ is expected. Compared to the predictions shown in Fig 3 this sensitivity tests of a whole set of theories and also the prediction from matter-antimatter asymmetry in cosmology ($d_e = 10^{-23} \ldots 10^{-26} \text{ e cm}$).

#### 3.2 Decay of the free neutron

The study of the decay beta decay of the free neutron $n \rightarrow p + e + \nu$ with a life time of $15 \text{ min}$ provides a wealth of information:

- Strength and structure of the weak lepton-quark interaction
- Strength and phase of the vector and axialvector coupling constants, $g_V$ and $g_A$
- Are there right handed currents in the weak interaction?
- Is the flavor symmetry perfect?
- Conservation of the weak vector current
- Is there a scalar or tensor coupling in weak interaction?
- Weak magnetism
- Search for the violation of time reversal symmetry
These parameters and questions can be experimentally investigated by measuring the
- neutron life time \( \tau \)
- most precise methods:
  - UCN population in a trap
  - UCN storage and detection of decay products
  - trap for decay protons
- angular correlation between the decay products
- parity violating asymmetry (coefficients A and B)
- test of time reversal (D coefficient, R coefficient)
- inner radiative correction
- decay into hydrogen atom

The most precise experiment on the neutron life time was performed recently by the Russian group of Morosov and Bondarenko at the UCN source of the ILL. They have measured the UCN population after different storage times and in addition the upscattered UCN during the storage. Using traps with different surface to volume ratios they obtain \( \tau = 8.85 \pm 0.9 \text{(stat.)} \pm 0.4 \text{(syst.)} \) s \[12\].

For the most recent A coefficient measurement the PERKEO 2 detector was used (see contribution to this symposium by H. Abele). A transversely polarized neutron beam passes through a strong, magnetic field. The decay electrons emitted into a half space are guided to one of the opposite detectors by the magnetic field. The asymmetry is measured by neutron spin flip. The result is \( g_n/g_v = -1.2740(21) \) \[13\], compared to the previous world average of -1.2670(35) \[14\]. From the neutron life time and the A coefficient the matrix element \( V_{ud} \) of the CKM matrix can be deduced and the unitarity of the matrix checked. With the present data the agreement with unitarity is poor.

For the D coefficient two groups are running experiments at present using somewhat different geometrical arrangements. The experiment TRINE is presented in this symposium by T. Soldner et al and has achieved from a part of the collected data the preliminary result \( D = (-3.1 \pm 6.2 \text{(stat)} \pm 4.7 \text{(syst)} \pm 4.7 \text{(stat-syst)}) \times 10^{-4} \) \[15\]. The motivation for the D experiments is competitive to the present limit of the EDM experiments.

**4 Conclusion**

- energy: \( \Delta E = 3 \times 10^{-22} \) (EDM)
- relative momentum \( \Delta p/p = 10^{-11} \) (neutron charge)
- neutron spin rotation \( = 10^{-6} \)
- asymmetry in spin flip measurements
  \[ N^{-} - N^{+} \]/\( N^{+} + N^{-} \) \( \approx 5 \times 10^{-8} \)

New experiments will profit from stronger neutron beams, development of neutron optics, new detectors and new secondary particle beams. Also multi detector arrangements and fast data acquisition systems are essential for further progress. Major progress is expected when more intense UCN sources are available. While the ILL UCN source provides an intense continuous flow of UCN, it is not a trap by itself. Production and accumulation of UCN in a trap will lead to higher UCN densities. At the rather weak cold neutron source at Los Alamos an UCN density comparable to that of the ILL was already obtain by the later method. A project at the new Munich reactor FRM II using a trap with an in-pile solid D2 aims at higher UCN densities. The work by Serebrov's group in Gatchina on solid D2 is also promising. The new EDM set-up at the ILL will produce the UCN in the trap filled with superfluid 'He and should lead to a high gain in sensitivity.

**References:**

Use of neutrons in chemistry at the molecular level

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The neutron techniques which are mostly used in chemistry are inelastic and quasielastic scattering, powder diffraction, and to a lesser extent small-angle scattering. They allow to locate hydrocarbons on surfaces and to study their dynamics. One can thus follow molecular adsorption, dissociation, or chemical reactions. These subjects are relevant to both fundamental research and industrial applications. Some recent results, mainly obtained at the ILL, are reported below. They concern essentially chemical reactions on surfaces and diffusion in porous media. Some improvements in the techniques are suggested.

1. Introduction
Chemistry has not a good reputation in the press and in the public because the word is immediately associated with pollution. However, a more positive image is obtained if one uses the words: fuel cells, green chemistry, energy storage and so on. In addition to developing clean processes, chemistry is engaged in treating existing pollutants in water or soils, in the discovery of new catalysts able to remove sulfur in fuels or to reduce the level of exhaust emissions from motor vehicles, or in the synthesis of new materials for storing nuclear waste.

To characterise the newly synthesised molecules or phases, or to understand the transformations and reactions occurring at interfaces, various physico-chemical methods are being used. With a vibrational technique such as inelastic neutron scattering (INS) one can identify the surface species resulting from molecular adsorption, dissociation or chemical reaction. Compared with optical methods, INS has unique properties such as the lack of selection rules, a high sensitivity towards hydrogen atoms, and a clear understanding of the different factors which govern the scattered intensities.

The mobility of molecules on reactive surfaces is one important step in chemical reactions. Strong confinement effects are found in microporous solids, such as zeolites, but measuring diffusion coefficients in these systems is quite complicated. It has been found recently in several cases that quasi-elastic neutron scattering (QENS) is the only technique which is able to determine reliable diffusivities. The combination of QENS and molecular dynamics simulations is a powerful tool to elucidate the mechanism and rate of dynamics in confinement, for simple molecules. However, for bulky or flexible molecules, the simulations do not provide yet precise diffusivities so that experiments are still required.

Neutron diffraction is another important tool in chemistry, using mainly powders, to characterise new materials and to determine the structure of host-guest compounds. In situ measurements can be performed with neutron diffraction to follow chemical reactions. In situ experiments are also possible with small-angle neutron scattering (SANS), one example is the template induced synthesis of zeolites [1]. In situ INS studies of catalytic reactions are not yet feasible, this may become possible with the ESS. Some examples of applications of neutron scattering techniques in chemistry will be given here, concerning mainly reactions on surfaces and diffusion in porous materials.

2. Environmental catalysis
Fossil fuels contain mainly hydrocarbons, which become by combustion carbon dioxide and water. However, incomplete combustion leads to carbon monoxide and other compounds. Further, fossil fuels also have some sulfur containing constituents, which yield

Fig. 1: Inelastic neutron scattering spectra resulting from the adsorption of H₂ on (a) MoS₂ (equilibrium pressure: 3 bar), (b) RuS₂ (equilibrium pressure: 0.5 bar).
emissions of sulfur oxides. The latest legislations in Europe concerning air pollution will oblige refiners to reduce considerably the sulfur level in diesel and petrol. ‘Hydrotreating’ refers to a variety of catalytic hydrogenation processes which saturate hydrocarbons and remove sulfur (also nitrogen) from petroleum streams in refinery. The catalysts are based on transition metal sulfides, with sulfur deficient sites on the surface to activate hydrogen. It has been shown by INS that different hydrogen species were present on MoS$_2$ and RuS$_2$ catalysts [2]. Only S-H groups and molecular H$_2$ is observed on MoS$_2$. In Fig. 1(a), the observed features are due to rotational transitions of molecular hydrogen, the broad band around 40 meV being due to recoil scattering. On the other hand, Ru-H species are found in addition to S-H groups on RuS$_2$, Fig. 1(b). This explains why RuS$_2$ is much more active than MoS$_2$ in hydrogenation and hydrodesulfurization reactions. It remains a challenge to observe Mo-H species on MoS$_2$, possibly at elevated temperatures or hydrogen pressures. Other INS studies have also been performed on TFXA (ISIS) or on IN1BeF, to follow surface reactions such as the reaction of formic acid on oxidised copper surfaces, to generate formates [3], the deactivation of Pd catalysts [4], or the hydrogenation of acetoneitrile on Raney nickel [5].

3. Interaction of water with acidic sites in a zeolite

Zeolites in the proton form are extensively used in acid catalysis. The active sites are formed by bridging hydroxyl groups, i.e. OH groups bonded to Si and Al atoms. A question which has been much debated is whether the Brønsted acidity of these solids is high enough to protonate water. The advantage of INS is that the spectra can be simulated from ab initio quantum mechanical calculations, using as inputs the theoretical frequencies and atomic displacements. This feature has been used to simulate the spectrum of water in H-ZSM-5 [6]. The experimental spectrum was compared to spectra calculated for the 2 possible structures: hydrogen-bonded water and hydroxonium ion (Fig. 2). The comparison clearly shows that only the hydrogen-bonded model reproduces the experimental spectrum. Since the spectrum from the dehydrated zeolite has been subtracted to obtain the experimental profile, the bending modes of the bridging hydroxyl groups appear as negative contributions (*) in the figure.

In other solids, such as solid acids, HM(SO$_4$)$_2$•H$_2$O [7] or heteropolyacids H$_3$PW$_{12}$O$_{40}$•6H$_2$O [8], the hydroxonium ion has been observed, which indicates a greater acidity. This vibrational spectroscopic technique is very important for chemists. To be able to follow chemical reactions, one needs to measure spectra at low Q values, with a better energy resolution. With a higher neutron flux, one could extend such studies to other environmentally important reagents such as CO and NOx in catalytic post-combustion.

4. Diffusion of benzene in porous media

In the gaseous state and in mesopores, the mean free path of a diffusing molecule is larger than the pore diameter so that collisions between a molecule and the pore wall occur more frequently than intermolecular collisions. A molecule hitting the wall exchanges energy with the surface with the result that it is reflected in any direction. The random aspect of this process gives rise to a Fickian expression for the flux, in which the diffusion coefficient depends only on the pore size and on the mean molecular velocity. This is known as Knudsen diffusion. There is thus a linear and moderate dependence of the diffusivity on the pore size, as shown in Fig. 3.
In microporous solids, such as zeolites, the size of the molecule is comparable to the pore size. This leads to diffusion limitations, and diffusion coefficients can be several orders of magnitude lower compared with mesoporous materials. For a small reduction in pore diameter: from 7.5 Å in NaX to 5.5 Å in ZSM-5, the diffusion coefficient of benzene is reduced by more than 3 orders of magnitude at 300 K (the points in Fig. 3 have been obtained using the IN16 and IN11 spectrometers). The chemical composition of the zeolite also influences the mobility of the molecule. For example, in NaY zeolite, the reduced number of sodium cations, compared with the number in NaX, enhances the potential energy barriers and thus reduces the diffusivity at room temperature (Fig. 3), although the dimension of the pores is the same for both zeolites.

QENS is the only microscopic technique which has been able so far to measure the diffusion of benzene in NaY [9], because large Y crystals are not available. The size of the crystals is unimportant in QENS so one can use crystals smaller than 1 µm without problems. It can be noted that this was the first investigation of the position of a hydrocarbon molecule in a zeolite by powder neutron diffraction [10]. The diffusivities obtained for benzene in NaY by various theoretical methods and by QENS are compared in Fig. 4. It appears that experiment and simulations (performed at infinite dilution) agree within 1 order of magnitude. The activation energies are also comparable. However, the KMC simulations predict that the diffusion coefficient should increase with the loading, which is in contradiction with the QENS measurements. This implies that some of the assumptions made in the simulations are not valid.

In the NaX zeolite, the sodium cations are distributed over a larger number of sites, compared with NaY. Since all these sites are not fully occupied, simulations in NaX are more difficult, and so far only one series of simulations have been performed for benzene in NaX [11]. The diffusivities obtained by this simulation and by several experimental techniques are shown in Fig. 5 (on a linear scale). The QENS diffusion coefficients [9] are very close to the frequency-response values, and lower than the PFG NMR data by a factor 3 to 4. The TZLC diffusivities are about 2 orders of magnitude lower at low loading and the loading dependence is at variance from those of all the other methods. The activation energies obtained by QENS are 17 kJ/mol at low loading and 16 kJ/mol at high loading. This is smaller than the values reported from the PFG NMR experiments, which are about 25 kJ/mol at low benzene concentrations and 20 kJ/mol at medium pore-filling factors. This discrepancy is not yet understood.

In the MFI structure (this 3 letter code refers to ZSM-5 and to its purely siliceous form, silicalite), the pores are about 5.5 Å in diameter, which is similar in size to the kinetic diameter of benzene. Therefore, strong variations of diffusion rates are expected. The diffusivity of benzene in ZSM-5 was too slow to be measured with conventional QENS instruments: time-of-flight and back-scattering spectrometers. However, it could be obtained by neutron spin-echo (NSE), because a higher energy resolution can be attained with this technique. Diffusivities could be derived by measuring the intermediate scattering function at different Q values, to check that the motion which was observed was due to Fickian diffusion [12]. This was the first measurement with a microscopic technique of the diffusion coefficient of benzene in the MFI structure (PFG NMR cannot be applied to this system). The NSE diffusivities are represented by crosses in the Arrhenius plot of
Fig. 6. Most of the diffusion coefficients reported by other experimental or theoretical methods are also shown in this figure for comparison. Whereas large discrepancies are often reported between microscopic and macroscopic diffusion coefficients, the diffusivities of benzene, as determined by the NSE technique, is in good agreement with macroscopic methods. Extrapolation to room temperature also gives a good agreement with a recent molecular simulation performed with a flexible framework (Forester & Smith [13]). Another simulation, performed with a rigid lattice (Snurr et al. [14]), yielded much lower diffusivities, by about 2 orders of magnitude.

5. Diffusion of methane-butane mixtures in the MFI structure

For small linear alkanes (up to n-hexane), the assumption of a rigid framework is valid and the diffusion is fast enough to be followed by traditional molecular dynamics (MD) simulations. This greatly reduces the computational expense. The agreement between the three microscopic techniques: QENS, PFG NMR and MD, is relatively well established for pure sorbates. However, few studies exist in the literature presenting direct comparisons between those techniques for mixed sorbates. The first attempt to compare results obtained from MD simulations and QENS experiments has been realised for a n-butane–methane mixture in silicalite, over a range of loadings and compositions at 200 K [15]. This system was chosen because of its practical applications and because its experimental and theoretical study was both worthwhile and feasible. The experiments were performed on IN5. Self-diffusivities calculated from the MD simulations were found to be in excellent agreement with the experimental QENS data, if one takes into account the errors associated with both techniques (Fig. 7). The self correlation function, $G_s(t)$, was calculated from the MD. After orientational average and Fourier transform, the incoherent dynamic structure factors $S_{inc}(Q,\omega)$ were found to show the expected Lorentzian shape. A direct comparison with experiment was performed through the half-width at half-maximum (HWHM) as a function of $Q$. For the low $Q$ values (in the linear, ‘Fick’s law’ regime), the agreement between MD and QENS was excellent. At larger $Q$ values, and undulating behaviour leading to a plateau value was seen in both MD simulations and in the experiments. This behaviour is a signature of a jump diffusion process. Models of jump diffusion, such as the Chudley-Elliott or a new model, were shown capable of providing a good representation of the experimental broadening. By monitoring and analysing the molecular motion in the simulations, it was confirmed that diffusion takes place through successive jumps between the interiors of adjacent channel segments. Precise and quantitative calculations mapping the MD trajectories onto a coarse-grained jump model revealed mechanistic aspects of the motion. Distributions of jump lengths and rate constants were accumulated for the various jump types executed by each sorbate species. Jump lengths were found to be widely dis-

![Fig. 6: Diffusivities of benzene in the MFI structure obtained at low loadings by various experimental and theoretical techniques [12].](image)

![Fig. 7: Orientationally averaged self-diffusivities obtained by QENS (□) and MD simulations (○) for methane in mixtures of methane and perdeuterated n-butane sorbed in silicalite at 200 K (a) as a function of methane loading (the n-butane loading is held constant at 4 molecules per unit cell). (b) as a function of n-butane loading (the methane loading is held constant at 4 molecules per unit cell).](image)
tributed between 0 and 15 Å, the mean jump length being a decreasing function of the loading. A second maximum appears in the calculated HWHMs as a function of Q. This could not be checked by experiment because of the presence of Bragg peaks in several detectors, even using a relatively long wavelength on IN5: 9 Å. Polarisation analysis would give access to the whole Q range, also at small Q values where small angle scattering due to the texture of the zeolite complicates the data analysis.

For this system, some basic assumptions made in the simulations: fixed framework and the united-atom model (CH₃ and CH₂ groups are represented by point masses), are valid. However, for branched alkanes or for long linear alkanes, deficiencies in the simulations have been observed so that QENS experiments are still unique [16]. Other groups have combined MD simulations with neutron scattering, to investigate the dynamics of various host-guests compounds, e.g. refs. 17-18.

6. Conclusions

Neutron techniques provide unique information on the structure and dynamics of molecular species at interfaces. For QENS, the ILL is still the best place in the world because a large range of observation times can be covered using time-of-flight, back-scattering, and NSE instruments. What is required for adsorbed molecular systems is a spectrometer with the largest dynamic range possible, a high intensity (to study single crystals), and polarisation analysis. Simulations are quite useful but they are not yet in a position to replace experiments. High resolution powder diffraction is also very important, so that the Super D2-B project is strongly supported. For inelastic studies, measurements of S(Q,ω) maps are possible at the ILL, on IN4, but up to 100 meV only. When the sample contains light elements, like hydrogen, larger energy transfers must be probed. At the ILL, this is only possible on IN1BeF so that any improvement in terms of flux or resolution would be welcome on this instrument.

References
The lecture commences outlining the common ground of the vastly different materials subsumed within the concept of soft matter. With some examples, I demonstrate the key role, static and dynamic neutron scattering has played in the molecular exploration of these materials. Considering recent advances I will then identify future trends, where neutrons are expected to be detrimental for further progress provided that more powerful instrumentation and sources are developed. (i) An important already unfolding research area will be the study of kinetics, transient and non equilibrium phenomena which today suffer significantly from intensity limitations. (ii) Relevant soft matter materials are multicomponent systems, therefore, complexity is an overarching issue in their understanding. This concerns, the structure and dynamics of the different components, which determine their role in the functioning of a material and includes the extremely important phenomenon of self assembly and structure formation. (iii) The trend to achieve a molecular understanding of rheological behavior brings in the new field of molecular rheology which combines analytic modelling, computer simulation and neutron scattering as an indispensable tool. (iv) Finally, it remains to be seen how far experimental and theoretical concepts developed for soft condensed matter systems will carry into biology.

1. Introduction
The concept of soft condensed matter subsumes a large class of molecular materials with great importance to our daily life and even ourselves as biological beings. Among these materials we find polymers, thermotropic liquid crystals, micellar solutions, microemulsions, colloidal suspensions and substances relevant for biology like membranes, vesicles or biological macromolecules. These materials exhibit a large variety of different properties which to large extend result from common physical chemical causes as they are (i) a large number of internal degrees of freedom, (ii) weak interactions between the structural units – often of the van der Waals type and (iii) a delicate balance between entropic and enthalpic contributions to the free energy. These material characteristics lead to large thermal fluctuation, a vast variety of forms and various metastable states, which all constitute the macroscopic softness of the materials and make them very sensitive to external forces and boundary conditions.

Soft condensed matter has a wide range of applications. Polymers are used as structural and packaging materials, as foams and adhesives, as fibers and fabrics, as additives to lubricants in order to stabilize the viscosity or to fuel oils in order to control waxing at low temperature, as rubbers in tyres and so on. Surfactants often together with polymers serve in detergents and shampoos, as cosmetics, as food additives and paints. Finally, the physical principles ruling soft matter also underlie matter in biology. Thus, research unravelling the behavior of soft materials may also help to understand general principles governing biological substances.

2. The unique role of neutrons

Neutrons are an nearly ideal probe for such studies, since they access simultaneously the important mesoscopic length and time scales. The momentum transfer range of neutron scattering covers spatial ranges encompassing the size of a macromolecule and reaches to distances characteristic of the single bond. Another key element of the importance of neutrons in soft condensed matter is the possibility to vary the contrast by hydrogen/deuterium exchange. By selective labelling and contrast matching, single components in complex structures may be deciphered. Similarly, neutron reflectometry accesses surfaces and interfaces in soft condensed matter. The high penetration of neutrons allows to study the behaviour of such materials under external fields and facilitates an observation e.g. under processing conditions. Finally, neutrons provide space time resolution and thereby access the molecular motions which underlie the viscoelastic and mechanical properties of these materials.

3. Contrast on a molecular scale

Today neutron small angle scattering (SANS) is the standard technique, in order to study conformations, detailed morphologies and interactions in polymer systems. The first great success of SANS was the experimental clarification of the chain conformation in the melt and in the amorphous state, where the random coil conformation was confirmed [1]. Thereby, the screening of the long range excluded volume interactions in the melt was established. This result decided between several competing models and facilitated a basic choice of concepts for the understanding of long chain molecules.

The Nobel price winner Paul Flory stated in 1969 “The comprehension of the configurational statistics of chain molecules is indispensable for a rational interpretation and understanding of their properties” [2]. The deep truth of this statement recently again has become evident as systematic investigations of the chain con-
formations revealed that entanglement formation can be understood solely from the packing properties of the polymer chains, which may be described by a packing length \[3\].

\[
p = \frac{\rho M}{M_0 \langle R^2 \rangle} = \frac{\nu_0}{C_\alpha l_0^2} \quad (1)
\]

where \(\rho\) is the polymer density, \(M\) is the molecular mass, \(M_0\) the monomer mass, \(\langle R^2 \rangle\) the mean square end to end distance, \(\nu_0\) the volume bond, \(C_\alpha\) the characteristic ratio and \(l_0\) the bond length. The viscoelastic properties of polymer melts are expressed by the plateau modulus \(G^*_N\) which relates to the network character of polymer melts: \(G^*_N = k_B T/d^2\), where \(d\) is the entanglement length. In terms of the packing length concept, the plateau modulus becomes a universal function of the packing length

\[
G^*_N \approx \frac{C_{\text{const}}}{\rho N_a} p^{-3} \quad (2)
\]

where \(N_a\) is the Avogadro number. Eq.(2) relates purely structural quantities with the plateau modulus, a mechanical property of the polymer melt. Fig.1 relates measured chain dimensions with measured plateau moduli for a large number of polyolefins. As may be seen, the prediction of Eq.(2) is very well fulfilled. This relationship between structural and mechanical properties may be used for the design of polymers with special properties. Eq.(2) has recently been exploited for achieving a new class of adhesives on the basis of simple polyolefins which work without any tackifying resins.

One of the key requirements for an adhesive is the so called Dahlquist criterion demanding for the plateau modulus \(G^*_N < 0.33\,\text{MPa}\). The criterion may be rationalized by the requirement that polymers on both sides of the adhesives should be able to interpenetrate quickly by significant amounts, the fast range of interpenetration being related to the entanglement length \(d\). The Dahlquist criterion thus means, that the entanglement length needs to be larger than a certain size. Using the Dahlquist criterion together with Eq.(2), it is immediately clear that polyethylene based copolymers of olefins are not able to meet the criterion. On the other hand polypropylene based copolymers lead to much larger entanglement distances. With this reasoning as a background in 1998 the Huntsmann company introduced Rextec - a new polypropylene based adhesive containing 40% butene. This example shows how a better understanding of polymer properties resulting from basic research may directly influence a development of novel products.

4. Polymer dynamics

Neutrons observe dynamical processes simultaneously in space and time. With the development of ultra high resolution techniques like neutron spin echo spectroscopy with the best in class instrument, the IN15, at the ILL, it become possible to observe the very slow motion of polymers in the melt and to decide between different theoretical concepts. In a melt the polymer chains are strongly entangled and these entanglements constrain the chain motions. According to de Gennes the constraints may be described by tube following the chain profile. In this tube the chain rattles around and finally creeps out of the tube. Recent neutron experiments could verify a large part of this intuitive molecular model. We will first look on the initial part of the chain motion, the rattling of the polymer chain in the tube. The polymer chain is subjected to entropic forces, which restore excursions from equilibrium. The dynamic model describing this motion, the so called Rouse model, predicts that the dynamic structure factor is universal function of the momentum transfer squared multiplied with the square root of time. Experimentally, this behavior may be studied uniquely by neutron spin echo spectroscopy.

![Fig. 1: Plateau modulus vs. packing length at 413K. The line is drawn with a slope of \(-3.0\). With a few exceptions the data points relate to polyolefins (see Table I in Ref.[3]).](image1)

![Fig. 2: Dynamic structure factor for polyethylene at T=473K. The data are superimposed according to the scaling relation due to de Gennes. The solid lines are the Rouse predictions including overall chain diffusion. The dashed line represents the Rouse model for infinite chain length.](image2)
The scaling properties originally predicted by de Gennes have been tested e.g. on polyethylene melts using different momentum transfers where $Q$ superimposed according to the scaling prediction (Fig. 2) [4]. Not only the prediction is extremely well fulfilled, but also the theoretical dynamic structure factor $S(Q,t)$ up to about 180ns. At early times the chain relaxes quickly causing a fast $Q$-dependent decay of the $S(Q,t)$ (Fig. 3). This part of the relaxation relates to the rattling around of the chain in the tube. Thereafter, the relaxation levels off into a plateau, which is a manifestation of the tube confinement on the relaxation process. The data were investigated in terms of a number of different models and it turned out that only the reptation model of de Gennes could fit these data.

5. Future trends in soft condensed matter

I have been asked to predict future trends in soft condensed matter research - a task which is nearly impossible. In order to start, I would like to remind on a few predictions, celebrities where giving in the past. Lord Kelvin, the president of the Royal Society in 1895 declared "heavier than air flying machines are impossible" - this was just a few years before the Wright brothers. In 1943 the chairman of IBM predicted that "I think there is a world market for may be five computers" and finally, even recently Bill Gates in 1981 thought "650K ought to be enough for anybody". As exemplified, predictions for future developments are difficult. Nevertheless, I like to try my best.

Soft condensed matter materials will be more and more multi-component structures of soft and soft and hard materials which are tailor-made for industrial applications. This increases the structural and dynamical complexity of such materials at all length scales. Here, neutrons together with isotope substitution will be an indispensable tool to decipher such complex materials. These soft condensed matter systems exhibit complex interaction potentials with different minima and different structures and will evolve according to mechanical or thermal history. Here kinetic experiments and in-situ studies will be extremely important, in order to observe the arrangements of such structures while they occur. For the mechanical behaviour of soft condensed matter systems, geometrical and topological interactions are of great importance. In the future we may be able to look on particular points, like cross links in branched polymers, to see how they determine the dynamic properties of such a system. Interfaces will play a key role in multicomponent systems. Neutron reflectometry could play a decisive role in their exploration and, finally, structural changes which are induced by external fields like shear fields, pressure or electric fields should be explored in in-situ experiments. In all of that, neutrons could play a decisive role and we have to ask, how neutrons can further and better contribute to this development.

In my opinion, there are two routes. First, we need to upgrade the ILL in order to exploit its opportunities as much as possible but, furthermore, in Europe we also have to build a next generation neutron source – the European Spallation Source (ESS). Such measures will bring more intensity at the detector, they will allow higher resolution in frequency, in Fourier time and also in real time and this will offer plenty of new opportunities.

Higher intensity will offer the opportunity, to measure on inherently small or dilute samples, to observe smaller cross sections, to measure over shorter times and to do in-situ real time kinetics experiments. This opens up many fields in soft condensed matter science including e.g. molecular rheology, surfaces, polymers and surfactant solution at low concentration, shampoos and emulsion, polyelectrolytes and biological molecules. Smaller cross sections will allow to go to the dynamics of branching points, to polymer additives in complex fluids, to detergents, paints and lubricants. Shorter measuring times will allow to explore extensively e.g. polymer phase diagrams or to do experiments in combinatorial chemistry. Finally, real time kinetic experiments will e.g. allow to address structure formation in external fields, precipitation kinetics of colloids, or adsorption phenomena at interfaces. In the following I will underline these opportunities by experiments of today, which often are at the limit of what can be done.

5.1. Kinetic experiments and non-equilibrium studies

The first example deals with an observation of micellar exchange kinetics between polymer micelles. Here, we deal with a process where polymers are exchanged between micelles in equilibrium. Such an experiment can be done beautifully with SANS if we start with ensembles of micelles which are structurally identical but which are different with respect to their deuteration. Assume, we have two containers, one with protonated and the other with fully
deuterated micelles. These micelles are in a solution which has the average contrast of the deuterated and the protonated micelles. At time equal zero we mix the two species. Then at the beginning we will see both the protonated and the deuterated micelles in the solution. If exchange processes take place, then after a while the contrast of the micelles will vanish and at the end we will have mixed micelles with the same scattering length density as the solvent [6].

In a two-dimensional representation Fig.4 presents SANS patterns reflecting the exchange process. The observed intensity is proportional to the contrast which is a square of the difference in scattering length. Thus, the square root of the intensity reflects the non-equilibrium distribution of the hydrogenated and deuterated polymers.

Looking on this quantity as a function of time, it was found that two different exchange processes are present. A fast one determining an initial fast decay and a slow one which dominates the long time part. This result is very unexpected, since for polymer micelles the unimer exchange was proposed and considered as the only exchange mechanism. If we look on the parameters, then this corresponds to the fast process. For the slow process at present there is no explanation.

Further examples are the in-situ observation of polymerisation reactions [7] or dewetting processes of polymer films [8]. Another very interesting field, where SANS has not yet contributed is the subject of biomineralisation. There, we deal with the growth of crystal structures in the presence of associating polymers. SANS experiments could help to understand how theses polymers are modifying the surfaces, where they go to and in which way biomineralisation takes place on a microscopic scale.

As an example for a non-equilibrium study we briefly inspect some older results on the spinning of fibers [9]. The strength of a semicrystalline fiber relates to the chain conformation which may be visualized by labelling of a fraction of chains. The question was, how many crystalline blocks within one fiber are connected on average by one polymer - obviously the strength of the fiber will depend on the amount of connections between different crystals - the experiment showed the feasibility of such investigations. However, in order to perform such studies routinely, much more intensity at the sample would be needed, in order not to use kilograms of deuterated polymers.

Summarizing, the field of kinetic and non-equilibrium studies offers plenty of new opportunities. Just to name a few, one could study chemical reactions like polymerisation, one could investigate processing like extrusion, reactive blending or spinning, one could look into non-equilibrium phases, on flocculation of colloids on transport through porous media, on lubrication phenomena, on the surface modifications under flow, on wetting and dewetting processes and so on.

5.2 Complexity

In this section, I like to address the general complexity of soft condensed matter systems and to demonstrate the observation of a key component in a multicomponent system by SANS. Surfactants which are amphiphilic molecules, where one part solves in oil and the other in water, facilitate thermodynamically stable mixtures of oil and water. We recently found, that small amounts of macromolecular surfactants of the type polyethyleneoxide/polyethylenepropylene (PEO/PEP) enhance the emulsification capacity of standard surfactants dramatically [10]. It was of great importance to understand the role of the polymer in such a system, a problem which in principle can be answered by SANS in matching water, oil and surfactant. This task, however, is tremendously difficult because the scattering intensities of the different components in the systems are grossly different. The bulk contrast, where oil scatters with respect to water is about 4 to 5 orders of magnitude more intense as a scattering from the polymer alone and therefore, a simple contrast matching experiment would not work.
The problem is solved by a twodimensional contrast variation scheme around the total matching point of oil, water and surfactant. Then, one may decompose the various scattering patterns into partial structure factors like the film-film or the bulk-bulk or the film-polymer structure factor and so on. As a result partial, all structure factors are then available, allowing to elucidate the complicated structural problem. As one important result, Fig.5 presents the polymer film partial structure factor. This term is dominated by the scattering amplitude of the polymer. The solid line compares the prediction for polymers in a mushroom conformation within the surfactant layer with the experimental data. In the range, where the approximation of a flat film should be good, we observe excellent agreement. Thus, we may conclude that the polymer sits in the mushroom conformation at the interface. From such an experiment, we also obtain the chain dimensions of the polymer. With this observation, we now are able to explain what is behind the emulsification boosting effect [11].

The polymers anchored in the interface change the surface elasticities $\kappa$ and $\bar{\kappa}$. This has been theoretically predicted [12].

\[
\begin{align*}
\kappa_{\sigma} & = \kappa + \frac{k_{-1}}{12} \left( 1 + \frac{\pi}{2} \right) \sigma (R_{s}^{2} + R_{c}^{2}) \\
\bar{\kappa}_{\sigma} & = \bar{\kappa} - \frac{k_{-1}}{6} \sigma (R_{s}^{2} + R_{c}^{2})
\end{align*}
\]

where $s$ is the surface density of the polymers and $R_{s}^{2}$ and $R_{c}^{2}$ are the end to end distances of the oil and water soluble parts of the blockcopolymer. Both elastic moduli are thus universal functions of $\sigma (R_{s}^{2} + R_{c}^{2})$. Taking into account that through the logarithmic renormalisation of the surface elasticity the stability limit of the microemulsion phase is an exponential function of the $\bar{\kappa}_{\sigma}$, we predict that the phase boundary should be a universal function of $\sigma (R_{s}^{2} + R_{c}^{2})$. For a number of different polymers and surface concentrations $\sigma$ in [11] it was shown that this is indeed the case.

Another nice example for complexity are recent developments for antifreeze agents for diesel fuel. If diesel fuel which contains a fraction of paraffins is cooled, then these paraffins form large plate like crystals which plug the filters and let the car stop. It turned out, that small amounts of self assembling diblockcopolymers, where one part is crystallisable, remedy the problem. Such diblockcopolymers crystallize in platelet like structures, where the crystalline core is covered on both sides by hairs of the amorphous polymer. Using contrast variation techniques, these structures including their interaction with wax have been investigated in detail by SANS [13]. It turns out, that already a very small fraction of these polymers in the order of few 100 ppm in the diesel oil produce enough nucleators, in order to inhibit the formation of large paraffin crystals. The remarkable part of this application of neutron scattering is that it took only four years from the discovery to commercialisation.

Complexity could also appear in a different way – namely, in combinatorial chemistry, where huge amounts of slightly different samples need to be characterized in a fast way. This is done today often with X-rays but obviously neutrons would be very favourable in many instances but at present intensities are not sufficient. Again future opportunities exist in many different areas, like the component behavior in multicomponent formations like oil additives, shampoos and detergents, food additives and cosmetics. They further include the self organisation of and at interfaces like surface phase transitions, polymers in surfaces, membrane-protein interactions, biosensors and compatibilisation problems. Further self assembly problems concern drug carriers, nanoreactors or smart materials. Mixtures of colloids and polymers are important. There e.g. the depletion interaction needs further to be explored. Also stabilisation layers on colloids and film formation are worth studying. Complex fluids in porous media is another important field. There the phase behaviour needs to be investigated and the transport through the porous media should be studied. Furthermore, wetting phenomena are extremely important.

5.3 Molecular rheology

Among the large number of problems for dynamic experiments, I will restrict myself to the molecular rheology of polymeric fluids, which relates the topology of the macromolecules with their dynamic response and finally with industrial processing. If we compare the rheology of linear polymers with stars, $H$-polymers, combs or trees, then we observe an enormously different rheological behavior. For any molecular design of properties it is essential to understand these phenomena on a molecular basis. We have seen before that for linear polymers reptation is the leading mechanism governing viscoelasticity. We now ask what is going to change for branched polymers. Obviously a branched polymer cannot easily creep out of the tube, but it has to disentangle its arms first.

A molecular understanding of these processes has a number of ingredients. We will just consider two of them. (i) Intuitively we guess that arm retraction will be important. That is the first process: the arms have to retract themselves out of their original tubes; (ii) secondly arm retraction will randomise the arms with the consequence of diluting the conformationally inner parts of the molecule. This process is called dynamical dilution. Furthermore, reptation still plays a role for the final relaxation. The considered mechanisms lead to a large range of time scales and allow, if understood, to tune the processability of polymers.

There are two approaches to study such phenomena. The first tries to quench defined relaxation steps and a study of the result at the SANS machine. This can be done with an in-situ quenching apparatus. Recently, such a device has been build in the frame of a European project at the Jülich facility. Here it is possible to quench a material, to anneal it at a well defined temperature for a given time and to quench it again. In this way the relaxation processes can be studied in-situ [14]. Fig.6a presents the SANS patterns from an $H$-polymer, where the cross bar was deuterated directly after stretch without relaxation. In this case, the poly-
mer is completely confined in the tube. Fig. 6b shows the SANS pattern after 37s. Then the polymer arms have retracted a lot and the tube should have been diluted. The experiment corresponds to a case where about 2/3 of the arms are already free.

The second approach involves dynamic experiments requiring small labels at different topological interesting positions along the branched polymer. Such experiments are a challenge both with respect to intensity and time scale and are most likely reserved for next generation neutron sources.

In the future, we should arrive at a prediction and an understanding of rheological and mechanical properties of polymers on the basis of molecular motion. This will allow us to understand processing and lubrication processes; in particular also non linear rheological phenomena. Mechanical properties like impact strength, brittleness and viscoelasticity could be investigated.

Fields outside molecular rheology involve e.g. conduction processes in rubbery electrolytes, the dynamics of stabilization layers in colloid, the effects of boundary conditions on the dynamics of complex fluids in porous media and so on.

5.4 Outline and link to biology

From the point of view of soft condensed matter research one of the basic problems concerns the suitability of soft condensed matter concepts for the field of biology. Do we understand biological phenomena better, if we try to transfer concepts which have been developed in soft condensed matter to biology? A typical example could be a membrane. In biology we deal with lipid membranes, in microemulsions we have surfactant layers which, as discussed above, could be decorated with polymers in a similar way as lipid membranes with proteins. I like to finish this review with one example, where experiments have been performed on membrane-biomolecular complexes. This has been done by neutron reflection using specular and off specular reflections on stacks of lipid membranes. Neutrons allow a very large range of observation, since they allow positive and negative angles of incidence and one can study the diffuse scattering or the off specular scattering in great detail. The diffuse scattering relates to the
fluctuation spectrum of the membrane which has been beautifully investigated by Münster et al. [15]. They found for example that the correlation length for the lateral fluctuation is in the order of a 1000Å. Furthermore, they have complexed the membranes with antimicrobial peptides. Fig.7 presents the effect of the peptides on the scattering profiles from the stacks.

Adding more and more of peptide leads to a broadening and finally a vanishing of the peak structures resulting from the membranes stacks. A detailed line shape analysis of the scattering profiles then led to models describing the peptide membrane structures. It turned out that the peptide is buried within the membrane. These are only small attempts to use soft condensed matter techniques, in order to approach more biologically oriented problems. Real biological membranes are much more complicated. They are complexes of surfactant like lipids and biomolecules which are highly complex. It remains to be seen how much in the future we can learn about such complex arrangements and interactions by neutron scattering.

6. Conclusion

With this short overview I hope to have shown that soft condensed matter research is a broad and rich field with close links to applications and may be also to biology. Neutrons play a key role in the investigations of this field because they allow to perform observations on the proper length and time scales as well as to exercise hydrogen deuterium contrast variation. Future developments will go in the directions of time dependent phenomena and real time experiments. They will look on non-equilibrium and transient phenomena, they will look on the complexity posed by multicomponent systems, on molecular rheology, in order to understand the functioning of materials, and they will try to exploit the link to biology.

Acknowledgment

I like to thank the Jülich soft matter group, A. Arbe and J. Colmenero from the University of San Sebastian as well as the members of the ESS soft matter group for their input and discussions, which led to outlook into the future of soft condensed matter research presented here.

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Life sciences
New developments for biological deuteration

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A new laboratory is being set up at the ILL/EMBL for the (bio)synthesis of deuterated biological macromolecules. The ability to deuterate samples has for a long time been a key issue for biological neutron scattering. In the past few years this issue has been highlighted by new results and techniques and in previous meetings of the ILL Biology Subcommittee has been flagged as one where a strong commitment would have a major impact on the biological science coming out of the ILL. The development we have proposed will benefit from the strong infrastructure that exists at the EMBL outstation and will provide a key resource for European workers in the field.

1. Background

Neutron scattering experiments provide important information in structural biology that is not accessible by x-ray scattering alone. At low resolution the contrast variation technique is particularly powerful both in solution and single crystal work [1,2]. In its simplest form it can be performed by varying the H2O/D2O content of the solvent to match alternately protein, nucleic acids, or lipids. However, if deuterium labelling of the constituent macromolecules is available, much more sophisticated experiments can be carried out. It becomes, for example, possible to investigate the shape of a single labelled protein within a multi-subunit protein complex or to measure the distance between two labelled subunits within a complex. At medium to high resolution, the ability to determine and distinguish H/D positions in single crystals provides unique information and insight into catalysis, protein-ligand interactions and the protein-solvent interface. Although increasing numbers of ultrahigh resolution x-ray diffraction studies will yield information on the location of well ordered hydrogen positions, x-ray data are unlikely to match neutrons for the positioning of more mobile hydrogen atoms. Support for this comes from the work of Habash et al [3] on concanavalin A, who have shown how neutron protein crystallography yielded more D2O positions than are available by ultrahigh resolution x-ray diffraction studies using cryocooled crystals. Moreover neutron diffraction allows such studies to be carried out at physiologically relevant temperatures. The importance of this type of information is highlighted by the development of the LADI diffractometer in recent years [4-6] and by the high demand for this instrument. In fibre diffraction the advantages of using neutron diffraction for the investigation of solvent structure and hydrogen atom positions around molecules such as DNA [7] and cellulose [8,9] are very clear – no comparable information has been obtained from X-ray diffraction, and instrument D19 at the ILL has a steadily growing portfolio of activity in this area. It should also be noted that the need for deuterated lipids, peptides and proteins is very clear in reflectometry studies of model membranes and of biological processes at interfaces [10]. Specific hydrogenation of deuterated proteins has been powerful in neutron inelastic scattering experiments to study protein dynamics. Here the dynamic information is contained in the incoherent scattering from hydrogen. Experiments on isotope labelled bacteriorhodopsin have provided evidence for inhomogeneous dynamics in this membrane protein, related to biological function [11,12]. Further information on this type of work is given by Zaccai (this volume).

A major challenge confronting neutron work is often the requirement for large sample sizes. For crystallographic and fibre studies in particular this is further exacerbated by incoherent scattering from hydrogen in the solvent and in the macromolecule itself.

Fig. 1: Structure of Inovirus protein sheath. The virion axis is vertical, and the N terminus of the subunit is towards the top. (a) A single coat protein subunit, viewed as if a subunit from the left side of (b) were moved further to the left. The dark circles represent the charged atoms of the acidic and basic sidechains. (b) The assemblage of subunits, each represented by a helical tube through successive C-alpha atoms. Three arbitrary nearest neighbours are indexed as 0, 6 and 11. From D.A. Marvin, Curr. Opin. Struct. Biol. 8, 150-158 (1998).
It is relatively straightforward to replace H2O solvent by D2O for these studies and this results in a huge decrease in the hydrogen incoherent scattering background. However, there is still a large problem arising from the hydrogen that is covalently bound to carbon atoms in the structure. This places severe limitations on sample size, data collection times, the interpretation of the data, and the quality of the final analysis. It has been estimated that for a neutron crystallographic study of a typical protein molecule one can expect a gain of a factor of 10 in signal to noise if the protein is perdeuterated. Experiments on perdeuterated myoglobin [13] and on perdeuterated DNA [14] clearly demonstrate these advantages.

2. The Deuteration Laboratory

Although the benefits of sample deuteration have been widely appreciated for some time, it has never been easy for individual biologists to deuterate their systems in a routine way that allows best use to be made of valuable central facility resources; the expertise is rather specialised and individual requirements vary quite considerably. The idea of creating a dedicated laboratory for this purpose has arisen over the last 2 years or so during which time the ILL, with advice from a number of external peer-review committees, has considered instrument upgrade options as part of its Millennium Programme. In addition to recognising the huge gains that are now possible for biological neutron work by exploiting modern instrumentation and detector technologies, it has also recognised the need to place strong emphasis on the unique opportunities that exist through selective and non-selective labelling of biological macromolecules, and has recommended that a deuteration laboratory be created within the infrastructure of the ILL and the EMBL Outstation. The ILL has therefore made provision for laboratory space within the ILL/EMBL infrastructure and has created a 5-year post for a molecular biologist to run the laboratory. The activities of this laboratory will be supported by a dedicated EMBL technician who is already experienced in in vivo deuteration.

We believe that the provision of such a laboratory is long overdue at the ILL. The neutron scattering facilities at the Institute are amongst the best in the world and we believe that it is essential to fully exploit these facilities with a strong initiative in the sample preparation area. The development of an ILL deuteration laboratory will have a critical impact on the quality and speed of neutron experiments in protein crystallogra-

Fig. 2: Structured water located in the major groove of A-DNA by neutron fibre diffraction. From Shotton et al. [14].

Fig. 3: Results from the work of Shu et al [13], illustrating the power of neutron protein crystallography in the determination of the location of hydrogen atom positions in protein molecules. (a) 2Fo - Fc x-ray map (6Å – 1.5Å data); (b) Fc neutron map, unlabelled protein (6Å – 2Å data); (c) 2Fo - Fc neutron map, deuterated protein (6Å – 2Å data).

Fig. 4: Life sciences

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phy, fibre diffraction, small angle scattering and inelastic scat-
tering, and will bring new science to the ILL in each of these
areas. It will also have implication for solution and solid state
NMR work.

3. Applications in Fibre Diffraction

Selective deuteration methods will be used in a number of fibre
diffraction projects. Two examples are given below. The first one
(see figure 1) concerns structural aspects of filamentous bacte-
riophage. These filaments, which can be lined up to form ordered
samples (with the aid of a magnetic field), consist of nucleic acid
at the centre of the molecule and an outer protein coat. Here there
are unresolved questions about the structure that have not been
clearly answered on the basis of x-ray fibre diffraction data.
There have been two proposals for the structure of the coat pro-
tein subunit itself; it is intended to deuterate parts of the coat
protein so that neutron fibre diffraction can be used to resolve
the issue. There are also questions about the relationship between
the DNA and the coat protein. This will be studied by assembling
phage samples containing (i) deuterated DNA & hydrogenated
protein (ii) hydrogenated DNA & deuterated protein.

The second example is one where deuteration methods can be used
to provide further insights into DNA polymorphism. DNA in the
A conformation has been studied previously by neutron fibre dif-
fraction at the ILL using instrument D19: clear water sites are
visible in the major groove of the molecule and it is likely that a
network of these water molecules and surrounding cations inter-
acting with DNA backbone & base atoms are responsible for sta-
bilising this structure. The aim of this work will be to investigate
the marked stability of A-DNA in certain repetitive base-pair
sequences. Most notable of these are homopolymer G-C sequences.
A-DNA molecules containing deuterated guanine or cytosine
residues (or both) will be used to study the stability of A-DNA.

4. Applications in Protein Crystallography

The advantages of using deuterated protein in neutron protein crys-
tallography have been summarised in section 1. Figure 3 demonstr-
ates many of these points very clearly. It shows the results of
a protein crystallographic study of deuterated myoglobin carried
out by Shu et al. [13]. Figure 3(a) shows a density map based
on x-ray data. The hydrogen atoms are not visible, even at a res-
olution of 1.5 Å. Figure 3(b) shows the type of density map that
can be expected from neutron data with normal (unlabelled)
protein; the hydrogen atoms can be seen but there are problems
associated with cancellation of the negative density from hydro-
gen and positive density from the surrounding atoms. Figure
3(c) shows how these problems are overcome with data recorded
from perdeuterated myoglobin. Deuterium and carbon positions
are all clearly visible.

Fig. 4: (a) Picture (provided by Shing Mok and John Squire) illustrating the actin,
troponin and troponin components of muscle. Experiments where these
components are made to interact in vitro can provide useful information about
the contractile process as shown in (b) where changes induced in troponin
following the addition of calcium, were studied by small angle neutron scattering
(see Stone et al. [15]).
Examples of crystallography projects being planned for the new laboratory are studies of the interaction between integral membrane proteins and lipids (deuterated lipids may help with the interpretation of X-ray studies), experiments to determine the protonation states in the active sites of various enzymes, detailed high resolution studies of eye-lens proteins (e.g., crystallin) to investigate the structure and dynamics of the protein-water interactions as a function of temperature.

5. Applications in Solution Scattering

Examples where deuteration methods can have a powerful impact on small angle neutron scattering work are not hard to find. Any multicomponent system can be studied in detail if various parts of it can be selectively deuterated, so that contrast matching can be used to study the shape and position of one component alone. For example, in vitro SANS studies of muscle components have been carried out. Stone et al [15] have studied troponin regulatory domains, illustrating changes in the relationship between the various troponin subunits following the binding of calcium (see figure 4).

Other solution scattering projects that may exploit the ILL/EMBL deuteration laboratory include studies of molecular complexes that are formed following infection, non-toxic penetration enhancers for the paracellular absorption of drugs, and structural studies of restriction-modification enzymes.

References

Biophysical studies of membrane-membrane and membrane-protein interactions require well controlled model systems. We have developed a new method to obtain a single lipid bilayer floating in excess water, in the vicinity of a fixed bilayer. It has been prepared in the gel phase and characterized using neutron and X-ray reflectivity. By increasing the temperature up to the melting transition of the lipid chains, one can observe a spectacular change in bilayer-bilayer interactions; this is likely due to a diminution of the bilayer’s bending modulus, which we have estimated above, at and below the melting transition. Above the melting temperature, the bilayer becomes fluid and is a stable, biophysically relevant substrate for protein-bilayer interaction studies.

The structure and composition of cell membranes is well known. Less known are the nature and mechanisms of interaction of membranes with other biological entities like peptides, proteins, DNA, etc. Simple, controlled physical models of membranes include lipid stacked multibilayers, vesicles, lamellae, monolayers on the water surface, bilayers on solid surfaces; each with advantages and disadvantages.

We have recently succeeded in preparing a new, promising system: the double phospholipid bilayer [1]. The first bilayer is adsorbed on the flat solid substrate; the second one, the floating bilayer, interacts less strongly with the solid substrate, and floats at 15 to 30 Å above the first. Its properties are remarkable: it fluctuates in bulk water, like real membranes, unlike stacked bilayers or monolayers; it lasts for days, and is stable in the biologically relevant fluid phase; it can be investigated alone (without collective or averaging effects implied by multilamellar systems) with Å-scale techniques, like neutron or x-ray reflectivity; finally it is useful to study how fluctuations influence the interactions of peptides or transmembrane proteins with the cell membrane.

Phospholipid bilayers exhibit a main phase transition from a gel phase, to a liquid crystalline phase where chains are disordered and fluid-like. Neutron specular reflectivity enabled us to study the structural modifications induced on double phosphocholine bilayers by changing the temperature around this transition. After preliminary experiments on the CRG reflectometer ADAM, data were collected on the diffractometer D16, specially adapted for reflectivity, and the new D17 configuration. The double bilayers were assembled on highly hydrophilic, Å-smooth silicon substrates with the Langmuir-Blodgett and Langmuir-Schaeffer techniques, see [1] for details. Phosphocholines were used since they are the main components of cell membranes: here hydrogenated DSPC (di-stearylphosphatidylcholine) in D2O, and deuterated DSPC in H2O or silicon-matched water.

Fig. 1 shows the reflectivity curves recorded at room temperature (25°C), in the pre-transitional phase (51.5°C), just above (53.4°C) and well above (64.1°C) the transition for fully hydrogenated DSPC in D2O. In the gel phase 25- 42°C; (b) 51.5°C; (c) 55.4°C; (d) 64.1°C. Solid lines are best fits with parameters represented in Fig. 2. To facilitate the comparison, vertical lines indicate the positions of minima in (a). Reproduced from [2].
immediately noticeable from the positions of the first minimum in Fig. 1). This free bilayer in fluid phase is an interesting substrate for biophysical studies [2].

The spectacular swelling around the transition temperature could be related to the expected [3] softening of the bilayer's bending modulus, which is visible when data from gel [4] and fluid [5] phases are plotted together (Fig. 3). In fact, the swelling could be due to an increased (entropic) repulsion between bilayers, originating in an increase of position fluctuation [6], which we measure independently. If this interpretation is correct, we estimate the membrane bending modulus (Fig. 3) [7]; the agreement with the completely independent data of refs. [4,5] is surprisingly good. We observe the same sharp minimum: a 250-fold decrease followed by a 6-fold increase over the same width of transition range, and even the same plateau followed by a further decrease at higher temperature. This is probably the first measurement in both lipid phases as well as at the transition between them, on the same sample and with a single method.

Off-specular X-ray scattering (and atomic force microscopy measurements, in preparation) provide information in the membrane plane. Preliminary analysis of the in-plane fluctuation spectrum lead to another independent measurement of the bending modulus, with compatible results; as well as an indication of the residual membrane tension (of order of a few mN/m) [8]. This technique could also apply to membranes containing proteins.

Fig. 2: Sample structure deduced from Fig. 1. Top: bilayer thickness (circles) and inter-bilayer distance (bullets), plotted vs temperature. Insert: inter-bilayer distance vs roughness. Bottom: schematic view drawn to scale along the vertical axis. Reproduced from [2].

Fig. 3: Bending modulus of DSPC bilayers deduced from these experiments in both phases. Published data for DMPC have been measured either in gel or in fluid phase; to facilitate comparison, the ordinate has been normalized, and the abscissa has been referred to the transition temperature.

REFERENCES

Concerted motion of protons in hydrogen bonds of DNA-type molecules

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We study the dynamical behaviour of the proton transfer in the hydrogen bonds in the base-pairs of the double helices of the DNA type. Under the assumption that the elastic and the tunnelling degrees of freedom may be coupled, we derive a non-linear and non-local Schrödinger equation (NLNLS) that describes the concerted motion of the proton tunnelling. Rough estimates of the solutions to the NLNLS show an intimate interplay between the concerted tunnelling of protons and the symmetry of double helix.

I. The recent direct observation of coherent proton tunnelling \cite{1} has focused the attention on systems allowing for the nontrivial dynamics of protons contained in hydrogen bonds. Perhaps, the most significant system of the kind is the DNA molecule. The importance of the phenomenon was noticed soon after the DNA double helix had been discovered (see \cite{2}). In fact from the chemical point of view the proton transfer is a so-called tautomeric reaction, that is a kind of transition that preserves the constituent atoms of a compound but at the same time changes their mutual positions. It has been believed that the tautomerism reaction could provide a mechanism for genetic mutations \cite{2}.

In the present paper we would like to draw attention to the fact that if the tautomeric transitions are coupled with a change in elastic properties of the DNA molecule, one could expect a concerted tunnelling of the protons in the hydrogen bonds. Taking into account the extremely sophisticated nature of the system, i.e. the DNA molecule, we aim at studying it in a qualitative framework, which takes into account, the main features of the molecule, i.e. the presence of the two strands, the helical structure, or the winding symmetry, and the dynamics of protons considered within the approximation of two-level systems.

II. Aiming at a simple model, we shall describe the states of the hydrogen bonds as those of a one-dimensional Bose oscillator, the two-level requirement being accommodated by considering only its ground state and the lowest excited one. In this sense the tautomeric reaction of the proton transfer is described by the excited state of an oscillator. Thus, we shall consider the protons inside the hydrogen bonds of a molecule of DNA as a quantum system described by the Bose operators $b_\uparrow, b_\downarrow$. We shall suppose that the system of the protons is in a weakly excited state that can be cast in the form of wave function

$$D(t) := \sum_n A_n(t) b_n^\dagger 0 >$$

in which $A_n(t)$ are complex amplitudes.

The Hamilton of the total system, that is the protons and the elastic part corresponding to the sugar-phosphates, reads

$$H = H_p + H_e + H_I$$

where $H_p$ is the proton Hamiltonian, $H_e$ is that of the elastic part, and $H_I$ is the interaction between them.

The standard procedure to treat the problem\cite{3,4} leads to a NLNLS equation. We are looking for the solution in the propagating wave (soliton). It is easy to find the first integral of the equation, i.e. the energy and obtain the asymptotic width of the soliton. The frequency of elastic oscillations is generally accepted to be within $10^{11} - 10^{13}$ Hz, but the average estimates for proton dynamics widely diverge. Consequently, the width of the solution varies $10 - 1000 \text{ Å}$, so that one may expect a concerted tunnelling of protons for the lower estimation of the width.

III. Concluding, we should like to draw attention to the fact that the existence of an appreciable interaction between the proton transfer inside the hydrogen bonds of the double helix, and elastic modes of the latter, could result in a concerted dynamics of the protons which is generally of non-linear character and governed by the non-linear and non-local Schrödinger equation. Of course NLNLS equation we obtained has a larger scope. It may not imply the existence of solitons in DNA, but could open another possibility, the possible existence of nonlinear localization leading to a collapse of an initially broad excitation into a highly localized deformation \cite{5}. Collapse does not occur in the standard one dimensional NLS equation, but the existence of nonlinearities with higher power in our NLNLS suggest that it could occur in this equation, although, as these terms are non local, no definite conclusion can be given without further studies of the equation. If this
hypothesis would be confirmed, a weak and broad perturbation of the hydrogen bonds of DNA molecule by the vicinity of an enzyme carrying local charges could trigger this nonlinear localization phenomenon and finally lead to the formation of a tautomerized form by the tunnelling of one proton.

REFERENCES
A novel histone octamer (O') and a novel histone tetramer (T') which are devoid of all their N-terminii (N tails) through totally selective cleavage of solubilized chromatin by an Arg-C endopeptidase (clostripain) were characterized by small- and wide-angle neutron scattering (SANS and WANS, respectively) in solution. An atomic model for O' was derived from the available 2.8 Å resolution X-ray structure of the nucleosome core particle by eliminating the DNA and the corresponding histone N tails. The calculated WANS curve appears to be closely related to the experimental curve, thus suggesting that O' in solution adopts a similar arrangement to that found in the nucleosome, independently of the conformationally less well-defined peripheral N tails. Using an atomic model for T' that is obtained by eliminating the H2A and H2B histones from the above mentioned O' model, the calculated WANS curve, although close, significantly deviates from the experimental one. It is tentatively concluded that T' in solution is conformationally distinct from the tetrameric central core within the intact nucleosome.

1. Introduction

The fundamental unit of chromatin in the eukaryotes is the nucleosome. It is made up of a stretch of double-stranded DNA superhelically wrapped around an octameric core that is composed of two each of the core histones H2A, H2B, H3 and H4 [1]. Extensive digestion of chromatin with micrococcal nuclease releases a stable nucleoprotein particle, the so-called nucleosome core particle (NCP) which contains ca. 146 bp of DNA and the central histone octamer (H2A.H2B.H3.H4), X-ray crystallography which led, in 1984, to the first determination of the topology of the nucleosome core particle at a resolution of 7 Å [2] has culminated in the past years in the elucidation of the three-dimensional organization of this nucleoprotein particle at 2.8 Å resolution [3]. In parallel, structural studies with the DNA-free histone octamer have led to the determination of its 3D structure by X-ray crystallography at 3.1 Å resolution, thus confirming the tripartite organization of the octamer [4, 5], as well as its intrinsic 2-fold symmetry, with a central tetramer (H3.H4), flanked by two peripheral dimers H2A.H2B. Each core histone involves two distinct domains within the octameric assembly: (i) a highly structured C-terminal region including about 80% of the residues, (ii) an unstructured (or conformationally variable) N-terminal tail (comprising about 20% of the residues) which interacts with the DNA at the periphery of the nucleosome. The histone N tails are substrates to a variety of post-synthetic enzymes and are intimately linked to chromatin function during replication and transcription, as well as in a more general manner to cell cycle progression [6]. It has been shown that the N tails of histones H3 and H4, at a low level of post-synthetic modification, are highly organized as DNA-bound polypeptide segments in NCP, with about half of their residues, taken together, being α-helical [7]. Recently, evidence has emerged that the central tetramer (H3.H4), by itself, could interact with DNA in chromatin and reg-
ulate its topological features (superhelicity) based on \textit{in vitro} experiments in which the DNA-free tetramer is bound to a short circularly closed DNA of controlled superhelicity [8]. Furthermore, the histone tetramers containing enzymatically hyperacetylated histones show preference for relaxed DNA over negatively supercoiled DNA [9], thus suggesting that the effect of histone N tail acetylation that facilitates transcription may be mediated via transient formation of a tetrameric particle with an \textit{open} structure. It has been established in our laboratory (JLB, JP) that all four core histones H2A, H2B, H3 and H4 can be proteolyzed with high selectivity in the chromatin complex by an Arg-C endopeptidase (clostripain) to yield a proteolyzed octamer $[H'_{2A}.H'_{2B}.H'_{3}.H'_{4}]_2$, or O’, which is devoid of all its N tails [10-12]. We report here on a comparative neutron scattering study (at small and wide angles) of O’ and T’ in solution, with the aim to understand the topological features of these DNA-free histone sub-assemblies in comparison to the presently known crystal structures.

\section*{2. Results and discussion}

As shown in Fig.1, both protein particles, O’ and T’, were characterized by SANS, thus yielding a gyration radius (Rg) value of 25.8 ± 0.4 and 20.3 ± 0.2 Å, respectively, in agreement with the general topology of each particle, as inferred from the crystallographic data (see above). The forward scattered intensities are in good agreement with the corresponding masses (to be published). O’ and T’ also differ markedly by their scattering features at wider angles (Fig.2). Two atomic models were selected to predict the scattering features of both particles. As shown in Fig.3, the octamer in the NCP crystal structure is closely related to our octamer O’, although some differences exist in particular for one of the H3 histones (chain A). The calculated WANS curve closely fits the experimental one (Fig.2A), with an Rg value of 26.4 Å close to the value determined by SANS (see above). An atomic model for T’ was then derived from the O’ atomic model upon elimination of both dimers H2A,H2B. As shown in Fig.2B, the predicted WANS curve, although close to the experimental one, significantly deviates from the latter at Q > 0.14 Å$^{-1}$ (of special interest is the « shoulder » at ca 0.2 Å$^{-1}$ in the calculated curve apparently absent in the experimental one; full details of these calculations will be given elsewhere). Independently of our calculations based on both atomic models, we also performed a modeling with spherical objects to account for the histone mass distribution in O’ and T’ based on the 7 Å resolution structure of NCP [2]. Besides affording a good fit (not shown) of the experimental O’ WANS curve, such geometrical modeling indicates that even small departures from the initial topology yield significant changes in the WANS curve of O’, as well as in that of T’. Such a combination of experimental (SANS+WANS) measurements and theoretical predictions could provide us with a rather accurate description of the conformational variability of these histones.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Wide-angle neutron scattering (WANS) measurements with: (A) the proteolyzed histone octamer O’ (6 mg/ml in D$_2$O buffer : 2M NaCl, 10 mM Tris-HCl, 1 mM EDTA, 0.2 mM PMSF at pH 7.75), (B) the proteolyzed histone tetramer T’ (3.7 mg/ml in D$_2$O buffer: 25 mM Na-succinate, 125 mM NaCl, 0.2 mM EDTA at pH 5.05; pH values uncorrected for 2H effects at 20°C), using the D11 scattering device at ILL, Grenoble (neutron wavelength 6 Å, sample-detector distance 120 cm ; all measurements at 34°C using 2 mm quartz cuvettes). Common symbols in (A) and (B): filled dots, experimental data; empty dots, simulated data (see text). Error bars lie within the symbols with the exception at large Q values for which they are apparent.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Comparison of the common domains in the clostripain-proteolyzed core histones H$'_{2A}$, H$'_{2B}$, H$'_{3}$ and H$'_{4}$ (as in the O’ octamer and the T’ octamer) and in the intact histones visualized on the X-ray crystallographic structures of the DNA-free native octamer (ref.4) and of the nucleosome core particle (ref.3).}
\end{figure}
tone assemblies in solution in comparison to the known structures in the crystal. This is certainly of paramount importance with regard to the possibility of a disassembling of the histone octamer under physiological conditions. A methodological caveat needs to be introduced at that level. As shown in Fig.4A, the O'-like octamer that is inferred from the NCP X-ray structure (upon removal of the DNA and the histone N tails) displays radial protuberances which are likely not to be present in the DNA-free octamer at high salt (see Fig.4B) and this could significantly bias our calculations. Similarly, T' in solution, at relatively low ionic strength (Fig.2B), might have a topology, in the absence of both dimers HA.HB, that differs from the topology in the integrated structures (i.e. the X-ray structures of NCP and of the DNA-free octamer). Finally, our present studies with crystals of T' could help understand the structural features of the isolated DNA-free histone tetramer.

Fig. 4: “Silhouettes” of two O'-type octameric assemblies (all atoms included with the exception of bound water molecules) viewed approximately along an axis perpendicular to the 2-fold axis of symmetry of the protein assembly, obtained from: (A) the NCP crystal structure after removing the DNA and, when possible, adjusting the histone N tail lengths to those in the clostripain-proteolyzed histones (see Fig.3). The long radial protuberance (upper left) is due to the N-terminal region (starting from residue 27) of H3 chain E. (B) the crystal structure of the DNA-free octamer (all N tails are shorter than required with the exception of H2A; see Fig.3).

REFERENCES
Dynamical Properties of Carbonmonoxy-Myoglobin Embedded in Trehalose Matrices of Different Water Content Studied by FTIR and Elastic Neutron Scattering

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Embedding myoglobin in a dry trehalose matrix strongly inhibits the non-harmonic contributions to the internal protein motions (protein specific motions). These contributions have been thought to arise from the thermal fluctuations of a protein molecule among different conformational substates. We report here on the dynamical behavior of carbonmonoxy-myoglobin embedded in trehalose matrices (trehalose coated) of different water content. In particular we measured the thermal interconversion among A substates (by FTIR) in the 263-323 K temperature interval and the mean square displacements of the hydrogen atoms (by elastic neutron scattering) in the 20-340 K temperature interval. The results indicate that both the non-harmonic contributions to the hydrogen atoms mean square fluctuations and the thermal interconversion among A substates depend on the sample water content in a parallel way. This shows the strict correlation at room temperature between the so-called protein specific motions, detected by the hydrogen mean square fluctuations, and the interconversion among MbCO A substates.

1. Introduction

Trehalose is a non-reducing disaccharide of glucose found in nature in some organisms (like some desert plants) that can afford conditions of extreme dehydration and exposure to high temperature, in a state of suspended animation, called anhydrobiosis. Under such conditions these organisms remain in the absence of any metabolic process; however, following re-hydration their vegetative cycle restarts. This property has been put in relation with the presence in these organisms, when in anhydrobiosis, of large concentration of trehalose [1,3]. Moreover, this sugar has been found to be the most active saccharide for the long preservation of biostructures, such as isolated proteins, membranes and liposomes [4-6].

Several studies showed that in a dry trehalose matrix the non-harmonic contributions to the protein motions (protein specific motions) of Carbonmonoxy-myoglobin (MbCO) are strongly hindered. This has been evidenced by several techniques, like CO rebinding after flash-photolysis [7,8], Mössbauer and optical absorption spectroscopy [9], neutron scattering [10] and molecular dynamics simulations [11]. In order to understand up to which extent the inhibition of protein specific motions in trehalose coated MbCO is related to the interconversion among conformational substates, we performed FTIR and elastic neutron scattering experiments on samples of trehalose coated MbCO with different content of residual water. FTIR experiments gave information on the thermal interconversion among A substates. These are the conformational substates which correspond to three specific environments experienced by the bound CO within the heme pocket [12] and are reflected in the splitting in three different sub-bands of the CO stretching band [13]. Elastic neutron scattering was used to measure the hydrogen atoms mean square displacement as a function of temperature.

2. Materials and methods

Horse myoglobin and trehalose were from Sigma (St. Louis, MO, USA) and Hayashibara Shoji (Okayama, Japan), and were used without further purification.

FTIR measurements were performed in the temperature range 263-323 K on a Jasco 410 FTIR spectrometer, with 2 cm⁻¹ resolution. A solid sample of trehalose coated MbCO was obtained by drying of a suitable solution of MbCO and trehalose [14,15]. The solid sample was then further dried for 15 h at 353 K, under room pressure and moisture. A first set of measurements was performed with the dry sample. The same sample was then overnight re-hydrated in a 60% relative humidity H₂O atmosphere, before performing a second set of measurements.

Elastic neutron scattering measurements were performed in the temperature range 20-340 K at the back-scattering spectrometer IN13 (ILL, Grenoble) on a solid sample obtained by drying of a suitable solution of MbCO and trehalose [10] treated as for FTIR experiments. The same sample was investigated both in the dry state and following overnight re-hydrated in a 75% relative humidity D₂O atmosphere.

In the elastic limit (ω=0), and for Q→0, the dynamical structure factor can be expressed within the framework of a Gaussian approximation [16]:

$$\lim_{\omega \to 0} \left[ \ln[S(Q, \omega = 0, T)] \right] = -<\Delta x^2> \cdot Q^2$$

where the quantity

$$<\Delta x^2> = -\left[ \frac{d \ln[S(Q, \omega = 0, T)]}{d Q^2} \right]_{\omega \to 0}$$
is the overall atoms mean square fluctuation taking place within the instrument timescale resolution (~100 ps). Fitting of the data was performed after standard treatment for instrument corrections.

3. Results

Fig. 1a,b shows the normalized absorption band of the bound CO in MbCO (which reflects the A substates), in the dry and in the re-hydrated sample, in the temperature interval 263-323K. Moreover, Fig. 1c,d shows the difference-spectra, obtained by subtracting from each spectrum of a given sample the spectrum at the lowest temperature of the same sample. As it is evident from the data shown, the spectral profile sizeably depends on temperature only in the re-hydrated sample. In agreement with previously reported data [14], this puts forward that the thermal interconversion among A substates strongly depends on the sample water content, although a small temperature dependence of the spectral profile is present also in the dry sample.

Fig. 2 shows the overall mean square displacements of the hydrogen atoms of the system, in the dry and in the D_2O re-hydrated sample, obtained in the neutron scattering measurements. As evident, the neutron scattering data fully agree with the ones obtained in FTIR measurements. Indeed, much larger non-harmonic contributions to \(<\Delta x^2>\) are present in the re-hydrated sample, thus confirming that these non-harmonic contributions stem from the interconversion among conformational substates. In a previous work Cordone et al [10] reported that in an extremely dry trehalose coated MbCO sample the hydrogen atoms mean square displacements obey the harmonic model in the whole temperature interval (20-310K) investigated, ad are of lower amplitude than the presently reported ones. Work is in progress to ascertain the origin of the slight differences between the presently reported mean-squared displacements in the dry sample and those reported in ref. [10]. It is worth to remind that the dry sample, used in the first run of neutron scattering measurement, contained MbCO, non-deuterated trehalose and traces of residual water (H_2O); for the second run of measurements the sample was re-hydrated with D_2O.

Acknowledgements

This work is part of a project co-financed by the European Community (European Funds for Regional Development).

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Incoherent Neutron Scattering Functions for Combined Dynamics

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Two dynamics models, the additive and multiplicative dynamics, constructed from the combination of the jump dynamics and diffusion inside a sphere are considered. The EISF and scattering correlation function are derived for these combined dynamic models. We find for the two models that the resulting EISF is essentially dominated at low Q by the EISF of motions with larger excursions, and the scattering correlation function at low Q has a biexponential relaxation in contrast to either jump dynamics or diffusion inside a sphere.

There are two kinds of conventional dynamic models that are often used in the incoherent neutron scattering analysis to study motions of particles (atoms, molecules, chemical species, ...) in biological systems: the jump dynamics between two sites and diffusion inside a sphere with impermeable surface [1-4]. In the jump dynamics, the particle is assumed to successively jump among two non-equivalent sites separated by a distance a with $\tau_1$ and $\tau_2$ being the residence times in each site. For this model, the incoherent intermediate scattering function, $I(Q,t)$, writes as $I(Q,t)=\frac{A_0(J(Qo))}{[1-A_0(J(Qo))]} C(t)$ where $A_0(J(Q))$ is the elastic incoherent structure factor (EISF) and $C(t)$ is the incoherent scattering correlation function given by

$$A_0(J(Q)) = 1-2p \ [1-p] \ [1-J_{1/2}(Qa)].$$

$$C(t) = e^{\Gamma t}$$

The $J(n)$ is the spherical Bessel function of the first kind of order l, $p=\tau_1/\tau_2$ is the probability of finding the particle in one of the sites and $\Gamma=\tau_1^{-1}+\tau_2^{-1}$ is the relaxation rate. The jump model has been found to be a reasonable approximation for describing the internal molecular motions and to interpret the dynamical transition in proteins [5-6].

In the other model, one assumes that the particle undergoes isotropic diffusive motion with the diffusion constant $D$ inside a sphere of radius $R$ with impermeable surface [2]. In this case also, the incoherent intermediate scattering function writes as $I(Q,t)=\frac{A_0(J(Qo))}{[1-A_0(J(Qo))]} C(t)$ where the EISF $A_0(J(Q))$ and the correlation function $C(t)$ are given by [2,7]

$$A_0(J(Q)) = \frac{3J_2(QR)}{QR^2}$$

$$C(t) = \sum_{n=\pi}^{\infty} \frac{A_1(Q)}{1-A_0(J(Qo))} e^{-\Gamma n^2 t}$$

The high order amplitudes $A_n(J(Q))$ and the roots $x_n\approx 2.082, 3.342, 4.493, \ldots$ are given in Refs. [2,7]. For $Q$ small, $C(J(Q),t) = e^{\Gamma t}$ where $\Gamma = 4.33D/R^2$ is the reciprocal of the typical time for a particle to diffuse over the entire sphere. In the opposite limit of high $Q$, we have $C(J(Q),t) = e^{\Gamma Q^2}$. Such an analysis has been used by several authors [4,8,9] to study, for instance, the internal dynamics, structure and dynamics of surface molecules in proteins.

In all these studies, the effective motions of particles (mainly hydrogen atoms) are assumed to be described by either the jump dynamics or diffusion inside a sphere, except for harmonic vibrational motions which are treated in the same manner. However, experimental evidence indicate that motions of H atoms reflect in fact the global behavior of a sample because they move with the larger chemical groups (such as amino acid side chains) to which they are bonded [10,11]. Since the subunits composing the larger group may undergo different dynamics, the H atom motions, and thus the neutron scattering profiles, could then originate from the combination of both the jump dynamics and diffusion inside a sphere. Various scenarios combining these dynamics can be envisaged. In this note, we consider two simplest combinations of jump dynamics and diffusion inside a sphere one can imagine.

1. **Additive Dynamics**

Consider that the protein system consists of a fraction $\phi$ of H atoms following the jump dynamics and the remaining fraction (1-$\phi$) undergoing diffusion inside a sphere. Such a situation stands when the system is dynamically heterogeneous. In this case, the scattering function is the incoherent summation, $I(Q,t)=\phi I(Q,t)+(1-\phi)I_0(Q,t)$ where $I(Q,t)$ and $I_0(Q,t)$ are the incoherent intermediate scattering function corresponding to the jump dynamics and diffusion inside a sphere, respectively. $I(Q,t)$ can be rewritten as,

$$I(Q,t) = A(Q)+[1-A(Q)] C(Q,t)$$

where the EISF and the correlation function are

$$A(Q) = \phi A_0(J(Q)+[1-\phi] A_0(J(Q))$$

$$C(Q,t) = \phi C(t)+(1-\phi) C_0(t)$$

with the corresponding $A_0(J(Q))$’s and $C(t)$’s given above.

Figure 1 shows the EISF in Eq.(4a) as a function of $QR$. When $Q$ is small and $\phi$ fixed, $A(Q)$ essentially follows the EISF of motions...
with a larger excursion. This corresponds to \( A_{\phi}(Q) \) of a sphere for \( r \leq R \) and to \( A_{\phi}(Q) \) of two sites for \( QR \). For higher \( Q \), however, \( A(Q) \) tends to \( A_{\phi}(Q) \) (which never reaches zero) since \( A_{\phi}(Q) \) goes down to zero as \( QR > \pi \).

The correlation function \( C(Q,t) \) in Eq.(4b) has a biexponential decay for both small and high \( Q \). This behavior is illustrated in Fig.2 for \( Q = 0 \) and for various \( \phi \) and ratio \( \Gamma' / \Gamma' \).

2. Multiplicative Dynamics

Now, assume that the position \( r(t) \) of the \( H \) atom particle can be decomposed into two independent parts, \( r(t) = r_j(t) + r_d(t) \), where \( r_j(t) \) and \( r_d(t) \) evolve following respectively the jump dynamics and diffusion inside a sphere as described above. Each position \( r_j(t) \) and \( r_d(t) \) may either represent the equilibrium position within the host heavy molecule and the displacement of the equilibrium position, or vice versa. In any case, the Green’s function describing the time evolution of \( r(t) \) for such a dynamics factorized as, \( G(r,t) = G_j(r,t) G_d(r,t) \), where \( G_j(r,t) \) and \( G_d(r,t) \) are the Green’s functions corresponding to the jump dynamics and diffusion inside a sphere, respectively. Thus, it follows from this that the resulting \( h(Q,t) \) of the system is a product, \( h(Q,t) = h_j(Q,t) h_d(Q,t) \) and can be rewritten as in Eq.(3) where the EISF and the correlation function are

\[
A(Q) = A_{\phi}(Q) A_{\phi}(Q),
\]

\[
C(Q,t) = \frac{1}{\Gamma' / \Gamma'} \{ A_{\phi}(Q) [1 - A_{\phi}(Q)] C_j(t) + A_{\phi}(Q) [1 - A_{\phi}(Q)] C_j(Q,t) + [1 - A_{\phi}(Q)] [1 - A_{\phi}(Q)] C_j(Q,t) \}
\]

with the corresponding \( A_{\phi}(Q) \)’s and \( C_j(t) \)’s given above.

Likewise, Fig.3 shows the EISF in Eq.(5a) as a function of \( QR \). As in the previous model, \( A(Q) \) is dominated by the EISF of motions with a larger excursion. That is to say that when \( Q \) is small, \( A(Q) \) is close to \( A_{\phi}(Q) \) of a sphere for \( QR \) and to \( A_{\phi}(Q) \) of two sites for \( QR \). While \( A(Q) \) tends to \( A_{\phi}(Q) \) as \( QR \) gets larger.

When \( Q \to 0 \), Eq.(5b) reduces to

\[
C(0,t) = \alpha e^{\Gamma t} + (1 - \alpha) e^{\Gamma t}
\]

\[
\alpha = \frac{5p(1-p) \beta^2}{5p(1-p) \beta^2 + 3K^2}
\]

This relation is exactly identical to Eq.(4b) at \( Q = 0 \) with the correspondence \( \phi = \alpha \). Accordingly, a may be regarded as the fraction of the motion experiencing jump dynamics. This feature is illustrated in Fig. 2 displaying the superimposition of \( C(0,t) \) in Eq.(6) with that in Eq.(4b). In the opposite limit of high \( Q \), however, Eq.(5b) reduces to a single exponential, \( \lim_{Q \to \infty} C(Q,t) = e^{\alpha \Gamma t} \).
3. Concluding Remarks

Additive and multiplicative dynamics models briefly discussed above represent the two simplest combinations of jump dynamics and diffusion inside a sphere one can consider. From their EISF, the two models appear to be substantially very different. At low $Q$, the resulting EISF is dominated by the EISF of motions with a larger excursion in both models A and B, while at high $Q$ it follows the EISF of jump dynamics, for model A, and the EISF of diffusion inside a sphere, for model B. Moreover, the mean-squared displacement of the particle is

$$\langle x^2 \rangle = -3 \left( \frac{d \ln |A(Q)|}{d (Q^2)} \right)_{Q \to 0} = \phi p (1 - p) a^2 + (1 - \phi) \frac{3 R^2}{5}$$  \hspace{1cm} (7a)

for the additive dynamics model and,

$$\langle x^2 \rangle = p (1 - p) a^2 + \frac{3 R^2}{5}$$  \hspace{1cm} (7b)

for the multiplicative dynamics model. Since $0 \leq \phi \leq 1$, it is clear that $\langle x^2 \rangle$ in the additive dynamics is smaller or equal to that in the multiplicative dynamics model.

Surprisingly, the scattering correlation function, $C(Q,t)$, are identical for the two models in the small $Q$ limit where the EISF (and thus the $\langle x^2 \rangle$) are quite different from each other. In this limit, $C(Q=0,t)$ has a biexponential relaxation with rates $\Gamma$ and $\Gamma_\gamma$ in contrast to either jump dynamics or diffusion inside a sphere. The difference between the two $C(Q,t)$ appears in the definition of fractions $\phi$ and $\alpha$ which may have different behavior with, for example, temperature. At high $Q$, the relaxation of $C(Q,t)$ remains biexponential for the additive dynamics while it reduces to a single exponential for the multiplicative dynamics.

Finally, it may be interesting to mention the limiting cases of the additive and multiplicative dynamics models. When $a \to 0$ and $\Gamma \to 0$ (or $R \to 0$ and $\Gamma_\gamma \to 0$) the additive dynamics model reduces to the Bellissent-Funel et al. [4] like analysis which deals with the fraction of mobile and immobile H atoms. The same kind of limits reduce the multiplicative dynamics model to the jump dynamics, for $R \to 0$ and $\Gamma_\gamma \to 0$, and to diffusion inside a sphere, for $a \to 0$ and $\Gamma \to 0$.

Acknowledgments

My thanks to E. Kats for critical reading of the manuscript.

References

Contrast enhancement in polarised neutron scattering by selective proton polarisation in macromolecules

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We aim at taking advantage of the possibility to create clusters of polarised protons in organic materials in order to investigate by polarised neutron scattering different parts of macromolecular structures in a more detailed way. Small-angle polarised neutron scattering in organic materials has shown that strong proton polarisation gradients can be created at free radical sites by dynamic nuclear polarisation combined with high frequency saturation and/or adiabatic fast passage polarisation reversal. Decay times of the non-uniform proton spin polarisation between 0.5 s and 20 s were observed by time-resolved experiments at D22 of the ILL. Work is in progress for the better understanding of the proton spin dynamics involved in view of an interesting, eventually powerful application of neutron scattering.

1. Introduction

Early experiments of polarised neutron diffraction from polarised proton spins in a single crystal of lanthanum magnesium nitrate were done at Harvard, Rutherford-Appleton Laboratory and the ILL in the seventies [1]. In the mid eighties the polarisation of protons and diols opened the way to nuclear spin contrast variation in biomolecules [2] and polymers [3], in which an existing contrast due to specific deuterium was enhanced by proton spin polarisation. In order to observe the influence of proton spin polarisation on polarised neutron scattering cleanly, the deuterons were depolarised selectively by a radio frequency scan through the deuteron NMR spectrum, while experiments of deuteron spin contrast variation required the selective depolarisation of proton spins. In the process it was observed that the depolarisation of proton spins near radical sites could be less readily achieved than for those in the bulk. This observation, confirming the prediction of Hayter, Jenkin and White [1], has suggested to investigate the possibility to perform polarised neutron scattering from selectively polarised proton spin domains in macromolecules. First results from experiments done at the ILL in August 2000 will be presented.

2. Nuclear spin polarisation in insulators

In most hydrogenous materials high degrees of nuclear spin polarisation can be achieved by the method of dynamic nuclear spin polarisation (DNP). In samples containing a few paramagnetic centres, at temperatures T ≤ 1 K and in magnetic field B > 2 T irradiation with microwaves at a frequency slightly off the electronic spin resonance will polarise all non-spinless nuclei to a degree which varies with the nuclear magnetic moment. The direction of nuclear polarisation with respect the external field can be chosen by applying different microwave frequencies.

3. Measurement and control of nuclear polarisation by NMR

NMR techniques are needed for the measurement of the polarisation of the various polarised nuclear spin systems in the sample as well as for selective nuclear depolarisation and adiabatic fast passage (AFP) spin reversal [4]. Radio frequency scans restricted to the peak area of the proton NMR will reverse the spins away from the radical site whereas an rf scan over the outer wings of the NMR line will affect the protons near the radical.

4. Solution studies on a metallo-organic complex

Solutions of an organic complex of Cr(V) (CrO₇C₈H₂O) (c=25 g/l) in a mixture of glycerol/water (1:1) with different degrees of deuterium have been studied by polarised neutron scattering. All samples were kept in a field of 3.5 T at a temperature of 1 K. In a first run, the protons of the sample were polarised and the polarisation of the proton spins of the bulk was reversed by AFP. As is shown in Figure (1) the polarisation of the protons of the Cr(V) complex (P=+24%) as obtained from neutron scattering differs from those of the solvent after AFP (P=-14%, from NMR) by almost 40%. The difference in proton spin polarisation decreases to 1/e in about 12 s and after 40 s the internal equilibrium has been reached at P = +4%.

Similar results were obtained from monitoring neutron scattering during DNP starting from a nearly unpolarised sample. The polarisation of the protons of the Cr(V)-complex reaches 25% after...
20s microwave irradiation, while the polarisation of the bulk protons in the deuterated solvent is about 8%.

The analysis of neutron scattering data is facilitated by the fact that the change of the contrast is almost entirely due to the polarisation of the protons in the Cr(V)-complex. As the concentration of the protons in the deuterated solvent is small – there is one proton among 30 deuterons - their influence on the contrast is almost negligible.

There is further a variation of the radius of gyration of the Cr(V)-complex with the proton polarisation. As the positive polarisation of the protons of the Cr(V)-complex decreases, the initial negative contrast of the Cr(V)-complex increases to even more negative values. The increase of radius of gyration is a clear hint that the hydrogen atoms of the Cr(V)-complex are close to the molecular surface.

With lower deuteration of the solvent the internal equilibrium is reached more quickly. The time of internal relaxation decreases to 2 s at 85% deuteration of the solvent and to some tenth of a second in the absence of deuteration.

5. Solution studies on a radical which is part of a protein

Catalase is an enzyme which decomposes hydrogen peroxide HOOH into water and oxygen. Peroxy acetic acid HOOCOCH₃ poisons the enzyme. For catalase from bovine liver, one conse-
quence of the inhibition is the formation of a tyrosyl radical within a couple of minutes after addition of peroxyacetic acid, which can be monitored by EPR [5]. Various tyrosins of the amino acid sequence have been proposed as candidates for tyrosyl formation. At present TYR-369 is the most probable one, with TYR-TYR distances which may vary between 16 Å and 26 Å inside the tetramer catalase molecule.

Neutron scattering from a frozen solution of 5% catalase with about 30% yield of tyrosyl dissolved in deuterated solvent shows that the tetramer has aggregated to octamers. There is a variation of the intensity of neutron scattering after DNP and AFP (as above) of the order of 1% within the first two seconds. As is shown in Fig. 2, the variation in intensity changes with the momentum transfer Q. It is positive with small Q and changes its sign at $Q = 0.06 \text{ Å}^{-1}$, $0.08 \text{ Å}^{-1}$ and $0.11 \text{ Å}^{-1}$. An analysis based on a spherical symmetric model shows that the average distance (45 Å) of the tyrosyl sites is about half the radius (75 Å) of the catalase particle.

Another internal relaxation follows at a time scale of 5s to 15 s. Its variation with Q is quite similar to that of the scattering intensity of the catalase particle, i.e. there is a change of the uniform proton spin polarisation of the protein. The exchange rate of polarisation across a boundary separating the protiated particle from the deuterated solvent is the same as that of the Cr(V) complex discussed above.

6. Conclusions.

Polarised neutron scattering from selectively polarised nuclear spin systems is an extremely sensitive tool for structural and dynamical studies on dilute paramagnets. The finite lifetime of the polarisation domains serves to localise the paramagnetic centres. Moreover, the method is extremely sensitive to changes in size and/or contrast of these domains due to the difference method of subtracting the scattering at different evolution times. Polarised neutron scattering from the creation and the decay of selectively polarised protons has been observed at 200 µM radical concentration where NMR ceases to monitor internal relaxation. Samples with still lower concentrations of paramagnetic centres are well within the reach of polarised neutron scattering which is of interest for the study of radicals in other macromolecular redox systems.

References
Supramolecular systems
Single chain motions in flexible polymers by neutron spin echo

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By means of neutron spin echo we have carried out a comparative study of the single chain motions in the melt and in dilute solution of the orientationally hindered polyisobutylene (PIB) and the dynamically very flexible poly(dimethyl siloxane) (PDMS) chains. Motional processes from the center of mass diffusion, the Rouse/Zimm dynamics to the more local relaxation processes were elucidated. In the melt, PIB displays a strong influence of local dynamics while PDMS follows the Rouse dynamics up to high momentum transfer values. Damping effects related to an internal viscosity of the chain are deduced to be the most important limiting factor for the universal dynamics in PIB. In dilute solution, the intrachain dynamics of PIB was evaluated on the basis of the PDMS results, which were taken to reflect as in the melt “ideal” relaxations. The so obtained characteristic relaxation time of the intrachain viscosity agrees well with the rotational barriers in PIB, corroborating the underlying physical idea of a delayed redistribution of conformational states to be at the origin of internal viscosity effects.

1. Introduction
The large scale motions in homopolymer melts and solutions are largely determined by chain connectivity effects or entropy and in solutions additionally by hydrodynamic interactions.[1] In a length scale regime where topological interactions are not yet important, the standard model for polymer chain dynamics in the melt, the Rouse model, considers the conformational entropy as the only source for restoring forces which stabilizes excursions from equilibrium. However, at shorter length scales where the simplifying assumptions of this model do not hold, the influence of the local chain structure becomes important. Both local stiffness as well as rotational potentials begin to play a role.[2] In order to determine the relevant limiting factors for the deviations from universal behavior in polymer chain dynamics, we have investigated the single chain structure factor \( S(Q,t) \) of two flexible polymers, polyisobutylene (PIB) and poly(dimethyl siloxane) (PDMS) in the melt and in dilute solutions. Both polymer chains show similar static flexibility (similar values of the characteristic ratio). Therefore, the finding of different dynamical properties leading to distinct deviations from universal dynamics should be attributed to the main difference between the two polymers: the value of the barrier for the rotation around the skeletal bonds.

2. Experimental
We have studied monodisperse chains of PIB (molecular weight \( M_w = 3870 \)) and PDMS (\( M_w = 6462 \)) with similar degree of polymerization: the chains contained 138 and 174 bonds respectively. The synthesis and characterization of the samples used are widely explained in Refs [3,4]. The neutron spin echo (NSE) experiments were performed by IN11 (ILL, Grenoble, France) and the Jülich NSE spectrometer (Forschungszentrum Jülich, Germany). PIB (PDMS) samples with 10% (15%) protonated chains in deuterated matrix were investigated, revealing the single chain \( S(Q,t) \) in the melt. Two temperatures, 390 K and 470 K, were investigated for PIB and one, 373 K, for PDMS. Similar experiments were performed on solutions of both kinds of protonated chains on deuterated toluene \( (\phi = 0.10) \) at different temperatures between the \( \theta \) temperature and the boiling point of the solvent. A momentum transfer \( (Q) \) range roughly between 0.04 Å⁻¹ and 0.4 Å⁻¹ was covered.

3. Results and Discussion
In the melt, the description of PIB data by the Rouse model is satisfactory up to \( Q \approx 0.15 \text{ Å}^{-1} \). Toward more local length scales, increasing deviations of the experimental behavior with respect to the Rouse prediction are evident. The chain relaxation is retarded compared with the theory.[3] In a different way, all PDMS data in the whole \( Q \)-range investigated, up to 0.4 Å⁻¹, can be described by the model.[4] Since both polymers exhibit the same static flexibility, it could be followed without further analysis that the chain stiffness does not cause the observed deviation from universal behavior on PIB chain dynamics. A thorough study of the effects on the dynamics of the local stiffness of this polymer was carried out in Ref. [3] applying the approaches of the all rotational state model and a bending forces model. Stiffness effects almost negligible were found when the proper values for the parameters giving account for the stiffness – those experimentally obtained from SANS measurements on the chain conformation – were introduced in such models. In order to look for the real source of the slowing down of the PIB chain dynamics with respect to PDMS at \( Q > 0.15 \text{ Å}^{-1} \), the internal viscosity produced by the local conformational changes as proposed by Allegra et al
[2] was considered. The relaxation process in this frame is simply described by one single relaxation time $\tau$. This internal friction at the intermediate scale motion produces a damping of the chain relaxation. A reasonable description of PIB melt data on this basis was achieved for all the $Q$ values investigated. However, some deviations in the shape of the decay of $S(Q,t)$ were found. Figure 1 compares the temperature dependence of the single relaxation time $\tau$ with that of the average time corresponding to other investigated relaxation processes on PIB, like the $\alpha$- and $\beta$-relaxations. The activation energy of $\tau$ resulted to be of about 10 kcal/mol. This value is in between those determined from the extrapolation of the low temperature region results for the $\alpha$- and $\beta$-processes. Nevertheless, within the experimental uncertainties, from inspection of Fig. 1, $\tau$ could be identified with the average value observed for the structural relaxation—the characteristic time for the decay of the interchain correlations in the system. This would imply that the local relaxation process invoked for explaining the deviations from the universal behavior toward local scales would relate to the origin of the $\alpha$-relaxation. However, this possible identification is not straightforward because the spectral shape of the $\alpha$-process is described by a Kohlrausch-Williams-Watts and not by a single exponential, as it is assumed for the local relaxation. It is clear that in the bulk the influence of the embedding melt prevents from a simple explanation of the mechanism behind the local conformational change represented by $\tau$. In absence of strong intermolecular interactions, this characteristic time should in principle show the activation energy corresponding to the rotational barrier of the skeletal bonds, that for hydrocarbons ranges typically between 3 and 3.5 Kcal/mol. To unravel the nature of the intrachain relaxation parameter $\tau$, the NSE on the solutions were crucial. In dilute solution the interchain friction effects are weak. However, the dynamics of the polymer chains are affected by the hydrodynamic interaction between different moving entities, complicating the interpretation of the data. At a first sight, nevertheless, by comparing the decays of $S(Q,t)$ for the two polymers, a similar effect to that in the melts can be found. At low $Q$-values ($Q < 0.1 \text{ Å}^{-1}$) the spectra corresponding to both systems decay in nearly the same way, indicating similar values for the translational diffusion coefficients. At higher $Q$, a retardation of the PIB $S(Q,t)$ with respect to that of PDMS becomes clear. To overcome the difficulties in the evaluation of the hydrodynamic interactions at high wavenumbers, we made use of the finding of identical translational diffusion coefficients and of the fact that the chain dimensions of the two polymers are nearly the same (the values of the radius of gyration $R_g$ are of 19.2 Å for PIB and 21.3 Å for PDMS). The description of the PDMS chain dynamics — free for intrachain viscosity, as deduced from the melt study—in the toluene solution in terms of the universal Rouse-Zimm model allowed us to get a starting point for the analysis of the PIB chain dynamics. The application of the Allegro model to PIB solution data on the basis of the PDMS reference of "unperturbed dynamics" led to a very good description of the NSE curves for all $Q$ and temperatures investigated. The resulting values for $\tau$ are depicted in Fig. 1. A value for the activation energy of 3.1 Kcal/mol is obtained. This value is well in the range previously given for the rotation barrier in hydrocarbons. Also the value of the preexponential factor in the Arrhenius law for this time lies well in the microscopic range (about 1 ps). We thus can follow that the damping mechanism origins from the conformational rearrangements in terms of crossing rotational barriers.

4. Conclusions
For flexible polymers the limiting factor for the universal (entropy driven) dynamics seems to be the interchain viscosity produced by the local conformational changes. The study of the chain dynamics in solution reveals that jumps across rotational barriers are the mechanism behind the internal viscosity, whereas in the melt the conformational changes responsible for this friction are affected by the embedding melt and are related to the origin of the $\alpha$- and $\beta$-relaxations.

Acknowledgements
We acknowledge support from the following projects: DGICYT, PB97-0638; GV, EX 1998-23; UPV/EHU, 206.215-G20/98. Support from "Donostia International Physics Center" is also acknowledged.

References
Using Neutron Spin Echo we have measured the dynamics of PIB polymer close to the glass transition in the q range around and below the first correlation peak. Previous measurements on deuterated polymer at and above the first correlation peak and at very low q on single chain dynamics indicated the possible existence of a universal power law q dependence of the relaxation times. Our more detailed study invalidates this expectation and we find a unusual nearly q independent relaxation at low q.

In a recent work on the relaxation of PIB [1] a very unusual power law dependence seemed to show up in very wide range of q values. Indeed mixing 10% protonated polymer chains into a matrix of identical but deuterated chains, the single polymer chain dynamics can be measured in the SANS q region. Unfortunately this dynamics can be followed only up to a limited value as the small angle signal quickly disappears in the increasing self correlation peak of the deuterated matrix. In ref [1] with optimized experimental work this SANS signal was followed to the highest possible q values (0.5 Å⁻¹). At low q, the polymer dynamics can be well described by the so called Rouse dynamics [2]. This model is based on the assumption that a) the actual polymer architecture is irrelevant as long as the length scale we are probing is large enough b) the polymer behaves like bead connected with (entropy driven) springs c) the local friction is the only dissipative interaction. The model has been verified to describe well the dynamics on several polymers. (see eg ref [3]) However at higher, q the local specific properties of the polymer chains come into play and deviations has been found. This has been analyzed in great detail in ref [1]. The result we want to point out here, is that even at this high q the intermediate scattering function, as measured via neutron spin echo (NSE), still maintains the characteristic stretched exponential character and approximately scales with the macroscopic viscosity.

On the other hand NSE measurements at much higher q (>1 Å⁻¹ at, and above the first correlation peak of the liquid structure) on fully deuterated polymer has been shown to follow very similar time and temperature dependence [4]. This is a very characteristic behavior in general around the glass transition temperature of many systems. To eliminate the strong numerical correlation between the beta exponent and tau decay time we will use an average tau defined as:

\[
S(q,t) = \exp \left[ -\left( \frac{t}{\tau_{\text{ave}}} \right)^\beta \right] \Rightarrow \langle \tau \rangle = \frac{\Gamma(1/\beta)}{\beta} \tau_{\text{ave}} \tag{1}
\]

The such defined average decay times closely follow a power law dependence over two decades in q with \( \langle \tau \rangle \propto q^{-3.1} \). However we were lacking experimental points on the fully deuterated sample below 1 Å⁻¹ where the scattered intensity is weak.

With the new IN11C multidetector option [5] (fig. 1) and its 25 gain in total intensity, it became possible to explore this q range now. Fig.2 shows in a condensed way all collected data. The IN11C measurements not only perfectly reproduce the previous (old IN11 data) points, but clearly show that the power law dependence is not followed by the collective relaxation (deuterated sample).

Two important features have to be recognized. First of all there is clearly a deGennes narrowing, slowing down of the relaxation at around the static structure factor peak. Secondly at the lowest q values, there is a very weak q dependence if any. With the above mentioned intensity gain factor it became also possible to measure the incoherent (or self) correlation function. (for NSE this is very unfavorable due to the reduced \( I/G \) scattered beam polarization). The self correlation shows no peculiar behavior, it is close to a \( \langle \tau \rangle \propto q^{-3.4} \) power law dependence. A priory the self and collective relaxation functions are only two manifestations of the same physical process, thus a relation must exist between the two. Unfortunately there is no theory giving this relation. The deGennes narrowing Eq. 2a. [6] is valid only for sim-
ple molecular liquids. Another possibility is the Skold ansatz Eq.2b. [7] which reproduces Eq. 2a. for the case of simple diffusion ($\tau_{self}^{-1} = Dq^2$)

$$\tau_{col}(q) \propto S(q)$$

$$\tau_{self}(q) \propto \tau_{self}(q'\sqrt{S(q)})$$

Both of them produces a maximum at around the structure factor peak position, but none of them is capable transform the strong power law dependence of the self relaxation to a q independent relaxation seen in the collective part.

Mezei et al. [8] have pointed out the possible importance of multiple scattering in amorphous systems in the forward scattering direction. They showed also that experimentally the safest check is to repeat the same measurement with long enough wavelength, such that the effective Bragg cut-off drastically reduces the chances of multiple scattering. We followed their way and repeated the low q measurements with 10Å and two additional points with 15 Å on the IN15 NSE spectrometer. (the original curves were measured with 5Å at the maximum flux of IN11) As can be seen on fig. 2 the points are reproduced quite well.

For the best of our knowledge, there is no theory yet describing our observations. Any propagating (diffusive, sub-diffusive) collective mode would have a strong q dependence. Undoubtedly we are dealing with some sort of localized modes. We can exclude the so called beta process as it is known to happen on a much shorter time scale, outside our NSE time window. From the q range where it is visible we have to suppose rather large scale (collective?) movements. Whether these hypothetical rearrangements can contribute sufficient density fluctuations to account for the scattered intensity, remains to be investigated.

REFERENCES:
Neutron reflectivity measurements on polyelectrolyte multilayers at the solid/liquid interface

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Polyelectrolyte multilayers adsorbed at the solid/liquid interface were investigated by neutron reflectometry. The multilayer systems were built up by alternate adsorption of polyanions and polycations from aqueous solutions. Former investigations showed that electrostatic attraction between polyelectrolyte and surface plays an important role for the adsorption process. The present results show that the thickness of the adsorbed film can be increased by the addition of salt to the dipping solutions up to the highest investigated salt concentration of 3 Mol/l NaCl. At such high concentration the electrostatic interactions are completely screened. This seems to be inconsistent with the electrostatically driven adsorption. One possible explanation to overcome this inconsistency would be density fluctuations of counterions. Although the salt effect on film structure is quite high during the adsorption there is no influence at all after the adsorption process is finished. The structure of the film seems to be determined by the adsorption conditions and cannot be changed either by salt or drying/re-swelling procedures afterwards.

1. Introduction

During the last 10 years a new kind of polymer films formed by the alternate adsorption of polyanions and polycations [1] has been investigated intensively. X-ray and spectroscopic measurements showed that the thickness of those films increases linearly with the number of dipping steps. These results indicate that the adsorbed films are layered systems [2]. Neutron reflectivity measurements performed on films composed of protonated and deuterated polyelectrolytes at the solid/air interface showed that adjacent layers are interdigitated to a large extent [3,4]. The driving force for the formation of a multilayer is the electrostatic attraction between the plain surface (and the surface of the former adsorbed polyelectrolyte, respectively) and the polyelectrolyte which is going to be adsorbed [5,6]. Recent experiments with different degree of polymer charges showed that charge overcompensation is necessary for the formation of a multilayer system [7]. Most of the structural investigations were performed on ‘dry’ films at the solid/air interface [8]. Adsorption kinetic and transport studies, however, were carried out on solvent swollen films at the solid/liquid interface. First neutron reflectivity measurements on such films at the solid/liquid interface which were compared with x-ray measurements on the same films at the solid/air interface indicated a shrinking of the films by 30% upon drying [9]. From these measurements it was concluded that not only the thickness but also the internal structure is changed upon drying. Former studies at the solid/liquid interface also showed an increase in film thickness with increasing ionic strength up to 1 Mol/l NaCl [9]. Despite the large number of investigations several important questions remain open: (i), is the structural change of these films observed upon drying reversible or not? (ii), since electrostatic attraction between polyelectrolyte in solution and surface of the film seems to be essential for the adsorption process, is there a plateau or even a decrease in film thickness with (at high) salt concentration? (iii), can the film structure of a prepared film be changed upon immersion into a aqueous solution of increased ionic strength? The neutron reflectivity investigations reported here specifically focus on the above raised questions.

2. Experimental section

Polyelectrolyte multilayers were formed by alternate adsorption of polystyrene sulfonate (PSS, Aldrich) and polyallylamin hydrochloride (PAH, Aldrich) from aqueous solutions. The fully protonated polyelectrolyte films were measured against D₂O. The neutron reflectivity experiments were carried out at ADAM at ILL (Grenoble, France). Single crystalline silicon blocks were used as solid substrates and served as individual tops of a flow cell. The direct beam was impinged on the substrate/D₂O interface from the solid side. A detailed description of the experimental setup can be found elsewhere [9]. The neutron reflectivity data were analyzed by applying a standard optical matrix method [10].

3. Results

Fig. 1 shows the thickness, d, of a double layer [PSS/PAH] as a function of the square root of the counterion concentration (including salt and polyelectrolyte counterions [10-2 Mol/l]). Below a concentration of 1 Mol/l NaCl d increases proportional to \(\sqrt{[\text{counterion}]}\). Above a salt concentration of 1 Mol/l the thickness increase is less pronounced, but, nevertheless, d increases up to a concentration of 3 Mol/l. No plateau or decrease in thickness is observed up to the highest experimental salt concentration. While the effect of ionic strength on the film structure during the adsorption process (‘in situ’) is well pronounced a change in
salt concentration has no influence on the structure of the pre-adsorbed film (‘ex-situ’). Fig. 2 shows the results for a film prepared without additional salt. The film was measured against D$_2$O and subsequently against a solution of 1 Mol/l NaCl in D$_2$O. No influence of the ionic strength of the environment on the film structure was observed. The reflectivity curves are similar. Fig. 3 compares the neutron reflectivity curves, subsequently obtained from a freshly adsorbed film against D$_2$O and after intermediate drying in air, measured also against D$_2$O. Even so the film shrunk by 30 % upon drying [9], the reflectivity curves of the freshly adsorbed and re-swollen film are quite similar. Hence, film swelling with solvent is a fully reversible process.

4. Discussion and Conclusion

The above results show that the film structure depends on the adsorption conditions (salt content of dipping solutions), but cannot be changed after the adsorption process is finished. The thickness increases with increasing salt concentration up to high ionic strength. This is due to a change in chain conformation from a rather extended to a more coiled chain, which gives a thicker adsorbed layer [11]. At the same time, the electrostatic attraction between film surface and polyelectrolyte in solution decreases. This counteracts the net increase in film thickness due to the coiling effects. Therefore, one would expect a plateau or even a decrease in film thickness at a certain ionic strength. At a salt concentration of 1 Mol/l the screening length as estimated from Gouy-Chapman theory is about 3 Å. This screening length is smaller than the diameter of a hydrated counterion and, as a consequence, electrostatic attraction should completely vanish. But, at even higher salt concentration the film thickness increases. Hence, mean field theories like the Gouy-Chapman theory are insufficient to describe the electrostatic field in front of the polyelectrolyte surface for our purpose. On the other hand, from experiments on film formation with polyelectrolytes with a varying degree of charge it is known that electrostatic attraction between film surface and polyelectrolyte in solution is a precondition for polyelectrolyte adsorption. One explanation of this paradox could be density fluctuations in the cloud of counterions, which make surface charges “visible” for a polyelectrolyte in front of the film surface.

The film structure cannot be changed by variation of the ionic strength ex-situ. This is due to the formation of complexes between the opposite charges of the polyelectrolytes upon adsorption by release of counterions [12]. These complexes “pin” the chains to the substrate. The replacement of a polyelectrolyte charge by a salt ion of equal charge, and in consequence the desorption of the polyelectrolyte chain from the surface would be accompanied by a loss of entropy of the system which is energetically unfavorable. Therefore, the film structure is determined by the adsorption conditions and cannot be changed afterwards. Removal of water leads to a shrinking of the film due to a collapse of the polyelectrolyte chains. Since this shrinking process does not influence the binding sites, the system can reswell in a fully reversible way.
Acknowledgement
The authors thank the Deutsche Forschungsgemeinschaft for financial support.

References
Inelastic neutron scatterings from hydrogenated and deuterated poly(methyl methacrylate) (PMMA) plasticized by dibutyl phthalate (DBP) was observed and the corresponding vibrational densities of states (VDOS) were determined. The total low-energy VDOS of the plasticized PMMA is well fitted by the sum of the ones of the PMMA and DBP components. However both components do not vibrate independently and the inelastic neutron scattering from DBP reflects the low-energy vibrations of PMMA.

1. Introduction

Recently an experimental study was carried out on the poly(methyl methacrylate) (PMMA) plasticized with dibutyl phthalate (DBP) [1]. Two interesting results were obtained. By small angle X-ray scattering a correlation peak was observed at about 1.5 nm⁻¹. This observation shows that the plasticizer is not distributed homogeneously in the polymer and that zones rich in plasticizer are alternated with other ones with a low content of plasticizer. The other interesting experimental result is the increase by plasticization of the excess of low-frequency Raman scattering (LFRS) or boson peak: the boson peak is more intense than the one obtained by adding the LFRS of the two components (PMMA and DBP) according to the composition of the plasticized polymer. The intensity of LFRS is proportional to the vibrational density of states (VDOS) and to the light-vibration coupling coefficient. The increase of the Raman boson peak may be due to the increase of either the VDOS, the coupling coefficient or both. The excess of VDOS can be determined from low-energy inelastic neutron scattering (LINS) and will be called neutron boson peak. It is why LINS measurements were carried out on plasticized and non-plasticized PMMA. On the other hand, in order to know the effect of the vibrations of one component on the other, two different plasticized PMMA were compared: one with hydrogenated PMMA, and the other with deuterated PMMA. Because the incoherent inelastic neutron scattering is much higher for the hydrogenated PMMA than for the deuterated one, it will be possible to separate the contribution of each component in the total VDOS.

2. Experiment

Four samples were compared: pure hydrogenated PMMA (PMMA-H), pure dibutyl phthalate (DBP), hydrogenated PMMA with 23 (mass) % of DBP (PMMA-H/DBP), deuterated PMMA with the same percentage of DBP (PMMA-D/DBP). The number average molecular weight of PMMA-H and PMMA-D is approximately equal to 500 000 g/mol. The percentage of deuteration of PMMA-D is 98%.

The inelastic neutron spectra were recorded on the time-of-flight instrument IN6. The wavelength of the incident neutrons was equal to 5.12 Å resulting on an elastic resolution of 80 meV, and an elastic momentum transfer range extending from \( Q = 0.22 \) Å⁻¹ to \( Q = 2.06 \) Å⁻¹. The spectra were recorded at 4 K for the determination of resolution and 30 K for the observation of the low-energy harmonic vibrations without anharmonic ones. The VDOS were obtained by taking the average over the range from \( Q = 0.22 \) Å⁻¹ to \( Q = 2.06 \) Å⁻¹. Because the first sharp peak of PMMA in the static structure factor is at \( Q = 0.95 \) Å⁻¹, a value that is lower than the upper limit of the experimental Q-range, the incoherent approximation was applied by using the total neutron scattering bound cross-section. The VDOS were calculated through the use of an iterative procedure described elsewhere [2]. The so-obtained VDOS were corrected by the Debye-Waller factor and for the multiphonon contributions.

The VDOS divided by the square of energy, \( G(E)/E^2 \), are plotted in the figure. It was not possible to obtain the absolute VDOS. However, as the shapes of the \( G(E)/E^2 \) for the different samples were observed to be identical (figure) at the energies higher than 4 meV, a normalization was obtained by coincidence of the curves from an energy of 4 meV. Obviously, this normalization does not allow...
to compare the total VDOS of the different samples, but it makes possible the comparison of the boson peaks which appear around 2 meV. Although the LINS of PMMA-D is expected to be very low, in view of its relatively weak neutron bound cross-section [3], \( G(E)/E^2 \) of PMMA-D/DBP and of PMMA-H/DBP are not very different (figure), while \( G(E)/E^2 \) of DBP is much lower than \( G(E)/E^2 \) of PMMA-H in the spectral range of the boson peak (inset of figure).

3. Discussion

As it can be observed in the figure, \( G(E)/E^2 \) of PMMA-H/DBP is very well fitted by adding the VDOS of respectively PMMA-H and DBP in the following proportion:

\[
G_{\text{PMMA-H/DBP}}(E) = aG_{\text{PMMA-H}}(E) + bG_{\text{DBP}}(E) \quad (1)
\]

The low-energy VDOS of the plasticized glassy polymer obeys the general addition law:

\[
g(E) = \sum C_i g_i(E) \quad (2)
\]

where \( g(E) \) and \( g_i(E) \) are the absolute VDOS, and the coefficient \( C_i \), the (mass) concentration of the component i. In our plasticized PMMA is 0.77 and 0.23 for respectively PMMA and DBP. The coefficients a and b in (1) are proportional to 0.77 and 0.23 respectively. From the good fit of the experimental \( G(E)/E^2 \) by Equations (1) and (2), it is concluded that the plasticization does not induce an enhancement of the low-energy VDOS excess or of the neutron boson peak.

In order to try to fit in a similar manner \( G(E)/E^2 \) of PMMA-D/DBP, it was taken into account that the observed VDOS \( G_i(E) \), depends on the total neutron bound cross-sections of the different atoms in the molecule. For the low-energy vibrational modes, which are mainly dependent on the intermolecular bonding and are studied in this work, the neutron bound cross-section proportionality \( G_i(E) \) of is approximately the following:

\[
G_i(E) \propto \beta_i g_i(E) \quad (3)
\]

where:

\[
\beta_i = \sum c_j \sigma_j / M_j \quad (4)
\]

with \( c_j \), \( \sigma_j \), and \( M_j \) respectively the (mass) concentration, the total neutron bound cross-section and the mass of atom j in the molecule or monomer i.

From these equations, the fit of \( G(E)/E^2 \) for PMMA-D/DBP corresponding to that for PMMA-H/DBP (1) is given by the following equation:

\[
G_{\text{PMMA-D/DBP}}(E) = a(0.98p + 0.02)G_{\text{PMMA-H}}(E) + bG_{\text{DBP}}(E) \quad (5)
\]

In this equation the fractions 0.98 and 0.02 accounts for the percentage of PMMA deuteration, that is equal to 98%. The coefficient \( p \) is equal to \( \beta_{\text{PMMA-D}}/\beta_{\text{PMMA-H}} \). Using the total neutron bound cross-sections of the different atoms in PMMA-D and PMMA-H in [3], it is found \( p=0.079 \). This weak value is due to the very large value of the incoherent cross-section of hydrogen in comparison with the total cross-sections of the other atoms including deuterium. The \( G(E)/E^2 \) curve given by (5) is plotted in the figure. As expected, due to the small value of \( p \), this calculated \( G(E)/E^2 \) curve is not very different from the experimental ones for pure DBP. One observes in the figure that the experimental \( G(E)/E^2 \) of PMMA-D/DBP is more intense at low-energies than the corresponding one calculated by (5). Furthermore, it is remarked (figure) that the \( G(E)/E^2 \) shapes of PMMA-H/DBP and PMMA-D/DBP are similar. The difference between the experimental and calculated \( G(E)/E^2 \) of PMMA-D/DBP is explained by the motion of the DBP plasticizer dragged along by the low-energy vibrations of PMMA-D and reciprocally. This exchange of VDOS between PMMA-D and DBP, like between PMMA-H and DBP, does not change the total VDOS. It is why a good fit is obtained for PMMA-H/DBP (figure).

The first interesting result of this neutron study is the fact that the VDOS of the plasticized PMMA is given by the sum of the component ones: the plasticization does not enhance the neutron boson peak, contrary to that it does for the Raman boson peak. As the low-energy vibrations depend on the intermolecular bonding, it is deduced that this intermolecular bonding is not significantly changed by plasticization and that, in other words, DBP molecules interact mostly between them in the plasticized PMMA, like PMMA ones. On the other hand, it is concluded that the observed enhancement of the Raman boson peak is due to the increase of the light-vibration coupling by plasticization, i.e., to the increase of the vibration modulated electric polarisability. These interpretations are in agreement with the inhomogeneous distribution of DBP in PMMA at the nanometer scale [1]. The vibrations in the spectral range of the boson peak correspond to the surface modes of nanodomains either DBP rich or DBP poor. There is a high polarisability modulated by the surface vibrations at the interface between different nanodomains, that explains the Raman boson peak enhancement. The observed exchange of low-frequency vibrational amplitude between DBP and PMMA occurs at the domain interface.

References

First inelastic neutron scattering studies on thin free standing polymer films

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Glass transition studies in free standing polymer films have revealed values of the transition temperature, \( T_g \), which were substantially reduced below the bulk for sufficiently thin films. Measurements at high molecular weight, \( M_w \), revealed a significant dependence on \( M_w \) suggesting that chain confinement was the dominating effect in the anomalous dynamics found. Here we report on the first tests by inelastic neutron scattering on stacks of free standing polystyrene films with thicknesses of 55 nm and 107 nm. We have employed the TOF spectrometer IN6 and the backscattering spectrometer IN16.

1. Introduction
The properties of confined glass forming materials have attracted much attention [1]. One way of introducing confinement is to make samples in the form of thin films, and a number of experiments have been performed which examine the dynamics and glass transition temperature, \( T_g \), of thin polymer films supported by substrates [2,3]. This study focuses on free standing films (membranes) with the advantage that both interfaces are identical. Measurements of the glass transition temperature in such samples have led to a number of fascinating observations. Most significantly, the measured \( T_g \) values in thin films show significant deviations from the bulk. These \( T_g \) reductions, which can be as large as 80 K, are observed to have a complicated dependence on the polymer film thickness and molecular weight \( M_w \). The data, which is shown collectively in figure 1, appears to display two distinct behaviours. For \( M_w \) values greater than 350,000 the \( T_g \) values display a surprising \( M_w \) dependence suggesting the existence of a chain confinement effect [5]. While some theoretical attempts have been made, a definitive theoretical picture of the mechanism by which chain confinement affects the dynamics and resulting \( T_g \) remains elusive. The lack of an unambiguous mechanism for the observation defines a strong need for more complete investigations into the dynamics. Despite the obvious importance for detailed measurements of the dynamics in thin free standing films of high \( M_w \) polymers there have been very few such measurements [8]. In this work we describe an attempt to use inelastic neutron scattering to probe the dynamics of free standing films in the ns- to ps- time region. On the ns time scale, one usually observes segmental motion for polymeric glass-formers only at temperatures far above \( T_g \), a range which is not accessible with free standing thin films. On the ps-time scale one observes at low temperatures the Boson peak, which is located for polystyrene at about 1-2 meV, and with increasing temperature a "fast relaxation" process which leads to an over-damping of the Boson peak. For PS-bulk samples the temperature dependence of the Boson peak and of the fast relaxation have been explored by neutron scattering [9]. In these experiments we aim to detect a change in the local polymer dynamics.

2. Sample preparation and experimental details
Monodisperse (\( M_w = 1.246 \times 10^4, M_w/M_n \approx 1.06 \)), PS was dissolved in toluene and spincoated onto freshly cleaved mica substrates. The samples were then annealed on mica at 388 K (\( T_g^{\infty} +17 \) K) for 12 hours in vacuum. The samples were cooled to room temperature at 1 K/min, and then were cut and floated onto a water surface. The films were captured on an Al foil grid (60 mm x 30 mm x 0.2 mm) which leaves 85% of the film free standing (see fig. 2). After transfer to the Al grids, the films were annealed at \( T_g^\text{load} = 371 \) K until all wrinkles in the films disappeared [1], and subsequently cooled at 1 K/min. A set of 12 films was taken at random from each series and floated onto Si for thickness determination with ellipsometry. Of all the samples prepared, the best free-standing films were chosen resulting in 70 films with thickness \( h = 107 \pm 2 \) nm and 140 films with \( h = 55 \pm 2 \) nm with roughly equal total stack thickness (7.5 µm and 7.7 µm). One additional

Fig. 1: \( T_g \) dependence of the film thickness for free standing PS films with molecular weights ranging from 120,000 to 9,100,000.
bulk sample was made for reference: a thick film with $h \approx 280 \mu m$. Each stack of films was assembled with the same number of Al foil sheets in order to maintain the same amount of Al in the beam (140 of the 55 nm films, 70 of the 107 nm films with 70 blank foils, and 1 bulk film mounted in a stack of 140 blank foils).

The inelastic neutron scattering experiments were carried out on the time-of-flight (TOF) spectrometer IN6 (5.1 Å) and the backscattering spectrometer (BS) IN16 (6.27 Å). In all experiments the exchange gas pressure was 1 Torr and temperature changes did not exceed 0.3 K/min. Experiments on IN6 were done at $T=300$ K and 357 K, while on IN16 elastic temperature scans were carried out between 2 K and 355 K, typically with a rate of 0.24 K/min. On both instruments a conventional background correction using standard ILL programs was impossible, due to the high sample transmission and the strong anisotropic scattering from the sample holder. Thus in this paper we compare the data from the different samples and compare them to the bulk and the empty sample holder.

3. Results

First we discuss results from the BS spectrometer IN16, which probes the local dynamics of the polymer on the timescale of ns. An example for an elastic scan in cooling on IN16 is shown in the upper half of Fig.3 for the bulk film, the 107 nm and the 55 nm film, all measured at $Q=1.8$ Å$^{-1}$. Because of the low scattering probability of the sample and the relatively high scattering of the sample the usual background corrections were not feasible. Therefore we compare the samples within the sample holder with the scattering of the sample holder itself. Clearly the sample holder shows a weaker temperature dependence compared to the samples plus sample holder. Furthermore this effect is $Q$-dependent.

For large $Q$-values the elastic scattering from the 55 nm film decreases somewhat faster with temperature than from the 107 nm film, whereas for low $Q$-values the curves do superimpose. This weak effect seems to be real, as shown by an evaluation of the $Q$-dependence and extraction of the average mean square displacements (msd) in Gaussian approximation. For such an evaluation we assume that vibrations lead to the observed $Q$- and temperature dependence of the elastic intensity. In this case the low temperature normalized elastic intensity can be written as $\ln(I/I_0) = -1/3 \left( <u^2(T)> - <u^2(2K)> \right) Q^2$, with the averaged msd, $<u^2>$. Fits of the $Q$-dependence at each temperature gives an effective msd. This is shown in the lower part of Fig. 3 for the two free standing films, the bulk film and the empty sample holder. The 55 nm film clearly has a larger msd, compared to the other samples which among each other show a similar temperature dependence.

For comparison we add literature values for bulk polystyrene [10], which are in good agreement with our bulk data. From the TOF experiments on IN6 we might expect to see some influence of the thin film confinement in the “Boson peak” region. For salol confined in porous matrices, a pronounced and pore size dependent decrease of the low frequency modes was observed [11]. Here, for PS, we have less favorable conditions concerning the Boson peak. First, the Boson peak in PS is located at relatively low energy and also, a clear inelastic hump is only observed at very low temperatures [9]. We had to limit these IN6 experiments to temperatures above room temperature ($T=300$K and $T=357$K) because we needed the undamaged sample for the following IN16 experiment. At these temperatures we are still in a range were additional relaxation processes, which lead to an over-damping of the “Boson peak”, are weak and therefore we might expect to see confinement effects.

Again, the standard data evaluation procedure does not work properly for IN6 data. The correction with either measured or calculated background corrections was impossible, due to the high sample transmission and the strong anisotropic scattering from the sample holder. Thus in this paper we compare the data from the different samples and compare them to the bulk and the empty sample holder.

Fig. 2: Sample holder geometry for the stacks of free standing films.

Fig. 3: upper part: Elastic scattering intensity as a function of temperature measured with 1µeV energy resolution on IN16. Crosses: empty sample holder; line: bulk, open circles 107 nm and filled circles 55 nm film, all in sample holder. Lower part: Effective mean squared displacements as a function of temperature, deduced from the elastic scattering intensity (same symbols and additionally literature data for bulk polystyrene [10] as stars).

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lated transmission factors leads to negative intensities in the elastic peak region, which we ignore. We show in Fig.4 the spectra for an elastic Q-value of $Q = 1.9 \, \text{Å}^{-1}$, which first of all prove that one is able to see the polystyrene signal. But, no evident shift or change of the spectral shape can be detected, comparing the 107 nm and 55 nm films. Only the expected changes with temperature are observed. Furthermore, unfortunately the Boson peak is already over-damped at these temperatures. Therefore one should measure at lower temperatures (i.e. less intensity) in future experiments. In order to check further a possible spectral change with thickness, we divide $S(Q,\omega)$ for the 107 nm film by $S(Q,\omega)$ for the 55 nm film at the same temperatures. This ratio is shown in the upper part of Fig.4. Again, no anomalous change is observed as a function of energy at both temperatures. The failure to observe of such changes might also be related to the fact that we have chosen temperatures which are too high.

4. Conclusions

These first feasibility tests of inelastic neutron scattering on very thin freely standing polystyrene films of 55 nm and 107 nm thickness illustrate that a total film thickness of 7.7 µm is just feasible, because we clearly see the signal from polystyrene. However, the amount of sample in the beam has to be increased and the sample holder signal to be reduced in order to get reliable information on a confinement effect from very thin free standing films. The small effect onto the mean squared displacement with film thickness observed on IN16 is encouraging, however some reservation remains due to the non-observation of a confinement effect on IN6. This type of experiments is clearly at the edge of feasibility for today’s inelastic neutron scattering instruments. Some improvements on the sample holder are planned.

References:
IN15 has been operated for the first time in time-of-flight mode and has shown an excellent instrumental resolution. Beside proving the feasibility of the NSE technique on a pulse source, it offers even more flexibility. A larger than ever dynamical range in one single run and variable monochromatisation. It is especially well suited for the study of relaxations in the small angle range.

IN15 is a joint venture between the ILL, HMI Berlin and FZ-Jülich to push further the limits of neutron spin echo spectroscopy. Substantial progress has been already achieved by reaching 350 nsec fourier times (or the equivalent sub neV energy resolution) [1]

In November ’99 we have passed a new milestone, for the first time IN15 has been operated in time-of-flight mode. This mode of operation is not only a feasibility test for future pulsed sources, but can offer some real advantages depending on the physical problem studied.

The main advantages of NSE are that a) the energy resolution is decoupled from the monochromatisation of the incoming beam, b) the intermediate scattering function $S(q,t)$ is the directly measured quantity, c) the maximum Fourier time is proportional to the magnetic field integral and to the third power of the wavelength. [2]

At a given wavelength with a now routinely applied configuration
In the test configuration the choppers were turning at a repetition rate of about 13 Hz and with a nominal wavelength band of 6-19 Å. Due the cut-off of the neutron guide in practice only the 7-19 Å band proved to be usable. The TOF electronics was set up to 128 time channels allowing 128 S(q,t) curves to be measured. As a first test the symmetry between the two sides was scanned (phase current) at a fixed precession field, to see if the echo group is found for all wavelengths. Fig 1 shows a 2D image of the scan (without normalization to the incoming intensity) with a horizontal cut at the time channels corresponding to 9 and 15 Å. As expected the center of the echo group is at the same position for all wavelengths.

Encouraged by this success the instrumental resolution was measured at 8.2° scattering angle on the usual standard graphite elastic scatterer. Even at the longest wavelength (time channel = 128) the resolution drops only to about 0.5. Finally for the real test we measured a polymer melt sample (15% protonated PEO) in the deuterated PEO matrix at T=140 Celsius. There is a very favorable match between the wavelength dependence of Q and instrumental resolution. Indeed at a given scattering angle long wavelength yields small Q and long Fourier time and vice versa.

In the case of polymer melt dynamics the relaxation time increases very fast about 1/τ ~ q¹ so the resolution is well matched to physical problem.

A further advantage is that at low Q (long wavelength) the scattered intensity (S(q)) is high partially compensating the lower incoming flux. As a demonstration we show the result of a fit of exp(-t/τ) at all q values (Fig 2). While the fitted function is not really appropriate for the polymer dynamics it illustrates the wide dynamical range which can be obtained in one single measurement.

Acknowledgement:

This successful start is evidently a result of a team work where the hard work of everybody has to be acknowledged. First of all C. Lartigue and A. Kollmar who started the construction. Later P. Schleger effectively started up the instrument and made the first real experiments[1]. The TOF option was put into operation in collaboration with G. Ehlers and Gy. Kali. We have to thank the ILL technical staff for design, testing and making the choppers, electronics work together, the Jülich technical staff for the time dependent power supplies and constant support on behalf of the “shareholders” F. Mezei from HMI, T. Springer and D. Richter from Jülich.
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Off-specular neutron scattering studies of the interface and surface formation in self-assembled polymer multilayers

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Most of block-copolymer films reveal after annealing an incomplete top multilayer in the form of islands, holes or “labyrinth”-type structures, which together with interfacial roughness of polymer multilayer film create an amount of off-specular scattering. We show that a comprehensive theoretical analysis of both specular reflectivity and off-specular scattering patterns measured over a broad range of incident and scattered wave vectors delivers a rather complete information on the surface topology and roughness correlations along each of the interfaces and across the multilayer stack.

1. Introduction
Symmetric diblock copolymers consist of two chemically different polymer chains linked end to end. They are micro-phase separated into macroscopic domains due to the immiscibility of the two polymers. The diblock copolymer diluted with a solvent is spin coated onto a flat substrate to obtain a thin film. During a following slow annealing above the glass transition temperature the micro-phase separation leads to a lamellar ordering parallel to the substrate. In general, the top layer relief structure depends on the preparation conditions during spin coating and annealing. During the annealing of the film with initial thickness $D$ a quantization must be respected due to the lamellar periodicity $L$ of the system. But in general $D \neq nL$ (with integer n) and thus the excess amount of the diblock copolymer $<L$ will form a non complete top layer. In this case the $nL$ thick film will have only partial diblock copolymer coverage on top of thickness $L$. This partial $1L$ thick top layer can consist of islands or of holes or of “labyrinth” structures. Thus the total film is composed of a basic stack $nL$ of diblock copolymer layers and of islands with thickness $L$ or holes in a top layer equally with a depth $L$. In view of current interest to fundamental problems of polymer surface formation, as well as due to the technological importance, these structures were intensively studied employing a number of different experimental techniques such as optical [1] and atomic force microscopy [2], transmission electron microscopy [3], x-rays [4] and neutron reflectometry [5,6]. However, none of them gave detailed quantitative information on both outer layer lateral arrangement and the roughness of inner interfaces. This information can be received by measuring the off-specular neutron scattering [7] using in particular advantages of high penetration depth and isotopic contrasting of particular structural elements. As an example we present the results of the investigation of a symmetric polystyrene-polybutylmethacrylate P(dS-b-nBMA) diblock copolymer multilayer using neutron specular reflection and off-specular scattering. The data were collected in a broad 2-dimensional range of momentum transfer and analyzed with a theoretical model using the Distorted Wave Born Approximation (DWBA) described in Ref. 7. It is found that the surface layer is incomplete and contains a set of holes (in contrast to the samples with islands [7]), while roughness of the interfaces is conformally correlated through the whole multilayer stack.

2. Experimental data and theoretical modeling
The investigated system is a thin film of a symmetric diblock copolymer of deuterated polystyrene, d-PS, and polybutylmethacrylate, PBMA, denoted P(dS-b-bMA) with the molecular weight $M_w=248300 \; $g/mol, polydispersity $M_w/M_n=1.03$ and a symmetric block ratio ($f=0.5$). The sample was prepared by spin coating of a toluene solution of the copolymer blend onto the glass substrate.

The experiment has been carried out on a time-of-flight reflectometer SPN (JINR, Dubna) [8] followed by a test on D17 (ILL, Grenoble) [9]. The neutron wavelength band was from 0.8 to 14 Å and the scattering angle of 11.4 mrad. The data collected over a broad range of incoming onto the surface and outgoing wave vectors and arranged into a 3-dimensional image of scattered intensity distribution are presented in Fig 1 (top). The specular reflection is the ridge along $p_\parallel = p_\perp$, where $p_\parallel$ and $p_\perp$ are the perpendicular to the surface components of the wave vector of the impinging neutron and the leaving neutron, respectively. Along the specular reflection, the total reflecting region is marked in black and is followed by a sequence of Bragg-peaks, the peak color ranging from black to light grey with vanishing intensity. The position of the Bragg-peaks is defined by the thickness $L$ of the PBMA-dPS-dPS-PBMA multilayer. The first Bragg-peak following the total reflecting region is hardly separated from the total reflecting region itself. The conformal roughness within the poly-
The polymer multilayer creates perpendicular to the reflectivity line the off-specular Bragg-sheet scattering, which shows up at each Bragg-peak and fulfills the condition of \( (p_i + p_f)_n = 2p_i = 2p_f \) (at the \( n \)th Bragg position with \( n = 1, 2, 3, \ldots \)).

From the model calculation the fitted neutron scattering length density profile perpendicular to the surface is obtained, which contains already a first information about a depleted density in the top stack with thickness \( L = 60 \pm 1 \) nm indicating a certain amount of holes.

The interfacial roughness creates not only Bragg-sheet scattering, but also some Yoneda-scattering. The intensity of the Yoneda-scattering is seen in stripes along \( p_i \) or \( p_f \) due to a reduced scattering length density in the island layer and has a different shape as a function of \((p_i, p_f)\). Indeed the experimental specular and off-specular data set is reproduced by the model calculation (Fig. 1 bottom) in very detail.

### 3. Conclusion

It is shown that polymer multilayers create very strong off-specular scattering, which must be included in the data analysis. This off-specular scattering itself contains information about the details of the multilayer structure and its surface. The evaluation of the 2-dimensional distribution of the reflected and off-specular scattered intensity delivers information absolutely necessary in order to determine unambiguously the objects giving rise to off-specular scattering.

### Acknowledgment

This work was supported by the German BMBF.

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Time-resolved SANS investigation of a shear induced lamellar-to-vesicle transition

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The mechanism and kinetics of a shear induced formation of multi-lamellar vesicles in a lyotropic lamellar phase of C10E3 (Triethyleneglycol-decylether) was investigated by rheology and time resolved small angle neutron and light scattering (SANS, SALS). Starting from a well defined, macroscopically oriented lamellar phase, the transition occurs in two steps. First, there is a formation of an intermediate structure oriented in the flow direction. This is compatible with multi-lamellar cylinders (tubuli). As shear is continued, multilamellar vesicles (MLVs) are formed.

1. Introduction
The influence of shear on the structure and orientation of complex fluids has attracted much interest in recent years.[1] Following the pioneering work of Diat et al.[2] particular attention was paid to lyotropic lamellar phases exhibiting two special features under shear. One is the flipping of planar lamellae[3] and the second concerns the formation of multi-lamellar vesicles (MLVs). While the shear induced formation of MLVs has been demonstrated in different systems, both with surfactants and block copolymers[4], neither the reason for, nor the mechanism of their formation is yet fully understood. Here we focus on the latter problem and present data from so called start-up experiments. Here a well defined lamellar state, having the bilayers aligned with their normal in the gradient direction (the so called c-orientation), is suddenly exposed to shear of a constant rate. The structural evolution from lamellae to MLVs is followed by time-resolved (i) viscosity measurements, (ii) small angle light scattering (SALS) and (iii) small angle neutron scattering (SANS). The system contains the surfactant C10E3 (Triethyleneglycol-decylether) dissolved in heavy water. The lamellar (L –) phase is stable at room temperature over a wide range of concentration. In this lamellar phase, MLVs can be formed upon shearing, however, the stability of the MLV state under shear relative to a planar bilayer state depends on temperature and the applied shear rate. For a given moderate shear rate the MLVs are stable at lower temperatures. At higher temperatures near the lamellar-to-L3 phase transition, the c-orientation is stable. The transition is fully reversible and the mechanisms are coupled to the shear flow and a given structure, lamellar or MLV, can be trapped, if the shear is turned off. Hence it is possible to prepare an oriented lamellar state by shearing at an elevated temperature and then bringing this structure down to room temperature while keeping the sample at rest. Turning the shear on again allows one to follow the formation of MLVs from an oriented lamellar state.

2. Experimental Details
SANS experiments were performed on the instrument D11 of the Institut Laue-Langevin. A thermostated Couette-type shear cell consisting of two quartz cylinders was used for SANS under shear. Two scattering configurations were used. i) In the so called radial position the neutron beam passes the sample along the velocity gradient direction, hence yielding information in the shear plane formed by flow and vorticity (neutral) direction. ii) The tangential position probes structures in the plane of velocity gradient and vorticity direction. Here the neutron beam passes through the gap of the Couette cell along the flow direction. For depolarized rheo-SALS studies, a Bohlin CVO-HR rheometer equipped with a quartz 3° cone/plate shear geometry was used in the rate-controlled mode.[5]

3. Results
The surfactant concentration was 40 wt.% C10E3 in D2O. In both, SANS and rheo-SALS experiments the sample was loaded at 25°C giving a polydomain lamellar phase as the initial state. Then the temperature was increased to 42°C and a shear rate of 10 s⁻¹ applied until the steady state was reached yielding planar lamellae in the c-orientation. Then the shear was stopped and the sample was cooled to 25°C retaining the oriented lamellar state. Sub-
studied the in

Bragg peak intensity
demonstrates the presence of MLVs. In the neutral direction the
peak both in the radial and tangential beam experiments which
total intensity has increased signifi-
cantly. Finally, after 1800s the intensity remained low during the first 300s. Then, after 300s the intensity
to parallel-to-perpendicular-to-MLV-to-SUV transition. Their sys-
tems was more dilute and reached a different

After the onset of shear at 10s⁻¹. The intensity scale is identical within each series but
different for radial and tangential beam data, respectively. To the right, sketches
of the structures in real space.

sequentlly the shear experiments were started and the transition
from planar lamellae to MLVs was investigated.

Fig. 1 shows the results from a depolarised Rheo-SALS experiment
performed at 10s⁻¹. Initially the viscosity is low as expected and the
depolarised SALS pattern is also typical for a c-orientation of pla-
nar layers. The viscosity began to increase immediately and after
about 300s we observed a small, but reproducible, plateau. The SALS
pattern at this stage displayed an elongated, two-lobe pattern per-
pendicular to the flow direction. Following this intermediate plateau,
the viscosity continued to increase and the two-lobe SALS pattern
evolved into a four-lobe pattern characteristic for MLVs. The vis-
cosity appeared to level off at long times although a clear steady
state was not fully reached at the end of the experiment after
1800s. At long times the SALS pattern had evolved further and at
1750s we observed strong structure factor peaks at \( q = 1 \mu m^{-1} \)
indicating a center-to-center distance of ca. 3µm which is in the order
of the gyration radius in the case of densely packed vesicles.

SANS experiments were performed in a \( q \)-range where the Bragg-
peak corresponding to the layer spacing is observed and the
first order peak was observed at \( q = 0.1 \mu m^{-1} \). SANS spectra were
recorded in intervals of 10s with an acquisition time of 2s. Fig. 2
displays 3D-SANS patterns recorded before the shear experiment,
at 300s and 1800s, respectively, after the onset of shear at 10s⁻¹.
Before the onset of shear a lamellar state with a c-orientation is
observed, as can be seen from the tangential beam data which
display strong Bragg peaks in the gradient direction. After 300s
the scattering in the tangential beam has become nearly isotropic
on the azimuthal trace of the Bragg peak. In the radial beam the
symmetry of the scattering pattern did not change, however, the
total intensity has increased significantly. Finally, after 1800s the
scattering was isotropic on the azimuthal trace of the Bragg
peak both in the radial and tangential beam experiments which

4. Discussion

The data presented here demonstrate that the transition from an
oriented lamellar state to a state of MLVs occurs in at least two
steps. First, an intermediate structure is formed, which in SALS
is characterised by a two-lobe pattern extended perpendicular
to the flow direction. In SANS we observe, at the same time, an
isotropic scattering ring in the tangential beam and a Bragg spot
in the neutral direction in the radial beam. This intermediate struc-
ture is transformed into MLVs as the shear flow continues. Two
possible structures are compatible with this scattering pattern
of cylindrical symmetry. The first possibility is that cylindrical sym-
metry occurs locally and we either have multi-lamellar cylinders
(tubuli) or lamellar bilayers are rolled up around the cylinder axis
like a "swiss roll". The second possibility is that lamellar domains
rearrange into a two dimensional powder, i.e. with the directors
of the domains evenly distributed in the gradient-neutral plane.
The same scattering pattern has been observed by Panizza et al.
in a thermotropic smectic liquid crystal by SAXS and was inter-
preted as multilamellar tubuli.[6] Further indications for the
presence of multilamellar cylinders in lyotropic lamellar phases
have been reported using NMR[7] and birefringence studies.[8]

The formation of multilamellar cylinders also fits in the concept
of membrane elasticity and curvature which was recently discussed
by Leon et al.[9] since the curvature of cylinders lies inbetween
planar bilayers and MLVs. Leon et al. studied the influence of the
saddle-splay modulus on MLV formation of an ionic surfactant and
found that the time necessary for shear induced MLV formation
increased with increasing salt concentration. On the other hand,
they described the MLV formation as a sequence of randomly
activated processes, whereas our results indicate a strain con-
trolled process. This difference can be due to the higher total sur-
factant concentration in our system and the different initial states.

Escalante and Hoffmann also reported experiments on the shear
induced lamellar to MLV transition in the lamellar phase of a pro-
tonated aminoxide surfactant. [10] They also observed a scaling
with the strain but interpreted their results with a polydomain-
to-parallel-to-perpendicular-to-MLV-to-SUV transition. Their sys-
tems was more dilute and reached a different final state. Our
experiments indicate a different structural evolution and it is con-
ceivable that the pathway can depend on the system. Further stud-
ies are necessary for a complete understanding.

In conclusion our experiments show that the formation of MLVs
of the concentrated \( C_{10}E_3/D_2O \) lamellar phase involves at least two
steps. First a formation of multilamellar cylinders as an inter-
mediate structure was observed which were then transformed into
closed vesicles. [11]
Acknowledgement

We thank the Deutsche Forschungsgemeinschaft and the Swedish NFR for financial support as well as the DAAD and the SI for a travel grant. J.Z. acknowledges a Marie-Curie fellowship of the EU.

References

Molecular systems
Excitations of quantum liquids in disorder

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We survey current knowledge of excitations of quantum liquids in porous media as revealed by inelastic neutron scattering. To date, liquid ⁴He in aerogel, xerogel, Vycor, Geltech silica has been investigated, examples of “bosons in disorder”. A key question is: how are the characteristic excitations modified by disorder and confinement and can these changes be related to superfluidity and Bose-Einstein condensation in disorder? Superfluid ⁴He in all the above media supports a well defined three dimensional (3D) phonon-roton mode. The energy and width of this mode is the same as in bulk liquid ⁴He at low temperature and as a function of T within current precision when the data is carefully taken and analyzed. A new excitation is also found in dense aerogel, Vycor and Geltech silica, a 2D layer mode that propagates in the liquid layers adjacent to the media walls. Evidence for Bose-Einstein condensation localized by disorder is presented. Directions for a promising new study are discussed.

1. Introduction

Measurements of the excitations of quantum liquids in disordered environments by inelastic neutron scattering were first reported [1] in 1994. Results for liquid ⁴He in aerogel, xerogel, Vycor and Geltech silica have appeared [2]. In contrast, the excitations of bulk liquid ⁴He have been extensively investigated since 1957. At temperatures below the normal-superfluid transition, Tₛ, bulk superfluid ⁴He supports the well known phonon-roton (p-r) excitation for wavevectors up to Q = 3.6 Å⁻¹. Normal liquid ⁴He (T ≥ Tₛ) however, supports only a broadened phonon mode up to Q ≈ 0.6 Å⁻¹. At the “maxon”, “roton”, and higher wavevectors there is no well defined mode in the dynamic structure factor S(Q,ω) of normal liquid ⁴He [3].

A central goal of measurements in porous media is to determine the impact of disorder and confinement on the p-r modes and whether new modes are created by disorder. A continuing aim is to relate the existence of the p-r modes (and possible new modes) to superfluidity and Bose-Einstein condensation. Disorder may be viewed as a means of “tuning” superfluidity. For example, the normal-superfluid transition temperature Tₛ is suppressed by confinement; from Tₛ = 2.172 K in the bulk, to Tₛ = 2.167 K in aerogel, to Tₛ = 1.95 K in Vycor and to Tₛ = 0.725 K in Geltech silica at SVP [4,5]. The temperature dependence of the superfluid density ρ_s(T) below Tₛ is also modified by disorder [4,5]. In addition, simulations and mean field calculations [6] suggest that disorder can localize BEC to specific regions so that it does not extend across the whole sample.

2. Excitations in Disorder

A broad picture of excitations of liquid ⁴He in disorder can be presented at this stage. [2] Superfluid ⁴He in fully filled aerogel and Vycor [7-9] supports well defined, phonon-roton excitations. Within current precision (± 5 meV), the p-r energies at low T are the same as in bulk superfluid ⁴He (see Fig. 1). In order to obtain the p-r excitations accurately, it is important to identify and subtract all other contributions to the scattering intensity and to make simultaneous measurements of the p-r energies in the bulk under identical conditions. When this is done, no difference in the phonon-roton energies and lifetimes are observed. The temperature dependence of the phonon-roton energies in aerogel and Vycor are also the same as in the bulk. As an example, Fig. 2 shows the temperature dependence of the roton energy in aerogel compared to that in the bulk. Similarly, the temperature dependence of p-r lifetimes is the same as in the bulk except perhaps at high temperatures near T_c, where the p-r peaks are very broad and a lifetime is difficult to define precisely. Particularly, Anderson et al. [10] have shown that the intrinsic width of the roton in aerogel is very small at low temperature, W ≤ 0.1 µeV at T = 0.08 K, as in the bulk.

In addition to the three dimensional (3D) p-r mode, 2D layer modes are observed in all media. Measurements of the filling dependence of S(Q,ω) show that these modes propagate in the liquid layers adjacent to the media walls [7]. The layer modes appear as additional intensity lying below the main 3D p-r peak and are

![Fig. 1: Dispersion curve of the elementary excitations in superfluid ⁴He in porous media. The three-dimensional (3D) phonon-roton curve is the same in Vycor (crosses), aerogel (not shown) and in bulk liquid ⁴He (line). The open and solid circles show the dispersion for the two-dimensional (2D) layer modes in aerogel and Vycor, respectively, which propagate in the liquid helium layers adjacent to the media walls. From Plantevin et al. (Ref. 9).](image-url)
observed only for wavevectors in the roton region (see Fig. 1). A 2D layer mode in Vycor having “roton” like dispersion as in Fig. 1 was proposed by Brewer et al. [11] from specific heat measurements. Brewer et al. [11] obtained a 2D mode “roton gap” $\Delta_{\rho_0} = 0.53$ meV which agrees excellently with the roton gap shown in Fig. 1 ($\Delta_{\rho_0} = 0.55 \pm 0.01$ meV). Similarly, Keiwet et al. [12] obtained a gap energy of 0.50 meV from measurements of the superfluid density $\rho_s(T)$ at low temperature ($T \leq 1.4$ K) in Vycor. The new dynamical feature in porous media that distinguishes excitations from the bulk is the 2D excitations with the 3D p-r excitations being the same as in the bulk (within current precision). A most interesting result is the temperature dependence of the intensity of the phonon-roton excitation in $S(Q,\omega)$. This temperature dependence suggests that there is localized Bose-Einstein condensation in porous media in the “normal” phase above $T_c$ (up to $T_c$). As noted, $T_c$ in porous media is suppressed below $T_c = 2.172$ K in the bulk. $T_c$ represents the critical temperature for superfluid flow across the whole sample as measured in a torsional oscillator experiment. [4,5] In bulk superfluid $^4$He the temperature dependence of the intensity of the single p-r excitation peak in $S(Q,\omega)$ scales approximately as the superfluid density $\rho_s(T)$ or the condensate fraction, $n_0(T)$ for wavevectors $Q \geq 0.7$ Å$^{-1}$. Particularly above $T_c$ in the normal phase there is no single excitation peak in $S(Q,\omega)$ for $Q \geq 0.7$ Å$^{-1}$. Bogoliubov [13] and Gavoret and Nozières [14] have shown that a Bose fluid at $T = 0$ K with BEC supports a well defined p-r mode with no other modes at low energy. Glyde and Griffin [15] have proposed that the weight in this single mode is proportional to $n_0(T)$. In Vycor [7] and Geltech silica we find that the weight in the single excitation peak does not scale with $\rho_s(T)$ in these porous media. Particularly, we observe a well defined maxon and roton peak in Vycor and Geltech silica above $T_c$ where $\rho_s(T) = 0$. Fig. 3 shows the roton peak in liquid $^4$He in Geltech silica at approximately 83% filling as a function of temperature. The roton peak shows no temperature dependence up to $T = 0.75$ K. If the peak intensity scaled as $\rho_s(T)$ in Geltech, there would be no peak at all above $T_c = 0.725$ K where $\rho_s(T)$ is zero. This suggests that there is localized BEC (localized phase coherence) above $T_c$ (up to $T_c$) that supports a well defined excitation above $T_c$. The regions of BEC are localized within the porous media and are separated by regions of normal fluid (or solid $^4$He). Only when the regions of BEC join so that there is phase coherence across the whole sample is macroscopic superfluidity observed as in a torsional oscillatory experiment [4,5]. Essentially neutron scattering is a probe of local BEC (local phase coherence and superfluidity) while a torsional oscillator measures phase coherence extended across the whole sample.

3. Future Proposals

Studies of liquid $^4$He in new porous media of varying pore size and geometry and under varying pressure are of great interest. Excitations of liquid $^4$He/$^4$He and their possible connection to the major changes in superfluid/normal phase boundaries observed in disorder remain to be explored.

References

Comparison of Neutron and X-ray Diffraction difference methods in the study of ionic hydration

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The difference methods of Neutron Diffraction and Isotopic Substitution (NDIS) applied to aqueous electrolyte solutions have revolutionised the manner in which the structure of ions and water molecules is now discussed. Additionally, the technique of Anomalous X-ray Diffraction (AXD) has been shown by us to offer an alternative means to NDIS in the provision of complementary information on the hydration structure of ions. This paper contains a critical comparison of these two prominent methods with reference to recent results on ions in the alkali series.

1. Introduction
X-ray and neutron scattering methods provide the best experimental means currently available to probe the atomic structure of aqueous solutions. Moreover, as we have clearly demonstrated, by working with differences between diffraction patterns it is possible to derive information on either the pair distribution function or the coordination number, the extent of local order around the specified ion, and as a critical examination of model potential calculations, [2]. Foremost among the difference methods is that of Neutron Diffraction and Isotopic Substitution (NDIS): combinations of differences between the scattering patterns of isotopically labelled samples can be used to obtain information directly on all aspects of an aqueous solution including that of the solvent (water), the solute and the solute-hydration [3]. The alternative method of Anomalous X-ray Diffraction (AXD) has recently been developed by us to give complementary information on ionic hydration structure for ions with atomic number greater than 30. Although less formally correct than NDIS it has the advantage over other diffraction and spectroscopic methods of providing structural information specific to a particular ionic species, [4-6]. In this paper we have selected some examples to illustrate the power of both methods listed above.

2. Difference Diffraction Methods
2.1 Neutron Diffraction and Isotopic Substitution NDIS
For an aqueous electrolyte solution of a salt (MXn) in water (H2O) the NDIS first difference method applied to cations or anions by isotopic exchange for M' for M or X' for X can be used to obtain information concerning aqua-ion structure in terms of the function Gα(r) or Gβ(r). In mathematical terms

\[ G_\alpha(r) = A g_{\alpha\alpha}(r) + B g_{\alpha\beta}(r) + C g_{\alpha\gamma}(r) + D g_{\alpha\pi}(r) + E \]

where \( A = 2c_\alpha c_\beta \Delta b_{\alpha\beta} \), \( B = 2c_\alpha c_\gamma \Delta b_{\alpha\gamma} \), \( C = 2c_\alpha c_\pi \Delta b_{\alpha\pi} \), \( D = c_\alpha^2(b_{\alpha}^2 - b_{\beta}^2) \), \( \Delta b_{\alpha\beta} = b_{\beta} - b_{\alpha} \), and \( c_\alpha \) is the atomic concentration of species 'α' whose neutron coherent scattering length is \( b_\alpha \).

A hydration number for an ion I in solution over the range \( r_1 < r < r_2 \) can be defined as:

\[ n^{H_2O}_I = 4\pi c_{H_2O} \int_0^{r_2} g_{\alpha\pi}(r) r^2 dr \]

or

\[ n^{H_2O}_I = 4\pi c_{H_2O} \int_0^{r_2} g_{\alpha\pi}(r) r^2 dr \]

depending on which of these functions can be more readily identified from \( G_\alpha(r) \).

2.2 Anomalous X-ray Diffraction.
AXD exploits the fact that the total atomic form factor \( f(q,E) \), which characterises the interaction between X-rays and the electrons of the atom, contains two anomalous terms, \( f'(E) \) and \( f'(E) \), in addition to the normal purely q dependent term \( f(q) \). By carrying out diffraction experiments in the neighbourhood of an absorption edge of a specific atom it is possible to obtain difference functions which contain structural information on the pairwise correlations around the specified atom.

The actual structure function \( \langle G_\alpha(r) \rangle \) is calculated from the Fourier transformation of the sum over partial structure factors \( S_{\alpha\alpha}(q) \) convoluted with their q-dependent X-ray atomic form factors. The effect of this convolution is to broaden peaks associated with the real structure as defined by \( g_{\alpha\alpha} \), and thereby obscure the structural information in the true \( G_\alpha(r) \). The peak positions, however, remain unchanged by the convolution process. Despite these drawbacks, we have demonstrated within the past few years, and coincidentally with the commissioning of X-ray diffractometers at the third generation synchrotron source at the ESRF, Grenoble, the viability of AXD in the determination of accurate information on interatomic correlations and coordination numbers, [4-5].

3. Results and Discussion
Both AXD and NDIS methods have been used to obtain information on ionic hydration in a variety of electrolyte solutions as a function of ion concentration, counterion type, and temperature and pressure. In recent years, NDIS methods have been extended...
to investigations of ionic hydration and hydrogen bond structure in aqueous electrolyte solutions under extremes of temperature and pressure, [7], and to studies of ionic hydration in aqueous solutions of complex molecules such as DNA and proteins, [8]. Over a similar period, we have developed experimental procedures and mathematical formalism needed to make AXD a competitive technique with that of NDIS, [4-6]. The power of each method is illustrated below with reference to studies carried on the hydration structure of alkali ions.

**Alkali Ions (Li+, Na+ isomorphic with Ag+), K+, Rb+)**

The NDIS first difference method has been successfully applied to Li+ as a function of concentration [9], and to K+ [10]. The sodium ion (Na+) hydration has also been investigated by the approximate method of XDIS and exploitation of the isomorphism between Na+ and Ag+ [6]. Recently AXD has been used to obtain information on Rb+ hydration in an aqueous solution of 4 molal rubidium chloride, [5]. These studies taken together show that as the ion size increases and the charge density is reduced, the hydration shell becomes broader. Interestingly however, it appears that the coordination number does not change significantly from a value of between about 5 and 8 (Table 1). The studies also show that the extent of the perturbations to the water structure is limited primarily to the range of the first hydration shell. Only Li+ has a significant second shell and even here only at very high concentration where counterion effects may contribute.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Solute (molality)</th>
<th>r_i(Å)</th>
<th>r_o(Å)</th>
<th>(\bar{n})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li+</td>
<td>LiCl (3.6)</td>
<td>1.95(2)</td>
<td>2.52(2)</td>
<td>6.0(5)</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>LiCl (1)</td>
<td>1.96(2)</td>
<td>2.52(2)</td>
<td>6.5(10)</td>
<td></td>
</tr>
<tr>
<td>Na+</td>
<td>NaClO4(4)</td>
<td>2.4(2)</td>
<td>-</td>
<td>4.9(10)</td>
<td>11</td>
</tr>
<tr>
<td>K+</td>
<td>KCl (4)</td>
<td>2.9 - 3.4</td>
<td>5.3(6)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Rb+</td>
<td>RbCl(4)</td>
<td>3.1</td>
<td>6.9</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

**4. Conclusions and Future Prospects**

The results above illustrate the contributions NDIS and AXD experiments have made to the definition of hydration structure in aqueous solutions. The information provided not only is useful as a systematic characterisation of ions within particular groups, but also can be used to assess the quality of computer simulation studies based on model potentials, [2], and helps in the interpretation of results obtained from spectroscopy and thermodynamic measurements.

The well-established NDIS method is generally superior to all other methods for structure determination at the level of interatomic pair coordination. It is limited to specific atomic nuclei and ions, and even then is only useful at concentrations above about 0.5 molal. The new method of AXD has the potential to answer long-standing questions about the structure around species with mass number greater than about 30. However, the low X-ray scattering power of hydrogen atoms means that it is never possible to resolve the full structure of the hydration shell of an atom or ion. At present AXD is also limited to studies of solutions at molal concentrations. In this sense EXAFS spectroscopy has a distinct advantage and studies which incorporate AXD or NDIS as a reference, together with extensive EXAFS measurements are likely to be the best way ahead in the short term to investigate ionic structure at low concentration.

**Acknowledgements**

We are grateful to EPSRC for providing funds to carry out investigations at sites such as ILL, Grenoble, and the ESRF, Grenoble. S.R. thanks the EU for a TMR Award to support her research studies for the Ph.D.

**References.**

Microscopic properties of simple fluids investigated through static and dynamic neutron scattering

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Accurate $S(k)$ and $S(k,\omega)$ measurements, together with theoretical and computer simulation predictions, provide valuable insight on the microscopic behaviour of classical and quantum fluids, especially when those studies are performed over extended density and temperature ranges. Some pertinent examples concerning static and dynamic properties of simple fluids are reviewed.

1. Introduction

In the past two decades the joint use of accurate experimental determinations of static and dynamic structure factors and of sophisticated theories and simulations has made possible extensive investigations on the microscopic behavior of simple fluids over wide density, temperature, exchanged momentum and energy domains [1-5]. We mention for example a couple of studies performed in the late eighties using the D4B diffractometer at ILL: with the first of them the possibility of extracting directly the pair potential from low density measurements of the static structure factor $S(k)$ was experimentally proved [6], while with the second one the familiar Lennard-Jones model for the interaction law was shown to be inadequate to quantitatively reproduce at a few percent level the structure factor in a broad range of liquid states [7]. This last study made also evident the marked sensitivity of the thermodynamic derivatives of $S(k)$ to the details of the potential, at least in proximity of the position of the main peak of $S(k)$. In the following sections we review some further examples of how experimental and theoretical determinations of static and dynamic structural quantities can provide valuable insight on the microscopic properties of classical and quantum fluids.

2. The low-$k$ structure of liquid Kr

A recent diffraction measurement performed using the small angle diffractometer PAXE (LLB, Saclay) extends at $0.8 < k/nm^{-1} < 4.1$ previous data [7] taken at the D4B instrument (ILL, Grenoble) on liquid krypton. Since the investigated thermodynamic states were quite close to the liquid boundary of the liquid-vapor phase transition, the data have been compared with theoretical results obtained using the soft-core hierarchical reference theory (SC-HRT), which had been previously demonstrated to be suitable for the description of the dense fluid properties near the liquid-vapor coexistence region [8]. In Fig. 1 the low-$k$ part of the experimental isothermal density derivatives of $H(k) = [S(k) - 1] / n$ at two different values of the number density $n$ is reported, together with SC-HRT predictions. The assumed model for the total interaction potential included a realistic pair contribution [9] plus an Axilrod-Teller triple dipole part of intensity renormalized in such a way that the critical parameters $T_c$ and $n_c$ of Kr could be reproduced within 1% of their experimental estimates. The results obtained from the well tested modified hypernetted chain (MHNC) theory are also reported as well as the $k=0$ thermodynamic limits. (a) $dH(k)/dn$ at $T=169 K$ and $n=14.40 \text{ nm}^{-3}$, (b) $dH(k)/dn$ at $T=199 K$ and $n=11.66 \text{ nm}^{-3}$. The derivative from the data of Ref.[7] is at the slightly different density $n=11.57 \text{ nm}^{-3}$.

Fig. 1: Experimental density derivative of $H(k)$ (dots with error bars). Data at higher $k$-values (open circles) are from Ref. [7]. The SC-HRT prediction based on the Ref. [9] $V_2$ pair potential plus (Axilrod-Teller) interaction (dash-dotted curve) is shown, together with the MHNC results based on the $V_2$ (dashed curve) and on the $V_1$ plus (Axilrod-Teller) interaction (solid curve). Full squares at $k=0$ are the thermodynamic limits. (a) $dH(k)/dn$ at $T=169 K$ and $n=14.40 \text{ nm}^{-3}$, (b) $dH(k)/dn$ at $T=199 K$ and $n=11.66 \text{ nm}^{-3}$. The derivative from the data of Ref.[7] is at the slightly different density $n=11.57 \text{ nm}^{-3}$.
a significant role in determining the structure for \( k \) values smaller than the position of the first minimum of \( S(k) \), and iii) both the thermodynamic properties and the low-\( k \) behavior of structural quantities are quite remarkably accounted for by SC-HRT using, as effective many-body potential, a triplet Axilrod-Teller interaction of renormalized (65\% higher) intensity.

3. Thermodynamic derivatives of the structure factor of liquid para-hydrogen

The study of the thermodynamic state dependence of \( S(k) \) can also profitably contribute to the knowledge of the quantum features of a liquid. In a first investigation in the vicinity of the triple point of liquid deuterium the density and temperature derivatives of \( S(k) \) were deduced from neutron diffraction data and the comparison with Path Integral Monte Carlo computer simulations performed with different interaction potentials allowed a clear discrimination among those models [10]. This analysis has been recently extended to liquid para-hydrogen in similar thermodynamic states [11] in order to investigate the effect of the mass difference on the quantum properties. The data were taken at the time of light neutron diffractometer SANDALS (ISIS, UK), along the \( T=17.1 \) \( K \) isotherm, and the \( n=22.2 \) \( \text{nm}^{-3} \) isochore, so that the thermodynamic derivatives of \( S(k) \) at constant temperature and density could be both evaluated. These are shown, together with the corresponding quantities for liquid deuterium, in Fig. 2a and 2b where quantitatively significant differences are evident. Assuming that hydrogen and deuterium experience the same intermolecular potential, these differences can only be attributed to the different quantum behaviours of the two molecules.

4. Quantum mechanical effects on the pair structure of ortho-deuterium

In the next sections we turn our attention to dilute fluids composed by almost spherical particles. In this case, it is convenient to expand structural quantities as \( H(k) \) as a function of the density \( n \): \( H(k) = H_0(k) + n H_1(k) + \mathcal{O}(n^2) \) where \( H_0(k) \), the F.T. of the zero-density limit \( g_0(r) \) of the radial distribution \( g(r) \), is completely determined by the pair interaction \( V_2(r) \) acting in the fluid. If \( H_0(k) \) is experimentally determined, \( V_2(r) \) can be obtained from the well known expression \( g_0(r) = \exp(-V_2(r)/k_BT) \) valid for classical monoatomic systems [6]. When the deviations from classical behaviour are significant, a quantum mechanical approach has to be applied as in the case of ortho-deuterium, recently investigated [12] through a diffraction experiment performed on \( D_4B \). The experimental data, taken at four low densities along the 36 \( K \) isotherm, were satisfactorily reproduced by a linear density behaviour, so that \( H_0(k) \) could be deduced and compared with calculations performed with the isotropic potential model of Schaefer and Köhler [13]. In Fig. 3 experimental, classical and quantum results are displayed: a significant disagreement between \( D_4B \) and classical data is evident, with the classical curve shifted towards higher \( k \) values. On the contrary, quantum results and diffraction data agree fairly well in almost all the investigated \( k \)-range. The main conclusions of this study [12] are therefore that quantum effects on the microscopic structure of deuterium are detectable also at 36 \( K \), where they are predominantly due to the diffraction of Boltzmann particles, and they can be adequately described using an accurate quantum mechanical scheme and a realistic isotropic intermolecular potential.
5. Pair contribution to the dynamic structure factor in a dilute gas

Analogously to the virial expansion of static structural properties, the dynamical correlation of density fluctuations can also be density expanded [14]. The intermediate scattering function can then be written as \( \frac{F(k,t)}{F(k,0)} = F(0)(k,t) + n F(1)(k,t) + O(n^2) \) where \( F(0)(k,t) = \exp(-k_B T k^2 t^2/2 M) \), and is related to two-body dynamics, i.e. pair interactions. If \( F(k,t) \) is known at densities low enough for the \( n^2 \) term to be negligible, the linear term \( F(1)(k,t) \) can be obtained from the above equation. This quantity, which is appreciably different from zero only at very low \( k \), was measured [15] by neutron scattering in \(^{36}\)Ar at room temperature and densities below 1.25 nm\(^{-3}\) using the small-angle multidetector of IN5 (ILL, Grenoble), and calculated by molecular dynamics simulation [16] of the corresponding Lennard-Jones (LJ) fluid. Numerical results for the equivalent hard-sphere (HS) system are also available from kinetic theory [17]. In Fig. 4 we show the comparison between experiment and calculations at four \( k \) values. It can be seen that the HS theory gives a good description of \( F(0)(k,t) \) at the lowest \( k \), but discrepancies increase with increasing \( k \). The simulation results are more similar in shape to the experimental ones and, at all \( k \), lie between the latter and the HS theoretical ones. This demonstrates the sensitivity of \( F(1)(k,t) \) to the interaction potential.

References

We have investigated the adiabatic evolution of a set of parameterized wavefunctions. Their relative phase change can be related to geometric measurable quantities that extend the familiar concept of Berry phase to the evolution of more than one state. These concepts can be applied to several physical systems. We discuss briefly an experiment on microwave cavities for which off-diagonal phases have been determined from published data.

The concept of geometric phase in quantum mechanics was introduced by Berry [1]. It has been a fruitful tool for interpreting disparate physical phenomena. In its original formulation, the geometric phase concerns the adiabatic evolution of a single eigenstate $|\psi_j(s)\rangle$ of a parameterized Hamiltonian $H(s)$. Berry showed that, when transported adiabatically along a closed loop, the state acquires a purely geometric (and measurable) phase factor. Open paths $\Gamma$ (joining $s_1$ to $s_2$) were considered by Pancharatnam [2], who showed that the phase of the projection $<\psi_j(s_1)|\psi_j(s_2)>$ of a parallel-transported state is measurable.

The phase factor $\sigma_{jk}^\Gamma$ of $<\psi_j(s_1)|\psi_k(s_2)>$ for two different eigenstates has never been investigated in detail so far. Indeed, $\sigma_{jk}^\Gamma$ can be rigorously defined and made independent of an arbitrary (continuous) phase change at each point along the path. As $\sigma_{jk}^\Gamma$ implies the relative phase of the two vectors $|\psi_j(s_1)\rangle$ and $|\psi_k(s_2)\rangle$ at the initial point $s_1$, a basic ambiguity is unavoidable. This phase relation is indeed arbitrary, as it relates orthogonal states. Such an arbitrariness can be eliminated by introducing a new quantity [3]:

$$\gamma_{jk}^\Gamma = \sigma_{jk}^\Gamma \sigma_{kj}^\Gamma$$

For a cyclic path, all $<\psi_j(s_1)|\psi_j(s_2)=(s_1)>$ (with $j\neq k$) overlaps vanish, and the only geometric phase information is represented by the diagonal Berry phases $\sigma_{jj}^\Gamma \equiv \gamma_j^\Gamma$. For a generic non-cyclic
path, both diagonal $\sigma^\Gamma_{jk}$ and off-diagonal $\gamma^\Gamma_{jk}$ phase factors carry the same kind of information, and should be considered on the same footing. When the final states are a nontrivial permutation of the initial ones, the diagonal scalar products $\langle \psi_j(s_1) | \psi_j(s_2) \rangle$ vanish and the usual Pancharatnam-Berry phase $\gamma^\Gamma_{jk}$ is not defined. In this particularly important situation, all but $n \sigma^\Gamma_{jk}$'s are undefined, since $| \psi_k(s_2) \rangle = e^{i \alpha} | \psi_j(s_1) \rangle$ (with $j \neq k$). Here the only phase information about the $n$ permuted eigenstates is contained in the off-diagonal products $\langle \psi_j(s_1) | \psi_j(s_2) \rangle$, and it is synthesized in the corresponding cyclic product(s) $\gamma^\Gamma_{jk}$.

A nontrivial permutation of the energy eigenstates occurs when the Hamiltonian changes sign at the ends of the path: $H(s_1) = -H(s_2)$. This is what happens in the deformed microwave resonator experiment performed by Lauber et al. [4], where off-diagonal phase factors can be easily measured for open paths. In this case, $s = (s \cos \theta, s \sin \theta)$ parameterizes the displacement of the upper right corner of the resonator away from the position of a conical intersection of the three energy levels. In this experiment, the three nearly degenerate adiabatic states are followed as the distortion is driven in small steps through a loop $\theta = 0$ to $2\pi$ around the degenerate point. In Fig. 1 we report the initial ($\theta = 0$), half-way ($\theta = \pi$) and final ($\theta = 2\pi$) eigenfunctions from the original pictures of Ref. [4]. The $\sigma^\Gamma_{jk} = \pm 1$ factors are easily identified in Fig. 1 from the recurrence of the wave patterns and the sign changes. In particular, the swap of states $| \psi_1 \rangle$ and $| \psi_3 \rangle$ shows that this system satisfies the symmetry relation $H(\pi) = -H(0)$ at mid loop. Thus, for the path $\theta = 0$ to $\pi$ the only well-defined diagonal phase is that of the central state $\sigma_{22} = \gamma_2 = -1$. The upper and lower states exchange, giving $\sigma_{31} = +1$ and $\sigma_{13} = +1$, thus an observable gauge-independent product $\gamma_{31} = +1$. Any correct theory for this system should recover this value. In Ref. [5] we compute these values in a perturbative scheme, and recover the observed phases. Similar off-diagonal phases, also in accord with our prediction, were observed for neutron spin states [6]. Photon spin is another promising field of investigation.

REFERENCES
We have built two shear cells for the investigation of sheared liquids: one for backscattering and time of flight and another one for reflectometry measurements. For aqueous solutions of the triblock copolymer P85 we report a macroscopic velocity distribution with the sample ‘sticking’ to the static and rotating disc. Also an enhancement of diffusion perpendicular to the shear gradient was found. For hydrophilic and hydrophobic coated polished silicon wavers we report different wetting behaviours which depend on temperature and shear rate and which include structural changes.

1. Introduction
Lubrication is a complex and barely understood phenomenon in physics. Insufficient lubrication may lead to premature wear and failure of mechanical components. The properties of lubricants can be optimised by additives for longevity or efficiency – and in the end for reduced economical costs. To approach this issue it seems essential to understand the fundamentals of lubrication and the dynamic processes in liquids on all length and time scales.

2. Sample
As a first sample we have prepared from the surfactant P85 a 33% in weight solution in deuterated water. This triblock copolymer consists of a core of 45 polypropyleneoxyde molecules with a hydrophobic character at temperatures above 15°C and with two end groups of 25 polyethyleneoxyde molecules, which are hydrophilic in the investigated temperature range between 10 to 80°C. Structural properties of this sample have been largely studied for different temperatures and concentrations by SANS for a large variety of phases embracing unimers, cubic or lamellar orderings [1].

3. Macroscopic and microscopic modes
Recently we have shown that the macroscopic flow dynamics of lubricants can be explored by inelastic neutron scattering [2]. To investigate this more carefully and to obtain in addition information on the diffusion processes parallel and perpendicular to the shear gradient we have built a shear cell specially for backscattering and time-of-flight scattering. The discs made from aluminium have a diameter of 200 mm, a thickness of 3 mm (making their scattering contribution negligible) and a minimum spacing down to 0.2 mm to prevent multiple scattering. Figure 1 shows a comparison between the sample at rest at 18°C and at a shear rate of 5000 1/s corresponding to a disk speed of about 1 m/s. This corresponds in 45° transmission geometry to a Doppler shift of 6.5 µeV for neutrons with an incoming energy of 2.08 meV as usual on IN10. In this case the scattering vector is parallel to the flow and inelastic scattering gives direct information about the macroscopic velocity distribution of the liquid. The data show a quasielastic line at the elastic position and well separated an inelastic line with a broadening contribution due to the velocity gradient relating to the beam size. The two peaks are well described by a fit with Lorentzians. This two peak structure shows that the sample under shear seems to stick to the plates. Such a veloc-

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Fig. 1: Neutron spectra of a 33% in weight solution of P85 in deuterated water at rest (left) and under shear (right) and the macroscopic velocity distribution between the plates.
ity distribution is contrary to that found earlier for motor oils at different temperatures [2] demonstrating dissimilar adhesive properties.

Broad and narrow Lorentzian lines were fitted to the spectra. Under a shear rate of 5000 1/s they become broadened from 1.24 µeV (full width half maximum) to 1.94 µeV and from 25.4 µeV to 32.2 µeV for the slower and the faster components, respectively. The increased diffusion perpendicular to the shear gradient indicates an anisotropic dynamic behaviour as it is known for the structural properties. Figure 2 shows the integrated and to monitor normalised intensity over the measured energy window, which is directly correlated to the width of the line for the faster modes. This mode disappears from the energy window of IN10 at a certain shear rate, implying a phase transition. Without shear the mode is found to become fast at about 40°C. This seems correlate with a drop in macroscopic viscosity which we found in rheological studies. For shear rates of about 5000 1/s this effect shifts down to about 28°C. At 55°C the modes become slowed down dramatically pointing toward a solid like behaviour.

4. Wetting and structural behaviour

To investigate the wetting behaviour of liquids at a hydrophilic (15 min in H2SO4:H2O2=5:1) and a hydrophobic (1min in 1% HF solution) coated polished silicon wafer under shear we have built a second shear cell. The coherent scattering length density of silicon (2.1*10⁻⁶1/Å), P85 (0.44*10⁻⁶1/Å) and deuterated water (5.77*10⁻⁶1/Å) are very different yielding good contrast between the components. Figure 3 shows the critical angles for total reflection of our sample at the different surfaces, shear rates and temperatures. For the hydrophobic plate a dramatic shift with temperature (without shear) is found from 0.19° at 18°C to 0.31° at 73°C implying a drop in polymer concentration c right at the surface from c=48% to c=12%. With shear the concentration drops from 52% to 29% for the same temperatures. A complete different behaviour is found for the hydrophilic plate. At temperatures of 18°C the concentration without shear is 38% and becomes increased to 43% at 73°C. Under shear it becomes temperature independent [3].

Figure 4 shows the spectrum on the linear detector at EVA for a angle of 0.7°, with the direct beam on the left, the reflected in the middle and a Bragg like reflection on the right. For the Bragg reflection we report a slight shift from Q=0.055Å⁻¹ at 18°C to smaller Q values at 73°C for both plates in good agreement with ref. [1]. Under shear in the hydrophobic case the peak slightly shifts to Q=0.050Å⁻¹ for 18°C and melts nearly completely for 73°C, showing a destruction of the long range ordering in direction of the shear gradient. For the hydrophilic plate the peak is not shifted. It even develops a reduced width and it becomes strongly enhanced meaning a more pronounced ordering in the same direction.

5. Conclusion

We have shown that macroscopic as well as microscopic dynamic of sheared liquids can be explored by neutron backscattering.
Macroscopic flow has been found to be strongly dependent on the coupling between the liquid and the solid interface as well as on temperature and shear rate. The diffusion perpendicular to the shear gradient becomes enhanced under shear. For different coatings of silicon wavers as contact materials strongly different wetting behaviours were found, which also affect the structure in the bulk medium.

Acknowledgement

We acknowledge the Fraunhofer Institut für Integrierte Schaltungen for the coating of the silicon wavers, Mr Gonzalez (IN10) for the test time, the team of Eva for the support during the experiment and the DFG for financial support (MA801/4 and ZA161/17).

References:

Combined neutron and x-ray diffraction for structural studies of liquids and glasses

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A proper understanding of many physical properties of glasses and liquids requires a knowledge of the partial structure factors (PSF), each of which describes the distribution of one atomic species around another. The technique of neutron diffraction with isotopic substitution (NDIS) [1], having been successful in determining the PSFs of several compounds [2], is nevertheless restricted to isotopes exhibiting sufficient contrast in neutron scattering length. On the other hand, the technique of anomalous x-ray scattering (AXS) [3] allows an adjustment of the x-ray scattering length (i.e. \( f \)) of one atomic species provided its absorption-edge energy is at once accessible and sufficiently high to give a good \( q_{\text{min}} \). The combination of neutron diffraction and x-ray diffraction can provide better scattering length contrast for a given compound, but requires a more careful data analysis in order to take into account properly the different systematic errors present in the two techniques [4]. We present a summary of the method and examples of our results [5,6,7].

1. Introduction.

The complexity of liquids and glasses as disordered systems has often led to overly phenomenological descriptions of their structure and dynamics. An important element of any quantitative microscopic description of polyatomic glasses and liquids is a set of partial structure factors (PSF). The partial structure factor \( S_{\alpha\beta}(q) \) is related to the measured scattered intensity due to correlations between the (instantaneous, ensemble-averaged) positions of atomic species \( \alpha \) and \( \beta \) in the liquid/glass. The PSF \( S_{\alpha\beta}(q) \) is unitless, converges to 1 at infinite \( q \), and can be Fourier transformed to obtain the corresponding partial pair distribution function (PPDF) \( g_{\alpha\beta}(r) \):

\[
g_{\alpha\beta}(r) - 1 = \int [S_{\alpha\beta}(q) - 1] q \sin(qr) \, dq / (2\pi^2 q^2) \quad (1)
\]

where \( \rho \) is the total number density of atoms and the integral is from 0 to \( \infty \). The PPDF \( g_{\alpha\beta}(r) \) is proportional to the probability density for finding an atom of type \( \beta \) around an atom of type \( \alpha \) at a distance \( r \). More specifically, the coordination number \( \bar{N}_\alpha \) of atoms around an \( \alpha \) atom, is given by

\[
\bar{N}_\alpha = 4\pi \rho \bar{C}_\alpha \int g_{\alpha\beta}(r) \, r^2 \, dr \quad (2)
\]

where \( C_\beta \) is the number fraction (i.e. concentration) of \( \beta \) atoms, and the integral is from \( r_1 \) to \( r_2 \) being the smallest consecutive radii giving minima in \( g_{\alpha\beta}(r) \). Minima at larger radii can thus define coordination numbers for second and third coordination shells, etc. The total structure factor \( S(q) \) is a weighted sum of the PSFs:

\[
S(q) - 1 = \sum_{\alpha\beta} \bar{C}_\alpha \bar{C}_\beta \bar{b}_\alpha \bar{b}_\beta \frac{[S_{\alpha\beta}(q) - 1]}{(\bar{S}_\alpha \bar{S}_\beta)}^2 \quad (3)
\]

where the summation indices range over all atomic species and \( \bar{b}_\alpha \) is the average (x-ray or neutron) scattering length for the \( \alpha \) atoms, called the coherent scattering length. Like the PSFs, \( S(q) \) is unitless, converges to 1 at infinite \( q \), and it has the useful thermodynamic limit of

\[
S(0) = \rho \chi \kappa_b T \quad (4)
\]

(only approximate for a polyatomic system) where \( \chi \) is the isothermal compressibility and \( \kappa_b \) is the Boltzmann constant.

The total differential scattering cross section is directly proportional to \( S(q) \) (plus the incoherent scattering) and can be written as

\[
(1/N) (d\sigma/d\Omega) = \sum_{\alpha\beta} \bar{C}_\alpha \bar{C}_\beta \bar{b}_\alpha \bar{b}_\beta \frac{[S_{\alpha\beta}(q) - 1]}{\bar{S}_\alpha \bar{S}_\beta} + \sum \bar{C}_\alpha \bar{b}_\alpha^2 \quad (5)
\]

where \( N \) is the total number of atoms in the sample illuminated by the beam. The first term of Eqn (5) tends towards 0 at infinite \( q \), and the second term containing the average of the square of the scattering length is commonly called the “self scattering” term.

2. Data analysis and results.

The experimentalist’s goal is then to go from a measured \( (d\sigma/d\Omega) \) to the \( S_{\alpha\beta}(q) \) and then \( g_{\alpha\beta}(r) \) and \( \bar{N}_\alpha \), which can be compared to those calculated from theoretical models of the local structure. For a binary system, there are 3 PSFs: \( S_{11}(q), S_{12}(q)=S_{21}(q), \) and \( S_{22}(q) \). If 3 chemically identical samples can be prepared having different average scattering lengths for one or both of the 2 atomic species in the system, and the \( (d\sigma/d\Omega) \) or \( S(q) \) measured for each, then Eqs (3) and (5) become 3 by 3 matrix equations from which the 3 PSFs can be determined. The average scattering lengths can be varied for x-ray scattering via anomalous dispersion (AXS), for neutron scattering via isotopic substitution (NDIS), or by combining x-ray and neutron diffraction data. The normalised determinant of the matrix gives a measure of the conditioning or
contrast of the set of experiments and therefore the final precision of the results. For NDIS the determinant is generally between 0.1 and 0.01. One can think of the value of the determinant as more or less the minimal precision needed in the measured \((d\sigma/d\Omega)\)s for a viable matrix inversion, e.g. one needs error bars smaller than 1\% for a determinant equal to 0.01.

Whereas neutron scattering lengths are generally independent of incident energy \(E\) and momentum transfer \(q\), the x-ray coherent scattering length of a given atom is dependent on both:

\[
b_x(E,q) = r_0 \left[ Z F(q) + \Gamma(E) + i \Gamma'(E) \right] \quad (6)
\]

where \(r_0 = 2.818 \text{ fm}\) is the classical electron radius, \(Z\) is the atomic number, \(\Gamma\) is the real part of the anomalous term which decreases by several electron units close to an absorption edge, \(\Gamma'\) is the imaginary part of the anomalous term which is proportional to the x-ray absorption, and \(F(q)\) is a form factor modulation varying from 1 \((q=0)\) to 0 \((q=\infty)\). The AXS technique therefore consists of combining \((d\sigma/d\Omega)\)s measured at different incident energies \(E\) close to and far from absorption edges of the elements in the sample. To obtain a good Fourier transform of the \(S_{\alpha\beta}(q)\) to \(g_{\alpha\beta}(r)\), a \(q\)-range extending to at least 10 \(\text{Å}^{-1}\) is usually necessary, roughly equivalent to an x-ray energy of at least 10 keV. The elements having K-edge absorption energies between 10 keV and 50 keV (generally the highest accessible at 3\textsuperscript{rd} generation synchrotron sources) range from Ga \((Z=31)\) to Gd \((Z=64)\). The advantages of AXS with respect to NDIS are that the data can be taken on the same sample and no expensive isotopes are needed, the disadvantages being that absorption effects are larger and the spatial resolution in \(g_{\alpha\beta}(r)\) is limited by the form factor modulation (i.e. the size of the electron clouds surrounding the atoms). The scattering length contrast obtainable with AXS is generally comparable to that for NDIS, the latter being better in the case of low \(Z\) atoms.

Since neutron scattering lengths are a function of atomic weight and not atomic number, they are not a priori correlated with x-ray scattering lengths, and a combination of x-ray \((X)\) and neutron \((N)\) diffraction \((d\sigma/d\Omega)\)s, e.g. for a binary system \(2X + N\) or \(2N + X\), generally has much larger contrast than that obtainable with only NDIS or only AXS. When one or more x-ray \((d\sigma/d\Omega)\)s are used, the matrix equations (3) and (5) naturally become \(q\)-dependent.

The proper combination of x-ray and neutron diffraction \((d\sigma/d\Omega)\)s implies a careful consideration of the different systematic errors inherent in the two techniques, since these errors will not "subtract out" in the matrix equation as much as in the case of one technique being used. For example, the \((d\sigma/d\Omega)\)s must be accurately normalised and (de)convolved for \(q\)-resolution differences, the background scattering must be completely subtracted, and accurate corrections for inelastic scattering must be performed. Aside from these experimental factors, any non-sphericity of electron density around atoms will modify slightly the isotropic \(F(q)\) modulation in Eqn (6). Finally, the near-edge variation of the anomalous terms \(\Gamma\) and \(\Gamma'\) is somewhat dependent on the chemical environment of the atom.

Taking into account these considerations, we have obtained good results for partial structure factor determination through combination of x-ray and neutron diffraction for liquid TiSe \((2N + X, 3 \text{ by } 3 \text{ matrix inversion})\) [5] and liquid Ga\textsubscript{2}Te\textsubscript{3} \((3N + 2X, overdetermined singular value decomposition analysis)\) [6], as well as for the covalent glasses PSe and GeO\textsubscript{2} [7].

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[3] Y. Waseda, NOVEL APPLICATION OF ANOMALOUS (RESONANCE) X-RAY SCATTERING FOR STRUCTURAL DETERMINATION OF DISORDERED MATERIALS (SPRINGER-VERLAG, BERLIN, 1984), LECTURE NOTES IN PHYSICS 204
In protonated lithium acetate dihydrate (LiAc-CH₃) the methyl groups show dynamical disorder. The methyl dynamics leads to a methyl proton density distributed on a square. This observation is explained by rotation-translation coupling. On partially deuteration of a methyl group the symmetry and the molecules rotational constant changes. Therefore a different dynamical behaviour is expected. Neutron diffraction offers a unique possibility to distinguish protons from deuterons due to the opposite sign of their neutron scattering lengths. The average scattering length of H₂D amounts to almost zero. Thus the H/D-density distribution of a dynamically disordered CH₂D-groups vanishes, whereas any preferred orientation shows up as positive and negative contributions of the deuteron and protons, respectively.

Our single crystal diffraction experiment showed that LiAc-CH₂D is isostructural to LiAc-CH₃ at 295 K, space group Cmmm. The methyl groups are dynamically disordered and consequently no contribution to the scattering density is found. At 20 K weak positive and negative contributions are found, indicating the onset of ordering. Below 5 K the compound undergoes a phase transition to Pman, where the methyl groups are localized. This phase transition is also observed in the perdeuterated, but not in the protonated compound.

1. Introduction:
Rotational tunneling of the methyl groups in lithium acetate dihydrate has been studied intensively in the past [2-7] because multiple tunneling peaks arise in the inelastic neutron scattering spectrum although only a single type of methyl group environment is present in the crystal [1]. The observed tunneling spectra have been interpreted in terms of coupled pairs of rotor [2-6] or rotor coupling in infinite chains [7]. However a neutron single crystal diffraction study at room temperature and at 3 K revealed that the methyl dynamics at both temperatures leads to a methyl proton density distributed on a square (Fig. 1). This observation is explained by rotation-translation coupling, i.e. a coupling of the methyl rotation to its centre of mass motion. In addition rotation-translation coupling allows for a consistent interpretation of the observed tunneling spectra [9].

Fig. 1: Section through the nuclear scattering density distribution observed in LiCH₃COO.2H₂O at 3 K, multiplied by -1. The section is parallel to the ac-plane, through the maximum of the methyl proton density.
2. Partially deuterated lithium acetate dihydrate:

On partial deuteration of a methyl group the symmetry and the molecular rotational constant changes. Therefore a different dynamical behaviour is expected. In addition neutron diffraction offers a unique possibility to distinguish protons from deuterons due to the opposite sign of their neutron scattering lengths ($b_H = -0.37$ fm, $b_D = 0.67$ fm). The average scattering length of H/D amounts to almost zero. Thus the H/D-density distribution of a dynamically disordered CH$_2$D-groups vanishes, whereas any preferred orientation shows up as positive and negative contributions of the deuteron and protons, respectively.

Our room temperature single crystal diffraction experiment showed that LiAc-CH$_2$D is isostructural with LiAc-CH$_3$, orthorhombic space group Cmmm. The methyl groups are dynamically disordered and consequently no contribution to the scattering density is found. At 20 K, however, although the methyl groups are still disordered, weak positive and negative contributions are found.
in the difference Fourier density map (Fig. 2), indicating the onset of ordering. In the structure refinement the methyl protons and deuterons may be described with a split atom model, where each atom is distributed over two positions, which are related by a mirror plane. However the individual occupation parameters do not add up to unity.

Below 5 K the compound undergoes a phase transition from orthorhombic Cmmm to Pman. At 4 K the C-centering and one of the mirror planes are lost. This phase transition is also observed in the perdeuterated [8], but not in the protonated compound. The negative contribution of the protons and the positive contribution to the scattering density in the difference Fourier map are clearly visible (Fig. 3). The partially deuterated methyl groups are well localized. This localization is accomplished by a freezing of the methyl carbon at a position at 0.03 Å away from the c-axis and a corresponding shift of the geometrical center of the H2D-triangle. Thus the observed phase transition inherits a rotational as well as a displacive component. This is in perfect agreement with the interpretation of the methyl dynamics in terms of rotation-translation coupling, where the rotation of the methyl group around its axis is coupled to the center of mass motion around the center of symmetry of the crystallographic site. Within this model, freezing of the dynamics will lead to symmetry breaking and result in a center of mass position shifted with respect to the previous center of symmetry.

References:

Accurate determination of the potential energy surface for crystalline benzoic acid

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Vibrational spectra of several isotopomers of benzoic acid (BA) crystals have been recorded by inelastic neutron scattering and are compared with spectra calculated for different potential energy surfaces (PES). These PES were obtained within the harmonic approximation from quantum chemical density functional theory (DFT) calculations made for the monomer, the isolated dimer and the crystal using different codes and different levels of basis functions. Without refinement of the force constants, the agreement between calculated and observed spectra is sufficient for an unambiguous assignment of all vibrational modes. The best agreement was obtained with periodic DFT calculations. The most prominent discrepancy between calculated and observed frequencies was found for the out-of-plane O-H bending modes. For these modes (as well as for the in-plane bending and the O-H stretching modes) the anharmonicity of the potential was calculated, and the anharmonic correction was shown to account for about 1/3 of the discrepancy. The origin of the remaining difference is attributed to the slight compression of the hydrogen bonds in the calculated structure of the dimer, which also leads to a significant lowering of the frequency of the O-H stretch mode.

1. Introduction

In order to predict the structure and the dynamics of a molecular system, the knowledge of the potential energy surface (PES) is required. In the condensed phase, the relevant PES has both intramolecular and intermolecular contributions. For systems containing a few hundred atoms, quantum chemical calculations using efficient codes and ever more powerful computers are the best tools to establish this PES, while for larger systems, empirical force fields have to be used. To establish the reliability of these methods, it is vital to confront predictions derived from a PES with experimental data. The equilibrium geometry of stable configurations can be obtained from diffraction measurements and the curvature around these positions from vibrational spectroscopy. Vibrational frequencies, related to the curvature of the potential energy surface, are directly observed in the spectra, while the corresponding eigenvectors determine the line intensities. In IR and Raman spectroscopy the calculation of these intensities is subject to some uncertainty, requiring the knowledge of the derivatives along the normal modes of dipole moments and of polarizability tensors. In contrast, in vibrational spectra obtained by inelastic neutron scattering, the scattering intensity is simply given by the product of the amplitude of the motion with the known scattering cross section of a nucleus, summed over all atoms of the system, so that precise predictions of INS spectra can be made for any given PES [1,2]. Of particular interest in the context of the present work is the fact that the scattering cross sections of the proton and the deuteron differ by a factor of 20, so that isotopic replacements, which at the level of the computations have no influence on the force field, lead to significant changes of the observed intensities. Selective deuteration can thus be employed to highlight the motion of a specific hydrogen atom.

The shape of a PES near stable positions can be derived either from experimental data or from calculations, but trajectories relating different stable configurations and saddle points between them can only be obtained via computations. This knowledge of transition states and reaction paths is essential for the understanding of the chemical dynamics of a system, so that the reliability of computational approaches becomes a central issue. With this motivation, the present work was undertaken in order to establish the ground state PES of benzoic acid (BA) crystals and to assess thereby the reliability of available computational methods for calculating this PES. In this contribution we summarize recent work, a full account of which is given in Ref. [3].

2. Benzoic acid: a model system for proton transfer

Benzoic acid (BA) crystal is a benchmark model system for proton transfer along hydrogen bonds [4]. BA, as many other carboxylic acids, forms symmetric dimers in the crystal, linked by two hydrogen bonds (Fig. 1). There exist two tautomers, which interconvert by a concerted transfer of the two acid protons, a reaction that is dominated by tunneling. The hydrogen bond length and strength in these dimers as well as the structural changes during the proton transfer are typical for a large number of hydrogen bonded systems.

Fig. 1: The two tautomers of benzoic acid dimers, which interconvert via a concerted transfer of the two acid protons.
In order to calculate these dynamics, the knowledge of the potential energy surface (PES) is required. Near the equilibrium positions, the PES is well represented within the harmonic approximation and normal modes describe the dynamics. For the description of the proton transfer reaction, however, this separation of variables becomes invalid since none of the normal mode coordinates of the ground state points in the direction of the straight-line path connecting the equilibrium configurations of the two tautomers. In addition, force constants of all coordinates change along the reaction path. The PES describing the proton transfer is therefore multidimensional and cannot be reduced to a one-dimensional cut along the reaction coordinate. This is illustrated in Fig. 2 by 2D cuts of the PES. Much current effort is directed toward a proper description of this PES. For moderately large systems such as BA, the establishment of the relevant PES becomes very computer-time consuming and calculations must therefore be optimized and reduced to the minimal information required to construct the PES. This task as well as the description of the dynamics in this PES and in particular the identification of the active (coupled) modes has recently been the object of a novel, successful approach [5].

3. Experimental and computational techniques

**Materials:** fully protonated, C₆H₅COOH (BA-H₆), and ring deuterated, C₆D₅COOH (BA-D₅H). BA were commercial products, fully deuterated, C₆D₅COOD (BA-D₅). BA were obtained from BA-D₅H by multiple exchange with heavy water. ¹⁸O labeled, C₆H₅C²⁰O¹⁸OH (BA-¹⁸O) BA was synthesized from correspondingly labeled water and subsequently exchanged with light water since the starting ¹⁸O water was deuterated to about 80%. The isotopic purity of the deuterated compounds was determined to be ≥99% and that of the ¹⁸O compound ≥98%. Prior to use, all materials were purified by extensive zone refining.

**Spectra:** Inelastic neutron scattering spectra were recorded on powdered samples at 20 K with the TFAX (now TOSCA) spectrometer at ISIS (Rutherford Appleton Laboratories) [6].

**Computations:** Different codes have been used to establish the harmonic force fields for the isolated molecule, the dimer, and the crystal. The details of these methods and the parameters used are given in Ref. [3]. The results for the crystal, shown here, have been obtained using the *ab-initio* total-energy and molecular dynamics program VASP (Vienna *ab-initio* simulation program) [7]. From force constant matrices, vibrational frequencies and eigenvectors were calculated for different isotopomers by diagonalizing the dynamical matrix constructed with the corresponding mass matrix. Inelastic neutron scattering spectra, including overtones, combinations (including combinations with lattice modes), were calculated from the normal modes using CLIMAX [8].

4. Results

We have measured, by inelastic neutron scattering, vibrational spectra of several isotopomers of BA. These spectra are compared in Figs. 3 and 4 with spectra calculated for a PES obtained within the harmonic approximation from periodic quantum chemical (DFT) calculations made for the crystal using the code VASP. Even without having recourse to a refinement of the force constants, the agreement between calculated and observed spectra is sufficient for an unambiguous assignment of all vibrational modes. This full assignment is discussed in Ref. [3]. Let us just note here a particularly important result concerning the lowest frequency internal mode of benzoic acid, the carbonyl out-of-plane torsion. We have established that this mode, with a frequency of 86-89 cm⁻¹, lies in the region of lattice and inter-monomer modes of the dimer. This result explains the failure of previous attempts to arrive at a complete, satisfactory force field of the internal modes based on the assumption of a higher frequency of this mode [9] and the difficulties in accounting for the observed number of bands in the low-frequency IR spectrum [10]. The insufficiency of the force fields employed in these studies was also borne out when using these force fields as a starting point for a refinement with the program CLIMAX [11]. The same statement holds for normal mode calculations based on different generic force fields [12]. Because of the relatively large number of modes, this failure is not so surprising.

The most prominent discrepancy between calculated and observed frequencies was found for the out-of-plane O-H bending mode, where the calculated value exceeds the experimental value by 7.3% (70 cm⁻¹). This discrepancy is best visible in the spectrum of BA-D₅H in Fig. 3. For this mode as well as the in-plane O-H bending and stretching modes, the anharmonicity was calculated. Figure 5 illustrates for the symmetric O-H stretch mode the excellent fit of a quartic potential to the calculated energy as

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Fig. 2: Representative 2-D cuts of the potential energy surface of carboxylic acid dimers, illustrating different types of coupling of the tunneling coordinate with transverse skeleton coordinates (CO₂ rocking and interdimer stretch). The lines between potential minima illustrate in addition to the straight path the minimum energy path (continuous line) and the tunneling trajectory (broken line).
a function of displacement. Fits of similar quality were obtained for the other modes. From these potential curves, the anharmonic corrections were calculated and were found to account for about 1/3 of the discrepancy. The remaining difference is attributed to the slight compression of the hydrogen bonds in the calculated structure of the dimer.

5. Conclusion
The excellent overall agreement between the calculated and measured vibrational spectra of the BA crystal demonstrates that for systems as large as this, with 60 atoms in the unit cell, reliable force fields can be obtained directly, without adjustment of force constants, from periodic DFT calculations. Comparison of the calculations for the isolated monomer and dimer as well as the crystal, shows that the most important couplings are within one dimer, and that the coupling of dimers within the crystal is fairly small for most vibrational modes.

Regarding the proton transfer reaction in the benzoic acid crystal, the two vibrations for which the tunneling splitting is predicted to increase significantly in the excited state are the inter-monomer stretch and rocking modes [13]. The frequencies determined here for these modes (129-136 cm⁻¹), which are illustrated in Fig. 2, are in very good agreement with the activation energy derived from the temperature dependence of the proton correlation time (125 cm⁻¹).

Acknowledgments
We are very grateful to Herbert Zimmermann, who has synthesized the ¹⁸O labeled compound and to the former thesis students and postdoctoral fellows Lukas von Laue, Richard I. Jenkinson, and Dermot F. Brougham, who have participated at some early stages in this work. Stewart F. Parker and John Tomkinson provided help and useful discussions during the measurements at ISIS. The discussions with Don Kearley have always been stimulating and useful. The authors are grateful to the Centre Grenoblois de Calcul Vectoriel of the Commissariat de l’Energie Atomique (CEA-Grenoble) for the use of computing resources.
References


Methyl group dynamics in glasses by neutron scattering: from rotational tunneling to classical hopping

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We propose a barrier distribution model for the temperature dependence of neutron scattering spectra of methyl group dynamics in glassy systems, covering the crossover from rotational tunneling to classical hopping. In this model, the total spectrum is obtained from the weighed superposition of the crystal-like spectra of the individual methyl groups, each one driven by a different rotational barrier. An operational definition of the “crossover temperature” – i.e., that of the onset of the classical hopping regime- for each methyl group allows to eliminate a large set of unknown parameters, so that the only free parameters are the average barrier and standard deviation of the distribution, together with the preexponential factor of the Arrhenius law for the classical hopping rate. The model has been checked successfully in several polymeric and low molecular weight glasses.

Incoherent neutron scattering is an adequate technique for the study of the dynamics of small rotors as ammonia, methane, ammine ions or methyl groups [1]. The height of the rotational barrier can be accurately determined by measuring the rotational tunneling frequency in combination with measurements of the torsional frequencies and the activation energy for classical hopping. Due to the relatively simple character of their dynamics, these rotors are often used as internal dynamics probes to obtain information about characteristics of the environment by measuring the influence of such effects on the barrier height [1].

Local disorder is reflected in distributions of rotational barriers [2]. When such distributions are sufficiently broad, as for methyl groups in structural glasses, the corresponding distribution of tunneling frequencies has its maximum beneath the neutron scattering peaks in the spectra even at liquid helium temperatures [3]. This fact makes difficult to determine the values of the barriers in the glass. In this work, this problem is tackled by a simple three-parameter model (rotation-rate-distribution-model, RRDM [2-6]) for the temperature dependence of neutron scattering spectra for methyl group dynamics in glassy systems, covering the crossover from rotational tunneling to classical hopping [4].

Now we briefly summarize the usual model for methyl group dynamics in crystalline systems [1] and expose the grounds of the RRDM. At very low temperature, the methyl group tunnels through a one-dimensional rotational potential V(φ), which generally is approximated to the threefold term of its Fourier expansion: V(φ) = V0(1-cos3φ)/2. The tunneling frequency ωt can be detected by neutron scattering as two inelastic peaks (for neutron energy gain and loss) for barriers V0 below ≈ 700 K [1]. When increasing temperature, the coupling to the lattice phonons drives a crossover to the classical hopping regime [7]. As a consequence, the tunneling peaks broaden leading to Lorentzian lines and shift to the central elastic line [7]. At the same time, a quasielastic Lorentzian broadening appears around the elastic line [7]. The temperature dependence of the shift and broadenings is well approximated by Arrhenius laws activated by the first torsional energy F0 [7]. At temperatures typically about 50-70 K, the onset of the classical hopping regime is reflected in the merging of the quasielastic and inelastic Lorentzians into a quasielastic Lorentzian, which broadens according to an Arrhenius law activated by the classical activation energy Fc [7]. Thus, if Γ is the Lorentzian half-width at half-maximum: Γ = Γ0 exp(E0/kT), with Γ0 a temperature-independent preexponential factor. The merging occurs in a quite narrow temperature interval (ΔT = 5-10 K) that we will approximate as a unique “crossover temperature” Tc. The corresponding incoherent scattering functions are [1]:

\[ S_{nc}^{ω}(Q, ω) = \frac{Aδ(ω)}{ω} + B\left[δ(ω) + δ(ω-ω_t) + δ(ω+ω_t)\right] \]

\[ S_{nc}^{ωω}(Q, ω) = \frac{Aδ(ω)}{ωω_t} + B[L(ω/ω_t) + L(ω-ω_t/ω_t) + L(ω+ω_t/ω_t)] \]

\[ S_{nc}^{ωωω}(Q, ω) = \frac{Aδ(ω)}{ωωω_t} + 3BL(ω/ω_t) \]

for the tunneling, crossover and classical regime respectively. In these equations A = [1+2j0(Qr)])/3, B = 2[1-j0(Qr)]/9, j0 being the zeroth-order Bessel function and r the H-H distance in the methyl group. L is a normalized Lorentzian function, and Γω, Γωω, Γωωω the half-widths at half-maximum for the quasielastic and inelastic crossover Lorentzians and for the classical quasielastic Lorentzian respectively. Δω is the shift of the tunneling frequency.

These features are well established in crystalline systems [1]. However, in a glass the different local environments yield a different barrier Vi for each methyl group and therefore, a barrier distribution, g(Vi) in the system [2-6]. As a consequence, the spectrum of the glass results from the superposition of the crystal-like spectra of the individual methyl groups, weighed by g(Vi). The incoherent scattering function for methyl group dynamics will therefore be calculated as S_{nc}^{ωω}(Q, ω, V) = \int dV g(V) S_{ncω}^{ωω}(Q, ω, V), where each individual function S_{ncω}^{ωω}(Q, ω, Vi) will be given by one.
of the Eqs. (1-3). While in the low- and high-temperature limits all these individual functions will be given respectively by Eq. (1) or (3), at intermediate temperatures it is not evident what functional form -the crossover-like of Eq. (2) below $T_c$, or the classical-like of Eq. (3) above $T_c$- must be taken for each methyl group. This problem is solved by introducing a functional relationship $T_c = T_c(V_3)$, that can be obtained by taking into account that the classical regime is reached when the rate for incoherent hopping becomes comparable to rate for coherent tunneling. Thus, we define the crossover temperature as that where $\Gamma = \hbar \omega_0$, or equivalently, $kT_c = E_A/\ln(\Gamma / \hbar \omega_0)$. $T_c$ defined in this way depends only on $V_3$, since $E_A$ and $\omega_0$ are obtained as direct functions of $V_3$, and it can be seen that, for a given system, $\Gamma$ can be taken as a barrier-independent quantity [2]. This definition allows to choose the functional form (2) or (3) for each individual function $S_{\alpha\beta}(Q, \omega)$. Moreover, by imposing a continuity condition $\Delta_{\alpha\beta}(T_c) = \Gamma(T_c) = \Gamma(T_\omega)$ and taking into account that $\Delta \omega_0(T_\omega) = \omega_0$, and that the first torsional energy $E_{\alpha\beta}$ is also a direct function of $V_3$, it is straightforward to see that the preexponential factors of the Arrhenius laws for the crossover shift and broadenings can be calculated for each barrier $V_\alpha$. After this procedure, all the quantities appearing in Eqs. (1-3) are unambiguously determined if the values of $V_3$ and $\Gamma_{\alpha\beta}$ are given, and the total scattering function $S_{\text{RRDM}}(Q, \omega)$ can be calculated in terms of $\Gamma_{\alpha\beta}$ and the parameters of the distribution $g(V_3)$. In all the systems studied up to now in terms of the RRDM, good descriptions have been achieved with Gaussian [2-5] or Gamma [6] distributions, that are characterized by only two parameters: the average barrier and the standard deviation. Finally, the total coherent contribution and the incoherent contribution of the other atoms in the molecule, both assumed to be elastic are added, and the total function is convoluted with the instrumental resolution for comparison with the experimental data. The suitability of the RRDM, that has been checked successfully in several polymeric and low molecular weight glasses [2-6], is illustrated in Figs. 1, 2 for glassy sodium acetate trihydrate as a representative example [5]. The water molecules were deuterated in order to attenuate their incoherent contribution to the total scattering. Fig. 1 shows the experimental spectrum at 2 K, measured at the backscattering spectrometer IN16 of the ILL. The spectrum does not show defined tunneling peaks, but a broad feature, that results from the distribution of tunneling frequencies that follows from $g(V_3)$. The spectrum of the crystalline sample has also been depicted for comparison. The evolution of the spectra is shown in Fig. 2 by depicting the temperature dependence of the integrated intensities in different inelastic windows of IN16. An excellent description of the experimental results was achieved with a Gaussian distribution of pure threefold barriers. The obtained average barrier, 417 K, is within the error bar, equal to the unique one of the crystal [1]. The values obtained for the other parameters of the RRDM were 205 K for the standard deviation, and 4.8 meV for $\Gamma_{\alpha\beta}$. Solid lines in Fig. 2 are the theoretical curves given by the RRDM, modulated by a Debye-Waller factor as described elsewhere [3]. Dashed lines correspond to a description exclusively in terms of classical hopping. The intensity excess below $\approx 60$ K is due to the fraction of methyl groups still having not reached their crossover temperature.

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Nanoscale magnetic materials are of growing interest since the molecule $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4$ was found to act as a nanomagnet at very low temperatures (below the so-called blocking temperature). There is a worldwide effort to produce new "single-molecule magnets" and to raise the blocking temperature. A rational approach involves a deeper understanding of the physics of such compounds. Inelastic Neutron Scattering (INS) is one of the best methods for investigating the magnetic properties of spin clusters. To show how powerful this method can be, we will present some of our recent results on the clusters $[\text{Mn}_4\text{O}_3\text{X}(\text{OAc})_3(\text{dbm})_3]$ ($\text{X} = \text{F, Cl, Br, OAc}$). We are able to determine not only the axial zero field splitting parameter $D$, but also the rhombic term $E$ and the fourth order term $B^4_0$. The latter two parameters are responsible for the quantum phenomena (e.g. tunneling effect) found in this class of molecules.

The recent discovery of quantum tunneling of the magnetisation vector in molecular complexes with large spin ground states has motivated a renewed interest in molecular magnets containing a small group of metallic ions embedded in organic ligands [1,2]. In such structures, each metallic cluster is magnetically isolated from its neighbours, and this permits the study of the collective quantum behaviour in systems with a finite number of magnetic atoms. In this rapidly evolving field, inelastic neutron scattering studies have provided extremely valuable information on the exchange and anisotropy parameters in a number of systems such as the celebrated $\text{Mn}_{12}$-acetate [3] and $\text{Fe}_8\text{Br}_8$ [4]. This route was shown to be successful in obtaining an intimate insight of the local anisotropy parameters that (i) characterise the ground states of those molecules and (ii) that drive the quantum tunneling of the magnetisation through the energy barrier [2]. In this contribution we report an inelastic neutron scattering (INS) study of the "single-molecule magnets" $[\text{Mn}_4\text{O}_3\text{X}(\text{OAc})_3(\text{dbm})_3]$ ($\text{X} = \text{Br, Cl, OAc and F}$) that allows us to determine the relevant parameters associated with the low-temperature magnetic properties. The axial and rhombic terms of the anisotropy tensor and, eventually, 4th order terms [5].

As represented in figure 1, the cluster contains one Mn$^{\text{III}}$ and three Mn$^{\text{IV}}$ ions where the X ligand acts as a bridge between the Mn$^{\text{III}}$ ions. Altering the chemical nature of X changes the Mn-X bonding which drives the exchange couplings and the anisotropy [5,6]. The exchange coupling in the (Mn$^{\text{III}}$)$_4$O$_3$X cube has been studied by magnetic susceptibility measurements. [6]. Assuming isotropic exchange interactions, the appropriate spin Hamiltonian is given by $H_{\text{ex}} = -2J_1(S_1S_4 + S_2S_4 + S_3S_4) - 2J_2(S_1S_2 + S_1S_3 + S_2S_3)$ with $S_1 = S_2 = S_3 = 2$ for the Mn$^{\text{III}}$ ions and $S_4 = 3/2$ for the Mn(IV) ion (see figure 1). In all compounds the antiferromagnetic Mn$^{\text{III}}$-Mn$^{\text{IV}}$ exchange interaction $J_1$ is dominant: $J_1 = -20$ to -34 cm$^{-1}$ while $J_2 = +5$ to +8 cm$^{-1}$ [5,6] depending on the X ligand. From magnetisation and susceptibility data, it was shown that,
throughout the present series, the cluster spin ground state is a S=9/2 multiplet whose degeneracy is lifted by a negative axial zero-field splitting (ZFS) parameter D of the order of D ≈ -0.3 cm⁻¹ [5,6], resulting in an energy barrier ∆ ≈ 6 cm⁻¹ between the “up” and “down” spin orientations (see figure 2 for a schematic representation). The S=9/2 ground state is well separated from the next higher excited states and we can safely restrict our analysis to the ground state multiplet.

As an illustration, figure 3 shows the INS spectra (IN5, λ = 7.5 Å) for X = OAc at several temperatures. At 1.8 K we observe a prominent inelastic peak at ω₁ = 4.013 cm⁻¹, labeled (I), corresponding to the transition between Mₛ = -9/2 and Mₛ = -7/2 in the ground state multiplet. As the temperature increases to 18K, inelastic peaks at lower energies appear on both the energy-loss and energy-gain side. These “hot” ∆Mₛ = ±1 transitions, labeled as II, III and IV in figure 3, result from the thermal population of higher-energy Mₛ states. From the determined energy levels and the relative INS intensities we can show that the inclusion of a rhombic term E and a quartic term B⁴ in the ZFS Hamiltonian is essential to account for the data. To describe the ground-state transitions we make use of the following ZFS Hamiltonian:

\[ H_{ZFS} = D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2) + B^4 O^4 \]

with \( O^4 = 3S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 + 6S(S+1) \). The obtained parameters for X = OAc are: D = -0.469 cm⁻¹, |E| = 0.017 cm⁻¹ and B⁴ = -7.9 × 10⁻⁵ cm⁻¹. The same procedure allows us to determine these parameters throughout the compound series [5]. INS turns out to be the most direct and accurate technique to determine independently the parameters that control the quantum tunneling probability determined from magnetic measurements at low temperatures.

Fig. 3: INS spectra (full lines) of a polycrystalline sample of [Mn₄(0)₂(0Ac)₃(dbm)₃] recorded on IN5 at λ = 7.5 Å for temperatures T = 1.8, 3.0, 6.0 and 18 K, respectively. The peaks are labeled at the bottom of the Figure. The dotted lines represent a convolution of the experimental background with the quasi-elastic and elastic peak features. The resolution is 0.261 cm⁻¹ at the elastic line.

References
The structure and the dynamics of carbon dioxide near the critical point have been investigated using Small Angle Neutron Scattering (SANS) and Neutron Spin Echo (NSE), respectively. By virtue of the short wavelength and well adapted energy, Neutron Scattering is the only technique able to investigate the structure and the dynamics of fluids in the critical regime as well as the crossover between critical and mean field regimes. From the SANS results, the universal scattering function $g(x)$ has been determined for the first time in an extended range as well as a precise evaluation of the critical index $\gamma$. The NSE results allowed to test the Kawasaki and dynamic scaling hypothesis in the critical and crossover regimes.

1. Introduction
Second order phase transitions are characterized by the appearance of large fluctuations of the order parameter which diverge at the critical point. An archetype of these transitions is the liquid-gas phase transition which occurs to carbon dioxide $\text{CO}_2$ at $\rho_c=0.468$ g/cm$^3$ and $T_c=304.23$ K, giving rise to the well known “critical opalescence”. Critical fluctuations are correlated defining a characteristic “correlation length” $\xi$ which diverges at the approach of the critical point. Although this phenomenon has been known for more than a century, the microscopic properties of the critical fluctuations close to the liquid-gas transition, and more particularly their dynamics, are not yet well known. Indeed most of the investigations were performed using light scattering; but the values of the momentum transfer $Q$ accessible by this technique does not allow to reach critical conditions defined by the product $Q\xi>1$.

2. Static properties [1]
On the critical isochore, correlation lengths diverge as $\xi = \xi_c t^\nu$ where $\nu$ is an universal critical index, $\xi_c$ a system dependent characteristic length and $t$ the reduced temperature $t = \frac{T - T_c}{T_c}$ with $T_c$ the critical temperature. The measurement of the correlation lengths which range from 10 to 1000 Å required small momentum transfers (0.001<Q<0.2(Å$^{-1}$) and a high stability in temperature (1 mK). The desired Q-range was obtained with the spectrometer D11 (ILL) using several sample-to-detector distances (1.7 to 37 m) and two wavelengths (6 and 10 Å). A good temperature stabilization and precision was obtained by adding a second stage temperature control inside a standard ILL orange cryostat and using calibrated platinum resistors. A few scattering curves are reported in figure 1 revealing a strong divergence at the approach of the critical point.

The strong scattering intensity observed at small Q at the approach of the critical point is governed by the universal scattering function $g(x)$, with $x = Q\xi_c t$ $\sim \xi^\gamma g(x)$ where $\gamma = 1.23$ is the critical index
related to the divergence of the isothermal compressibility.

Far enough from the critical point (i.e. \( x << 1 \)) the diffusion intensity obeys the Ornstein-Zernike law

\[
g_{\text{OZ}}(x) = (1 + x^2)^{-1}
\]

At the critical limit \( x \to \infty \), \( g(x) = C_x x^{2+\eta} \), where \( \eta \) is a critical index whose value is about 0.03 in the critical regime and strictly zero in mean field. The function is not analytical in the crossover region (\( x = 1 \)). Several semi-empirical approximations have been proposed; the most accredited is due to Fisher and Langer [2]:

\[
g(x) = C_x x^{2+\eta} \left[ 1 + C_i / x^{1+\eta} + C_i / x^{1-\eta} \right]
\]

We were able to produce the first experimental determination of \( g(x) \) in an extended range (0.01<\( x <60 \)); the function \( h(x) = \ln[g(x)/g_{\text{OZ}}(x)] \), i.e. the excess of \( g(x) \) from \( g_{\text{OZ}}(x) \), is reported in figure 2 as well as a few semi empirical evaluations in the crossover region. The best experimental evaluation of the critical index \( \eta \) is 0.042(6).

3. Dynamics

In the critical region, two regimes may also be identified depending on the value of the relevant parameter \( x = Q_\xi \).

The dynamic scaling hypothesis, predicts the following Rayleigh linewidth at the critical limit \( x>>1 \):

\[
\Gamma_x = D_x Q_x^2 \xi^{2+\nu} \nu = D_x Q_x^{2+\nu} (Q_\xi)^{2+\nu} = D_x Q_x^{2+\nu} (Q_\xi)^{2+\eta}
\]

with \( 1+2\nu = 2\gamma \) and \( \gamma \) the critical index relative to the divergence of the thermal conductivity.

In another approach (Kawasaki [3] mode coupling theory), the width of the quasielastic Rayleigh line is supposed to vary as:

\[
\Gamma_x = A\eta F(x), \quad \text{with} \quad F(x) = \frac{2}{\pi} \left[ x^\nu + x^2 + (1 - x^2) a \tan(x) \right]
\]

and \( A=k_BT/16\eta \), where \( k_B \) is the Boltzmann constant, \( T \) the temperature and \( \eta \) the shear viscosity assumed to be independent of \( Q \) and \( \xi \).

In the hydrodynamic regime (\( x<<1 \)), neutrons probe at a scale larger than the correlation length of the critical density fluctuations; therefore the hydrodynamic regime is controlled by \( \xi \). Indeed \( F(x) \to 8/3\pi x \) and \( \Gamma_x = 8\pi Q_x^2/3\xi_x = D_x Q_x^2 \), with \( D_x \) the thermal diffusivity. In the critical regime (\( x>>1 \)), the dynamics is probed inside the correlated volume and the relevant parameter is therefore the momentum transfer \( Q \); \( F(x) \to 1 \) and \( \Gamma_x = A\eta Q_x^2 \).

The Kawasaki approximation does not satisfy the boundary condition imposed by the dynamic scaling hypothesis in the large-\( x \) limit and varies like \( x \) rather than \( x^{2+\eta} \). Burstyn et al. [4] improved the Kawasaki function by taking into account the frequency and wave-vector dependence of the viscosity. Their approximant \( F(x) = R_x F(x) \left[ 1 + (x/2)^{1/2} \right]^{1/2} \) satisfies both boundary conditions of the dynamic scaling i.e. \( D \propto \xi_x^{-\nu} \) for \( x \to 0 \) and \( D \propto Q_x^{2+\eta} \) for \( x \to \infty \).

Neutron spin echo spectroscopy which directly measures the intermediate scattering function \( S(Q,t) \) gives a direct access to the relaxation time \( \tau_x \) of the density fluctuations (figure 3); \( \tau_x \) and \( \Gamma_x \) are related by \( \Gamma_x (\text{mu}eV) = 0.6583 / \tau_x (\text{ns}) \).

Figure 4 displays the experimental results of the Rayleigh linewidth giving a nice evidence of the dynamic scaling and of the crossover between the hydrodynamic and critical regime.

**References**


Small-angle neutron scattering in nanocrystalline glass ceramics in potassium niobium silicate system

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On controlled heat treatment at temperatures slightly above the glass transition temperature \( T_g \), potassium niobium silicate glasses (KNS) of the general formula \( xK_2O \cdot y\text{Nb}_2\text{O}_5 \cdot (1-2x-y)\text{SiO}_2 \) show optical non-linearities (e.g., second harmonic generation - SHG) while remaining transparent and “X-ray amorphous”. Although the detailed mechanism of SHG generation in KNS glasses is not yet fully understood, this behaviour is attributed to formation of nanometric clusters and/or nuclei of non-centrosymmetric phase in the bulk glass. Prolonged heat treatment at elevated temperatures leads to gradual onset of opalescence and eventual crystallisation. Small-angle neutron scattering of these materials clearly shows the development of inhomogeneities on the length scale of 5-20 nm with duration of the heat treatment, giving a direct evidence of non-linear optical nanostructure in KNS glasses. The studies enable us to correlate the SHG efficiency with the average size of inhomogeneities and to optimise the technological parameters leading to well transparent non-linear optical materials of a novel type.

1. Introduction

On controlled heat treatment at temperatures slightly exceeding the glass transition temperature \( T_g \), potassium niobium silicate (KNS) glasses exhibit liquid-type phase separation leading to spectacular optical non-linearities – in particular second harmonic generation (SHG) [1]. The possible cause of this behaviour is the growth of (possibly non-centrosymmetric) clusters on nanometric scale in the bulk of glass, but the detailed microscopic mechanisms of SHG generation are not yet quite clear [2]. Since their relative SHG efficiency is rather high, these materials present not only scientific but also practical interest – as an alternative to crystals for non-linear optical applications.

At the earliest stages of phase separation, the glass remains amorphous from the point of view of X-ray diffraction since the clusters are evidently too small and/or too distorted to show X-ray Bragg reflections. With prolonged heat treatment at elevated temperatures, however, opalescence usually starts to develop and is eventually followed by crystallisation, leading to loss of transparency.

To test the idea of nanoclusters and to characterise the inhomogeneous structure of these glasses, we carried out small-angle neutron scattering (SANS) experiments on selected glass samples in the KNS system, i.e. \( xK_2O \cdot x\text{Nb}_2\text{O}_5 \cdot (1-2x)\text{SiO}_2 \) with \( x = 0.18-0.25 \), as a function of prolonged heat-treatment at elevated temperatures. The spectra were recorded using the D11 neutron diffractometer of ILL, Grenoble.

2. Results

SANS studies of initial and heat-treated KNS glasses were carried out both at room temperature and in the 680-850°C range at a wavelength of \( \lambda = 0.45 \text{ nm} \). Initial glasses (prior to heat treatment) were homogeneous, in accordance with their vanishing SHG efficiency.

As proposed by Guinier [3], the behaviour of the scattering curve, \( I_s(q) \sim (\bar{U} - <\bar{U}>^2) \exp(-q^2 R_g^2/3) \), at small \( q \) makes it possible to estimate the characteristic size parameter \( R_g \) (Guinier radius) of the inhomogeneities, provided their density \( \bar{U} \) differs from the average density \( <\bar{U}> \). On the other hand, we can analyse the \( q^2 I_s(q) \)

Fig. 1: Guinier plots of the SANS intensity of the \( x=0.25 \) glass for heat treatment at several temperatures.
dependences to estimate the integrated averaged square of the nuclear density \( \langle \rho^2 \rangle \), which is proportional to the area under the \( \rho \langle q \rangle \) curves and characterises the total degree of inhomogeneity of the two-phase medium [4].

We show in Fig. 1 the Guinier plots (\( \ln I_S \) vs. \( q^2 \)) obtained for an initially homogeneous sample of \( x=0.25 \) composition \( (T_g = 688 \, ^\circ C) \) as a function of heat treatment in the furnace during successive measurements. Corresponding \( I_S q^2 \) vs. \( q \) plots in Fig. 2 shows qualitatively the degree of inhomogeneity of the sample (as proportional to the area below the broad peaks). The curves indicate that this glass remains homogeneous up to \( \sim 700^\circ C \). On prolonged duration of heat treatment at \( 706^\circ C \), nanometric inhomogeneities start to develop in the bulk. At this temperature, the inhomogeneities continue to grow slowly in size, with a clear tendency to saturation with time. The average radius \( R \) of these inhomogeneities estimated from the plots is shown in Fig. 3 as a function of the heat treatment duration at \( 706^\circ C \). Assuming spherical shape, the limiting diameter \( 2R \) remains here below \( \sim 10nm \). We note that total degree of inhomogeneity increases with time too, showing similar trends like \( R \). Small sizes of nanoclusters and absence of their growth on prolonged treatment at this temperature is typical for the nucleation stage - i.e. liquid-like phase separation - in controlled bulk crystallisation of glass. This state of the samples correlates well with the onset of efficient SHG generation (Fig. 4). Further increase of temperature and duration of the heat treatment leads to a steep rise of \( R \) accompanied by strong opalescence and decreasing SHG signal.

**Fig. 2:** \( I_S q^2 \) plots of the SANS intensity of the data of Fig. 1.

**Fig. 3:** Average diameter of the inhomogeneities in the \( x=0.25 \) glass vs. heat treatment duration at \( T_{HT} = 706^\circ C \).

Similar behaviour is shown by KNS glasses of the \( x=0.22 \) composition \( (T_g = 705^\circ C) \); SANS data on other samples evidence that nanostructuring of KNS glasses takes place even outside the phase separation region [2].

**3. Conclusions**

Our measurements of KNS glasses made it possible to observe the nanostructuring process from initial homogeneous glassy state to the creation of well-defined nanostructure penetrating the whole volume of the samples. Correlation of the SANS results with SHG provide a unique possibility to characterise the nanometric structure of transparent glass with nonlinear optical properties and, eventually, to optimise the technological parameters leading to good transparence and efficient SHG. Further SANS studies complemented by other techniques are needed to provide new information on nanostructuring of glasses of differ-
ent composition in the KNS system, on nucleation and growth kinetics, on the nature of phase separation and on the origin of non-linear optical phenomena in KNS glasses.

Particularly interesting are glass compositions outside the phase separation region (e.g. with $x=0.16$ and those with K$_2$O-to-Nb$_2$O$_5$ ratio different from unity), which show moderately efficient SHG and good transparency (no opalescence). Also, a detailed SANS study of the behaviour of the $x=0.18$ glass, which is characterised by disappearance of opalescence at higher temperatures, would be of great interest for the physics of non-linear phenomena in glasses, because in this case the liquid immiscibility process is not obscured by crystallisation processes (taking place in glass compositions close to $x=0.25$).

The results on nanostructured KNS glasses are expected to contribute to our understanding of the mechanisms underlying the non-linear optical behaviour and to shed new light on the nature of the medium range order in glass.

**Acknowledgements**

The authors are grateful to Charles Dewhurst of the ILL staff for efficient assistance with the D11 diffractometer.

**References**


We present a preliminary investigation of the dynamics of glassy Polycarbonate by means of Quasielastic Neutron Scattering (QENS) and Dielectric Spectroscopy (DS). The momentum transfer dependence of both, the coherent and incoherent scattering functions, reveals the existence of some complex chain motion likely also involving phenyl ring \( \pi \) -flips. On the other hand, the similarity of the energy landscape deduced from both techniques, DS and QENS, points to the idea that the carbonyl unit movement is highly influenced by the motions observed by QENS.

1. Introduction

Most of the engineering thermoplastics - materials with a well-known technological significance - are glassy polymers, and many of their desirable properties are directly related with the dynamical processes occurring at the molecular scale. For the design of new materials with improved properties is thus essential to understand the relationship between molecular dynamics and mechanical properties of these polymers. Polycarbonate (PC) is a typical example. Its dynamics has been thoroughly investigated by means of different techniques (NMR, DMS, DS, PALS...) [1-6] for a long time, and by different approaches, like the study of various copolymers, blends, and substituted (ring and main chain) polycarbonates. Some computer simulations also add to this list [7-9]. Nowadays it is widely accepted that the dominant large amplitude motion for the main chain in glassy PC involves a 180\(^\circ\) phenylene ring \( \pi \) -flip [7 and references therein]. However, the exact mechanism leading to the occurrence of these flips is not yet clear. There is not a consensus on questions like, e.g., up to which extent and in which way do the inter and intrachain interactions affect the flipping process, whether the ring flips need cooperative motions of different units along the chain or not, or the influence of the chain packing [10-13] on the process. In order to contribute to these questions, we are carrying out a combined study on glassy Polycarbonate dynamics by means of Dielectric Spectroscopy (DS) and Quasielastic Neutron Scattering (QENS). This last technique is an essential tool for revealing the molecular mechanisms responsible for a given dynamics, because i) they offer space-time resolution at a molecular level and ii) due to the difference between the scattering lengths of hydrogen and deuterium, the system can be selectively studied at atomic level.

2. Experimental

QENS measurements were performed by means of the backscattering spectrometer IN16 at the Institute Laue Langevin ILL, Grenoble. An incident wavelength of 6.27 Å was used, covering a Q range between 0.2 Å\(^{-1}\) and 1.9 Å\(^{-1}\) and an energy window from –15 to 15 µeV with 1 µeV (FWHM) resolution. The coherent scattering related to the atom pair correlation function was obtained from measurements on a fully deuterated sample (PCd14), and the incoherent scattering corresponding to the selfcorrelation function of the protons in the phenyl rings dominates the cross sections obtained from a sample with deuterated methyl groups (PCd6). Temperatures up to about the glass transition temperature \( T_g = 420 \text{ K} \) were investigated.

In DS experiments, the complex dielectric permittivity \( \varepsilon^* = \varepsilon' - i\varepsilon'' \) was measured in the frequency range \( 10^{-2} - 10^6 \) Hz and at temperatures between 125K and \( T_g \).

3. Results and Discussion

Neutron Scattering: The elastic incoherent intensity measured begins to deviate from the decay corresponding to harmonic vibrations, the Debye Waller Factor (DWF), at about 200 K [14]. At the same time, an increase of the quasielastic intensity is observed, indicating the onset of a motion in the dynamical range accessible by IN16 (see Figure 1). The Q modulation of the inco-

![Fig. 1: Incoherent quasielastic intensity as a function of Q for different temperatures. Solid lines: modelled data for EISF=1/4(1+(sinQd)/Qd)*(1+(sinQD)/QD) with d=4.3 Å, D=2 Å and a distribution of activation energies with <Ea> =0.42eV and \( \sigma =0.12eV \). The dashed line shows the expected Q-dependence for pure phenyl ring \( \pi \) -flips.](image)
herent signal is similar for all the temperatures investigated. This leads to a factorable dependence of the quasielastic intensity on the geometry and on the dynamics. According to this, and taking into account the localized character of the dynamical processes involved in the sub-$T_g$ region, the incoherent scattering function has been assumed to be:

$$S_{inc}(Q, \omega) = DWF \{EISF + (1-EISF)f_{inel}(\omega)\}$$  \hspace{1cm} (1)$$

where EISF is the so-called Elastic Incoherent Structure Factor, a quantity only spatially dependent, and $f_{inel}(\omega)$ gives account for the dynamical dependence. The exact functional form of EISF depends on the way in which the scattering unit (protons in our case) moves, so the EISF monitors the geometry of the motion, provided it is local. The first approach was to model the geometry considering pure phenyl ring p-flips. The EISF for a scatterer performing jumps between two equivalent positions is given by $1/2[1+\sin(Qd)/Qd]^{15}$, where $d$ is the jump distance, 4.3Å in this case. The $Q$ dependence given by this EISF describes well the observed quasielastic intensity modulation below $Q \sim 1.3$Å (see dashed line in Figure 1), while at higher $Q$-values the quasielastic intensity corresponding to a $\pi$-flip is lower than that experimentally observed. The occurrence of isolated phenyl ring $\pi$-flips is thus not enough to explain the QENS spectra. Moreover, the coherent scattering data obtained from the PCd14 sample show a quasielastic intensity that increases with $Q$. Since motions which do not alter the configuration of the system (and phenyl ring flips do not) do not give rise to coherent inelastic signal, our observations indicate the existence of some centre of mass motion in addition to the rings flips. The experimental behavior of the incoherent scattering function can indeed be better explained considering an EISF equal to $1/2[1+\sin(QD)/QD] + 1/2[1+\sin(QD)/QD]$, with $d = 4.3$Å fixed and $D$ fitted to the best value adjusting data, $D=2$Å. In this framework, the centre of mass would undergo a displacement of about 2Å.

In order to model the dynamics, an explicit form for the frequency dependence of $S_{inc}(Q, \omega)$, i.e., for $f_{inel}(\omega)$ has to be assumed. A Gaussian distribution of thermally activated Debye processes originated by local disorder gives usually account for the dynamical behavior of sub-$T_g$ processes. Under this hypothesis, the experimental data at all the temperatures below $T_g$ were successfully described with the distribution of activation energies shown in Figure 2. A preexponential factor $\tau_0=10^{-13}$s in the Arrhenius law corresponding to all the activated jumps was assumed. The full modelled quasielastic intensity is depicted by solid lines in Figure 1, where a good agreement between theory and experiment can be appreciated.

Dielectric Spectroscopy: A distribution of activation energies originated by local disorder has also been assumed in the analysis of the DS data. Due to the marked asymmetric shape of $\varepsilon'$ vs Logf(Hz)[14], a $\chi^2$-type distribution was used for describing the data, instead of a Gaussian function.

Figure 2 shows the distribution functions of energy barriers obtained from both kinds of techniques. As can be seen, though the shapes are different, the average value for the activation energy and the width of the distributions are similar. These findings support the idea that the carbonyl unit movement is strongly influenced by the motions observed by QENS.

4. Conclusions

The occurrence of only phenyl ring $\pi$-flips is not enough to explain the QENS experimental data of PC below $T_g$. The $Q$ dependence of the incoherent data together with the coherent ones indicate the existence of a more complex chain motion also involving phenyl ring $\pi$-flips. We hope that a deeper investigation of the coherent intensity will provide a better understanding of the geometry of the motion. Work in this direction is currently in progress. On the other hand, the similarity of the energy landscapes for the carbonyl units accessed by DS and for the phenyl groups obtained by QENS supports the idea that the carbonyl unit movement is highly influenced by the motion observed by QENS.

Acknowledgements

S. Arrese-Igor acknowledges the grant of the Basque Government. We also thank the support received from "Donostia International Physics Center" and the following projects: DGICYT, PB97-0638; GV, EX 1999-11; UPV/EHU, 206.215-G20/98.
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High-frequency brillouin scattering from strong glasses: state-of-the-art and prospects

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At the present time, neutron Brillouin scattering is possible with triple-axis spectroscopy only in glasses for which the sound velocity is quite low, owing to kinematic reasons and achievable resolutions. An example will be shown for glassy selenium. On the other hand, inelastic X-ray scattering (IXS) does not suffer from kinematic constraints. This recently allowed to observe acoustic phonons and their crossover to diffusive modes in the particular case of densified silica. However, the IXS instruments rarely allow to explore the true plane-wave phonon regime. There clearly remains inaccessible gaps in the scattering vector and energy regions that were important to explore in order to make progress on the physics of glasses. An approach is to investigate with neutrons model disordered systems that have kept Bragg periodicity. A more ambitious plan is to develop new instruments. Some possibilities will be reviewed.

1. Introduction

The nature and properties of collective vibrations in glasses is a matter of current interest. At first sight, owing to the absence of Brillouin zones, only acoustic vibrations of small wavevectors $q$ can be expected in a structurally disordered medium. As far as the medium can be considered as a continuum at the scale of the acoustic wavelength, plane-wave phonons are approximate solutions for the equations of motion. In vitreous silica, $\nu$-SiO$_2$, experiments over a broad frequency range, from 1 MHz to 400 GHz, have shown that weakly damped acoustic waves propagate in glasses [1,2]. The damping originates mainly from relaxation and resonant interactions with local excitations associated with structural disorder. A still open question concerns the vibrations at very large wavevectors, where the wavelength of phonons becomes of the order of the largest structural fluctuations in the glass structure. In fact, the plateau observed near 10 K in the thermal conductivity of most glasses gives evidence for a limit in the propagation of acoustic phonons at frequencies $\Omega$ around a few meV [3,4]. It is thus of crucial interest to investigate high frequency acoustic vibrations in coherent spectroscopy experiments in order to observe a possible end of the acoustic branches. This could also allow to improve our understanding of glass structure.

2. Experimental results

Inelastic X-ray spectroscopy experiments performed on several glasses for scattering vectors $Q$ in the nm$^{-1}$ range give evidence for Brillouin-like scattering peaks in the meV range [5]. However, serious difficulties arise in the interpretation of the data. In most experiments, the weak Brillouin-like peaks appear on the tail of the strong Lorentzian line associated with elastic scattering. It is thus hard to extract the profile of the inelastic signal with an accuracy sufficient to allow a significant comparison with theoretical models, in particular in the low frequency region of the spectra. This has been the origin of a debate on the nature of high frequency collective excitations in glasses [6]. Analyzing the data in $\nu$-SiO$_2$, with a model which assumes an inhomogeneous scattering of plane waves by structural disorder, we concluded that acoustic phonons cease to propagate at a Ioffe-Regel crossover frequency, $\Omega_{ir} \sim 4$ meV [7,8]. This Ioffe-Regel frequency marks the crossover to strong scattering of plane waves above which they cease to propagate, the eigenmodes of the problem being very different from plane waves at these frequencies. The main difference between the predictions of the models for the inelastic structure factor, $S(Q,\omega)$, occurs in the low frequency part of the spectrum [9]. Thus, to allow for a discrimination between the different pictures, the glass investigated must have a high sound velocity, in order to obtain a maximum frequency shift between the Brillouin peaks and the elastic line. On the other hand, scattering vectors in the nm$^{-1}$ range probe the material at a scale of a few nm. A better structural homogeneity at this scale would allow the propagation of plane waves up to larger $q$-values, opening a wider frequency window for the experiment. It might also lead to smaller intensities for the elastic line. The above requirements are met in densified silica, $d$-SiO$_2$. IXS measurements in $d$-SiO$_2$ have given evidence for a crossover to strong scattering, with $\Omega_{ir} \sim 9$ meV [10]. More recently, a similar crossover was evidenced in ($B_2O_3$)$_x$($Li_2O$)$_{1-x}$ glasses [11].

High frequency longitudinal acoustic vibrations in non-periodic materials can also be studied by inelastic neutron scattering (INS) on high resolution triple-axis instruments. However, within the present possibilities of the instruments, kinematic conditions restrict the experiments to materials of low sound velocity. This requirement precludes most strong glasses from being investigated in neutron spectroscopy. Brillouin scattering from high-frequency acoustic modes was measured in glassy selenium [12]. In this case, the crossover to strong scattering was
found at Ω ~ 3.4 meV. In addition, diffuse Umklapp scattering gives information on transverse acoustic modes. It shows that all acoustic excitations cease to propagate beyond ~ 5 meV in that case.

3. Prospects

To progress on these questions one can consider the use of either IXS or INS. In the former case, efforts are currently made to improve the contrast of the spectrometer by reducing the wings of the instrumental functions. This is described elsewhere [13]. In the case of INS, one could select to investigate systems that are structurally crystalline but dynamically disordered. Such is the case for alloyed crystals of Si-Ge. Preliminary results [14] show that transverse acoustic phonons experience considerable temperature-independent broadening owing to the disorder. One hopes to be able to observe the Rayleigh scattering by disorder, and to investigate its modification upon the approach of the zone boundary. Quartz crystals partially amorphized by fast neutron irradiation provide another opportunity to investigate the influence of structural disorder on the propagation of high-frequency acoustic phonons.

A more ambitious INS project were the construction of a dedicated instrument offering very high Q- and ω-resolution for neutrons of high energy. A step in this direction is the work on BRISP [15]. The advantage that this will bring is restricted to work in liquids or compressed gases for which it opens a small window. In the case of glasses one would like neutron velocities of at least 4000 m/s if not higher, in order to investigate a broad choice of materials. This implies incident energies of 150 to 200 meV with resolution of ~ 1 meV and very small scattering angles of ~ 0.1°. A possible design for such an instrument has already been proposed [16]. The proposed design relies on the optimal use of a focussing crystal monochromator, but one should keep in mind that in this energy range a pulsed source based chopper spectrometer might overcome in efficiency at equal resolution [17]. A case study with a specific implantation is necessary. Anyhow it is sure that a fully optimised instrument with the specifications discussed above would open new perspectives in the understanding of the vibrational dynamics of glasses.

References
High-resolution neutron diffraction and Raman spectroscopy were carried out on germanium-rich binary \( y\text{GeS}_4/(1-y)\text{GeS}_2 \) glasses. These experiments show new structural features: highly distorted sphalerite-like elements \( \text{GeS}_4 \) at \( y \geq 3 \) becoming predominant at \( y \approx 0.7 \).

1. Introduction

Binary chalcogenide glasses were extensively investigated in the seventies and eighties using various diffraction and spectroscopic techniques. However, the resolution in real space of conventional diffraction methods was not sufficient caused by a limited range of scattering vectors \( Q \) [1-3]. High-resolution neutron diffraction on a spallation source, anomalous wide-angle X-ray scattering and high-energy X-ray diffraction on a 3rd generation synchrotron light source allow more structural features to be distinguished. Over the past ten years, these experiments were carried out mostly on stoichiometric chalcogenide glasses [4-7]. In this paper, we report the results of high-resolution neutron diffraction and Raman spectroscopy measurements for non-stoichiometric \( y\text{GeS}_4/(1-y)\text{GeS}_2 \) vitreous alloys.

2. Experimental details

Neutron diffraction (ND) experiments were carried out on GLAD (IPNS, Argonne National Laboratory, USA), SANDALS (ISIS, Rutherford-Appleton Laboratory, UK) and 7C2 (Laboratoire Léon Brillouin, Saclay, France) diffractometers. Raman spectra were measured on a DILOR XY system equipped with a Si CCD detector and using the 647.1 nm line of a Kr laser as excitation source (Centre d'Études et de Recherche en Spectrométrie (EUDIL), Lille, France).

3. Results

Typical structure factor \( S(Q) \) for the investigated glasses is presented in Fig. 1, taking glassy \( \text{GeS}_2 \) as an example. Distinct oscillations in the \( S(Q) \) can be observed till 30 Å\(^{-1} \) and even at higher \( Q \) allowing high resolution of real-space functions after Fourier transform. The first sharp diffraction peak (FSDP) at \( Q = 1 \) Å\(^{-1} \) is indicative of a significant intermediate-range order mainly caused by Ge-Ge correlations at 6-7 Å [8]. Figure 2 shows the total correlation functions \( T(r) \) for selected glasses obtained by Fourier transform of \( S(Q) \) using a Lorch window function. Four peaks can
easily be identified in this particular case. The feature at 2.22-
2.23 Å corresponds to Ge-S first nearest neighbours in a GeS_{4/2}
tetrahedron. The intensity of this peak decreases with increasing
y. The second peak at ≈ 2.5 Å corresponds to Ge-S and Ge-
Ge first neighbour correlations in ethane-like units, at least at
y ≤ 0.3. This feature becomes predominant at y > 0.7. The Ge-
Ge second neighbour contacts in edge-shared GeS_{4/2} tetrahedra are
responsible for a small peak at ≈ 2.9 Å (GeS-poor glasses) and
≈ 2.8 Å (GeS-rich glasses). The fraction of the edge-shared tetrahe-
dra f_{es} for the stoichiometric GeS_{2} glass, f_{es} = 0.44(3), is com-
parable with that for the high-temperature crystalline α-GeS_{2}
modification (f_{es} = 0.5) [9], but increases significantly with y. The
peak at ≈ 3.5 Å corresponds to Ge-Ge second neighbour correla-
tions in corner-shared tetrahedra and S-S second neighbours.
Typical Raman spectra of the yGeS (1-y)GeS_{2} glasses are given
in Fig. 3. One can observe very systematic changes with increasing
GeS content. In accordance with many experimental results
and theoretical calculations [10-13], there are two groups of lines
in g-GeS_{2}: (i) the A_{1} mode in corner-sharing (CS) GeS_{4/2} tetrahe-
dral units at ca. 343 cm^{-1}; and (ii) two modes at 373 and 435 cm^{-1}
characteristic of edge-sharing (ES) GeS_{4/2} tetrahedra. At y = 0.1-
0.2, two new spectral features at 260 and 406 cm^{-1} clearly
appear. Usually, they are attributed to Ge-Ge vibrations in ethane-
like units [13]. The peak at 260 cm^{-1} is asymmetric and contains
a shoulder at ≈ 237 cm^{-1}. Above y = 0.3, this shoulder transforms
in a broad peak, whose position seems to be shifted to lower fre-
frequencies from 230 to 200 cm^{-1}. In contrast, the feature at 260
cm^{-1} disappears. As expected, the CS-GeS_{4/2} tetrahedral feature
at 343 cm^{-1} decreases with y. However, the fraction of the ES
tetrahedra increases with y, consistent with the obtained ND
results, while the fractional intensity of the lines at 373 and 435
cm^{-1} increases compared to that of the 343 cm^{-1} one.

4. Discussion
The composition dependence of the first neighbour coordination
numbers exhibits a surprising behaviour (Fig. 4). The expected
trends were found only in the composition range below y = 0.3,
i.e., the extrapolated intensity of the first peak at 2.22-2.23 Å goes
to zero at y → 1, and that of the ethane-like units to 1 with the
local coordination number of germanium, N_{Ge,X} = 4 (3 Ge-S and
1 Ge-Ge bonds). At y ≥ 0.4, the structural organisation of the
glasses seems to be changed. A clear indication of that is rep-
resented by new composition trends, N_{Ge,X} (2.23 Å) → 1 and
N_{Ge,X} (2.5 Å) → 3 at y → 1. The suggested structural changes
are consistent with the Raman scattering results.
The following scenario could be proposed for the investigated yGeS
(1-y)GeS_{2} glasses. Between y = 0 and 0.2, only ethane-like units
coexist with the regular CS and ES GeS_{4/2} tetrahedra in the glass
network. They are GeX_{4} = GeS_{3}Ge tetrahedra with N_{Ge-X} = 4 and
N_{Ge-X} = 2, seen in the ND results. Above y = 0.3, the third type
of structural units appears in the network, most probably highly
distorted sphalerite-like units GeS_{4/4} (3 Ge-S bonds of 2.5 Å and

Fig. 3: Typical Raman spectra of germanium-rich Ge-S glasses. (\lambda_{exc} = 647.1 nm).

Fig. 4: Ge first nearest neighbour coordination numbers for structural features at
≈ 2.23 Å (○) and ≈ 2.5 Å (●). The average Ge environment is always
tetrahedral (□).
1 Ge-S bond of 2.23 Å with $N_{GeS} = N_{GeS} = 4$. Between $y = 0.3$ and ca. 0.7, the fraction of the GeX$_4$ ethane-like units decreases and that of the highly distorted GeS$_4$ units increases. Above $y = 0.8$, the regular GeS$_4$ tetrahedra and sphalerite-like units coexist with the progressively diminishing fraction of regular GeS$_4$. Finally, pure amorphous GeS is assumed to be built by the distorted sphalerite-like units only. The appearance of the sphalerite-like units changes the intermediate-range ordering of the regular GeS$_4$ tetrahedra, the fraction of the ES units increases from $f_{ES} = 0.44$ ($y = 0$) to 0.7-1.0 ($y \geq 0.7$). These changes in the intermediate-range order can also clearly be seen in the composition dependence of the FSDP parameters. For example, the FSDP height decreases markedly above $y = 0.3$ (Fig. 5), in contrast to Ge-poor glasses. This decrease of the FSDP amplitude as well as of the glass transition temperature with increasing $y$ indicates that the GeS$_4$ units play the role of the network modifiers and not of the network formers, in excellent agreement with their local structural organization. Actually, similar assumption was first made by Kawamoto et al. [1] thirty years ago in analyzing the thermal properties of Ge-rich germanium – sulphur glasses. One should also note that $^{119}$Sn-Mössbauer spectroscopy experiments on Ge:Sn-S glasses [11] also showed multiple Sn sites and drastic changes in the hyperfine interaction parameters above $y = 0.22$. Boolchand et al. [11] proposed distorted NaCl-type units to be predominant in this composition domain.

5. Conclusions

High-resolution neutron diffraction and Raman spectroscopy measurements exhibit new structural features in germanium-rich binary Ge-S glasses. In addition to regular corner- and edge-shared GeS$_{4\text{e}}$ tetrahedra and GeX$_4$ ethane-like units, the highly distorted sphalerite-like structural elements GeS$_{4\text{d}}$ (3 Ge-S bonds of 2.5 Å and 1 Ge-S bond of 2.23 Å) appear in the $y$GeS (1-y)GeS$_2$ glasses at $y \geq 0.3$ and become predominant above $y = 0.7$. These units seem to be the network modifiers and change considerably short- and intermediate-range ordering in the glasses.

Acknowledgments

The authors would like to thank C. Benmore (Argonne National Laboratory, USA), B. Beuneu (Laboratoire Léon Brillouin, Saclay, France), A. Hannon (ISIS, Rutherford-Appleton Laboratory, UK), A. Lorriaux (Centre d’Etudes et de Recherche en Spectrométrie (EURIL), Lille, France), D. Price (Argonne National Laboratory, USA) and P. Salmon (University of Bath, UK) for many useful discussions.

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Preparation of practical SMA devices involves quenching from high temperature phases. Remnant effects stay frozen for long times in beta phase, and can be monitored via high resolution resistance measurements. In beta phase, long time after the quench, transformation temperature (Ms) dependencies related to temperature and time have been quantified. A time and temperature predictable analysis can be done, and the low temperature ageing processes can be simulated and optimised. The predictable analysis gives the set of conditions (temperature and time) best suited to detect the structural changes in the samples. The first visualisation of time dependent structural changes at constant temperature after a temperature step, shows that the time evolution presupposes an average structural deformation of the material, producing displacements of the diffraction peaks. The measurements suggest that the appropriate choice of time and temperature scales is the tool for time dependent structural studies.

1. Introduction

The Shape Memory Alloys (SMA) are passive smart materials: they can be used as sensor and actuator [1-2]. Cu-Zn-Al, one of the most studied alloys, can be considered as a SMA prototype [3-4]. The martensitic transformation in SMA originates their particular properties: the shape memory effect and the pseudoelasticity, with high potential interest in industrial applications. Use of shape memory alloys as smart material require a long time guaranteed behaviour. This supposes invariance or only controlled changes in the transformation temperature Ms. The parent and the martensite are metastable phases obtained by quenching of high-temperature equilibrium phase [3]. Classically, the Cu-Zn-Al presents two kinds of evolution acting on the hysteresis cycle and on Ms [3]. The first has a mechanical origin. The thermo-mechanical cycling and the thousands of martensite domains facilitate the dislocation creation [4]. The second has a diffusive origin. In the first hours after the quench, large Ms changes can be observed [4]. The dependence of Ms with the atomic order [3] and with the structural evolution [5-6] has received permanent interest. In the present state of the art, only some structural time evolution has been established in the first hours after quenching [7-8]. In this work the characteristics of the appropriate samples for the structural analysis are established from long term resistance measurements. Via neutron diffraction it has been realised a first visualisation of structural changes at constant temperature after a temperature step in beta phase.

2. Experimental

Single crystals of Cu 68.4at%, Zn 15.3at% Al 16.3at%, were used. The homogenisation thermal treatments were 1123 K for 15 min. and water quench (or, eventually, air quench) to room temperature (293 K). Electrical resistance measurements were done with a computer-controlled device, operating continuously in a thermostated room. Temperature control and stability better than 0.01°C is necessary to check for small changes in the resistance value, as described in [9]. Neutron scattering is a well suited technique to follow atomic order changes. Experiments were conducted at ILL-D9 single crystal diffractometer. The detector has 32*32 pixels of 4 mm² each pixel. Samples of 2*2*2 mm³ were used. In the measurements, the expected resolution (in 2θ) is close to 0.2°.

3. Results: Time evolution of resistance and transformation temperature

It was observed that when a temperature step is done, the electrical resistance evolves roughly in a nearly exponential way. After several temperature steps and 25 thermal cycles (8 months after the quench), the time constant t against temperature could be written as:

\[ \ln \tau = -18.094 + \frac{10001}{T} \]  (1)

Then, the physical state of the sample can be represented by an order parameter T', which follows the equation:

\[ \frac{dT'}{dt} = - \frac{T'(t) - T(t)}{\tau(T)} \]  (2)

The time dependent Ms values are computed from the T'(t) (hidden order parameter), usually starting in a steady state at external temperature T by:

\[ Ms(t) = Ms(T^0) + a_1 (T'(t) - T^0) \]  (3)

The previous expressions allow to obtain the Ms changes induced from variable “room” temperature patterns [10-11]. The low temperature ageing processes can also be easily simulated and optimised (fig. 1).
tion takes place in the first hour, and the data acquisition, following a only few diffraction peaks, needs near one hour. The results allow the detection of a change in intensity of the superstructure diffraction peaks, but show a relatively large incertitude (fig. 2 left). A temperature step to 339 K was done, in order to have appropriate time constant to detect time evolution in two days. Results of time evolution of diffraction peak positions are shown in fig. 2 (right). The experiment was repeated with another sample with similar results. The electrical resistance of a parallel sample subject to the same temperature step is shown in fig. 2 (right-E).

5. Conclusions
The predictable analysis gives the set of conditions (temperature and time) best suited to detect the structural changes in the samples. The first visualisation of time dependent structural changes, at constant temperature after a temperature step, shows that the time evolution, due presumably to atomic order changes, presupposes an average structural deformation of the material, producing displacements of the diffraction peaks. The measurements suggest that the appropriate choice of time and temperature scales is the tool for time dependent structural studies, together with sufficient resolution and high counting statistics provided by the source.

Acknowledgements
Dr. F.C. Lovey and Dr. J.L. Pelegrina for fruitful discussions. Neutron diffraction measurements at D9-ILL in the frame of proposal 5-15-458 (1999). Partial support from CICYT is acknowledged.

4. Results: Neutron diffraction
The initial cell parameter used at 295 K (0.585 nm) relates the basic DO3 (L21) cubic cell, near to the value from [12]. Some experiments were done in samples air quenched in situ in the goniometer furnace, from 1073 K to 295 K. Even though a relatively large change in atomic order is suspected after the quench, it is difficult to quantify and follow because the larger part of the evolution takes place in the first hour, and the data acquisition, following a only few diffraction peaks, needs near one hour. The results allow the detection of a change in intensity of the superstructure diffraction peaks, but show a relatively large incertitude (fig. 2 left). A temperature step to 339 K was done, in order to have appropriate time constant to detect time evolution in two days. Results of time evolution of diffraction peak positions are shown in fig. 2 (right). The experiment was repeated with another sample with similar results. The electrical resistance of a parallel sample subject to the same temperature step is shown in fig. 2 (right-E).

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REFERENCES

We present new results on the separation of the atomic-partial vibrational density of states for the ternary quasicrystal i-AlCuFe. The decomposition into atomic-partial functions has been performed self-consistent with the calculation of the multi-phonon contributions.

1. Introduction

The lattice vibrational and thermal properties of quasicrystals are not well understood. Specific heat results for i-AlCuFe [1] show a non-integer power for the lattice specific heat at low T: $C_{latt} \propto T^{3.55}$. This deviation from Debye-behaviour down to low temperatures indicates that low-lying non-acoustic vibrational states must exist in addition to the well-known longitudinal and transversal acoustic branches. It is then an important question for the understanding of the quasicrystalline structure to ask of the microscopic nature of such localised states. The most important characteristic would be to identify the atomic species involved. Our goal was first to obtain the individual atomic-partial vibrational density of states of i-AlCuFe quasicrystal in a model-independent way. This will allow a further test of the presence and character of localised states. The atomic-partial vibrational DOS can be obtained for several different cases using inelastic nuclear-resonant absorption of synchrotron radiation [2].

This requires an appropriate nucleus with a low-lying Mössbauer nuclear transition ($^{57}$Fe, $^{119}$Sn). Previous measurements at the ESRF of the iron-partial vibrational density of states of i-AlCuFe [3] have shown the surprising result that there is more detailed structure in the atomic-partial vibrational DOS of quasicrystals than previously seen in the INS experiments for the neutron-weighted "generalised" vibrational DOS [4]. This has led us to re-open the study of the vibrational DOS of i-AlCuFe using INS but with isotope-enriched samples.

2. Experiments:

Our method is isotopic substitution: $^{65}$Cu and $^{57}$Fe and inelastic neutron scattering at IN6 of ILL (see [5]). The following table gives the scattering cross-sections in barns of the different samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>$\sigma_{Al}$</th>
<th>$\sigma_{Cu}$</th>
<th>$\sigma_{Fe}$</th>
<th>$\sigma_{total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a:</td>
<td>nat Cu &amp; Fe</td>
<td>0.93</td>
<td>2.05</td>
<td>1.45</td>
<td>4.43</td>
</tr>
<tr>
<td>b:</td>
<td>$^{65}$Cu, nat Fe</td>
<td>0.93</td>
<td>3.70</td>
<td>1.45</td>
<td>6.08</td>
</tr>
<tr>
<td>c:</td>
<td>nat Cu, $^{57}$Fe</td>
<td>0.93</td>
<td>2.05</td>
<td>0.13</td>
<td>3.10</td>
</tr>
</tbody>
</table>

It is clear from the table, that sample b strongly weights the Cu scattering whilst sample c strongly suppresses scattering from Fe. The raw data (for 300K, Fig. 1) show a strong variation in intensity with scattering cross section which is non-homogeneous over energy. The low-E region intensity increases strongly with increasing $\sigma_{Cu}$. The high-E region decreases strongly with decreasing $\sigma_{Fe}$. This observation led in Ref.[5] to a simple first-order model which suffices to calculate the multi-phonon contributions. This was composed of three different Debye-like bands with differing effective masses: a low band for Al$_{62}$Cu$_{25.5}$, a middle band for Al$_{62}$Fe$_{12.5}$, and an upper band for Al. The resulting multi-phonon-corrected neutron cross-section-weighted vibrational DOS form the starting point in the self-consistent calculation presented here. In order to be self-consistent, it is necessary in addition to calculate the partial Debye-Waller factors and perform the multi-phonon corrections at the same time.

Fig. 1: Generalised frequency distributions for the three samples given in the table at 300K.
3. Model calculations:
In the one-phonon incoherent approximation the neutron-weighted vibrational density of states (denoted G(E)), obtained from the experimental data, is
\[
G(E) = \sum_i (c_i \sigma_i / M_i) g_i(E) e^{-2W_i},
\]
where \(c_i\) is the atomic concentration, \(\sigma_i\) is the neutron scattering cross-section, \(M_i\) is the atomic mass, \(g_i(E)\) is the partial vibrational spectrum and \(W_i\) the thermal Debye-Waller factor for the \(i\)th element. In all the calculations the following normalization was used:
\[
\int G(E) dE = \sum_i (c_i \sigma_i / M_i) e^{-2W_i}.
\]
In a first approximation it was supposed that \(e^{-2W_i} \approx 1\). The partial spectra for Cu, Fe and Al atoms were restored as a difference of the experimental \(G(E)\) for different samples with different weighting factors:
\[
\begin{align*}
g_{\text{Cu}}(E) &\approx G_b(E) - G_a(E) \\ g_{\text{Fe}}(E) &\approx G_a(E) - G_c(E) \\ g_{\text{Al}}(E) &\approx G_b(E) - \alpha g_{\text{Cu}}(E) - \beta g_{\text{Fe}}(E)
\end{align*}
\]
where: \(\alpha = C_{\text{Cu}} \sigma_{\text{Cu}} / M_{\text{Cu}}\) and \(\beta = C_{\text{Fe}} \sigma_{\text{Fe}} / M_{\text{Fe}}\) and \(a, b\) and \(c\) denote the samples given in the table. Since \(W_i = (u_i^2 Q^2 / 2kT) dE\), it is possible to calculate the partial Debye-Waller factors by means of an iteration process with starting values of \(g_i(E)\) taken from Equation 1 with \(e^{-2W_i} = 1\). From this we obtain the first approximation for the partial vibrational spectra \(g_{\text{Cu}}(E), g_{\text{Fe}}(E), g_{\text{Al}}(E)\) and for density of vibrational states: \(g(E) = \sum_i g_i(E)\), where \(i = \text{Al}, \text{Cu and Fe}\).
Using this first approximation as input, we calculate the partial contributions of 2- and 3-phonons scattering. The sum of these contributions (after appropriate normalization) and the calculated background (due to frame-overlap) were subtracted from the raw data and one-phonon \(G(E)\) have been obtained. Now we return to step 1 and repeat all the calculations in the second iteration. The difference between 2- and 3-iterations was very small and after 3-iterations, the process of calculations has been finished. The resulting atomic-partial vibrational DOS as well as the concentration-weighted total DOS are shown in Figure 2. The respective curves shown are normalised to the concentration C (respectively 0.125 for Fe, 0.255 for Cu, 0.62 for Al and 1 for the total). In the figure, the abscissa major divisions are all equal, making comparisons easier. The surprising result is the sharpness of the atomic-partial Cu \(g(E)\), as sharp as that for Fe, but at much lower energy, and the broad featureless character of that for Al.

4. Conclusions
We are able to present new results on the separation of the partial vibrational density of states of a ternary quasicrystal. The calculation corrects for the effect of multiphonons as well as calculating the atomic partials in a self-consistent way. The results show the surprising property for the icosahedral quasicrystal that the partial DOS for both Fe and Cu are very sharp, whilst that for Al is broad and featureless.

Acknowledgements
This work was partially supported by the DFG Focus Program “Quasikristalle: Struktur und physikalische Eigenschaften”.

References

Fig. 2: Atomic-partial vibrational DOS for Fe, Cu and Al, as well as the concentration—weighted total DOS (from top) as calculated from the self—consistent calculation presented for the data at \(T = 300K\).
Anharmonicity and aperiodicity in complex perovskites: complementarity of synchrotron and neutron diffraction experiments

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Translational periodicity is a nice concept for a crystallographer since it results in a considerable reduction of the amount of information necessary to model the structure of solids. Any deviation from this ideal description is usually included in the thermal displacement parameters, handled within the Debye-Waller approximation. Nevertheless, periodicity and harmonic lattice vibrations give a very rough picture of these ferroelectric compounds. In particular, the atoms in ferroelectric solids generally present local off-site displacements (e.g. multi-well potentials). Our aim is to go beyond the average structure approximation.

The interesting dielectric properties of ferroelectric materials spring from the coupling of the electric field to polar distortions of the crystal lattice. In the soft-mode framework, the progressive softening of a lattice vibrational mode in the neighbourhood of a phase transition brings about a dramatic rise in the value of the dielectric constant. The resulting very large relative permittivities (in the thousands range) have found important technological applications as high density capacitors, actuators, pyroelectric detectors and piezoelectric transducers [1]. From a practical point of view, however, the development of materials with a desired response faces the difficulty of trying to separate experimentally the influences of many effects: composition, structure, domain configuration. There are also open theoretical issues such as whether the relevant phase transitions are indeed associated to the above-mentioned “soft-mode” (and are thus of “displacive” character) or exhibit “order-disorder” characteristics. Various new experimental techniques like, e.g. EXAFS, PDF, NMR [2] have recently revealed that many perovskite ferroelectrics show locally polarized clusters which are not compatible with the undistorted high-temperature paraelectric phase. The object of this work is to go beyond the average structure approximation usually obtained in conventional Rietveld refinements and to compare different approaches to better model these deviations from the ideal structure (superspace approach, anharmonic treatments ...). Two examples will illustrate these approaches: PbMg₁/₃Nb₂/₃O₃ and Pb₂CoWO₆.

Table 1: Results of the refinement

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reflections</th>
<th>Ideal structure (4 parameters)</th>
<th>Free rotator model (5 parameters)</th>
<th>Gram-Charlier expansion 4th order (6 parameters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>873 K</td>
<td>55</td>
<td>R=0.22% Rw=2.42%</td>
<td>R=5.13% Rw=1.80%</td>
<td>R=0.317(5) Å</td>
</tr>
<tr>
<td>673 K</td>
<td>60</td>
<td>R=0.49% Rw=2.70%</td>
<td>R=4.89% Rw=2.07%</td>
<td>R=0.309(5) Å</td>
</tr>
</tbody>
</table>

Fig. 1: Typical diffraction pattern recorded at ESRF; the classical sources cutoffs are also shown.
In the ideal perovskite model, high u-factors are observed for lead atoms; nevertheless, the R-factors do not show a very good agreement within this hypothesis, leading to a systematic overestimation or underestimation of the diffracted intensities of several reflections. Since no evidence is given of a macroscopic deviation from the cubic symmetry, this result can be interpreted by the existence of a high degree of spherical disorder: to take into account this in the microscopic model for the structure of PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3}, we have chosen to modify the structure factor of lead atoms. The x-ray structure factor is given by the Fourier transform of the electronic charge density. In the eventuality the Pb atom sits randomly at a given distance R from the ideal position, the structure factor can be factored into an atomic lead form factor times the Fourier transform of a thin shell of radius R, eventually modulated by the angular distribution of the atoms. For a spherical distribution, the leading term in the spherical harmonic expansion of the charge density is Y\textsubscript{00}, the spherically symmetric contribution. Therefore, the modified form factor is proportional to S(q) = J\textsubscript{0}(qR) Y\textsubscript{00}, where J\textsubscript{0} is a spherical Bessel function. This model is more appealing than split atom models requiring additional adjustable parameters (i.e., the displacement directions). Accordingly, we believe that this fit captures most of the important features of the data and, therefore, it is more appealing (Fig. 2).

A more sophisticated way to model these data is to introduce an anharmonic contribution in the Debye Waller factor, using the Gram-Charlier expansion. The main advantage of this method is that no \textit{a priori} hypothesis is made on the static or dynamic character of the Debye Waller factor. The counterpart of the model is that within the single particle potential of the PDF approach [3], the atomic correlations are not taken into account. The analysis in terms of anharmonicity is more precise and less constraining than the static models (like the split-atom or the rigid...
rotator models) for the simple perovskites and for the ordered perovskites as well and it allows an accurate modelling of the behaviour of these compounds close to the critical temperatures. Obviously, the chemical and site selectivity of X-ray scattering (and also of neutron scattering) represent a serious advantage for splitting the individual local atomic potentials (Fig. 3). Though our data are well modelled within the anharmonic treatment at high temperature, this model fails completely at room temperature and below it because of the onset of diffuse scattering condensating near the Bragg peaks, witnessing the presence of correlated displacements. In this case, another approach has been considered to model the total intensity, borrowed from the usual aperiodic structure superspace formalism. This is also consistent with the idea that a large portion of the ferroelectric polarization is provided by Pb displacements (to accommodate the lone-pair electrons), and these displacements are closely coupled to the rotation of the BO₆ octahedra. Therefore, this picture provides a possible framework for understanding relaxor behavior at the atomic level. Since the coupling of the Pb polarization to the environment and the ease of rotation of the BO₆ will have different energy scales, the random distribution of the B cations on the sites might be expected to lead to the relaxor behaviour. The above illustrates the status and shortcomings in the present understanding of the structure of the conventional relaxor ferroelectrics (Figs. 4, 5).

2. Aperiodicity in Pb₂CoWO₆

Most of the structural studies of modulated incommensurate phases are developed using single crystal diffraction data. Nevertheless, many compounds are not easily synthesised as single crystals or the interesting phases present complex polydomain structures, so that the study of the structure by single crystal techniques is very complex, or even not possible. Powder refinements are generally less performing than single crystal ones as the three-dimensional information contained in the reciprocal lattice is reduced onto a one dimension diffraction pattern. In spite of this limit, many structural determinations and refinements were successfully performed (Figs. 6, 7). This is exactly the situation we encounter in the low temperature phases of Pb₂CoWO₆ and we have applied the Rietveld method for refining the incommensurate structure. Among the main advantages of this method, we can identify the better accuracy of the incommensurate metrics. Another advantage, intrinsic to the method, is that all the reflections, whatever their intensity, are included in the refinement. As a matter of fact, the presence of weak reflections is very helpful for phasing the modulated displacements. These reflections are often missing in single crystal refinements. The critical point for a good refinement is the accurate modelling of the profile lineshapes, otherwise the estimation of weak satellite peaks near the main ones is rather poor. The superspace approach allows to locate the displacive or substitutional disorder and to describe the local atomic environment. In the present case, we were able to point out the particular behaviour of the Pb-O bonding in the incommensurate ferroelectric phase of Pb₂CoWO₆ (T_c=298K). Pb-O bondings display a very pronounced adaptative character to the framework defined by the octahedra. In T-space (i.e. along the modulation vector) Pb describes a pendular trajectory around an O atom whom it is always bonded to, whatever the section in the 4D structure.

Fig. 6: Schematic representation obtained from DIA data at the ILL of the octahedra framework of Pb₂CoWO₆ in two different sections of the aperiodic structure.

Fig. 7: Representation of Pb-O bonds in Pb₂CoWO₆ in the incommensurate phase.

References
For the analysis of the dynamics and the structure of the hydrogen bond network of the hydrous layer silicate Na-RUB-18 ¹H NMR and Neutron diffraction experiments were carried out. The temperature encoded NMR spectra showed that the low field signal of the strongly hydrogen bonded proton disappears at higher temperatures indicating a phase transition. The Rietveld analysis of Neutron powder data confirmed the crystal structure of the non-hydrogen atom structure and also revealed the hydrogen bond network which is local at temperature below the phase transition and extended in 1 dimension above.

**Introduction**

Layer silicates are common minerals which occur e.g. as weathering products of rocks or constituents of diagenetic processes in nature. Their crystalline structure is characterized by a regular sequence of silicate species followed by intercalated water. Often, the water rich part contains cations compensating the charge of the anionic silicate layer. Because of the weak bonding interaction between the silicate part and intercalated water crystallinity of the solid is poor leading to diffraction powder pattern typical for disordered materials. Since at the same time the materials are not stable in vacuum electron diffraction experiments on these class of materials for the study of the local order is difficult and requires freezing techniques. Therefore only few crystal structures have been investigated in detail with atomic resolution.

In these materials the silicate/water interface simulates the termination of a dense silicate structure and, with limitations, is a good model for the water/silicate interaction at the external surface of silicate minerals. The three dimensionally ordered layer silicate crystal, therefore, can be studied with conventional diffraction techniques in order to elucidate the structure and dynamics of the water species located directly at the water/silicate interface.

Na-RUB-18, Na₈[Si₃₂O₆₄(OH)₈]·32H₂O, is a layered silicate hydrate with high water content. The material is highly ordered and an exception in the layer silicate family. The crystal structure has been solved from X-ray powder data and refined to atomic resolution [1]. Between silicate layers there are intercalated sodium cation which are octahedrally coordinated by water molecules. The hydrate octahedra are edge linked and arranged in chains. The sodium cations compensate the charge of the semi-deprotonated silicate layer. However, the details of the proton ordering and their dynamics could not be analyzed.

Here we report on the Rietveld analysis of a Neutron powder data set for the analysis of the proton sites in the RUB-18 structure and temperature resolved ¹H solid state NMR experiments on their dynamics.

**Experimental**

Na-RUB-18 was synthesized using a slightly modified procedure compared to that reported in literature. CsOH as additive has been omitted. For the synthesis of Na-RUB-18 for the Neutron diffraction experiment, D₂O instead of H₂O was used as solvent. The degree of deuteration was determined to 71.5%.

Diffraction experiments were carried out at 250K in the 2θ range from 7 to 150° at the high resolution Neutron powder diffractometer D2B at the ILL, Grenoble, France. Further details of the instrument are described in the yellow book available at http://www.ill.fr/YellowBook/D2B/. The subsequent Rietveld analysis of the data set was carried out with the Rietveld refinement program FullProf [2]. A summary of the results of the refinement is given in Tab. 1.

### Tab. 1: Summary of the Neutron Rietveld refinement of Na-RUB-18

<table>
<thead>
<tr>
<th>N of reflections</th>
<th>490</th>
<th>Rמוס</th>
<th>27.30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N of struct. parameters</td>
<td>95</td>
<td>Rman</td>
<td>35.70%</td>
</tr>
<tr>
<td>N of restraints</td>
<td>38</td>
<td>Rexp</td>
<td>16.10%</td>
</tr>
<tr>
<td>χ²</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹H NMR experiments were performed on a Bruker ASX 400 with standard Bruker probes.

**Results and discussion**

¹H solid state NMR NOESY experiments show that at temperatures above 327 K 4 out of 8 hydrogen atoms of the intercalate water exchange with the strongly hydrogen bonded proton of the silanol group of the silicate layer [3]. In addition temperature encoded single pulse proton NMR spectra show that the low field signal of the strongly hydrogen bonded proton disappears at temperatures above 377 K (Fig. 1). This indicates a phase transition where the proton of the silicate surface interacts with the surface near hydrate water and becomes involved in dynamic interactions.
processes of the hydrogen bond net of the intercalate water. Apart from the phase transition described above there is another phase transition at temperatures below 250 K. 

\[ ^1H \text{ NMR spectra change considerably and are not understood so far [4]. Powder diffraction diagrams also show significant changes at 150 K and below and could not be indexed so far.} \]

The Rietveld analysis of the low temperature phase at 250 K Neutron diffraction data set confirms the structure of the non-hydrogen atoms obtained from a X-ray Rietveld structure refinement (Fig. 2). In addition the positions of the hydrogen atoms clearly showed up. The silanol proton involved in the strong hydrogen bond has been refined on a centered position between the two siloxane oxygen atoms. The O-O-distance is below 2.4 Å with the oxygen-hydrogen distance \( d(O-H) \) of 1.18 Å. The water molecules of the edge linked \([Na(H_2O)_6]\) octahedron are divided in two groups, the isolated apical molecules with 4 protons and the axial molecules with four more protons sharing two octahedra. Those axial hydrate water molecules form strong hydrogen bond to the silicate surface, however, without affecting the strong hydrogen bond of two siloxane groups sharing one proton (Fig. 3a). Difference Fourier maps clearly show strong scattering contribution from well ordered hydrogen localized between water and silanol oxygen atoms. The oxygen-oxygen bond length is ca. 2.7 Å with an average O-H bond length of 1.07 Å and an average O......H bond length of 1.70 Å. The apical water molecules with their protons interact only weakly with the silicate layer. In addition, there seems to be a weak bonding interaction between neighboring octahedra. Difference Fourier maps indicate distinct maxima

Fig. 1: 1H NMR showing the low field line disappearing with increasing temperature.

Fig. 2: Residual plot of the Rietveld analysis of deuterated Na-RUB-18.

Fig. 3a: Na-RUB-18 with the local hydrogen bond net between 4 hydrate water molecules.

Fig. 3b: Na-RUB-18 with the 1-dimensional hydrogen bond net including the silanol proton of the silicate layer.
for the deuteron with a high degree of positional disorder. Theoretical simulations of the structure support these observations. Based on the Neutron structure analysis of the low temperature form of Na-RUB-18 and the NOESY NMR spectra in the temperature range between RT and 373 K analyzing the proton exchange between hydrate water and the silanol proton, the single pulse $^1$H NMR spectrum of the high temperature form indicates that the strong hydrogen bond between the surface siloxane groups disappears in favor of distinct surface silanol groups. These silanol groups are connected to the intercalate hydrate water via hydrogen bridges now extending in one dimension (Fig. 3b). This supports pulsed field gradient NMR measurements on Na-RUB-18 which found increasing proton conductivity at higher temperatures [4]. The structure refinement of the high temperature form of Na-RUB-18 with the detailed analysis of hydrogen bonding in the high temperature form is in progress.

Acknowledgment

The authors acknowledge the financial support of the ILL and assistance during data collection by Dr. E. Suard.

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Electronic systems
Structural and magnetic disorder in crystalline materials - an opportunity for ILL?

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In ‘conventional’ powder diffraction one measures the elastic (Bragg) scattering which gives information on the time average crystal/magnetic structure. However for many materials of recent technological interest, e.g. high Tc superconductors, colossal magnetoresistance (CMR) materials and fast ion conductors, it is vital to also understand the local correlations. These can be investigated using total (energy integrated) scattering. Within the past 15 years a number of groups have begun to develop this method, but most work has been done at pulsed sources since a high maximum $Q$ is required to enable direct Fourier transform of the data (the ‘PDF’ method). However a reactor source offers many advantages for such experiments, despite the more limited maximum $Q$, including better data in the lower $Q$ region (e.g. for magnetic materials) and better systematic accuracy (single wavelength corrections). A reverse Monte Carlo method of data analysis [1,2] has been developed that overcomes the $Q$ range problem and allows treatment of magnetic scattering (not possible with direct transform methods). The total scattering technique is currently limited by the accuracy of the data that can be obtained, rather than the method of analysis. There is an opportunity for considerable progress if optimised instrumentation were available.

1. Introduction

In powder diffraction it is normally assumed that all sharp peaks in the scattering pattern represent elastic scattering, that is Bragg scattering. All other scattering in between or ‘under’ the sharp peaks, which we will refer to as diffuse scattering regardless of its origin, is simply subtracted and not used in the structural analysis. The elastic (Bragg) scattering gives information on the time average structure, i.e. on correlations between the time average positions of atoms. However if one analyses the total scattering, that is both the elastic (Bragg) and diffuse scattering, then this gives information on the instantaneous structure, i.e. on correlations between the positions of atoms at one instant in time. In a crystalline system with long range order and in thermal equilibrium the time-average correlations within the unit cell are equivalent to the space-average instantaneous correlations, hence the total scattering contains more information than the Bragg scattering (for relevant equations see e.g. [3]).

This is of course obvious, since all scattering provides information. However, diffuse scattering is often weak and relatively unstructured, i.e. broad oscillations rather than sharp peaks, so it has often been assumed that the relative information content is low. This is incorrect - the information content is simply different. Even broad scattering has a definite shape and can provide very detailed information if precisely measured. For example, determination of thermal parameters from Bragg scattering data normally proceeds under the assumption that there are no specific local correlations (and that the thermal displacements are small). This should lead to diffuse scattering that increases monotonically with $Q$; if the diffuse scattering differs from this prediction (which in fact it almost always does!) then either the time average positions or the thermal parameters can be misleading. Even in ‘good’ crystalline materials the existence of phonons implies correlations which affect the shape of the diffuse scattering, typically giving maxima underneath Bragg peaks. It has been suggested that total scattering data can be used to derive phonon dispersion curves [4]. However in practice this may only be possible in simple cases where an appropriate form of the interatomic potential is already known. In more disordered crystals, e.g. certain proton conductors, the derivation of a time average (H) position with a thermal displacement can be completely meaningless (see e.g. [5]).

2. Experiments and data analysis

Even if the diffuse scattering contains information, one of course needs to be able to measure it with sufficient accuracy and to analyse the data and extract that information. The vast majority of total scattering studies on crystalline materials have been carried out using diffractometers on pulsed neutron sources (e.g. [6,7]). This gives a high maximum $Q$, typically above 30 Å\(^{-1}\), which means that the data can be directly Fourier transformed to obtain the pair distribution function, ‘PDF’. This is then generally analysed by a comparison to what would be expected from the time average structure [8]. Note that truncation problems can still occur, even with high maximum $Q$ data, so care should be taken. In addition direct transform methods should not be used for magnetic systems; except in the simple case of uncorrelated magnetic scattering (i.e. paramagnetic) the effect on the PDF can be significant and not easily predicted. In the case of some highly disordered crystalline materials (e.g. high temperature fast ion conductors [9]) a maximum $Q$ of 10 Å\(^{-1}\) can be adequate for obtaining the PDF. However in most cases a direct transform method cannot be used - an inverse method of data analysis is required. One such method is reverse Monte Carlo modelling, in particular the RMCPOW program [1,2]. With-
out the use of such data analysis, total scattering studies at reactors will only generally provide very qualitative information; however the combination of software and source has many advantages. Reactors offer easier systematic corrections (single wavelength) and generally better data at low \( Q \), particularly for magnetic scattering. The \( Q \) space resolution varies in a more systematic way and is included in the analysis so the results are directly comparable to Rietveld refinement, though they should not necessarily be the same since Rietveld considers the Bragg scattering only. In addition magnetic scattering can be dealt with properly.

Within the space available we can only mention a few selected examples of total scattering studies using reactor sources. There have been several studies of Ag and Cu based fast ion conductors that have provided detailed information on conduction mechanisms, including possibly the earliest total scattering study (on AgBr) [9]. The existence of a high correlation between \( \text{SO}_4^- \) group rotation and proton transport was shown in CsDSSO\(_4\) [4], and the preferred rotation direction of ND\(_4^+\) molecules in ND\(_4\)Cl [10]. In these two cases similar information can be obtained indirectly through model dependent analysis of quasi-elastic neutron scattering data, however with much less detail. The existence of lattice and magnetic polarons in the CMR material La\(_2\)Sr\(_x\)MnO\(_y\), and the detailed correlations between the local atomic arrangement and magnetic ordering, have been demonstrated [11]. Some of this information can be obtained from Bragg scattering alone, or magnetic small angle scattering (i.e. diffuse scattering alone), and the correlations can be surmised. However only total scattering provides a single self-consistent model and gives information on the spin-lattice correlations directly.

### 3. Future developments.

Of course there is no unique solution, but nevertheless the combination of precisely measured Bragg and diffuse scattering is (in relevant cases) significantly more powerful than Bragg scattering alone (or diffuse scattering alone). It is also possible to obtain information on local correlations between atomic positions and magnetic moments. (e.g. spin-lattice coupling). Other methods, e.g. spherical neutron polarimetry, may provide more specific information but are more limited in their application (e.g. single crystals), require considerably more time and in the end still require ‘data interpretation’.

There are many classes of material, often of technological interest, for which total scattering could provide key information, such as colossal magnetoresistance materials, high temperature superconductors, spin glasses, ferroelectrics, fast ion conductors, proton conductors, hydrogen in metals and hydrogen bonded systems. However, the development of the total scattering technique is at present limited by the quality of the experimental data that can be obtained, rather than the intrinsic limitations of the method itself or the data analysis. The diffractometers used have not been specifically designed for such studies. Those that have been designed for normal powder diffraction have good control over the definition of angles and the \( Q \) space resolution, e.g. to obtain accurate lattice parameters, but the backgrounds can be too high, particularly at low scattering angles. They also tend to use longer wavelengths, to obtain better resolution, whereas shorter wavelengths (higher energies) are needed for total scattering since it is an energy integration technique. Diffractometers that have been designed for studies of liquids and amorphous materials tend to use shorter wavelengths, and have good control over the background (e.g. to measure weak, broad diffuse scattering) but not over angle definition and \( Q \) space resolution. In addition most total scattering studies will involve variation of the sample in some way (e.g. \( T, P \ldots \)) where more useful information can certainly be obtained by smaller steps (i.e. needing higher flux). There is therefore a strong case for the provision of optimised instrumentation at a high flux neutron source, for example ILL.

### References

Polarization Study of the Singlet-Triplet Modes in a Quantum Spin System

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S=1/2 dimer clusters represent an excellent example for singlet-triplet magnetic units which can be assembled into spin chains, spin ladders or more complicated models of quantum magnetism. The microscopic characterization of the resulting ground-state and elementary excitations constitutes a lively research field, involving neutron scattering at its forefront. In Cu²⁺ KCuCl₃, S=1/2 dimers are at the origin of well-defined singlet-triplet modes, which propagate in reciprocal space above a finite energy gap of quantum nature. The spin symmetry of these collective quantum excited states was investigated by polarized neutron scattering on single crystals. Complete experimental results concerning the transversal and longitudinal components of the triplet modes are presented in the context of an S=1/2 dimer model. The assumption of spin isotropic Heisenberg interactions finds confirmation in the polarization factors measured along the three crystallographic axes.

PACS index categories: 75.10.Jm, 75.30.Et, 78.70.Nx

Cu²⁺ KCuCl₃ is a quantum disordered antiferromagnet near to the dimer limit. The dynamical scattering function S(Q,ω) studied by inelastic neutron scattering (INS) is well reproduced within the framework of an S=1/2 dimer model H=Hᵢ+Hᵢ, where Hᵢ describes the strong intra-dimer bond and Hᵢ the weaker inter-dimer bonds as in Ref. [1]. Despite the three-dimensional nature of the inter-dimer bonds, KCuCl₃ retains down to the lowest temperatures a collective singlet ground-state. Elementary excitations at T~2K are well-defined triplet modes which propagate in reciprocal space above a finite energy gap of quantum origin, Refs. [1-3]. The spectrum of KCuCl₃ compares to a number of quantum antiferromagnets including alternating chains, even-leg ladders and dimerized spin Peierls compounds. In the latter however, dimerization is driven by magneto-elastic interactions, invalidating the effective separation between spin and lattice degrees of freedom. Polarized INS studies of the triplet modes in KCuCl₃ is presented in the following. Measurements were performed on the cold neutron spectrometer IN14 (ILL) operated at constant final energy E₉=4.7meV. Standard set-up with a bender polarizer and Heusler analyzer was used to determine the spin-flip (SF) and non spin-flip (NSF) scattering along the three quantization axes of the neutron polarization P. The latter is set in the local coordinates {x,y,z} so that z is out of plane, x parallel and y perpendicular to the scattering vector Q. The efficiency of the instrumental components was calibrated at selected nuclear Bragg positions, following the procedure detailed in Ref. [6]. We accordingly denote the polarized scattering by Iᵢⱼ, where the index i=[0,1], j=[0,1] reflects the

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Fig.1: Polarization dependence of the triplet modes in KCuCl₃ at T~2K. Lines are simple guides from Eqs. (3), (4) as explained in the text. The scattering vector corresponds to the spin excitation gap at Q=(0 4 0) [r.l.u.].

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status of the spin flipper before and after the sample. Opposite quantization between the polarizer and analyzer imply for the present measurements SF scattering at $P^s, P^t$ and NSF scattering at $P^o, P^p$. Excellent flipping ratios were reported, with minimal variations upon changing the neutron polarization $P$ but a tendency towards lower merits for increasing incident energy. Conserved estimates of the averaged polarizer-analyzer and flippers inefficiency yield $1-\Phi = 0.025$ and $F_1 = F_2 = 0.02$, respectively, in the notation of Ref. [6]. Complete excitation profiles at $T-2K$ were measured along the crystallographic axes $Q \parallel a^*, b^* \text{ and } c^*$, for which $P^o$ and $P^p$ were determined in the three polarizations $P^0 = [x, y, z]$ each. Experimental observations confirm that the magnetic excitations in KCuCl$_3$ consist of three degenerate components which are accessed according to the cross section in Eq. (1). Longitudinal and transverse components to the neutron polarization $P$ are consistently separated into NSF and SF scattering, respectively. Within experimental accuracy, the total spectral weight is found to be equally distributed in spin space. Typical polarized neutron profiles are presented in Figure 1, to be explained in the following. Justified by the simple experimental observations, we restrict our considerations to the magnetic only term in the polarized neutron cross section and anticipate quantitative agreement with spin isotropic interactions. Additional comments will be addressed in the conclusion. The magnetic cross section

$$I(Q, \omega) = \langle k / \hbar \rangle \langle g / 2 \rangle \left| P(Q) \right|^2 \sum_{\omega} \left( \delta_{\omega, Q^2 / 2} \left( \delta_{\delta_{\omega}, Q^2 R^2} \right) S^0(Q, \omega) \right)$$

(1)

determined here in the usual notation, simplifies in the case of $S=1/2$ to

$$S^0(Q, \omega) = \sin \left( \delta_{\omega, Q^2 / 2} \right) \left( 1 + \left( \delta_{\omega, Q^2 / 2} \right)^2 \right)$$

(2)

where $\alpha, \beta = \{x, y, z\}$ denote the spin component, $R$ is the separation vector of the spins within the dimers and $J$ the isotropic exchange bond in $H = -JS^0 S_x$. The polarization dependence of the cross section reduces from Eq. (2) to the simple expressions

$$P^o(Q, \omega) = \left| 1 + \left( \delta_{\omega, Q^2 / 2} \right)^2 \right| I(Q, \omega) / 2$$

(3)

$$P^p(Q, \omega) = \left| 1 - \left( \delta_{\omega, Q^2 / 2} \right)^2 \right| I(Q, \omega) / 2$$

(4)

where $P^o + P^p = I$ for all settings, and individual $P^o, P^p$ depend on the angle subtending polarization and scattering vector, see Ref. [7] for example. The polarized scattering from quantum disordered dimers resembles that of ideal paramagnets, but the spectral weight in the former is strictly inelastic instead of quasi-elastic, Ref. [8]. Moreover, the characteristic dimer structure factor from Eq. (2) introduces an intrinsic $Q$ dependence of the total scattering, which reflects the dominant bond vector $R$. Normalized Eqs. (3), (4) yield in the notation already introduced the expectations $P^o = 100.0$ for $P \parallel x$, and $P^p = 50.50$ for both $P \parallel y, P \parallel z$. Simple gaussian peaks to the above are shown in Figure 1, on top of a common background at fixed centre position and fixed total intensity. In spite of the neglect of individual fit parameters and instrumental inefficiency, excellent qualitative agreement is reported - confirming the high instrumental confidence and justifying the model simplification. The quantitative determination of the polarization factors in KCuCl$_3$ at $T-2K$ relies on global least squares fits to the observed profiles, under explicit consideration of instrumental peak shapes and individual intensity contributions. The latter are summarized in Table 1 for the polarization setting $P \parallel x$ scaled to 100 counts at each $Q$ point. Corresponding model expectations from Eqs. (3), (4) corrected by the instrumental inefficiency (Table 1, bottom line) are in full agreement with the overall experimental results. Summing over the three sets of measurements from Table 1 we obtain the high statistics estimates $P^o, P^p = 95.0(2.4):5.0(1.1)$ for a total of nearly 3 days $P \parallel x$ beam time. Within experimental accuracy it is concluded that the nature of the singlet-triplet modes investigated in KCuCl$_3$ at $T-2K$ is well described assuming spin isotropic Heisenberg interactions.

This finding is substantiated by the remark that Cu-Cl-Cu dimers are located at inversion centres of the unit cell, implying that the antisymmetric DM interaction leading order $H_z$ is forbidden. Early ESR investigations in KCuCl$_3$, were however interpreted in terms of the DM interaction in Ref. [9]. As demonstrated in the present INS investigations, its eventual influence through weaker $H_z$ on the nature of the ground-state and elementary triplet modes is modest, lying beyond the sensitiveness of the complete three-dimensional polarized cross section. Experimental efforts based on advanced three-dimensional polarimetry (see Ref. [10]) would prove of advantage in order to strengthen the above conclusions.

<table>
<thead>
<tr>
<th>$Q \parallel a^*$</th>
<th>SF/100</th>
<th>NSF/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O \parallel b^*$</td>
<td>95.2(3.5)</td>
<td>4.8(1.3)</td>
</tr>
<tr>
<td>$O \parallel c^*$</td>
<td>95.1(4.3)</td>
<td>4.9(2.1)</td>
</tr>
<tr>
<td>expected</td>
<td>95.7</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Tab. 1: Normalized polarization factors of the triplet modes in KCuCl$_3$ at $T-2K$, measured along the three crystallographic axes at $Q=(1.5 0 0), (0 0 1.5)$ for the $P \parallel x$ setting each. Theoretical expectations from Eqs. (3), (4) corrected by the instrumental inefficiency are compared in the bottom line.

**Acknowledgment**

Fruitful discussions with L.P. Regnault are gratefully acknowledged. This study was partially supported by the Swiss National Science Foundation.

**References**

This paper describes neutron inelastic scattering measurements of the magnetic excitations in a single crystal of PrBa$_2$Cu$_3$O$_{6.2}$. The measurements probe (1) the Cu spin excitations on the antiferromagnetically-ordered CuO$_2$ layers, and (2) the dispersion of the exchange-split doublet ground state of the Pr ions at low temperatures. Experiments were performed on the chopper spectrometer MAPS at ISIS, the thermal triple-axis spectrometer IN8 at the ILL, and the cold-source triple-axis spectrometer TAS6 (RITA) at Risø. We obtain a good description of the measured dispersion using a spin Hamiltonian for the coupled Pr–Cu system containing intra- and inter-layer Cu–Cu exchange constants $J_{||}$ and $J_{\perp}$, and a nearest-neighbour Pr–Pr exchange constant $J_{pp}$, and a pseudo-dipolar interaction constant $K_{sp}$. The value of $J_{pp}$ for PrBa$_2$Cu$_3$O$_{6.2}$ is found to be a factor 2 smaller than that for YBa$_2$Cu$_3$O$_{7-x}$ whereas $J_{pp}$ for these two materials is similar. Both the Pr–Pr and Pr–Cu couplings are found to be important in determining the relatively high Pr magnetic ordering temperature.

1. Introduction

One of the characteristics of the cuprate family of superconductors is the insensitivity of the superconducting properties to the presence of magnetic rare earth ions. In the K$_x$Ba$_{2-x}$Cu$_3$O$_{6+y}$ family (R = rare earth or Y) superconductivity occurs at temperatures as high as 95 K, and magnetic ordering of the R sublattice coexists with superconductivity at temperatures around 2 K or below [1]. Antiferromagnetic (AF) ordering of the Cu sublattice is observed in non-superconducting samples with low oxygen doping levels (typically $x < 0.4$), but superconducting samples with higher doping levels do not exhibit any conventional form of Cu magnetic order [2].

A striking exception to this behaviour is the case of PrBa$_2$Cu$_3$O$_{6+y}$ (PrBCO). Superconductivity is not observed for any $x$ in samples of PrBCO prepared by standard methods, and AF ordering on the Cu sublattice occurs below a temperature $T_c \approx 300$ K only weakly dependent on the x. Magnetic ordering on the Pr sublattice is observed below a temperature $T_m$ varying from 11 K ($x = 0$) to 18 K ($x = 1$), much higher than the rare earth ordering temperatures in superconducting YBCO compounds, and unusual magnetic structures are observed below $T_m$ [3]. These anomalous features of PrBCO remain a puzzle, the more so given recent reports of superconductivity in PrBCO crystals grown by the floating-zone method [4]. Models for the electronic structure have revealed a tendency for Pr 4$f$–0 2$p$ hybridisation, causing a localization of doped holes in O 2$p$ orbitals and thus inhibiting superconductivity [5,6]. Such hybridisation might be expected to influence the magnetic couplings within and between the Pr and Cu sublattices, and so measurements of the exchange interactions could provide information on the underlying electronic structure.

Broadly speaking, the magnetic excitations in PrBCO fall into two categories: (1) Cu spin wave excitations with a large dispersion in directions parallel to the CuO$_2$ layers, and (2) single-ion excitations between levels of the Pr 4$f$electrons split by the local crystalline electric field. The spectrum of crystal field excitations has been studied previously with polycrystalline samples, and found to extend in energy to $\sim 100$ meV [7]. Moreover, the peaks exhibit an intrinsic width of several meV indicating a coupling of some sort, most likely hybridization or a magnetic interaction. Below $T_m$, the Pr excitations are expected to exhibit dispersion due to cooperative crystal field excitonic modes.

The aim of this work, therefore, was to obtain values for the principal Cu–Cu, Pr–Pr and Cu–Pr exchange interactions from the dispersion of the magnetic excitations studied in a single crystal of PrBCO, and to compare these with values found in YBCO and related materials. Measurements on a crystal should also point towards the origin of the broadening of the crystal field transitions. In this paper we summarise the results obtained for oxygen-deficient PrBCO [8].

2 Experimental details

The experiments were performed on a single crystal of PrBCO prepared from a flux by the top-seeded pulling method. The as-grown crystal had a mosaic spread (FWHM) of $\sim 1^\circ$, and after annealing in Ar to establish an oxygen content $x = 0.2$ the crystal was found to have a Pr ordering temperature $T_m \approx 13$ K. In order to access the full range of energies characteristic of the Cu and Pr magnetic excitations three different neutron spectrometers were used, (1) the MAPS chopper spectrometer at the ISIS spallation neutron source, (2) the IN8 triple-axis spectrometer at the ILL, and (3) the TAS6 (RITA) spectrometer at the DR3 reactor, Risø.
MAPS is designed for the study of magnetic excitations single crystals, and is characterized by a large area coverage of position-sensitive detectors extending to low angles. This affords the possibility of very good Q resolution which is necessary in order to study the highly-dispersive in-plane Cu spin waves in PrBCO. The crystal was aligned with the c axis parallel to the incident neutron wavevector. This arrangement means that surfaces of constant energy transfer are approximately parallel to the $a^*\cdot b^*$ plane in reciprocal space.

IN8 has a very high flux of thermal neutrons, and the option to curve both the monochromator and analyzer allows the flux to be increased further at the expense of Q resolution. These are ideal conditions for determining the Cu optic mode energy gap at the antiferromagnetic zone centre because here the spin wave branch is locally independent of energy. Measurements were made in the horizontal scattering plane containing the reciprocal lattice vectors $(1, 1, 0)$ and $(0, 0, 1)$.

TAS6 (RITA) has both a flexible analyzer system and a position-sensitive detector. We curved the analyzer blades so as to focus the neutrons onto a strip in the centre of the detector. The outer edges of the detector were then useful for assessing the background and for identifying spurious scattering. Once again, the ability to relax the Q resolution was an advantage for measuring the weakly dispersive Pr excitations. TAS6 was situated on the cold source at the DR3 reactor, and the high flux of low energy neutron enabled us to study the dispersion of the exchange-split doublet ground state of the Pr ions in the Pr ordered phase ($T < T_n$).

3. Results

3.1 Cu spin excitations

To a good approximation, we can regard the Cu spin arrangement as a square-lattice bilayer antiferromagnet, and the coupled spin excitations can be calculated from the Heisenberg Hamiltonian

$$H_{Cu} = \frac{1}{2} J_{||} \sum_{i, j} S_i \cdot S_j + \frac{1}{2} J_{\perp} \sum_{i, j} S_i \cdot S_j'$$

including nearest-neighbour interactions only. The pairs of spins are on the same layer in the first summation, and on adjacent layers in the unit cell in the second summation. $J_{||}$ and $J_{\perp}$ are the intra- and inter-layer exchange constants respectively. The dispersion curve derived from Eq. (1) has two branches, differing according to whether neighbouring spins on adjacent layers rotate in the same sense (an acoustic mode) about their average direction, or in the opposite sense (an optic mode). As the AF zone centre is approached the acoustic branch tends to zero energy with a slope proportional to $J_{||}$. The optic branch has a minimum energy of $2(J_{||} J_{\perp})^{-1}$ at the AF zone centre. Because of the bilayer structure in the unit cell the scattering intensity from acoustic and optic modes is modulated by factors $\sin^2(\pi z l)$ and $\cos^2(\pi z l)$ respectively, where $z$ is the interlayer spacing as a fraction of the $c$ lattice parameter ($z = 0.295$ for PrBCO).

Figure 1(a) shows a constant energy surface measured on MAPS at a temperature of 20 K with neutrons of incident energy 200 meV. The plot focuses on the region of reciprocal space around the $(1/2, 1/2, l)$ AF zone centre. The data have been averaged over energy transfers between 80 meV and 120 meV and projected onto the $(hk0)$ plane. The ring of scattering centred on the point $(1/2, 1/2, 0)$ corresponds to the acoustic branch of the Cu spin excitation spectrum. (b) The Cu acoustic mode dispersion obtained from MAPS data such as that shown in (a). The line is the best-fit theoretical dispersion calculated with an in-plane Cu-Cu exchange constant $J_{||}$ of 127 meV.

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The $l = 5.5$ position is close to the maximum of the $\sin^2(\pi z/l)$ acoustic mode modulation factor, and so the ring in Fig. 1(a) represents scattering from the acoustic spin wave branch. The scattering is approximately circular because at this energy the spin wave wavevector extends less than halfway to the Brillouin zone boundary in the $a^*-b^*$ plane.

Runs with incident neutron energies of 80 meV and 300 meV were also performed, and rings similar to that shown in Fig. 1(a) were observed over a number of different energy ranges. By fitting these rings to Gaussian-broadened circles we found their radii and hence arrived at the dispersion curve shown in Fig. 1(b). The data were fitted by the theoretical expression for the acoustic spin wave dispersion derived by Tranquada et al. for YBCO [9], leading to a value for the in-plane Cu-Cu exchange constant $J_\parallel$ of $(127 \pm 10)$ meV. The best-fit dispersion curve is shown in Fig. 1(b).

Next we consider the Cu optic mode. We used the IN8 triple-axis spectrometer with a constant final energy of 34.8 meV and a graphite filter installed in the scattered beam. In order to measure the optic mode gap at the AF zone centre we performed a series of constant-Energy scans in the $(h, h, 0)$ direction through the position $(1/2, 1/2, 6.75)$ in reciprocal space, close to where the optic mode structure factor $\cos^2(\pi z/l)$ is a maximum. Fig. 2(a) shows a number of these scans measured at $T = 20$ K. At $E = 45$ meV there is no signal, but for $E = 55$ meV and 65 meV there is a peak centred at $h = 1/2$. On Fig. 2(b) we have plotted the amplitude of this peak as a function of energy. The intensity increases stepwise with energy, and we deduce the optic mode gap to be 53 meV, at the mid-point of the step. This energy gap and the above-mentioned value of $J_\parallel$ gives $J_\perp = (6 \pm 1)$ meV.

3.1 Pr magnetic excitations

The low energy magnetic excitation spectrum of polycrystalline PrBCO measured at $T = 5$ K is dominated by two peaks centred at approximately 1.7 meV and 3.4 meV [10]. These peaks have an intrinsic width of 1–2 meV, and correspond to the doublet ground state and singlet first excited level of the $^3H_4$ term of the Pr$^{3+}$ ion split by the local tetragonal crystal field. The doublet is further split by the exchange field associated with the magnetic ordering. Constant-$Q$ scans of these low energy peaks were performed on TAS6 at a temperature of 1.8 K for a large number of $Q$ positions. The scattered neutron energy was fixed at 5 meV, and a beryllium filter was placed in the scattered beam. For illustration we show in Fig. 3(a) the scan at $Q = (0.75, 0.75, 0)$. The data have been corrected for the non-magnetic background and elastic peak contamination with scans measured on a similar-sized crystal of YBCO. Two peaks consistent with the polycrystalline data are observed, labelled A and B in the figure. Both peaks have an intrinsic width larger than the resolution (~0.4 meV), supporting the hypothesis that $f-p$ hybridisation occurs even in undoped PrBCO. We note that single crystal measurements are necessary to separate such intrinsic broadening from the effects of dispersion. Peak A was found to exhibit a weak dispersion within the $a^*-b^*$ plane, and to quantify the dispersion we fitted the peaks with damped harmonic oscillator response functions (including detailed balance). The fitted curve is shown on Fig. 3(a), and the results for the dispersion of peak A are plotted in the $(1, 0, 0)$ and $(1, 1, 0)$ directions in Fig. 3(b). Unfortunately, peak B was too broad and weak to allow a determination of the dispersion of its energy, and its lineshape was held constant during the fitting.
The simplest model to describe the dispersion of peak A would include just the crystal field and an exchange coupling between nearest neighbouring Pr ions. This model is represented by the Hamiltonian

$$H_{\text{Pr}} = H_{\text{CEF}} + \frac{1}{2} J_{\text{Pr}} \sum_{ij} \left( \mathbf{J}_i \cdot \mathbf{J}_j \right) \left( \mathbf{J}_j \cdot \mathbf{J}_i \right)$$  \hspace{1cm} (2)

where $H_{\text{CEF}}$ is the single-ion crystal field Hamiltonian and $\mathbf{J}_i$ is the angular momentum operator for a Pr ion at site $i$. We calculated the excitations from Eq. (2) using the pseudo-boson approximation, including only the ground state doublet. The resulting dispersion is shown as the broken line in Fig. 3(b). The agreement with the data is seen to be reasonable, but there are discrepancies close to the AF zone centres where the Pr mode crosses the Cu acoustic spin wave dispersion. Coupling between the Cu and Pr magnetic sublattices is most likely responsible for the discrepancies. A Pr-Cu interaction was earlier inferred from the existence of a twist reorientation that takes place in the Cu magnetic structure when the Pr spins order below $T_{\text{Pr}}$ [12], and it was shown that an interaction with dipolar symmetry could account for the observed reorientation [13]. This so-called pseudo-dipolar coupling can be described by the off-diagonal components in the second rank exchange tensor $K$ linking the Pr and Cu sublattices as follows:

$$H_{\text{Cu-Pr}} = \frac{1}{2} \sum_{\alpha \beta} K_{\alpha \beta} \left( \mathbf{S}_\alpha \cdot \mathbf{J}_\beta \right) \left( \mathbf{S}_\beta \cdot \mathbf{J}_\alpha \right)$$  \hspace{1cm} (3)

The calculation of the dispersion of the exchange-split doublet from the full Hamiltonian $H_{\text{Cu}} + H_{\text{Pr}} + H_{\text{Cu-Pr}}$ followed a similar method to that described by Sachidanandam et al for Nd$_2$CuO$_4$ [14], and good agreement with the data, as indicated by the line in Fig. 3(b), was obtained for the parameters $J_{\text{Pr}} = 0.025$ meV and $K_{xy} = 0.30$ meV.

### 4. Discussion and conclusions

The central scientific result of this work has been the set of exchange constants $J_{\|}$, $J_{\perp}$, $J_{\text{Pr}}$, and $K_{xy}$ determined for PrBCO for the first time. These constants are important because they reflect...
exchange pathways that may be influenced by hybridisation of O 2p and Pr 4f states, and hence they contain indirect information on the electronic structure of PrBCO. The value of $J_{||}$ for PrBCO found here is the same within experimental uncertainty as that reported for YBCO with the same oxygen content, but surprisingly $J_{||}$ is a factor 2 smaller than for YBCO. This shows that Pr has a significant influence on the inter-layer exchange coupling. The values of $J_{\perp}$ and $K_{xy}$ can be compared by means of a mean-field estimate of $T_{c}$ [8]. This indicates that Pr-Pr and Pr-Cu coupling are responsible in roughly equal measure for the large value of $T_{c}$.

This work nicely illustrates the strengths and complementarity of modern spallation and reactor neutron instrumentation. Because the sample was relatively small the ability to focus the resolution ellipsoid in order to improve the scattering intensity was crucial. For the measurement of the very steep acoustic Cu spin waves the data were typically averaged over a 30 meV energy range while maintaining a wavevector resolution of 0.02-0.04 r.l.u. This was possible because of the fine pixellation of the MAPS detector and the particular geometry used in the experiment. Similarly, the ability to curve the monochromator and analyser arrays on triple-axis spectrometers permits a relaxation in the wavevector resolution without degradation to the energy resolution, and this suited the measurement of the rather flat energy dispersion of the Pr excitations and the Cu optic branch at the AF zone centre. Provision of these and other types of flexibility in the operation of neutron spectrometers would be of great value for enabling even more difficult and challenging experiments to be performed in the future.

Acknowledgements

We are grateful to the scientists and technical staff at the neutron sources for developing the world-class spectrometers on which these measurements were made, and in the light of the recent closure of the DR3 reactor we thank in particular the neutron group at Risø for their hospitality, friendship, and the excellence of the facilities they developed. We acknowledge financial support from the EPSRC for the work at ISIS and the ILL, and from the EU TMR programme for the work at Risø.
In this paper we discuss the experimental possibilities as well as the instrumental requirements for inelastic neutron scattering experiments on single crystals to investigate the magnetic dynamical response function of strongly correlated \( f \)-electron systems. After introducing the scientific framework, we present as an illustrative example the recent inelastic neutron scattering investigations on the heavy fermion superconductor \( \text{UPd}_2\text{Al}_3 \). The results are compared to those on \( \text{UNi}_2\text{Al}_3 \) as well as on \( \text{UGa}_3 \). We conclude the paper on the instrumental requirements to meet the future experimental needs for such studies.

1. Introduction:

The information obtained from inelastic neutron scattering experiments characterizes the dynamical response function of a material. In this paper we concentrate on the magnetic response of antiferromagnetic materials lying in the strongly correlated \( f \)-electron regime. In general the dynamic response of such materials is complicated as it can have more than one pole in momentum space and extend over a large frequency range. Moreover, the magnetic interactions near additional low temperature phase transitions, such as superconductivity (\( T_c \) usually below 2K) are of particular interest.

Strongly correlated \( f \)-electron systems are intermetallic compounds, containing Ce, Yb or light actinide atoms. The magnetic properties are most unusual, ranging from strong antiferromagnetism via intermediate valence behavior to heavy fermion superconductivity [1]. Many of those materials are close to a magnetic instability and by variation of an external parameter, such as doping or pressure, the physical behavior can drastically change. Note that a similar proximity to a magnetic instability has been observed for high \( T_c \) materials, GMR compounds or low dimensional magnets, and it is the existence of an universal phase diagram and the physical concept of a quantum critical point, which mutually increased the interest in all those strongly correlated compounds [2].

2. Experimental example:

In the following we will discuss recent inelastic neutron scattering results from what is probably the most prominent example of a magnetic heavy fermion superconductor: \( \text{UPd}_2\text{Al}_3 \) [3]. In this compound, effective heavy electrons (\( \gamma = 150 \text{mJ/moleK}^2 \)), superconductivity (\( T_c = 2 \text{K} \)) and antiferromagnetism (\( T_N = 14 \text{K} \), propagation vector \( \mathbf{k} = (0 0 1/2) \), \( \mu \sim 1 \mu_B \) perpendicular to the hexagonal c-axis) co-exist at low temperatures.

Inelastic neutron scattering experiments have been performed on ILL’s cold neutron three-axis spectrometer (TAS) IN14 using a large single crystal mounted inside a dilution refrigerator. Fig. 1 shows a map (reconstructed point by point from the TAS measurements) of the magnetic response within the basal plane of the hexagonal structure (h 0 1/2). The plot covers 2 magnetic Brillouin zones. Besides some dispersive feature starting at the magnetic zone centers (0 0 1/2) and (1 0 1/2), a broad inelastic feature is observed close to the magnetic zone boundary (1/2 0 1/2) [4].

In the normal state the dispersive feature exists in conjunction with a quasi-elastic signal centered around (0 0 1/2) (Fig. 2b, c). In the superconducting state the quasielastic signal is replaced by a low-lying inelastic mode in conjunction with an almost unchanged dispersive feature at higher energies (Fig. 2d and 3) [7]. Suppressing the superconducting state with temperature or by applying a magnetic field suppresses the low energy magnetic mode.
underlining that this signal is related to the formation of the superconducting state. Polarisation analysis reveals that the quasielastic and both inelastic features have the same polarisation in the magnetic channel. Based on these experimental results several theoretical descriptions have been put forward, all describing the magnetic interactions in the normal state as well as the relation between magnetic order and superconductivity [8], which reveal the symmetry of the order parameter [9], and show that the superconductivity is mediated by magnetism, as also suggested by tunnel spectroscopy [10].

3. Comparison to UNi2Al3 and UGa3
The experimental results may be compared to the dynamic response of other related compounds. Similar experiments have been performed on the heavy fermion antiferromagnetic superconductor UNi2Al3. Because all transition temperatures (T_N = 4.5K, T_c = 1K) and the magnetic moment (μ ~ 0.2µB) are lower, the statistical error in the data is higher. Nevertheless the normal state data are well described by the same features and a similar model with an adjusted parameter set [11].

Underlying that this signal is related to the formation of the superconducting state. Polarisation analysis reveals that the quasielastic and both inelastic features have the same polarisation in the magnetic channel. Based on these experimental results several theoretical descriptions have been put forward, all describing the magnetic interactions in the normal state as well as the relation between magnetic order and superconductivity [8], which reveal the symmetry of the order parameter [9], and show that the superconductivity is mediated by magnetism, as also suggested by tunnel spectroscopy [10].

Fig. 2: Temperature dependence of the magnetic response of UPd2Al3 close to the magnetic zone center (0 0 1/2). Quasi-elastic scattering is observed above T_N = 14K [panel (a)], but at T = 7K [panel (b)] and 1.8K [panel (c)] in the normal state a dispersive feature exists in conjunction with a quasi-elastic signal centered around (0 0 1/2). In the superconducting state [panel (d)] the quasielastic scattering is replaced by a low-lying inelastic mode in conjunction with an almost unchanged dispersive feature at higher energies (data taken from [8]).

UGa3 is an itinerant antiferromagnet with a significant orbital moment (T_N = 67K); once again at least part of the f-electron density of states resides in the conduction electron band. Fig. 4 shows that similar features as in the case of UNi2Al3 are observed; notably even down to lowest temperatures an inelastic dispersive feature co-exists with strong quasi-elastic scattering [12]. This co-existence then appears to be a common feature of these magnetic f-metals.

4. Conclusions:
We now turn to the instrumental requirements for such kind of investigations: To quantify χ_q(ω) our experiments start with a general “mapping” of the response function, and then more selective scans in the regions of interest are done, often involving polarisation analysis to isolate the magnetic cross section.
Therefore single crystals are necessary and, often weak, signals at (possibly) several positions in momentum space need to be characterised. The flexibility and good signal to noise ratio make the three axis spectrometer invaluable for these studies. Of particular interest are the interactions near additional phase transitions, such as superconductivity, which occurs usually below 2 K. This requires good cryogenics, adequate energy resolution (~ k_BTc), and the use of other complementary techniques such as Spherical Neutron Polarimetry [13] (which helps to quantify the interaction between magnetic excitations and lattice dynamics) or magnetic fields (which allow access to different parts of the phase diagram).

Acknowledgements:
We acknowledge the excellent help of the ILL technical services, and also our many collaborators, who are identified on the published papers.

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Neutron time-of-flight (TOF) spectroscopy on LiV$_2$O$_4$

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Neutron scattering is the most powerful technique to study magnetism on a microscopic scale. Current scientific research focuses on the study of strongly correlated electron systems exhibiting a wealth of exciting phenomena including high-$T_c$ superconductivity, CMR materials and heavy fermion properties. Frequently, new materials are - for a certain time after their discovery - only available as polycrystalline samples. Consequently, the method of choice to investigate the magnetic interactions on polycrystalline materials is TOF neutron spectroscopy. Concerning neutron flux, energy range and polarization options, ILL offers several unique instruments of TOF spectrometers. This field of research will remain a domain of neutron scattering in the years to come. Continuous effort should be spent to maintain ILL’s role in the study of new magnetic materials by TOF spectroscopy. As an example, we present some results of neutron scattering studies on LiV$_2$O$_4$. LiV$_2$O$_4$ has been considered as the first example of a heavy fermion compound without $f$-electron element. Quasielastic neutron scattering revealed the typical features of a heavy fermion system. However, increasing experimental and theoretical evidence favours an explanation of the heavy fermion behaviour of LiV$_2$O$_4$ in terms of spin fluctuations of a magnetically strongly frustrated system. Currently, polarized neutron scattering on D7 is in progress to establish a firm basis for the interpretation of the unusual ground state properties of LiV$_2$O$_4$.

1. Introduction

Electronic correlations represent one of the most formidable problems in modern condensed matter physics. From a theoretical point of view, the comparable low densities and strong interactions require non-perturbative calculational approaches. The large class of strongly correlated electron materials exhibit a wealth of exciting phenomena including high-$T_c$ superconductivity, colossal magneto-resistance (CMR) effects, heavy fermion behaviour and metal-to-insulator transitions. These unusual properties are the result of the cooperative behaviour of interacting microscopic degrees of freedom (spin, charge, orbital and lattice degrees of freedom). Current scientific research focuses on unconventional superconductors with non s-wave symmetry like the heavy fermion superconductors, the cuprates and the ruthenates and its interplay with magnetism. Whereas the exact pairing mechanism is still under debate, it is generally accepted that magnetic excitations play a crucial role for the formation of the superconducting state. In several compounds deviations from conventional Fermi liquid behaviour is found on the verge of a magnetic instability. Concerning the CMR manganites, which display a rich variety of electronic ordering phenomena the role of mesoscopic-scale selforganization behaviour (stripe phases) for the metal-to-insulator transition and the low temperature ferromagnetic metallic state is still unclear. In all these prominent cases the low energy magnetic excitations dominate the physical properties of these compounds.

2. Neutron time-of-flight (TOF) spectroscopy

Neutron scattering is the most powerful technique to study magnetism on a microscopic scale. To elucidate the physical properties of strongly correlated electron systems, the determination of the corresponding magnetic excitation spectrum is required. Most detailed information can be obtained by means of polarized neutron spectroscopy on single crystalline samples. However, single crystals of suitable size and quality are usually very difficult to synthesize. Therefore, for a significant time, new materials exhibiting extraordinary new phenomena are frequently available in polycrystalline form only. Consequently, the method of choice for such materials is neutron spectroscopy employing the TOF technique. Since the physical properties of strongly correlated electron systems are determined by the low energy magnetic excitations involving weak magnetic moments, the requirements for successful experimental studies are high neutron flux, low incident neutron energy and good resolution. Quasielastic neutron scattering experiments provide a unique characterization of the dynamic properties of a magnetic system. The most fundamental property is the dynamical susceptibility $\chi(Q, \omega, T)$ that can be measured via the dynamic structure factor $S(Q, \omega, T)$. In the absence of interactions, a local magnetic moment will give a sharp delta-function peak in $S(Q, \omega, T)$. Exchange interactions with conduction electrons will yield Lorentzian line shapes and the corresponding width $\Gamma(Q, T)$ at low temperatures corresponds to a characteristic energy scale. Additionally, due to the large detector arrays of TOF spectrometers, it is often possible to determine the relevant regions in reciprocal space. This information not only determines the magnetic excitation spectra to a large extent, but additionally provides a basis for subsequent measurements on single detector three-axis spectrometers which oth-
erwise may be lost in reciprocal space. Concerning neutron flux, energy range and polarization options, ILL offers several unique instruments of TOF spectrometers such as IN6 or D7.

3. LiV$_2$O$_4$

Based on a wealth of experimental results, in particular specific heat, NMR and µSR measurements, LiV$_2$O$_4$ has been considered as the first example of a heavy fermion compound without $f$-electrons [1]. Traditional heavy fermion systems rely on the Kondo physics of two different electronic systems. Well localized $f$-electrons hybridize with band states of conduction electrons. This in turn gives rise to a renormalization of the electronic properties which may be described by a large effective electronic mass. Though there are attempts to map the electronic structure of LiV$_2$O$_4$ onto the periodic Anderson model usually adopted for the description of heavy fermion compounds [2,3], it is hard to imagine how this scenario could work in the present case of LiV$_2$O$_4$.

An alternative explanation supported by an increasing amount of theoretical [4] and experimental evidence is based on the strong geometrical frustration inherent to the spinel structure of LiV$_2$O$_4$. Strong magnetic fluctuations as arising from the geometrical frustration may lead to a similar behaviour like heavy fermion systems. The underlying physics is, however, completely different. We have performed a quasielastic neutron scattering study on LiV$_2$O$_4$. As shown in Fig. 1, the following main results are obtained [5]: LiV$_2$O$_4$ exhibits a residual quasielastic line width of $\Gamma(T \rightarrow 0) = 0.5$ meV, followed by a square root temperature dependence. No significant $Q$-dependence could be observed for $T<40$ K. A dramatic change of the magnetic response takes place between 40K<$T<$80K, where a pronounced $Q$-dependence starts to develop and the system behaves like a weak ferromagnetic metal [5], in accord with the results of NMR measurements [6]. However, we also observed a significant $Q$-dependence of the intensity at low temperatures ($T<40$ K) corresponding to antiferromagnetic fluctuations. According to conventional models of heavy fermion systems, the $Q$-dependence of the intensity (correlations in space) and the line width (correlations in time) are not independent of each other [7]. This strongly points away from a conventional heavy fermion ground state in LiV$_2$O$_4$. In order to study the vital role of the geometrical frustration, we have performed a study of the diffuse scattering on the TOF spectrometer D7. Full polarization analysis of this unique instrument allows for a separation of the nuclear and magnetic, as well as of the coherent and incoherent scattering cross sections, respectively. Due to the weak signal, the instrument was used in its diffraction mode, only. After correction for detector and polarizer efficiency and for background, the resulting magnetic scattering signal clearly revealed the onset of antiferromagnetic spin fluctuations for $T<40$K. These results support the interpretation of the heavy fermion behaviour of LiV$_2$O$_4$ as arising from strong (antiferromagnetic) spin fluctuations. To further elucidate the magnetic properties of LiV$_2$O$_4$, we have recently performed a quasielastic neutron scattering study on Li(V$_{1-x}$Ti$_x$)$_2$O$_4$ for $x=0.1$ and $x=0.3$. In contrast to the substitution of Li by Zn in Li$_{1-x}$Zn$_x$V$_2$O$_4$ [8,9], Ti doping directly disturbs the magnetic sublattice of V ions, corresponding to hole doping of the $d$-electron system. Furthermore, Ti doping introduces atomic disorder and leads to a slight lattice expansion of 0.4% for $x=0.3$. The results are shown in Fig. 2. Again, we observe a residual quasielastic line width of the order of 0.5 meV, followed by a square root temperature dependence. Above $T>40$ K, a significant narrowing (for mean elastic low $Q$ values) of the line width strikingly resembles the behaviour.
observed for pure LiV$_2$O$_4$. The stability of the magnetic response of LiV$_2$O$_4$ upon hole doping up to 30% again demands for an alternative explanation than a Kondo physics based heavy fermion ground state. An interesting scenario of the magnetic properties of LiV$_2$O$_4$ has recently been put forth by Fulde et al. [10]. They divided the mixed-valent V sublattice into rings and chains of a S=1/2 (corresponding to V$^{4+}$ ions) and a S=1 (V$^{3+}$ ions) spin system. The low energy excitations of the S=1/2 subsystem dominate the magnetic properties of LiV$_2$O$_4$, since the S=1 system reveals a finite energy gap [10]. Within such a scenario, hole doping would reduce the number of S=1 ions, but hardly effect the excitation spectrum of the relevant S=1/2 system.

4. Conclusion

The determination of the magnetic excitation spectra of strongly correlated electron systems is a prerequisite for an understanding of the exciting physical properties of these compounds. On behalf of pure and doped LiV$_2$O$_4$, we have shown the power of TOF neutron spectroscopy to unravel the microscopic origins of the unusual magnetic ground states of novel materials. This field of research will remain a domain of neutron scattering in the years to come. The high demand for neutron beam time related to the study of strongly correlated electron systems on TOF spectrometers at the ILL shows its competitiveness, based on high neutron flux, good resolution and unique polarization options. Therefore, continuous effort should be spent to maintain ILL’s role in the study of new magnetic materials by TOF spectroscopy.

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Magnetically disordered systems, studied using neutron polarization analysis

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Neutron polarization analysis (NPA) studies of both nuclear and magnetic correlations in disordered alloys and compounds provide a unique insight into the character and extent of magnetic disorder in these systems and its dependence on the local atomic environment. A review of polarization analysis studies of magnetic and structural defects in a variety of materials, performed using the diffuse scattering spectrometer D7 at the Institut Laue-Langevin is here presented. The diverse range of magnetic materials studied using D7 includes spin-glasses, frustrated itinerant electron systems, pyrochlores and quasicrystals. While NPA is undoubtedly an extremely valuable technique, it is severely flux limited, and is thus restricted to the study of massive (~20g) large moment systems. The rebuild of the primary and secondary spectrometers of D7 as part of the ILL millennium project will result in an increase in counting statistics of a factor of 60, opening up NPA as a routine technique for the measurement of small and weakly scattering samples.

1. Introduction

The diffuse scattering that is found beneath the nuclear and magnetic Bragg peaks in a diffraction pattern, and which is often considered as merely an annoying "background" contribution, provides detailed information on magnetic local order or disorder, and upon the interplay between such local magnetic configurations and any local atomic defect structures which may be present in the system under investigation. However, such magnetic disorder scattering contributions are generally weak, and often co-exist with nuclear (chemical or isotopic) incoherent scattering and nuclear-spin incoherent scattering contributions. In order to separate each of these contributions to the scattering, and look at each one in isolation, it is necessary to use polarized neutron scattering techniques. These techniques fall into four major categories:

i) Polarized beam neutron diffraction: in which the incident neutron beam is polarized, but the scattering beam is not analysed for its polarization direction. This technique is used in the study of ferromagnetic systems, in particular with single crystals.

ii) The Parallel-Perpendicular (ll - l) method: in which the incident neutron beam polarization is oriented first parallel and then perpendicular to the momentum transfer vector, Q, and then the scattered beam polarization analysed in the relevant direction. Using this technique, magnetic scattering may be separated from the other scattering contributions. Note that this technique may only be used on single-detector neutron instruments.

iii) The XYZ Technique (3-directional polarization analysis): in which the incident neutron beam polarization is oriented parallel and antiparallel to 3 orthogonal x-y-z axes with the x-y plane being defined by the plane of the detectors. This technique allows for separation of magnetic scattering from other contributions on a multidetector instrument. However, this separation only works with multi-orientational magnets, e.g., paramagnets, multi-domain antiferromagnets, spin-glasses, etc. In particular, ferromagnetic and helimagnetic systems cannot be studied accurately using the XYZ technique.

iv) Full 3-dimensional neutron polarimetry: in which the orientation of the incident beam is fully controllable and the scattered beam polarization vector (magnitude and direction) is measured, rather than just the polarization component in a specified direction, as is the case with the other two polarization analysis techniques. The direction of the final polarization depends on 16 separate contributions to the scattering cross-section (nuclear, magnetic and interference terms included) all of which may be deduced, and any magnetic system may be measured using this technique. Like the ll - l method, it may only be used on single detector instruments.

We shall restrict our attention from now on to the XYZ technique, which is used on the diffuse scattering spectrometer, D7 at the ILL. This remains the only method where magnetic scattering is separable on a multi-detector, and is ideally suited to studies of disordered magnetic systems. In such systems, the magnetic scattering is generally diffuse and weak, and so D7 is optimised for high-flux and low Q-resolution, employing a double focusing pyrolitic graphite monochromator. D7 employs cold neutrons (E, from 2.3meV to 8.5meV). This is a general requirement of diffuse scattering spectrometers since multiple Bragg scattering may add considerably to the apparent diffuse scattering. Experiments are therefore performed at wavelengths beyond the Bragg scattering cut-off of the sample under investigation.

2. Diffuse Magnetic Scattering from Antiferromagnets, Paramagnets and Spin-Glasses

The diffuse magnetic scattering from an antiferromagnet of the form $A_{B_{1-c}}$, provides information on the moment fluctuations of the A and B species about their mean values. Both the chemical and the magnetic environment of the A or B atoms will in principle, affect these
moment fluctuations. Assuming that all the moments of a binary antiferromagnet are parallel or antiparallel to a unique moment direction \( \mathbf{n} \), then the defect (diffuse) scattering cross-section, assuming linear superposition of defects, will be [1],

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{res}} = \left( \frac{y e^2}{2m} \right)^2 |1 - (\mathbf{\tilde{n}} \cdot \mathbf{\tilde{f}})|^2 c(1 - c)S(\mathbf{k} - \mathbf{\tau}) \left[ \mu f_1(\mathbf{\kappa}) - \mu f_2(\mathbf{\kappa}) + M(\mathbf{\kappa}) \right]^2
\]

(1)

where, \( \mathbf{\tau} \) is the antiferromagnetic propagation vector of the host lattice and, \( S(\mathbf{k} - \mathbf{\tau}) \) and \( M(\mathbf{\kappa}) \) are the nuclear and magnetic structure factors, respectively. The major advantage of neutron polarization analysis with respect to antiferromagnetic scattering is that the nuclear structure factor, \( S(\mathbf{k} - \mathbf{\tau}) \), may be independently deduced from the nuclear (Non-Spin-Flip) scattering. For a polycrystalline (powdered) sample, \( |1 - (\mathbf{\tilde{n}} \cdot \mathbf{\tilde{f}})|^2 \) spherically averages to 2/3. In general, analysis of spherically averaged data is more complicated than for a single crystal since there will be contributions to the scattering from more than one Brillouin zone [2]. Polarization analysis studies of binary Cr alloys [3] and \( \gamma \)-Mn [4] have revealed detailed information of the defect structures of these alloys. Moreover, deviations from the strictly collinear model in \( \gamma \)-Mn revealed in anomalous diffuse scattering around the (001) reciprocal lattice point have shown that \( \gamma \)-Mn has an exotic triple-\( Q \) tetrahedral spin structure.

It is in the study of disordered magnetic systems such as spin-glasses and paramagnets that neutron polarization analysis comes into its own, since the magnetic cross-section in these systems is usually weak. For a fully (long-range) disordered magnet, the diffuse magnetic cross-section will be of the form,

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{res}} = \frac{2}{3} \left( \frac{y e^2}{2m} \right)^2 \sum_{\mathbf{k}} S(\mathbf{k}) M(\mathbf{k}) F(\mathbf{k})
\]

(2)

where \( M(\mathbf{k}) \) is the Fourier transform of the spatially varying magnetisation density \( M(\mathbf{r}) \). \( M(\mathbf{k}) \) can be written as,

\[
M(\mathbf{k}) = g^2 \bar{S}(S + 1) \sum_{\mathbf{s}} \frac{S(S+1)}{S(S+1)} e^{\mathbf{k} \cdot \mathbf{s}}
\]

(3)

where \( S_0 \) and \( S_i \) are the atomic spin vectors at an impurity origin and the \( N \)th atom, respectively, \( S(S+1) \) is the self-correlation term. Factorising Eq. (1.3) into near neighbour shells and taking the polycrystalline average gives,

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{res}} = \frac{2}{3} \left( \frac{y e^2}{2m} \right)^2 \sum_{\mathbf{k}} S(\mathbf{k}) M(\mathbf{k}) F(\mathbf{k})
\]

(4)

where \( R_i \) and \( N_i \) are the radius and coordination number of the \( i \)th near-neighbour shell, and where we have implicitly assumed that there are no concentration driven magnetic moment fluctuations arising from any nuclear short-range order, so that \( S(\mathbf{k}) = 1 \) in Eq. (2). In cases where this assumption cannot be made, the calculation of the spherical average of \( F(\mathbf{k})S(\mathbf{k})M(\mathbf{k}) \) must be made explicitly. In all but the simplest structures (see for example [3]) this calculation is extremely difficult, and numerical modelling methods must be employed to take full account of the nuclear and magnetic driven contributions to the magnetic diffuse cross-section.

### 3. Recent Neutron Polarization Analysis studies on D7

Recent investigations of magnetic correlations in disordered magnets on D7 include such diverse systems as kagomé antiferromagnets [5,6], 2d-honeycomb networks [7], pyrochlore lattices, dilute chromium alloys, itinerant electron frustrated antiferromagnets [1,8] and high-temperature superconductors [9]. Three examples of studies performed on D7 are given here.

#### A. Cu-5at.%Mn spin-glass alloy

It is widely believed that the Mn atoms in dilute CuMn alloys freeze randomly into a spin glass magnetic ground state. Recent work by Murani [10] on single crystal Cu-5 at% Mn, following on from the work of Cable and co-workers [11] on the Cu-25 at% Mn alloy, has observed strong magnetic correlations, consistent with a short-range spin-density-wave (SDW) structure, superimposed on a "background" cross-section due to randomly oriented spins.

Figure 1 shows the nuclear and magnetic cross-sections of Cu-5at.% Mn with \( Q_1 \) along the [100] direction and \( Q_2 \) along the [110] direction at a temperature of 1.5K (\( T_\gamma = 25 \)K). The broad humps in the nuclear cross-section indicate that the Mn atoms are preferentially surrounded by Cu atoms (anticlustering behaviour) while the magnetic correlations appear to be peaked at the same positions as the nuclear correlations, but also in the forward scattering direction close to (000) and at incommensurate (1/2 ± 8 0) positions, as well as other positions in k-space. The "pitch" \( d \) of the SDW-like peaks varies as a function of Mn concentration. This is thought to be due to the varying periodicity of the KKK-interaction between the Mn spins, as electrons are donated to the band and the Fermi wavevector \( k \) evolves. The magnetic scattering also features a uniform background level associated with randomly ordered 3d spins. Evidence suggests that this background scattering dominates in very dilute CuMn alloys, while in the more concentrated alloys the SDW-like incommensurate structures are enhanced relative to the background level.

#### B. Zn-Mg-Ho Rare-Earth Quasicrystal

Recent neutron diffraction studies by Sato and co-workers have observed strong diffuse magnetic scattering in the Zn-Mg-Ho icosahedral rare-earth quasi-crystalline system [12]. The magnetic susceptibility of this alloy shows spin glass like irreversibility behaviour below \( T_\gamma = 2 \)K. However, the magnetic scattering from a single crystal at low temperatures, shown in figure 2 is dominated by the diffuse peaks, with a relatively weak background contribution from randomly ordered Ho moments. In an icosahedral quasicrystal, reflection positions need to be indexed by six numbers, the Bragg positions being regarded as projections in 3d reciprocal space of six-dimensional hypercubic reciprocal lattice points. As a preliminary result, Sato has found a magnetic mod-
ulation vector of $Q = (3/4\ 0\ 0\ 1/2\ 3/4\ 1/2)$ which can reproduce the data in each of the planes studied. The correlations are found to be antiferromagnetic in each of the six virtual dimensions. It is remarkable that a system which exhibits typical spin glass behaviour in its bulk susceptibility, should display such strong "short-range" order, with a relatively small random background.

C. β-Mn Alloys

As an illustration of the extraction of short-range nuclear and magnetic correlations using computational Monté-Carlo techniques, we shall consider the work of Stewart and co-workers on the polycrystalline concentrated spin glass $β$-Mn$_{0.9}$Al$_{0.1}$ [13]. Although the underlying symmetry of $β$-Mn is simple cubic, the point symmetry is non-centrosymmetric. Thus, for any arbitrary origin the nuclei do not fall within well-defined shells and application of Eq. (4) results in gross over parameterisation of the data with, for example, 24 near neighbour shells covering a radial distance of only 7.8Å. To overcome this problem, reverse Monté-Carlo techniques as described in [13] are employed to model first the nuclear diffuse and then the magnetic diffuse scattering. In this way the magnetic correlations driven by nuclear short-range order are automatically taken into account, since the modelled lattice is used as the basis for the magnetic model. The nuclear and magnetic diffuse cross-sections are shown in figure 3 along with the modelled cross-sections from the Monté-Carlo simulations. This work has shown that: a) the Al nuclei have a tendency to anticluster; and b) the Mn-Mn spin correlations are antiferromagnetic in nature, but of moderately short range. The results obtained from $β$-Mn$_{0.9}$Al$_{0.1}$ have considerable bearing on the question of moment localisation and the spin-liquid to spin-glass transition. Pure $β$-Mn is characterised by massive zero-point antiferromagnetic spin fluctuations associated with a frustrated tri-angually coordinated Mn sublattice. The addition of Al impurities dampens the magnetic fluctuations and results in partial localisation of the Mn moments [14], while simultaneously relieving the topological frustration of the Mn moments.

4. Outlook

While neutron polarization analysis is an invaluable tool in the study of disordered magnetic materials, it remains a severely flux-limited technique. Taking into consideration that the combined transmission of the polarizer/analysers on D7 is currently around

Fig. 1: the nuclear and magnetic cross-sections of single crystal Cu-5at.%Mn measured on D7. The data show distinct nuclear short-range order (SRO) peaks at the (1 1/2 0) reciprocal lattice points and SDW-like magnetic short range order peaks at the (1 1/2 + δ 0) positions.

Fig. 2: the magnetic cross-section of single-crystalline Zn-Mg-Ho. The 10-fold magnetic symmetry is clearly shown up in the relatively sharp SRO peaks. The white circles denote the nuclear Bragg peak positions, showing that the magnetic correlations are basically antiferromagnetic.
5% and that 6 separate measurements are required to deduce the magnetic scattering, one can expect counting times in excess of 150 times that of a conventional diffraction measurement. The D7 Millennium Project, which started in January 2001, seeks to address this problem. With state-of-the-art supermirror technology, it is reasonable to expect a combined polarizer/analyser transmission of around 16%. In addition, the solid angle coverage of the detector banks on D7 is set to increase by a factor of 7.5, and the incident flux by a factor of 3. Taking these together, the new rebuilt D7 (scheduled for completion by 2005) will provide counting rates of between 30 and 60 times the current counting rate, thus enabling experiments which currently average two weeks duration, to be completed in less than a day. This upgrade will also open up neutron polarization analysis to new fields, such as biology, where the sample size is generally small, and to time-of-flight spectroscopy – which is currently available on D7, but rarely used due to the inordinately long counting times involved.

5. Conclusions

The theory of neutron polarisation analysis with regard to diffuse scattering studies of disordered magnetic materials has been presented, as well as some of the more recent and exciting results obtained from the diffuse scattering spectrometer D7 at the ILL, Grenoble. Diffuse scattering has done much to enhance our knowledge of disordered magnets, and will undoubtedly continue to do so, particularly in view of the advances being made in supermirror and 3He spin-filter technology and in anticipation of the intense 3rd generation pulsed neutron sources (SNS, ESS).

References

In-Situ neutron powder diffraction study on the pathway for the formation of Tl-2223 and Tl-1223

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The pathway for the formation of the high Tc cuprates Tl2Ba2Ca2Cu3O10 (Tl-2223) and TlBa2Ca2Cu3O9 (Tl-1223) was investigated by means of in-situ neutron powder diffraction on D1B. Three samples with nominal compositions Tlm(x)Ba2Ca2Cu3Oz (x = 1.1, 1.7 and 2.3) were prepared from Tl2O3, pre-reacted BaCuO2 and pre-reacted Ca2CuO3, and sealed in evacuated quartz tubes. They were then heated to 1078 K (x = 1.7 and 2.3) or 1180 K (x = 1.1) and held at this temperature for different periods while the diffraction patterns were collected every 5 minutes. For x = 1.1, the formation of Tl-1223 implies two phases of the binary TlO 1.5-BaO system and the double TlO layer phases Tl-2212 and Tl-2223 according to the sequence: Precursors/oxides → Tl2BaO4 → Tl2BaO13 → Tl-2212 → Tl-2223 → Tl-1223.

The formation temperatures for Tl-2212 and Tl-2223 are as low as 860 K and 1070 K, respectively, whereas, for Tl-1223, it is around 1180K. For x = 1.7, the conversion from Tl-2223 to Tl-1223 does not occur while for x = 2.3, the only stable superconducting phase is Tl-2212. These results are in complete agreement with a previous study on phase equilibria in which we have established that for x > 2, the equilibrium involves Tl-2212, TlCa2O6, (Ca,Tl)1-xCuOx, and CuO.

1. Introduction

The Tl-based high Tc superconducting cuprates form two homologous series of phases, the single TlO layer family with ideal composition TlBa2Ca2Cu3O8+x (n = 1-4) and the double TlO layer family with ideal composition Tl2Ba2Ca2Cu3O8+x (n = 1-4) [1,2]. Compounds of both series are of interest for practical use. The Tl-2223 phase has received great attention for power applications due to its superior current-carrying capability in high magnetic fields [3]. Concerning the double TlO layer phases, high quality Tl-2212 thin films have been used in a variety of passive microwave superconducting devices. The higher Tc of the Tl-2223 phase (Tcmax = 128 K) relative to the Tl-2212 phase (Tcmax = 110 K) suggests that devices with Tl-223 films could be operated at higher temperatures [4]. For both grain growth and film morphology, it is of great interest to know whether a liquid phase is implied or not in the formation path for Tl-1223 and Tl-2223.

For this reason, we have undertaken an in-situ neutron powder diffraction study.

2. Experimental

For the three starting compositions, Tl1.1Ba2Ca2Cu3O9 (sample Tl11), Tl1.7Ba2Ca2Cu3O9 (Tl17) and Tl2.3Ba2Ca2Cu3O9 (Tl23), the appropriate amounts of Tl2O3, BaCuO2 and Ca2CuO3 powders were thoroughly mixed, pressed into a pellet, tightly wrapped in gold foil and sealed in an evacuated quartz tube. About 9 g were prepared for each sample in order to ensure good counting statistics during the in-situ neutron diffraction experiments. Variable temperature neutron data were collected on the high-flux powder diffractometer D1B at the Institut Laue Langevin (ILL) in Grenoble (λ = 2.524 Å, Graphite (002) monochromator, 6° ≤ 2θ ≤ 86°, 0.2° 2θ step). The samples were rapidly (+10 K/min) heated from room temperature to about 700 K. The heating rate was then reduced to +2 K/min until the maximum temperature was reached, 1172 K for Tl11 and 1078 K for Tl17 and Tl23. After an annealing treatment, the samples were cooled to room temperature. The compositions of the Tl17 and Tl23 reacted samples, estimated from the weight changes attributed to Tl2O losses.

Fig. 1. Low angle part (6° < 2θ < 26°) of the first 120 diffraction patterns of Tl17 (300 K < T < 1078 K).
were found to be Tl$_{1.65}$Ba$_2$Ca$_2$Cu$_3$O$_z$ and Tl$_{2.25}$Ba$_2$Ca$_2$Cu$_3$O$_z$, respectively. However, the Tl content in Tl11 could not be determined because of reactions in vapour phase at the interface superconductor-foil.

The reacted samples were further characterised by AC susceptibility measurements and scanning electron microscopy (SEM).

### 3. Results and discussion

The reaction pathway was found to be:

Precursors/oxides $\rightarrow$ Tl$_2$BaO$_4$ $\rightarrow$ Tl$_6$Ba$_4$O$_{13}$ $\rightarrow$ 2212 (Tl$_{23}$) $\rightarrow$ 2223 (Tl$_{17}$) $\rightarrow$ 1223 (Tl$_{11}$).

A 3D plot of the low angle part of the first 120 patterns for Tl$_{17}$ is given in Fig. 1. From such graphs, we were able to identify all phases involved in the formation path. For all samples, the decomposition of BaCuO$_2$ and Tl$_2$O$_3$ begins at about 680 K and is followed by the formation of Tl$_2$BaO$_4$ and Tl$_6$Ba$_4$O$_{13}$. At the same time, CuO appears and its amount increases progressively as expected. In addition, an unknown U-phase was detected on four diffraction patterns (between 750 K and 780 K), just before the formation of the two binary compounds, Tl$_2$BaO$_4$ and Tl$_6$Ba$_4$O$_{13}$. The two low angle reflections ($2\theta = 10.8^\circ$ and $20.0^\circ$) which can be unambiguously attributed to this phase, do not correspond to any other equilibrium compound of the Tl$_2$O$_3$-BaO system which was studied in detail by Jondo et al [5], nor to any known phase of the other subsystems of Tl$_2$O$_3$-BaO-CaO-CuO. They do not correspond to any carbonate either. It is therefore believed that this U-phase is metastable and does not play a major role in the formation path. The Tl$_2$BaO$_4$ phase vanishes at 880 K while the amount of Tl$_6$Ba$_4$O$_{13}$ still increases until it reaches a maximum at about 905 K. Then Tl$_6$Ba$_4$O$_{13}$ starts to decompose and Tl-2212 is progressively formed. The latter phase appears at 860 K and the integrated intensity of one of its characteristic peaks ($2\theta = 19.3^\circ$) reaches its maximum value at 1075 K. For Tl$_{23}$, this is the final equilibrium state which implies Tl-2212, Tl$_{2}$Ca$_3$O$_6$, (Ca,Tl)$_{1-x}$CuO$_{z}$ and CuO as already demonstrated in a previous work [6]. The sample has a T$_c$ of 100 K and SEM images (Fig. 2) reveal small grains (<5µm in size) with sharp edges characteristic of the absence of a liquid.

For Tl$_{17}$, which diffraction patterns are shown in Fig. 1, and Tl$_{11}$, the conversion from Tl-2212 to Tl-2223 occurs at about 1070 K. As expected, it is accompanied by a significant decrease of the weight fractions of Tl$_2$Ca$_3$O$_6$, (Ca,Tl)$_{1-x}$CuO$_{z}$ and CuO. Tl-2223 is the equilibrium phase in Tl$_{17}$ with a sharp superconducting transition at T$_c = 115$ K (Fig. 3). As indicated in the introduction, the appearance of a liquid phase during the formation of Tl-2223 is detrimental to the morphology of thin films dedicated to passive microwave superconducting devices [4]. Both in-situ diffraction experiment and SEM analysis (Fig. 4) show explicitly that the Tl-2212 $\rightarrow$ Tl-2223 conversion occurs through an entirely solid state route which is thought to imply the diffusion of the Ca and Cu species and the restructuring of the Tl-2212 lattice.

Finally, in Tl$_{11}$, the Tl-1223 phase is formed from Tl-2223 at 1175 K. The reaction pathway through the double TIO layer phases is for the first time directly evidenced. We showed in a previous report [6] that the Tl-2223 $\rightarrow$ Tl-1223 conversion occurs by a progressive de-intercalation of TlO layers in the solid state. This non-equilibrium process results in the formation of transient intergrowth phases (e.g. 1223/2223/2223) which could not be unambiguously identified during this experiment due to the low resolution of the instrument. The reacted sample, which is in the equilibrium state, is mainly a mixture of Tl-2223 and Tl-1223 because of the high Tl content. The critical temperatures for the two superconducting phases are 122 K and 108 K, respectively.

The formation path in an evacuated closed system differs from that observed in air or in oxygen. Three points may be discussed:

- the Tl-2201 phase is not observed prior to the formation of Tl-2212 which may be explained as follows. In vacuum at 700 K, the Tl$_2$O vapour pressure becomes high enough to induce the

![Fig. 2. Secondary electron image of the sample Tl23.](image)

![Fig. 3. Real and imaginary part of the AC susceptibility as a function of temperature for Tl17.](image)
decomposition of BaCuO$_2$. The resulting free BaO reacts with the Tl$_2$O vapour and forms Tl$_4$BaO$_6$. As the decomposition of BaCuO$_2$ proceeds, the amount of free BaO increases which results in the formation of Tl$_4$Ba$_4$O$_{13}$. The latter phase then reacts with Ca$_2$CuO$_3$ and CuO to form directly Tl-2212 at 860 K. In air or in oxygen, the Tl$_2$O vapour pressure is lowered and the process is better described as a solid state diffusion of Tl$_2$O$_3$ in the mixed oxide BaCuO$_2$. The resulting pathway then implies the three phase field Tl-2201-BaCuO$_2$-CuO so that Tl-2201 is effectively observed.

• the formation of Tl-2212 and Tl-2223 occur at 860 K and 1070 K, respectively, which is about 200 K and 75 K lower than what is observed in air or in oxygen.

• in contrast, the formation temperature of Tl-1223 does not depend on the atmosphere. It is always around 1175 K.

The present study mainly shows that Tl-2223 may be formed through an entirely solid state route at relatively low temperatures under suitable conditions i.e. in evacuated closed system. As a consequence, the production of Tl-2223 films with a microstructure suitable for the patterning of narrow line structures can reasonably be anticipated [4].

Acknowledgements

The financial support by the Région Rhône-Alpes through the program Avenir is greatly acknowledged.

References


Fig. 4. Secondary electron image of the sample Tl17.
Recent structure results on High-\(T_c\)’s and related compounds from D2B data

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The crystal structure of \(\text{Ca}_{4.78}\text{Cu}_{6}\text{O}_{11.60}\) \((P2/c, a=10.9456(4) \text{ Å}, b=6.3192(2) \text{ Å}, c=16.8408(5) \text{ Å}, \beta=104.952(2)\)°\) has been solved and refined using neutron powder diffraction. It is closely related to the NaCuO\(_2\)-type structure. The phase stoichiometry and the displacements of atoms with respect to their positions in the previously reported substructure are explained by the minimization of the Ca-Ca repulsion and by a relaxation towards a more regular octahedral environment for Ca atoms. The crystal structure of the high-\(T_c\) superconducting cuprate \(\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y\) was reinvestigated. The identification of all impurity phases including \((\text{Ca,Tl})_{1-x}\text{CuO}_y\) allowed us to perform a full profile Rietveld analysis with no excluded regions. The main new feature is a displacement of the Tl site along the cell axis which, combined with that of the O site located in the same layer, results in a distorted tetrahedral coordination for Tl atoms with a mean observed Tl-O distance of 2.19 Å. Finally, we present the results of a study on \(\text{Nd}_{1.9}\text{Ba}_{1.1}\text{Cu}_3\text{O}_{7.31}\), the Nd-rich limit of \(\text{Nd}_{123ss}\). The ordering between Ba and Nd atoms in the bridging (Ba,Nd)O layer gives rise to a 4-fold superstructure \((Bmmm, a=7.7679(3) \text{ Å}, b=3.8539(2) \text{ Å}, c=22.9591(9) \text{ Å})\) with respect to the orthorhombic cell of \(\text{NdBa}_2\text{Cu}_3\text{O}_7\).

1. Crystal structure of \(\text{Ca}_{4.78}\text{Cu}_{6}\text{O}_{11.60}\)

\(\text{Ca}_{4.78}\text{Cu}_{6}\text{O}_{11.60}\), which related compound \((\text{Ca,Tl})_{1-x}\text{CuO}_y\) plays an important role in the formation of Tl-2223, was first reported for composition \(\text{CaCuO}_2\) by Roth et al [1] who proposed an orthorhombic subcell with \(a=10.588 \text{ Å}, b=2.812 \text{ Å} \text{ and } c=6.325 \text{ Å}.\) Weak superstructure reflections seen on precession photographs indicated a monoclinic supercell with \(a=10.95 \text{ Å}, b=6.35 \text{ Å}, c=33.72 \text{ Å}, \beta=105.5^\circ\). Using X-ray single crystal diffraction, Siegrist et al [2] confirmed that the subcell was orthorhombic. A refinement based on substructure reflections and carried out in space group \(Fmmm\) \((a=2.807(1) \text{ Å}, b=6.351(2) \text{ Å}, c=10.597(3) \text{ Å})\) showed that the average structure was closely related to the NaCuO\(_2\)-type structure (Fig. 1). It contains linear chains of edge-shared CuO\(_4\) squares directed along [100] with Ca atoms located in half of the octahedral sites in the channels produced by the chains. Extensive electron diffraction and microscopy work by Milat et al [3] revealed that the supercell was actually monoclinic with \(a'=16.80 \text{ Å}, b'=6.32 \text{ Å}, c'=10.95 \text{ Å}, \beta'=75^\circ\) and a sto-
superstructure. On the contrary, the displacements of Ca atoms, mainly along [001], and of O atoms along [010] (Fig. 2) are by far larger and may be understood in terms of a relaxation towards a more regular octahedral environment for Ca atoms. As a result, the average Ca-O distances lie between 2.34 and 2.41 Å and the average Ca-O distances between 1.81 and 2.04 Å. Bond valence sum analysis shows that the valences of Cu5 and Cu8 are definitely close to +1 and +3, respectively. This result could give additional clues for the understanding of the low temperature magnetic properties of the phase. The average bond sum for Ca is found equal to 2.02 which gives further confidence in the internal consistency of the refinement. The reason why the stoichiometry is not CaCuO2 is easily understood. Adding a sixth Ca site in the channels would result in too short Ca-O and Ca-Ca distances.

2. Disorder within the TIO layers of Tl-2223

Despite a large number of studies on the crystal structure of Tl-2223 (I4/mmm), there are still controversies over the cation distribution and the displacive disorder within the TIO layers. The reduced scattering density from the Tl site has been ascribed to Cu substitution, Ca substitution or, simply, Tl vacancies. The oxygen site within the same layer was found displaced from the ideal position on the 4-fold axis (4(f) 1/2 1/2 1/2 z) to 16(a) 1/2 y z in [4] whereas both Tl and O sites were split to the 16(d) 1/2 y 1/4 z position in [5]. The identification of all impurity phases, including the newly discovered (Ca,Tl)1-xCuO2 [6], allowed us to perform a full profile Rietveld analysis on neutron powder diffraction data with no excluded regions. We find that both Tl and O sites within the TIO layers are displaced in the basal plane along the cell axis to 16(a) 1/2 y z (Table 2). This results in four short Tl-O distances. Each Tl atom is therefore preferably linked to four O atoms (<Tl-O>=2.19 Å) which form a distorted tetrahedron. This tendency to a tetrahedral environment for Tl atoms has already been reported for Tl-1223 [7] and the displacement of the Tl site is further supported by the results of an ionic-type interatomic potential computer simulation by Chaplot [8]. Finally, we find that Cu does not substitute at the Tl site which is therefore either partly vacant or, most probably, partly occupied by Ca atoms.

Table 2. Atom coordinates, displacement parameters and site occupancies in the structure of Ca4.78Cu6O11.60.

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<th>y</th>
<th>z</th>
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<td>4(g)</td>
<td>0.2368(14)</td>
<td>0.4484(23)</td>
<td>0.4709(9)</td>
<td>0.58(3)</td>
<td></td>
</tr>
<tr>
<td>O11</td>
<td>4(g)</td>
<td>0.3769(14)</td>
<td>0.5422(22)</td>
<td>0.1498(10)</td>
<td>0.58(3)</td>
<td></td>
</tr>
<tr>
<td>O12</td>
<td>4(g)</td>
<td>0.3895(15)</td>
<td>0.4775(24)</td>
<td>0.3074(10)</td>
<td>0.58(3)</td>
<td>0.88(4)</td>
</tr>
</tbody>
</table>

Fig. 2. (Top) Schematic drawing of the structure of Ca4.78Cu6O11.60. Arrows indicate the displacements of atoms with respect to their position in the starting model. (Bottom) Oxygen sublattice projected along [100].
3. Crystal structure of Nd_{1.9}Ba_{1.1}Cu_{3}O_{7.31}

Recently, Goodilin et al. [9] showed that the solubility limit of the Nd(Ba_{1-x}Nd_{x})_{2}Cu_{3}O_{7+δ} solid solution is as high as x=0.45 at 995°C and found an orthorhombic domain above x=0.25. Evidence of a 4-fold superstructure (2a, 2b, 2c) was given by electron diffraction experiments [9] and confirmed by a structure refinement based on neutron powder diffraction data [10] for x=0.45. In agreement with the latter study [10], we find that the structure is satisfactorily described in space group Bmmm with a=7.7679(3) Å, b=3.8539(2) Å, c=22.9591(9) Å (Table 3) and that the coordinates and occupancies of the cation and O2-O6 sites are equal within standard uncertainty. However we find an extra O7 site in the chain layer, below Nd1 site located in the bridging layer, and a positional disorder of the O1 site (Fig. 3). The superstructure with respect to the orthorhombic cell of YBCO is due to ordering between Nd and Ba atoms in the bridging layer and to the related ordering of O atoms in the chain layer which give usual coordinations for the latter cations.

Acknowledgements

The authors thank E. Suard for fruitful discussions and assistance with data collection. The financial support by the Région Rhône-Alpes through the program Avenir is greatly acknowledged.

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Structural and magnetic properties of YCo$_{4-x}$Fe$_x$B compounds investigated by neutron diffraction

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The limited substitution of Co for B in RCo$_5$ leads to a family of compounds of formula R$_n$Co$_{n+1}$B$_n$ (n = 0, 1, 2, 3, ∞). The Fe for Co substitution induces serious modifications of the magnetic feature. In order to understand the influence of each sublattice (rare-earth and 3d metal), the YCo$_{4-x}$Fe$_x$B (n = 1) compounds with x ≤ 3 have been synthesised. Neutron diffraction experiments made on the D1A high-resolution powder diffractometer of the I.L.L. show a preference of iron for the 2c crystallographic site of the structure. The substitution of Fe for Co enhances both the Curie temperature and the saturation magnetisation. Therefore, we have evidence that the magnetic moment are significantly higher for the atoms situated on 2c site in comparison with these of the atoms situated on the 6i site. Diffraction measurement as a function of temperature has been performed on the D1B diffractometer (French C.R.G.). It demonstrates that the phenomena of spin reorientation occurring in the YCo$_4$B compound at low temperature disappear upon the Fe for Co substitution.

1. Introduction
The rare-earth cobalt intermetallic compounds such as RCo$_5$ (R = rare-earth) have attracted considerable attention for many years because of their large magnetic anisotropy. It is possible to substitute B for Co in RCo$_5$ to obtain the family of compounds R$_n$Co$_{n+1}$B$_n$, with n = 0, 1, 2, 3, ∞ [1], which form a unique series of crystal structures changing with n. All these structures are derived from the CaCu$_5$-type structure and can be described by an ordered substitution of B for Co in RCo$_5$.

The compound YCo$_4$B (n = 1) is obtained by the ordered substitution of Co by B in every second layer of the YCo$_5$ structure. One method currently used to study the magnetic properties of the 3d sublattice is by the substitution of Fe for Co that induces significant modifications to the crystal structure and to the magnetic properties of the YCo$_4$B phases. Neutron diffraction allows us to measure both the ordering scheme and the evolution of the magnetic moment of each atom upon the substitution of Fe for Co.

2. Experimental details
The neutron experiments were performed at the Institute Laue Langevin using the high-resolution 2-axis powder diffractometer D1A which description can be found elsewhere [2]. Further neutron diffraction patterns as function of temperature were obtained using the high flux powder diffractometer D1B (French CNRS-CRG instrument), to study the thermal evolution involving possible spin reorientation. Refinements of the diffraction data were performed using the Rietveld method as implemented in the software FULLPROF [3]. The polycrystalline samples were prepared by melting the starting materials (minimum purity 99.9 %) in a high frequency furnace under an argon gas atmosphere. The samples were synthesised using $^{11}$B rather than natural B in order to avoid both the incoherent scattering contribution and the absorption due to the natural boron. To increase homogeneity, small pieces of the ingots were annealed at 1223 K for at least a week.

The Curie temperature (T$_c$) was measured using a Faraday–type balance with a heating and cooling rate of 5 K per minute. Magnetisation measurements were performed using the extraction method in a continuous field of up to 7 T.

3. Results and discussion
The X-ray and neutron diffraction spectra of random powders of the YCo$_{4-x}$Fe$_x$B system show the formation of single-phase samples with the hexagonal CeCo$_4$B-type structure for an iron content of x ≤ 3. The YCo$_4$B crystal structure can be derived from the CaCu$_5$ structure and has two different crystallographic sites for Y (1a and 1b), two other sites for the transition metal elements (2c and 6i) and one site for the B atom (2d). The lattice parameter $a$ increases significantly until x = 1 and then levels off for the higher Fe concentrations. After a slight decrease until x = 1, the parameter $c$ shows a sharp increase as the iron concentration is increased. We have performed neutron diffraction studies in order to determine if the evolution of the lattice parameters with the substitution of
Table 1: Structural and magnetic properties of the YCo₄₋ₓFeₓB compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Tc (K)</th>
<th>Mₛ at 5 K µₛ/μ₀</th>
<th>Iron occupancies</th>
<th>Magnetic moments (μₛ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2c</td>
<td>6i</td>
<td>2c</td>
<td>6i</td>
<td>2c</td>
<td>6i</td>
</tr>
<tr>
<td>YCo₄B</td>
<td>5.020 (3)</td>
<td>6.893 (4)</td>
<td>380 (4)</td>
<td>2.9 (1)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>YCo₂FeB</td>
<td>5.066 (3)</td>
<td>6.859 (4)</td>
<td>635 (4)</td>
<td>4.3 (1)</td>
<td>74 (2)</td>
<td>10 (2)</td>
</tr>
<tr>
<td>YCo₂Fe₂B</td>
<td>5.070 (3)</td>
<td>6.911 (4)</td>
<td>655 (4)</td>
<td>5.5 (1)</td>
<td>87 (3)</td>
<td>39 (2)</td>
</tr>
<tr>
<td>YCoFe₂B</td>
<td>5.071 (3)</td>
<td>6.973 (5)</td>
<td>674 (4)</td>
<td>6.1 (1)</td>
<td>88 (3)</td>
<td>72 (2)</td>
</tr>
</tbody>
</table>

Fe for Co is linked to a preferential filling scheme of iron. An example of the diffraction patterns obtained on the D1A instrument is shown in Figure 1. Fe preferentially occupies the 2c site, as shown in Table I. The 6i site begins to fill with iron as the 2c site reaches the maximum of its occupation for YCo₂Fe₂B [4]. This preferential substitution scheme cannot be explained by a volume effect since the two Co/Fe sites (2c and 6i) have almost the same Wigner-Seitz volumes, 10.9 Å and 10.8 Å, respectively in YCo₄B and the atomic radii of Fe and Co are the same. Consequently, we propose that a chemical effect is at the origin of the preferential location of Fe atoms on the 2c sites.

As shown in Table I, a large increase of the Tc is observed upon the substitution of Fe for Co. A dramatic enhancement occurs between x = 0 and x = 1 whereas only a slight increase is observed for higher Fe concentrations. For 0 ≤ x ≤ 1 the sharp increase of Tc corresponds to the filling of the 2c site by Fe atoms. The subsequent filling of the 6i site observed for higher Fe concentration corresponds to a much smaller increase of Tc. A similar evolution is found for the saturation magnetisation (Mₛ) where the filling of the 2c site leads to a more significant increase of Mₛ. These measurements are in good agreement with the refined magnetic moments determined by neutron diffraction. Our neutron diffraction investigation reveals that the measured magnetic moments of the 2c site are twice those of the 6i site (Table I). It is to be noticed that during the refinement the magnetic moment of Co was fixed to the known values of YCo₄B in order to allow the determination of the Fe moment. This feature is observed for both Co and Fe atoms. Consequently the filling of the 2c site between x = 0 and x = 1 results in a large increase of Mₛ. As a comparison, the filling of the 6i site that occurs between x = 2 and x = 3 induces a much smaller increase of the Mₛ. The main difference between the Co (6i) site of YCo₄B and the Co (3g) site of YCo₄ is the change in the species (B for Co) of half of the nearest neighbours. This environmental change induces a dramatic decrease of the magnetic moment from 1.7 μₛ for the Co (3g) site of YCo₄ to 0.5 μₛ for the Co (6i) site of YCo₄B. This is a consequence of the hybridisation between B atoms with their Co (6i) near neighbours, which implies that B atoms donate valence electrons to the Co (6i) atoms. The key point is probably the mixing of the 3d-states of Co with the 2p-states of B. On the Co (2c) site, which is much farther from B atoms, the value of the magnetic moment in YCo₄ (1.8 μₛ) is close to that measured for the 2c site in YCo₄B (1.5 μₛ).

Previous studies have shown a spin reorientation phenomenon in YCo₄B occurring at 140 K [5]. This phenomenon is due to the competition between the opposite individual site anisotropies of Co atoms situated on the 2c and the 6i sites. Neutron diffraction patterns recorded at both 2 and 220 K on YCo₄B are presented in Figure 2. A significant decrease of the intensity of the (0 0 1) Bragg peak is observed when the temperature increases. This is related to the decrease of the magnetic contribution to this Bragg peak, and shows that the easy magnetisation direction (EMD) changes from the basal plane at 2 K to the c-axis at 220 K. The diffraction patterns recorded on the iron containing samples shows that the EMD remains unchanged from 2 to 300 K. That is, the spin reorientation observed for YCo₄B has disappeared in the Fe containing samples.

Acknowledgements

The authors wish to thank Dr E. Suard for her help during the preparation of the experiments. The Institute Laue Langevin is acknowledged gratefully for providing the neutron diffraction facilities.

References

In this paper we present a kinetic neutron diffraction study of the crystallisation and subsequent phase transformations of an amorphous Y₇Fe₃ alloy. The final product of the crystallisation process is the C15 Laves phase compound YFe₂, however a novel intermetallic compound, close to the composition YFe, forms at intermediate temperatures. In addition to the structural study of the phases formed during recrystallisation, the magnetic properties of the new Y-Fe phase, as determined by neutron diffraction, ⁵⁷Fe Mössbauer spectroscopy, muon spin relaxation and dc magnetisation are also discussed.

1. Introduction
For many years neutron diffraction has been used routinely by physicists and chemists to determine the crystallographic and magnetic structure of materials. However, the recent advent of intense neutron sources and concomitant improvements in instrumentation have now made it possible to collect high quality diffraction patterns in a few seconds. This dramatic decrease in counting times has thus provided us with the possibility of using neutron diffraction to explore the kinetics of solid-state processes in real time, and hence enabled us to monitor phase formations and transformations in materials under the conditions at which they occur. In this paper we present the results of an in-situ crystallisation of high purity, amorphous Y₆₇Fe₃₃ melt-spun ribbons. Using this technique we have synthesised a new Y-Fe compound and, via Rietveld refinement, have determined its structure.

2. Experimental details
Amorphous precursors of Y₆₇Fe₃₃ were prepared by RF melt spinning. The recrystallisation process was studied by collecting diffraction patterns collected every four minutes while the temperature was ramped from 230°C to 510°C at 40°C per hour. The magnetic properties of the new phase were studied using a range of techniques: Mössbauer spectra were collected in zero field at several temperatures between 5K and 200K. Muon spin relaxation (μSR) spectra were collected on warming in zero field at several temperatures between 5K and 300K. DC magnetisation measurements were carried out in a 12T Oxford Instruments VSM. Hysteresis loops were collected in fields of +/- 5T. To determine the magnetic structure high statistics neutron diffraction patterns were collected on D1B as the temperature was ramped from 1.5K to 100K at 8K per hour.

3. Results and Discussion
3.1. Structural properties
The neutron thermogram collected on D20 is shown in fig. 1. A detailed description of the recrystallisation process is given in [1], and only a summary of the salient features is presented here. From the figure it can be seen that partial crystallisation of Y₆₇Fe₃₃ first occurs at approximately 300°C when a pure HCP elemental Y phase is formed (P6 3/mmc with a=3.650(1) Å, c=5.77(1) Å, γ=120°), with the Fe atoms segregating to form an Fe-rich amorphous phase. Above 390°C there is a dramatic crystallisation of the entire sample, witnessed by an abrupt loss of the amorphous contribution to the diffraction pattern. At this temperature new Bragg peaks appear signifying the formation of an intermediate phase which coexists with the Y matrix to ~450°C. From the composition of the precursor material, the intensity of the pure Y peaks and the intensity of the Y and YFe₂ peaks in the final phase, we have identified the composition of this intermediate phase as close to stoichiometric YFe. Using FulProf, we have established that this YFe phase crystallises with the hexagonal space group, P6/mmc with extremely large cell dimensions of a=12.8893(7) Å and c=11.7006(9) Å. As yet, we have not determined the exact positions of the Y and Fe atoms in this structure, although it is clear that a cell of this volume will contain a large number of atoms. Examination of the Fe-Fe and Y-Fe distances in other Y-Fe phases (~2.6 Å and ~3.5 Å respectively) and assuming a density of 7g.cm⁻³ we propose a structure containing ~100 atoms/unit cell. Above 450°C the Bragg peaks associated with the intermediate phase decrease in intensity, accompanied by a further increase in the intensity of the Y peaks, and the cubic C15 Laves phase YFe₂ emerges. A two-phase Rietveld refinement shows that the final crystallisa-
tion product is YFe$_2$ (Fd3m with $a=7.416(3)$ Å) coexisting with crystalline elemental Y (P6/mmc with $a=3.659(1)$ Å and $c=5.791(4)$ Å). With the exception of a small peak at $2\theta \sim 59^\circ$, no peaks other than those associated with either Y or YFe$_2$ are observed.

3.2 Magnetic properties

Mössbauer spectroscopy, µSR and dc magnetisation measurements all show that the intermediate YFe phase undergoes a magnetic transition at $\sim 55$K where ordered Fe moments of approximately 1$\mu_B$ are found. The Mössbauer spectroscopy measurements suggest that there are two crystallographically distinct Fe sites at high temperatures and four magnetically distinct Fe sites below the transition. However as these measurements were taken in zero field it is not possible to decide if the magnetic order is ferro- or antiferromagnetic in nature.

The µSR spectra were fitted with a simple exponential model $G_z(t) = a_1 \exp(-\lambda t)$ plus a flat background to account for muons landing in the silver sample holder. The temperature dependence of both the relaxation rate, $\lambda$, and the initial asymmetry, $a_1$, show that YFe is magnetically ordered below $\sim 54$K. Spectra collected below 55K are oscillatory in nature and indicate the presence of static magnetic fields of approx 0.3T at 30K, below 30K the magnetic fields appear to decrease. The susceptibility of the sample was obtained by fitting the high field magnetisation curves to a straight line. The susceptibility peaks at $\sim 58$K and a plateau is observed in the below 30K Neutron diffraction patterns were collected at 1.5K, well below the magnetic transition, and at 75K, well above the transition. The difference pattern (1.5K-75K) shown in fig. 2, shows only one peak at $2\theta \sim 16^\circ$. This peak does not lie at the position of a nuclear Bragg peak and it appears that a simple ferromagnetic model is not a good description of the magnetic order in system. Diffraction patterns were also collected every five minutes on warming to study the temperature dependence of the magnetic Bragg peak (fig 3). The Bragg peaks at $\sim 12^\circ$ and $\sim 18^\circ$ are the (100) and (101) reflections in the hexagonal space group described above and the magnetic peak is seen at $2\theta \sim 16^\circ$. From the temperature dependence of the intensity of this peak, the magnetic ordering temperature is found to be close to 60K in good agreement with the values determined via other magnetic techniques.

It is interesting to note that there are marked deviations from a smooth curve below 30K in the intensity of the magnetic neutron peak, the ac susceptibility and the frequency of the muon signal. This is possibly due to a spin re-orientation at around 30K but further analysis is required to confirm this.

4. Conclusions

Generally the agreement between the experimental data and the predictions of ASW [2] and LMTO [3] band structure calculations of the interplay of structural, electronic and magnetic properties in the families of inter-metallic compounds upon which our investigations are based are extremely good. However, the parameter space available to the theoreticians is often restricted by the lack of appropriate stable intermetallic compounds against which the calculations can be tested. Through in situ neutron diffraction techniques we are already synthesising relevant crystallographic and magnetic phases which should stimulate further calculations and provide a stringent test of the predictive capabilities of these methods.

Acknowledgements

The authors are grateful to Drs Convert and Hansen for their help during the D20 experiment and to Prof Cywinski for his comments.

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Fig. 2: Neutron diffraction patterns taken at 1.5K and 75K. The bottom figure shows the magnetic scattering obtained by subtracting the 75K data from the 1.5K data.

Fig. 3: Temperature dependence of the magnetic Bragg peak intensity as determined using ABFFIT.
The powder diffractometer D2B is due to its choice of wavelengths and collimations certainly the most powerful existing high resolution diffractometer. With a Q-range extending to low values magnetic features often not detectable on spallation source instruments are visible, the well defined peakshape allows smooth refinement of data. Discussing possible projects for the Milenium program the idea of extending the size and number of the existing detectors was partly criticized as leading only to “more of the same science”. The impossibility to use the highest resolution mode of D2B on a regular basis has, however, in the past proven to be a major drawback when performing so called ‘hot topic’ science. The coexistence of several phases, the availability of only small samples, the necessity to perform high resolution scans as function of B, P or T, all these aspects call for a higher data acquisition rate to open up the possibility to do ‘more of new science’. Recent results of diffraction studies on D2B are presented which show the need for increasing the available (detected) neutron flux and the benefit of using the highest available resolution more routinely on this machine.

1. Phase segregation in GMR manganites
Manganites of type $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ are famous for their giant magnetoresistance (GMR). The most recent idea to explain this phenomenon is based on the existence of a phase segregation between metallic ferromagnetic and insulating antiferromagnetic (often charge-ordered) regions. Apart from the magnetic signature these different phases leave in form of magnetic Bragg peaks (which can be misinterpreted as stemming from spin-canting) the best means to detect the presence of different phases is of course the determination of the differing cell parameters. Highest resolution is necessary to determine coexisting phases and to detect slight deviations from the parent orthorhombic structure. High intensity is, however, simultaneously needed to detect the panoply of magnetic peaks: it is of outmost importance to be able to measure the coexisting phases and the magnetic peaks simultaneously so as to be able to couple the nuclear scale factors of the different phases to the refinement of the corresponding magnetic structures and moment values. Highest resolution data on D2B show that $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is phase segregated at low temperatures into an orthorhombic ferromagnetic phase, a charge...

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**Fig. 1:** Refinement of 3 nuclear and 3 magnetic phases present in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

**Fig. 2:** Low angle region of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$: A field of 6 Tesla leads to the suppression of the CE-type magnetic peaks as the monoclinic phase transforms into the orthorhombic ferromagnetic phase.
ordered CE-type antiferromagnetic monoclinic phase and an orthorhombic antiferromagnetic phase of A-type (figure 1). Application of an external field leads to a structural phase transition of the charge ordered phase (figure 2) and therefore to the suppression of the CE phase and the increase of the ferromagnetic phase [1]. Due to the small amount of sample available only 1 temperature could be measured with only the ‘second’ best resolution.

2. **Distortions, octaedra rotations, phase coexistence in double perovskites**

Double perovskites of type A,MM'O₆ with A = earth alkaline and M, M' = transition metal became a subject of highest scientific interest as the half metallic ferromagnetic character of Sr₂FeMoO₆ was discovered. Magnetoresistive effects at high temperatures (RT and higher) are originating in the alignment of grains in the external field permitting the tunneling of electrons between neighboring grains. The discovery that the magnetic transition in Sr₂FeMoO₆ is accompanied by a structural distortion (figure 3) triggered a lot of work on D2B. Using the high resolution mode it was discovered that the coordinated rotation of metal-oxygen octahedra can be hosted in a metrically still cubic lattice (figure 4). Together with the finding of phase separation in Ca₂FeReO₆ (figure 5) this leads to numerous aspects under which these compounds have to be inspected: the cation distribution, the possible tetragonal distortion and the rotation of the octahedra (in the Sr based compounds), the coexistence of phases and finally the magnetic structure and the magnetic moment formation. Highest resolution and high intensity over a large Q-range are needed when dealing with these different aspects.

3. **Distortions and magnetoelasticity in quaternary Nickel-Boron superconductors**

The new family of nickel-boron-carbides RNi₂B₂C has shown the coexistence of magnetism and superconductivity for R=Tm, Er, Ho and Dy. Highest resolution data of D2B showed a distortion of the tetragonal unit cell for Dy, Ho, Er and Tb compounds in the

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**Fig.3:** The magnetic moment of Fe and the tetragonal distortion as a function of T in Sr₂FeMoO₆.

**Fig.4:** A rotation of Mo₆ octahedra is found in the unmagnetic state in Sr₂Fe₀.₇₅Mn₀.₂₅MoO₆. N stands for nuclear, M for magnetic and R for nuclear intensity resulting from the rotation of the octahedra.

**Fig.5:** T-dependence of the (040) reflection of Ca₂FeReO₆ displaying the phase coexistence.
magnetic state. The knowledge of the distortions are important with respect to the interpretation of the superconducting properties as the electronic structure which is responsible for the nesting feature of the Fermi surface are influenced. A very time consuming experiment in highest resolution mode (figure 6) showed the linear dependence of the lattice distortion on the squared value of the ordered magnetic moment [6].

Fig. 6: Squared value of the magnetic moment and the lattice distortion in TbNi$_2$B$_2$C and ErNi$_2$B$_2$C.

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**Super-D2B and the structure of new materials**
*Dedicated to the late Cliff Shull, father of Neutron Powder Diffraction*

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D2B is among the ILL instruments that attract the largest number of proposals and produce the greatest number of publications; it has also produced the ILL's most cited papers. Indeed, neutron powder diffraction has been among the essential techniques applied to all new inorganic materials. In particular, it has proved important for the study of mineral and magnetic structures, structural transitions, ferro-electrics, solid liquids and gases, ice structures, hydrogen in metals, zeolites, solid electrolytes, quasi-crystals, heavy metal oxides, mixed valence, superconductors, GMR materials, and many others. The super-D2B proposal submitted to the EPSRC by a group of 5 UK universities will increase the efficiency of the machine by an order of magnitude, and allow the highest resolution to be applied to the study of new materials, even when they are only available in small quantities.

**Introduction**

Since the award of the 1994 Nobel Prize to Cliff Shull for pioneering neutron powder diffraction, large investments have been made at the British, French and German neutron sources in response to user demand for this technique. ISIS has recently spent ~30 MFF on a single machine (GEM), while the D2B-type diffractometer SPODI is one of the first on the new Munich reactor. With only 2 dedicated powder diffractometers, D2B and D20, ILL has fallen behind the national labs in both the number of machines, and in using the latest technology; both D2B and D20 were conceived some 20 years ago!

Yet, the user demand for powder diffraction at ILL (fig.1) has increased with the discovery of new materials such as superconductors, CMR ceramics and zeolites. Demand is strong even from the UK community, with significant growth from French, German and Spanish users. Very often, these are scientists who are not traditional neutron scatterers. Indeed powder diffraction is one of the few neutron techniques, with SANS and 3-axis spectroscopy, that has reached out to the general scientific community, and had a major impact there.

Curiously, this very success and lack of investment is used to argue that ILL powder diffractometers are no longer "unique" or "best in the world". Machines may be "unique" simply because no-one thinks it important to copy them - and a mention in the Guinness book of records is hardly a guarantee of scientific excellence! The evidence is that neither investment in lower flux national laboratories, including spallation sources, nor the advent of 3rd and 4th generation synchrotrons, has

Fig. 1: ILL proposals 1998-1999 showing that 3 powder machines are among the 7 attracting half of all ILL proposals.
dampened the demand for neutron powder diffraction at ILL. Surely it is time to consider the actual evidence of user demand, productivity and scientific impact, rather than rely on subjective predictions. D. Dubbers has therefore analyzed the number of ILL experiments for the years 1997-1999 and the resulting number of publications for the years 1998-2000. This shows that 37% of all proposals are for diffraction group instruments, which also contribute 1/3rd of all ILL publications. Publication statistics over a 5-year period show that 6 ILL instruments produce half of ILL scientific papers, and 3 of these are powder diffractometers (fig.2)! These neutron powder papers feature in the most influential journals, such as Nature and Phys.Rev.Letters, while the Science citation index shows that 10 of the 40 most cited ILL experimental papers, out of more than 5000 since statistics began, were produced on either D1A or D2B!

**What do we propose?**

A high-resolution powder diffractometer like D2B was first proposed by B.E.F. Fender when the UK joined the ILL in 1973. Because there was no remaining beam position, a less ambitious machine (D1A) was built on a less intense thermal guide tube. Following the success of D1A, money was made available in the ILL’s “Deuxième Souffle” programme 20 years ago to build the current machine, which was completed in time for the high temperature superconductor discoveries. High-resolution neutron powder diffraction played a major role in the characterization of these new materials. In particular, D1A produced the most cited experimental paper in the field in 1988, and D2B produced the most cited of all ILL publications in 1990, establishing the “charge reservoir” concept, which lead to the discovery of more new materials. More recently, D2B has been essential for much work in zeolite chemistry, superconductors, new CMR materials, and in the earth sciences as illustrated by a recent Nature paper on new forms of ice. The superconductor and CMR work has made neutron diffraction one of the best-known techniques for the study of metal-insulator transitions, one of the hottest current topics in solid-state science. But often only mg quantities of new materials are available when they are produced under high pressure. Similarly, new forms of meta-stable ice have recently been discovered on D2B, but again working at high pressure means very small samples and high resolution to sort out the different ice phases.

These new demands have led to the current proposal, to increase both the flux and resolution of D2B. This has been supported as being of the highest priority by ILL users and independent experts, but central ILL funding has not been available. We propose to build a unique new type of pseudo-2D high-resolution position sensitive detector. In the horizontal plane, high resolution will be obtained by scanning a large bank of very fine 5-minute collimators. In the vertical plane, lower resolution would be obtained using linear wire position sensitive detectors. This vertical resolution is needed to correct for the curvature of the diffraction cones. We already have prototypes of 300 mm high collimators built by Euro-Collimators in Cheltenham, and the detectors too are commercially available in Europe. Such a detector would collect 6 times as many neutrons for the same resolution. Following this proposal, a similar detector has been planned for the new Munich reactor, but with lower resolution and flux. Indeed, if we do not modernize our own equipment, we will lose the advantage of our
high flux reactor.
In a second stage, we propose to upgrade the monochromator and neutron optics to give even more intensity and a larger choice of wavelengths. The total gain would be an order of magnitude in intensity, which would allow the highest possible resolution to be used for most experiments. This project is complementary to the new GEM machine at ISIS, which has higher intensity, but lower resolution.

The new Super-D2B will be ideal for studies requiring the following factors:
- Good resolution and counting statistics for high-quality Rietveld refinements.
- Small samples (geological samples, special isotopes, high pressure materials).
- Special environments (high pressure and high temperatures; reaction cells).
- A wide d-range (long d-spacings for magnetic structures and low-d data for Rietveld refinement).
- Parametric studies (e.g. of many samples; at many temperatures, pressures, times for kinetics studies, etc.)

**Details of the Proposed Super-D2B Project**

Neutrons are scattered from a powder in cones of a fixed angle, depending on the wavelength and “d-spacing” of crystal planes. At present, we only collect those neutrons scattered within a narrow band in the equatorial plane. The essence of the proposal is very simple, to increase the height of the detector to collect a x3 larger band (fig.3), and to double the number of detectors for a total gain of x6 (fig.4).

Of course, in practice it is not quite so easy. Because our linear detectors intersect cones of radiation, the peaks are broadened if we average over a longer detector, and the centers of intensity of the peaks shift; this is unacceptable on a high resolution machine. We can only increase the height if we use some kind of position sensitive detector to correct for the curvature of the cones. Fortunately we only require a low-resolution detector in the vertical direction, since we still only intersect a relatively small segment of the cones, except at very low and very high scattering angles. A simple linear wire detector, with a resolution of 2-3 cm is sufficient.

**References**


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**Fig. 3**: Prototype 5' high-resolution 300mm high collimator (with CD to show the scale).

**Fig. 4**: The proposed new 128 linear wire detector/collimator for the ILL super-D2B project.
Magnetic field induced change of lattice symmetry in rare earth intermetallics

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Some of the rare-earth intermetallics RCu2 (R = Ce, Pr, Nd, Tb, Dy) show unusual behavior in high magnetic fields called “Ising axis conversion” [1]. It is characterized by an irreversible change of the easy magnetization axis. The temperature dependence of the conversion field of several compounds was investigated by magnetization measurements, showing that the conversion is also observed in the paramagnetic state, i.e. above the Néel temperature $T_N$. Beside the anomalous magnetic behavior giant magnetostrictive effects $DL/L \geq 1\%$ were found at the axis conversion process. Neutron diffraction experiments on DyCu2 single crystals, performed at the D15 spectrometer of the ILL [2], detected a change of the lattice symmetry from the original, low symmetric, orthorhombic CeCu2-type structure to the high symmetric, hexagonal AlB2-type structure of the converted state. In this context future experiments related to structural and dynamic properties of this class of compounds will be discussed that may give a deeper insight into the microscopic processes driving the “Ising axis conversion”.

1. Introduction
The magnetic properties of the RCu2 intermetallics, which crystallize (with the exception of LaCu2) in the orthorhombic CeCu2 structure, were intensively investigated for most members of the series. Their complex magnetic order can be well explained by anisotropy effects due to crystal field and bilinear exchange. They are, therefore, basic compounds for the investigation of anisotropic magnetic interactions.

Already some years ago a new magnetic phenomenon, the conversion of the Ising axis in high magnetic fields, was discovered in DyCu2 [1]. Magnetization measurements at low temperatures showed unusual large hysteretic effects. Surprisingly, after application of a high magnetic field along the crystallographic c-direction the magnetization curve measured along the c-axis resembles closely the magnetization curve of the (original easy) a axis and vice versa. The change of the direction of the magnetic moments is illustrated in Fig. 1. The axis conversion can be reversed by increasing the temperature above 150 K. The experiments show that the effect also occurs in the paramagnetic state, i.e. above $T_N = 27$ K. In the paramagnetic range the magnetic field at which the conversion starts (“conversion field”) increases linearly with temperature.

Studies on other RCu2 compounds revealed a similar effect for $R = $ Ce, Pr, Nd and Tb. [3,4]. Neutron scattering experiments were performed in order to find out the interplay between the magnetic and the lattice properties at the conversion process as a key point for understanding the effect.

2. Experimental results
At first, magnetostrictive measurements were done using a dilatometric method [5]. They show that the axis conversion in DyCu2 is connected with a giant magnetostriction (GMS). The crystal expands 1.5% in c-direction at $T = 30$ K and $p_xH = 3.5$ T: at 4 K the magnetostriction is even as large as 4% [6]. At the same time the crystal contracts in a-direction, whereas the lattice parameter $b$ stays nearly unchanged in the conversion cycle. Because of the fact that the orthorhombic CeCu2 type structure (space group Ima2) can be viewed as a distorted hexagonal AlB2 type (space group $P_g/mnm$; note that in the orthorhombic description a and c form the hexagonal plane) the idea was born that the drastic change of the lattice parameters $a$ and $c$ may be connected with a change of the lattice symmetry.

To confirm this idea elastic neutron scattering experiments have been performed at the D15 diffractometer of the ILL Grenoble with wavelengths of 0.085 nm and 0.117 nm. The neutron scattering experiment consisted of three parts. At first a complete determination of the crystallographic structure was done at $T = 1.5$ K yielding the well known CeCu2 type structure ($a = 0.4294$ nm, $b = 0.6742$ nm, $c = 0.724$ nm, cell volume $V = 0.2097$ nm$^3$). Then the temperature was increased to 30 K and a magnetic field of 5 T was applied along the c-direction with a ramp rate 0.05 T/min. To see the influence of the magnetic field on the lattice properties we measured the intensity of several reflections simultaneously while ramping the field. Thereby, the expected drastic changes of intensity of certain reflections could be seen and related to the transition between the CeCu2 and AlB2 structure. Then, after the axis conversion, the field was removed and the temperature set back to 1.5 K. Again a complete structure determination was performed resulting in $a_{conv} = 0.4227$ nm (this corresponds to a GMS of -1.55 % with respect to the unconverted state), $b_{conv} = 0.6747$ nm (+0.07 %), $c_{conv} = 0.7340$ nm (+1.3 %), $V_{conv} = 0.2093$ nm$^3$ (-0.17 %). In the converted state the c/a ratio is $c_{conv}/a_{conv} = 1.7318 \pm 0.2093$ with the special value indicates a change from orthorhombic to hexagonal symmetry induced by a high magnetic field. Moreover, the observed changes in inten-
sity and position of the reflections before and after the axis conversion were a strong proof that the axis conversion is indeed associated with a change from the orthorhombic CeCu$_2$ to the hexagonal AlB$_2$ structure, both structures can be seen in Fig. 2.

3. Discussion and outlook

The investigated conversion process of the easy axis increases the symmetry of the lattice. To our knowledge this is one of the first experiments that shows a change from low to high symmetry by application of an external magnetic field. The magnetoelastic coupling in rare earth intermetallics may arise from a strong strain dependence of either the magnetic two-ion exchange or the single-ion crystal field interactions. By investigation of the magnetic structure at $T = 1.5$ K after the conversion process we find the characteristic commensurate structure with $\tau = (2/3 1 0)$ as before the conversion in DyCu$_2$ [2] but with different moment directions, see fig. 1 (At NdCu$_2$, a small shift of the propagation vector is observed [4]). For that reason the two-ion exchange interaction does not depend much on the lattice strain. Therefore, we conclude that a strong single ion magnetoelastic coupling must be the reason for the observed symmetry change of the lattice [2].

In order to get a deeper insight into the axis conversion effect more detailed experiments are necessary. Investigations of elementary excitations (crystal fields, phonons etc.) could be such experiments. Moreover, the crystal field - phonon - coupling in RCu$_2$ compounds is of basic scientific interest. The equipment of the ILL Grenoble offers a wide variety for experiments. An important improvement of the experimental possibilities in our case would be a cold-transfer system that allows to keep a sample cold which was converted in an external magnet and insert it in a simple-to-handle cryostat. Only with such a system do the properties of the sample stay unchanged and can then be investigated by neutrons without the geometrical restriction imposed by a high field magnet. This would allow a complete study of the static and dynamic properties of the converted crystal. Further development of the experimental possibilities could also be directed to high magnetic fields. Cryomagnets with maximum fields above $\mu_0H \sim 10$ T, vertical as well as horizontal, should be available.

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![Fig. 1: Principle of the change of the easy magnetization direction in DyCu$_2$ induced by a high magnetic field (“Ising axis conversion”)](image)

![Fig. 2: Lattice structure of DyCu$_2$ before and after the magnetic axis conversion; left: orthorhombic CeCu$_2$ structure, right: hexagonal AlB$_2$ structure](image)
References


Nuclear spin excitations in Nd

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We have investigated the low energy excitations in Nd in the µeV range by a back-scattering neutron spectrometer. The energy scans on Nd revealed inelastic peaks at $E = 2.67 \pm 0.06$ µeV at $T = 60$ mK on both energy gain and energy loss sides. The inelastic peaks move gradually towards lower energy with increasing temperature and finally merges with the elastic peak at zero energy transfer at the electronic magnetic ordering temperature $T_N \approx 19.8$ K. At about 5 K we observe a second peak at $E = 1.8 \pm 0.3$ µeV which also decreases in energy with increasing temperature. This second peak disappears at about 15 K. We interpret the inelastic peaks as low energy nuclear spin excitations arising due to the Shull-Nakamura indirect interaction.

The coupling of nuclear spins through Shul-Nakamura indirect interaction gives rise to nuclear spin waves [1]. This interaction takes place as follows: Each nuclear spin sees the electronic spin on its own ion, through the effective hyperfine coupling $A(I)$. The electronic spins of all the ions are coupled by exchange interaction. An interaction of the nuclei therefore arises via the low-lying excited states (spin-waves) of the electronic system as intermediate states. That is to say, a nuclear spin excites a spin wave through the hyperfine coupling, and another nuclear spin causes it to be reabsorbed through its hyperfine coupling. This process gives rise to the so-called Shul-Nakamura indirect interaction [2,3]. Although the polarized nuclear spin system is far from being in perfectly ordered state, it does possess long-range order of the average oriented nuclear spin because of the long range of the Shul-Nakamura interaction; and therefore as pointed out and justified by de Gennes et al. [4], there exists a spin-wave-like spectrum of excitations of the nuclear spin system. There exists indirect evidence of nuclear spin waves which causes lowering of the antiferromagnetic resonance (AFR) and the nuclear magnetic resonance (NMR) frequencies at low temperatures [5]. Nuclear spin waves are expected to have energies which are about three orders of magnitudes lower than those of electronic spin waves and lie in the µeV range. The nuclear spin wave spectrum should have dispersion at lower Q range which is inversely proportional to the range b of the Shul-Nakamura indirect interaction.

Among the light rare earth elements the magnetic structure of Nd has been intensively studied for several decades. However the observed neutron diffraction patterns of Nd at different temperature are so complex that a complete understanding of the complex magnetic structure of Nd has not yet been achieved [7]. Nd has a double hexagonal closed packed (dhcp) crystal structure with the stacking ABAC. In the dhcp crystal structure atoms on the A layer have neighbour distribution typical of the cubic structures whereas those on B and C layers have hexagonal nearest neighbour environments. The existence of two kinds of sites (cubic and hexagonal) with different local symmetry is a further complication. Nd orders at $T_N = 19.8$ K with a longitudinal sine-wave amplitude modulated phase on the basal plane of the dhcp structure. The modulation vector lies in the basal plane of the b direction and is incommensurate with the crystal structure. The magnetic moments also lie in the basal plane. The moments on neighbouring hexagonal sites are ordered antiferromagnetically. Simultaneously a c axis moment (plus a small component in the basal plane) with the same wave vector are induced on the cubic sites by the anisotropic two-ion coupling. As the temperature is lowered further a first-order transition to a double-structure takes place with the wave vectors $k_1$ and $k_2$ aligned approximately along a pair of b axes but canted slightly such that the angle between them is somewhat less than 120 degrees. In the double-structure two modulation waves with the wave vectors $k_1$ and $k_2$ exist simultaneously in the crystal. The polarization vectors of the moments in the two waves are also canted away from the corresponding b-axes towards each other but by a different value. The waves are no longer purely longitudinal. The arrangement increases the average ordered moment and is favoured at lower temperature. A further increase of the ordered moment occurs by squaring up the waves as indicated by the appearance of the third order harmonics in the neutron diffraction pattern. The periodicity of the wave increases simultaneously. In a double-structure, the third harmonics would not only be $3k_1$ and $3k_2$, but also $2k_1 \pm k_2$, etc. Observation of such intermodulation harmonics confirms the existence of double-structure in Nd. At 8.2 K the planar components of moments on the cubic sites begin to order. At temperature well below $T_N$, the magnetic moments in the double-structure are approximately perpendicular. Several phase transitions occur in Nd as the temperature is lowered further and finally at the lowest temperature a complex quadruple-structure is realized.
We performed neutron scattering experiments on Nd single crystals at millikelvin temperatures by using the high resolution back-scattering neutron spectrometer IN16. The sample was placed either in 3He–4He dilution cryostat, 3He cryostat or a conventional 4He cryostat. The base temperature attained with the dilution cryostat was about 0.060 K and that of 3He cryostat was about 0.370 K. The temperature variation of the inelastic scans were conveniently performed with the conventional He cryostat. The conventional He cryostat gave the lowest temperature of 1.2 K.

We observed inelastic signals in Nd at energy $E = 2.67 \pm 0.06 \text{ } \mu\text{eV}$ on both energy gain and loss sides at $T = 0.06$ K. To our knowledge this is the first observation of the low energy inelastic signal in Nd metal at millikelvin temperature by neutron scattering. The energy of the inelastic signal decreases continuously as the temperature is increased and disappears at $T_N = 20$ K. At $T = 5.5$ K a second inelastic peak develops at $E = 1.8 \pm 0.3 \text{ } \mu\text{eV}$. The energy of the second peak also decreases with increasing temperature up to $T = 7.5$ K then it remains practically constant at $E = 1.2(3) \text{ } \mu\text{eV}$. The second peak disappears at about $T = 15$ K. Fig. 1 shows typical inelastic scans of Nd at several temperatures. The continuous curves are the results of the fit of the data with 3 or 5 Gaussian functions convoluted with the instrumental resolution function determined by vanadium scans. The scattering from the empty sample holder has been subtracted.

![Fig. 1 - Typical energy scans of Nd at several temperatures. The continuous curves are the results of the fit of the data with 3 or 5 Gaussian functions convoluted with the instrumental resolution function determined by vanadium scans. The scattering from the empty sample holder has been subtracted.](image)

Fig. 2 - (a) Temperature variation of the energies of two inelastic peaks of Nd corresponding to the hexagonal and cubic sites of the dhcp structure. (b) Temperature dependence of the intensities of the inelastic peaks of Nd.

![Fig. 2](image)
which are still poorly understood after several decades of intensive investigations. Also the inelastic signals contain information about the cooperative nuclear spin excitations and may yield Shul-Nakamura interaction strength in Nd.

We interpret the inelastic signal observed in Nd metal to the excitations of the Nd nuclear spins \( I = \frac{7}{2} \) of the isotopes \(^{143}\text{Nd}\) and \(^{145}\text{Nd}\). The abundances of \(^{143}\text{Nd}\) and \(^{145}\text{Nd}\) isotopes in natural Nd are 12.3% and 8.3% respectively. In a first approximation one can consider these inelastic peaks to arise to the transitions between the hyperfine-field-split nuclear levels. This is the single-nucleus effect [8]. However the nuclear spins are coupled through Shul-Nakamura interaction. So one expects nuclear spin wave excitations (cooperative lattice effect) discussed in [3] according to which the nuclear spin waves should have dispersions at a very small q. In our experiment, due to the insufficient Q resolution of the back-scattering spectrometer, we could not measure the expected dispersion of the nuclear spin waves. To measure the dispersion of the nuclear spin waves one needs to use a neutron spin echo (NSE) spectrometer. We note that the inelastic signal persists at least up to \( T_N \) in both the samples. It is known [8] that nuclear spin waves can exist in magnetic materials at quite high temperatures when the nuclear spin system is in a disordered paramagnetic state. In this respect nuclear spin waves differ from the electron spin waves (magnons), because magnons can usually be observed only at temperatures below that of the magnetic ordering of the electron spin system. The existence of the nuclear spin waves in a paramagnetic system of nuclear spins is due to the macroscopic dimensions of the regions of spatial correlation in the motion of the electron magnetisation. These dimensions reach \( r_c = (10^2 - 10^4)a \), where a is the average interatomic distance within the crystal.

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Cerium usually comprises a mixture of polycrystalline FCC and DHCP allotropes. Single-crystal Ce has been stabilised in Ce/Pr and Ce/Nd superlattices grown using molecular beam epitaxy. It is found that DHCP and FCC phases can be obtained depending on superlattice composition and growth conditions. The structure and magnetic ordering has been studied at low temperature by neutron diffraction using the triple-axis spectrometer D10. For DHCP superlattices the magnetic ordering resembles either $\beta$-Ce or Nd, but these two types of antiferromagnetic structure cannot coexist in the same superlattice. Furthermore the propagation of magnetic order through intermediate layers is considerably reduced compared to other light rare-earth superlattices. We find that the electronic transition to a collapsed phase observed in bulk FCC Ce is suppressed in superlattices.

1. Introduction

In the standard model of rare-earth magnetism an integral number of $4f$ electrons are localised on each ion, and the moments interact with the crystalline electric field and indirectly with each other via the conduction electrons [1]. However, for Ce hybridisation of the $4f$ electron with the conduction band leads to more exotic intermediate-valence and heavy-fermion behaviour. So far the greatest theoretical interest has been in the properties of FCC Ce, which undergoes an isomorphic transition from $\gamma$-Ce to a collapsed nonmagnetic phase $\alpha$-Ce at low temperature. This unusual phase transition is attributed to an electronic transition from a state with the localised $4f$ electrons characteristic of the other lanthanides, to a phase that exhibits metallic $4f$ behaviour [2]. The low-temperature properties of the DHCP phase $\beta$-Ce are very different, and the localised $4f$ moments order with an antiferromagnetic structure below $T_N \sim 13.5$K [1]. In elemental form Ce comprises a mixture of DHCP and FCC allotropes, and it is not possible to obtain bulk single-crystal samples. However, single-crystal Ce can be stabilised in superlattices grown using molecular-beam epitaxy, and the structure and magnetic ordering in these samples can be investigated by neutron diffraction. By varying the superlattice composition it is possible to control the epitaxial strain and, since this will alter the delicately balanced electronic structure, this may dramatically change the magnetic behaviour. This paper describes neutron-diffraction studies of Ce/Pr and Ce/Nd superlattices.

2. Experimental procedure

The superlattices were grown by molecular-beam epitaxy on sapphire substrates with a Nb buffer using techniques developed for other light rare-earth superlattices [3]. It was found that good single-phase Ce epitaxy could be established using a DHCP Pr seed layer on the Nb (rather than the usual hcp Y seed or growth directly onto Nb). High-quality DHCP Ce/Pr and Ce/Nd superlattices were obtained with growth temperatures in the range 150-270°C. The compositions were $[\text{Ce}_{20}/\text{Pr}_{20}]_{60}$, $[\text{Ce}_{10}/\text{Nd}_{30}]_{60}$, $[\text{Ce}_{20}/\text{Nd}_{20}]_{60}$ and $[\text{Ce}_{30}/\text{Nd}_{10}]_{60}$, where the subscripts inside the brackets refer to the number of atomic planes of each element in one bilayer, and the subscript outside is the number of bilayers. The FCC phase was stabilised in $[\text{Ce}_{30}/\text{Pr}_{10}]_{60}$ with a growth temperature of 400°C.

Neutron-diffraction measurements were carried out on the D10 instrument at the Institut Laue-Langevin. The superlattices were mounted inside a variable-temperature cryostat designed to fit within the four-circle cradle, and measurements were performed over the temperature range 2-300K. The incident energy was fixed at 14.8meV and higher-order contamination was suppressed using a pyrolytic graphite filter. The elastic magnetic signal from the superlattices is very weak, and it was necessary to suppress the inelastic background using an energy analyser crystal.

3. Results

3.1 Structure

Figure 1 shows the x-ray scattering intensity from $[\text{Ce}_{10}/\text{Nd}_{30}]_{60}$ along the [1 0 q] direction of the DHCP lattice. This scan is typ-
ical of all of the superlattices grown at lower temperatures, and it shows that they adopt a DHCP structure uncontaminated by FCC Ce. The intensities of the superlattice peaks displaced from the DHCP reflections at positions corresponding to the bilayer thickness indicate that there are sharp interfaces. The mosaic spreads are about 0.2° and this indicates that they are good single crystals.

The structure of the [Ce$_{30}$/Pr$_{10}$]$_{60}$ sample grown at 400°C is different. The neutron scattering intensity along the [1 0 0] direction reveals the presence of FCC and DHCP phases, see Fig. 2. The width of these peaks indicates that the coherence of the stacking sequence is confined within individual blocks. It is assumed that a large fraction of the Ce in this superlattice adopts the FCC structure. The change in the FCC lattice parameter between $T = 300$ and 2 K is less than 0.7%, which is an order of magnitude smaller than the 6% change observed for bulk FCC Ce. Thus the electronic transition to the collapsed phase is suppressed when Ce is constrained within a superlattice.

3.2 Magnetism

For DHCP [Ce$_{30}$/Pr$_{10}$]$_{60}$, the magnetic structure resembles that of β-Ce [4] and Ce-Y alloys [5]. Figure 3 shows a scan of wave-vector transfer $Q$ through a magnetic reflection in the [1 0 0] direction of the DHCP lattice. The magnetic correlation length $\xi$ may be estimated from the width of the peak using the relation $\xi \sim 1/\Delta Q$, and the magnetic ordering is found to be confined to individual Ce blocks. The ordering in the [Ce$_{30}$/Nd$_{10}$]$_{60}$ superlattice is found to be very similar, with the Ce magnetism confined to single blocks and no ordering detected in the Nd blocks.

The magnetic ordering in the [Ce$_{30}$/Nd$_{10}$]$_{60}$ and [Ce$_{20}$/Nd$_{20}$]$_{60}$ samples is very different, and no β-Ce type magnetism is observed. Instead the magnetic structure more closely resembles that found in bulk Nd [6]. Figure 4(a) shows the temperature dependence of the scattering at (0.14 0 3) which is due to an antiferromagnetic ordering of the hexagonal sites of the DHCP structure. The magnetic component at (1,0,0) due to ferromagnetic ordering of the cubic sites is shown in Fig. 4(b). The antiferromagnetic order is only coherent over about two bilayers, whereas the ferromagnetism is coherent over many bilayers, possibly due to induced ferromagnetism in the Ce layers.

Fig. 2: The neutron scattering intensity along the DHCP [1 0 0] direction from [Ce$_{30}$/Pr$_{10}$]$_{60}$ showing the presence of the FCC phase.

Fig. 3: The magnetic scattering at $Q = (1.5$ 0 0) from [Ce$_{30}$/Pr$_{10}$]$_{60}$ at $T = 2$ K. The width of the peak indicates that the magnetic ordering is confined to single Ce blocks.

Fig. 4: The temperature dependence of the two types of magnetic ordering in [Ce$_{30}$/Nd$_{10}$]$_{60}$. (a) the intensity at (0.14 0 0) due to antiferromagnetic ordering on the hexagonal sites. (b) the magnetic intensity at (100) due to ferromagnetic ordering on the cubic sites.
4 Discussion and conclusions

Long-range magnetic ordering is usually observed in rare-earth superlattices in which both elements adopt the DHCP crystal structure [7,8]. However, the magnetic ordering in DHCP Ce differs markedly from Nd and Pr, indicating that the Fermi surfaces must be very different. This must lead to a de-coupling of the magnetism in Ce/Pr superlattices. The same $\beta$-Ce-type magnetism is observed in the Ce-rich Ce/Nd superlattice, but Nd-type magnetism is found in the superlattices with more Nd. This coexistent ferromagnetic and antiferromagnetic order is observed in bulk Nd under applied pressure [9], and may well be a consequence of the epitaxial strain. However the magnetic interactions between the constituents are also important since the results indicate that the $\beta$-Ce and Nd-type magnetic ordering cannot coexist in the same superlattice.

In summary single-crystal Ce-based superlattices have been stabilised using molecular beam epitaxy. For the superlattice containing FCC Ce the electronic transition to the collapsed phase is suppressed. The magnetic ordering in the DHCP Ce/Pr and Ce/Nd superlattices reveals the effects of the epitaxial strain and the magnetic interactions between the constituents of the superlattice.

References

Growth conditions and magnetic ordering in Fe/Cr multilayers

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The magnetic structure of [Cr(10Å)/Fe(18Å)]₈ multilayers on sapphire substrate has been investigated with polarised neutron reflectometry. The samples were grown at different substrate temperatures in order to vary the interface structure. Off-specular scattering, detected only adjacent to the half-order Bragg-peak and the total thickness oscillation maxima, indicates a big magnetic domain size. The coupling angle between the layer magnetisation direction of adjacent Fe-layers was determined for different growth temperatures. The highest coupling angle obtained for a growth temperature of 180°C corresponds to the highest Giant Magneto-Resistance (GMR).

1. Introduction

Considerable attention has been given to magnetic multilayers displaying a wide array of exciting properties like GMR and specific cases of magnetic ordering. An intimate feature of Fe/Cr multilayers is the complicated co-existence of in-plane domain structure and non-collinear Fe layer ordering. Different growth conditions influence both effects and in particular the varying non-collinear Fe-layer ordering may influence the GMR. Here we report on a study of the magnetic structure of Fe/Cr multilayers with polarised neutron reflectometry and off-specular scattering. The measurements were performed with full polarisation analysis. We studied the influence of the growth temperature on the Fe-Cr interlayers in order to trace correlations between interface structure and magnetic coupling in Fe/Cr multilayers. A series of Fe/Cr samples were grown on (101) Al₂O₃ substrates at different temperatures in the range of 20 - 500°C. An increased growth temperature means that the Cr interdiffusion affects additional Fe monolayers adjacent to the Cr layer. In our series of samples such interface regions consisting of 2 to 4 monolayers were detected depending on the growth temperature [1]. Magneto-resistance measurements were made in the standard dc four contact scheme for a current along the layer plane. The consequence of the growth temperature on the GMR is shown in Fig.1. The optimal temperature to gain the highest GMR is 180°C.

2. Discussion of the coupling angle

The polarised neutron reflectivity experiment with full polarisation analysis was performed on ADAM at a wavelength of 4.41Å [2]. The scheme of the analyser part of ADAM is shown in the bottom of Fig.2. The analyser works in transmission and reflection so that non-spin flip (nsf) and spin flip (sf) components are measured simultaneously. The intensity of specular reflected and off-specular scattered neutrons was recorded with a position sensitive detector.

The intensity map for sample 3 (see Fig.1) is shown in Fig.2 for neutrons impinging on the sample with (+) polarisation. (+) and (−) assign the neutron spin parallel or antiparallel with respect to the external magnetic field, respectively. After the analyser the (+ +) nsf and (+ −) sf components were recorded as shown in Fig.2. The two vertical modulated intensity bands show the measured intensity oscillations arising from the total thickness of the multilayer and, as the most prominent feature, from the 1/2 order Bragg peak in sf scattering originating from the Fe-Cr bilayer thickness with antiferromagnetic components [3]. Also the first full order Bragg peak is visible in nsf scattering. Off-specular scattering is concentrated close to the reflectivity line.

![Fig.1: Magneto-resistance in % as a function of growth temperature for 4 Fe/Cr samples with the same composition. The depicted coupling angle for each sample measured in an external field of 0.5 kG is formed by the two magnetisation vectors in two subsequent Fe-layers.](image)
Here the discussion is focussed on the orientation of the Fe-layer magnetisation. The angle between the direction of the magnetisation vectors in two subsequent Fe-layers is the coupling angle. These angles were obtained from the fit to the data and are depicted in Fig. 1 for the 3 investigated samples. It is evident from the presentation in Fig. 1 that the sample with the highest antiferromagnetic component shows the highest GMR.

It should be noted that each pair of magnetisation vectors has to be turned for all samples in Fig. 1 by a canting angle, which turns both magnetisation vectors together by an angle of 5 to 10 deg. The understanding of the origin of this canting angle with respect to the easy magnetisation axis [3] needs further investigation. The off-specular scattering, which does not extend much left and right from the reflectivity curves, indicates a big domain size of the order of 1000 nm compared to 200 nm in Ref. 3, so that an influence on the GMR from the side of the domain size seems to be not probable. A more detailed discussion is under preparation.

The sample 4 in Fig. 1 shows a very enhanced interdiffusion of Fe and Cr due to the high growth temperature [1] and only a negligible antiferromagnetic coupling.

3. Conclusion

It was found that the increase in the substrate temperature during the multilayer growth causes a change of the interlayer magnetic coupling. The sample with the highest antiferromagnetic component in the magnetic coupling shows the highest GMR, a plausible combination in view of a high spin-flip electron scattering at the interfaces. This is one important finding in the search for parameters, which govern the GMR.

Acknowledgement

RFBR (Grants No. 00-15-96745 and 01-02-17119) and BMBF supported this study.

References

We describe a continuous-flow He cryostat with spherical geometry and a novel open-cycle dilution stage that allows gravity-insensitive operation with nearly unrestricted access in all three angles of the Eulerian cradle of the four-circle triple-axis spectrometer D10 at the ILL. Experiments attempted with this cryostat include verification of the hyperfine-induced nuclear polarisation in Nd$_2$CuO$_4$, and solution of the non-collinear magnetic structure of Cu(ND$_3$)SO$_4$.D$_2$O below 0.4 K. The difficulties in studying fissile materials near 150 mK are described.

1. Introduction

Until now single-crystal neutron (and X-ray) experiments below 2K were restricted primarily to a single scattering plane because of the limited mobility of bulky conventional dilution cryostats. Yet magnetic transitions at such low temperatures often form complex structures whose solution and characterization require access to all three dimensions of reciprocal space. We have developed a four-circle cryostat that avoids the influence of gravity by using a capillary dilution chamber devised originally for operation in satellites [1].

2. Cooling by gravity-insensitive dilution

Below 0.7 K the phase diagram of 3He-4He shows a forbidden region in which a mixture separates into two co-existing phases, one diluted in 4He, the other concentrated. The enthalpy of 4He is very much greater in the diluted phase than in the concentrated; thus in going from the concentrated phase to the diluted, 4He absorbs heat, just like an evaporating liquid. The net enthalpy when diluting 4He with 3He is positive under ideal conditions down to 130 mK. To achieve lower temperatures the dilution process should be cycled along the phase-separation boundary. The usual technique, by back diffusion of 4He up the 4He injector from a voluminous mixing chamber to stabilize the boundary between the phases (Fig. 1a), is unsuitable for a four-circle cryostat because of its sensitivity to gravity (4He is lighter than the mixture). In the cryostat described here this limitation is overcome by using a small-diameter mixing chamber so that the excess 4He forms bubbles that drift along the exit tube to provide cooling power ideally down to 85 mK along the full length of the heat exchanger (Fig. 1b) [1].

3. Hardware

The 1.6 K primary stage is a development of the He-flow cryostat that has been used with great success on the four-circle triple-axis spectrometer D10 at the ILL for over 20 years [2]. The sample is supported on an externally-driven shaft (φ), which has one end at room temperature, the other at the desired sample temperature. The mixing chamber of the dilution stage is a 10-cm long Cu-Ni capillary, with internal diameter 0.3 mm, fixed rigidly to a copper cold head at the end of the φ shaft (Fig. 2). A supplementary 4He circuit, in the form of a long spiral capillary that allows 360° rotation of the φ shaft thermalizes the end of the φ shaft nearest the sample at 1.6 K. Similarly, spiral capillaries are used to deliver the diluents and remove the mixture (Fig. 3). The cryostat is mounted on the 400 mm offset Huber Eulerian cradle of the four-circle triple-axis spectrometer D10, with the φ goniometer inverted to increase the distance between the sample and the φ goniometer in order to facilitate construction and maximize the thermal path along the sample shaft. The cryostat does not extend the existing blind regions of the cradle. Control of the flows of the pure He gases and the mixture, filtering of the gases via cold traps, and recuperation and recompression of the mixture is carried out in a 60 x 60 x 200 cm bay adjacent to the cryostat. Extended spiral tubes are wrapped around the φ and χ axes of the liquid-He transfer siphon to feed the He gases between the bay and the cryostat. Re-distillation of the He isotopes is made off-site.
4. **Software**

The heater power is regulated by a graphical user-friendly C program on a ubiquitous Macintosh personal computer reading one of the carbon, germanium or ruthenium-oxide thermo-resistors in the cryostat via a Barras temperature controller. This program also controls the cooling of the 1.6 K stage and the flows of He and He gases to the cryostat according to the desired temperature and the difference between the current and the desired temperatures, to minimize consumption of expensive He. The long-term response of the cryostat is stored and displayed graphically by the same program, which in turn is interfaced to the diffractometer control program to allow automatic control of the sample temperature.

5. **Performance**

Temperatures down to 150 mK can be achieved within two hours. The minimum temperature is about 110 mK, somewhat higher than the ideal value due principally to conduction along the \( \phi \) shaft. The consumption of He is 12 pmol/sec at 150 mK; the cooling power of the dilution stage is 2 \( \mu \)W at 200 mK, increasing as \( T^2 \). The 50 L of recuperation volume for the expended mixture gives an autonomy of nearly 24 hrs at the lowest temperatures. The total heat loss on the 1.6 K stage is 1.3 W.

Rotating the \( \phi \) shaft puts in further heat due to compression and expansion of the spiral part of the heat exchanger and to friction in the shaft bearing. The experiments are usually planned to minimize \( \phi \) rotation. There is also considerable torsional flexibility in the \( \phi \) shaft, amounting to 0.5° at the \( \phi \) limits, due to the compromise in the mechanical strength of the shaft, and the spring force of the spiral capillaries. A backlash correction of 1° is sufficient for most experiments for \( \phi \) between -90° and +90°.

6. **Scientific Results**

Thus far fourteen diffraction experiments have been conducted with this cryostat on problems which required access to more than one plane of reciprocal space. Half of these showed scientific features that are not observable above 1.6 K. The very first experiment was a re-investigation of the hyperfine-induced nuclear polarization in Nd,CuO\(_4\) [3]. Another notable experiment was the solution of the ground-state structure of the spin-1/2 Heisenberg antiferromagnet Cu(ND\(_3\))(SO\(_4\))\(_2\)D\(_2\)O for which \( T_N = 370 \) mK [4].
Three days were spent searching in three dimensions for the first weak magnetic reflection (Fig. 4). The other half of the experiments gave null results, interesting \textit{per se}, but not so exciting for the cryostat! One of these, on a-uranium, was compromised by fissile heating of the sample in the neutron beam during the experiment, estimated to be about 3 µW; low temperatures could only be reached by attenuating the beam. Even the thermal conductivity of the cement used to mount the sample had an effect on the minimum temperature attainable; without attenuation of the beam, 370 mK was the minimum with the black Stycast cement that was used.

\textbf{Acknowledgements}

We are very grateful for the enthusiasm and patience of the users of D10 during the development of this cryostat.

\textbf{References}


Formation of Magnetic Solitons Lattice in CuB$_2$O$_4$

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Elastic neutron scattering single crystal measurements have been performed to investigate the magnetic ground-state of copper metaborate CuB$_2$O$_4$.

The compound exhibits a second order phase transition from a paramagnetic to a commensurate antiferromagnetic phase (CP) with $k$=0, followed by second order transition to an incommensurate one (ICP) at $T^*$=10K. The association of the Dzyaloshinskii-Moriya(DM)-interaction and tetragonal anisotropy leads to the formation of a magnetic soliton lattice.

Introduction

Copper metaborate, CuB$_2$O$_4$, belongs to the exotic group of magnetic materials which show a phase transition into a helimagnetic phase.

In insulators, the origin of helimagnetism is either due to competing exchange interactions like in MnO$_2$ [1] or in NiBr$_2$ [2,3], or due to relativistic effects expressed by the Dzyaloshinskii-Moriya interaction. This latter can be represented as the antisymmetric, anisotropic part of the 3x3 exchange tensor $J^\leftrightarrow$ in the general expression of the Heisenberg exchange interaction $S^\alpha_1\cdot J^\leftrightarrow\cdot S^\alpha_2$ and can be written as a cross-product $D^\alpha\cdot [S^\alpha_1\times S^\alpha_2]$, where $D$ is the so-called Dzyaloshinskii-Moriya-vector [4]. The symmetry of the crystal governs the existence of this interaction and determines its direction.

Elastic neutron diffraction on single crystal measurements were performed on the four-circle diffractometer D10 at ILL with $\lambda$=2.36Å. The neutron diffraction results shows that CuB$_2$O$_4$ orders below $T_N$=21K in a commensurate magnetic arrangement with a propagation vector $k$=[0 0 0]. Group analysis of magnetic structures has been used to restrict the number of possible spin arrangements compatible with the crystal symmetry [8].

From the originally 5 irreducible representations of the point group 42m only the one-dimensional representations $\Gamma_1$ and $\Gamma_2$, and the two-dimensional representation $\Gamma_3$ are possible for both sites simultaneously. While $\Gamma_3$ corresponds to an antiferromagnetic ordering along the z-axis, the modes associated with $\Gamma_3$ describe non-collinear arrangements in the basal plane, i.e. a 90° configuration.

The refinement of 25 purely magnetic reflections shows that both, Cu(A) and Cu(B) spins, are confined in the tetragonal plane. The spin arrangement is characterised by a 90° angle between the spin of the two sublattices compatible with the magnetic modes of $\Gamma_3$. A slightly better result could be obtained by adding the magnetic modes of $\Gamma_3$ for Cu(A) which leads to a small...
tilting of about 14 degrees out of the plane for the magnetic moments of this site.

The magnetic moments for the two sublattices Cu(A) and Cu(B) are different. While at \(T=12\,\text{K}\) Cu(A) is close to the expected value for the spin-only moment of Cu\(^{2+}\) of 1 \(\mu_B\), the moment of the Cu(B) spin reaches only 0.2 \(\mu_B\).

Below \(T^*=9.7\,\text{K}\) a broadening of the magnetic peaks sets in, indicating a phase transition to the IC phase. Two satellites appear at the positions \((0,0,\pm q)\) which shift their central peak position to higher \(q\)-values as the temperature goes down. As it is shown in figure 1 the \(k\)-dependence is smooth within the temperature steps of \(T=0.1\,\text{K}\). The black line in figure 1 is an interpolation of the form \((T-T^*)/T^*\) with \(\nu=0.48\).

The refinement of the neutron data shows that the magnetic structure below \(T^*\) consists of an helix along \(c\), which changes its period continuously with temperature up to a value of \(c/0.15\approx 40\,\text{Å}\) at \(T=1.5\,\text{K}\). The amplitude of the magnetic moments shows no modulation. While the moments at the A-site keep there value of about 1 \(\mu_B\) by lowering the temperature, the B-moments increase their values from 0.25 to about 0.75 \(\mu_B\) at \(T=2\,\text{K}\). An extrapolation gives a value of 1 \(\mu_B\) at \(T=0\,\text{K}\) (see figure 2). Strong additional diffuse scattering has been observed around the \([1,1,q]\) position in the neutron scattering obtained using the triple-axis spectrometer TASP at the SINQ spallation source and D10 at ILL. This diffuse scattering is observed over the whole temperature range below \(T^*\). This intensity is absent in \((0,0,q)\) neutron-scans. The only difference for scans along \((0,0,q)\) and \((1,1,q)\) is the orientation of the scattering vector \(Q\), i.e. the influence of the polarisation factor in the neutron cross-section. This indicates that the fluctuations are restricted along the \(c\)-axis.

The integrated intensity of these diffuse scattering using a Lorentz-function of the form \(Ak/\mu^*l/k^2+q^2\) as a function of temperature is shown in figure 3. It has a maximum at the phase transition \(T^*\). The solid line in the figure is a guide to the eye. Below \(T=9.5\,\text{K}\) shoulders can be observed at each side of the two satellites (see figure 4). They can be clearly distinguished as higher harmonics with further cooling. They are indexed as \(\pm 3k\) satellites at all temperatures, where \(k\) is the value for the first order satellite. As one can see from figure 4 the intensity for the third order harmonics goes down very quickly, so that they are only visible in a small temperature range of about 0.2K below \(T^*\). The experimental resolution is given by the FWHM of the central peak, i.e 0.0018 r.l.u. The larger FWHM of the satellites is caused by the large gradient \(dk/dT\) near \(T^*\). Even small fluctuations in temperature of 0.01K leads to the observed broadening and a value of 0.0026 r.l.u.

The appearance of higher harmonics as well as the presence of the DM-interaction and an additional anisotropy of 4\(a\) order in the plane [9] suggest the formation of a magnetic soliton lattice near \(T^*\) [10]. Our conclusions are in agreement with the theory developed by Dzyaloshinskii on the basis of Landau theory of phase transition and later adapted for the neutron case by Izyumov [11].

Without anisotropy with a DM-vector pointing along \(c\), the magnetic moments, forced by the DM-interaction, turn smoothly from layer to layer along the \(c\)-axis i.e. a regular helix. This gives rise to the (first order) satellites in neutron diffraction pattern around the magnetic zone centers. The \(k\)-values give the periods of the helix.

The presence of the additional anisotropy (or a magnetic field) in the basal plane distorts the regular helix and tries to align the moments along the easy magnetisation directions within the plane. As a compromise the spins form ferromagnetic domains along \(c\), but change abruptly their direction over several lattice sites in one of the easy axes of the plane [11]. The length of the domains as well as the length of the microscopic Bloch-walls (or solitons) depend on the strength of the interactions in the crystal.
Fig. 4: Temperature dependence of the third order satellites around the IC-C transition temperature $T^*$. 

REFERENCES
Kohlrausch Relaxation in Random Anisotropy Magnets

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The nature and evolution of the spin dynamics above the glass temperature, $T_g$, in the spin glass-like amorphous random anisotropy magnet $a$-Er$_7$Fe$_3$ have been explored using the neutron spin-echo technique. The time-dependent spin correlations are found to follow the stretched exponential or Kohlrausch form, $\exp(-t/\tau^\beta)$. The exponent $\beta$ is temperature dependent, decreasing to 1/3 at the glass transition, whilst the relaxation time, $\tau$, is Arrhenius-like. It is suggested that this behaviour is closely analogous to that observed in studies of structural relaxation processes in fragile glasses above $T_g$.

1. Introduction
The nature of glass and the glass transition has been described as the deepest and most interesting unsolved problem in solid state theory [1]. Consequently structural glass transitions and their associated dynamics have been extensively studied, but are nevertheless still relatively poorly understood. In many cases the structural dynamics above the glass transition, $T_g$, are characterised not by a simple exponential relaxation function, but by a stretched exponential form, $\exp(-t/\tau^\beta)$, in which the characteristic relaxation time, $\tau$, exhibits an Arrhenius or Vogel-Fulcher-like temperature dependence. Stretched exponential relaxation, named after Kohlrausch who first reported the phenomenon in 1854, is now recognised as an almost ubiquitous form of relaxation in disordered and strongly interacting electronic and molecular systems. For several such systems (eg colloidal glasses, Lennard-Jones glasses, polymer glasses, Ising models of structural glasses [2]) $\beta$ is found to be temperature dependent, almost universally decreasing from unity to 1/3 as the glass transition is approached. Ngai [3] has attempted to classify glasses according to their relaxational dynamics above $T_g$: “Fragile” or Type A glasses exhibit stretched exponential or Kohlrausch relaxation with a temperature dependent $\beta$, whilst “Strong” or Type B glasses have a $\beta$ which is independent of temperature. However, the origin of Kohlrausch relaxation itself is still not well understood, although it is widely attributed to a broad distribution of intrinsic relaxation times.

2. Spin glass dynamics
Whilst the dynamics of structural glasses are extremely difficult to model, fortunately much can be learned by studying their magnetic analogues, spin glasses. In such systems magnetic spins freeze with random orientations below $T_g$, usually because of random or frustrated exchange interactions. In common with structural glasses, spin glasses exhibit (magnetic) creep and anomalous non-exponential (spin) relaxation above $T_g$. Extensive Monte Carlo calculations by Ogielski [4] based upon a 3d $\pm J$ Ising spin glass model have shown that above the spin glass temperature the dynamical spin autocorrelation function should take the form

$$q(t) = \langle S_i(0)S_i(t)\rangle \propto \exp(-t/\tau^\beta)$$

As the exponent $x$ is generally small, the spin relaxation is dominated by the stretched exponential. The exponent $\beta$ is found to be temperature dependent, decreasing from $\beta=1$ at high temperatures (~4$T_g$) to 1/3 at $T_g$ whilst the relaxation time, $\tau$, diverges at $T_g$. Ogielski’s simulations therefore suggest that spin glass dynamics, at least within the $\pm J$ Ising spin glass model, are similar to those of Type A or fragile structural glasses. Although the dilute spin glasses that have been studied using the neutron spin echo technique (eg CuMn, PdMn, AuFe [5]) show Type B behaviour characterised by a temperature independent $\beta$ of 0.5 or 0.6, there is new and growing evidence, particularly from our own $\mu$SR studies, that Kohlrausch relaxation of the Ogielski form, with $\beta$ approaching 1/3 and $\tau$ diverging at $T_g$, may be a universal characteristic of concentrated spin glasses and highly disordered magnets. Indeed the muon spin relaxation function is itself a stretched exponential with the behaviour of both the exponent $\beta$ and the muon spin relaxation rate mirroring that of the spin relaxation [6].

We have attempted to confirm this apparent Type A spin glass-like behaviour in complex spin glass systems by using neutron spin echo to measure the evolution of the spin dynamics with temperature in an amorphous random anisotropy magnet. The ground state of amorphous rare earth–transition metal alloys is defined by the Harris-Plishke-Zuckermann Hamiltonian [7] in which the random single ion anisotropy associated with the topological crystalline disorder dominates the magnetic exchange. It is this random anisotropy, rather than random exchange interactions, that give rise to spin glass-like behaviour. Our ac susceptibility [8] and $\mu$SR studies of such systems indicate strongly non-exponential relaxation above $T_g$, associated with a distribution of spin relaxation times which broadens considerably as $T_g$ is approached from above.
3. Neutron Spin Echo Measurements

The spin dynamics in the model random anisotropy magnet a-Er₇Fe₃ were measured using the IN11 spectrometer with 5g of amorphous melt-spun Er₇Fe₃ ribbon as the sample. a-Er₇Fe₃ has a glass temperature (determined by ac susceptibility) of 25K, and it should be noted that the Fe atoms do not carry a magnetic moment. The resulting temperature dependence of the essentially Q-independent spin relaxation function is shown in Figure 1. It can be clearly seen that the relaxation is strongly non-exponential. The solid lines represent least squares fits to the Kohlrausch relaxation function exp(-t/τ)^β.

The temperature dependence of the parameters τ and β extracted from the fits are shown in Figures 2a and 2b. β is found to decrease to an asymptotic value of 1/3 at the glass transition of 25K, whilst τ is Arrhenius-like, with an effective activation energy, E_a/k, of 130K. The spin dynamics above T_g in the glassy random anisotropy magnet a-Er₇Fe₃ therefore follow the predictions of Ogielski’s 3d ±J Ising spin glass model, and are also closely analogous to the structural dynamics in Ngai’s Type A fragile structural glasses.

4. Discussion

The precise origin of Kohlrausch relaxation and the apparent universality of the temperature dependence of β in many structural and spin glass systems remains an open question. An elegant explanation has been offered by Campbell [9] who assumes a model of hierarchical intrinsic relaxation processes based upon phase space morphology. The phase space for N Ising spins can be mapped onto the 2^N corners of an N-dimensional hypercube and turning one spin is equivalent to a step from one microstate (ie one corner) to a near neighbour state (ie near neighbour corner). The probability, p, that any one microstate is accessible is proportional to temperature, and there is a critical value of p at which a closed space analogue of a percolation transition takes place. Beyond this critical value, p_c, there is a giant cluster of linked corners, whilst below p_c only small isolated clusters exist. For a random walk on the percolation cluster the average of the square of the distance from the initial point varies with time as <L²> ≤<t> and for N>6, β=1/3 at percolation, p_c. Any point on the random walk is equivalent to the instantaneous configuration of spins in phase space, and as time increases memory of the starting configuration is lost. On the hypercube the equivalent of a random walk with exponent β is a memory function defined by a stretched exponential also with exponent β. For p>p_c, equivalent to high temperatures, progress on the random walk is rapid and β tends to 1, but as p approaches p_c, the time scale of the random walk diverges and β approaches 1/3.

Our own calculations suggest instead that β, rather than being intrinsic, simply reflects the relative width of the distribution of relaxation times within the system, with β asymptotically approaches 1/3 when any such distribution becomes sufficiently broad in comparison to the effective time window of the experimental probe.

At first sight it would appear that the Campbell model would be directly applicable to the Ising-like spins of the random anisotropy magnet studied here, implying that β should approach 1/3 at T_g irrespective of the experimental probe. Surprisingly, however, our µSR measurements on non-S-state a-RE₇TM₃ alloys show that β...
approaches 1/3 and τ diverges at approximately an order of magnitude higher in temperature than T_g measured by ac susceptibility. On the other hand, for the S-state Gd alloys, a-Gd,TM, which behave more like conventional spin glasses and which have a much narrower distribution of relaxation rates, µSR indicates that β approaches 1/3 and τ diverges precisely at T_g. These results suggest that the simple model invoking the effects of a limited experimental time window might be the more appropriate.

It is clear that considerable work is still necessary in order to ascertain whether Kohlrausch relaxation and the associated characteristic temperature dependence of β is intrinsic and a reflection of the complexity of phase space geometry of spin glass, or indeed structural glass, systems, or whether the temperature dependence of β is imposed by the time window of the measuring technique. These preliminary neutron spin echo measurements have shown that the random anisotropy magnets a-RE,TM may well be excellent model systems with which to study this fascinating problem.

Acknowledgements

The authors are indebted to Dr. Bela Farago for his considerable experimental help and advice in the course of the neutron spin echo measurements.

References


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The Application of Novel Polarised Neutron Techniques to Better Investigate Exotic Magnetic Systems - The D3 Millennium Project

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In order to improve the characteristics and extend the fields of science investigated with the polarised hot-neutron diffractometer D3, we propose to take advantage of the novel 4He neutron spin filter developed at the ILL. This will both add polarisation analysis of the scattered beam and improve the peak count rates by optimising the monochromator irrespective of the spin selection process. As its highest polarised flux will be at short wavelength and it can be used in combination with either a 10 Tesla cryomagnet, for optimised flipping ratio measurements and uniaxial polarisation analysis, or a dedicated zero-field neutron polarimeter Cryopad, for carrying out 3-dimensional polarisation analysis experiments, the new instrument will be the most powerful and flexible in its class. Among the new fields of science, it will probe exotic magnetic structures and the precision measurements of antiferromagnetic form factors over a large Q range.

1. Scientific case

The diffractometer D3 uses the technique of polarised neutron diffraction (PND) to determine precise quantitative magnetisation distributions in single crystals that are ferro- or ferri-magnetically ordered under an applied magnetic field. PND is a very sensitive method for the observation of the distribution of unpaired electrons in the entire unit cell. It reveals unambiguously delocalisation, the polarisation sign, the shape of spin density, and so permits direct characterisation of magnetic interactions. It can be applied successfully to 3d transition metal complexes, free radicals, heavy fermions, high-Tc superconductors, transition metals, and actinide alloys [1-5]. The versatility of this instrument also permits unusual polarised neutron experiments to be carried out such as the study of the parity-violation in the vicinity of the p-wave neutron resonance of 139La [6].

In order to open this instrument to new fields of science, we propose to add polarisation analysis and to take advantage of new polarised neutron techniques. In elastic mode, the use of a 4He neutron spin filter is simpler and better than a polarising crystal (flux x 5 to 10). Other advantages are the possibility to use a position sensitive detector with which to compare directly spin dependent cross-sections (there is no convolution by a third axis). Uniaxial polarisation analysis may also be used with a large energy window to investigate the paramagnetic scattering of 3d transition metals using single crystals synthesised from single isotopes. Short-range magnetic correlations are expected well above the ordering temperature as an outcome of the very fast hopping processes, which will lead to a scattering function that contrasts sharply with that of insulators or any other localised magnetism. The addition of polarisation analysis will also make possible the use of a Cryopad with which to carry out spherical neutron polarimetry (SNP) experiments [7]. This unique technique gives access to the 16 measured quantities related to the 16 independent correlation functions involved in the most general nuclear-magnetic scattering process. Using SNP, both the longitudinal and transverse components of the final polarisation vector are measured, which is not possible by uniaxial polarisation analysis: with the sample in a magnetic field, transverse components cancel and only longitudinal components are accessible. In the case of magnetic structures, SNP therefore allows the direct determination of the direction of the magnetic interaction vector. Hence, SNP is the most powerful tool for solving non-trivial antiferromagnetic structures: chiral spin configurations, complex helices, configurations in which symmetry centres are lost, etc. In recent years, the technique has been used to correct major errors in magnetic structures determined previously from data obtained with other techniques. Furthermore, because transverse components contain most of the information related to the nuclear/magnetic interference terms, SNP is the best method to study antiferromagnetic compounds for which the magnetic and nuclear information are located at the same place in the reciprocal space.

Among the new fields of research that will be opened are the antiferromagnetic ground states of geometrically frustrated lattices which are the subjects of numerous discussions. In principle, those systems, such as Kagomé and pyrochlore antiferromagnets, possess an infinite number of degenerate ground states and "spin-liquid" phases have been predicted. Neutron powder diffraction studies of various pyrochlores have discovered diffuse magnetic scattering that appears similar in form to a liquid structure factor. Recently, we have also shown that using SNP, we are able to determine precise antiferromagnetic form factors [8]. Providing a Cryopad with a rotating sample environment giving 3D access to Bragg peaks, we expect to generalise this for the first time to the magnetisation determination. Furthermore, the basic improve-
ment to the instrument through the decoupling of the optical functions and spin selection will give higher resolution and better flux. This will provide better data at higher Q where the magnetic signal weakens, and so will improve again the performance of the world leader D3.

With the new 10 Tesla cryomagnet, we anticipate an increase in the present overload of D3. Furthermore, by adding polarisation analysis, the opening up of new fields of science should result in a tangible growth of the user base. In addition, some of the kinds of experiments that were performed on D5 with the polarisation analysis option will be accommodated with significant improvement in data quality.

The D3 Millennium project is split in two parts: the polarisation analysis options will be added during the period 2000-2002 and the flux and resolution of the instrument will be improved in 2003-2004.

2. Polarisation analysis options

We propose to add polarisation analysis using a 3He neutron spin filter [9]. Compared to the use of a Heusler crystal, at 0.843 Å, it leads to a reasonable increase of the flux into the detector: \( \times 4.7 \) for \( P_{3He} = 55\% \), \( \times 5.9 \) for \( P_{3He} = 70\% \) and more at shorter wavelengths. The crucial challenge of this project resides in the ability to shield the inhomogeneous and large stray field coming from the 10 Tesla cryomagnet. This is necessary to keep the polarised 3He cell in a homogeneous magnetic field, as is required for long relaxation time of the polarisation.

A new device called Cryopol, being developed in collaboration with the CEA-Grenoble, should remove this difficulty. Briefly, Cryopol is a superconducting cylinder surrounded by a \( \mu \)-metal box in which we trap a homogeneous magnetic field [10]. Tests recently performed with a prototype show that it is a very promising device. With magnetic fields lower than 7 Tesla in the cryomagnet, we have measured a relaxation time greater than 80 hours. This result is in agreement with the simulations made in order to check the project feasibility, and to define the geometry of Cryopol.

Cryopad, developed and presently uniquely existing at the ILL, is the only device which can accomplish SNP measurements. However, in order to determine magnetic structures and distributions, we need general 3D access to Bragg reflections over a large Q range. To carry out elastic SNP experiments, we therefore propose to build a new Cryopad optimised for short wavelengths that will be able to host the Cryocradle, i.e. a cryostat containing a fully non-magnetic cradle. Compared to the Cryopad-II [10], the handling of the polarisation vector should be improved thanks to the new nutators and precession coils designed after detailed simulations. In particular, the nutators will accept larger beams and the precession coils will be decoupled by combining Meissner screens and \( \mu \)-metal yokes (fig. 1). The Cryopad has also been designed in order to host a standard cryostat or a dilution fridge. The Cryocradle has been extensively studied in order to control the thermal expansion and minimize play in the mechanics. The first prototype will consist of two circles mounted inside a cryostat fixed on a rotating plate \( \omega \) (fig. 2). The first circle supports the cryostat and fixes the angular position \( \chi \). The second one is connected to the axis of the cryostat with a gear and provides \( \phi \) angle positioning. Both circles will be motorised using tangential axes, with the motors outside the zero-field chamber of Cryopad. The cradle/sample chamber will be cooled using a pulse tube cryorefrigerator. With the present geometry, the 2θ Bragg angle of a beam diffracted by a 1 cm wide sample may vary from -40° to +120°.

As spin analyser, we will use a cryogen-free device called Decpol which is a compact single detector with spin analysis. As the stray field of the nutators is weak, we can use an end-compensated horizontal coil surrounded by a \( \mu \)-metal screen to provide the homogeneous field required to maintain the 3He polarisation. However, in order to rotate adiabatically the beam polarisation, small identical coils were added at both ends and compensation coils were modified accordingly. This device was simulated, designed.
and built in the year 2000. The relative homogeneity of the field used to maintain the $^3$He polarisation is of the order of $5 \times 10^{-4}$ cm$^{-1}$ and the depolarisation of the beam is less than 1% for $\lambda > 0.33$ Å.

3. Flux and resolution improvement

In a PND/SNP experiment, the data measured are the ratios between the intensities observed for both polarisation states of the incident neutron beam at the peak of Bragg reflections. Incoherent scattering is subtracted from the Bragg intensity by measuring the background intensity away from the peak. In order to improve the quality of the dataset, one must seek to increase the peak count rate significantly, i.e. increase the incident flux and improve the energy resolution.

Because Heusler polarising crystals provide a modest energy resolution, we have proposed to decouple the neutron spin selection from the optical functions by using a non-polarising focussing monochromator combined with a $^3$He neutron spin filter. For PND experiments, the global improvement has been estimated by comparing the actual use of a Heusler single crystal in symmetric Laue geometry with different non-polarising single crystals in focussing symmetric Laue geometry [12]. Roughly, with a Cu (200) monochromator and $P_m=70\%$, simulations show that the peak count rate may be improved by a factor 2 to 4 depending on the wavelength when the magnetic signal weakens beyond a momentum transfer of 2.5 Å$^{-1}$. The option of a reflecting monochromator is also envisaged. This may lead to a further improvement if there is sufficient room available in the present monochromator shielding.

4. Conclusion

The present polarised hot-neutron diffractometer D3 of the Institut Laue-Langevin is mainly used to determine precise quantitative magnetisation distributions of ferro- and para-magnetic samples. The D3 Millennium project consists in adding polarisation analysis and improving the flux and resolution of this instrument by taking advantage of new polarised neutron techniques. This project will open D3 to new fields of science: investigation of exotic antiferromagnetic structures, precise determination of antiferromagnetic magnetisation distributions, search for spin liquids or short-range ordering in paramagnetic phases, etc.

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Spin structure of the free-radical 2,4,6-triphenylverdazyl (TPV)

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The organic free-radical 2,4,6-triphenylverdazyl (TPV) is a linear chain antiferromagnet (spin 1/2) with a Néel temperature of 1.78K. Below this temperature a weak ferromagnetic component appears. The magnetic structure of TPV has been investigated by neutron diffraction on a single crystal sample. Several magnetic Bragg reflections have been collected below (1.37K) and above (2.20K) the Néel temperature using the CRG diffractometer D23. A collinear spin structure model with the magnetic moment pointing along the b-axis and the same collinear model with the magnetic moment along the a-axis were found to give a similar agreement between observed and calculated intensities for the measured magnetic reflections. The former one is consistent with magnetization measurements and the refined magnetic moment for this model is μ=0.39μB, a value which is considerably reduced compared to the expected value 1μB for a spin 1/2. This result can be interpreted in terms of spin reduction in Heisenberg S=1/2 chains.

1. Introduction

Up to now magnetic neutron investigations have been concentrated mainly on 3d and 4f electron systems, and very few on 2p systems. 2p systems are different in many respect from the 3d or 4f ones, in particular because the magnetism arises from unpaired electrons in molecular orbitals spread over different atoms in the molecules built from light elements such as H, C, N, O... Therefore organic magnetic materials are interesting targets for neutron investigations. However, measurements on such materials are difficult because on the one hand the background is very high due to the hydrogen atoms included in the molecules and on the other hand the magnetic signal is very weak due to a low spin density delocalized over large molecules. Getting large single crystals is in addition often difficult.

The organic compound TPV is a stable free radical of formula C29N4H17. This molecule is planar and is built of a verdazyl ring surrounded by three phenyl groups. It crystallizes in the orthorhombic space group (P212121) with four molecules in the unit cell forming zigzag chains along the c-axis. This compound is a linear S = 1/2 Heisenberg antiferromagnetic chain with a Néel temperature of 1.78K [1]. Below this temperature a three dimensional antiferromagnetic order develops and at the same time a weak ferromagnetic component appears. A former neutron investigation allowed, from the measurement of a few Bragg reflections, to propose a model where antiferromagnetic chains along the c-axis are coupled antiferromagnetically in the a-c plane and ferromagnetically in the b-c one, the moments pointing along the b-axis [2]. However, the counting statistics, the low number of observations and the lack of the low temperature crystal structure were obstacles to draw definitive conclusions. Therefore we decide to reinvestigate the magnetic structure of this radical.

2. Neutron Experiments

We first refined the crystal parameters at 4.2K using the CRG diffractometer D15 of the ILL. A TPV crystal with a weight of 24mg was cooled down and 4262 peaks reducing to 1571 independent reflections were collected. The magnetic contribution (about 10 % of the total signal). A clear signal is visible in the difference, with a width comparable to the instrument resolution; it is an evidence of a long temperature is about 1.78K, in good agreement with the data already reported [2]. 63 different magnetic reflections were collected.

3. Results and Discussions

We calculated magnetic intensities for several possible models to determine the spin structure. A collinear spin model [2] where antiferromagnetic chains extend along the c-axis was found to give a good agreement with the experimental data. Another model of the same spin configuration but with the spins pointing along the...
a-axis was also found to give a comparable agreement. The magnetization measurements [3] seem to support the former model. However, the present analysis was based on a simple model about the spin density distribution. Indeed, we have assumed a magnetic form factor calculated from a model where the spins 1/2 are equally shared by the four nitrogen atoms of each TPV molecule, in 2p Slater-type atomic orbitals. This model is a very simple one, and the spin density must be determined experimentally to confirm this assumption. A polarized neutron investigation is presently in progress.

The refined magnetic moment for the two models either along the b-axis or the a-axis are respectively 0.39µB and 0.43µB at 1.37K, values which can be extrapolated to 0K according a S=1/2 Brillouin curve to 0.53µB and 0.59µB. These values are considerably reduced compared to 1µB expected for a spin 1/2, and this can be interpreted as a spin reduction in Heisenberg linear chain. This is a very interesting problem, but our measurements were done just below the Néel temperature (T/T_N=0.77), far from the saturation of the magnetic moment, and therefore data measured at lower temperature are needed to further discuss this problem.

References

Fig. 1 Magnetic part of (101) peak.
We present the results of a polarized neutron experiment on UCoAl single crystal. Experimental data have been analyzed by a maximum entropy method and within an atomic model. The main magnetic contribution originates from the uranium atoms. The ratio $\mu_L/\mu_S$ between the orbital and spin moment is slightly reduced in comparison to the uranium free ion value and remains nearly unchanged between 1 and 8 T. Induced magnetic moments of nearly same magnitude and similar field dependence are observed on the two cobalt sites. An additional magnetization density is observed around the aluminum positions.

1. Introduction

UCoAl crystallizes in the ZrNiAl-type hexagonal structure (space group P6$_3$2m) and exhibits a paramagnetic ground state. When a magnetic field of $\approx$ 1 T is applied along the c-axis of UCoAl below 13 K, a metamagnetic transition to a high-field ferromagnetic state with uranium magnetic moments parallel to the c-axis is observed [1]. The magnetization along the c-axis does not saturate above the metamagnetic transition but shows a strong, almost linear increase with increasing field ($M_{\mu} = 0.334 \mu_B$, $M_{8T} = 0.445 \mu_B$). We present polarized neutron diffraction study of this compound performed on a single crystal.

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**Fig. 1:** Density of magnetic moment within the U-Co plane in 1 T (a) and 8 T (b) and within the Al-Co plane in 1 T (c) and 8 T (d) reconstructed by maximum entropy method. The contours are at 0.01 $\mu_B/\AA^2$, dotted contours represent negative values. Above 0.1 $\mu_B/\AA^2$ (center of the uranium position), the contours are at 0.1 $\mu_B/\AA^2$.

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2. Experimental

The UCoAl single crystal used for our neutron diffraction study has a shape of a flat plate (4x0.8x3 mm) perpendicular to [001] direction with a length of 3 mm along [001] direction. To refine the structure parameters, integrated intensities of 131 non-equivalent nuclear reflections have been measured on the D15 diffractometer at ILL Grenoble at 0.851 Å. The polarized neutron diffraction experiment has been performed on the D3 diffractometer at the ILL. The flipping ratios of 86 non-equivalent reflections have been measured for λ = 0.514 and 0.843 Å, in magnetic fields of 1 and 8 T applied parallel to the c-axis of the UCoAl crystal at T = 2 K.

3. Results and discussion

The refinement of measured integrated intensities (including the absorption and extinction corrections) confirmed the ZrNiAl-type crystal structure, which consists of two types of basal-plane atomic layers along the c-axis. One of them contains all of the U atoms (in (x,0,1/2), (0,x,1/2) and (x,x,1/2) positions) and 1/3 of the Co atoms (the Co2 position: (0,0,1/2)). The other one contains the rest of the Co atoms (the Co3 position: (1/3,2/3,0) and (2/3,1/3,0)) together with all of the Al atoms (in (y,0,0), (0,y,0) and (y,y,y)). Our refinement gives the values of x(U) = 0.5788(1) and y(Al) = 0.2358(2).

The experimental flipping ratios R were analyzed by two different approaches: the maximum entropy method [2] which makes no assumption on the magnetization distribution and by a classical refinement of an atomic model which considers that the magnetic moments are carried by atomic sites. The magnetization-density maps obtained by maximum entropy method are shown as projections onto the basal plane in Fig. 1(a-d). The main contribution comes clearly from the uranium atoms. Much weaker magnetization clouds are located on the Co2-positions. In the Al-Co plane, magnetization clouds are observed on the Co3-positions and close to the Al-positions. Analysis of the magnetization density along the c-axis shows clearly that these positive densities are located in the Al-Co plane. Magnetic moment induced on aluminum or an atomic disorder between the cobalt and aluminum sublattice could be an explanation.

<table>
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<th></th>
<th>µ(U)</th>
<th>µ_c</th>
<th>- µ_s</th>
<th>-µ_s/µ_c</th>
<th>µ(UCo)</th>
<th>µ(UCo)</th>
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<td>0.059(11)</td>
<td>0.051(6)</td>
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<td>0.327(4)</td>
<td>0.602</td>
<td>0.275</td>
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Table 1: Results obtained by integration in the magnetization density maps, fit to the magnetic structure factors calculated from these maps and the direct refinement of the measured flipping ratios. Magnetic moments are given in µB/atom; µ_spd is obtained by comparing the sum of all moment with the bulk magnetization and is given in µB/atom. By * we denote the results obtained assuming magnetic moment described by cobalt form factor on Al-site. Magnetic moments obtained by direct integration in the maps, as well as the results of the refinement based on the atomic model (fit to magnetic structure factors calculated from the magnetization maps and direct refinement of the experimental flipping ratios) are given in Table I. The results are not very sensitive to the uranium valence, so we cannot make any conclusion about it. We present the results obtained assuming U3+ ions. The ratio -μ_s/μ_c determined from our data is reduced compared to the U3+ free ion value of 2.57, but the reduction is smaller than in the isostructural UNiGa (-μ_s/μ_c = 1.98) [3], UNiAl (-μ_s/μ_c = 1.79) [3] or URhAl (-μ_s/μ_c = 1.81) [4]. The large orbital contribution is remarkable for a material such as UCoAl, which is considered as one of the UTX compounds with rather delocalized 5f electrons. We shall note that both μ_c and μ_s are strongly reduced with respect to the corresponding free-ion values. When increasing the magnetic field: both μ_c and μ_s increase and their ratio remains almost unchanged.

The magnitude of the magnetic moments induced on cobalt is about 20% of the uranium moments, less than in URhAl (30%) or URuAl (45%) [4]. This is expected because the 4d wavefunctions of Rh or Ru are more expanded in space than the 3d-states of Co. A large anisotropy of the hybridization between the uranium 5f-states and transition metal d-states has been observed for URhAl and URuAl [4]. Our study does not show any indication for such a large hybridization anisotropy in UCoAl. The moment on Co is slightly larger than that on Co2, and both moments increase when increasing the magnetic field. Comparing the results obtained for URhAl, URuAl [4], UNiAl, UNiGa [3] and UCoAl, one could speculate that the hybridization is strongly anisotropic (occurs mainly within the U-T1 plane) for the 4d-series, while no such strong anisotropy appears for the 3d-series. The U-T1 and U-T2 distances are very close to each other in all the mentioned compounds, and cannot thus serve as an explanation for such a different behavior. The nature of the d-states plays probably the crucial role. In this context, it would be highly interesting to investigate an isostructural UTX compound from the 5f-series, e.g. UPAI which is a simple ferromagnet with uranium moments aligned along the c-axis [5].

Electronic systems
Acknowledgements

We acknowledge the support from ILL technical services. The work was supported by the Grant Agency of the Czech Republic (grant #202/98/P245 and 202/99/0184).

References

First neutron tests of the renewed IN20 polarization analysis spectrometer

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The IN20 is a thermal beam three-axis spectrometer equipped with a Heusler crystal monochromator and analyzer for neutron scattering with polarization analysis in the thermal energy range. The new beam tube of 170 mm diameter and a large doubly focusing Heusler monochromator provide a gain factor of 10 in monochromatic polarized flux at sample position as compared to the old configuration. In combination with the horizontally focusing analyzer installed last year the sensitivity of the instrument has increased more than 30 times as compared to the configuration with only vertically focusing crystals in use till 1999.

1. Introduction

The thermal beam three axis spectrometer (TAS) IN20 has been designed for excitation studies in the 10-60 meV range using polarized neutrons and represented the state of the art in its domain in the 1980’s and 1990’s. The experiments carried out on IN20 involve elastic and inelastic scattering with 1D and 3D (CRYOPAD) polarisation analysis as well as the thermal beam spin-echo technique (TASSE). In reality the energy scale of excitations covered on IN20 extended only to about 35 meV due to a severe cut-off of the monochromatic flux at incident neutron energies higher than 60 meV, caused by the small size of the old Heusler monochromator saturated by a horizontal magnetic field. In addition, even at lower neutron energies the data acquisition rate was a factor 30-100 lower than for an equivalent configuration with unpolarized beams, which in most cases excluded a polarized beam continuation of a typical experiment needing a week of beamtime already on an unpolarized TAS like IN8.

We have therefore proposed to rebuild the spectrometer in such a way that the incident neutron energy range would extend above 100 meV (wavelengths down to about 0.8 Å) and the overall luminosity would permit inelastic scattering experiments to be carried out within a time comparable to that needed previously with an unpolarized beam (ie. about one week for samples of 1 cm³). The essential parts of the new setup are the new beam tube, which increases the neutron source diameter to 170 mm, a heavy input slit of variable width, playing the role of a virtual source for monochromatic focusing, and a new doubly focusing Heusler monochromator 230 mm wide and 150 mm high with vertical magnetisation. At a later stage a second monochromator (Si 111 or PG 002) will be added for occasional non-polarized work.

For more details on the technical solution the project report in the ILL Millenium Programme [1] can be consulted. The exact geometry of the primary spectrometer has been optimized using RESTRAX Monte-Carlo ray-tracing calculations [1,2]. For the new Heusler monochromator these predicted a monochromatic polarized flux of about 8 x 10⁷ n cm⁻² s⁻¹ in the range of the neutron wavelengths of 1.2-1.5 Å (k = 4 – 5 Å⁻¹, maximum of the thermal spectrum).

2. The new Heusler monochromator

The key part of the upgraded setup is the new Heusler monochromator. Its design is based on detailed RESTRAX simulations permitting to define the optimum size of its active surface as well as to optimize the size and number of crystal plates used in the assembly. Since most of the present experiments require a good...
energy resolution but allow a relaxed momentum resolution, we have opted for a variable horizontal focusing geometry. As a consequence, the Heusler crystals are saturated by a vertical magnetic field closed by a C-shaped iron yoke on the rear side of the monochromator; this solution is ideal for work at low Bragg angles where it does not impose any limits on the neutron beam. The exact layout of the magnetic circuit with NdFeB permanent magnets, saturating the Heusler crystals, was then defined on the basis of 3D finite-element calculations and validated by reference calculations for the horizontally focusing IN20 Heusler analyzer, built and implemented in 1999/2000.

The new monochromator, displayed in Fig. 1, consists of 75 crystal plates mounted in 15 columns, pivoting around vertical axes to provide variable horizontal focusing. Moreover, the five plates in each of the columns are glued on precision supports with their (111) crystallographic planes inclined by angles corresponding to vertical focusing, optimized and fixed at $k_i = 4.1 \text{ Å}^{-1}$. With an active surface of 230 x 150 mm$^2$ it is probably the largest polarizing crystal assembly ever built.

3. Results of neutron tests.

The polarized monochromatic flux delivered at the sample position has been measured with the same calibrated monitor used since decades to obtain flux values given as a reference for different ILL instruments. The measurement was performed in the usual way with the orientation of the monitor adjusted for maximum signal and the horizontal curvature of the monochromator reoptimized for each neutron wavelength separately. The data obtained are displayed in Fig. 2 as a function of the neutron wavenumber, $k = 2\pi\lambda [\text{Å}^{-1}]$, in comparison with various results of the RESTRAK ray-tracing simulations and with the output flux of the old monochromator. The calibration constant and the correction factors for higher order contamination, effective below $k_i = 4.5 \text{ Å}^{-1}$, are the same as for the old configuration. Although this appears as a plausible hypothesis in the first approximation, detailed verification of the harmonic contamination is due at a later stage of the commissioning tests.

The beam polarization has been checked using the horizontally focusing Heusler analyzer and a 111 reflection from a silicon single crystal sample, which is free of the $\lambda/2$ harmonic and, moreover, contains no magnetic or nuclear-spin incoherent component in the signal. A flipping ratio of 26 has been obtained at $k_i = 2.66 \text{ Å}^{-1}$, which is somewhat better than the usual values of 20-22 for the old setup and which indicates that the Heusler crystal assembly, despite its size, is properly saturated. At higher $k_i$ this value reduces to about 13, which is most probably due to a lack of adiabaticity at the interface between the new monochromator and the old spin guide between monochromator and sample, still to be rebuilt.

The energy resolution widths of 0.8 meV and 3.0 meV obtained with the combination of the new monochromator with the horizontally focusing analyzer from vanadium scans at $k_i = 4.5 \text{ Å}^{-1}$ and 4.1 $\text{ Å}^{-1}$, respectively, are by 0.2 meV smaller than those of the old set-up. These scans, however, were taken with the input slit in front of the monochromator relatively wide open (35 mm). A detailed survey of the optimum choice of the slit aperture and its impact on flux, energy resolution and signal/noise ratio remains a matter for further tests. The comparison of the present vanadium data with those obtained in the previous configurations demonstrates the dramatic increase in the sensitivity of IN20: at unchanged energy resolution width the peak count-rate passed from 3 cts/sec for IN20 with vertically focusing monochromator and analyzer in 1998 to 15 cts/sec after implementation of the horizontally focusing analyzer in 2000 and became more then 100 cts/sec with the new monochromator in 2001.


The purpose of the above results, obtained within the first few days of testing, is to demonstrate that the essential goals of the IN20 renewal - a significant increase in monochromatic flux (factor 10 at $k_i = 5 \text{ Å}^{-1}$) and an extension of the incident neutron energy range beyond 100 meV - have been achieved. The forthcoming months will see in parallel more extensive tests and the first user experiments, the results of which will serve as basis for further finetuning of the performance of the instrument.

Acknowledgements.

The development of the RESTRAK program and the IN20B Monte-Carlo simulations have been partly supported by the European TMR network PECNO (ERB-FMRX-CT96-0057).

References.

High Energy Spin-Orbit Excitations in the $\gamma$ and $\alpha$ Phases of Ce

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We have performed measurements of the spin-orbit excitations at high energies in Ce using the beryllium-filter technique on the IN1B spectrometer on the hot source at ILL. With this technique, the high energies of the excitations necessarily imply measurements at high momentum transfers $Q$. Thus, the observed spin-orbit excitation at 260 meV in the $\gamma$-phase corresponds to a momentum transfer of ~11 Å$^{-1}$. On cooling below 110 K Ce undergoes a first order phase transformation to the $\alpha$-phase, and the spin-orbit excitation is found to be broadened and shifted to ~500 meV ($Q$ ~ 15 Å$^{-1}$). This observation is consistent with the strongly hybridised but essentially localised single-ion character of the 4f state of Ce in the controversial $\alpha$-phase.

1. Introduction

The $\gamma \to \alpha$ phase transition in Ce has remained enigmatic ever since its discovery about four decades ago [1]. Despite considerable theoretical and experimental work over the years there appears to be, as yet, no real consensus about the possible physical mechanism associated with the transition. The current debate on the subject can be loosely considered as divided between two principal schools. One of them believes that at the $\gamma \to \alpha$ transition the 4f electronic state undergoes a transformation from a localised to an itinerant 4f band [2]. The other school, however, considers that the 4f state in the $\alpha$ phase is essentially localised but is influenced by strong Kondo coupling [3] or is strongly hybridised with conduction electrons [4].

Within the Russell-Saunders coupling scheme, the spin-orbit interaction splits the 4f state of Ce with orbital momentum $L=3$ and spin $S=1/2$ into two states with total angular momenta $J = 3 \pm 1/2$, viz. the states $^2F_{5/2}$ and $^2F_{7/2}$ separated in energy by ~270 meV in the free ion [5]. In the solid, particularly in the metallic state, changes in the nature of the two spin-orbit states of the Ce$^{3+}$ ion (4f$^1$) are expected due to the crystalline field as well as interactions with other electrons, including conduction electrons. The changes would be quite dramatic, however, if the 4f state transforms to an itinerant 4f band. This is because itinerant band formation quenches the orbital moment significantly while possibly also reducing the spin moment by a smaller amount, relatively.

A number of measurements of the paramagnetic response of the ground multiplet $^2F_{5/2}$ of both $\gamma$ and $\alpha$-Ce as well as a number of $\alpha$-Ce-like systems have been reported in the literature, and provide a wealth of information about the $^2F_{5/2}$ state. In general, these systems show a broad Lorentzian-like spectral response at low temperatures centered on characteristic energies ranging from ~40 – 60 meV for systems like CeSn$_3$ [6], CePd$_3$ [7] to ~140 – 180 meV for CeNi$_2$ [8], CeRh$_2$ [9], and $\alpha$-Ce [10]. Indeed, values as high as ~500 - 600 meV are observed in very strongly hybridised Ce-compounds like CeFe$_2$, CeRu$_2$ [11] which show a saturation valence of ~3.3, as in several Ce compounds [12].

Measurements of the spin-orbit excitations have been performed earlier on an alloy of Ce with 7 at. % Sc using high-energy neutrons on a time-of-flight spectrometer [10]. In addition to the expected spin-orbit excitation in the $\gamma$-phase at ~260 meV the data give clear evidence for the existence of a broad excitation at an elevated energy of ~500 meV in the controversial $\alpha$-phase. These measurements using the time-of-flight technique were performed in the forward direction probing relatively low momentum transfers, $Q$ ~ 5 - 6 Å$^{-1}$. Consequently, the excitations were observed as shoulders on the broad magnetic scattering from the ground state. Intrinsic to the technique, the present investiga-

![Fig. 1: Ce$^{3+}$ form-factor $F_2(Q)$ and the structure factor of the $^2F_{5/2} \to ^2F_{7/2}$ excitation calculated by Balcar and Lovesey [15]. The inset shows the same data normalised to unity at $Q = 5$ Å$^{-1}$, close to the Q-vector where the measurements of the spin-orbit excitations were performed on the time-of-flight spectrometer HET [10].](image-url)
tion using a beryllium-filter spectrometer could only be performed at relatively high Q’s (~ 11 - 16 Å⁻¹). Despite the overall reduction of the intensity of the spin-orbit excitation to ~ 1/3 relative to that at ~ 5 Å⁻¹ this is, nevertheless, an interesting Q-range for its measurement because the reduction in intensity of the F₁/₂ ground state response is even greater, by about an order of magnitude, as shown in figure 1. As a result, the spin-orbit excitation can be observed prominently as a peak rather than as a shoulder on the broad ground state response.

2. Experimental Details

We have used the same ~ 60g sample of Ce containing 7% Sc as used in the earlier measurements on the time-of-flight spectrometer HET at ISIS [10]. Additions of small amounts of scandium has the effect of stabilising fcc Ce against the unwanted dhcp β-phase which forms sluggishly on cooling below ~ 200 K. Gschneidner et al. [13] have observed that addition of ~ 7% Sc suppresses the formation of β-phase to below ~ 1% level, and addition of up to 10 % Sc has negligible influence on the relative volume change ∆V/V at the transition.

The measurements were performed on the IN1B beryllium-filter spectrometer situated on the hot source at ILL. In this technique the sample is irradiated by monochromatic neutrons with incident energy Ei and the scattered neutrons with final energies ω < 5 meV transmitted by a nitrogen-cooled beryllium filter are counted by He³ detectors placed immediately behind it. Energy scans are performed by varying the incident energy Ei which is, in general, large compared with the final neutron energies of <5 meV. Hence, the scattering vector Q is very closely represented by 2π/λ, with the incident wavelength λ = Ei/ω. High-energy scans therefore necessarily imply measurements at high Q-values. For example, at the energy transfer of ω = 250 meV the Q-value is ~ 11 Å⁻¹ and at ω = 500 meV a Q-value of ~ 15 - 16 Å⁻¹ is reached. The present measurements of magnetic scattering at relatively high Q-values are possible because of two principal reasons:

i) The structure factor for the F₁/₂ → F₃/₂ excitation (for the free Ce³⁺ ion) decreases rather slowly with Q above 5 Å⁻¹ (see fig. 1), and

ii) The high luminosity of the hot source at ILL for energies up to ~ 500 meV, and possibly beyond.

One of the drawbacks of the beryllium filter technique, however, is that the background scattering is, in general, higher compared with the time-of-flight method, for example. This is because filter discrimination for neutrons with incident energies > 5 meV, although very high, is not perfect (say, 99.9⋯9.9%). Considering the high magnitude of the integrated signal from other processes, particularly elastic scattering, a very small but finite transmission for these unwanted neutrons translates into a small, non-negligible sample-dependent background signal.

Another particularly difficult source of background is from fast neutrons that come through with the incident beam. These are scattered by the sample, transit the filter suffering some attenuation before reaching the detectors. Additionally there is always the constant, time-invariant background due to neutrons (as well as γ-rays) from the surrounding instruments that reach the detectors, despite the elaborate shielding. Assuming that the incident flux of fast neutrons coming through with the main beam is roughly constant, independent of Ei, the background due to this latter source should be proportional to the counting time. Since the incident flux of useful neutrons of energy Ei decreases with increasing energy due both to decreasing luminosity of the source as well as decreasing reflectivity of the monochromator, the counting times become progressively longer, for the same monitor preset, i.e. incident flux, with proportionate increase in the background. We have subtracted out this source of background including other time-invariant contributions assuming their proportionality to counting time.

3. Results and Discussion

In fig.2 we show the results obtained in both phases for energy transfers ω < 700 meV. We observe a well-defined peak around ~ 260 meV representing the spin-orbit excitation F₁/₂ → F₃/₂ in the γ-phase which almost completely disappears in the α-phase from the energy window ω < 300 meV, except for a small residual contribution which may be due to a small amount of β-phase which could form on cooling or even hydrogen related impurities (CeH, for example). The other ‘structures’ in the data between 100 and 200 meV are seen equally in both α and γ phases and can be attributed to hydride impurities commonly seen at these energies in rare earth systems. We have performed a smooth fit to the γ-phase data above 300 meV using a polynomial of 2ⁿ order, shown by the dashed line. Taking this dashed curve as the base-line for the measured α-phase data above 300 meV, we have fitted the α-Ce data in the energy region above 300 meV to a polynomial of 3ⁿ order shown by the long dashed curve, which helps to define the broad hump representing the spin-orbit excitation F₁/₂ → F₃/₂ situated around ~ 500 meV. A Lorentonian fit also results in a very similar curve to that obtained with the polynomial fit yielding the following parameters: centroid ~ 500 ± 50
meV, half-width ~ 150 ± 30 meV. These results thus confirm and supplement our earlier observations of the spin-orbit excitations in γ and α-Ce at lower Q (~ 5 Å⁻¹) [10].

Finally, we address the question of the physical interpretation of the observed broadening and enhancement of the spin-orbit excitation energy which could be the key to our understanding of the intrinsic physical phenomenon associated with the γ → α phase transition. To our knowledge, there are no calculations for the structure factor of the spin-orbit excitation between the itinerant 4f sub-bands in α-Ce. However, as a result of the predicted (substantial) quenching of the orbital moment and of the spin moment to a lesser extent, the spin-orbit interaction ζL.S should be reduced in proportion, with direct consequence for the magnitude of the splitting of the spin-orbit sub-bands. It is evident that within the itinerant band models any observable spin-orbit sub-band excitations should occur at a lower energy compared with the free-ion spin-orbit energy. Hence, the observed enhancement of the spin-orbit excitation energy goes counter to the idea of itinerant band formation.

Our earlier measurements of the 2F5/2 ground state response of α-Ce show all the characteristic features of a single ion magnetic response. The Q-variation of intensity of the spectral distribution determined, for example, at the maximum in the distribution (~ 170 meV) has been shown to follow the Ce³⁺ magnetic form factor and the overall spectral shape is also well described by the single-ion spectral form such as the Lorentzian (with a constant Q-independent spectral width) or the single-ion spectral form of Kuramoto and Müller-Hartmann [14] which closely resembles a Lorentzian except at very high energies. In summary, the present observations at high Q-values of the energy-enhanced spin-orbit excitation in α-Ce lend support to the earlier observations indicating a single-ion character of the 4f state in this phase.

References:
Nuclei & particles
A new class of symmetries in nuclei, and their empirical discovery, will be discussed. These symmetries apply to nuclei at the critical points of phase/shape transition regions and represent entirely new paradigms of structure.

1. Introduction

Dynamical symmetries play a central role in our understanding of the atomic nucleus. They provide benchmarks or paradigms of structure, and analytic solutions to the complex nuclear many-body problem for the structural idealizations they portray. Three such benchmarks were recognized in the 1950s: the vibrator [1], the axially symmetric deformed rotor [2], and the \( \gamma \)-soft axially asymmetric rotor [3]. These structures were later recognized as the distinct dynamical symmetries, U(5), SU(3) and O(6), of the group U(6) in the context of the Interacting Boson Approximation (IBA) model [4]. Examples of all three symmetries have been discovered in actual nuclei, largely using data from the GAMS spectrometer at the ILL [5-8]. These research achievements provide a basis for our current understanding of the structure of the nucleus as a macroscopic, collective, many-body object.

However, it remains true that the vast majority of nuclei do not satisfy one of these dynamical symmetries: they are in regions of changing structure between a pair of symmetries. This is illustrated in the symmetry triangle of Fig. 1, where the vertices denote the symmetries and the legs the transitional regions between them. Most collective nuclei lie on or near one of these legs, and sequences of nuclei as a function of proton and neutron number typically lie along a trajectory following one of them. Valuable as these symmetries are, virtually all realistic calculations of nuclei to date have therefore required numerical solutions to Hamiltonians deviating from the symmetries.

2. Critical Point Symmetries

Particularly interesting are the transition legs between the vibrator and \( \gamma \)-soft limits and the vibrator and axial rotor limits. Analysis of the geometrical shapes involved shows that these correspond to second and first order phase transitions, respectively. Experimental evidence that finite nuclei do indeed exhibit phase transitional behavior has been recently discovered [9,10]. This has directly inspired a major theoretical breakthrough [11,12], with ramifications far beyond nuclear physics into molecular and other mesoscopic systems, namely the discovery of a new class of dynamical symmetries that give analytic descriptions of nuclei at the critical points. Two specific symmetries of this class have been developed, called E(5) [11] and X(5) [12], that describe nuclei at the critical point of the second and first order phase transitions mentioned above.

The locations of these new symmetries, which represent the first entirely new analytic paradigms of nuclear structure since the 1950s, are schematically indicated in Fig. 1. It is worth noting that the wave functions, energies, and transition rates of E(5) and X(5) result from solutions to differential operator Hamiltonian...
equations: they are not related to the boson ansatz of the U(6) group of the IBA. For example, the eigenvalues are defined in terms of the zeros of spherical functions [e.g., Bessel functions of irrational order for X(5)]. Nevertheless, both E(5) and X(5) are dynamical symmetries in the group theoretical sense, albeit of a different kind than normally encountered. (See ref. [12] for further discussion.)

Immediately upon the recognition of these symmetries, experimental evidence for their realization in actual nuclei was presented — in $^{134}$Ba (ref. [13]) for E(5) and $^{152}$Sm (ref. [14]) for X(5). The $^{152}$Sm – X(5) comparison is particularly extensive and compelling. As shown in Fig. 2 (see ref. [14] for additional comparisons), the agreement is excellent. It is worth stressing that the predictions are entirely parameter-free (with the exception of energy and transition rate scale factors).

The predictions for the X(5) symmetry are actually still under development. The key task is to better incorporate the $\gamma$ degree of freedom and $\beta$-$\gamma$ coupling. This is expected to improve the agreement with experiment and allow the quasi-$\gamma$-band states to be incorporated into the scheme.

In summary, a new class of dynamical symmetry, applicable at the critical points of phase transitions, has been developed, with applications both within and beyond nuclear physics. Two members of this class are called E(5) and X(5), and empirical examples have been found in actual nuclei.

**Acknowledgements:**

I am very grateful to N. V. Zamfir and F. Iachello for collaboration in all phases of this work. Work supported under U.S. Department of Energy Grant No. DE-FG02-91ER-40609.

**References:**

[14] F. Iachello, to be published
Applications of gamma-ray spectroscopy with $10^{-4}$ resolving power are presented. The extraordinary resolution and precision obtained allows determining lifetimes of excited nuclear levels, inter atomic potentials, and fundamental constants. We report on recent achievements of ILL’s high-resolution facilities.

1. Precision gamma-ray measurements at ILL:
   An historical outline
   The aim to obtain the highest possible resolution and precision in a measurement has always been one of the major challenges for experimental physicists. A gain in resolution generally results in progress by opening up insights in new fields of applications. Originally, high resolution $\gamma$-ray spectroscopy at the Institut Laue Langevin (ILL) was developed to determine with high accuracy the energies of $\gamma$-ray transitions and to separate doublet structures not resolvable by other means. Three decades ago the first generation DuMond type crystal spectrometers built at ILL allowed to obtain a resolution $\Delta E/E$ in the order of $10^{-4}$. Later on, efforts were made to approach $10^{-5}$ [1]. In that period the data obtained were mainly used to construct nuclear level schemes with the aim to do that as completely as possible. A well-known example of that time is $^{168}$Er [2] where - within the spin window which can be reached in neutron capture - a complete level scheme was established up to an excitation energy of close to 2.5 MeV. Due to the completeness achieved it became a famous testing ground for theoretical models. Another example is $^{197}$Pt [3], the level scheme of which was the first one associated with the O(6) limit of the Interacting Boson Model. A bit more than a decade ago one succeeded to achieve a resolving power close to $\Delta E/E = 10^{-5}$ and a precision close to $\Delta E/E = 10^{-7}$. This was done by introducing a new geometry using the two axis flat crystal spectrometers GAMS4 which is operated in an ILL/NIST collaboration. An example for a high-precision measurement is the determination of the mass of the neutron with an accuracy of $10^{-7}$ [4]. This was obtained by comparing the neutron binding energy in deuterium (obtained by precise measurement of the 2.2 MeV deuterium line) to the deuterium/hydrogen mass difference. The ultra high resolving power then finally also allowed to observe the tiny Doppler shifts produced when nuclei recoil after the emission of gamma rays and this led to the possibility to determine lifetimes of excited states populated after thermal neutron capture.

2. GRID: Gamma-Ray Induced Doppler Broadening
   In thermal neutron capture the product nucleus is excited to an energy of typically around 10 MeV, depending on its neutron binding energy. The capture state will decay preferably by the emission of $\gamma$-rays. Each emitted $\gamma$-ray of energy $E_\gamma$ induces a recoil of the nucleus. These velocities are in the order of $10^{-4}$ to $10^{-6}$ of the velocity of light:
   \[ v/c = E_\gamma / Me^2 \]
   with $c$ the velocity of light, $E_\gamma$ (typically several MeV) the energy of the gamma ray causing the recoil, and $M$ ($\sim A \cdot 931$ MeV) the mass of the nucleus. The low average incident energy of thermal neutrons ($\sim 25$ meV) can generally be neglected. The measured Doppler shifts of subsequently emitted secondary $\gamma$-rays of energy $E_\gamma$ are correspondingly small:
   \[ \Delta E_{\gamma,\nu} \approx E_\gamma v/c \]
   for unslowed recoiling nuclei. They can be detected with $10^{-4}$ resolution using the crystal spectrometers Gams4 and the new Gams5, now available at the ILL [5,6]. Because there is no preferred direction for the emission of primary $\gamma$-rays, the measured profiles of secondary $\gamma$-rays will show a Doppler broadening rather than a Doppler shift. The obtained line shapes depend - besides the magnitude of the original recoil - on two time scales: The lifetime $\tau$ of the nuclear level which is depopulated by the measured $\gamma$-ray and the slowing down time $t$ for the recoiling atom to thermalize. The corresponding technique is called GRID (Gamma Ray Induced Doppler broadening) and more details of the basic principles may be found elsewhere [8]. At the low recoil velocities the slowing down time $t$ is quite short and this limits the determination of lifetimes to below ~10 picoseconds. However, there is in principle no lower limit as below ~1 femto second one can measure experimentally the natural width $\Gamma(\text{eV}) \sim 6.6 \times 10^{-9} / \tau \text{s}$ of the corresponding transitions.

If one wants to extract details about atomic motion from GRID measurements an almost precise realisation of the concepts of classical mechanics is needed. This can be achieved by introducing molecular dynamics (MD) simulations, which model the motion of a system of $N$ atoms interacting with each other via a particular inter-atomic potential. This method becomes especially precise when oriented single crystals are used as targets. Due to the
regular arrangement of atoms in a single crystal the rate of slowing down in such samples depends on the direction of recoil due to blocking and/or channelling effects. Therefore the shape of the observed Doppler profiles depends directly on the orientation of the target crystal with respect to the spectrometer. Fine structure appears which allows the determination of interatomic potentials and/or the lifetimes of excited nuclear states. First GRID measurements were carried out with light nuclei [8,10-14] where the recoils - due to the small mass - are relatively large (in the 100 eV region). The situation gets more difficult in heavy nuclei where the recoil energies are smaller because the intensity of feeding γ-transitions is generally much more fragmented and the mass of the recoiling nuclei much higher. Therefore it was evident that one needed to push resolving power to its limits. It was a major event when it turned out that it was possible to mount crystals almost completely stress free. At present the line shapes obtained are almost exactly equivalent to the ones predicted by dynamical diffraction theory.

The first (and since heaviest) nucleus studied after these improvements with the GRID technique was 196Pt [15]. The experimental success of the Pt-measurement then triggered i) further efforts to still improve the resolution - less dramatic now, and in the order of altogether about a factor of 2 - and ii) follow up experiments in the region of heavy nuclei. It was an important fundamental result when an experiment at the ILL [16] found a level in 168Er which could be associated with the 2-phonon γ-vibrational mode. This result for 168Er led to experiments, by others, to confirm this result (which they did [17]), and at ILL it led to searches for multi-phonon states in other nuclei.

In spite of the many achievements already obtained concerning resolution and precision there are still ongoing efforts to even further improve the performance of ILL’s high-resolution gamma-ray spectrometers.

References
Neutron $\beta$-decay, $V_{ud}$, and the question of quark mixing

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The Standard Model of particle physics describes free neutron decay with two parameters, namely $\lambda = g_A/g_V$, the ratio of axial-vector to vector coupling constant, and $V_{ud}$, the first entry in the Cabibbo-Kobayashi-Maskawa (CKM) matrix. Neutron decay experiments determine these parameters and, together with other data from particle and nuclear physics, many tests of the Standard Model become possible. We check the unitarity condition of the CKM matrix by comparing neutron decay data, based upon quark decays of the first particle family, with the results of quark and muon decays of the second and quark decays of the third family. Neutron decay input are the lifetime $\tau$ and the $\beta$-decay asymmetry $A$ measured with our instrument PERKEO II.

1. Introduction

Particle physics tries to reveal structure and strength of particle interactions and particle properties. In the Standard Model of elementary particle interactions, the fundamental fermionic constituents of matter are leptons and quarks and the leptons and quarks are found in three generations or families. Neutron decay experiments provide us with information about the first family. Involved are the following, fundamental particles: in neutron $\beta$-decay, the d-quark couples to an u-quark and the electron couples to the electronantineutrino via W-boson exchange.

Neutron physics study a number of interesting questions from the field of particle physics and cosmology and tries to shed light on the following topics: quark mixing and the universality of the electroweak interaction, the coupling strength of charged weak currents, a hypothetical violation of time reversal invariance, and the origin of parity violation. Parity is maximally violated in low energy scale. However, we do not have a fundamental justification for parity violation. It is particularly interesting that modern grand-unified theories support a left-right symmetrical universe right after the start of the big bang. Parity violation arises only due to a spontaneous symmetry breaking at some intermediate energy scale. Parity violation is not 100% and right handed contributions in the weak interaction should be found. Measurements of the correlation coefficient B, the correlation between neutrino momentum and neutron spin, are sensitive to right handed current contributions in the weak interaction. However, we have no evidence for right handed currents so far. Another peculiarity of the electroweak interaction is quark mixing. As is well known, the quark eigenstates of the weak interaction do not correspond to the quark mass eigenstates. The weak eigenstates (primed) are related to the mass eigenstates (unprimed) in terms of a $3 \times 3$ unitary matrix $V$. The value of individual matrix elements are determined from weak decays of the relevant quarks. Unitarity requires that the sum of the squares of the matrix elements for each row and column is unity. So far precision tests of the unitarity condition are only possible for the first row of $V$, namely

$$|V_{ud}|^2 + |V_{us}|^2 + |V_{ub}|^2 = 1$$

The Standard Model requires unitarity, that is $\Delta = 0$. Usually, $|V_{ud}|$ is derived from superallowed nuclear $\beta$-decay experiments, combined with kaon, hyperon- and $\beta$-decays.

2. $V_{ud}$ and neutron $\beta$-decay

A determination of $V_{ud}$ involves combining the neutron lifetime $\tau$ and $\lambda$ from a measurement of correlation $A$ or $a$.

$$|V_{ud}| = \sqrt{\frac{k}{f \cdot 1 + \frac{\Delta}{\tau}} \cdot \frac{1}{1 + \frac{3\lambda^2}{2}}}$$

Natural constants and $G_F = (1.16639 \pm 0.00002) \cdot 10^{-5} (hc)^2/GeV^2$ are summed in $k = 861.076s$, $f = 1.71482(15)$ is Wilkinsons [3] radiative corrected phase space factor adjusted for the new neutron-proton transition energy $Q$. Inner radiation corrections $\Delta_1$ [2.4.5] reduce $V_{ud}$ by about 1.2%. For the neutron lifetime, we use $\tau = 885.8 \pm 0.9s$. This value is the Particle Data Group value [1], updated by the new measurement [6]. When we insert our $\lambda = 1.274(2)$ from the PERKEO experiment [7,8], we obtain for $V_{ud}$ from neutron decay

$$|V_{ud}| = 0.9713 \pm 0.0014$$

The unitarity test according to Eq. 1 reads

$$|V_{ud}|^2 + |V_{us}|^2 + |V_{ub}|^2 = 0.9917(29)$$

This value differs from one, the Standard Model prediction by $\Delta = 0.0083$ and the difference is 2.9 times the stated error. In its analysis on the "CKM quark-mixing matrix", The Particle Data Group uses $|V_{ud}| = 0.9728 \pm 0.0012$ from neutron decay. Still, the unitarity gap is 2.2 times the stated error. If we ignore neutrons for now and use $V_{ud}$ from nuclear $\beta$-decay, we still find a $2 \sigma$ standard deviation from unity. This was pointed out earlier by [2.5]. However, some radiative corrections in nuclear $\beta$-decay are difficult to calculate, and therefore the Particle Data Group doubles the error in $|V_{ud}|$, such that without neutron $\beta$-decay data
the unitarity condition is restored to one. An earlier unitarity check can be found in [9]. Fig. 1 shows $|V_{ud}|$ as a function of $\lambda$ with information from nuclear $\beta$-decay, higher quark generation decays and neutron $\beta$-decay. Tab. 1 summarizes information on $|V_{ud}|$.

A violation of unitarity in the first row of the CKM matrix is a challenge to the three generation Standard Model. Data so far do not preclude being more than three generations and CKM matrix entries deduced from unitarity might be altered when the CKM matrix is expanded to accommodate more generations. [1,10]. A deviation $\Delta$ has been related to concepts beyond the Standard Model like couplings to exotic fermions [11,12], to the existence of an additional Z boson [13,14] or the existence of right-handed currents in the weak interaction. [15]. The next section describes measurements of correlation coefficients in the decay of free neutrons with instrument PERKEO II. PERKEO II is the successor of PERKEO I [16].

### 3. Measurement of $\beta$-asymmetry coefficient $A$ and neutrino-asymmetry coefficient $B$

The instrument PERKEO II was designed to measure correlation coefficients in the decay of free neutrons. For a measurement of coefficient $A$, it has been installed at the PF1 cold neutron beam position at the High Flux Reactor at the Institut Laue-Langevin, Grenoble. Cold neutrons are obtained from a 25 K deuterium cold moderator near the core of the 57 MW uranium reactor. The neutrons are guided via a 60 m long neutron guide of cross section 6 x 12 cm$^2$ to the experiment and are polarized by a 3 x 4.5 cm$^2$ supermirror polarizer. The deBroglie wavelength spectrum of the cold neutron beam ranges from about 0.2 nm to 1.3 nm. The degree of neutron polarization was measured to be $P = 98.9(3)$% over the full cross section of the beam. The polarization efficiency remained constant during the whole experiment. The neutron polarization is reversed periodically with a current sheet spin flipper. The main component of the PERKEO II spectrometer is a superconducting 1.1 T magnet in a split pair configuration, with a coil diameter of about one meter. Neutrons pass through the spectrometer, whereas decay electrons are guided by the magnetic field to either one of two scintillation detectors with photomultiplier readout. The detector solid angle of acceptance is truly $2 \pi$ above a threshold of 60 keV. Electron backscattering effects, serious sources of systematic error in b-spectroscopy, are effectively suppressed. The measured electron spectra $N(E_e)$ and $N_i(E_e)$ in the two detectors $(i=1,2)$ for neutron spin up and down, respectively, define the experimental asymmetry as a function of electron kinetic energy $E$. From this experiment we get for correlation

$$A = -0.1189(7) \text{ and } \lambda = 1.274(2) \text{ \cite{7}}$$

Errors and corrections entering Equ. (5) are listed in Tab. 2. The previous world average [1] for $\lambda$ is -1.2670(35). The new world average is $\lambda = 1.2703(28)$ and includes a scale factor of 2.07. The spectrometer PERKEO II is now installed at the new beam position PF1B for a measurement of coefficient $B$. The basic principle of a coefficient $B$ measurement is to measure the charged decay particles in neutron decay in order to reconstruct the neutrino momentum with respect to the neutron spin. Usually this is done with one electron and one proton detector. PERKEO has one electron detector and one proton detector in each hemisphere. This is an advantage over other experiments because it maximizes the sensitivity on $B$. What is more, $B$ shows in a reasonable range no energy dependence on the decay electrons. Systematic errors due to the detector response function should be small. The prob.

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Tab. 2: All corrections and uncertainties entering the determination of $A$. The corrections shown in parentheses are already included in the fit function and thus do not enter in the sum of the corrections that have to be applied to $A$ [6,7].
ton will be measured in coincidence with a decay electron. The $\beta$-detectors are made of plastic scintillators. The proton detectors also make use of the $\beta$-detectors. The idea is to convert a proton into an electron signal. A proton will be accelerated up to 30 keV and eventually hit a thin foil of carbon. About five secondary electrons will be created and detected with the electron detectors. This method of proton detection was already used by Stratowa et al. [17] for a measurement of coefficient $a$. Measurements are underway and first results are expected for the beginning of next year.

4. Summary

To summarize, for the first time, $|V_{ud}|$, the first element of the CKM matrix, has been derived from particle physics, where neutron decay experiments provide precise information on quark $d \leftrightarrow u$ transitions. This new value of $|V_{ud}|$ has been compared with a prediction from higher generation quark decays, taking the unitarity condition of the CKM matrix into account. The prediction differs from $V_{ud}$ based on our neutron decay measurement by $2.9\sigma$ standard deviation. This research was made possible in part by grants from the BMBF under contact number 06HD953.

References

The neutron electric dipole moment (EDM) experiment has continued to be developed by the RAL/Sussex group at ILL and to produce high-quality data. A new world best upper limit to the neutron EDM of $6.3 \times 10^{-26}$ e cm was published [1] in January 1999 based upon data taken at ILL during the period 1996 to 1998. Results from data taken since 1998 now surpass that from the published result and indicate that we are on course to measure, or to set limits upon, this fundamental quantity with a precision approaching $10^{-26}$ e cm by 2004. This is the only operational neutron EDM experiment [2]. For particles to have electric dipole moments, the forces concerned in their structure must be asymmetric with regard to space-parity (P) and time reversal (T). P violation is a well-known intrinsic feature of the weak interaction, but CP (and hence T) violation, which is believed to be responsible for the baryon asymmetry of the universe, has thus far only been positively measured in the $K^0$ system. Significant CP violating effects are however expected to be measured shortly in the $B^0$ system. Such limited information leaves open a wide range of possibilities for competing theories [3] attempting to explain the origin of CP violation. Extensions to the Standard Model of the electroweak interaction, such as additional Higgs fields, right-handed currents or supersymmetric partners typically give rise to dipole contributions which are of order $10^{-25}$ to $10^{-27}$ e cm. Dipole moments of this size might also come from CP violation in the QCD sector of the strong interaction. Experimental measurements of particle EDMs, and in particular that of the neutron, are providing some of the strongest additional constraints on these theories (Fig. 1) and a continuing null result creates for particle physics both Supersymmetric CP and a Strong CP problems.
2. Experimental set-up and techniques

The principle of the EDM experiment is to use the Ramsey resonance technique and measure, with very high precision, the precession frequency of spin polarised ultracold neutrons (UCN) in a weak magnetic field. The precession frequency will change in the presence of an electric field if the neutron has an EDM $d_n$ since the additional torque will either increase or decrease the precession frequency. The Larmor frequencies of the neutrons in an electric field parallel and anti-parallel to the magnetic field, $\nu_{dd}$ and $\nu_{df}$ respectively, relate to $d_n$ via $\hbar(\nu_{dd} - \nu_{df}) = 4d_nE$. The experiment is designed to measure, with the highest possible precision, any shift in the transition frequency $\nu$ when a strong $E$ field is reversed relative to $B$. Our experiment incorporates a magnetometer [4] based on atomic $^{199}$Hg stored simultaneously in the same cell as the neutrons. Fig. 2 shows a schematic of the apparatus.

The error due to counting statistics noise alone is

$$\sigma(d_n) = \frac{h}{2\alpha EN\sqrt{N}}$$

At the moment we take data with $E = 7.5$ kV/cm and $T = 130$ sec when we have $\alpha = 0.65$ and $N = 18000$ neutrons per batch; with each batch cycle taking about 210 s. From one day of data therefore, and allowing for pauses between runs, $\sigma(d_n)$ is about $4 \times 10^{-26}$ cm.

The neutron storage cell has a volume of 20 litres and is made with two flat, circular, aluminium electrodes, separated by a hollow right circular cylinder of quartz, which also acts as a high voltage insulator. The electrodes are coated with a hard, “diamond-like” carbon layer [5]. During the past year we have increased the value of the polarisation product $\alpha$ from 0.45 to 0.65. This represents nearly a 50% gain in EDM sensitivity and has been achieved by developing neutron polarisers with 1000 Å films of pure natural iron sputtered onto 50µ aluminium or silicon substrates. The performance of the mercury magnetometer has been described in some detail [4]. It has considerably reduced magnetic field drift as a source of systematic uncertainty. Surface-barrier charged particle detectors are used for monitoring the incoming UCN flux, and measuring spectral dependence of guide tube efficiencies. These detectors are made using evaporated films of $^{10}$B and $^6$Li as neutron converters. They are also now forming the basis for a new generation of detectors to be used in a cryogenic environment.

Overall the efficiency of the EDM experiment has been considerably enhanced and a figure of merit incorporating all these gains in neutron flux, high voltage, polarisation and running efficiency is shown in Fig. 3 which demonstrates that the sensitivity of EDM data taking has improved by over an order of magnitude since data taking started with this apparatus.

3. Neutron EDM results

The results from ten ILL reactor cycles taken whilst the experiment was still under development were published [1] in 1999 as $d_n = (1.9 \pm 5.4) \times 10^{-26}$ cm. The systematic error is believed to be about 20 times less than the statistical error. This new result [1] when combined with our earlier experiment [6] yielded a new upper limit of $6.3 \times 10^{-26}$ cm. The new experiment has now surpassed the sensitivity of the previous experiment, and the result has the advantage of much lower systematic uncertainties. This is demonstrated in Fig. 4, which shows the measurements resulting from 322 individual runs; the $\chi^2$ for this set of data is 0.98 per degree of freedom using neutron and photon counting-statistics error predictions alone.

A further 320 data runs have been taken since 1998 using an improved experimental set up of higher field gradient and larger diameter storage cell.

4. Future plans for neutron EDM measurements

From this point onwards we can foresee several more phases, each aiming for increased precision, driven on by the knowledge that, at some level, a finite, non-zero, EDM must exist. The first of these phases is to finish the EDM measurement in progress. This programme exploits what is, for the moment, the most potent UCN source in the world; that at the ILL.
We aim to increase our EDM measurement sensitivity from its current level of $4.0 \times 10^{-25} \text{ e cm/day}$ to $2.0 \times 10^{-25} \text{ e cm/day}$ over the next year. At the same time we would take data as intensively as possible over the next three years, reaching an overall statistical error close to $1 \times 10^{-26} \text{ e cm}$. Fig. 5 shows the evolution of the statistical error that we have obtained with its expected future evolution if further data is taken under 3 assumptions: (a) running as now; (b) with a 30% increase in UCN, 10% increase in HT and neutron polarisation and (c) with a 50% increase in neutron numbers and 20% increase in both HT and neutron polarisation. We are optimistic we can obtain at least some of these projected gains in sensitivity.

References

Experimental challenges in neutron decay

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Neutron beta decay offers various possibilities to study the weak interaction at low energy. Experimental access to many different observables enables us to determine important parameters like the weak coupling constants of the neutron and to perform several tests of the electroweak standard model. The latter comprise tests of the unitarity of the weak quark mixing matrix, searches for left-handed currents, searches for scalar and tensor admixtures to the weak Hamiltonian and tests of time reversal invariance. This contribution briefly states some of the possibilities, highlighting work to be done next.

Physics goals
The decaying neutron is an excellent object of study to answer various questions of weak interaction physics. This simple semileptonic transition has exactly known Fermi and Gamow-Teller matrix elements, well-known radiative corrections, and there are no nuclear structure effects. Many observables with impact to particle physics can be measured with high precision. The most intensely studied observables have been the neutron lifetime and a few “classical” angular correlations between the spins and momenta of the particles involved in the decay process. Other quantities and phenomena, not measured so far, are within reach during the next few years. Recent years have seen substantial progress at all fronts of experimentation. A new beam for nuclear and particle physics with unprecedented neutron flux density and total intensity is now available at the ILL. Beam diagnostics, in particular neutron polarisation analysis, has reached a new level of quality. In the center of these developments stand new devices to study the details of neutron decay with much reduced systematic uncertainties. This short contribution shall focus on work to be done next, in accordance with the intention of this symposium.

1) A cosmological argument makes a connection between the neutron lifetime $\tau_n$, the number $N$ of particle families, the ratio $b/\gamma$ of baryons to photons and the helium to hydrogen ratio He/H of the universe. The availability of a precise value of $\tau_n$ permitted to exclude a fourth family of light neutrinos before it was definitely fixed to $N=3$ at LEP/CERN [1]. The argument can now be reversed to calculate a value of He/H. A recent new prediction of this ratio requires $\tau_n$ to be measured better than actually known [2]. Since further progress is to be expected in the rapidly developing field of astrophysics, the challenge is to provide a reference value of $\tau_n$ with best possible precision. New techniques of magnetic trapping of ultracold neutrons (UCN) will help to avoid anomalies in neutron wall interactions governing the fate of lifetime measurements [3,4]. Stronger UCN sources than presently available are needed to exploit the full potential of magnetic UCN trapping in vacuum.

2) The weak interaction is known to mix the eigenstates of the strong interaction. This mixing is described by the unitary Kobayashi Maskawa matrix. Its unitarity can be tested experimentally by measuring the size of its elements. Any deviation from unitarity points at a problem in the current understanding within the standard model (SM). Ultimately, the first element of this matrix, $V_{ud}$, can be determined most precisely in neutron decay. As an obvious advantage with respect to nuclear beta decay no nuclear model dependent effects occur. At present, the combination of the neutron lifetime and the beta asymmetry provides a best value of $V_{ud}$ from neutron decay. The beta asymmetry is sensitive to the ratio $\lambda=g_A/g_V$ of the axial-vector to vector weak couplings. Recent results obtained with Perkeo II indicate a violation of the SM by three standard deviations [5]. Since theoretical uncertainties are believed to be under control even below the present level of precision [6], further improved beta asymmetry measurements are needed. In addition, alternative paths to measure $\lambda$ should be taken as well. The neutrino electron angular correlation and the proton asymmetry have comparable sensitivity to $\lambda$ but they encounter rather different systematic effects. If the knowledge of $\lambda$ can be improved by a factor 3±5, model dependent radiative corrections will start to dominate the analysis, wherefore theoretical efforts are required as well.

3) The helicity structure of the weak interaction can be investigated in neutron beta decay exploiting the fact that, owing to angular momentum conservation, the angular distribution of the decay products depends on the helicity states involved. Today it seems to be well established that the weak currents contain only vector minus axial-vector type contributions, corresponding to left-handed neutrinos. It is now generally believed that this fact is due to a spontaneous breaking of a left-right symmetry which would be restored at a certain high energy. In accelerator experiments one attempts to produce the corresponding heavy gauge bosons in high energy particle collisions. It is noteworthy that neutron decay products with their kinetic energies below 1 MeV can tell us competitively whether or not bosons as heavy as several 100 GeV do exist which mix some right-handedness into the weak interaction. The present mass limit from neutron decay in the minimal left-right symmetric model is ~ 300 GeV at zero mixing angle [7,8] and further progress is within reach. An ultimate yes/no test...
is offered by the rare process of neutron decay into the hydrogen atom [9]. One of its hyper fine states cannot be populated if the neutrino had no right-handed component. The idea is similar to the beautiful Goldhaber experiment. Even with the new cold beam at ILL it will be hard to detect the process, and this experimentum crucis probably has to wait for a next generation spallation neutron source.

4) Several extensions of the SM predict scalar and tensor type weak interactions. Their existence in the real world can be tested in neutron decay in several ways. If non-zero, scalar and tensor couplings appear in most observables as a quadratic admixture, which makes it difficult to reveal them at the percent level. However, there are also observables which contain them linearly. One is the Fierz interference term which can be measured via the electron spectrum or by comparing the values obtained from the beta asymmetry and the neutrino electron angular correlation [10]. A second observable of this type is a triple correlation between the electron momentum and the spins of neutron and electron. This correlation tests the presence of imaginary scalar and tensor interactions. In addition, it changes sign under reversal of time and thus provides a test of time reversal invariance. Hence, containing two "miracles", its first measurement with neutrons, being planned at the new strong beam at PSI, may provide a surprise comparable to the discovery of parity violation in the late fifties [11].

5) A classical test of time reversal invariance (tri) in neutron decay measures the triple correlation between the neutron spin and the momenta of the electron and the neutrino. This observable has recently been remeasured by two groups. The emiT collaboration already published a new limit on the $D$ coefficient at the $10^{-3}$ level of precision [12]. An upgrade of the experiment TRINE [13] shall reach the low $10^{-4}$ region of precision in near future. An interesting property of tri-violating correlations in neutron decay is that for any non-zero result even down to the $10^{-6}$ level one can exclude final state effects to mimic true time reversal violation. To approach ultimate limits set by theory will continue to be a great challenge to experimentalists.

Conclusions

Meeting the experimental challenges requires work in two directions. The development of new neutron decay spectrometers is needed as well as a further improvement of sources and beams. At the cold neutron front, a new milestone was set with the recent commissioning of the upgraded polarised neutron beam facility PF1. In order to make efficient use of its excellent properties, high quality auxiliary devices should be provided. These are (1) a new large surface polariser which does not deteriorate the small divergence of the beam, (2) a neutron focussing device, (3) implementation of a new method for polarisation analysis developed recently at ILL [14], (4) a stable flux monitor in the primary beam and improved flux distribution measurements. Experiments sensitive to inhomogeneities in the neutron polarisation would profit from the development of a large surface $^{3}$He or proton spin filter as primary beam polariser.

References

Quantum states of the neutron in the gravitational field

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100 years ago, Max Plank introduced the concept of minimal energy quantum, which can be transmitted through physical interactions. Soon it became evident that quantum (discrete) properties of matter are dominant in a variety of phenomena: quantum states of electrons in an electromagnetic field are responsible for the structure of atoms, quantum states of nucleons in a strong nuclear field are responsible for the structure of atomic nuclei. An example for quantum effects in the weak interaction is the possible neutrino oscillations. We report here on the first observation of quantum states in the gravitational field.

1. Introduction
The Pauli principle couples the Plank constant to the minimum values of the distance \( \Delta z \) and the velocity \( \Delta v \) at which the quantum phenomena become dominant for the particle with the mass \( m \):

\[
\Delta z \Delta v \sim h/m (\Delta v \ll c).
\]

The smaller are \( m \) and \( \Delta v \), the larger is \( \Delta z \).

When the particle is placed in a potential well during time period longer than \( \Delta \tau \sim h/\Delta E \), quantum states with an energy difference \( \Delta E \) can be resolved. In order to allow for an experimental observation, all other interactions must be so small that their interference with the gravitational quantum phenomena can be neglected. The choice of a neutron, a neutral long-lived particle, satisfies the above mentioned conditions. To our knowledge, the Plank constant and the neutron acceleration in the gravitational field have been considered simultaneously only in few papers (see for instance refs. [1,2,3]). As pointed out in ref. [4], it is possible to observe quantum states of neutrons in the Earth’s gravitational field. Earlier, a complete analytical solution of the mathematical problem related to the quantum states of particles in a gravitational field was published in textbooks on quantum mechanics (see for instance [5,6]). Ultracold neutrons [7,8] provide a convenient method for such a study. The experimental technique using ultracold neutrons was developed during the last 30 years. Recently a one-component neutron gravitational spectrometer of high resolution was built at ILL [9]. The first measurement at the ultra cold neutron beam [10] with this device showed the existence of the lowest neutron quantum state but hinted also to the potential for further investigations [11].

2. Experiment
When neutrons with extremely low energy fall down in the Earth’s gravitational field – above a reflecting mirror – then they do not move continuously along the vertical direction but rather jump from one height to another one. Obviously, the Earth’s gravitational field alone does not create such a potential well as it does not allow particles only to move upwards too high; the other wall of the well is obtained by introducing a horizontal reflecting mirror. A description of the interaction of neutrons with surface can be found in textbooks on neutron physics (for instance [12,13]). As in such a situation no forces act in the horizontal plane, quantum states can only be observed in the vertical direction. Fig.1 illustrates how quantum states of neutrons in the Earth’s gravitational field can be observed. The neutron wave is reflected from the bottom mirror and interferes with itself. Such self-interference provides a standing wave of neutron density. In a vertical slice, the neutron beam above the bottom mirror consists of plane neutron “jets” with a neutron density, which depends on the distance from the mirror. One lets “flow” neutrons with a cer-

Fig.1: Quantum states of neutrons are formed in the potential well between the Earth’s gravitational field on top and the horizontal mirror on bottom. The probability of finding neutrons at the height \( z \) corresponding to the \( n \)th quantum state, is proportional to the square of the neutron wave function \( \psi_n(z) \). The vertical axis \( z \) gives an idea about the spatial scale of this phenomenon.
tain horizontal velocity distribution through a slit. An absorber/scatterer placed above the incident neutrons and the reflecting mirror below act as a selector for the vertical velocity component. From fig.1 we expect a stepwise dependence of the neutron flux as function of the height of the absorber: if its height is smaller than the spatial width of the lowest quantum state, then the neutron transmission should be zero. When the height is equal to the spatial width of the lowest quantum state then the transmission is expected to increase sharply. The height of such a step is equal to the first state population. Further increase in the absorber height should not increase the neutron transmission as long as the height is smaller than the spatial width of the second quantum state. Then again the transmission should increase stepwise. At sufficiently high absorber position one should approach the classical dependence and the stepwise increase should be washed out.

3. Results
Measurements at small absorber height showed the existence of the lowest quantum state; at sufficiently large absorber height the purely classical behaviour is observed (fig.2) [11]. The observed effects are consistent with the non-transparency of the slit formed by the bottom mirror and the absorber/scatterer for neutrons as long as the absorber height is smaller than the spatial width of the lowest quantum state. Careful analysis of the experiment allowed to rule out any systematic errors. In particular, the shape of the transmission curve (figs.2, 3) does not depend on the value of the horizontal velocity component but it depends only on the vertical velocity component, as expected. A 15µm-wide slit is not yet transparent for neutrons but it is sufficiently large to observe its transparency for visible light. This is a good check of the setup as the light wavelength of ~0.4µm is much larger than the neutron wavelength of ~0.01µm. Evidently, the difference results from the fact that under normal laboratory conditions the Earth’s gravitational field does not act noticeably to the light beam but it forms bound quantum states for neutrons. Fig.3 shows in a larger scale and with additional statistics the initial part of the dependence analogous to fig.2. One can even notice here indications of the stepwise character of such a dependence not only for the lowest quantum level.

4. Conclusion
This first experimental observation of quantum state in the gravitational field showed once again the universality of the quantum properties of matter. As the parameters of quantum states are defined in such a system mainly by the interaction of the neutron with the gravitational field, the presented phenomenon can be considered as a tool for further investigations of fundamental properties of matter.

References:
Mini-D₂: A powerful source of ultracold neutrons at FRM-II

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The new Munich high-flux reactor FRM-II offers the possibility to install a unique source for ultracold neutrons (UCN), the Mini-D₂ UCN source. A small volume of solid deuterium, positioned close to the cold source of FRM-II and kept at a temperature of about 5 K, will be used as a converter. This new source, best suited for storage experiments, is designed to be much superior to any existing UCN facility. In pulsed mode it shall provide UCN densities up to 10⁴ n/cm³ for neutrons with energies below 250 neV, orders of magnitude larger than the source at ILL (~50 n/cm³). Operated in the continuous mode, up to 5·10⁵ n/cm²s may be extracted. At the moment the technical design is in its final stage.

1. The principle of the Mini-D₂ source

A new, powerful source of UCN shall be installed in the beam tube SR-4 of the Munich high-flux reactor FRM-II. It employs a small amount of solid deuterium at a temperature of about 5 K, positioned very near to the cold-neutron source inside a long evacuated tube. The UCN are produced by down-scattering the cold neutrons in the D₂ converter and accumulated in the tube. Within a few minutes a UCN density of about 10⁴ n/cm³ builds up in the storage tube. By opening the valve at the end of this tube the experiment will be periodically supplied with up to 2·10⁸ UCN. Operated in continuous mode the source will provide a UCN flux of about 5·10⁵ n/cm²s. In the case of good matching of the attached experiment to the source – which is especially simple for Mini-D₂ – it is feasible to extract and transport up to 25% of the neutrons to the experimental setup.

The principle of the Mini-D₂ source is illustrated in Fig.1. Its concept is based on the following ideas:

- The temperature of the converter for the production of UCN by down-scattering of faster neutrons is kept low enough to let the equilibrium of UCN production and losses no longer be determined by up-scattering, but by absorption in the converter (super-thermal source). Solid deuterium at 5 K temperature meets this requirement [1,2].
- The Mini-D₂ source is best suited for storage experiments. The experimental volume is refilled with UCN periodically every few minutes. In the meantime the continuously produced UCN are accumulated in the storage tube, which then delivers the UCN to the experiment. Accumulation takes place as the losses in the storage tube are negligible compared with those in the converter (storage source).
- The converter is placed as close as possible to the cold-neutron source. Feeding the converter with cold neutrons reduces its optimum size down to a few centimeters – roughly the UCN self-absorption length (Mini-D₂)[3].

2. Technical design

The end piece of the in-pile part of the source is shown in Fig. 2. The storage tube is made from an aluminum alloy and covered on the inside with Ni and Be. It is cooled by helium gas at 25 K. The end part of the storage tube, which contains the converter, has a separate cooling circuit operated with super-critical helium.
at 4.7 K. By this condition the deuterium is solidified only in the end part. The central cold finger serves to improve cooling of the solid D₂.

The in-pile cryostat is a strong double-wall construction made of zircaloy. It is cooled by helium gas at room temperature. Figure 3 shows a cut-away view of the source in the SR-4 beam tube. The length of the in-pile part is 4 meters; the total length of the storage tube from the converter to the attached experiment exceeds 8 meters, the diameter is about 6 cm.

Detailed information on the Mini-D₂ UCN source may be found in the internal report [4]. It includes a description of the physics background, associated calculations and detailed technical proposals for cooling circuits and mechanical design for all systems of the source. Special attention is paid to safety problems.

3. Status of the project
The project was initiated in 1998. Currently it is in an advanced stage of the technical design and of the official approval. The start of the source operation is scheduled for 2003.

REFERENCES
A detector for ultracold neutrons (UCN) based on a silicon PIN diode has been developed. To minimize the reflectivity for UCN, multilayers consisting of $^{62}\text{Ni}$ and $^{6}\text{LiF}$ were evaporated onto the surface of the diode. The intrinsic detection efficiency is nearly 1, as in addition to the low reflectivity either the 2.06 MeV a particle or the 2.73 MeV triton is detected. In a short running time at the PF2 beam line at ILL in February 2000, the UCN detection efficiency was measured and was found to be higher than that of a $^3\text{He}$ gas detector over the entire UCN energy range. The development of UCN PIN diode detectors with multilayers composed of different materials is being continued.

Ultracold neutrons (UCN) have kinetic energies below 200 neV, which corresponds to velocities of about 7 m/s. This makes them ideal for storage in material and magnetic bottles and thus for experiments like EDM or life-time measurement.

To detect UCN with a semiconductor device, a converter which produces charged particles is needed. Commonly, a material with a high cross section for neutron capture reactions such as $^7\text{Li}$ or $^10\text{B}$ is used. This material is then evaporated onto the surface of the detector. The TUM UCN detector uses $^6\text{LiF}$ as converter, because the $^6\text{Li}(n,\alpha)\text{t}$ reaction is a two-body reaction with a rather high Q-value (2.06 MeV for the a, 2.73 MeV for the triton). As the n is nearly at rest, the a and the triton will be emitted at an angle of 180° with respect to each other. Thus, one of the two will reach the detector with a high probability, making the intrinsic detection efficiency nearly one.

A typical spectrum, as recorded in a test run at the ILL PF2 beam line in 2000, is shown in Fig. 1. More results of the test run may be found in [1].

One problem is the fact that the surface potential and therefore the reflectivity of $^6\text{LiF}$ for UCN is very high. To remedy this, we use a multilayer structure consisting of materials with both positive ($^6\text{LiF}$) and negative ($^{62}\text{Ni}$) scattering potentials for UCN. Ideally, the two should cancel each other, making the surface potential for UCN zero.

Underneath the multilayer structure is a layer of $^{62}\text{Ni}$ which has a high reflectivity for UCN. In case a neutron passes through all layers without being captured by $^6\text{Li}$, it will be reflected back and pass through the $^6\text{LiF}$ and $^{62}\text{Ni}$ layers again. Hence almost every neutron will be detected once it is inside the multilayers.

Figure 2 shows the calculated reflectivity of a typical multilayer structure versus the neutron energy. The reflectivity $R$ was obtained using a neutron optics program, where the reflected amplitude, and thus $R$, is calculated by matrix multiplication [2]. The structure calculated has the following composition:

1) A V layer of 50 Å thickness on top,
2) 90 layers, each consisting of one layer of $^{62}\text{Ni}$ (with a thickness of 30 Å) and one of $^6\text{LiF}$ (with a thickness of 45 Å),
3) the same as 2), but 115 layers and the thickness of the $^6\text{LiF}$ layer is 70 Å,
4) one layer of $^{62}\text{Ni}$ as reflector (with a thickness of 850 Å).

This setup will be tested at ILL in April 2001.
The tests described in [1] were done with a less complex structure, containing 150 multilayers, each consisting of one layer of $^{60}$Ni and one of $^4$LiF; the thicknesses were 30 and 60 Å, respectively.

The detector efficiency was measured for different energies using a gravity spectrometer shown in Fig. 3. It consists of a cylindrical storage cell which may be connected to a UCN inlet and a vertically mounted detector tube made from stainless steel. After 40 s filling time the UCN are stored for another 40 s and energy selected (0-38 neV) by an adjustable absorber. Finally, the detector, mounted at height $L$, is exposed to the UCN. The height $L$ shifts the selected energy range.

The results were promising; a detector efficiency of up to 80% was measured in the energy range between 100 and 200 neV. This experimental setup will also be used to test the new multilayer structure described above.

This work is partly supported by a programme “Grant-in-aid for the specially promoted research” (No.10101001), Ministry of Education, Japan.

**Fig. 3: Gravity spectrometer.**

**References**


Neutron Physics as a Key to the Quantum Chaos Problem

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A new approach to the quantum chaos problem is briefly discussed, which resulted as a generalization of the neutron compound resonance theory.

While the importance of classical chaoticity is well understood by now, the mere possibility of chaos in quantum systems is still opened to discussion. Since the concept of trajectory and its Lyapounov’s instability, underlying the classical chaos foundations, can not be applied to quantum systems, it is often suggested (see, e.g. [1]) to search only for the "quantum signatures" of the classical chaos. In order to do this, one takes two classical systems, one of which is regular and the other chaotic. Using the correspondence principle one constructs two Schroedinger's equations and compares all the properties of their solutions in hope to find some difference, which might be called such a "signature" of chaos. The only more or less generally accepted "signature" found in such a way is the nearest level distribution law (see, e.g. [2]). For the quantum chaotic system the probability to find the neighbouring level, which differs from a given one by the energy ε is defined by Wigner law:

\[ P(\varepsilon) = \frac{\pi \varepsilon}{2D^2} \exp \left\{ -\frac{\pi \varepsilon^2}{4D^2} \right\} \]  (1)

Here D is the system's average level spacing. The specific feature of (1) is level repulsion: \( P \to 0 \) for \( \varepsilon \to 0 \).

Since, however, there is no generally accepted definition of the quantum chaoticity this empirically found "signature" of chaos still lacks the fundamental explanation.

One should keep in mind that the law (1) was first observed in the low-energy neutron scattering on nuclei and perfectly described the distribution of compound nuclei resonances. One of the main features of these resonances is the absence of any good quantum numbers (integrals of motion) but for the trivial ones (such as energy and spin). This fact urged us to consider the problem of chaos in a more general way [3 - 5].

It is well known in classical mechanics that the Hamiltonian system with N degrees of freedom might have \( M \leq N \) independent first integrals of motion (conservation laws), which according to Noether's theorem, result from the symmetry of the system. According to Liouville-Arnold theorem the system is integrable and its motion is regular if \( M = N \). If the systems' Hamiltonian is perturbed in such a way that \( M \) becomes less than \( N \), the system becomes chaotic.

The concept of symmetry (unlike the trajectory) can be applied to both classical and quantum mechanics. One should only substitute the classical integrals of motion by the "good" quantum numbers (eigenvalues of the operators commuting with the Hamiltonian). Thus the regular quantum system is the one whose symmetry is so high that it has \( M = N \) integrals of motion. It becomes chaotic if its symmetry is broken in such a way that \( M < N \).

A rather typical feature of the quantum Hamiltonian \( H_0 \) with high symmetry is the high degree of degeneracy of its energy levels. The perturbation \( V \) which breaks its symmetry removes the degeneracy. This removal is the essence of Wigner's level repulsion law. However, this perturbation also mixes the eigenfunctions \( \psi_0 \) of \( H_0 \) corresponding to the energy eigenvalues \( \varepsilon_0 \). Now we expand the eigenstates \( \psi \) of the non-integrable Hamiltonian \( H = H_0 + V \) over the "regular" basis \( \phi_i \):

\[ \psi = \sum c_i \phi_i \]  (2)

and look for the probability \( P(E) = |c_i|^2 \) to find the original "regular" component \( \phi_i \) in different \( \psi \). From the theory of the neutron strength functions \( S(E) \) we know (see, e.g. [6]) that the probability \( P_i \) is centered around the "original" energy \( \varepsilon_i \) and tends to saturate to unity over the characteristic interval \( \Gamma_{\varepsilon_i} \):

\[ S(E) = \frac{|c_i|^2}{D} = \frac{\Gamma_{\varepsilon_i}}{2\pi(E - \varepsilon_i)^2 + \Gamma_{\varepsilon_i}/4} \]  (3)

Here D is the average level spacing of the non-integrable system and \( \Gamma_{\varepsilon_i} \) is defined [3] by the m.s.r. matrix element \( \bar{\nu} = \sqrt{|\nu|^2} \) of the perturbation mixing the basic states \( \phi_i \) and by the degeneracy rank \( N_i \) of the initial level \( \varepsilon_i \):

\[ \Gamma_{\varepsilon_i} = \bar{\nu} \sqrt{N_i} \]

Thus the system becomes formally non-integrable as soon as \( \Gamma_{\varepsilon_i} \) deviates from zero. However, while the ratio:

\[ \kappa = \frac{\Gamma_{\varepsilon_i}}{D_0} \]  (4)

(\( D_0 \) is the level spacing of the initial regular system) is smaller than unity the traces of the initial good quantum numbers (and initial symmetries) are quite obvious as isolated maxima of the strength function. This is the case of the "soft chaos".
When $\kappa$ exceeds unity these traces of regularity disappear since it is impossible to distinguish between the successive strength function maxima corresponding to the different values of the original quantum numbers. This means that we approach the domain of the complete stochasticity or the “hard chaos”. Thus the experience accumulated in studies of the neutron compound resonances allows us not only to formulate the general definition of chaoticity (both classical and quantum), but also gives us quantitative measures $\Gamma_{spr}$ and $\kappa$ of the quantum chaoticity. We had demonstrated (see, e.g. [3]) that in the classical limit the quantity $\Gamma_{spr}/\hbar$ transforms into the Lyapounov exponent $\Lambda$ or into the Kolmogorov-Sinai entropy. We also showed [3 - 5] that our quantum chaoticity criteria apply well to the investigation of transitions from regularity to chaos for the quantum analogues of the most popular systems (Henon-Heiles and diamagnetic Kepler problems) studied in classical chaos.

References

Test of Time Reversal Invariance in Neutron Decay

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In the decay of free, polarised neutrons, time reversal invariance can be tested by measuring the triple correlation between the spin of the decaying neutron and the momenta of electron and antineutrino. An observation of this correlation, described by the coefficient \( D \neq 0 \), would be a strong hint on physics beyond the Standard model of particle physics. Previous measurements were mainly limited by statistics, but current measurements scratch a range where systematic effects get important. We describe requirements for experiments that could go down to the range \( D \approx 10^{-4} \) and concentrate thereby on the neutron beam properties.

1. Motivation

It was believed for a long time that physical laws do not distinguish between the world and the mirrored world, between a world made of particles and one made of antiparticles, or between two worlds differing just by the direction of time. Consequently, the laws of classical mechanics or electrodynamics are invariant under the discrete symmetries P (Parity), C (Charge conjugation) and T (Time reversal). For weak interactions, however, only the renunciation of these symmetries, first proposed by Lee and Yang in 1956, allowed a consistent description of the observed phenomena. P and C seem to be maximally broken here, whereas only a tiny violation of the combined symmetry CP was found in the neutral kaon system in 1964. Several theories came up to explain this tiny violation, and the situation was clarified only recently by the proof of direct CP violation in favour of the explanation within the Standard model. However, the deeper origin of the violation of these symmetries is not understood. Furthermore, the baryon-antibaryon asymmetry in the universe seems to request a CP violation that goes beyond the Standard model.

CP violation is related to T violation via the CPT theorem. To evaluate different theoretical models, T and CP violation have to be tested in various systems. In neutron decay the correlation coefficient \( D \) is a sensitive parameter. The Standard model predicts \( D \approx 10^{-12} \) whereas several theories allow values up to \( 10^{-4} \). Final state interactions play a role only two orders of magnitude below the current experimental world average of \( D = 0.5(1.4) \times 10^{-4} \) [1] (as reported by particle data group, the latest published single measurement \( D = (0.6 \pm 1.2 \pm 0.5) \times 10^{-3} \) [2] is not included yet).

2. Requirements for a D Measurement

The differential decay probability of polarised neutrons can be written as [3]:

\[
\frac{dW}{dE_e d\Omega_e d\Omega_\nu} = G(E_e) \left[ 1 + a \frac{\vec{p}_e \cdot \vec{p}_\nu}{E_e E_\nu} + b \frac{m_\mu}{E_e} + \frac{\sigma_\nu}{\sigma_e} \left( A \frac{\vec{p}_e \cdot \vec{p}_\nu}{E_e} + B \frac{\vec{p}_e \cdot \vec{p}_\nu}{E_e} + D \frac{\vec{p}_e \cdot \vec{p}_\nu}{E_e} \right) \right]
\]

Here, \( \vec{p}_e \) and \( E_e \) are the momenta and energies of electron \( e \) or antineutrino \( \bar{\nu} \), respectively, \( \vec{p}_\nu \) the spin of the neutron, and \( G \) the phase space factor. \( a \) and \( b \) are decay coefficients that exist already in a P, C or T invariant theory whereas the coefficients \( A \) and \( B \) are related to parity and \( D \) to time reversal violation. The values reported by particle data group [1] are \( a = -0.102(5) \), \( A = -0.1162(13) \), \( B = 0.983(4) \), \( D = 0.5(1.4) \times 10^{-4} \); \( b = 0 \) in standard V-A theory. Parity is violated in neutron decay whereas only upper limits have been found on time reversal violation.

For the determination of the \( D \) coefficient the count rate of a combination of an electron detector \( i \) and a proton detector \( j \) has to be measured for both neutron spin directions. These count rates are related to \( D \) by integrating (1) over the acceptance of the detector combination. By calculating the asymmetry

\[
\alpha^i = \frac{N^i - N^\bar{i}}{N^i + N^\bar{i}} = \frac{1}{2} \left( \frac{\vec{k}^i_x + \vec{k}^\bar{i}_x}{\vec{k}^i_x + \vec{k}^\bar{i}_x} \right) \left( \vec{H} \vec{k}^i_x + \vec{B} \vec{k}^\bar{i}_x + \vec{D} \vec{k}^i_x \right)
\]

one gets independent on homogeneous detector efficiencies. The \( \vec{k}^i_x \) are vector apparatus constants that describe the sensitivity of the detector versus the coefficient \( \eta \in \{A,B,D\} \). Since \( \vec{k}^i_x \propto \vec{p}_\nu \) whereas \( \vec{k}^\bar{i}_x \propto \vec{p}_e \) and \( \vec{k}^i_x \propto \vec{p}_e \) one can design apparatus with \( \vec{k}^i_x \parallel \vec{k}^\bar{i}_x \parallel \vec{k}^i_x \). For such apparatus, the influence of the coefficients \( A \) and \( B \) vanishes if the polarisation \( \vec{P} \) is parallel to \( \vec{k}^i_x \). But any small deviation (misaligned polarisation, nonzero beam divergence) can cause huge systematic effects since \( A, B >> D \). Therefore, the detector has to fulfils the following conditions:

1. There exist two orthogonal mirror planes of the decay volume.
2. For each detector combination, there exist also all detector combinations mirrored at both planes.

The simplest arrangement that fulfills (i) and (iii) is given in Fig 1. One finds

\[
4D \vec{P} \cdot \vec{k}_x = \alpha^1 - \alpha^\bar{1} + \alpha^{1-} + \alpha^{1+}
\]

which is insensitive to \( A \) and \( B \) in first order. This is still true for small deviations of the polarisation from the detector axis (defined
by the line of intersection of the two mirror planes) and for a divergence of the beam compatible with (i). In fact, the last detectors for \( D \) show at least these symmetries. It should be mentioned that an optimisation of the statistical sensitivity of the apparatus suggests a modification of the simplest arrangement to include larger angles between electron and proton detector. One finds that the statistical sensitivity is maximised for angles of about 135° (see [2,4] for details).

3. The Trine D Measurement

Trine is the latest and up to now most precise measurement of the \( D \) coefficient. It was carried out in 2000 at ILL. The apparatus consists of four plastic scintillators and four wire chambers for electron detection and of 12 detector planes with four PIN-diodes per plane for proton detection. A cross-section can be found in Fig. 2. The detector fulfills the conditions (i) and (ii). The magnetic guiding field for the neutron spin was provided by a long coil with correction loops at the ends; the earth field was shielded using a mu metal tube.

In 2000, approximately 50 million events were collected. Presently 30 million events are already analysed giving the preliminary result \( D_{\text{prelim}} = (-3.1 \pm 6.2_{\text{stat}} \pm 4.7_{\text{syst}} \pm 4.7_{\text{syststat}}) \cdot 10^{-4} \). The systematic error can be divided into a detector related contribution of \( \delta_{\text{det}} D_{\text{prelim}} = 2.3 \cdot 10^{-4} \) and a beam related contribution of \( \delta_{\text{beam}} D_{\text{prelim}} = 4.1(4.7) \cdot 10^{-4} \) which was determined experimentally and includes therefore the statistical uncertainty syststat. Although \( \delta_{\text{beam}} D_{\text{prelim}} \) is still consistent with 0 first Monte Carlo simulations indicate a significant deviation from 0 of a few times \( 10^{-4} \). This systematic error was caused by the inhomogeneous beam profile (Fig. 3) that does not fulfill condition (i) and opens the door for an influence of \( A \) and \( B \) via the slightly misaligned magnetic field (misalignment \( <5 \cdot 10^{-3} \)). The reason for this profile is an inhomogeneous transmission of the focusing polariser used. It should be mentioned that already the neutron beam at the guide exit of PF1 is inhomogeneous due to upstream experiments that use parts of the beam.

For the present Trine measurement, the spatial resolution provided by the wire chambers and the large number of detector planes was essential to keep the systematic error to an acceptable value. See [4] for a detailed analysis.

4. Conclusions and Outlook

The precision of a \( D \) measurement is determined not only by the detector but also by the provided beam. The neutron beam determines the statistical and the systematic precision of the experiment. For a low systematic error, a homogeneous beam with a small divergence is essential. For the future equipment of the new cold neutron beam facility PF1b at ILL we derive the following:

1) The neutron beam must not be interrupted for upstream exper-

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Fig. 1: Simplest symmetrical detector for \( D \).

Fig. 2: The Trine detector. A to D indicate the scintillators, 1 to 4 the wire chambers for electron detection and a to d the PIN diodes for proton detection. The neutron beam is in the centre, the polarisation perpendicular to the plane of the drawing.

Fig. 3: Horizontal (left) and vertical (right) cuts of the neutron beam intensity at three different positions in the decay volume (0=centre). The beam is inhomogeneous in \( y \) direction.
iments to avoid inhomogeneous neutron beam distribution and a decreasing flux. 2) A nonfocusing polariser exploiting the large guide cross-section and with homogeneous transmission should be developed. 3) $^3$He spin filters exhibit homogeneous transmission, do not increase the beam divergence, and produce almost no gamma background. They are an interesting alternative to standard supermirror polarisers and should be made available for long term experiments. With these conditions, an improved alignment of the magnetic field, and an upgraded detector a precision of the order of $10^{-4}$ for $D$ seems achievable.

References
Experimental approach to search for the origin of the T-odd triple correlation in ternary fission

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The experimental possibilities to search for the origin of T-odd triple correlation in ternary fission, discovered at ILL by the Collaboration of ITEP-TU-DTU-ILL-PNPI-KI are discussed.

1. Introduction
A few years ago the left-right asymmetry of long-range \( \alpha \)-particle emission in ternary fission of \( ^{235}\text{U} \) induced by cold polarized neutrons has been discovered by the Collaboration of ITEP-Tuebingen University-Darmstadt Technical University-ILL-PNPI-Kurchatov Institute [1]. Such an experiment had been proposed many years ago to test the time reversal invariance (TRI) [2]. The observed correlation can be described by the expression:

\[
W = \text{const.}(1+D_{\alpha} S \cdot [P_{\nu}, P_{\alpha}])
\]

(1)

where \( D \) is the correlation coefficient, \( S \) a unit vector in the direction of neutron polarization, \( P_{\nu} \) and \( P_{\alpha} \) are unit vectors in the directions of light fragment and \( \alpha \)-particle momenta, correspondingly. The expression (1) looks to be T-odd because it changes its sign under time reversal. However theory predicts that such a correlation may also be simulated by an interaction in the final state of the reaction. In this case the coefficient \( D \) must involve a phase factor which also changes its sign. The experimental value of \( |D| \) is equal \( 3 \cdot 10^{-2} \) although it could be as large as \( 10^{-2} \) taking into account the (unknown) average degree of compound nuclei polarization. Digressing from the problem of TRI, such a large magnitude of this correlation coefficient in the reaction with a colossal number of final states is very surprising. Of course, we have other examples of a similar large correlation in fission such as the P-odd correlation [3] which arises from a weak interaction of nucleon in nucleus or a P-even correlation [4] due to the interference of s- and p-waves in the entrance channel of the reaction. The semi-classical model [5] explains this phenomenon as a result of interference of transitional amplitudes from opposite parity states in saddle to final states. The angular part of the wave function at saddle already shows the correlation of the pear-shaped nucleus with the spin of a fissionable nucleus. It is evident that this model is useless for the case of ternary fission.

2. Possible explanation of observed correlation
More probably that observed correlation is a result of interactions in the final state. It can be an electromagnetic or/and strong interaction between \( \alpha \)-particle and deformed nucleus at scission point, or between \( \alpha \)-particle and two fragments after scission (three-body problem!). The experimental data [1] show that the magnitude of \( D \) depends on the kinetic energy of \( \alpha \)-particles – the absolute value of \( D \) rises with \( E_{\alpha} \). This is very important because it is the oblique evidence that correlation (1) arises from interaction in final state. It should be pointed out that the coefficients of P-odd and P-even correlations in binary fission do not depend on mass/energy of fragments. There is a simple explanation for the large magnitude of the T-odd correlation: the magnitude of the effect for definite final state is an order of unit, the number of final states for the \( \alpha \)-particle is not so large as for fragments. As a result of summation over \( 10^4 - 10^6 \) final states the magnitude of this effect is \( 10^{-2} - 10^{-3} \).

3. Experimental possibilities
To verify the hypothesis about the final state interaction origin of the correlation (1), we have proposed to investigate the dependence of the correlation coefficient \( D \) on incident neutron energy. In the case of final state interaction, the magnitude of the effect must not depend on the excitation energy of fission nuclei by definition. Of course, in principle, the dependence of \( D \) on compound nucleus spin value is possible. In the case of s-neutron capture the spin value of the compound nucleus is \( I = J \pm 1/2 \), where \( J \) is the spin value of the target nucleus. At any neutron energy the ratio of two values of \( I \) population is defined by energy position of resonances with spins \( I = J + 1/2 \) and \( I = J - 1/2 \). There are two target nuclei \( ^{235}\text{U} \) and \( ^{239}\text{Pu} \) for which the complete data concerning partial spin-dependent fission cross section are available for the neutron energy region \( 0.025 \text{ eV} - 0.4 \text{ eV} \). Thus, if measurements will show any dependence of the correlation coefficient \( D \) (normalized to 100% of fission nuclei polarization) on neutron energy, it will mean that the observed correlation cannot be explained by interactions in the final state. Otherwise it will be necessary to distinguish between electromagnetic and strong interactions in the final state. For that we proposed to search for the same correlation for a neutral ternary particle.
So called “ternary fission” is the binary fission accompanied by a light charged particle, such as α, D, T, He and so on. According to many theoretical models the third light particle originates in the neck before or during scission. It is obvious that the emission of a neutron by the same mechanism cannot be forbidden. Moreover, because there is no Coulomb barrier for a neutral particle the neutron emission probability should be larger than the probability of proton emission. There is a lot of experimental data concerning the angular distribution of prompt fission neutrons. To fit these data with the assumption that neutrons are emitted by entirely accelerated fragments it is necessary to add from 3% up 35% [6] of the spherically symmetric part which, therefore, should be emitted before scission. More probably, they are emitted by neck, i.e., such a mode of binary fission may be considered as the “neutral component” of ternary fission.

Of course, in addition to charge difference there is another essential difference between the α-particle and the neutron. The latter has non-zero spin and, therefore, spin-orbit interaction is possible too. So, the magnitude of correlation coefficients for the neutron and α-particle should not be the same. Moreover, the magnitude of the real asymmetry for neutrons should be suppressed by a background of neutrons which are emitted from fragments. But due to essential differences in the angular and energy distributions of scission and fragment neutrons there is a possibility to evaluate the true value of D using two neutron detectors situated at 90° and 45° relative to the fission axis. If non-zero asymmetry is found, by fitting the result of measurements D(90°) and D(45°) it is possible to evaluate not only the true asymmetry coefficient but also the ratio of scission neutrons to fragment neutrons.

Indeed, the correlation under discussion looks like:

\[ W = \text{const.}(1 + D_s S[ P_{\alpha}, P_{ns}]) \]  

where \( P_{\alpha} \) is the unit vector in the direction of scission neutron momentum.

Thus the count rate of coincidence between light (or heavy) fragment and scission neutron in binary fission induced by longitudinally polarized neutrons can be expressed as:

\[ N = N_0(1 + D_s P B) \]  

Where P is the polarization degree of fissile nuclei, and B is the average value of the angular function S[ P_{\alpha}, P_{ns}] which depends on the geometry of the experiment. The sign of B can be changed by reversal of the neutron polarization direction (+ and -). The maximum value of IBR takes place for an orthogonal geometry of 3 vectors. Therefore, for two opposite directions of neutron beam polarization we have:

\[ N(+) = N_0(1 + DP<B>) \]  
\[ N(-) = N_0(1 - DP<B>) \]

and measured asymmetry equal to:

\[ A = \{N(+) - N(-)\}/\{N(+) + N(-)\} \]  

The magnitude of the correlation coefficient D is equal to:

\[ D = A/\text{P}<B> \]  

In the presence of background from fragment neutrons, which should not display an asymmetry (6) it is easy to find that the measured asymmetry will be suppressed by a factor \((1 + N_{\text{fn}}/N_{\text{ns}})\), i.e.:

\[ A^* = A/(1 + \delta) ; \delta(\theta) = N_{\text{ns}}(\theta)/N_{\text{ns}} \]  

where \( \theta \) is the angle between the axis of the neutron detector and the fission axis. As was pointed out above, the scission neutron angular distribution is spherically symmetric while fragment neutrons correlate with the fission axis and its angular distribution depends on the kinetic energy of neutrons. Moreover, the mean energy of scission neutrons is less than the mean energy of fragment neutrons. Therefore, by measuring the asymmetry of the coincidence count rate at \( \theta = 90^\circ \) and \( \theta = 45^\circ \) for different regions of neutron kinetic energy it is possible to evaluate the true asymmetry coefficient \( D_{\text{ns}} \) for the “neutral component” of ternary fission:

\[ A^*(90^\circ,E_\alpha)/A^*(45^\circ,E_\alpha) = <B>(45^\circ)/<B>(90^\circ) \]  

Equation (9) is the basic one for evaluation of \( \delta \) by Monte-Carlo simulation using the well known angular distribution of fragment neutrons as a function of neutron energy. The magnitude of B(\( \theta \)) can also be calculated using M-C simulation. Of course, this is possible only in the case where the measured asymmetry does not equal zero. In the last case, the upper limit for the correlation coefficient can be found.

The preliminary runs of measurements of \( D_\alpha \) for 233U and 239Pu targets have been performed on the polarized neutron beams of the MEPhI and ILL reactors. We can already conclude that \( D_\alpha \ll D_\alpha \) for 233U under the assumption that the ratio of scission to fragment neutrons is equal to 0.35 [6], i.e. \( \delta = 2.86 \).

**Acknowledgements**

This work is supported by RFBR (grant 00-02-16011) and Russian State program “Fundamentalnaya Yadernaya Fizika” (grant 134-06).

**References**

Complete Lifetime Spectroscopy of $^{168}$Er

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A complete set of lifetimes of nuclear excited states below 2.2 MeV in a well deformed nucleus, could form a unique database for the study of nuclear structure. Over the past decade a series of experiments at the GAMS4 spectrometer aimed at such a goal using the GRID method. The results of these experiments are reviewed in the context of our understanding of the nuclear many-body problem with relation to phonon excitations.

1. Introduction

The combination of the high neutron capture cross section of 670 barns with the relatively high ground state spin of $7/2^-$ makes thermal neutron capture in $^{168}$Er an ideal tool to perform complete low-spin spectroscopy in a well deformed heavy nucleus. Therefore $^{168}$Er became a classical example of a deformed nucleus, since the work of Davidson et al. in the mid seventies [1]. This study revealed most intrinsic excitations, labeled by the quantum numbers $K^\pi$ and on which rotational bands are built. The intrinsic excitations arise by collective nuclear vibrations. Those are collective motions of many nucleons which move in a deformed common mean-field potential. Because they are fermions they need to fulfill the Pauli Principle. How to treat at the same time the collective and single particle degrees of freedom is one of the major questions needed to be solved in nuclear structure. The lowest collective vibration in $^{168}$Er is the first excited $K^\pi = 2^-\gamma$-vibration. In order to establish its collectivity it is very useful to study the double excitation. This double $\gamma$-vibration leads to a $K^\pi = 4^+$ and a $K^\pi = 0^+$ band. Davidson et al. were able to show that the first candidate for the $K^\pi = 4^-$ excitation is the 19th rotational band in $^{168}$Er. This observation raised intensive theoretical debates [2].

2. Measurement of absolute decay rates

A major drawback of the use of thermal neutron capture to study atomic nuclei was, however, the lack of an appropriate method to determine short lifetimes of nuclear excited states. The GRID method [3] solved this problem by combining ultra-high resolution gamma-ray spectroscopy with Doppler Shift Attenuation and opened the possibility to perform also complete lifetime spectroscopy in $^{168}$Er. Such a program is now since a decade pursued using the GAMS4 spectrometer (Fig.). Nine candidates for intrinsic vibrations were up to now studied via their absolute electromagnetic decay. The first major result showed the first $K^\pi = 4^-$ band to be a collective excitation and therefore a candidate for the two phonon gamma-vibration, leading to a worldwide search for other candidates (some of them using the GRID method). After this success the next collective vibration, the so-called $\beta$ vibration was studied. This $K^\pi = 0^+$ vibration is also highly debated and much less understood than the $\gamma$-vibration [5]. Although at the limit of sensitivity the GRID results showed for the first time the weak collectivity of this intrinsic vibration [6].

The third series of experiments dealt with the octupole vibration, the lowest collective vibration with negative parity. Because of the high multipole, this vibrations splits up in several intrinsic states with $K^\pi = 0^-, 1^-, 2^-$ and $3^-$. To locate these vibrations, lifetimes of excited states in five negative parity bands were measured using the GRID technique [7]. The results allowed to identify clearly the $K^\pi = 0^-$ and 2$^-$ octupole vibrations via their absolute decay and to rule out the candidate for the $K^\pi = 3^-$ excitation.

3. Conclusion

In conclusion, over the last decade we have measured lifetimes and limits thereon for seventeen excited states in $^{168}$Er allowing to study the collectivity of eight intrinsic excitations. The collective character of the $\gamma$ vibration could be clearly established as well as the one of the octupole vibrations. Less clear is the collectivity of the $\beta$ vibration and therefore our next experiment will try to determine more lifetimes of states in $K^\pi = 0^+$ bands. A maybe related question concerns the non-observation of the $K^\pi = 0^+$ double-$\gamma$ vibration. On the theoretical side a better knowledge of the interplay between collective and single-particle degrees of freedom was obtained, notably on double excitations of intrinsic vibrations.
Acknowledgements

We would like to acknowledge many discussions with R.F. Casten and E. Kessler in the context of this work.

References

Several new microsecond isomers were recently observed in the mass range $A=125-134$, in neutron rich nuclei of Sn, Sb, Te and Xe, around the doubly magic $^{132}$Sn nucleus. These nuclei are produced by thermal neutron induced fission of $^{235}$U or $^{239,241}$Pu. The detection is based on time correlation between fission fragments selected by the LOHENGRIN spectrometer at ILL and delayed $\gamma$-rays or conversion electrons from the isomers. These new data substantially extend the experimental knowledge on these nuclei and give the opportunity to follow the evolution of several high-spin configurations, like the $\nu(h_{11/2}^\pi)^{10+}$ isomer for example, from a pure shell model state towards a more collective structure. This $10^+$ state decays by an E2 isomeric transition and we have shown that its $B(E2)$ strength is strongly enhanced from Sn to Te isotopes. A theoretical interpretation is proposed to explain this new feature and we suggest that analogous effects are expected in other region of closed shell nuclei.

1. Experimental procedure
The details concerning the experimental set-up are given in [1,2]. The fission fragments were produced by thermal neutron induced fission of $^{235}$U or $^{239,241}$Pu. The LOHENGRIN spectrometer at ILL has been used to separate the fission fragments (FF) recoiling from thin targets of about 400 $\mu$g/cm$^2$, according to their $A/q$ ratios. The FF are detected by an ionization chamber of 13 cm length, and subsequently stopped in a mylar window of 12 mm thickness. The delayed $\gamma$-rays de-exciting the isomeric states were detected by two large volume Ge detectors and the conversion electrons were detected by two cooled Si(Li) detectors covering a total area of 2x6 cm$^2$ and located 7 mm behind the mylar window. The gas pressure of the ionization chamber was tuned to stop the fission fragments at about 2 mm from the outer surface of the mylar window. The electron detection efficiency is about 30 %. This set-up is designed to measure X-rays and conversion electrons down to 10 and 15 keV, respectively.

2. Results
Several new isomers have been observed in $^{129}$In, $^{125,127,129}$Sn [1], $^{131}$Sb[2], $^{130,132}$Te [3], $^{134}$Xe [3], and $^{133}$Sb [4]. This mass region has a large number of isomers. This is specially evident in fig. 1 where the level schemes of $^{129}$In and $^{133}$Sn nuclei are reported. One observes that a large amount of angular momentum is brought to these isomers by the fission process. Particle excitation is very likely the main origin of the angular momentum of these nuclei close to the doubly magic $^{132}$Sn.

These new data substantially extend to high spins the previous ones obtained mainly in $\beta$-decay experiments and give the opportunity to follow the evolution of several high-spin configurations, from a pure shell model state towards a more collective structure. As an example we shall discuss the systematic behaviour of the $\nu(h_{11/2}^\pi)^{10+}$ isomer in the Te and Sn isotopes and its decay properties.

Fig. 1 Level schemes of $^{129}$In and $^{133}$Sn nuclei. The data on $^{129}$In are from this work and from [6,8].
In fig. 2 are reported the $B(E2, 10^-\rightarrow 8^-)$ reduced transition probabilities in the Sn and Te isotopes versus the neutron number. These $10^-$ and $8^-$ states have a rather pure $\nu(h_{11/2}^n)$, seniority $v=2$, configuration. The values of $^{128,130}\text{Te}$ [2] and $^{128,130}\text{Sn}$ [5] are the new data obtained in this work, while $^{128,130}\text{Sn}$ [5] were re-measured. A strong enhancement of the $B(E2)$ values is observed for the Te isotopes and these values increase when the neutron number decreases, while the trend is inverted for the Sn isotopes. In the $Z=50$ magic shell Sn nuclei, the observed trend reflects the filling of the $\nu h_{11/2}$ neutron subshell which shows a deep minimum for 73 neutrons, corresponding to the mid-subshell: at this point 6 neutrons occupy the $\nu h_{11/2}$ orbital. Hence, one may conjecture that in the Te isotopes the effect of subshell filling is completely masked by some admixtures with other configurations. In fact the most efficient way to increase the $B(E2)$ strength in the Te isotopes, with two valence protons outside the $Z=50$ magic shell is to suppose that the $\{\nu(10^+) \times \pi(0^+)\}_{10^+,8^+}$ configurations are mixed with the $\{\nu(10^+) \times \pi(2^+)\}_{10^+,8^+}$ ones, where a proton pair is excited to a $2^+$ configuration. The underlying cause of the mixing is the p-n interaction. Then the transition takes place between the initial state:

$$|10^+> = [\nu(10^+) \times \pi(0^+)]_{10^+,8^+} + \epsilon_1 [\nu(8^+) \times \pi(2^+)]_{10^+,8^+}$$ (1)

and the final state:

$$|8^+> = [\nu(8^+) \times \pi(0^+)]_{8^+} + \epsilon_2 [\nu(10^+) \times \pi(2^+)]_{8^+}$$ (2)

with coefficients $\epsilon_1, \epsilon_2 \ll 1$.

It is easy to show that the $<8^+||E2||10^+>$ matrix element between the Te wave functions defined in eqs. 1, 2 can be evaluated as a function of the elementary $<\nu(8^+)||E2||\nu(10^+)>$ and $<\pi(0^+)||E2||\pi(2^+)>$ matrix elements. Finally, the $B(E2)$ reduced transition probability in the Te isotopes can be written as:

$$B(E2(\text{Te}), 10^-\rightarrow 8^-) = [\sqrt{B(E2, \nu(10^-\rightarrow 8^-))} + \epsilon_1 1.9 \sqrt{B(E2, \pi(2^-\rightarrow 0^+))}]^2$$ (3)

with the additional simplification that $\epsilon_1=\epsilon_2=\epsilon$. One observes in eq. 3 that the $B(E2)$ value in Te is now the sum of a neutron and a proton contribution. These values can be approximated by the experimental $B(E2(\text{Sn}), 10^-\rightarrow 8^-)$ value taken from the Sn isotopes having the same neutron numbers as the Te isotopes and the $B(E2(\text{Te}), 2^-\rightarrow 0^+)$ value taken from the same Te nucleus; the latter $B(E2)$ value is much larger than the former which occurs for a magic nucleus. Therefore, even a rather small mixing amplitude can lead to a large enhancement of the total $B(E2)$ value in Te. In fact we have found that values $\epsilon=0.08-0.17$ are able to produce the very strong enhancement of the $B(E2)$ values as observed experimentally from Sn to Te. In contrast the energy shifts of the $10^-$ and $8^-$ states in Te isotopes due to the p-n residual interaction are always smaller than 20 keV, which indicates that the energies are only very weakly affected by the mixing.

In conclusion, the proposed mechanism is able to explain the large observed difference in the behavior of the $B(E2)$ strengths in the Sn and Te isotopes, although the leading configuration of the $10^-$ state is the same in both isotopes. We expect that this feature is more general and is very likely present in other closed shell regions of the nuclear chart, but it is easier to observe in the Sn-Te region.

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Mass and Isotopic yields for the reaction $^{245}$Cm(n$_{th}$,f) at Lohengrin

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Recently, a new specific interest for fission yields of “minor” actinides arose, due to the development of new reactor technologies and transmutation projects of actinides and nuclear wastes. The SPIN program (for SéParation-INcinération) has been launched at the CEA (Commissariat à l’énergie atomique, France) to search for solutions allowing to partition and transmute long-lived radioactive waste in order to reduce their volume and toxicity and to investigate new fuel cycles. From the standpoint of the inventory of transuranium elements in Pressurised Water Reactor (PWR) and of their radiotoxicity, Curium and in particular Curium 245 is the third most important nuclide after Plutonium and Americium. Within these aspects we investigated the reaction $^{245}$Cm(n$_{th}$,f) at the mass spectrometer Lohengrin. A new technique using an ionization chamber and an absorber has allowed to measure the isotopic yields from Z=34 (Se) up to Z=47 (Ag). Moreover, mass and kinetic energy distributions up to mass A=167 have been investigated. We present the measurement techniques and preliminary results.

1. Introduction

The inventory of transuranium elements in Pressurised Water Reactors (PWR) and their radiotoxicity shows that Curium (in particular $^{245}$Cm) is the third most important nuclide (after Plutonium and Americium). Several experimental efforts for measuring yields in thermal neutron induced fission of $^{245}$Cm have been made in previous years. Whereas the situation concerning chain yields was adequate for the light peak of the distribution, a pronounced deficit existed concerning the independent yields of single nuclides for masses above A=94. Earlier data provided only isolated values, such as the independent yields of the nuclides $^{86}$Rb and $^{136}$Xe [1] and the fractional cumulative yields of $^{132}$, $^{134}$Te [2] and of $^{135}$I and $^{139}$Ba [3] as well as the fractional independent yield of $^{132}$Xe [4]. Reference [5] provides 12 fractional cumulative yield values. A few recent measurements [6] performed at the Lohengrin mass separator provided accurate values for the nuclear charge distribution from A=76 to 94 using an ionization chamber with a split anode. New experimental results on the nuclear charge distribution of $^{245}$Cm(n$_{th}$,f) for the region from A=85 to A=115 were obtained from the measurement presented in this page. Furthermore, the mass yields and kinetic energy distributions have been extended up to mass A=167 with the ionization chamber alone.

2. Experimental setup

The initial target material which originated from PNPI in Gatchina, Russia, had an isotopic composition of 8.7 % for $^{244}$Cm and 91.3 % for $^{245}$Cm (± 10 %). The targets were purified and conditioned at the Institut für Kernchemie in Mainz, Germany, by means of electrodeposition of Curium in the form of Cm$_2$O$_3$ on circular Titanium foils (diameter 3 cm, thickness 50 µm) in the shape of a round spot of 4 mm diameter. The cross section of $^{245}$Cm and of $^{246}$Cm for thermal neutrons is approximately 1.2 barns and 2000 barns respectively. The contribution of the first isotope to the total activity measured in experiment is negligible compared to that of $^{246}$Cm.

All experiments were performed at the Lohengrin mass spectrometer, Institut Laue Langevin (ILL), Grenoble, France : see figure 1. This mass separator for unslowed fission products, consists of a condensor and a magnet [8], and is installed at the high flux reactor in Grenoble which has a flux of $5 \times 10^{14}$n.s$^{-1}.cm^{-2}$ at its disposal. This device makes use of electric and magnetic deflection fields to separate fission products according to their mass number A, their kinetic energy $E_{kin}$ and their ionic charge. Par
cles are separated in the magnetic field according to the mass over ionic charge (A/q) ratio and in the electric field they are separated according to the kinetic energy over ionic charge (Ekin/q) ratio. The action of the two fields together focuses particles of equal A/q and Ekin/q ratios on the same point in the focal plane. Points corresponding to the same value of A/q but different energies are located on a parabola which, in practice, can be approximated by a straight line. In this spectrometer the energy dispersion is along the parabolas and the mass dispersion is perpendicular to the parabolas. The selection of a particle with desired characteristics (A, Ekin, q) is done by setting the appropriate electric and magnetic fields. By limiting the exit slit length at a maximum of 72 mm, the maximum energy band width accepted by the spectrometer is $E = E_0 \pm 5\%$. The mass resolving power is $M/\Delta M = 800$ for a target of 4 mm width.

To increase the luminosity and to decrease background, a second magnet (RED magnet for Reverse Energy Dispersive) has been added at the end of the spectrometer. With the RED magnet using 40 cm of the exit slit of the mass separator, the multiplication by a factor of 7 in the count rate can be achieved. This facilitates the study of rare binary and ternary fission events [9].

The selected fission fragments were detected with a small ionization chamber [10]. This chamber was located at the exit of the RED magnet. As a working gas isobutane was used at a pressure of 30 mbar. To conserve a pressure of 10⁴ mbar in the condenser, a poly-propylene window with a density of 40 µg.cm⁻², supported by a tungsten grid, with 90 % of transmission was placed at the entrance of the chamber.

3. Measuring technique

It is known from [10] that solid absorbers have better separation power for different nuclear charges Z that gaseous ones. The solid absorber used here was a stack of 12 foils Parylen C of thickness 0.58 µm (± 10 %) each. The main requirement of this material is to have a homogeneous surface which implies the same energy loss across the total area of the absorber. The only observable is the $E_{ion}$ signal for fission fragments being stopped in the ionization chamber. The chamber was operated in the • E-$E_{rest}$ mode in order to discriminate from false events having passed through the Lohengrin field arrangements. According to their nuclear charge, fission fragments have different energy loss in the absorber. The Figure 2 shows an example of a measurement for A=93, $E_{rest}$=102 MeV and q=20. Five nuclear charges can easily be seen.

4. Results

Five targets with amounts of $^{245}$Cm ranging from 13 to 16 mg have been exposed to a thermal neutron flux of 5.10⁻¹⁰n.s⁻¹.cm⁻² for 10 days each. The targets were protected by a nickel foil of 0.25 µm which prevents sputtering and uncontrolled loss of the target material. Isotopic yields have been measured from mass 85 to 115 for kinetic energies 92, 97, 102, 108, 113 and 118 MeV and for one or two ionic charges; mass yields have been measured from A=130 to 167 for the whole kinetic energy and ionic charge distributions. Results are presented in figure 3.

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Future Nuclear Structure Physics at PN1 ("Lohengrin")

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Many areas of physics and chemistry can be studied with the "Lohengrin" mass separator. Only one area for possible future physics is discussed, the nuclear structure of exotic neutron-rich nuclei. The advent, last decade, of large 4π-arrays of high-resolution germanium detectors [1] for γ-ray spectroscopy revolutionised nuclear physics, allowing the observation of such exotic effects as superdeformation [2]. The next generation of these arrays is at present under development, and these will facilitate the tracking of γ-rays through a detector. The future use of such an array at "Lohengrin" would be the first use of an efficient γ-ray detector array for the analysis of fission fragments from a reactor. The investigation of exotic neutron-rich nuclei towards the neutron drip line (the point beyond which bound nuclei cannot exist) would become possible.

One of the major goals of nuclear physics is to test how well nuclear models describe exotic nuclei. Present models have only been tested with nuclei close to stability. Such exotic effects as nuclear skins, nuclear phase transitions and the disappearance of shell gaps have already been hinted at. Magnetic moment measurements would also be possible, which are known to be sensitive probes of the nuclear wavefunction. This region is also important to astrophysics as these nuclei lie along the path of the r process. The r process is thought to be the method of synthesis for about half of the matter heavier than iron found in nature [3]. Measurements of nuclear properties in this region are therefore of great importance to astrophysics. The recently installed beam switching facility on "Lohengrin" will allow measurements of the β-decay half-lives of these nuclei to be performed. It will soon be possible to measure delayed neutron decays from these nuclei, with the neutron detector currently being assembled.

1. Introduction

Nuclei are one of the fundamental building blocks of the universe, sitting in between atoms and hadrons. Nuclei make up more than 99% of the known mass in the universe; therefore it is of fundamental importance to understand their properties and structure. Stable nuclei constitute less than 10% of all the nuclei thought to be bound systems. Nuclear physics experiments have so far only been able to investigate nuclei close to stability. The use of an efficient γ-ray detector array at facilities such as "Lohengrin" now allows more exotic nuclei to be studied.

2. The "Lohengrin" Mass Separator

Very neutron-rich nuclei are created at the PN1 ("Lohengrin") impile position by the neutron-induced fission of uranium, or transuranium, isotopes. These nuclei are then separated, according to their mass and charge, by the electromagnetic fields of "Lohengrin" [4]. Nuclei with excited-state isomers of a microsecond, or longer, then decay by γ-ray emission. Excited states can also be created in nuclei, at the exit slit of "Lohengrin", by β decay. It is from observations of the γ-rays emitted by these excited states that much information can be obtained about the structure of nuclei.

3. Structure of Neutron-Rich Nuclei

Knowledge of the energies of excited states in nuclei is essential to determine the structure of a nucleus. High-resolution γ-ray spectroscopy is one available method to determine the energies of excited states. The measurement of angular correlations between γ-rays, from the same nucleus, is a well-established method for determining the spins of excited states in nuclei, the characteristic anisotropy of the position of detection of many pairs of γ-rays from nuclei being related to the initial and final spins of the levels. To perform these measurements good detector angular resolution is needed, which requires placing conventional γ-ray detectors some distance (~ twenty centimetres) from the decaying nucleus. Placing detectors further away from a source reduces the solid angle covered by each detector, hence reducing the detection efficiency per detector. Thus for good detection efficiency many detectors are required, greatly increasing the cost. For nuclei populated weakly very large arrays, such as EUROBALL (~ 10% efficient), with hundreds of detectors must be used. The latest generation of γ-ray detectors, such as MINIBALL [5], facilitate the tracking of γ-ray interactions through the germanium crystal, thus giving excellent position resolution, whilst still retaining the ability to be placed close to the γ-ray source. This new technology will allow angular correlations to be measured for very weakly populated nuclei with as few as eighteen detectors (MINIBALL ~ 13% efficient).

Magnetic moments of nuclei are known to be sensitive probes of the nuclear wavefunction. For instance the predicted g factor, gen-
erated by single-particle motion (Schmidt moment), of the 5-state of $^{130}$Sn is $-0.385 \mu_N$, whereas it is expected to be $-0.26 \mu_N$ when the interacting boson model is used [6]. For excited state lifetimes of 1 ps, or less, the best method for measuring magnetic moments of nuclei is to observe perturbed $\gamma$-ray angular correlations. This method has been used successfully for excited-state lifetimes as short as 1 ps, with a variety of different techniques being available to the experimenter. The high angular resolution obtained using the $\gamma$-ray tracking facilities of MINIBALL would make it ideal for these experiments.

Little is known about the magnetic moments in the neutron rich region towards the drip-line around mass 150 and mass 100, the two regions most strongly populated by neutron-induced fission. The disappearance of closed shells has already been hinted at in this region by the measurement of the magnetic moments of neutron-rich barium and cerium nuclei [7]. Use of the MINIBALL at “Lohengrin” for magnetic moment experiments should further extend the knowledge of nuclear structure in this important region. This region of the nuclear landscape is important not only to nuclear structure studies, but also to astrophysics.

Measurements of nuclear properties around closed shells are the prime source of information about nuclear forces. The simple structure of these nuclei, a closed inert core with a few valence nucleons makes them particularly suitable for interpretation using the shell model. Until now only nuclei around the doubly magic nuclei $^{208}$Pb and $^{132}$Sn have been studied, but advances in experimental techniques, such as highly-efficient MINIBALL $\gamma$-ray detectors, now allows the properties of nuclei around $^{64}$Ni to be examined. The mass 100 region is a particularly interesting region of the nuclear chart as nuclei undergo a rapid shape change from a spherical to a deformed shape, with the addition of just a few nucleons [8]. The cause of this shape change is not understood. Detached shells of neutrons outside an inert core, called nuclear skins, are expected to exist in this region, which would provide a unique opportunity to study interactions in matter consisting almost entirely of neutrons.

### 4. The Astrophysical $r$ process

The astrophysical $r$ process is thought to be the method by which half of the matter, heavier than iron, in nature was created. These nuclei are synthesised by neutron capture during a supernova explosion. Predictions about the path of the $r$ process, and the predicted yields of the nuclei vary widely from those observed in nature. Nuclear structure information, for $r$-process nuclei is essential for the development of this important model. For instance quenching of shell gaps is required by $r$-process calculations to give the observed isotopic abundance found in nature. Accurate $\beta$-decay lifetimes are essential to calculate the speed at which the $r$ process proceeds. When neutron binding energies drop below about 2 MeV neutron capture is inhibited and the nuclei must first undergo $\beta$ decay, before more neutrons can be added to the nucleus. The nuclei on the $r$-process path pausing for $\beta$ decay are called waiting point nuclei. The recently installed beam chopper at “Lohengrin” will allow a pulsed beam of fission fragments to be produced. Timing measurements between the start of the beam pulse, and the observation of $\beta$ particles is one possible method available to determine the $\beta$-decay half-lives of very neutron-rich $r$-process nuclei.

### 5. Delayed Neutrons

Delayed neutrons emitted from $\beta$ decay have implications for reactor control dynamics. The neutron detector currently being assembled at “Lohengrin” will allow the study of these neutrons. The study of delayed neutrons, in coincidence with $\gamma$-ray emission, will also be of use to nuclear structure studies as delayed neutrons populate different excited states to those populated by $\beta$ decay. Very little study has been made of delayed neutrons, and the excited states in their daughter nuclei.

**References**

Possible improvements to the precision gamma-ray spectroscopy facilities at the ILL are considered. The suggested improvements take into consideration the existing facilities and the likely future emphasis of the gamma-ray spectroscopy program at the ILL. Future measurements will likely benefit from better resolution ($\Delta \lambda$), increased throughput of the spectrometers (ability to measure weaker sources), and more accurate angle measurements. In addition, some efforts to reduce the background, improve the environmental control, and improve the ease of using and maintaining the spectrometers are in order.

1. Introduction

Gamma-ray spectroscopy at the ILL has evolved from single-curved-crystal spectrometers (GAMS1 and GAMS2,3) [1] which have high throughput and limited resolution to a double-flat-crystal spectrometer (GAMS4) [2] which has lower throughput and higher resolution. An improved second double-crystal spectrometer (GAMS5) has been developed for use with both flat and curved crystals. Experience with these spectrometers suggests four areas for future improvements: resolution of the spectrometers, throughput of the spectrometers, accuracy of the angle measurements, and the general laboratory conditions. The resolution and throughput of the spectrometers are mainly dependent on the crystals. The perfection of the crystals as well as the available crystal planes and thickness are important parameters. The diffraction angles are measured with angle interferometers that exhibit drifts and calibration instabilities that limit the quality of the most precise measurements. Alternate interferometer schemes are being considered as a means to obtain more accurate angle measurements. In addition to the critical crystal and angle measurement areas, the GAMS facilities would benefit from upgrades of a number of technically less-demanding items.

2. Crystals

The existing flat crystals for the GAMS facilities have been manufactured at NIST. Diffraction occurs on a crystal slab that extends from a post used to support the crystal and provide an optical alignment reference (see Ref. [2] for more details concerning the flat crystals). At the present time there are 8 Si crystals (performance approaching dynamical diffraction theory) and 4 Ge crystals (somewhat less good) with thickness ranging from 1.3 mm to 7.0 mm. For a particular measurement problem, the crystal type, reflection, and thickness are chosen to provide the most appropriate resolution and throughput. In Fig. 1 we show theoretical dynamical diffraction profiles for the (440) reflection in Ge and Si at an energy of 2 MeV. Note that the width, intensity, and crystal thickness are quite different for these two profiles and that a significant gain in throughput is available from high-quality Ge crystals. In order to maximize the crystal performance for the variety of measurement problems proposed for the GAMS facility, the inventory of available crystals needs to be expanded. The current crystal configuration makes the production of new crystals very labor intensive. We are considering alternative crystal designs that will preserve the robustness of the crystal quality and alignment, but make them easier to manufacture. Finally, in a very recent measurement we have installed the ability to sequentially record profiles from the top and bottom portions of the beam. The shift of these profiles may be a measure of the crystal misalignment that can be corrected by using a PZT tipper on one of the crystals, leading to some improvement in crystal performance.

A major step in improving the efficiency of the spectrometers will consist in the implementation of a double bent crystal geometry. It is known that a DuMond geometry using a single bent crystal has a very high luminosity. On the other hand the resolution of such a spectrometer is limited by the finite thickness of the
source. The double bent crystal geometry overcomes this disadvantage and should theoretically have the same resolving power as a double flat crystal geometry. This requires bending perfect single crystals to a cylindrical shape with an accuracy of about $5 \times 10^{-8}$ rad. This technologically demanding process is currently underway.

3. Angle measurements

The present angle-measuring scheme for the two crystal spectrometers is a Michelson interferometer illuminated by a commercial two-frequency laser [2]. The laser emits two orthogonal linearly polarized frequencies having a frequency difference of 1.8 MHz. This interferometer has two distinct disadvantages: one, the use of the two-frequency laser and the polarization-sensitive beam splitter allows some mixing of the two frequencies in the two interferometer paths which can lead to significant periodic angle errors ($\approx 2 \times 10^{-9}$ rad), and two, the use of a rather high frequency difference (1.8 MHz) increases the difficulty of accurately measuring the phase difference between the measurement and reference signals.

An alternate angle interferometer scheme that is completely free of frequency mixing is shown in Fig. 2. [3] Results achieved with this interferometer suggest that periodic errors will be in the neighborhood of $5 \times 10^{-11}$ rad. In this scheme horizontally polarized light from a single-mode stabilized laser is split by a beamsplitter into two beams which are directed toward the moving retro-reflectors. Each of these beams passes through an acousto-optic modulator (AOM) and the two AOMs are driven at frequencies $\nu_M$ and $\nu_R$, respectively. The polarization-insensitive AOMs divide the beams into a reference channel and a measurement channel. The beams in the reference channel are frequency shifted by $\nu_M$ and $\nu_R$ and are combined to form a reference signal with frequency $\nu_M - \nu_R$. The beams in the measurement channel pass through the retro-reflector, roof prism, quarter-wave plate, and mirror assemblies. The return beams are vertically polarized and pass again through the AOMs where they are frequency shifted by $\nu_M$ and $\nu_R$ and combined to produce a measurement signal also with frequency $\nu_M - \nu_R$. The phase shift of the measurement signal with respect to the reference signal is a measure of the angular rotation of the retro-reflector arm. In this scheme there is no frequency mixing that can lead to periodic errors. The measurement and reference signals are generated symmetrically which makes the interferometer immune to some potential drifts. The retro-reflectors are passed 4 times which increases the angular sensitivity by a factor of two over the current design. The frequency $\nu_M - \nu_R$ can be chosen in the 10s of kHz range leading to an easier measurement of the phase difference between the measurement and reference signals. Low expansion materials will be used in implementing this scheme.

4. General laboratory upgrades

Although considerable care has been taken to make the GAMS spectrometers immune to environmental disturbances, they are still affected by temperature and humidity changes. Some effort to provide a more stable temperature and humidity environment is in order. The reduction of background radiation by moving the GAMS4 spectrometer farther away from the reactor will make it easier to measure weak transitions. Remote adjustment of the collimation will make it much easier to optimize the performance of the spectrometers. Finally, providing more working space around the spectrometers in order that crystal changes and spectrometer maintenance are easier would be a significant help to the experimenter.

References

Industrial relevance of neutrons
Actinide diffusion in zirconium and the role of oxidation

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Nuclear fuel devices of Pressurised Water Reactors are composed of uranium oxide pellets which are enclosed in zircaloy cylinders. During reactor operation different processes occur. In the contact with the fuel the zircaloy oxidises nonuniformly in depths of order of some micrometers. Further on, energy deposition of fission recoils leads to sputtering of uranium onto the inner surface of the cladding material. Thus, sputtered uranium ions start to migrate outwards. This paper presents first the results of experiments performed on the Lohengrin spectrometer in order to simulate the alteration of cladding tubes in contact with the nuclear fuel during irradiation. The energy loss of selected fission products is correlated to an oxygen mass gain. From these experiments, we deduce the oxidation kinetics constant under irradiation at a mean temperature of 400°C. These results are compared with those of a thermal oxidation. Following oxidation the fission product kinetic energy is stabilised, but still a broadening of the energy distribution is observed, which is characteristic of actinide diffusion inside the zirconia target. Using the Fick model, an actinide diffusion coefficient into zirconia under irradiation is deduced.

1. Introduction
Fuel cladding tubes of Pressurised Water Reactors have been subject to numerous investigations to understand their behaviour. The oxidation process on both sides of the zircaloy tubes has been in particular thoroughly characterised [1, 2]. The cladding tube inner surface is known to be oxidised by reduction of the UO2 pellets which are in slight contact with the Zr cladding [3]. The oxidation kinetics during nuclear operation is subject to discussion as it depends on several conditions: temperature, residual oxygen pressure and irradiation conditions. In addition, fission products are implanted by recoil in this inner oxide layer and energy deposition of fission recoils leads to sputtering of uranium onto the inner surface of the cladding material. The as-sputtered uranium can then migrate outwards. It is of primary importance to determine the diffusion parameters of the fission products and actinides in the cladding. Consequently, this work will be presented into two parts. The first part is devoted to zirconium oxidation measurements in reactor conditions performed on the ILL (Institut Laue Langevin) neutron experimental reactor in Grenoble. The oxidation kinetics constant deduced from these experiments are compared to thermal oxidation measurements obtained in the same temperature and pressure conditions. The second part presents the study of uranium diffusion in the oxidised zirconium.

2. Experimental set up
2.1 The ILL Lohengrin mass spectrometer
Zirconium oxidation and uranium diffusion in reactor conditions have been performed at the Lohengrin mass spectrometer. This spectrometer allows to irradiate an uranium-oxide target in a high neutron flux of 5x1014 n cm⁻² s⁻¹. Uranium is enriched in 235U to about 99%. Fission rates of standard targets (50 to 100 µg cm⁻²) reach about 10¹⁰ particles s⁻¹. The high energetic fission products leaving the UO₂ target transverse a Zr foil of 2µm thickness and 3.5 cm² surface which is to be investigated and placed in front of the target. The fission fragments are analysed in mass and kinetic energy in two successive magnetic and electric fields respectively. The separated fragments are detected in a high resolution ionisation chamber [4]. The process of oxidation and diffusion can be detected by scanning over the kinetic energy distribution of a selected fission product mass at successive times. The kinetic energy evolution of A=90 and Q=18 selected fission fragments is

\[ \Delta E = 19.7 \text{ MeV} \]

\[ t = 62 \text{ h} \]

\[ t = 0 \]

Fig. 1: Evolution of the energy distribution of fission products (A=90, Q=18) during 62 hours.

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presented in figure 1. In experimental configuration, the Zr foil is heated by the \( \gamma \) radiation from the ILL reactor and by the fission fragments from the UO\(_2\) target which are slowed down in the foil. Taking into account the \( \gamma \) heating in the in-pile position (about 0.6 W g\(^{-1}\)) and the heating by the fission product (45 MeV energy loss per fragment), the temperature of the Zr foil is of the order of 400°C with an error of about 25% [5]. The estimated partial oxygen pressure inside the beam tube is around 10\(^{-4}\) mbar.

2.2 Coupling of thermal annealing and RBS analysis

The zirconium thermal oxidation has been investigated at an oxygen partial pressure of 10\(^{-5}\) mbar and at a 400°C temperature. Samples are placed inside an stainless steel tube. Vacuum is obtained thanks to a turbomolecular pumping and adjusted by using a dry air variable leak valve. The furnace temperature is regulated at \( \pm 3°C \) and controlled by a thermocouple. For each annealing time, zirconium oxidation is measured by Rutherford Backscattering experiments performed using 1 MeV \( \alpha \) particles. At this incident energy the sensitivity is about 5x10\(^{16}\) oxygen atoms cm\(^{-2}\). In figure 2 the RBS \( \alpha \) yield on a non oxidised sample is compared to those of oxidised ones respectively after 2 and 18 hours annealing.

3. Results

3.1 Comparison between oxidation under irradiation and thermal oxidation

At ILL, we have performed systematic energy measurements as shown in figure 1. After an irradiation of 62 hours the complete oxidation of the zirconium foil has occurred which corresponds to an energy shift of 19.7 MeV. From the experimental mean kinetics energy loss, the oxygen mass gain in the Zr foil was calculated by using the stopping tables for heavy ions in solids from Ziegler [6]. In the considered energy range corresponding to the oxidation process, the mean oxygen stopping power value is equal to 1195 eV/10\(^{15}\) at cm\(^{-2}\). After the oxidation phase no more shift of the mean energy value is observed as shown in figure 3. At this stage, the whole foil is oxidised and the stoichiometry corresponds to ZrO\(_2\).

The oxidation kinetics of zirconium under irradiation at 400°C is presented in figure 4. No parabolic evolution is noted which means that oxidation is not limited by the oxygen diffusion. This can be interpreted by the presence of numerous defects created by fission products. The slope of the straight line gives the kinetics constant to be equal to 1.5x10\(^{17}\) oxygen at cm\(^{-2}\) h\(^{-1}\). This result needs to be compared to the kinetics constant of thermal zirconium oxidation in the same conditions of temperature and pressure (400°C and 10\(^{-5}\) mbar).

In thermal oxidation experiments the oxidised thickness is deduced for each annealing time from the fits of the RBS distributions. The results are presented in figure 4 (dotted line). It appears that the oxidation kinetics is much smaller compared to that under irradiation. The slope of this curve leads to a kinetics constant of 0.7x10\(^{17}\) oxygen at cm\(^{-2}\) h\(^{-1}\). This factor 2 can be attributed to the defects induced by the fission product energy loss in the zirconium foil.

3.2 Uranium diffusion

After the oxidation phase, the fission product energy is stabilised but a broadening of the energy distributions is observed. Such an evolution is presented in figure 5. It is characteristic of the
actinide diffusion inside the zirconia target. Within 240 hours, the half width of the almost gaussian energy distributions increases from 12.73 MeV to 17.27 MeV. An analysis of these data has been performed assuming a gaussian shape of the energetic distributions. The initial distribution is assumed to be the one after 62 hours of irradiation when the whole zirconium foil is oxidised and the final distribution is the last measurement (after 240 hours). We have simulated the uranium distribution evolution by subtracting the two distributions mentioned above. The resulting curve is then deconvoluted into 5 gaussian distributions dividing the surface region into 5 slices, the first one corresponding to the initial uranium distribution. The amplitude of each gaussian is considered as proportional to the uranium concentration whereas the energy is converted into depth of zirconia. An analytical solution of the Fick law is given by an erf function distribution of uranium.

It is thus possible to reproduce the experimental data with a diffusion coefficient of uranium in zirconia equal to $2 \times 10^{-16}$ cm$^2$ s$^{-1}$.

**Conclusion**

In this paper, the cladding surface behaviour under irradiation has been investigated. An oxidation kinetics constant has been deduced together with a diffusion coefficient of uranium in zirconium. Compared to thermal oxidation, a factor 2 in the kinetics constant has been found. Further experiments are now being done including two main improvements: a precise measurement of both the target temperature and the oxygen residual pressure in the ILL beam tube. This will allow to compare the uranium thermal diffusion to that under irradiation.

**Acknowledgements**

The authors are very grateful to J. C. Duclot and D. Rochman for their help during the ILL experiments.

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Due to the high penetrating power of neutrons they can be used to non destructively determine (residual) stresses deep inside matter. Applications range from mock-ups for materials research to “real” engineered components for industrial testing. The size of specimens ranges from cm³ to meters length and weights from grams to several hundred kilograms. The lateral resolution of the instrument should be adaptable to the problem and enable measurements at interfaces and surfaces as well as in the bulk material, providing enough neutron flux to penetrate big samples. These demands can only be fulfilled on a machine dedicated to the measurement of residual stresses. As part of the Millennium Programme, ILL is constructing a new strain imager in collaboration with the University of Manchester. The new instrument will have collimating optics for best lateral resolution and a Steward platform for the sample table which will load more than 500 kg and allow complicated sample movements.

1. Introduction
The neutron strain imaging technique has become an important tool in engineering science and applied research and is getting a more and more important tool for industry. During the past five years a standard has been developed in two international working parties (VAMAS TWA 20 and RESTAND) which will soon be installed. Furthermore the number of proposals for neutron beamtime for strain scanning has been increased during the past years. The advantage of neutrons is their high penetrating power, which enables measurements in large samples in a suitable measuring geometry and without the need of special sample preparation. The ILL is actually running a strain imager which is an optional set-up on the high-resolution powder diffractometer D1A. But only an instrument dedicated to the measurement of residual stresses can really exploit the full bandwidth of applications. ILL decided to construct a dedicated strain imager in the frame of the ILL Millennium Programme, which started in January 2000. Since December 2000 we work in collaboration with Prof. Philip Withers of the University of Manchester and holding an EPSRC grant which partially funds the project.

2. The neutron strain imaging technique
The principle set-up of a strain imager at a monochromatic neutron source is shown in figure 1. The neutron beam coming from the monochromator passes optics which create a well defined beam in the sample. In combination with secondary optics a gauge volume is defined, which is of the size of typically 1 mm³ but can be varied according to the requirements of the measurement. A Position Sensitive Detector detects a Bragg reflection, diffracted by the polycrystalline sample. The variation of the scattering angle is related to the strain inside the crystals from which stresses can be calculated using Hooke’s law. In order to map the strain distribution, the sample it is scanned.

3. Neutron guide and beam optics
High neutron flux, angular- and lateral resolution are the first demands on a strain imager. This is only possible by optimising all of the optical parts in combination: neutron guide, monochromator and beam defining optics. Since only one Bragg reflection is determined at a time the angular resolution – it determines the accuracy of strain measurements – can be optimised for this scattering angle. A double focusing monochromator using bent perfect crystals has been chosen. It provides best resolution for a chosen scattering angle and focalises the neutrons very efficiently onto the sample. Jan Saroun from the Nuclear Physics Institute in Rèz near Prague was invited to perform Monte Carlo simulations on guide and
monochromator in combination with beam defining optics. The calculations show that a super-mirror neutron guide with a factor of reflectivity of \( m=2 \) provides the optimum flux. A guide with \( m=3 \) would provide again higher flux but more divergent neutrons which cannot be focalised onto the sample and would therefore not increase the available intensity.

Furthermore the calculations verify that radial collimators are well suited to a focusing monochromator. They take advantage of the divergence in the primary beam and define the gauge volume very precise and reliable.

The concept of radial collimators for the definition of the gauge volume has been developed for D1A. It shows many advantages concerning resolution and operation of the instrument. Slit apertures, which are often used at strain-imagers, should be positioned as close as possible to the sample in order to achieve best resolution and intensity. Radial collimators stay in their focal distance, which is in our case 150 mm, and leave space for large specimens and sample movement and provide at the same time high resolution at any point in the sample \([1,2]\). This simplifies the alignment since the collimators need not to be moved which saves valuable beam time.

Another important feature is that the use of a primary radial collimator reduces the surface effect drastically, which leads normally to huge errors when measuring across surfaces or interfaces. Using collimators, the maximum error depends only on the dimension of the gauge volume and is typically about 400 \( \mu \) [3]. Since it depends only on geometrical parameters it can be analytically corrected.

To sum it up it can be said that radial collimators fulfil the request for lateral resolution and measuring on large samples at the same time with efficient and reliable operation. For an easy change of the size of the gauge volume three sets of collimators shall be mounted on carrousels: Two sets in the primary beam for the vertical and horizontal dimension of the volume and one secondary. Another advantage of the neutron strain imaging technique is that the scattering angle can be chosen and adapted to the specimen. For this reason the new instrument will have a variable take off angle, which allows a choice of wavelength between 0.13 nm and 0.45 nm.

### 4. Sample table

The reliable and precise positioning of samples of any shape and size is the major requirement on the sample table. We have chosen a Steward platform which allows most flexible movements. It shall load samples of more than 500 kg weight and position them to better than 10 \( \mu \)m. The range of translation will be up to +400 mm in the horizontal plane and 380 mm vertically. Tilts of at least +30° and omega rotation of +80° will be possible. The position of the hexapod is extendable on a big granite table so that samples of up to 2 m length can be scanned. Fig. 2 shows a drawing of the proposed instrument which shall be operational in 2004.

### 5. Operation

The control of the sample table, the optimisation of the monochromator, the programmation of the scan and quick and reliable alignment of the specimen are the necessary tasks to perform a measurement. Special software will be developed to help setting up experiments quick and reliable and to allow user-friendly operation. A special feature will be that the scans can be programmed beforehand on a computer model of the specimen, which can be achieved from a CAD drawing or a 3D-scanner. Furthermore a base plate, which was developed in VAMAS TWA 20, will be available onto which the sample can be mounted and orientated before the measurement and will then be placed on the sample table by using dowel pins. In this way the sample co-ordinate system with respect to the instrument is well defined and samples can easily be changed.

![Fig. 2: The future strain imager drawn on a photograph of the actual work area. A train wheel is mounted on top of the Steward platform. The sample table slides on a big granite table on which it can be moved to extended positions so that large samples can be scanned. The position of the radial collimators and the detector are shown in a 90° scattering geometry. A variable take off angle allows the choice of wavelength between 0.13 nm and 0.45 nm. For wavelength changes the whole instrument moves on air pads on a marble floor.](image)

**Acknowledgements**

The calculations for the monochromator and guide would not have been possible without the help of Jan Saroun of the Nuclear Physics Institute in Rèz near Prague. The author thanks Stephen Rowe and William Hutt (both part of the project team) for the design drawing of the instrument and the fruitful collaboration in the project. We acknowledge the EPSRC for funding.

**References**


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**Industrial relevance**

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Engineering research infrastructure at the ILL

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The ILL is the European centre for neutron beam research and it provides most of its visiting scientists with excellent support and facilities. Engineering research has been conducted at the ILL for many years but only to a limited extent, and rarely by engineers. The most established engineering activity at the ILL is strain scanning which began in the early 1980s. Now there is an established and very active international community but it is still small and most members have, and at present need to have, a scientific rather than an engineering background. Engineering research could become a major activity at the ILL but is presently constrained by the lack of dedicated equipment and by the cultural entry barrier that most engineers have to overcome before they can begin an experiment at the ILL. Additionally some of the most important and pressing engineering problems that could be addressed by neutron scattering may, quite rightly, be judged to have little or no scientific merit, presently the sole proposal assessment criterion of the ILL. The paper discusses the special needs of engineers and the actions that might be taken by the ILL to make the facility useful and attractive to them.

1. Introduction
Materials Engineering Research at the ILL
Scientists (including Materials Scientists) are generally well catered for at the ILL because:

(i) the facilities and equipment were designed for science by scientists; (ii) scientists generally have appropriate background knowledge and training to exploit such facilities; (iii) Local Contacts are well-qualified scientists with similar and complementary knowledge and culture to the visiting researcher; (iv) most scientific experiments involve relatively small ‘homogeneous’ samples that are scanned as a whole in ‘reciprocal space’ (over a range of angles) whilst a controlled environment (Temperature, Magnetic field, Pressure, etc.) is changed. The ILL has excellent facilities for these types of measurements. Relatively few experiments involve scanning a sample in ‘real space’.

Engineering research is conducted at the ILL, but usually by scientists (or by engineers initially trained as scientists), rather than by formally-trained engineers who generally will have little or no knowledge of neutron (or X-ray) scattering. Relatively few traditionally-trained engineers are currently aware of the existence of the ILL and even fewer know of its considerable potential for engineering research. Those who are aware are often unable to make optimal use of the facilities because of barriers between the two disciplines. Engineers, who have the essential specialised knowledge to direct and to define the priorities and critical features of engineering research, generally do not have the necessary scientific background to conduct experiments at the ILL, nor is the ILL structured or equipped to meet their special needs. Likewise, most of resident ILL staff (scientists and administration) have only a limited engineering background and are unable to provide engineers with the complementary assistance that most of them require in order to make best use of the facilities. As a result engineers are generally less likely to apply for time at central facilities, and find them more difficult to use than scientists. This is principally because:

(i) the facilities and equipment were not designed for engineering or engineers; (ii) engineers do not generally have appropriate scientific background knowledge and training; (iii) Local Contacts are generally not engineers with similar and complementary knowledge or culture to engineering users; (iv) most engineering experiments involve complex ‘non-uniform’ samples of all shapes and sizes that are scanned in ‘real space’ (over the volume of the sample), sometimes under static or dynamic mechanical (or thermo-mechanical) load, usually requiring extended and precise 3-dimensional translation and sample manipulation. The facilities for these measurements are rarely well-developed.

If the ILL intends engineering (and other technical applications disciplines such as medical and veterinary) research to become a mainstream activity at the ILL it will be necessary for them to reconsider and to reform their relevant administrative structures, marketing and resource allocations.

2. Strain Imaging
The most established engineering activity at the ILL is strain imaging, used to determine non-destructively the residual stresses in engineering materials and components. The first neutron strain measurements were made in the early 1980s [1] and there are now established and very active European and international communities. Currently the community is developing, through VAMAS TWA20 [2], the first international standard for residual stress measurement using neutrons. An accepted standard is a
prerequisite for wider industrial and engineering adoption of the technique. European members, in close collaboration with industry, are also developing in parallel the first European standard through the EU-funded RESTAND project. They are due to issue their common draft standards early in 2001. Synchrotron X-ray strain imaging began in the early 1990’s but is now developing rapidly as a complementary technique particularly for high-resolution measurements in lighter-element materials. Much of the research and development is taking place at the ESRF. It is anticipated that, within the next few years once sufficient experience has been gained and techniques have been refined, the neutron and synchrotron X-ray strain imaging materials engineering communities will merge so that members will use both or either of the techniques, as appropriate, to solve a particular problem. For example, at the present time, neutrons are generally preferred for medium-resolution internal measurements within larger components made of denser materials whereas synchrotron X-rays have advantages for surface studies, high-resolution measurements and low-density materials.

3. Administrative Structure, Resource Allocation and Marketing

Administrative Structure

At the present time beam-time at the ILL is allocated through the six-monthly proposals system on the basis of scientific merit, presently the sole proposal assessment criterion of the ILL. Some of the most important and pressing engineering research problems that could be addressed by neutron scattering may, quite rightly, be judged to have little or no scientific merit. The present route for review of strain imaging proposals is through College 5A ‘Crystallographic structures’, sub-section 5-26 ‘Special applications: texture, stress, unit-cell indexing, ab initio structure determination’. Considering its constitution and remit the College appears to do a surprisingly good job when assessing strain imaging proposals, possibly because it chooses to ignore, or to interpret very broadly, the ‘scientific merit’ criterion. However, it is now time that the ILL followed the lead of other Central Facilities in introducing alternative criteria that would envelop engineering merit, technical usefulness, environmental benefit, etc. ISIS, for example, incorporated ‘Engineering merit’ as an alternative criterion in 1988 and ESRF has a Committee for ‘Materials Engineering and Environmental Matters’ which has, in addition to ‘scientific merit’, the alternative criteria: “practical usefulness of the expected results and the relevance of the findings to technical or environmental applications”. They should also consider how applied disciplines (such as Materials Engineering) should be formally incorporated into the College structure.

Resource Allocation

The ILL is now building, within the framework of the Millennium programme, in collaboration with EPSRC and a consortium led by Manchester University, a new Strain Imager [3]. This project includes a significant ILL resource commitment, in particular to upgrade guides and to provide an optimised beam to the instrument. This is most welcome and should enable the ILL to benefit from the upsurge in activity that is expected academically, and industrially, when the new international and European standards for stress determination by neutron scattering are issued. This commitment to materials engineering could be extended to fast, time synchronised, strain scanning (D20), SANS, radiography and tomography.

Marketing

The provision of an appropriate administrative structure, and engineering-user-friendly equipment and support, are necessary but not sufficient conditions for materials engineering to develop its potential at the ILL, particularly with increasing competition from other neutron (and synchrotron) facilities. The facility also needs a marketing focus on the European academic (and industrial) engineering community (in particular Materials, Mechanical, Aerospace and Electronic engineering) who are as yet largely unaware that the ILL exists.

Acknowledgements

Special thanks are due to the Scientists, Directorate and Support staff who have over the years supported strain scanning at the ILL. Thanks also to colleagues in the VAMAS TWA20 and RESTAND programmes who have done so much in the last four years to advance the subject.

References

Small angle neutron scattering from polymers using polarised neutrons

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We describe an experimental set-up used on D7 to investigate the scattering from solid polystyrene samples in the ‘low angle’ region. This procedure is related to standard small angle scattering (SANS) experiments.

1. The rationale

“Finally, there is one method that has not been widely used so far in SANS and which can measure directly the actual level of incoherent scattering: polarization analysis. It is to be hoped that, in future, SANS spectrometers will have polarization analysis as a standard option, thus obviating the need to estimate the level of incoherent scattering.” [1, p.67].

It is well known that before a coherent scattering function $S(Q)$ is chosen to fit a set of SANS data obtained on polymers, the measured data has to be normalised and the incoherent background removed. While the former can be achieved in terms of absolute calibration [1,2], the latter is not straightforward. Several procedures were developed over the years, but the main assumption, namely that the incoherent background is independent of $Q$, has been shown to be false by us [3, 4]. When the scattering of polarised neutrons with spin polarisation option is employed, the coherent and incoherent parts of the scattering are measured separately in the same experiment; in addition when the internal calibration is used, the scattering function is obtained in absolute units [5,6].

However, until now polarisation analysis was mainly available on instruments accessing high $Q$ range, of which D7 at the ILL is the primary example [7]. In what follows we describe a small angle set-up implemented on D7 for measuring the scattering from solid polystyrene and its ionomers samples. This experiment has a double purpose: 1. to investigate the possibility of using a small angle set-up on D7 simultaneously with wide angle measurement; 2. to analyse intermediate angle SANS data obtained on polystyrene and its ionomers in this little investigated region. This is the $Q$ region where the subtraction of the ‘flat’, incoherent background is the most questionable [1].

2. Experimental

2.1 Equipment

The small angle set-up on D7 consisted of one analyser with supermirrors [8] arranged horizontally. They lied concomitantly in a steady horizontal magnetic field produced near the sample.

Fig. 1: Sketch of the small angle scattering set-up with polarisation analysis (see text)

An array of 16 detectors, each 1.2 cm wide, with the sample-detector distance of 1.68 m covered an angular range of 9° (Fig. 1). An angular resolution of 0.01 Å⁻¹ was achieved for the incident wavelength $\lambda = 5.72$ Å. The resulting $Q$ ranged from 0.02 to 0.16 Å⁻¹. The finite flipping ratio for small angle scattering was measured using a strong scatterer, Vycor glass, which scatters without flip. In order to determine the flipping ratio at wide angles a quartz sample was used.

The experimentation with polarised neutrons on D7 has been extensively described before [5,6,9]. We mention only that one measures the coherent and incoherent parts of the scattering in the same experiment. After appropriate corrections the coherent cross-section is normalised to the incoherent one, yielding absolute calibration in barns:

$$\frac{\partial \sigma_{coh}}{\partial \Omega} = \sigma_{inc} \frac{I_{coh}}{4\pi I_{inc}} \quad (1)$$

2.2 Samples

Samples used were solid atactic and isotactic polystyrene and its sodium sulphonated ionomers. Some samples were selectively deuterated. Sample preparation is described in detail in [6] where also an extensive account of wide angle scattering results is given.

3. Results and discussion

An additional interest in these measurements is that at small angles the scattering pattern from some ionomers shows a peak, termed the ‘ionomer peak’ [10]. Our wide angle measurements
showed no evidence of the ordering which would result in a structural peak at small angles [6]. We saw no evidence of such peak in small angle measurements on D7 either.

Data presented in Figure 2 is a small selection of our measurements, plotted as the Guinier and Kratky plots; the latter as $IQ^2$ vs $Q$. Note that I is in absolute units.

The results of data fitting are listed in Table 1. Here $n$ is the number of monomers.

<table>
<thead>
<tr>
<th>sample</th>
<th>$R_g$, small $Q$</th>
<th>$n$, small $Q$</th>
<th>$R_g$, large $Q$</th>
<th>$n$, large $Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD63</td>
<td>51.9</td>
<td>110.5</td>
<td>19.1</td>
<td>3.2</td>
</tr>
<tr>
<td>HD</td>
<td>53.9</td>
<td>27.4</td>
<td>16.7</td>
<td>0.8</td>
</tr>
<tr>
<td>HD08</td>
<td>56.0</td>
<td>33</td>
<td>16.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 1: The values of $R_g$ and $n$ obtained from the Guinier plot...

The Guinier plot (Fig. 2a) shows that there is a qualitative difference in the behaviour of samples with high and low degrees of sulphonation. For example scattering curves for HD63 (which is 6.3 mole% sulphonation) lie above that of neutral polymer (HD) and low HD08 (meaning 0.8 mole% sulphonation) lie below it. First attempt at data analysis indicated, that for high degrees of sulphonation more monomer units contribute to the small angle scattering, whereas the radius of gyration does not show any systematic changes. For sulphonated samples, the Kratky plots (not shown) have the same general behaviour as the Guinier plots. Figure 2b shows the Kratky plot for selectively deuterated polystyrene, with DH - chain deuterated, HD - ring deuterated, and DD - fully deuterated polystyrene. In the Kratky region, the values of $R_g$ are in broad agreement with those quoted in the literature (e.g. [11,12]), however more detailed comparison would be only possible by using exactly the same samples on different instruments.

We have subsequently carried out SANS measurements on D11 for comparison with two major results: 1. The shape of the scattering patterns obtained on both spatial scales is the same, indicating a scaling behaviour [13] 2. There is no indication of the ‘ionomer peak’. This confirms our wide and small angle results on D7 and the hypothesis that the appearance of the ionomer peak is mainly due to the sample preparation process [6].

We mention in passing that polarisation analysis in the wide angle region enabled us to calibrate results obtained on the high $Q$ detector of the SANS instrument LOQ for another sample [14].

4. Conclusions

In this brief paper we demonstrated the feasibility of SANS measurements with polarisation analysis. It is clear that there is a need of combining data obtained in different $Q$ ranges in order to obtain a better understanding of the structure of polymers in the bulk. Especially the intermediate scattering range is difficult to interpret, and polarisation analysis offers the unmatched possibility of experimental separation of the incoherent background. Moreover, recent advances in molecular modelling give an additional insight into the conformation of polymers on the ‘semi-local’ scale. Purely coherent scattering gives the most accurate measure both for fitting procedures and refinement of theoretical models.

In the measurement on a series of polystyrene and its ionomers we found and agreement with the results obtained from wide angle measurements. In addition we performed complementary measurements on the same samples on D11 which gave the same type of scattering patterns. Preliminary data analysis indicated that the scaling laws could explain our results in the most consistent way.

Finally, the presence or absence of a short range order in amorphous polymers is still a rather controversial subject.

Fig. 2: Purely coherent scattering from polystyrene and its ionomers. a) Guinier analysis for HD63 (2_1.dat), HD (2_2.dat) and HD08 (2_3dat) samples. b) Kratky graph for DH (1), HD (2) and DD (3).

Industrial relevance of neutrons
It is therefore a fitting field of research for the next millennium. In the eighties’ and nineties’ experiments carried out at the ILL were at the forefront of science. We hope that this tradition will continue in the future, and that the scientists will be encouraged to tackle controversial subjects in innovative ways.

References
[13] Full data analysis in progress
The performance of thermally sprayed coatings is significantly influenced by residual stresses [1]. In the present research project five different spraying techniques (Vacuum, Atmospheric and Water Stabilized Plasma Spray, Flame Spray and Wire Arc Spray) were applied to manufacture metallic NiCrAlY deposits of diverse types of microstructures. Residual stress measurements were performed by the technique of neutron diffraction at the strain scanner D1A at the Institute Laue-Langevin in Grenoble / France and by bending measurements using laser profilometry [2]. The recently designed set-up at D1A allowed to employ two radially focusing collimators, defining a gauge volume of 0.65x1x10 mm³ [3]. Strain profiles in the substrate and in the deposit of about 1 mm thickness were obtained up to 50 mm near the interface. Estimated average stress values deduced from the neutron strain profile agree with results from bending measurements.

1. Introduction

A wide range of microstructures as well as spray technique dependent substrate and impact particle temperatures are known to vary significantly residual stress states within thermally sprayed coatings. Deposition thicknesses are often limited by a lack of adhesion due to build up of residual stresses. Knowing macroscopic average stress values as well as stress profiles - especially in the interface region - could help to better optimize the spraying parameters.

To characterize the microstructure of the deposits, one technique employed is small angle neutron scattering. By this method the total specific surface area as well as mean dimensions of the pores and stress induced cracks are determined. It can be expected that there is a connection between the void system, micro cracks and residual stresses. In this paper, we focus on the residual stress measurements recently performed at the instrument D1A.

2. Experimental

A commercially available NiCrAlY powder (Ni 67%, Cr 22%, Al 10%, Y 1%) was used as feedstock material and construction steel as substrate material. After cutting the substrates, they were heat treated to relax macroscopic stresses. To increase the adhesion, the substrates were grit blasted before the spraying process, as it is usually the case. The dimensions of the substrates were 100×25×6.4 mm³. Thicknesses of the coatings varied between 0.95 mm and 1.25 mm. All samples investigated were sprayed by optimized spray parameters.

Through thickness strain measurements were performed at the instrument D1A. The reflections Ni \{111\} in the deposit and Fe \{110\} in the substrate were chosen at a wavelength of 2.994 Ångstroem to achieve scattering angles values near 90 degrees for optimum spatial resolution. The configuration at the strain scanner D1A allows horizontal as well as vertical scans with high lateral resolution of 1 mm. The advantage of vertical scanning is the non existent surface error. Unfortunately the long path length in the high absorbing deposits does not allow vertical scans in reasonable measuring time. But thanks to the primary horizontal focusing collimator the surface effect is very small. The maximum error in this configuration is only \(\Delta d/d = 600 \times 10^{-6}\). Data shown are corrected by an experimental surface error obtained from scanning a stress free powder sample through the gauge volume.

The set-up for horizontal sample scans in transmission and reflection mode for strain measurements in the surface plane and perpendicular to it is shown in Figure 1. The sample position with respect to the neutron beam was obtained from the amplitudes of the Bragg peaks of the scan. From this position and the size of the gauge volume, the center of mass of the scattering material was calculated. Peak positions were converted into strain values implicitly employing the Bragg law by:

\[
\varepsilon = \frac{d_{\text{hkl}} - d_{\text{hkl},0}}{d_{\text{hkl},0}} = -\Delta \theta \cot \theta_0
\]
where \( d_{\text{ref}} \) is a stress free reference value obtained from an annealed feedstock powder and wire eroded free standing samples. The samples were mounted on a translation table and scanned through the gauge volume in steps of minimal 0.1 mm. To determine macroscopic average stress values, bending measurements were performed by applying laser profilometry. An UBM laser profilometer was used with a resolution of 30 data points per millimeter on the uncoated side of the substrate. For each sample analysed three subsequent scans along the extended direction were made: One scan after cutting and annealing, one after grit blasting and a final scan after spraying. An average strain value is obtained by Stoney’s equation for thin coatings:

\[
\sigma_{\text{Deposit}} = \frac{\kappa E_{\text{Deposit}} H_{\text{Deposit}}}{6h_{\text{Deposit}}(1-\nu_{\text{Deposit}})}
\]  

where \( \kappa \) is the curvature parameter obtained by the inverse radius of a circle fitted to the bending data. The difference in curvature between the grit-blasted and sprayed specimen reflects the stress induced by the spray process. The resulting \( \sigma_{\text{Deposit}} \) is the calculated constant in-plane stress value in the coating. In case of the discussed atmospheric plasma sprayed coating the following values were applied: Thickness of substrate and coating: \( h_{\text{subst}}= 4.6 \) mm and \( h_{\text{Deposit}} = 0.95 \) mm and elastic modulus and Poisson ratio of the substrate \( E_{\text{subst}}= 209 \) GPa and \( \nu_{\text{subst}}=0.33 \) [1].

### 3. Results

The strain profile in an Atmospheric Plasma Sprayed deposit and its substrate, determined by neutron strain scanning, is shown in Figure 2. Generally, the strain information obtained by the technique of strain scanning has to be regarded as the average over the region sampled by the gauge volume. This implies that near surfaces the spatial resolution is as high as the gauge volume has penetrated the sample. It is gradually reduced when the gauge volume is more and more filled with diffracting material. In case of the deposit, the gauge volume even exceeds the deposit thickness and therefore the strain values from the middle of the deposit have to be interpreted accordingly by keeping in mind that all regions of the deposit contribute to this strain information.

Table 1 contains the curvature data obtained for the APS sample by profilometry. Different signs of the curvature imply a bending of the sample in different directions. The compressive strain introduced by grit blasting is overcompensated by tensile "quenching" stresses induced during the deposition. From equation (2) a macroscopic average stress in the coating of \( \sigma_{\text{Deposit}} = 221 \) MPa is calculated.

Figure 2 displays the in-plane strain, oriented parallel to the surface, as a function of depth into the coating as well as into the substrate for the Atmospheric Plasma Sprayed NiCrAlY sample. In the coating the strains are tensile and highest at the surface. This can be explained by the fact that the spray process generates tensile quenching stresses in the coating, and that on top no more layers under tensile strain are deposited which could introduce compressive strains in the deeper layers and partly compensate the tensile strains. The data point nearest to the interface is already in the compressive region. In the substrate compressive strain is found near the interface, whereas deeper inside, near the uncoated surface, the stresses tend to be tensile. The compressive strain near the interface can be explained by the fact that the tensile stresses in the coating must be balanced by compressive strains in the substrate.

### 4. Conclusion and prospects

For an Atmospheric Plasma Sprayed deposit a residual strain profile in the coating as well as in the substrate obtained by neutron strain scanning is presented and compared with the bending results. As seen from figure 2, the technique of neutron scattering is able to resolve existing gradients - limited by the spatial resolution due to the size of the gauge volume. Quantitative agreement is found with the average macroscopic stress value obtained from curvature measurements within the assumptions of neutrons.

Table 1: Curvature data of the NiCrAlY APS coating obtained from profilometry

<table>
<thead>
<tr>
<th>curvature ( \kappa ) [1/m]</th>
<th>After grinding and annealing</th>
<th>After grit blasting</th>
<th>After spraying</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.1</td>
<td>0.091</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2: Through thickness strain profile in an atmospheric plasma sprayed NiCrAlY deposit and its substrate.
made. Particularly stresses near surfaces i.e. at the interface between the substrate and the deposit can be determined, though the data have to be corrected for the surface error. Measurements on samples manufactured by the remaining spraying techniques will be performed to analyse spray technique specific stress profiles and average stress values with the aim to relate the residual stresses to the microstructure and properties of the deposits. A strong influence between residual stresses and the void structure is expected due to microcracking, depending on the particular spraying technique.

Acknowledgements
The authors would like to acknowledge the partial EUREKA/KTI grant $\Sigma 1973$ obtained by the THERMETCOAT project.

References
In this work, three Ti6Al4V welded plate-shaped specimens have been studied by neutron diffraction. The effect of thickness on the residual stress field induced by welding was investigated in a thick walled welded sample (thickness 6 mm), and two thin ones (1.6 and 2 mm thick).

Experiments have been performed on the D1A diffractometer at the ILL, Grenoble (France) for the 6 and 1.6 mm thick specimens and on the E3 diffractometer at the HMI-BENSC, Berlin, Germany, for the 2 mm thick sample.

The unstrained interplanar distance \( d_0 \) has been evaluated with the plane stress hypothesis for each investigated gauge point. Large variations of \( d_0 \) have been found inside the heat affected zone (HAZ) and the weld pool, probably due to the large grain size, and some composition and precipitation gradients.

Basically, lower tensile stresses have been found in the thinnest sample, whereas the stress level is almost the same for the 6 and the 2 mm thick specimens. The strong similarity between the latter two samples is confirmed by the non-zero tensile stress state found far from the weld in both of them. The hoop stress lies always higher than the axial, which oscillate around zero for the 1.6 and the 6 mm samples.

**1. Material and samples**

The use of Ti6Al4V alloy for building spacecraft fuel tanks is well established [1]. From the microstructural point of view, it is considered to lie in the mixed \( \alpha+\beta \)-Ti alloys, as Vanadium stabilises the presence of the b-phase (bcc structure) at room temperature. In the parent material (PM), this implies the presence of globular \( \alpha \) precipitates in a matrix of finely dispersed \( \alpha \) embedded in residual \( \beta \), and a lamellar mixed \( \alpha+\beta \) structure in the Heat Affected Zone (HAZ) and in the Weld Pool (WP). Here the grain size is considerably larger and at the boundary between HAZ and WP it reaches 500 µm [2]. The volume fraction of the \( \beta \)-phase is slightly lower in the WP than in the PM, where it reaches 6-7%.

The tanks are built by joining two drawn half-cylinders, and successive cold worked. The thickness of the half-cylinders is usually a few millimetres and their external diameter is of the order of 0.5-2 metres. They are usually joined by TIG (Tungsten Inert Gas) welding. It is very important to know the stress state in the weld region, in order to ensure safety during both storage on earth and launch, and to increase the vehicle lifetime. The stress state due to fuel pressure and weight can be easily calculated, and therefore the total stress evaluation needs the determination of residual stresses already present in the tank. The investigated specimens, a thick-walled welded sample (thickness 6 mm), and two thin ones (1.6 and 2 mm thick) are schematically shown in Fig.1.
2. Experimental conditions

Despite the experimental difficulties linked to high incoherent background and small signal-to-noise ratio, measurements in the three principal strain directions were performed in all samples. Due to long counting times, only 4 gauge points (1 in the weld, 1 in the HAZ and 2 in the parent material) could be investigated at HMI, while thanks to the highest neutron flux available at ILL more points could be considered, namely 5 inside the weld, 5 in the HAZ and 1 far from the weld, with a signal-to-background ratio between 5 and 12.

Experiments have been performed at the D1A diffractometer of the ILL, Grenoble (France) for the 6 mm and the 1.6 mm thick and at HMI for the 2 mm thick sample. The α-Ti (011) Bragg peak was considered in the experiments at ILL, with a neutron wavelength of 2.99 Å, whereas at HMI-BeNSC the wavelength was 1.38 Å and two peaks (the (211) and the (203), both around 2θ = 90°) could be investigated. A gauge volume of 0.9 x 1 x 12 mm³ was used for the 1.6 mm thick and 0.9 x 4 x 8 mm³ for the 6 mm thick sample at ILL. The gauge volume used at HMI was 2 x 2 x 2 mm³.

3. Results

Measurements were performed in three perpendicular directions (this implies the scattering vector to be oriented along those directions), namely the hoop, axial and radial (Fig.1), supposed to be the principal directions of stress. As the geometry of the specimens suggests and because of the choice of the gauge volume, the unstrained interplanar distance d₀ has been evaluated with the plane stress hypothesis for each sample and in each investigated gauge point. Large changes of d₀ have been found (Fig. 2), especially inside the weld, due to the variation of the grain size and some composition and precipitation gradients between the molten zone and the HAZ, as mentioned above.

The Young’s modulus and the Poisson’s ratio, depending on the crystallographic plane under investigation, have been derived from literature: for the (011) peak the ones measured in [3] (E_011 = 98.9 GPa, ν_011 = 0.323), whereas for the (211) and the (203) peaks the values measured in [4] and from a Kröner model have been used respectively (E_{211} = 110.8 GPa, ν_{211} = 0.329; E_{203} = 113.8 GPa, ν_{203} = 0.322).

In this frame, the radial stress, which has been imposed to be vanishing, assumes a different meaning: it will be a check of the validity of the plane stress hypothesis. In all the cases it lies around zero, within the error bar. The stresses are plotted in Figs. 3-5. Despite the low number of investigated points for some of the measurements (the ones at HMI) the stress profiles look very similar. Higher stresses (in the hoop direction) are not (or not only) obtained inside the WP, but in the transition region between the WP and the SAZ (strain affected zone). The latter is in this case corresponding to the HAZ. To some extent an effect of the cap passes is to be reckoned.

The measured stress values in the weld region (250/350 MPa in the hoop direction) are comparable to results from previous strain gauge measurements (180 MPa) [5]. The difference could be ascribed to texture, grain size effects and to the presence of 2nd order stresses, which are not detected by strain gauge methods. This kind of stresses are probably due to the presence of a few percent of β-phase (see for example [2]).

Fig. 2: The variation of d₀ for the thickest (6 mm) sample. It is clear that regions of interface bring large jumps. The far-from-weld sides reach the same interplanar spacing, thus confirming the validity of the plane stress hypothesis.

Fig. 3: The axial and hoop stress for the thickest sample: values around 300 MPa are attained in the weld, but they decay rapidly outside. The far field level is not zero, but around 100-200 MPa.

Fig. 4: The axial and hoop stresses for the thinnest sample: lower values (max. around 180 MPa) are reached in the weld, and in the far field level is zero.
For both the 6 and 2 mm thick samples a non-zero value is attained far from weld. This suggests that this far field stress state probably comes from the drawing process or the successive cold-working after weld. This is confirmed by the fact that the stress state is in-plane homogeneous, which is typical for drawn samples.

Lower tensile stresses have been found in the thinnest sample and zero values are reached far from the weld pool. Once again, the highest stress values are obtained at the molten zone interface. This confirms that most of the stress in this type of alloy comes from phase transition and grain size effects.

4. Conclusions
A comparison can be drawn out between samples of different thickness. It is apparent that the 6 and 2 mm thick samples behave very similarly, whereas the 1.6 mm specimen shows somewhat complementary features. This can be summarised into the following points:

The far field stress level is not zero for the first two samples. This indicates a clear influence of the machining of the specimen. Due to a probable overlap of the machining stresses, the weld stresses reach higher values (and always tensile) in the first two samples. The thinnest one seems to be relaxed or it may be thought that the freedom to straining brings it to lower RS.

There are in any case many points in common between the investigated samples:

The stress profile is asymmetric with respect to weld centre. This depends on the order of the weld passes, at least in the thicker sample.

The highest stress values are reached at the transition region between HAZ and WP.

Some oscillations appear in the stress profile, above all in the WP. This is due to the coarse-grain structure of the molten zone, but also to the effect of the phase transitions on the weld stresses, as shown in [6] and [7].

The last points can be thought to characterise the specific alloy under investigation, and not only the single sample.

Acknowledgements
The Neutron sources (HMI, ILL) where the measurements have been carried out are acknowledged for the financial support in the frame of the EU Large Scale Facilities Programme. Mr.J. Linhart and Prof.W. Reimers (HMI) are acknowledged for the technical and scientific help.

References
On-line rheometry and small angle neutron scattering from complex fluids

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A technological important extension of classical scattering techniques is to investigate soft matter systems under non-equilibrium conditions. Especially mechanical deformation is known to have a strong influence on the morphology of complex fluids as colloidal dispersions, polymer and surfactant solutions or liquid crystals. Thus, it is necessary to monitor shear induced structural changes in-situ with shear flow. Although many different systems have been studied under shear during the last few years, in many cases the exact influence of the particular experimental parameters like shear rate, stress, strain or frequency remains to be investigated properly.

1. Experimental equipment

It is obvious that the combination of the powerful instrumentation for small angle neutron scattering (SANS) at the Institut Laue-Langevin (ILL), Grenoble, France, with a state-of-the-art rheometer will provide a unique possibility to directly correlate rheological properties of complex fluids with the underlying microstructure. For this purpose we installed a commercial rheometer (BOHLIN CVO 120 HR) on the SANS instrument D11 at ILL. The rheometer allows to perform many different rheological tests like simple shear flow either at constant shear stress or constant shear rate, creep and creep recovery as well as low and large amplitude oscillatory shear deformation. Since high quality quartz cylinders are used for the shear cell, excellent scattering data with lowest background can be obtained even in the range of very low q available at D11. A thermostated Searle-type shear cell has been developed in collaboration with Forschungszentrum Jülich, Germany (cf. Figure 1). It consists of two concentric cylinders made of quartz glass (HELLMA). The outer fixed cylinder is mounted in a steel jacket, which is connected to a water bath. The inner rotating cylinder fits into the Bohlin rheometer fixtures. Gap widths of the shear cell are either 1mm (sample volume 7.5ml) or 0.5mm (sample volume 4.5ml), depending on the diameter of the inner (rotating) cylinder. The rheometer is mounted on a translation table which enables a precise computer controlled positioning with respect to the neutron beam. Two different configurations are possible: one with the incident beam aligned along the direction of the velocity gradient (“radial” beam configuration) and another where the beam is along the flow direction (“tangential” configuration) [1]. The equipment is now available for user operation at ILL.

2. Example

As an example, we demonstrate the influence of added, watersoluble polymer on the structure and flow behaviour of a lyotropic lamellar phase without and with added, water soluble polymer (cf. Figure 2). Obviously, the flow curve of the sample was extremely altered when 0.5 wt% of poly(N-isopropylacrylamide, PNIPAM) was added. Without polymer, the sample was shear thinning, whereas shear thickening and shear thinning was observed when the polymer was present. The microstructure of the samples under shear was investigated by SANS at D11 simultaneously to the rheological measurement [2], [3].

SANS spectra shown in Figure 2 were measured in the tangential beam configuration as a function of increasing shear stress. For the sample without polymer, a shear induced alignment of the lamellae was found. It can be characterized by comparing the orientation of the layer normal with the direction of flow, the direction of the velocity gradient and the vorticity (neutral) direction, respectively.

The real-space orientation is denoted parallel when the layer normal points along the velocity gradient direction, and perpendicular when the layer normal points along the vorticity direction, respectively. At low shear stresses the Bragg peak is observed
along the velocity gradient direction thus the lamellae are aligned parallel to the walls of the shear cell. With increasing shear, the layers flip to the perpendicular orientation, which is characterized by the scattering peak along the neutral (vorticity) direction. The data clearly show that the shear thinning is correlated with a reorientation process of the surfactant double layers.

A different behaviour was observed when a small amount of the water soluble polymer was added to the aqueous surfactant solution. The SANS spectra obtained at low and high shear stresses were similar to those obtained from the sample without polymer. At intermediate shear stresses, however, the Bragg peak was observed along the entire azimuthal trace of the two dimensional multidetector in the tangential beam configuration, as shown in the upper part of Figure 2. From the isotropic Bragg scattering one can deduce the presence of multilamellar vesicles because the radial symmetry of such “onions” gives rise to an isotropic distribution of layer normals. Again, the simultaneous detection of rheological data and SANS spectra allows a direct correlation of flow properties with the (shear induced) microstructure. Obviously, the vesicles are destroyed at high shear and a perpendicular orientation of planar layers was found.

Fig. 2: Flow curve of a lyotropic lamellar phase without and with added, water soluble polymer, together with SANS spectra as measured at D11 with the tangential beam configuration

References
Instrumentation
Operation of sealed Microstrip Gas Chambers at the ILL

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1- ILL, GRENOBLE • 2- LURE, ORSAY

Microstrip Gas Chambers (MSGCs) were introduced at the ILL as a response to the problem of fabricating the large area neutron detector of the D20 neutron powder diffractometer. This banana-like detector consists of 48 MSGCs, each comprising 32 counting cells. It was in operation during 18 months before being stopped due to the progressive deterioration of the anode strips. In order to increase its lifetime, significant modifications were introduced in the recently assembled new version. Another instrument, was equipped with a modular uni-dimensional detector made of 9 MSGCs, each of them in an individual gas vessel. The ILL has also developed bi-dimensional MSGCs with a charge division readout. All these detectors employ sealed vessels containing a gas mixture at a pressure which can be as high as 15 bars, necessitating very clean conditions. This paper describes the experience acquired at the ILL in the fabrication and operation of these detectors.

1. Introduction

A Microstrip Gas Chamber has several advantages, compared with a Multi Wire Proportional Chamber: precision and mechanical stability of the strips; reproducibility of the fabrication; better counting rate and better position resolution. But it has also some disadvantages: its maximum amplification gain is significantly lower, and it is not resistant to sparks induced by highly ionizing particles. Furthermore, charging up of the surface and electrochemical reaction of the glass under high electric field must be avoided through a careful choice of the substrate. These restrictions severely limit the use of MSGC in High Energy Physics, and solutions using a pre-amplification stage have been proposed [1]. In neutron instrumentation, the detection conditions are simpler for the following reasons: counting rates are moderate, there is no constraint on the thickness or the density of the substrate, and the primary charge produced by the interaction of a neutron in the gas is 2 or 3 orders of magnitude higher than with minimum ionizing particles.

2. Fabrication outlines

The main difficulty of fabricating neutron gas detectors rests in the fact that, due to the cost of $^3$He used as the neutron converter, it is not possible to flush the gas through the detector, and, as it is well known, the long term stability of any sealed gas detector can only be obtained with a very low outgassing of its components. In addition to $^3$He, $^4$He, is added as the stopping and quenching gas. The nuclear interaction of a thermal neutron with an atom of $^3$He releases 764 keV of energy, shared by 2 ionizing particles, a proton and a triton, of different track lengths. This difference induces an error of localization which, to a good approximation, is given by $0.8 R_p$, where $R_p$ is the proton range [2]. $^4$He, is used for its short attenuation length, but this gas is known to contain freon impurities, which are electronegative and corrosive. Only gas of very high purity are used. In order to decrease the outgassing of the detector during its operation, internal parts are made of ceramic, glass, and metal, and the detector is heated to 150°C, and pumped with a turbo-molecular pump. Among the different parameters influencing the stability of an MSGC, the material of the substrate has been rapidly identified as one of the most important one. Actually, at the ILL, only detectors made with the Schott S8900 glass have given satisfaction concerning the long term stability, and all MSGC are made with this substrate. This glass has also the special property that it makes it possible to fabricate MSGCs with anode strips on one side of the glass, and cathode strips on the other side. This configuration, the so-called ”virtual cathode”[3], provides signals with the same amplitude, but of opposite sign, on the anode and on the cathode. Furthermore, we have measured amplification gain greater than $10^5$. The S8900 glass plate is polished and controlled under grazing light before fabrication of the MSGC. As an additional control for series of more than 10 plates we test the glass melt by first fabricating a single MSGC with this melt. Chromium has excellent mechanical properties and adheres very well to the glass substrate. The time spreading of the signals induced by the electrical resistivity of chromium is not a limitation for neutrons, regarding the time development of the signals they produce in gas detectors. This resistivity has in fact been turned into an advantage for charge division readout detectors by engraving a resistive line directly on the substrate. A very important point to consider is the quality of the electrical contact. For this reason, chromium strips are locally gold plated, and each readout strips of the MSGC is connected with a copper-Beryllium spring.

3. The multi-MSGC D20 detector

The D20 instrument, was the first large area detector at the ILL to make use of microstrip technology. A complete description of this detector can be found in [4]. The functional parameters of this detector are the most demanding at the ILL : 1536 readout
channels, each of the cells 2.57 mm wide (corresponding to an angle of 0.1 degree), sustaining a counting rate of 50 kHz/channel; a very good counting uniformity over the whole length of the detector (no dead space, nor dead channels), and a counting stability better than 0.1% over several days. A 128 channels MWPC prototype was first fabricated, but small uncertainties in the position of the sensitive wires, and of their mechanical tension, resulted in insufficient uniformity and stability. Therefore, the concept of the Microstrip Gas Counter was applied [5]. At the beginning of 1997 the D20 detector started its first phase of operation. It worked during 18 months without interruption, and produced scientific results of high quality. Unfortunately, the detector had to be stopped following a serious degradation of its performances due to a progressive destruction of the anode strips. An analysis of the electrodes was performed by Auger electron spectroscopy. This analysis showed that the chromium metal of the anodes was partially replaced by chromium-oxide. It resulted in a reduction of the effective width of the anodes, which subsequently induced destructive sparks. Before dismounting the D20 detector, we irradiated one of the plate locally with the primary neutron beam during several days. The integrated intensity was equivalent to the dose received during several months in normal conditions. We could not observe any specific degradation of the plate related to this test. It follows that the origin of the anode destruction had nothing to do with irradiation, and it suggests that the oxidation of the anode strips was initiated by the impurities present in the gas, or on the surface of the MSGC.

Several actions were performed in order to improve the life time of the detector. The most significant are the following: We suspected that the cleaning procedure of the MSGC didn’t remove completely residues coming from the engraving procedure. It has been reinforced with a bath of de-ionized water at 60°C during 30 minutes. The first machine used to control the electrical continuity of the anodes contained a gold needle scanning continuously the surface of the MSGC. In some cases, there were traces of gold attached to the surface, and even small scratches. This machine was replaced by a motionless system connected to a PC, which allows the simultaneous measurement of the resistivity of all the anodes of a MSGC plate.

The gas tightness is provided by 2 O-rings. The internal one wasn’t gas-tight. The two new O-rings were commissioned. For reason of ease of mounting, the MSGC anodes were connected together in two groups. This configuration creates a large electrical capacitance, and exposes the whole detector to the effect of high energy sparks. To reduce the energy of these sparks and their propagation, we changed the circuit of the anodes by individually filtered connections.

During the detector outgassing procedure (150°C during 2 weeks), a mass spectrometer has been used to control the content of the residual gases. This measurement wasn’t done the first time. The new detector is monitored continuously in real time with a multiplexed analyzing system which measures the pulse height spectrum of every MSGC.

The optimal pressure of the detection gas was determined as following: 1) it should not exceed 4 bars to avoid safety annual inspections, 2) the 4He pressure should be as high as possible to get the maximum of efficiency and 3) the CF4 pressure should be at above the value required to prevent double counting events. The D20 detector, which was at the origin of the development of micro-pattern gas detectors, is again in the users’ hands since September 2000.

4. The modular D4C detector

D4C is a liquid and amorphous materials neutron diffraction instrument. Its detector is made of 9 one-dimensional MSGCs, 64 channels each, included in an individual gas vessel containing 15 bar of 4He + CF4. Each module is sealed with a metallic joint Helicoflex. The modular configuration of D4C allows a quick repair in case of failure, and guarantees the continuous availability of the instrument. This detector, described with more details in [6], started its operation in August 2000.

5. Bidim80 Two-dimensionnal detectors

The first version of this series of detectors is described in [7]. The MSGC plate is made of a 127x127 mm2 Schott S8900 glass, 0.5 mm thick. The sensitive area is 80 x 80 mm². The front side structure consists of a pattern of chromium anodes, 1500 Å thick, 10 µm wide, with a pitch of 1 mm. In the direction perpendicular to the anode strips the localization is measured by charge division with a resistive line of 5 kΩ engraved on the substrate. The second coordinate is measured on the opposite face of the substrate with the cathode made of rectangular strips orthogonal to the anodes, or with a backgammon geometry parallel to the anodes. 5 detectors have been installed at the ILL, the first one in 1996.

5. Conclusion

Fast and accurate detectors are developed at the ILL to fully benefit from the neutron flux of the high power reactor. The large area D20 banana was the first detector to make use of Micro Strip Gas Chamber, but also the most complex one, and in that sense, represents an ideal tool for observation of this technology. A significant effort has been made to improve the lifetime of sealed MSGC detectors, and the experience acquired over 12 years is now converging towards stable fabrication requirements. A new large area 2D MSGC bidim200 has been fabricated for the future D19. It has been tested very recently, and is actually in a phase of commissioning. New conditions of detection imposed by the future spallation sources will reinforce the interest for these detectors.
References


What the general public knows of neutrons is, at best, the bomb and nuclear reactors; even the majority of the scientific community is not much aware of neutron science. The CD-ROM is thus designed to advertise for the neutrons. When available, it will present many aspects of neutron science, techniques, applications and facilities. It is not a physics course but rather an overview of the above topics in a form which is as much visual as possible (images, animations, simulations, videos).

This CD-ROM is a sister project of “Synchrotron Light”, a CD-ROM designed by the ESRF and commercialized by Springer Verlag since March 2001. Both have the same technical designer: iMedia Software <http://www.imediasoft.fr/>.

1. Why a CD-ROM about neutrons?

In 1992 ILL physicists declined participating to the general public exhibition “La science en fête” because they claimed had nothing to show they could put on a table. Thus, in three months, an early interactive multimedia presentation of neutron science mixing interactive slide shows and interactive simulations was designed [1] and shown on self served computers (Fig. 1). The debriefing of the festival [2] concluded that the interactive video was a success and that the ILL should go on.

First conclusion: “Scientific communication must go interactive!”

In 1996 the French Neutron Society (SFN) felt very much concerned with a slow decrease of the number of French proposals for neutrons experiments. Therefore the SFN organized a workshop(1) at the ILL in October 96 to give a chance to university professors to meet neutrons scientists and to work together on that problem.

The conclusion was that neutron science lacks visibility. In France it is totally unknown from the general public. In laboratories and universities, ILL and LLB are only known from a few experts. In the industry nobody is aware of possible neutron solutions to given problems. Neutrons are barely taught and teachers said “How can we design a neutron course? We lack good and up-to-date text books, we lack ready to use examples, we lack attractive documents, etc.” The SFN thus decided of several actions and the early CD-ROM “Video_ILL_interactive” [3] was distributed to the SFN workshop participants.

Second conclusion: “Doing good neutron science is one thing but we must communicate towards teachers, students and the general public!”

March 1998: The ESRF was already involved in the CD-ROM project “Synchrotron light” [4] together with InterMedia Software. Dan Bog, the boss of the company, convinced the ILL to start a sister project about neutron science.

Third conclusion: “Major scientific editors like Springer Verlag may help promoting our science.”

2. Today project status

Today the five parts of the CD-ROM have the following completion levels: Sources (90%, 62 screens); Science (70%, 300 screens); Tools (50%, 50 screens); Applications (30%/100%, 115 screens)(2); Facilities (?) (3).

On the technical side, the CD will be Mac/PC compatible and both English and French. It was originally designed with MacroMedia Director and with the usual window size of 640x480 pixels for 13” screens. However, since these screens are disappearing, a window size of 800x600 pixels is now more convenient. Therefore iMedia Software recently decided to fully redesign the CD at a 800x600 size and with Flash, a vectorial technology (Fig. 2). This means that the existing animations are also being redesigned to Flash and this will save space for more videos but at the expense of extra developing efforts.

The current cost for the ILL is about 3.5 man/year. The project

(1) “Réunion de la Bienvenue”, 30-31 Oct. 96, Grenoble
(2) 30% is the real status; 100% means that we cannot go farther with the current manpower, despite of obvious incompleteness of that part.
(3) These pages were provided by the labs who already decided to participate to the CD-rom: ILL, ISIS, Forschungszentrum Jülich, LANSCE, LLB. Labs willing to participate should contact Dan Bog <bog@imediasoft.fr>.

Fig. 1: The ILL stand at “La fête de la science” (1992). But where is the interactive presentation? Very young to very old people often crowded around the computers to play with it.
is supported by the Neutron Round Table (8000 €). IMedia Software
receives no money from the ILL but is confident that a major
multimedia editor like Springer will fund the project.
The timetable is summer 2001 for scripts for Sources, Science,
Tools ; a beta CD-rom should be available by the end of the year
and about six extra months will be necessary for corrections, test-
ing and various technical adjustments.

3. How to participate to the CD
Everybody is warmly welcome to participate since we don’t want
this CD-rom to be ILL centric. The most obvious needs are for
the chapter “Applications” since its present contents (see table
1) is far from reflecting the current status of neutron applications.
A “Guide to author’s” is available in the form of a set of html pages
either from <filhol@ill.fr> or from the Millennium’s web page on
<http://www.ill.fr>.

4- Conclusions
The forseen project duration will be about four years to be com-
pared to the three and a half years for the Synchrotron Light proj-
ect. In fact the neutron project is more ambitious (more physics
inside) but less funded and with less manpower. When finished
the set of scripts will be equivalent to a 1000 page book or more.
The main difficulty we see for the close futur will be the need for
a bunch of courageous volunteers (physicists and students) for
the beta testing. But are there any volunteers ? Please send a mes-
sage to filhol@ill.fr.

References
[3] ILL internal note, DS/CS-AF 024/97

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Table 1: Foreseen CD-ROM contents.
Your participation to this part of the CD would be greatly appreciate since the
current CD team will not have time to prepare scripts for the “desirable topics”
indicated by ???.
Light grey: scripts already available; Dark grey: scripts being prepared; ???:
desirable topics.
D20: New Developments and Experiments at the Intensity Frontier of Neutron Powder Diffraction

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D20 is a 2-axis diffractometer, providing high intensity with a large stationary, curved linear position sensitive detector. In the future, a radial oscillating collimator will suppress background contributions from sample environment. A variably vertical focussing Germanium monochromator will allow for higher resolution at higher take-off angles of 63 to 122°. Two new copper transmission monochromators, with optimised fixed vertical focussing for the small take-off angles 42° and 28°, will improve flux and peak-shape.

1. Introduction: high intensity and versatility

D20 was conceived as an improved high intensity powder diffractometer in the reactor. Today, two vertically focussing monochromators, 4 take-off angles, and optional Soller collimators provide a large choice in Q-space, resolution, wavelength, and flux. A large position sensitive detector (PSD), with a good angular definition provides high, simultaneous counting rates. The high intensity adapts D20 for one-shot diffraction studies of chemical kinetics with time constants down to a second, or fast cyclic phenomena below 100 µs, using a stroboscopic data acquisition mode. The high intensity and the stability of the detector permit high precision in intensity measurements, needed for differential acquisitions in magnetism and physisorption, or studies on disordered systems.

1.1 Neutron optics and present monochromators

The two present monochromators of D20 provide fixed vertically focussing. A monochromator of pyrolitic graphite HOPG (002) in reflection position offers $\lambda \approx 2.4 \ \text{Å}$ at a take-off angle of 42°. A preceding pyrolitic graphite filter of 6 cm thickness in the incident beam suppresses second harmonics. The transmission at 2.4 Å is about 70% [1]. A copper monochromator Cu (200) in transmission gives wavelengths of $\lambda = 0.82, 0.88, 0.94$ or 1.3 Å at take-off angles of 26°, 28°, 30° or 42°. At $\lambda = 1.3 \ \text{Å}$ the monochromatic beam has its highest flux of about $6 \cdot 10^7 \ \text{n·cm}^{-2} \cdot \text{s}^{-1}$. Soller collimators allow to reduce the natural divergence (27') of the incident polychromatic beam down to $\alpha_s = 10'$ or 20'.

1.2 The new position sensitive detector (PSD)

The PSD housing of aluminium provides a detection zone of about 4 m long and 150 mm high. The PSD is filled with 3.1 bars He and 0.8 bar CF₄ and has a detection gap of 53 mm. For this large PSD the micro-strip gas chamber (MSGC) technology has been developed [2]: chromium is sputtered on the polished surface of electronically conducting glass plates. Then the chromium is etched to create conductive micro-strip electrodes (alternately 4 cathodes and 4 thin anodes per detection cell). The detection plates have each 32 cells of 2.568 mm (0.1") each, covering in total 3.2", as mounted on a radius of 1471 mm. The current PSD covers 153.6", as 48 plates were mounted. The 32 cells of one plate have 32 independent outputs from the detector through a metal-ceramic plug. The major interests of the micro-strip detection system for the instrument D20 are the precise and perfectly stable geometry, resulting in a very homogeneous response and a very high stability, a high gaseous amplification with a low high voltage (750 V) between anode and cathode, and the possibility of very high counting rates because of the small distance between anode and cathode (170 µm) giving a fast evacuation of the positive ions.

All 1536 cells are connected to as many amplifiers, followed by the same number of anti-coincidence logics (CLET): After the amplifier signal first passed the discriminator threshold for a particular cell, its neighboured cells are prevented from counting a same event a second or third time during 1.5 µs. 2.5 µs after having passed the threshold a cell may count again an event. Therefore, the total dead time is about 5.5 µs (in three different cells). Because of this parallelism, the counting rate is only limited to about 50000 ± per cell (dead time 27.5%). The amplifiers and discriminators are regrouped by 32 in one of the 48 boxes directly plugged at the backside of the detector.

The data acquisition system (DAS) has a parallel input for up to 1600 cells. The dead time between two successive diagrams is 20 ns. This allows recording a series of short diagrams, typically a few seconds each, to observe a kinetic irreversible phenomena. If the kinetic process is much faster and reversible, one can reproduce it many times in a cyclic way, and the DAS works in stroboscopic mode. Today, up to 256 complete diagrams or ‘slices’ can be recorded, with a minimum active counting time ‘window’ (open ‘gate’) of 1 µs inside each slice of at least 30 µs (so a maximum slice frequency of 33 kHz).

2. Instrument performances

2.1 Flux and detected intensity

The flux $\phi(\lambda)$ resulting from the Maxwellian flux distribution

$$\phi(\lambda) \propto (\lambda/\lambda_0)^2 \cdot \exp(-\lambda/\lambda_0)$$

with $\lambda_0 = 1.8 \ \text{Å}$ from the thermal source of the high flux reactor (HFR) is at 0.82 Å 55% of that at 1.3 Å and at 2.4 Å 18% of that at 1.3 Å at the monochromator...
position. Absolute flux measurements by means of gold platelet activation had been performed for several configurations at the sample position: $1.7 \cdot 10^7$ n/cm$^2$/s at 0.82 Å, $6.0 \cdot 10^7$ n/cm$^2$/s at 1.3 Å, and $3.7 \cdot 10^7$ n/cm$^2$/s at 2.4 Å. This results from the monochromator reflectivity, increasing with $\lambda^3$, and the different geometric circumstances. The finally detected intensity depends additionally on the wavelength dependent scattering of the sample ($\propto \lambda^3$) and the efficiency $e_D$ of the detector. The latter depends on the wavelength by $e_D = 1 - \exp(-b \cdot \lambda)$ with the constant b of $b = 0.07417$ bar$^{-1}$cm$^{-1}$ after the continuous scan in about 300 steps of 0.1 Å.

3.7·10$^7$ n/cm$^2$/s at 2.4 Å. This results from the monochromator reflectivity, increasing with $\lambda^3$, and the different geometric circumstances. The finally detected intensity depends additionally on the wavelength dependent scattering of the sample ($\propto \lambda^3$) and the efficiency $e_D$ of the detector. The latter depends on the wavelength by $e_D = 1 - \exp(-b \cdot \lambda)$ with the constant b of $b = 0.07417$ bar$^{-1}$cm$^{-1}$ after the continuous scan in about 300 steps of 0.1 Å.

2.2 Resolution and peak-shape

Resolution curves have been determined empirically from powder patterns of standard samples like silicon and subsequent determination of the parameters of the Cagliotti function via a full profile pattern matching procedure or application of the Rietveld method. They can be estimated as well from geometrical considerations, or, more precisely, using an existing Monte-Carlo ray-tracing simulation of the instrument by means of McStas [4].

A pseudo-Voigt function does not fit well the observed shape of Bragg peaks at high diffraction angles, as the mixing factor $\eta$ of this linear combination of Gaussian and Lorentzian line shape becomes negative. Monte-Carlo ray-tracing reproduces precisely the observed peak-shape, so a mistake in the instrumental setup can be excluded. This observed super-Gaussian shape is the result of convolution of several beam profiles, which are not only Gaussian (as approximately the monochromator mosaic) but also as well triangular (Soller collimator), rectangular (not collimated primary beam), or circular (sample cylinder). A good fit can be obtained by using a convolution function of a rectangle and a Gauss or pseudo-Voigt function. There is no further benefit from introducing a circular or triangular component. A peak asymmetry due to the interception of the curved Debye-Scherrer cones with linear, 15 cm high detection cells is observed at low angles. This effect can be described analytically, using the height of the sample and of the zone of detection and the distance from sample to detector [5]. Vertical monochromator mosaic, vertical divergence due to vertical focussing with a small number of monochromator blades, and subsequently a non-homogenous illumination of the sample height, make this phenomenon only roughly describable by the three mentioned parameters.

2.3 Detection response and stability

efficiency and angular calibrations

The threshold values of all 1536 discriminators have been adjusted to level out locally the different efficiency of the preceding amplifiers. The static noise in the uncorrected counting rate of the PSD could so be reduced to about 0.3%. This does not include the regular, homogenous efficiency variations with the periodicity of 32 cells (one MSGC plate), which is in the order of up to 2% in the plate centres and down to -5% on the plate borders. An efficiency correction is applied to the raw data, which is calculated from a $2\theta$ scan in about 300 steps of 0.1° (one cell-width) over a mostly incoherently scattering vanadium sample. The relative efficiencies are concluded from the comparison of counting rates from different cells at the same angular position.

To obtain the response curve or each detector cell, the PSD has been scanned with a very narrow neutron beam (cadmium slits of 1 mm width close to the PSD entrance window) in little steps using the programmable $2\theta$ movement of the detector. The centre of counting rate of each cell gives the angular position for an angular calibration. The positions are not exactly equidistant in angle and consequently, widths are not exactly 0.1° per cell. The curved PSD entrance window and the polygonal arrangement of the MSGC plates result in periodical variations of about 5% of cell width (and consequently in efficiency), as mentioned above, due to a slight deformation of the electrical field, in a first approximation homogeneously parallel and perpendicular to the entrance window. A ray-tracing simulation reproduces this scan exactly, confirming the observation. The PSD has been shown to be completely error-free. During four months of operation, only about 1% of the detector cells changed their efficiency in the order of 1% due to noisy amplifiers. There is no evidence of any degradation of the PSD.

3. Projects

3.1 Germanium monochromator

A variable vertical focussing Germanium monochromator (113) will allow for higher resolution, as higher take-off angles of 65°, 90°, and 120° ($\pm 2\theta$) become accessible, resulting in wavelengths from 1.8 (63°) to 3.0 Å (122°) for (113), down to between 0.6 (63°) and 1.1 Å (122°) for (119), one of several available out-of-plane reflections, profiting in resolution and flux from the Fankuchen effect [6]. The resolution will approach $D_d/d = 10^3$, whilst still having a considerable flux of $5 \cdot 10^7$ n/s/cm$^2$ at the sample position. The mechanical support with the variable focussing mechanism is ready, as well as the mosaic crystal blades, the new monochromator is planned to become operational in 2001 after modification of the instrument’s surrounding biological protection.

3.2 Copper monochromators

The vertical focussing of the existing copper monochromator is optimised only for a compromise in between the take-off angles of 42° and 28°±2°. As it consists of two columns of crystals so it gives a slight decrease of intensity in the beam centre. Additionally these columns are of different reflectivity, giving an additional asymmetric component to the peak-shape, when using the full monochromator. Therefore, today, in order to obtain good peak-shapes, one half of the monochromator is hidden in most cases by the horizontal monochromator slits to improve peak-shape. Two new copper (002) transmission monochromators, with optimised fixed vertical focussing for both take-off angles, 44° and 28° ($\pm 2\theta$), will provide a higher flux of up to $10^8$ n/s/cm$^2$ at 1.3 Å (take-off 42°). With only one column of larger mosaic crystal blades (packed wafers), these monochromators will also provide a clean
peak-shape. The blades will be optimised in thickness and horizontal mosaic spread for each of both take-off angles: 4 mm and 13’ for 28˚ and 6 mm and 17’ for 42˚. The vertical mosaic will be kept at a feasible minimum of about 4’.

3.3 Radial oscillating collimator
D20 offers different dedicated sample environments, among them a vacuum vessel, a cryostat with vanadium tail, and a furnace with vanadium heater. Screens of cadmium, respectively B₄C in the case of the furnace, mask the parasitic Bragg-peaks of the aluminium wall of any of these vessels. It is foreseen to use a radial oscillating collimator (ROC) for suppressing background contributions of other sample environments of the ILL pool or from external users, becoming an issue with increasing number of in situ experiments. A ROC will exclude contributions to the diffraction pattern from sample environment construction materials at a certain distance from the sample. Additionally, it will improve to a certain extend, depending on its focus aperture, which has to be chosen carefully, resolution and peak-shape due to its nearly triangular transfer function: $T = 1 - \frac{\sin (d/r_o) - \sin (d/r_i)}{p}$ with the inner radius $r_i$, the outer $r_o$, the angular pitch between blades $p$, and the distance $d$ from the centre of the focus, in a plane perpendicular to the neutron vector.

References
The main requirements for a reflectometer are high flux, flexible resolution, accurate collimation and precision neutron detection. D17 has all of these properties. This article shows some of the first results taken with D17 using the time-of-flight (TOF) option including data from the first official experiment.

The principal reason for having a TOF option on this instrument was to enable experiments on the kinetics of planar materials to be performed. This is possible because a range of q is measured simultaneously using a white beam as opposed to the monochromatic mode where the sample angle has to be rotated for each point in q. The TOF is less efficient than the monochromatic mode in terms of the flux available at each q point as the flux at the extremes of usable wavelengths are much lower than the peak flux used in the monochromatic mode. Having a chopper system where the resolution can be continuously varied, however, compensates for this as flux can be gained when high resolution is not required. A second advantage is that when setting up experiments it is easy to check the alignment of the sample after only a few seconds of data acquisition. For example figure 1 shows raw data from counting for only 10 seconds. The vertical resolution of the detector has been summed resulting in a picture with X-pixels horizontally, corresponding to $2\theta$, and the vertical pixels representing wavelength. It can be seen that above the critical wavelength where total reflection occurs there is no intensity in the direction of the incoming beam. This means that no neutrons fly past the sample surface and this surface is under illuminated and correctly aligned with respect to the incoming beam. The picture demonstrates the fact that neutrons obey simple optical laws. It can be seen that below the critical wavelength the transmitted beam is refracted towards the horizon showing that neutrons, unlike light, have a refractive index less than one (for a material with positive scattering length density). The curvature of the diffracted beam with wavelength is due to the fact that the formula for neutron refractive index has a wavelength squared term.

In one of the first officially scheduled experiments involved investigating model living cells in the form of adsorbed lipid bi-layers at a silicon/water interface [1]. Complexes of cationic lipids and DNA have been shown to transfect cells in vivo and in vitro, which has lead to much excitement in the area of gene therapy. The mechanism by which the lipid improves the transfection efficiency of DNA into cells, however, is not well understood. In order to investigate the interaction of these lipid structures with a cell membrane, neutron reflectivity has been used. A model cell membrane of deuterated lipid was deposited on a silicon block, and protonated cationic liposomes added to the bulk solution in the absence of DNA. Over time a change is seen in the reflectivity curve of the model membrane. It was thought that the lipid liposomes would collapse onto the model membrane to form an additional, positively charged bilayer. In fact this appears not to happen, instead, exchange occurs between the deuterated lipid of the model membrane and the protonated lipid of the cationic liposomes. Thus the composition of the model membrane changes from deuterated to protonated lipid and becomes positively charged. If a similar process occurs in the presence of DNA, then it would be expected that the negatively charged DNA would be
bound to the surface of the model membrane where this exchange has occurred. Additional data has been collected for this system in the presence of DNA, and is currently being treated to determine whether this is indeed the case. The q-range explored on D17 (see Figure 2) was larger than that measured in the past on this kind of sample as the lowest reflectivity is usually limited by background from bulk water and sample cell. With the high flux and wide-angle multi-detector reflectivities of \( \sim 10^{-3} \) could be measured in the reasonable time of one hour.

In addition to the ability to subtract incoherent backgrounds more efficiently there is another advantage to having a large area multi-detector. About the specular reflection there can be off-specular scattering arising from surface roughness or as in the case described below, low angle diffraction. The sample was a diffraction grating consisting of a glass substrate with thousands of strips of nickel, 900Å deep separated by 10µm (Ott and Menelle, Saclay). If this grating were placed perpendicular to the incoming beam then 10Å neutrons would be diffracted only a few thousandths of a degree (\( q_x = 6 \times 10^{-4} \text{ Å}^{-1} \)), beyond the range of any existing small angle instrument. However, if the incoming beam strikes the grating surface at a glancing angle then many diffraction orders can be seen in both the reflected and transmitted beams at measurable angles of deflection (figure 3). In addition to information on the stripe separation, the depth profile (consistent with 900Å) is revealed in the ripples of intensity found running along the specular line and the various reflected diffraction orders. The diagonal line of intensity coming from where the specular line just totally reflects is a Yoneda wing and is a consequence of the roughness along the surface of the nickel strips. D17 is ideally suited to investigate not just structures as a function of depth but also within the plane such as magnetic grain boundaries or polymer droplets.

Recently both the monochromatic and the polarised neutron modes of the instrument have been successfully tested.

<table>
<thead>
<tr>
<th>Useful wavelength range</th>
<th>2-20Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qz range (normal to a surface)</td>
<td>( 2 \times 10^{-4} - 4 \text{ Å}^{-1} )</td>
</tr>
<tr>
<td>Qx range (within a surface)</td>
<td>( 1 \times 10^{-4} - 2 \times 10^{-3} \text{ Å}^{-1} )</td>
</tr>
<tr>
<td>White beam flux</td>
<td>( 10^8 \text{ n/s/cm}^2 )</td>
</tr>
<tr>
<td>Detector size</td>
<td>250 x 500 mm</td>
</tr>
<tr>
<td>Detector distance</td>
<td>1.1-3.4 m</td>
</tr>
<tr>
<td>Detector resolution</td>
<td>1.8 x 3 mm</td>
</tr>
</tbody>
</table>

**Conclusions**

The D17 instrument has finished the period of commissioning and is operating with scheduled experiments. The ability to explore low reflectivities, explore wider q-range with flexible resolution and enable kinetic experiments provides the opportunity for new science in the areas of solid and solid/liquid interfaces.

**Reference**

MCNP4C Calculations for the ILL HFR Reactor

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The Monte Carlo MCNP4C code was applied to simulate the characteristics (e.g. neutron flux) of different ILL beam tubes and in case of the new BRISP instrument to determine the expected radiation dose outside the primary shielding

1. The MCNP Method

MCNP is a general Monte-Carlo particle transport code for neutrons, photons and electrons. The statistical sampling process of the Monte-Carlo method is based on the selection of random numbers. The individual probabilistic events that comprise a process are simulated sequentially. When Monte Carlo methods are applied to processes such as the interaction of nuclear particles with materials individual histories are chosen by following each of many particles from a source throughout its life to its death in some terminal category (absorption, fission, escape, etc.). Probability distributions are randomly sampled using transport data to determine the outcome at each step of its life. For MCNP calculations the model must be properly divided into geometric cells of specified materials in which the particles (neutrons, photons) can interact. MCNP uses continuous-energy and atomic data libraries. The primary data sources are ENDF (Evaluated Nuclear Data File), ENDL (Evaluated Nuclear Data Library), ACTL (Activation Library) and T2 (Applied Nuclear Science Group, LA). [3,4,5].

2. The ILL HFR MCNP Model

The ILL High Flux Reactor model has been developed by Ageron / Gross / Mahling-Ennaoui / Jahn. It provides principal characteristics of the reactor such as neutron flux, neutron spectra and relative reactivity properties. Instrument shielding calculations were divided into three parts because a single step neutron transport over large distances and the whole solid angle can not be computed with sufficient statistics due to the fact that the neutron flux from the beam tube bottom to the instrument monochromator is decreased by several orders of magnitude. Therefore the following three successive MCNP calculations had to be performed: (1) calculation of the beam tube bottom characteristics (neutron flux [n/s.cm2] and source strength [n/s]), the critical reactor itself was considered to be the neutron source, therefore this calculation is called MCNP critical calculation; (2) streaming of the neutrons through the beam tube and definition of a virtual neutron source at the beam tube exit, again characterised by a neutron flux [n/s.cm2] and a source strength [n/s] at a particular position (flange position) of the tube exit. In these calculations neutrons (and photons) were transported from the beam tube bottom to the beam tube exit. The beam tube bottom was considered to be a neutron surface source. The neutrons have been calculated in two energy groups: thermal neutrons and faster than thermal neutrons; (3) simulation of the radiation field around the monochromator shielding produced by neutrons from the virtual source and secondary photons. The biological dose equivalent rates were determined using the corresponding dose rate conversion factors: neutron dose factors (mSv/h) ICRP 74, and gamma dose factors (mSv/h) ICRU 47, 1992a [1,2,7].

3. BRISP MCNP Model

BRISP will be a thermal neutron Brillouin scattering spectrometer that exploits the time-of-flight technique and is optimised to operate at small scattering angles with good energy resolution. This instrument will enable the investigation of the dynamics of low momentum transfer excitations in condensed matter, particularly in magnetic and disordered systems, to study fundamental properties of liquids, interatomic forces, etc. [8]. BRISP will be placed at the inclined beam tube H3 of the ILL. The MCNP geometry model for the H3 beam tube and the shielding of the monochromator chamber is shown in figure 1.

3.1 H3 Neutron Fluxes

The calculated H3 neutron fluxes for the beam tube bottom and for the exit are shown in table 1. The corresponding measured thermal flux at the exit of H4 (very similar to H3) at r=598 cm core distance is 1.64E+10 [n/s.cm2].

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**Fig. 1:** reactor model cut 45 cm from the core axis with the inclined beam tube H3 and the BRISP monochromator shielding, fluxes were calculated for 58 MW reactor power
3.2 IH3 Bottom Spectrum

The calculated IH3 bottom neutron spectrum is shown in figure 2. In a successive MCNP neutron streaming calculation it is used for source characterisation. The gamma spectrum at the beam tube bottom has not been studied in detail because, according to the Security Report [3], the influence of the primary photons can be neglected compared to the secondary photon production. Test simulations showed that photons from the beam tube bottom lead to a non-negligible dose only behind the beam stop in a small area around the direct beam.

3.3 BRISP Instrument Shielding

MCNP shielding calculations were necessary for the construction of the BRISP primary spectrometer. Due to the special position of the instrument on a platform the weight of the shielding had to be minimised under the condition that radiological and seismic restrictions were still fulfilled. The calculated dose rates are shown in figure 3.

4. Benchmarking the Thermal Neutron Flux Properties and Conclusions

A comparison of measured and calculated flux data in table 2 showed, that the model provides a systematically overestimated neutron flux. The factors between calculated and measured fluxes are varying between 1.5 - 2.0, taking into account, that the measured and calculated positions were not exactly corresponding. Reasons for the discrepancies might be due to the fact that: first: not all (neutron absorbing) structures in the reflector are modelled, second: the power normalisation does not include the influence of the turbines, third: better data (including cross section libraries) for material compositions, temperature effects etc. might be available. These effects on the model need to be studied in more detail in upcoming calculations. Furthermore for long range neutron transport calculations all available variance reduction techniques should be applied in a next step, such as weight windows, Russian roulette and source biasing. This should lead to a strong reduction of computing time, especially for critical calculations, which are running on a 800 MHz Linux IBM PC about two to three weeks! MCNP provides a source creating subroutine that is very helpful for calculations of long range neutron transport, but it can be only used with properly adjusted variance reduc-

<table>
<thead>
<tr>
<th>Energy bin</th>
<th>Calculated bottom r = 61 cm</th>
<th>Calculated bottom r = 574 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flux</td>
<td>Error</td>
</tr>
<tr>
<td>Thermal</td>
<td>6.25E-07</td>
<td>9.82E+14</td>
</tr>
<tr>
<td>Epithermal</td>
<td>5.50E-03</td>
<td>1.68E+13</td>
</tr>
<tr>
<td>Intermediate</td>
<td>8.21E-01</td>
<td>1.91E+12</td>
</tr>
<tr>
<td>Fast</td>
<td>1.00E+01</td>
<td>6.64E+11</td>
</tr>
</tbody>
</table>

Table 1: IH3 inclined beam tube neutron flux [n/s.cm²], r - distance to the core centre.

Fig. 2: Neutron energy spectrum at the IH3 beam tube bottom. It was calculated in two critical calculations running 10 000 cycles each (corresponding to 10 000 neutron generations) for thermal and faster than thermal neutrons, respectively. The results are compared to a Maxwellian distribution in the thermal range and to HFR security data for higher energy neutrons [3].

<table>
<thead>
<tr>
<th>Beam tube</th>
<th>Core distance (cm)</th>
<th>Measured flux</th>
<th>Core distance (cm)</th>
<th>Calculated flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>H9</td>
<td>60</td>
<td>5.30E+14</td>
<td>59.58</td>
<td>8.54E+14</td>
</tr>
<tr>
<td>IH3</td>
<td>598.00 (IH4)</td>
<td>1.64E+10 (IH4)</td>
<td>574.00</td>
<td>2.80E+10</td>
</tr>
<tr>
<td>H13</td>
<td>502.72</td>
<td>5.70E+10</td>
<td>468.55</td>
<td>1.15E+11</td>
</tr>
</tbody>
</table>

Position of the bottom nose centre (cm) for neutrons and photons (underlined numbers) are shown at different positions near the shielding.

Table 2: Calculated vs. measured beam tube neutron fluxes [n/s.cm²] and beam tube positions.
tion techniques. The new intermediate version of MCNP4C called MCNP4C2 should provide visual features for generated weight windows not depending on cell structures but on individually generated and superimposed weight windows. Nevertheless, the work presented here was absolutely necessary to prove the basic physical assumptions of the ILL HFR MCNP model. When using sophisticated statistical sampling methods a systematic error (under- or overestimated flux) is likely to happen [5, 6, 7].

Acknowledgements
The authors like to thank W. Kaiser, J. Tribolet and other people from the radio protection for providing flux measurement data, the staff in the ILL construction office for technical information concerning beam tube constructions, F. Pinet for helpful support when optimising the computing time and H. Faust for fruitful discussions. Furthermore we would like to acknowledge G. Fieg and F. Fischer from the Forschungszentrum Karlsruhe for their advice at the start-up of the shielding calculations.

References
[3] ILL HFR Sicherheitsbericht
We study the possibility of improving both the neutron flux and the dynamic range of the backscattering spectrometer IN16 at the ILL by using the Phase Space Transformation (PST) technique. In order to obtain reliable information about the possible gain in flux that could be achieved in this way, we have performed several Monte Carlo simulations comparing the performance of the existing instrument with that of an hypothetical IN16B, resulting that a gain up to a factor of 8 can be expected.

1. Introduction

The backscattering (BS) spectrometer IN16 became operational at the ILL in 1995, representing a major improvement over existing backscattering instruments. Thus, IN16 was the first BS spectrometer of the second generation, i.e. the first that maintained the perfect BS condition at the monochromator side. This is achieved by using a focusing deflector and a deflection chopper, together with a large monochromator (25-45 cm²) mounted on a Doppler machine that operates at a maximum frequency of 14 Hz, allowing to study energy transfers in the sample up to ±15 µeV [1]. In the standard setup, using deformed and unpolished Si(111) crystals the spectrometer offers an excellent energy resolution of 0.9 µeV (FWHM) with a nearly gaussian shape. The ideas used in the construction of IN16 have been applied later to other BS spectrometers, such as the HFBS instrument at NIST [2] or the future BS spectrometer at the FRMII reactor in Munich [3]. Additionally, in those two instruments a new concept is applied: the use of a phase-space-transformation (PST) chopper, so realizing the idea proposed by Schelten and Alefeld [4]. Basically, it consists in using a crystal moving on the direction perpendicular to its reciprocal lattice vector to reflect an incoming neutron beam that has an angular divergence given by the critical angle of reflection inside the guide and a large spread of wavelengths. The effect of the reflection on the moving crystal is to produce a beam that has a smaller spread of wavelengths and a larger divergence than the incident beam (see [3,4] for details). Of course, the momentum-space volume remains unchanged, but there is a transformation from “white” to “wide”: a primary beam relatively well collimated and not monochromatic is transformed into a diffracted beam with increased divergence and relatively well monochromized [4]. This effect is shown on Fig. 1, where we plot the energy distribution of the neutrons reflected by the IN16B deflector (see next section) when we use a stationary crystal or a crystal moving at different velocities. It appears clearly that one can get a significant increase on the neutron flux at a particular energy, so we have investigated by means of Monte Carlo simulations if IN16 could be modified to apply the same principle to a future IN16B and which gain could be obtained compared to the existing instrument.

2. Technical information

In order to get reliable information on the possible gain that can be obtained by applying the PST principle to IN16 we have performed several Monte Carlo simulations using the McStas package [5]. As a first step, we simulated the present instrument to check the validity of the simulation results. Thus, we use a source that mimics the neutron beam coming out from the H53 guide and impinging on the first deflector. This is a pyrolitic graphite (PG) crystal (002) formed by 9 lamella that focus the beam at a distance of 1.5 m. Each of the lamella is composed of three different crystals of isotropic mosaicity (in the simulation we used η=30', angle between crystals = 0.4°). A supermirror focusing guide formed by two segments (the reflectivity of the first segment is m=2 and that of the second is m=3) reduces the cross section of the neutron beam from 60×120 mm² to 27×27 mm² and conducts the neutrons to the second deflector, which is also composed by three PG(002) crystals assembled together (η=80', angle between crystals = 0.4°) mounted on a chopper disc moving at 70 m/s (the variation in the angular velocity due to the finite beam size has been neglected). The monochromator has been simulated as a cut 25×45 cm² into a perfect spherical Si(111) crystal with a radius of curvature of 2 m.

Fig. 1: Energy distribution obtained after reflection of a “white” neutron beam on a crystal moving at different velocities (in all cases, 10⁹ events were generated at the neutron source).
In order to simulate an hypothetical IN16B we used the same neutron source as before and we moved the spectrometer along the H53 guide in order to place it after the instruments EVA and ADAM. Then, at the end of the H53 guide we put a supermirror focusing guide (SMG) and a moving crystal of high mosaicity (see values below) that sends the neutrons to the Si(111) monochromator. The characteristics of the SMG, as well as the mosaicity and the velocity of the deflector and the size of the monochromator were optimised in a series of simulations. The results obtained both for IN16 and for the IN16B project are shown in the next section.

3. Results

The calculations performed on the IN16 spectrometer were done with the aim of validating the simulation by comparing their results with those of several test experiments. Thus, we compared the beam coming out of the SMG, the rocking curves of both the first and the second deflector (see Fig. 2) and the calculated resolution with real data. As exemplified by Fig. 2 the agreement between the calculation and the experimental measurements is good, so giving us confidence on the possibility of using the simulation to obtain reliable estimates about the possible characteristics of a future IN16B.

Therefore, as explained before, we have performed a full series of simulations of the projected instrument IN16B in order to optimise several parameters. We have studied the influence of: a) the reflectivity of the SMG (m = 1, 2 or 3); b) the horizontal and vertical mosaicity of the crystal mounted on the PST chopper; c) the velocity of the PST chopper; and d) the size of the monochromator. The best results are obtained using the SMG with m=3 and a deflector crystal with an anisotropic mosaicity (η, = 10°, η, = 2°) moving at a speed around 300-350 m/s. Additionally, a big monochromator (50x50 cm²) is needed to recover all the neutrons of the highly divergent beam coming from the deflector.

The number of neutrons detected at the sample position as a function of the velocity of the PST chopper is shown in Fig. 3 for three different kinds of SMG. Although the best results are obtained for the SMG with m=3, the relative gain produced by the PST — g = I_{300 m/s}/I_{0 m/s} — decreases when the beam divergence offered to the deflector is increased (g = 3.0 for m=1, 2.7 for m=2, and 2.4 for m=3); similar results have been reported by Kirstein [3]. Thus, the gain obtained by the focusing at the SMG and by the reflection at the moving crystal are not independent.

Finally, we have performed a quantitative comparison between IN16 and the "optimised IN16B" by simulating the flux at the sample position for both instruments (using a monitor of size 3x5 cm²). When considering the case of the static monochromator (ΔE = E_{mono} – E_{anal} = 0), the ratio I_{IN16B}/I_{IN16} where I is the number of neutrons detected, gives a gain factor G=5, while for the cases of the monochromator moving at a velocity of ±2.25 m/s (corresponding to an energy transfer ΔE = ±15 µeV) we get G=4 and G=8, respectively.

A more refined estimate of the expected gain was achieved by calculating the total number of neutrons within the energy window (−ΔE, +ΔE) that are reflected from the moving Doppler monochromator into the sample area. When ΔE = 15 µeV we obtain G = 5, while if we extend the dynamic range of the instrument [6] the gain increases: G = 6.7 when ΔE = 30 µeV and G = 8.0 for ΔE = 50 µeV.

Fig. 2: Comparison of the simulated and measured rocking curves for the first and the second deflectors of IN16.

Fig. 3: Number of neutrons arriving at the sample position (in an area of 3x5 cm²) as a function of the velocity of the PST chopper and for three different reflectivities of the focusing guide in IN16B (10⁷ neutrons were generated at the source).
4. Conclusions
We have performed Monte Carlo simulations in order to optimise the parameters of an hypothetical new backscattering spectrometer IN16B that would use the PST principle and to obtain a reliable estimate of the gain on intensity that could be achieved if the present instrument was modified in that sense. Our results show that, in agreement with the experience at NIST and the calculations for the FRMII-BS spectrometer at Munich, a considerable intensity gain can be achieved by applying supermirror focusing techniques and the PST principle at a neutron guide end position.

References
[6] The comparison with IN16 is done by supposing that the Doppler machine is changed to allow to achieve higher monochromator velocities, but keeping unchanged all the other parameters of IN16, notably the characteristics of the second deflector
A new perfect crystal option will be available on IN16: Si(311) monochromator and analysers are added which extend the Q-range up to 3.8 Å⁻¹ and are increasing at same time the maximum energy transfer to ± 28 µeV, without changing the present Doppler drive. First tests indicate an excellent energy resolution of about 2 µeV (FWHM) with a Voigt line shape between Gaussian and Lorentzian. We discuss the new experimental possibilities and some technical aspects of the Si(311) analyser setup.

1. Introduction

The backscattering spectrometer IN16 at the ILL is operating successfully in user mode since 1995 using perfect backscattering geometry from Silicon single crystals with (111)-orientation. The use of large spherically deformed crystals results in a nearly Gaussian energy resolution function, which, together with the high flux and the good signal to noise ratio, made this instrument unique. Now new monochromator and analyser crystals will further enhance the versatility of IN16 by extending the momentum transfer and energy range.

In the standard configuration of IN16 deformed single crystals of Si(111) are used in perfect backscattering geometry at both monochromator and analysers [1,2,3]. This allows for measurements with high energy resolution of ~ 0.9 µeV (FWHM) in a Q-range between 0.06 and 1.9 Å⁻¹. The energy resolution can be improved for Si(111) to about 0.3 µeV (FWHM) by using a polygonal sphere of small, polished single crystals, preserving the same Q-range.

For many applications in molecular spectroscopy an extension of the Q-range is desirable. As it is well known, the spatial extend and geometry of a molecular motion determines the modulation of both, intensities and line width in Q. For a reliable determination of the type of motion a wide Q-range is needed as well as a good energy resolution to separate the elastic scattering. Applications can be found in a wide scientific field, ranging from diffusion in metals over relaxation of small molecules or side-groups to complex systems like polymers or biological macromolecules. A very simple example is illustrated in Fig.1 for a 3-fold jump on a circle of e.g. methyl group protons. The elastic incoherent structure factor and its inelastic counterpart are shown as a function of Q. The Q-range which is accessible on IN16 with Si(111) analysers is indicated by an arrow. It is clear that the Q-range is not really wide enough to see the characteristic oscillations of the intensities, like the minima and maxima. Of course this point was realized since quite some time and this was one reason for building IN13 [5] and for having Si(311) analysers on IN10 [6] and now on IN16. The maximum Q-limit reached by the Si(311) analysers is high enough to detect in this example easily the first minimum. IN13 covers the whole Q-range shown. In reality the limiting factors for accessing high Q-values are intensity and Debye-Waller factor. The (Q,ω)-range which is accessible by the backscattering instruments (except IN10B) is shown in Fig.2.

2. The new IN16 Si(311) setup

The Q-range on IN16 is now substantially extended to 3.8 Å⁻¹ by the use of Si(311) analyzer crystals (see Fig.2). At the same time the maximum energy transfer is increased at the same Doppler monochromator speed. Backscattered neutrons from Si(311) single crystals have a wavelength of 3.275 Å corresponding to an energy of E = 7.63 meV. Therefore the Bragg angle at the first graphite (002) deflector of IN16 is small (θ = 29.2°) and the instrument is located roughly as shown in Fig.3.

For the new Si(311) analysers crystals the well approved technique of deforming large single crystal wafers, which was first introduced for Si(111) on IN10 [2,4], was adopted. Hexagon-
shaped Si(311) wafers with a side length of about 4.6 cm and thickness d = 0.25 mm were deformed and glued onto spherical Aluminium supports of radius R = 2 m. The single crystals were purchased from Holm-Siliziumbearbeitung and were iteratively oriented by X-rays and then test cut. The intermediate cutting steps were checked again and corrected that the reciprocal lattice vector showed less then 0.1° deviation against the surface normal. The pieces were cut into thin wafers, which were finally checked again by X-rays. Nevertheless some deterioration from the initial value was found. The use of relatively thin wafers ensures a good energy resolution. The deformation contribution to the energy resolution is given by $\Delta E_{\text{def}} \sim \mu_{\text{Poisson}} E_i d / R$ ($E_i = \text{neutron energy for } 90^\circ \text{diffraction}, d \text{ the wafer thickness and } R \text{ radius of curvature}$). Thus in order to maintain the same absolute energy contribution arising from deformation about half the thickness of Si(111)-wafers was chosen.

First tests were carried out using the new Si(311) monochromator and the first analyser. Figure 4 shows the vanadium spectrum measured at $Q = 0.9 \ \text{Å}^{-1}$ (dots) compared with the quasi-elastic scattering signal from a viscous liquid sample (triangles). The upper part of the figure is shown on a linear scale normalised to maximum and the lower part on a logarithmic intensity scale. In the lower part fits for the resolution function are added. Clearly a Gaussian (dotted line) or a Lorentzian function (not shown) do not fit the experimental resolution function well. The shape is much better described by a Voigt function, which involves a Gaussian

![](image1.png)

**Fig. 2:** Momentum-energy transfer range of the Si(311)-option compared to the (0,0)-range of other crystals on IN16 and IN10 (besides IN10B) and to IN13.

and a Lorentz component. The solid line is a fit with a Voigt function of FWHM 1.85 ± 0.03 μeV with about 37% Lorentzian contribution. From these first tests, it was found that the instrument was not yet optimized, a signal to noise ratio of about $S/N \sim 100$ was found. This value is comparable to IN13, but much worse than the value achievable on IN16 with Si(111) ($S/N \sim 1500$). As expected the flux is considerably lower than for

![](image2.png)

**Fig. 4:** IN16 vanadium resolution in the Si(311) configuration (dots, count time 3hrs) compared with the quasielastic spectrum (triangles) from a viscous liquid. Upper part on a linear intensity scale, normalized to maximum and lower part on a logarithmic scale. Lines are fits with a Gaussian (dotted) and a Voigt function (solid line).

![](image3.png)

**Fig. 3:** Schematic view of the new Si(311) position of IN16.
Si(111), roughly a factor of 4. Concerning the flux it has to be noted that the present deflector chopper speed on IN16 is too low and that about half of the pulse which returns from the Doppler monochromator arrives on the reflecting segment. Thus we expect that both factors, flux and S/N, can be increased by improving the background shielding and by building a faster chopper device.

We want to mention a further detail. The flexible construction of IN16 with its total mobility of the instrument on air-pads permits to work with the Si(311) configuration in two different positions (see Fig. 5). Up to now only the small take-off angle or small Bragg angle position was tested as mentioned above. But furthermore it is possible to move the instrument to the other extreme of the technically reachable take-off angle range. In this low take-off angle position the graphite (004) reflection is used. The advantages and disadvantages of the different positions remain to be tested, but one can already note some properties: i) Using the graphite (002) reflection at a relatively small Bragg angle, a wide $\Delta \lambda / \lambda$ is obtained, allowing for a wide dynamical range. Also in this position there is no shadow from the deflector chopper onto the analysers, however the background might be higher due to a more direct view towards the H53 guide. ii) Using the graphite (004) position with a large Bragg angle, a smaller wavelength band $\Delta \lambda / \lambda$ is offered to the spectrometer. Depending on the wavelength range which is usable on the Doppler monochromator, this might be more favorable. Also the background might be reduced. The major disadvantage would be the chopper shadow at scattering angles of about 80°.

3. Status and perspective

Currently one Si(311) monochromator and three large angle analysers are available on IN16, where one analyzer is tested. Further three large angle analysers are to be built. It is envisaged to complete the low Q-range with small angle analysers for which the aluminium supports and adjustment mechanics are still needed. Thus a wide Q-range is then available simultaneously with Si(311). Strictly speaking, the low Q part which overlaps in the Q with the range accessible with Si(111) would not be needed. However, because all the Q-range is measured simultaneously, the overlap range is for “free” and allows a good control in joining two different experiments. A major progress would be the construction of a fast graphite deflector chopper, which increases the intensity by about a factor 2, besides another considerable gain which can be expected from a better graphite.

References

Possibility of an advantageous exploitation of symmetric/asymmetric diffraction geometry of bent perfect crystal (BPC) monochromator has been studied with the aim of a further increase of detector signal and/or resolution of a powder diffractometer. In our contribution we present resolution and relative detector signal of several reflections of a polycrystalline sample for opposite asymmetric diffraction geometries of cylindrically BPC monochromator. The presented results document that along with the thickness, curvature and choice of the monochromator reflection, its asymmetry cut as a free parameter which is often not considered, can play an important role in optimization of a powder diffractometer, namely, diffractometers dedicated to strain scanning.

1. Diffraction by a bent perfect crystal monochromator

BPC monochromators can combine focusing in momentum space with real space focusing onto the sample at any take-off angle. However, concerning the detector signal along the integrated reflectivity of the bent crystal (dependent on the "effective mosaicity") and the peak reflectivity, the asymmetry cut of the crystal should also be considered. Imaging by a thin cylindrically BPC slab follows the lens formula \( \frac{f_a}{a} + \frac{f_b}{b} = 1 \) where \( f_a = (R \sin (q_{\mu} + \Psi))/2 \) are the focal lengths on the image or object side, respectively, which are dependent on the asymmetry cut. The positive or negative value of \( \Psi \) correspond to the asymmetric monochromator reflection with a beam extension or compression, respectively (see Fig. 1). Symmetric geometry means \( \Psi = 0 \). If the whole bent crystal is irradiated by the incident polychromatic beam, then from the point of view of the total flux of selected monochromatic neutrons, for a fixed curvature both asymmetric geometries are equivalent. In practice, the monochromator-sample distance \( L_{MS} \) is fixed and should coincide with \( f_b \), eventually with the image distance \( b \). Then, it is clear that for the fixed value of \( L_{MS} = f_b \), the value of \( R \) is determined by the asymmetry cut and therefore the bent crystal has in opposite diffraction geometries different peak and integrated reflectivities. In the case of the BPC slab, the "effective mosaicity" \( \delta_{h,0}(Q,\Psi) \) in the incident/diffracted beam direction can be expressed as

\[
\delta_{h,0}(Q,\Psi) = (D / \sin (\theta \pm \Psi)) \cdot (1/Q) \cdot H(\theta,\Psi) \tag{1}
\]

Here, \( D \) is the thickness of the crystal slab, \( H(\theta,\Psi) = (\cos \Psi / \cos \theta) \cdot [1 - (1 + \sigma) \cdot \sin (\theta \cdot \Psi) \cdot \sin (\theta + \Psi)] \), is the asymmetry parameter (see Fig. 2) and \( \sigma \) is the Poisson ratio. Assuming a constant peak reflectivity \( r(Q,\Psi) \) throughout the angular range \( d\theta(\Psi) \) and unit cross-section of the incident beam, the integrated reflectivity \( r(\Psi) \) of the bent perfect crystal can be written in the form \( r(\Psi) = A(\mu) \cdot A(\rho) \), where \( A(\rho) \) is the attenuation factor \( [2] \).

The expression for \( r(\Psi) \) was derived in the form

\[
r(\Psi) = [1 - \exp(-Q \cdot R \cdot A(\theta,\Psi))] \cdot [3],
\]

where \( Q \) is the kinemat-
Fig. 3: Schematic layout of the focusing performance of a neutron powder diffractometer.

Fig. 4: Monte Carlo calculation of the dependence of the $\Delta d/d$ - resolution on the scattering angle $2\theta S$.

Fig. 5: Intensity and resolution optimization vs $(1/R)_M$ of the diffractometer at $2\theta_s = 64^\circ$ and $2\theta_s = 84^\circ$.

Instrumentation
ical reflectivity of the crystal unit volume. These formulae document that even though a drastic increase of $d(\theta(K,\Psi))$ (by increasing $1/R$) is followed by a decrease of $r(K,\Psi)$ [4], the integrated reflectivity $r(\theta(K,\Psi))$ is still a monotonously increasing function of $(1/R)$ having an upper kinematical limit. Then, when estimating the flux of monochromatized neutrons delivered onto the sample, due to different curvatures for focusing, both opposite geometries can differ in product $(D/\sin(\theta_{\pm\Psi}))\cdot(1/R)\cdot|H(\theta_{\Psi})|\cdot|r(R,\Psi)|$.

2. Focusing in the powder diffraction case

The focusing neutron diffraction performance (see Fig. 3) consists basically of the following steps and properties [4-6]: Monochromatic neutrons selected by the bent monochromator from a white spectrum are focused on a sample (real space focusing). There is a strong correlation between divergences of incoming and outgoing beams with respect to the sample as $\Delta\theta_{2} = \Delta\theta [2(\tan \theta_{s}/\tan \theta_{w})(1 - L_{w} / 2a_{w}) - 1]$ which can easily be manipulated by changing the radius $R_{M}$. Then, by setting a value of $R_{M} = (2L_{w}/\sin(\theta_{s} - \Psi))/(2 - 1/a_{w})$, $\Delta\theta_{2} = 0$, which results in a parallel output beam for a chosen scattering angle $\varphi = 2\theta_{s}$. There are small blurring effects which come from the effective mosaicity of the BPC slab and the width of the sample and which can be easily evaluated [5]. They bring about the diffraction beam being slightly divergent (quasiparallel) and determine the line-width at some angle $\varphi = 2\theta_{s}$ (see Fig. 4). Therefore, depending on the curvature, the peak intensity and FWHM of the diffraction line achieves its maximum and minimum, simultaneously, as demonstrated in Fig. 5.

3. Experimental results

The monochromator tests and comparisons were carried out on the SPN-100 diffractometer set at the monochromator take-off angle $2\theta_{w} = 66^\circ$. As a sample we used a well annealed Fe-nail ($\alpha$-phase) of 2.7 mm diameter (no slits were used). For the monochromator tests we used two Si-slabs in the form of sandwich with the main surface parallel to the lattice planes (311). Each slab had the dimensions 200 x 30 x 3 mm$^2$ and the total thickness of the sandwich was 2x3 mm. By simple rotation of the slabs 180° round the longest axis, we could carry out the experiment on 422 planes with $\Psi = \pm 10^\circ (\lambda = 0.121$ nm) and compare both asymmetric geometries under the same experimental conditions.

4. Conclusion

It can be seen from Figs. 5a-5d that asymmetric geometry with the beam extention ($\beta = 43^\circ$) is superior over its opposite counterpart in both parameters, detector signal and FWHM, simultaneously. Similar effect was observed also in relation to the symmetric diffraction geometry ($\Psi = 0^\circ$), but it was not so pronounced. This favourable effect of using the asymmetric geometry with the beam extention can be succesfully exploited in the case of residual strain measurements which are usually carried out on chosen individual lines. On the other hand, it should be pointed out that the gain due to the asymmetry is at the expense of the flatness of the linewidth behavior versus $2\theta$ for constant curvature as it is used in the conventional powder diffractometry [6].

Acknowledgement

Bragg diffraction optics investigations are supported by the Grant Agency of the Czech Rep. No. 202/97/K038, Grant Agency of CAS No. A1048003 and the TMR-Network ERB FMR XCT 96-0057.

References

Renewal of the D11 collimation

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After about 26 years of continuous operation, the D11 collimation system will now be completely renovated within the ILL Millenium programme. The project includes a replacement of all neutron guides with new glass guides of cross section 30x50 mm over the whole length of 38 m, as well as an introduction of two new collimation distances at 27 m and 1.5 m away from the sample position.

1. History of the D11 collimation
The collimation of the incident beam of the cold neutron guide H15 is carried out at D11 by a system of moveable neutron guides after the velocity selector, following the principles described by Ibel [1]. The guides have a cross section of 30 x 50 mm and are made of boronated glass. The number of collimation lengths available was increased in 1991, allowing a better matching of the collimation distance to the infinitely variable sample-to-detector distance [2]. Thus, the exit of the closest neutron guide can be placed at 2.5, 4.0, 5.5, 8.0, 10.5, 13.0, 16.5, 20.5 and 40.5 metres away from the sample. Following modifications during the HFR shutdown between 1991 and 1995, all guide sections between 2.5 and 40.5 m are motor driven and under computer control, allowing for rapid and programmable simultaneous change of the collimation and detector positions.

2. Experience and problems between 1995 and 2000
As a consequence of the possibility for programming complete series of measurements (scattering or transmission, attenuator OUT or IN, various detector- and collimation distances, wavelength changes, changes of sample environment parameters such as sample position, temperature, magnetic field, pressure, shear gradient etc.) all mechanical components are heavily used under normal operating conditions at D11. Mechanical degradation is particularly critical for the original parts of the instrument (≈ 30 years old). For instance, the 20 m collimating section which is inside the casemate along the instruments DB21 and IN10 is still driven by a bicycle chain. Some problems have appeared in the past, such as failures of the bearings and of the motor couplings at some of the moveable neutron guides due to heavy use. Access to this guide section is sometimes extremely difficult and at some places impossible without dismantling the heavy concrete shielding.

Standard calibration measurements which are periodically performed at D11, reveal significant variations of the instrumental constant (C(λ)/A) with time. The instrumental constant is a parameter describing the stability of the instrument in terms of neutron flux per unit solid angle. These fluctuations could be interpreted as being a consequence of mechanical imprecisions of the collimation- and attenuator positioning, i.e. the tolerance of the movements is too large. Moreover, systematic neutron flux measurements at the sample position (by gold foil activation and by using a calibrated monitor) reveal a loss of about 34% with respect to the incident neutron flux at the entrance of the collimation section (after the selector). This loss is probably due to an aging of the neutron guides.

3. Renewal Project 2001
The complete refurbishment of the D11 collimation system has recently been programmed. The main work of the renewal project as described below will start during the summer shutdown 2001 and then continue during the long winter shutdown 2001/2002.

3.1 Replacement of 38m glass neutron guides
Monte-Carlo flux simulations as a function of wavelength and collimation distance for various guide coatings show that pure, boronated glass is indeed the best compromise for the D11 collimation system [3]. No significant flux increase can be gained by using other coating materials, such as natural Nickel, 58Ni or super-mirrors. In order to maintain the low background of the instrument it has been decided to replace the 30 year old guides by new glass guides over the whole lengths of 38 m. The new glass guides will have improved surface properties and will be twice as long (100 cm) as the old guides (50 cm), hence reducing the number of connecting joints.

3.2 Refurbishment of the selector area
According to the Monte-Carlo flux simulations [3], a considerable loss of neutrons occurs around the selector area, 40 m away from the sample. The present configuration includes two short guide pieces at either side of the short Dornier velocity selector, 4 air gaps and 8 windows. Space can therefore be optimized in this area. The standard Dornier selector will be displaced directly in front of the entrance to the collimation section, close to the beam monitor. A similar intermediate guide piece in front of the selector will be removed and replaced by one single Nickel-guide between the secondary D11 beam shutter and the selector.
entance. Consequently, the number of air gaps and windows will be reduced and a considerable flux gain is to be expected. Furthermore, a second 9% DORNIER velocity selector will be purchased as spare equipment.

3.3 Installation of two new intersections
A new collimation distance at 27m from the sample position will allow use of a detector position, intermediate between 20m and 36.7m, with optimized flux conditions. Another new collimation distance at 1.5m (minimum distance so far 2.5m) will allow for a considerable flux gain of about 45% in the high Q range (at shortest detector distance L=1.1m). This flux gain is particularly important in view of the new generation of the fast 2 MHz SANS detectors for D11 & D22, which are under development at ILL.

3.4 Diaphragm changers
Installation of a system of motorized and variable diaphragms at the sample position as well as at intersections 1.5m, 5.5m, 10.5m and 20.5m will allow for improved resolution. The option of a rectangular slit aperture at 20.5m will allow better to take into account the parabolic neutron flight path for wavelengths above 16Å and long detector distances.

3.5 Renewal of motors, mechanics and control automate
The mechanics of all guide sections will be completely upgraded; improvements of the motorisation will result in a more precise guide positioning. All components, including the new vacuum control system, the attenuator control and the detector security control, will be incorporated into the general instrument control system.

3.6 Refurbishment of the sample area
A complete refurbishment of the D11 sample area will lead to larger space and improved working conditions at the instrument (handling of cryostats and other heavy equipment).

4. Summary
D11 is one of the "work horses" at the ILL with an average use of about 160 days beam-time per year, corresponding to about 70 experiments of both fundamental research and commercial users. Recent modifications (1998), such as the replacement of the old BF3 detector by a refurbished 3He detector and the installation of the light-weight DORNIER velocity selector, have already improved neutron flux and detection efficiency by about a factor of 3.5, compared to 1990. The current project for renewal of the collimation system is a another step in order to maintain the reliability of this worldwide unique SANS facility and towards an increase of D11’s performance. The work is scheduled for completion in 2002.

References
Laue Diffraction: Updated Tool

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The concept of the diffraction in white beam with neutrons for study of phase transitions (p. t.) and modulations in crystalline networks has been published in 1978. It has already been shown that the Laue diffraction allows: - to make a study of subtle structural p. t. as a function of temperature and magnetic or pressure field by the observation of reflections in superstructures, especially in the cases of spiral or incommensurate modulations; - to dress the design of diffraction phenomena at long-distance (twin and domains) or short-range-order-diffuse scattering near p. t. as periodic and local properties. All this is disclosed easily with polychromatic beam. Today new tools for detection allow to increase the quality of the neutron Laue diffraction for this research work. This is developed through digital 2D detectors, planar or cylindrical, covering a large solid angle that replace the couple of film-thin flexible sheets (coated with layer of luminescent screens). For this, on the S42 instrument dedicated to test the quality and alignment facility, progressively it is put into place a technique offering rapid data collection.

1 Introduction

25 years ago was experimented, in April 1976 as scheduled program, on magnetic hematite crystals the magnetic neutron Laue diffraction [1] as a new tool for magnetism on the special instrument S42 (Single Crystal Laue-Diffraclrometer) accepted as “long term experiment” by the ILL Scientific Council of October 1976. This proposal simplified another complementary approach introduced by Hohlwein with a neutron Weissenberg camera. These two geometries, using large area detectors in the ‘80s were useful. In fact, a large number of experiments performed at the ILL on 4-circle diffractometers have failed or turned out to be very difficult, owing to the lack of knowledge of the reciprocal space. The use of the Laue (S42) or the Weissenberg (D12) method has already demonstrated his intrinsic quality in the study of magnetic ordering at low temperatures and modulated phases [2, 3] of the condensed matter.

The Laue-diffraction spectrometer simply consists of an optical bench, a collimator to define an incident beam of neutrons, a goniometer head for the sample support, ancillary equipment (as top loading cryostat, magnet, pressure, or furnace) to control certain physical parameters (low temperature in the range 0.2-300 K, magnetic field up to 1.8 T, uniaxial pressure, furnace from T = 300 to 950 K) and an flat area (photographic and now image plate) detector or counter to survey the scattering from the specimen. On figure 1, the main photo refers to a close up of S42, today test instrument in the diffraction group as Laue crystal alignment facility. The insert gives a general view with J.C. Marmeggi in the background.

The Laue arrangement is suitable for studying a number of features arising from scattering by magnetic domains, structures and phase transitions using intensities of equivalent Laue spots in positions when the crystal symmetry is lowered. The white beam elastic diffraction with area detectors provides a first rational approach to detect the set of propagation vectors on single crystals for incommensurate (crystallographic or magnetic) structures.

Several approaches have been developed to collect high-quality diffraction pattern using neutron flat area detectors. First in the ‘overall approach’, the information is integrated over the whole irradiated sample volume. The Laue pattern is recorded on: - a Kodak “Regulix” film (130x180 or 260x380 mm²) sandwiched between two scintillate screens (ZnS and LiF in a plastic matrix) with a resolution of = 0.3 mm, - a flat image-plate...
as position-sensitive detector based on a thin sheet coated with 150 µ layer of photostimulable phosphor (BaFBr doped with Eu<sup>2+</sup> ions) with Gd<sub>2</sub>O<sub>3</sub> added that create a cascade of gamma-rays and conversion electrons, acting as thermal neutron scintillator with a resolution of 0.2 mm. Secondly in the ‘local approach’ (‘topography’), the result is recorded on X-ray Kodak “Periapical Ultra-Rapide” film (18x34 mm<sup>2</sup>) backed by a 50 µ thick gadolinium foil with electron internal conversion and a resolution of <0.05 mm. Thirdly the diffuse scattering in “white beam” diffraction use energy-marks to determine the amplitudes of wavevectors $k$ and their variation under the influence of external parameters [4]. The loss of intensity implied by the reflectivity coefficient of the monochromator is avoided in the Laue technique; thus small effects can be detected with more ease, e.g. phonon diffuse or magnetic inelastic streaks from single crystals. The main updates technical characteristics of S42 are summarised in Table 1.

<table>
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<tr>
<th>Max. flux at specimen:</th>
<th>10&lt;sup&gt;6&lt;/sup&gt; n.cm&lt;sup&gt;-2&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident wavelengths:</td>
<td>&lt;0.08 mm &lt; $\lambda$ &lt; 0.35 mm (max. flux at 0.15 nm)</td>
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<tr>
<td>Single-Crystal Diffractometer Specification</td>
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</tr>
<tr>
<td>Size of specimen:</td>
<td>1 mm&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Diameter of beam:</td>
<td>usually 3 mm</td>
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<tr>
<td>Angular range:</td>
<td>2° &lt; $\theta$ &lt; 68° or 112° &lt; $\theta$ &lt; 178°</td>
</tr>
<tr>
<td>Distance crystal-film range:</td>
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<td>Beam divergence:</td>
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<tr>
<td>Min. angular distance to separate 2 spots:</td>
<td>15°</td>
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<td>Accuracy of intensities:</td>
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Main characteristics of the white beam instrument S42 on the guide tube H24

### 2. Some experimental results

#### 2.1 Identification of the sublattice magnetization by comparison of the intensities of the (311) magnetic reflections associated with a NiO single T-domain

NiO is a collinear type II antiferromagnet below the Néel temperature $T_N = 520$ K, consisting of ferromagnetic (111) sheets, staked in an antiferromagnetic order in the <111> direction [5,6]. Domains associated with different {111} sheets are usually characterised as $k$ (or $T$, for twin as introduced by Roth [6]) - domains, a star of four equivalent magnetic propagation vector $k$ of type <1/2 1/2 1/2> is possible, because they are associated with a crystallographic twinning. Within these domains, due to the symmetry of the <111> $k$ vectors, three S-domains arise from the equivalent spin direction in a (111) sheet. By magnetic neutron Laue diffraction it has been identified directly through the measure of the intensities of the magnetic reflections the direction of the sublattice magnetisation in S-domains distribution [7]: the magnetic moments are aligned along the <112> directions. Comparing with the local approach that use topographies in monochromatic beam there is some advantage like: the time of data collection (nearly divided by 20 with respect to the usual topography), and the use of ordinary sample (not limited, to a high-resolution area detector or, in counterpart to large enough domains to be imaged [8]). Crude topographies of not so big S-domains from [311] magnetic reflections in white beam were useful, and took advantage [7, (1979)] from a parallel work using monochromatic beam and recording splendid topographies one by one [8, (1981)] of so big magnetic domains. Recently an imaging plate detector [IP-ND] has been used to study a multi-domain crystal. The image plate data [9] gave similar scientific results compared with film but the pattern is easier to manipulate and to analyse.

#### 2.2 Phase transitions and incommensurate phases

We recall some experiments already successfully carried out as demonstration of the structural nature of a transition and the study of incommensurate phases: in this case the area (photographic or image plate) detection of neutrons is incomparably more powerful than detection by counter and often the only possible technique to investigate whole areas of reciprocal space. As already mentioned, one of the most important applications has been the study of magnetic phases. In particular, the reflections of incommensurate magnetic structures can be found. In the substance NaMnCrF<sub>6</sub> at 4.2 K a ferromagnetic phase with propagation vector of the form [0, 0, 0.018] has been detected [2] resolving the magnetic and nuclear reflections on the Laue diagram for a long period superstructure of about 27.5 nm.

Structural phase transitions have been observed and followed as a function of temperature in alpha-uranium. The projection of $k$ in a plane perpendicular to $a^*$ is rotating about 10° away from the $c^*$ axis to be set up at 22 K parallel to <011>. In the range 22-36 K the interesting feature in the interpretation of the Laue pattern is a floating unlocked incommensurate structure which appears embedded in the orthorhombic matrix [2]. After this detection and localisation of phenomena affecting the reciprocal lattice more quantitative studies are required, completed on a neutron diffractometer and a triple-axis spectrometer.

At 87 K, a 'locked-in' commensurate antiferromagnetic spiral transition in 4% Ga doped FeGe, with a star of four propagation vectors (1±δ, 0, 0), (0, 1±δ, 0) has been determined with the prototype version of the thermal image-plate Laue Diffractometer (LADI) on the beam H22 for test experiments on problems in physics and chemistry [10]. The location of Laue instruments in front of varied neutron beams spectra like H24 and H22 are beneficial to optimise data collection (an example is given in [2]). This is to be realising today with the arrival on the thermal guide H22 of VIVALDI (Very-Intense, Vertical-Axis, Laue Diffractometer) with its image plate detector incorporated and a higher neutron flux at small wavelengths compared to H24, in the ILL’s Millennium Programme.
3. Conclusion

Some typical experimental results have given information in the intensity data and on spatial imaging or topography. These are two applications (micro- and macroscopic approaches) of the Laue method. With the developing of IP-ND and television imaging that liberate the detection technique from the Schwarzschild effect, it is expected to be able to measure local and periodic properties very near phase transitions.

Acknowledgements

I am very grateful to C. Wilkinson (ILL) for supply of an IP-ND prototype.

References

The scientific case for the ILL Millennium Programme project, VIVALDI, an image-plate Laue diffractometer that will accept a variety of standard and adapted sample environments for fast single-crystal experiments in physics, chemistry and materials science, is presented. Using the Laue technique with single crystals and a thermal beam, the two-dimensional projection of a large volume of reciprocal space of small-unit-cell materials can be seen in a single exposure. Complete structural data can thus be obtained in a time shorter by one-to-two orders of magnitude than for a monochromatic experiment, with only a modest loss in precision. This allows structural and magnetic phase transitions (which often result in complex incommensurable structures) to be observed and followed as a function of temperature or pressure. VIVALDI will provide a tool for development of new diffraction experiments, and will be complementary to existing ILL diffractometers. Construction is based on proven components, and is scheduled to be complete in spring 2001.

1. Introduction
A detector employing neutron-sensitive image plates is comparatively cheap and capable of high spatial resolution, has good homogeneity, a large dynamical range, extended linearity and no dead-time, and can be constructed to subtend very large angles at the specimen. The neutron-sensitive image plates are based on the same storage phosphor (BaFBr doped with Eu$^{2+}$ ions) used for X-ray image plates, but with Gd$_2$O$_3$ added; the Gd nuclei act as neutron scintillators by creating a cascade of $\gamma$-rays and conversion electrons. Dramatic gains in data collection rates should be possible with such a detector in combination with the Laue technique on a (quasi-) white beam. LADI - an ILL/EMBL collaboration [1]. LADI is now in scheduled operation at the end of a cold neutron guide, and has been shown to give good quantitative structural information in macromolecular crystallography [2].

2. Trials with LADI on a thermal neutron guide
While not optimized for small unit-cell investigations, LADI has occasionally been moved to the thermal beam H22 for test experiments on problems in physics and chemistry. The test experiments have included:

- Rapid structural studies: Gains in efficiency between one and two orders of magnitude compared with monochromatic experiments on the same or similar compounds are achieved, with only modest loss of precision in bond lengths and angles.
- Reciprocal-space surveys: The large detector surface combined with the white beam allows rapid survey of large continuous regions of reciprocal space, and facilitates identification of complex features due to incommensurability and twinning.
- Very small samples: Crystal volumes 10 to 100 times smaller than those usually studied are now feasible because of the gain in efficiency. This is particularly attractive for high-pressure experiments, or for first investigations of new topical materials where the wand of crystal growth has still to wave its magic.
- Phase transitions: Complete data collections are possible in just an hour or so, which allows the nuclear or magnetic structure to be followed in detail with temperature, magnetic or electric field or pressure, for example, through phase transitions. This is particularly relevant to structures where individual reflections are not directly related to the order parameter.

Figure 1 illustrates some of the advantages of a Laue experiment. Fig. 1a shows ~1/4 of the room-temperature Laue diffraction pattern of 4% Ga-doped FeGe$_2$ [3]. Exposure times of a few minutes are sufficient to give integrated intensities of good statistical qual-
ity for structural refinement. Ga-doped FeGe$_2$ undergoes a number of magnetic transitions, which give rise to additional Bragg reflections whose positions vary with temperature. Due to the high spatial resolution of the detector, even very subtle changes in the positions of the reflections could be followed with temperature. Below 180 K the material locks into a non-harmonic spiral magnetic phase with propagation vector of exactly 1/10, as shown in Fig. 1b.

### 3. Proposal for a thermal Laue diffractometer

Based on our experience from these trials we have proposed a development of the LADI scanner, better adapted to the demands of physicists and chemists, to be combined with a high-wavelength rejection filter to provide a thermal beam of optimum width, and a time-of-flight analyzer to monitor the incident spectrum. The new instrument was accepted as one of the first five instruments of the Millennium Programme of the ILL as VIVALDI - Very-Intense, Vertical-Axis, Laue Diffractometer. Like LADI, VIVALDI consists of a cylindrical image-plate detector 40 cm long and 100 cm in circumference, first held stationary while the crystal which lies on the axis of the cylinder is irradiated by the white beam, and then spun around its axis for on-line read-out. Unlike LADI, the axis of the cylinder is vertical to facilitate access by heavy cryostats and pressure cells, and the irradiated surface of the image plates will be read directly to give a 2- to 3-fold gain in efficiency. The sample/cryostat support is a robust high-precision rotation unit, which sits above the detector and can be lowered into the detector for the measurement. The detector height is also variable to suit most beams at the ILL. A schematic diagram of the image-plate detector is given in Figure 2.

Ancillary equipment will include a dedicated cryostat with longer diimensions whose positions vary with temperature. Due to the high spatial resolution of the detector, even very subtle changes in the positions of the reflections could be followed with temperature. Below 180 K the material locks into a non-harmonic spiral magnetic phase with propagation vector of exactly 1/10, as shown in Fig. 1b.

Ancillary equipment will include a dedicated cryostat with longer and narrower tails than the standard ILL, 'Orange' cryostat to offer temperatures from mK (with a dilution insert) to 600 K. The long-wavelength filter is a stack of Ni/Ti multilayer supermirrors with length optimised for 3 Å [4]. For most experiments the transmitted beam with wavelengths shorter than 3 Å will be used, but it will also be possible to rotate the entire instrument on its air-pads and to the long-wavelength reflected beam to investigate small-q reflections free of harmonic overlap. A single-channel time-of-flight analyzer will be located downstream of the scanner. The diffraction patterns will be analyzed with user-friendly software based, as with LADI, on the CCP4 Laue suite.

The construction of the scanner and associated control electronics and software has been undertaken by an outside firm (SICN Veurey, in consultation with EMBL-Grenoble). Delivery is expected in the spring of 2001, and the scanner will be first tested with neutrons behind LADI on H142. VIVALDI will eventually be positioned at the end of the thermal guide tube H22, in the position used for the tests with LADI. The data collected in these tests show that a clean neutron beam with low γ-ray background can be delivered to this position (image plates are γ-ray sensitive and would otherwise need extensive protection). Waves, high-pressure studies and structural phase transitions. When (even small) single crystals of a material are available, it will provide a tool more powerful than powder diffraction for preliminary investigation of topical structures. In many cases the data collected would be adequate to give an answer of sufficient precision to render subsequent experiments unnecessary. The detector should also be suitable for some types of diffuse scattering experiments on a monochromatic beam.

### Acknowledgements

We provide the scientific impetus for this project, but many more people from the ILL and SICN are involved in the construction. They are too numerous to name all individually here, however we would like to acknowledge especially Christian Bard and his team at SICN, Serge Pujol (ILL) and Steven Rowe (ILL). We are also indebted to François Dauvergne and Jean-Charles Castagna (both EMBL) for their expert technical assistance during the trials with LADI.

### References


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Status of the ILL's renewed thermal three-axis spectrometer IN8C


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ILL's first fully-optimised high-flux thermal-neutron three-axis spectrometer IN8C is now being installed on site and will be operational at the end of the year 2001. In this paper we summarise the technical details and the status of the renewed instrument. Finally we discuss other instrumental developments for a three-axis spectrometer which will improve the quality of the signal and that can constitute a common option for all ILL TAS instruments.

1. Introduction

The unique power of three-axis spectroscopy (TAS) for the study of excitations in condensed matter is due to the fact that it is possible to perform selected scans to explore specific sections in momentum $Q$ and energy $E$ space. The relevant quantities for a TAS instrument are thus luminosity, resolution widths ($\Delta Q$, $\Delta E$) and the signal-to-noise ratio. As inelastic neutron scattering is intensity limited, "flexibility" is an important issue; it means being able to trade in the most practical way resolution against luminosity.

ILL's thermal TAS instrument IN8B is installed on beamtube H10 [1]. It was built about 25 years ago but is still one of the most powerful instruments of its kind. The IN8C project consists in rebuilding the primary spectrometer of IN8, and – as it was pointed out recently [2] - the above mentioned needs are addressed by (i) increasing the monochromatic flux using large double focusing monochromators, short distances and a wider beamtube, (ii) reducing the background level by adopting a beam geometry with a horizontal virtual source (HVS) and (iii) improving flexibility by enlarging the range of accessible scattering angles.

The IN8C project has been undertaken by the ILL in collaboration with its Spanish scientific partners. The design study and the manufacturing have been subcontracted to Spanish industry. In the first part of the paper it will be presented the technical details of the new elements introduced in IN8C, in the second a brief report of the status of the project is given, and finally we present some new options that can be introduced in a TAS instrument in order to improve the quality of the signal measured.

2. Technical details

The horizontal virtual source (HVS) is introduced at a fixed distance $d = 2284$ mm before the monochromator [3]. This matches the monochromator - sample distance and allows monochromatic focusing without degrading the $E$-resolution. To illuminate the HVS - an adjustable horizontal slit device made of (fast) neutron shielding materials - the beamtube diameter has been enlarged from $\Phi = 100$ mm for IN8B to $\Phi = 200$ mm for IN8C. As the HVS aperture is smaller than for IN8B’s "flat" geometry, we expect the background of IN8C to be lower as compared to IN8B. Converging collimators and diaphragms are placed in the beam path to reduce the penumbra.

The double-focusing monochromator has three faces equipped with PG002, Cu200 and bent Si111 crystals, respectively. A new design concept for the focusing mechanics has been explored by TEKNIKER, Eibar, Spain. The first two faces consist in 9 x 11 elements of (W x H) 25mm x 17mm which build up an active area of (W x H) 233mm x 197mm. The horizontal and vertical curvature can be varied independently. The Cu200 crystals will have an anisotropic mosaicity of 30° horizontal and 10° vertical. The fixed horizontal curvature of the Si111 face will be realised by bending a sandwich of five perfect Si blades [3] of (W x H) 260mm x 17mm. We use 11 benders to realise a variable vertical curvature.

![Fig. 1: General overview of the double-focusing monochromator. In the picture the Cu200 and the PG002 faces are shown.](image-url)
3. Status of the IN8C project
The status of the different elements of IN8C is the following:
(i) The drum, casemate, control unit, support lines, electronics and D15 platform are currently installed “on site”.
(ii) The optical elements: chariot, beam shutters, diaphragms, collimator exchanger and slits; are under manufacturing and the reception is foreseen during the second half of May.
(iii) Recently work on the double-focusing monochromator has been carried out from both sides, the ILL and TEKNIKER, its Spanish industrial partner for the monochromator. The mechanics of the three faces of the monochromator was tested at TEKNIKER. The reception of the monochromator is foreseen in the beginning of May. Figure 1 shows a general overview of the monochromator, in which the faces for the mosaic PG and Cu crystals are visible. The work on aligning and mounting the monochromator crystals for all three faces is currently being carried out at ILL. Most recently, the Si crystals for the third face (not visible in Fig1) were mounted on the benders (5 Si blades for each bender) and were tested on the hard X-ray laboratory of the ILL. Two diffraction patterns were obtained, one for the <220> reflection, in order to use it as a reference to bend the crystals to a fixed curvature of 8 m, and the other for the <224> reflection, to estimate possible vertical misorientations of the 5 Si crystals in each bender. Figures 2a and 2b show the <220> and <224> reflections of the Si crystals of one bender obtained with hard X-rays. As a result, all crystals were found to be bent to the same curvature and a vertical misorientation of < 0.1° in each sandwich could be obtained. All benders were sent to TEKNIKER to be mounted on the monochromator mechanics.

4. Other instrumental developments for a three-axis spectrometer
Other instrumental options are explored in parallel such as a time-of-flight (TOF) option, a focusing-imaging analyser (FIA) and a position-sensitive-detector (PSD) option.
The TOF option consists in introducing a counter-rotating double-disk chopper in the white beam and gating the detector. This allows not only to suppress higher order contamination (as a velocity selector would do), but might be used to reduce the background due to elastically scattered neutrons.

Using focusing/imaging analysers together with position-sensitive-detectors for three-axis spectroscopy not only improves the precision of the data collection, but simplifies the identification of parasitic signals and allows to investigate efficiently the vicinity of a chosen position in (q,E)-space. It allows to reach high intensities without sacrificing Q-resolution. A PSD option of the secondary spectrometer is used on the cold-neutron TAS instrument RITA at Risø [5].

We acknowledge discussions with and help from J. Kulda and A. Wildes.

REFERENCES
New secondary spectrometer dedicated to replace the existing beryllium filter-analyser on IN1 is described. The project aims to substantially open the aperture of the spectrometer using a large area crystal analyser focussing the scattered neutrons onto a single detector. Potential gains in instrument luminosity, energy resolution and signal-to-noise ratio are discussed.

1. Introduction
The beryllium-filter (BeF) secondary spectrometer is a distinct option of the hot-source instrument IN1. It replaces the crystal analyser of the three-axis spectrometer (TAS) for the measurements which do not require high sensitivity to momentum transfer, for instance, such as phonon densities of states. The existing beryllium filter-analyser spectrometer has been effectively exploited during last 20 years by the ILL reactor users for the studies of high-energy atomic and molecular vibrations in condensed matter systems. The important information on atomic bonding and location has been obtained for different hydrides, catalysts, biological objects. Recent experiments demonstrated advantages offered by IN1-BeF for studies of magnetic neutron scattering and single crystal samples. Current trends in the fields of application of the beryllium filter spectrometer ensure long term user need in such a versatile, high luminosity instrument.

2. Current set-up
The beryllium filter-analyser of IN1 is the simplest type of a neutron spectrometer. It consists of a cooled polycrystalline block of Be metal followed by a counter (Fig.1). Such an analyser allows for a transmission, ideally, only of neutrons with energies below the Bragg cut-off of beryllium (5.2 meV) while the energies above the cut-off are to be effectively scattered out. In reality the optimisation of transmission and filtering properties imposes particular demands to the quality the filter design and the filtering material itself. For instance, the grain size of beryllium polycrystal should not be very small (to avoid decrease in transmission of the low-energy neutrons due to small-angle scattering) or very large (to minimize extinction in the Bragg scattering). On the other hand the lateral dimensions of a filter block should be considerably smaller than its length along the beam and such a block is to be well covered with the absorbing material. To this end the actual Be-filter of IN1 is cut onto rods (altogether $4 \times 4 = 16$ pieces) shaped to respect the divergent geometry of the beam scattered from the sample and separated by Cd spacers (Fig.1). Such a design allows one to avoid a considerable deterioration of the filtering power for high energy neutrons due to multiple scattering processes in the body of the filter while keeping reasonably large solid angle subtended by the detector. The multiple scattering becomes the primary reason for the leakage through the filter of the monochromatic line which is elastically scattered by a sample. This most intense component in the scattered beam before the filter may be five or more orders of magnitude stronger than the useful inelastic signal and it represents the main source of the experimental background. The instrument in its present design is very well suited for the medium energy resolution studies (e.g. 5-8% in energy transfer range 50-300 meV) for what it provides spectacular count rates. For example, hydrogen vibrations in metal hydrides can be reliably studied with samples containing amount of hydrogen equal to that in few cubic mm of water in spite of relatively small solid angle for the scattered beam: $\Delta \Omega \sim 0.06$ Steradian or 0.5% of $4\pi$. This high intensity results largely from the well optimized primary spectrometer with a set of exchangeable vertically focussing copper crystal monochromators and the available take-off angles allowing for scanning in the very broad incident energy range of $\sim 10$-1000 meV. However the performance gets down in case of lower scattering substances with excitation spectra distributed over large energy range. The instrumental background is observed to increase considerably at energy transfers above 300 meV, very likely due to progressive deterioration of the absorbing power of Cd used as the main protection component. Another drawback of a Be-filter analyser becomes crucial when better resolution is needed for...
the most demanded range of medium energy transfer below 100-150 meV where the main contribution to the total resolution stems from the relatively large energy window of the beryllium Bragg cut-off.

For the ILL Millennium Programme we propose a modernisation of the secondary spectrometer of IN1-BeF which will result in higher intensity together with improved energy resolution and significantly lower background.

3. Proposed modernisation

The proposed project does not affect the primary spectrometer of IN1 which is shared with the liquids diffractometer D4. Its central point consists in introducing a large reflecting surface around the sample-to-detector axis which focuses the diverging scattered neutrons onto a relatively small single detector, as schematically shown in Fig.2. The proposed scheme has several important advantages as compared to a possible way of increase in the instrument luminosity by putting more filters and counters around the sample. First, it allows for a considerable enhancement of the acceptance angle $\Delta \Omega$ for scattered neutrons without corresponding increase in the sensitive volume of the counter. Second, the counter can be protected against direct exposure to the intense elastic scattering from the sample, which is the major source of the background in the currently used instrument. Third, using single crystals as the reflecting surface gives the possibility to improve the energy resolution $\Delta E$ of the secondary spectrometer. The use of the single crystals, however, implies filtering out higher order Bragg reflections.

Estimation of the factors which influence the performance of the proposed instrument could be based on a model where the reflecting surface represents a part of an ellipse of rotation with its two focal points at sample and counter positions, as in the Fig.2. Such an ideal mirror would focus all the rays emitted in one focal point onto another focal point. In reality such a surface could be approximated by an assembly of flat single crystals with finite size and mosaic spread. This, together with a finite size of the sample, will result in a smearing out of the focused beam both in real space (geometrical broadening) and in reciprocal space (finite energy width of the reflected beam).

For example, with the sample-detector distance of $\sim$1 m and using $\sim$0.7 m long pyrolytic graphite reflector made of $\sim$4 cm large individual crystals of mosaic spread $\sim$3 degrees, for the average reflected energy of $\sim$4.5 meV we have approximately equal contributions to the energy resolution from the linear crystal dimensions, mosaic spread and difference in the Bragg angle at the top and the edges of the reflecting surface. The resulting resolution of the analyser is estimated to be $\Delta E \sim 0.6$ meV instead of $\sim 3$ meV for a Be-filter analyser. With this value the total energy resolution of the whole spectrometer drops down to below 2% at around 100 meV energy transfer, which is a characteristic figure of high-resolution instruments.

With the selected value of scattered energy the peak reflectivity of graphite crystals is still as high as $\sim$70% at 2 mm crystal thickness even with this relatively broad mosaicity. A counter with linear dimensions of $\sim$10 cm will intercept about 70% of the geometrically broadened beam (larger counter sizes would give rise to a disproportion between gain in signal and increase in background level). Altogether about 50% of the neutrons with the nominal final energy will reach the counter (to be compared to $\sim$70% in the case of present Be-filter).

For the referred sizes of the reflecting surface the acceptance angle $\Delta \Omega$ for scattered neutrons becomes as large as 3 Steradian or $\sim$25% of $4\pi$, that is 50 times larger than on IN1-BeF at present. The total surface to be covered with crystals appears to be slightly less than 2 m$^2$ (the diameter of the largest cross-section of the ellipsoid is $\sim$0.8 m) what results in the overall gain in the luminosity $\Delta \Omega \cdot \Delta E$, of about an order of magnitude. This gain may be doubled if a second analyser is built up on the other scattering side as well. We outline that in spite of relatively large reflecting surface the optimal choice for the graphite grade turns out to be a comparatively inexpensive broad-mosaic material so that the total price may keep relatively low. Note that the solid angle $\Delta \Omega$ might be kept at the same value with reduced linear dimensions of the whole analyser (a limitation is imposed by the dimensions of sample environment). This allows one to optimise the cost of the reflecting surface which shrinks as fast as square of these linear dimensions. One of the assets of the design is a possibility to fill in, first, a part of the reflecting surface (less than a square meter) and to enlarge it subsequently so that the financial load might be staggered.

The reliability of the estimates of the gain in luminosity has been verified experimentally using the three-axis spectrometer of IN1 with a double-focussing graphite analyser set to reflect $\sim$4 meV neutrons and a sample of Ti hydride with a band of hydrogen vibrations at about 140 meV. The ratio of intensities measured on BeF and TAS and calculated in the same way as above has been found to coincide within 15%. The estimate of the background level is

![Fig. 2: A schematic view of the proposed secondary spectrometer. The reflecting surface represents a part of ellipsoid of rotation. The surrounding protection is not shown in the figure.](image-url)
more difficult to approve in such a test experiment. As expected, the background could be also improved several times, up to an order of magnitude (this is a typical ratio of the count rates measured at about boundary energy of a spectrum with and without a sample on the present Be-filter analyser). Nevertheless the inherently open design of the large-area analyser demands certain attention to its performance with respect to the level of noise.

The proposed construction envisages a cooled beryllium block dedicated to filtering out higher order reflections from graphite crystals. Without filtering this scattering is well persistent up to at least 6-th order where it appeared to be comparable to the inelastic signal, as it was observed in the referred test on the IN1-TAS spectrometer. On the other hand the higher order contamination is much lower in intensity than the primary elastic scattering from the sample so that this Be-filter block will be smaller in thickness and simpler in design than the filter-analyser. For the purpose of attenuation of this scattering the filtering Be-block will perform equally well either right after the sample, as depicted in Fig.2, or just before the counter. At the same time the level of background, stemming from parasitic scattering from construction materials behind the reflecting surface or from graphite material itself, may be not indifferent with respect to its position. Radial cone-collimators may serve as an effective measure to screen the counter against neutrons scattered by the filter block itself. A part of background can be removed by filling in the volume of the analyser "barrel" with helium or argon gas in order to suppress air scattering. In case if the inelastic scattering in graphite crystals would appear to be a significant source of background, cooling down the reflecting surface could be envisaged.

4. Conclusion

The anticipated parameters of the new spectrometer will permit the characterisation of much smaller samples, inherent in novel materials studies, the use of weakly scattering samples, a more detailed probing of external parameters like temperature, pressure, chemical composition, magnetic field etc., studies of time-dependent processes. With presently available flexibility in choosing the appropriate monochromator reflecting plane and collimation of the incident beam, the modernised IN1-BeF will become a unique high-intensity instrument for studies of excitations in the several-hundred-meV range. It will complement and extend the capabilities of the best existing spectrometers of similar destination at ILL and elsewhere.
Design study of a novel multi detector unit for a triple axis spectrometer

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Triple axis spectrometry is an old and highly developed technique for studying excitations in condensed matter. Although many developments concerning focusing in real and reciprocal space have been made in the past, one problem was not attacked in the same manner, namely the use of several scattering angles simultaneously. A novel multi analyser detector system for a triple axis spectrometer is described in this contribution. Asymmetrically cut and bent silicon crystals will be used in a transmission geometry. The crystals are positioned on an arc around the sample. All channels together perform a constant energy scan. This setup is well suited for “excitation fishing” in the momentum/energy transfer space, as in e.g. 2D magnetic systems. The layout is not restricted to the scattering plane and analyser crystals and detectors can be positioned also in the vertical direction.

1. Introduction
The development of the triple axis spectrometer (TAS) started in the fifties with a first set up built by Brockhouse in Canada [1]. The TAS has the inherent advantage that one can reach each allowed point in the momentum-energy space in different scan directions. This high degree of flexibility will be paid by one main drawback: the instrument measures step by step. One of the first attempts in the development of multi detectors for TAS was an upgrading of a horizontal focusing analyser system [2,3]. In this arrangement a linear detector was positioned behind the focusing point of the scattered neutrons. Further contributions have been made by the groups in Risoe and at NIST, with the RITA design [4-6]. The analyser part consists of several individual analyser crystals combined with a position sensitive detector in a short distance. Also a vertical arrangement has been studied with the flat cone detector at HMI [7].
A different set up for a TAS has been built in Garching, which works in a horizontal geometry. It uses the principle of monochromatic defocusing [8]. The analysers are set around the sample position on an arc and behind them there are the detectors arranged (“defocusing”). Each analyser is set to the same end energy (“monochromatic”). All channels are separated from the others with absorbing blades to prevent cross talk. To avoid second harmonics one solution is to use crystals with diamond structure and choose lattice planes with odd indices. Further advantages of bent perfect crystals are a homogeneous and high peak reflectivity and in the case of silicon also the low prize. In the monochromatic defocusing geometry one has to use an asymmetric cut of the silicon crystals (see Fig. 1).
A practical simple solution may be commercial silicon wafers. Within a silicon rod in (111) grow direction a further Si (11-1) lattice plane can be chosen at a cutting angle of 70.5°, which gives a Bragg angle of 19.5° (λ=2.09 Å). For intensity reasons one has to add several wafers and bent them to a radius of about 1m, which is also the distance to the sample.

2. Resolution and Intensity
For this arrangement the energy resolution has been calculated analytically. With the Restrax program (ILL) calculations for resolution and intensity have been done. For the energy resolution we have used the following formula [9]: \[ \frac{\Delta k}{k} = \frac{D}{R} \cot(\theta) \cot(\beta) \]
D is the thickness of the analyser crystal, R is the bending radius and \( \beta \) the outgoing angle. This expression determines the longitudinal wavevector spread. Introducing realistic values, \( \beta = -51^\circ \) and D = 15 mm for a Radius of R = 1 m gives \( \frac{\Delta k}{k} = 0.034 \). Fig. 2 shows the results of Restrax calculations for this setup with silicon in transmission geometry. One can see from the picture, also in this transmission geometry resolution values comparable with a reflection geometry can be obtained.
The resolution volume of the secondary spectrometer has been used as a measure for the expected intensities. The resolution volume for the transmission geometry is smaller by about 30% compared with a reflection geometry under the condition of nearly same resolution. Now we are under the way to optimise the intensity concerning cutting angle, crystal thickness, distances and detector dimensions.

Fig. 1: Sketch of the analyser geometry with asymmetric cut silicon crystals. The thick lines in the crystals mark the lattice planes.
3. Conclusion
A novel multi detector setup with bent perfect silicon crystals in transmission geometry has been described. Resolution and intensities have been calculated and show that this arrangement can compete with a setup in reflection geometry. One can extend this arrangement out of the horizontal plane also in the vertical direction through adding several analyser banks. Then a huge solid angle “excitation scanner” emerges.

References:

Fig. 2: Projections of the resolution ellipsoids calculated with Restrax for a transmission geometry.
Cascade: A New Large Area, Efficient and Position Sensitive Detector for Thermal Neutrons

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We present the CASCADE-detector, a new concept for efficient and position sensitive detection of thermal neutrons on large areas. The detector concept is based on solid neutron converter layers in a common gas detector system, which guarantees insensitivity to γ-rays. High detection efficiency is reached by cascading several solid neutron converter layers each coated onto a charge transparent carrier substrate. The GEM-foils are employed as such a transparent substrate. In this design position information, the locus of neutron conversion, can undistortedly be imaged through a cascade of several converter layers onto a readout structure underneath. The detector works with ordinary counting gases under normal pressure. Lightweight, easy to handle and in particular large area detectors can be constructed at low costs. A constant flow of fresh, purging counting gas avoids ageing effects, which guarantees long term stability as well as long lifetime. The use of GEM-foils provides a high dynamic range from single neutron counting up to high count rates of 10^7 n/cm^2 s and sub-µs absolute time resolution. This feature is required for modern spallation source instrumentation and opens the door towards new ambitious TOF applications. The concept of the detector, together with first results from a prototype device are presented.

1. Introduction
Neutrons are employed as research tools in almost all the natural sciences like Chemistry, Biology, Bio-chemistry, Physics, Material Sciences and Medicine. Modern applications, employing these neutron research tools, strongly demand two dimensional detector arrays, that allow to detect simultaneously all the neutrons of interest. Furthermore, modern time-of-flight (TOF) measurements as well as the instruments at the various spallation sources in operation and construction have a strong need for much enhanced time resolution in the sub-µs range. This time resolution depends primarily upon the time, neutrons can spend in the converter material and thus scales with the thickness (typically 0.5 cm – 2 cm) of the converter volume.

The 3He-filled proportional counter tube has been the standard neutron detector, ever since free neutrons became available. With 3He pressurised to several atmospheres in a proportional counter tube, a very high detection efficiency of up to 95% accompanied with a high insensitivity to γ-rays can be achieved. It is a robust and easy to handle construction. However, this detector is very limited in count rate as well as position and time resolution.

The CASCADE-detector overcomes all the limitations of the 3He-counter tube while maintaining all the advantages. It is a high efficiency detector employing a solid converter material that has about 3 mm spatial resolution, ultra low background and MHz count rate capacity on every channel. It is the universal detector concept of ultra high dynamic range for lowest intensity, background critical applications, as well as for highest intensity applications. Even for modern, challenging time critical experiments it provides time resolution in the sub-µs range. The completely unpressurised detector can be built into a lightweight housing. This allows to completely cover any region of interest by tiling several detectors, with very little blind surface of less than 8% of the active area.

2. Design Considerations
The principle change from a gaseous to a solid neutron converter allows to employ any cheap counting gas under normal pressure for charge amplification and detection. Convenient ambient pressure can be used because detection efficiency is now independent from gas pressure. Furthermore, lightweight, easy to handle and in particular large area detectors can be constructed. They can even be arranged in an array configuration with very limited loss to blind areas. Further, semi-spherical constructions, ideally suited for scattering applications are now easily feasible. In order to maintain the negligibly low gamma sensitivity of gas detectors, their enormous advantage over other detector concepts, a solid converter of Li or, alternatively 10B is used. Both, for their low Z, produce hardly any photo-electrons on γ-impact. 10B has, as opposed to Li, a much higher cross-section of absorption for thermal neutrons. The primer advantage of B, however, is its chemical inertness, so that the material can be exposed to roughly any harsh environment. The charged conversion products (α-particle and Li-nuclei) of the neutron capture reaction in 10B produce very high ionization densities in adequate counting gases even at atmospheric pressure. The center of gravity of the charges produced is limited to a range of 1-3 mm around the point of conversion. This results in a spatial resolution of 2-6 mm, by far sufficient for many applications. Cleaning by constant throughput of fresh counting gas avoids ageing effects, which guarantees long term stability and long lifetime of the detector.
2.1 The Problem of Insufficient Detection Efficiency

The principle challenge when using solid converters is the detection of the charged particles emerging from the conversion process. Most of these charged products are absorbed within the solid converter itself so that they cannot deposit their energy in the detection medium, e.g. a surrounding counting gas. Only if the conversion products manage to leave the bulk of the converter they can be detected. So apart from neutron capture cross-section the ratio of surface to volume of the solid converter determines the overall detection efficiency for neutrons. The advantage of high density of nuclei in a solid converter is jeopardized by the insufficient escape probability of the charged fragments from the bulk of the solid converter.

Up until now it was impossible to use several thin layers of solid converter material in a cascade in order to enhance detection efficiency, as the subsequent layer was impenetrable for the ionization signal, a cloud of electrons and ions. Extraction in other directions inevitably spoils the information on position. An ideal carrier substrate for the converter material would have to be completely transparent for the charges produced.

2.2 Charge-Transparent, Solid Neutron Converting Layers, the GEM

Since 1997 a substrate is available that has this property of charge transparency, the GEM [1]. The GEM was developed by F. Sauli at Cern in 1997 as a Gas Electron Multiplier. GEMs are Kapton foils (50-100 µm thick), that are coated on both sides by a thin layer of copper (5-15 µm thick) (Fig. 1). Most importantly, these foils are covered with a regular pattern of through going holes, 50 µm in diameter and at a lattice spacing of about 150 µm. Both layers can be individually contacted electrically. If the potentials on these electrodes are chosen adequately, homogeneous field lines far above the hole structure will be channeled right through these holes and the GEM. The fields are formed in such a way, that charges from above the GEM will be channeled and imaged undistorted to below the GEM. In an intuitive manner, these GEMs can thus be cascaded one behind the other. Application of a thin coat of a solid neutron converter material onto such a GEM provides the charge-transparent, solid neutron converter layer.

With charge transparent layers of a solid neutron converter available, the complete technology of standard gas detectors can readily be employed towards the construction of a neutron detector. The transparency for charges allows to cascade several such layers one behind the other collecting single layer detection efficiencies. In such a cascade, an overall detection efficiency for an impinging neutron can be obtained that challenges the standard single channel $^3$He counter tube.

3. The CASCADE-Detector

The CASCADE neutron detector is a detector constructed from a cascade of several GEM-foils which are coated with a layer of neutron converter material such as $^10$B. This detector is operated at ambient pressure. The robust detector can easily be built to cover large areas with a lightweight housing (approx. 1-2 kg for 10 000 channels and a surface of 30 x 30 cm$^2$) (Fig. 2). Furthermore, flowing cheap counting gases through the detector avoids ageing effects and guarantees long term stability and long lifetime of the detector.

The planar stack of the converter foils can be read out by means of a simple readout structure. This structure can be adapted to meet specific needs such as e.g. pure azimuth resolution and integration over polar angle or simply 2D resolution. With a stack of
several (5-10) converter sheets, detection efficiencies of about 50% for incoming thermal neutrons (1.8 Å) can be achieved. (Fig. 3). With a drawback in spatial resolution, even 80% detection efficiency is feasible when using 'LiF as converter material. For typically employed neutron wavelengths of 3.5 Å, only half the number of converter sheets is needed, that is six singly or three doubly coated GEM foils!
The use of GEM-foils allows high count rates up to $10^5$ n/cm² s [2] and because of the low-Z of $^{10}$B, because of the high energy of the charged conversion products and together with the property of being a gas detector the detector is free of γ-underground. Furthermore, the detector provides sub-µs absolute time resolution, opening the door towards new TOF applications.

4. First Experimental Results
By now, first completely functional, natural boron coated GEM-foils (sensitive area 4 x 4 cm²) have been successfully employed in a cascaded setup, proving their functionality as cascadable, charge-transparent substrate for the neutron converter coating. In a four, singly coated layer cascade, spatial resolution was found to be 3 mm. Position information was undistortedly imaged through the four layer cascade onto a charge-detection structure (e.g. MSGC [3]). Detection efficiency was determined to be 4% in agreement with theoretical expectations. The detector has now successfully been scaled up to a sensitive surface area of 8 x 8 cm² (Fig. 4). A two-dimensional readout was additionally installed so that first imaging experiments with data presented here could be carried out (Fig. 5).

5. Final Remarks and Outlook
The further expansion of the sensitive area to a size of 30 x 30 cm² is prospected. This larger detector will be equipped with GEM-foils coated with isotopically pure $^{10}$B, which will further enhance detection efficiency by a factor of five. The final goal is the construction of a full sized (30 x 30 cm²) detector of 50% detection efficiency for incoming thermal (1.8 Å) neutrons. This detector will be constructed with 10 doubly coated cascade layers.

REFERENCES
Neutron detector development at ILL

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During the last years, with D20, D4C and bidim projects, microstrips detectors have been subject of development at ILL. New requirements have been induced by the modernization of the instruments at ILL (millenium program) and are also motivated by the projects of future spallation sources. New developments made by “Service Détecteurs de Neutrons” at ILL are reviewed. The Bidim200 detector, (64 x 64 cells with a 3mm pitch and individual readout) exists in two versions: MWPC which is in operation and MSGC which is in phase of commissioning. The Bidim300 MWPC, (128 x 128 cells with a 2mm pitch and individual readout) is under construction. CCD readout of GEM based detector, in collaboration with Coimbra University, has given its first images of neutrons. Neutron Optical Readout Detector (6LiF / ZnS : Ag scintillator, optical fibers and photomultipliers) is studied in collaboration with CERN. A 2D neutron beam monitor is designed; the use of nitrogen as a very weak efficiency detection gas has been confirmed. A small angle neutron scattering detector (SANS-2MHz) is described in another paper in this symposium [1].

1. Bidim200 MWPC 64 x 64

The Bidim200 MWPC (Multi-Wire Proportional Chamber) detector (Fig. 1) has been recently completed. Its main features are:
detection gap: 30mm; anode-cathode distance: 3mm; anode plane: 30µm stainless steel wires with a pitch 3mm; first cathode plane: 100µm Cu-Be wires (soldered) with a pitch 1mm and grouped by 3; second cathode plane: 2.8mm wide Cu strips on poly-imide printed board with a pitch 3mm; internal connections with 4 “kapton” flexible printed boards (no outgassing) and 37 points feed-through connectors with knife joint.
The detector has been outgassed for two weeks at 150°C before it was filled with the gas mixture composed of 3 bars He + 2 bars CF₄. The electrode potentials are: guard 400V, cathode 450V, anode 3100V.
The acquisition chain is based on individual readout 64X by 64Y. 128 channels (amplifiers and discriminators) are distributed on four mother boards (2 X and 2 Y). The selection of the largest signal is made from X channels and the same is done for Y channels. Then the XY coding (2x6 bits) is made during a coincidence window (0.2µs) and the resulting address is sent to the acquisition system.

This detector have been tested for a few days on the D16 diffractometer and comparison with the D16 detector made with the attenuated direct beam. The peak profiles were the same, the background to peak ratio, qualitatively good, could not really be compared because of an unsuitable shielding of the Bidim. The global count rate of the Bidim200 is much better, greater than 150kHz (Fig. 2). It will be increased to 500kHz with the amplifiers of the next generation currently under development.

Fig. 1: Inside view of the Bidim200 MWPC.

Fig. 2: Comparison of measured count rate of D16, D11 and Bidim200 MWPC.
The Bidim200 MSGC (Micro-Strip Gas Chamber) detector (Fig. 3) is the microstrip version of the Bidim200 MWPC. It is made in view of the detector modernization of the D19 instrument. The microstrip plate is made of S8900 Schott glass. The structure used is the so-called "virtual cathode" where anodes are etched on one side and cathodes on the other. The cathodes use the backgammon pattern [2]. Guard electrodes made of S8900 glass homogenize the electric field in the drift region between the microstrip plate and the entrance window. The microstrip connections are gold plated. In the future, these connections, presently designed for individual readout, will be modified to implement charge division readout along each strip. The detector is baked at 150°C under ultra vacuum. The microstrip plate was delivered very recently and 3 days later tested (1st April 2001) with an Am-Be neutron source. It was perfectly working with a good uniformity without any threshold adjustment of signals which is a general property of microstrip plates.

The design of Bidim300 MWPC is presently under completion. It is an extrapolation of Bidim200 in a more compact vessel. It is intended to replace the current D16 detector. Its main characteristics are: anode: 25 µm golden Rh-W wires, pitch 2mm; cathode 1: 100 µm Cu-Be wires, pitch 1mm, grouped by 2; cathode 2: 1.8mm Cu strips, pitch 2mm; distance anode-cathode: 2mm, detection gap: 30mm.

4. Active gas scintillator

Optical readout of GEM (Gas Electron Multiplier) based neutron detectors operated with a gaseous mixture of 3He and CF4 has been investigated in collaboration with Coimbra and Delft Universities [3]. Preliminary studies have shown that avalanche scintillation in He-CF4 is sufficiently high to allow the development of detectors with CCD readout. Using a detector operated with two 5 x 5 cm² GEM foils spaced by 2mm, some basic measurements of cascaded GEM operation were made. Special custom ordered GEMs with several hole diameters were used. A CCD system operating in the 400-1000nm band was used to collect the light of the scintillation of the GEM avalanches. Spectroscopic data on the visible and NIR scintillation of He-CF4, data on gain, transfer fields and light emission were collected. An image of the proton and triton tracks obtained with neutrons at the ILL is shown (Fig. 4).

5. Neutron Optical Readout Detector

The Neutron Optical Readout Detector (NORD64), based on a scintillator coupled to multi-anode photomultipliers via optical fibers, is studied in collaboration with a CERN team (Kuroda). A prototype has been tested at ILL, giving promising results: 60% effi-
ciency with 2.5Å neutrons combined with a good rejection of gamma rays. The construction of such a detector with 64 x 64 cells at a pitch of 2mm has been undertaken. A 4LiF / ZnS:Ag scintillator (from Applied Scintillation Technologies) and two 8 x 8 multi-anode photomultipliers (H7546 from Hamamatsu) will be used, linked by optical fibers (Y11 from Kuraray) giving optimal wavelength shift between the scintillator and the photomultiplier (Fig. 5). The first side of the 0.5mm thick scintillator will be covered by 256 square fibers 0.5 x 0.5 mm² grouped by 4. The 64 resulting groups will transmit the collected light to the 64 anodes of one photomultiplier. The same will be done on the other side but in the perpendicular direction. The anode signals will be amplified, filtered (gaussian shape) and then sent to a discriminator followed by an individual readout acquisition chain. The prototype tests have shown a count rate limitation due to the decay time of the scintillation light (tenths of µs). Next step will be the use of other scintillators like Li-glass which is much faster (of the order of ns) and should overcome this rate limitation. This fast and accurate detector will find applications in neutron radiography and spallation sources.

6. 2D neutron beam monitor

The study of a thin position sensitive monitor has been undertaken. The main features are: charge division localization made along resistive wires at a pitch of 1cm, thickness of aluminum windows 0.5mm, total thickness 2cm, sensitive area 10 x 10 cm², detection gap 1cm. The design of this monitor is now achieved (Fig. 6).

Fig. 6: Design of the 2D neutron beam monitor.

The neutron pulse height spectrum measured with a monitor filled with 12mb of nitrogen is shown (Fig. 7). The conversion gap was 3.3 cm. To shorten the range of the proton and to reduce the edge effects, 400mb of CF₄ was added. This spectrum was measured on the direct beam of CT1 across a 25mm circular diaphragm during 1000s. The counts in the 40 first channels are due to gamma radiation and can be easily discriminated from the neutron counts. The detection efficiency is 3.5 10⁻⁶.

Acknowledgements
Thanks to: B. Demé for Bidim200 MWPC testing, S. Rowe for 2D neutron beam monitor drawings.

Fig. 7: Neutron pulse height spectrum with nitrogen as detection gas.

Thanks to their better energy resolution, gas monitors are intrinsically superior to monitors based on a thin converter layer (Uranium or Boron) in terms of counting stability, but they suffer from a limitation of the minimum detection efficiency they can achieve. The capture cross section of ³He is equal to 5350 barns for thermal neutrons. Using a 1cm conversion gap, a detection efficiency of 10⁻⁵ can only be obtained with a ³He filling pressure equal to 0.075mb, which is very difficult to control. For this reason, we investigated nitrogen as a detection gas. The nuclear reaction is: ¹⁴N + n → ¹H + ¹⁴C + 627 keV (this reaction is the one which allows the ¹⁴C dating). The proton energy is 585 keV and the carbon one is 42 keV. The capture cross section for thermal neutrons is 1.8 barn, corresponding to a detection efficiency of 9.05 10⁻⁶ p.l (p pressure in bar, l length of the conversion gap in cm), 10⁻⁶-10⁻⁷ can be attained with pressure of the order of a few mb of N₂ which is easily obtainable.

The neutron pulse height spectrum measured with a monitor filled with 12mb of nitrogen is shown (Fig. 7). The conversion gap was 3.3 cm. To shorten the range of the proton and to reduce the edge effects, 400mb of CF₄ was added. This spectrum was measured on the direct beam of CT1 across a 25mm circular diaphragm during 1000s. The counts in the 40 first channels are due to gamma radiation and can be easily discriminated from the neutron counts. The detection efficiency is 3.5 10⁻⁶.

REFERENCES
High count rate detectors for Small Angle Neutron Scattering

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1. Detector structure

The present detector of D22 is made of a large area single vessel M.W.P.C. using He-3 gas at 1.85 bar plus some CF4. It contains 2 orthogonal sets of 128 cathode wires, and the position information is extracted by finding a coincidence on an X and a Y signal. Such a structure is limited to a counting rate of at most a few hundred kHz.

In order to achieve the high counting rate specified, we opted for a segmentation of the active surface in 128 independent, one-dimensional position sensitive detectors, based on the principle of charge division. Indeed, on a small prototype, a spatial resolution of 3 mm at 1600 V and of 6 mm at 1400 V, a dead time of 2.2 microseconds (corresponding to overall dead-time losses of 10% at 5 MHz) and good spectral separation of photons and neutron events will be demonstrated.

The aim of the SANS-2MHz project is to develop and build a real-time neutron detector for small angle scattering applications that can achieve at least a 2 MHz count rate with dead-time losses no larger than 10 %, a factor of 40 higher than the maximum counting rate obtained with the actual D22 detector. Although the project is aiming at defining a technical solution for the 2 SANS instruments of ILL, D11 and D22, we have concentrated our efforts on D22, which has stronger requirements. The future detector should have a resolution of at least 7.5 mm x 7.5 mm on an active surface of 960 mm x 960 mm and a neutron detection efficiency of about 75 % for neutrons at 5 Angstrom wavelength. It should have a gamma rejection capability at least comparable to that of the current detector. Results will be presented that show that the main requirements for such a detector can comfortably be achieved using an “organ pipe structure” of 128 independent tubular position-sensitive detectors, based on the principle of charge division. Indeed, on a small prototype, a spatial resolution of 3 mm at 1600 V and of 6 mm at 1400 V, a dead time of 2.2 microseconds (corresponding to overall dead-time losses of 10% at 5 MHz) and good spectral separation of photons and neutron events will be demonstrated.

The « Y » coordinate of an interaction will be given by the number of the tube in which this interaction took place, and the « X » coordinate will be determined by resistive charge division in that tube – each anode wire being read out at both ends by charge amplifiers. The « Y » coordinate will be given by the number of the tube in which this interaction took place, and the « X » coordinate will be determined by resistive charge division in that tube – each anode wire being read out at both ends by charge amplifiers.

If we call R the resistance and L the length of the anode wire, Z the input impedance of the amplifiers and x the distance from one end (A) of the anode wire at which a total charge Q has been deposited (e.g. a neutron event), the charges A and B observed at both ends are given by equation (1).

$$A = Q \left( 1 - \frac{x}{L} \right) \frac{R + Z}{R + 2Z} \quad B = Q \frac{\frac{x}{L} R + Z}{R + 2Z}$$

In order to extract the position information, we calculate the ratio of the difference to the sum of these charge signals, as given in equation (2). The amplification factor of the amplifiers cancels.

$$\frac{A - B}{A + B} = \frac{L - 2x}{L} \times \frac{R}{R + 2Z}$$

The first factor contains the position encoding in an interval (-1,1). The second factor reduces this range. We call the second factor the useful dynamic range. In our case, the impedance Z is of the order of 100 Ohm thanks to an improved structure of the preamplifier, while the wire resistance is about 6KOhm, resulting in a useful dynamic range of essentially 100 %.

2. Spatial resolution and electronic noise

The determining factor of the spatial resolution in charge division is the electronic noise added to the signals A and B. This noise has two different kinds of sources: on one hand, there are the noise sources due to the preamplifiers, on the other hand there is the thermal Johnson noise due to the resistive anode wire itself. If we call $v_i$ the spectral voltage noise density and $i_i$ the spectral current noise density of an amplifier, R the wire resistance, and T the absolute temperature of the wire, then the total equivalent spectral current noise density can easily be calculated. On a single signal (A or B), this density is given in equation (5). On the difference and on the sum of the signals A and B, the densities are given by the equations (3) and (4) respectively.

$$\sqrt{i_A^2 + i_B^2 + 8 \frac{v_i^2}{R} + \frac{16k_iT}{R}}$$

$$\sqrt{2i_A^2 + 8 \frac{v_i^2}{R} + \frac{16k_iT}{R}}$$

$$\sqrt{2i_A^2 + 8 \frac{v_i^2}{R} + \frac{16k_iT}{R}}$$
\[ |i_A + i_B|_{RMS} = \sqrt{2 \times i_t} \quad (4) \]
\[ |i_A - i_B|_{RMS} = |i_A|_{RMS} = \sqrt{\frac{i_t^2 + 2 \nu_n^2 + \frac{4k_BT}{R}}{R}} \quad (5) \]

When unplugging an amplifier from the detector, the only contribution to the equivalent current noise density is \( i_t \) itself. Taking the values \( i_t = 1.6 \text{pA}/\text{Hz}^{1/2}, \nu_n = 1 \text{nV}/\text{Hz}^{1/2}, R = 5.6 \text{kOhm} \), we calculate a noise current density of 4.15pA/Hz\(^{1/2}\) for the difference signal, 2.26pA/Hz\(^{1/2}\) for the sum signal and 2.36pA/Hz\(^{1/2}\) for a single signal.

After r.m.s. integration of these spectral noise densities over the transfer function of the preamplifier-amplifier chain, one obtains the standard deviations due to electronic noise on the sum (A+B) and the difference (A-B) output signals. The errors on the sum and the difference are statistically independent if the amplifiers are identical while the individual errors on A and B are statistically correlated. In our case, the standard deviation has been measured to be 6.3mV on the sum signal, and 12mV on the difference signal. The individual channels have measured standard deviations of 6.9mV each. Without the detector, the standard deviation is 4.5mV on both channels. These measurements are in agreement with the ratio of the calculated current noise densities.

The propagation of these statistical errors in the expression \((A-B)/(A+B)\) is given in equation (6).
\[ \delta \left( \frac{A-B}{A+B} \right) = \sqrt{\frac{(A-B)^2}{(A+B)^2} (\delta_{A-B})^2 + \frac{1}{(A+B)^2} (\delta_A)^2} \quad (6) \]

In this expression, the second term under the square root is dominant (and essentially determined by the Johnson thermal noise in the anode wire) and position-independent (A+B is the amplified total charge). The smaller contribution of the first term is position-dependent: it vanishes in the middle of the detector and has its largest contribution at both extremities of the detectors (the "U-effect"). It is due to the current noise of the amplifier.

Given the fact that \( 1/(A+B) \) has an average value of about 1/2.8V when operating the detector at 1400V, we calculate a spatial resolution of 5mm (F.W.H.M.) in the middle of the detector and about 6mm (F.W.H.M.) on the borders.

3. Counting rate issues
Assuming that the physical processes in the detector are not introducing any noticeable extra dead time, the total dead time (and hence the counting rate) of one detector will be essentially determined by the total pulse width of the shaping circuit. In order to optimize noise bandwidth and pulse duration, we opted for a 4-th order pure pole approximation of a Gaussian pulse shaper, with a total pulse duration slightly larger than 2 microseconds.

4. Experimental results
At an operating voltage of 1400V (150V below the nominal voltage), we obtained spatial resolutions (F.W.H.M. derived from a Gaussian fit) of the order of 5.5mm in the middle, and less than 7mm near the border of the detector, as shown in figure 1. Note that these observations are in quite good agreement with the theoretical prediction (5mm resp. 6mm). When operating the detector at 1600V (50V beyond the nominal voltage), the spatial resolution obtained in the middle was about 3mm. These...
results were obtained using a low count rate (of the order of 1kHz) and a highly collimated beam of 2.5 Angstrom neutrons\(^{(1)}\). When comparing the count rates of the detector with those of a low efficiency monitor, using a less collimated but intense beam, we measured a decrease in relative efficiency in agreement with a dead time of 2.2 microseconds\(^{(2)}\), as shown in figure 2. This is fully in agreement with the pulse width of the shaping electronics. While at 1400V, the energy spectrum of the neutron interaction has undergone a non-linear effect (non-proportional region of the avalanche amplification) a separation of the gamma peak and the neutron energy range is still visible, as demonstrated in figure 3. This allows for a good separation of both events by a threshold on the A+B signal.

**5. Conclusion**
The main goals set out initially for the SANS-2MHz project can be achieved comfortably using the detector structure as described in this paper. The principal difficulties to overcome were spatial resolution (we are well below the 7.5mm specified) and counting rate (we are well below the 5 microseconds dead time specified). The good agreement with the calculated predictions show that we master the essential parameters of this detector on the theoretical side. Preliminary experimental results show that both these requirements are not mutually exclusive. Having used high voltage levels well below the nominal voltage, the detector elements will not face a serious aging problem and will be mechanically robust. Photons can be discriminated from neutron interactions. We have strong indications that the demanded overall efficiency can be reached for several different configurations of these position sensitive detectors.

**Acknowledgements**
The authors wish to thank Michel Gamon, for his professional wiring up of the electronics, Steve Rowe for his excellent mechanical drawings and Fabrice Horst for his highly valuable suggestions in eliminating electromagnetic perturbations.

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A New Multidetector at IN11

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A two dimensional position sensitive neutron detector based on the Multiwire Proportional Counter principle is being installed at IN11. The main requirements for this detector are: (1) active detector area of about 150mm x 150 mm, (2) light weight construction that fits in the existing environment of the spectrometer, (3) a simple data acquisition system, (4) a small volume, and (5) relaxed spatial resolution (of the order of a few mm). The neutron detection is based on classical neutron absorption in ³He.

1. Introduction
The ESRF has made considerable progress in the development of gas-filled particle detectors. By implementing the necessary technology for Multiwire Proportional Counter (MWPC) construction in a clean room environment, the ESRF has established a solid base for reliable and reproducible detector fabrication.

Long term experience has proven that the MWPC invented in 1940s during the Manhattan Project [1] does not suffer from stability and reliability problems and can be built to any size required. Further, the achievable electron amplification on a single stage MWPC is at least an order of magnitude higher than for other detector types. This and the complete lack of any substrate make them largely insensitive to eventual electronegative gas contamination and charge collection problems.

2. Technical Parameters
The neutron detector built for IN11 has an active aperture of 185 x 185 mm². The anode is made from 6 µm gold-coated W(Re) wires at 1 mm pitch fixed onto a polyimide frame. The two cathode frames have a similar structure but the wire thickness is 30 µm. The cathode wires are connected to the lumped parameter delay line nodes. The delay line (DL) serves to encode the position of the neutron capture. At both ends of the delay lines impedance-matched preamplifiers (PAs) are placed. These are transimpedance (100 kΩ) current amplifiers made in-house using modern components developed for high speed fiber optics communication. The output pulses from the PAs have a nearly triangular shape with a rise time in the order of 25 ns. The fast rise time is essential for timing measurements and allows to handle high count rates. The DL based data acquisition principle is the fastest and most precise method between the global encoding techniques (charge division etc...). Actually it measures the difference of the arrival times of the pulses due to the same neutron at the ends of the DL, the difference being proportional to the position of the neutron capture.

The detector is filled with a 2 bar ³He and 1 bar CF₄ gas mixture. The composition’s partial pressures are optimized to obtain the required detection efficiency and positional resolution. Due to the applied DL encoding (only 5 + 2 hermetic gas tight connectors being required) the detector body is rather compact and contains all the necessary preamplifiers. Such a way the immunity to Electromagnetic Compatibility (EMC) is maximized. The position encoding principle is depicted in Fig.1. Discriminated pulses (by Phillips Model 715 constant fraction discriminator) are timed by a time to digital converter (TDC) with a precision of 0.8 ns. The TDC measures the time between the anode pulse and any other pulses occurring on each delay line. All these data are passed to a VME processor, which computes the neutron position. An intelligent pulse recognition algorithm finds the pulses belonging to the same neutron, as the time sum of two opposite cathodes (x or y) is always equal to the delay line length. This time sum check allows the rejection of noise and recovers neutrons with overlapping coincidence windows.

3. Installation and first results
The detector was first installed at IN11 in December 2000. Initial tests with neutrons were continued in June 2001, but have not yet been completed. The final installation, including the shielding, correct detector position, VME and the fiber optics link between the experimental zone and the instrument control computer is under way. The routine operation is expected to be starting in the 4th reactor cycle in 2001.

We now report on some results obtained during the tests. As working conditions an anode voltage of 2850V and a drift voltage of...
−2000V were chosen. To estimate the sensitivity to γ radiation, the detector was completely shielded by a Cd mask. This mask converts all neutrons to γ radiation. The measured numbers can be found in table 1. From these numbers a γ sensitivity of the order of $1 \times 10^{-4}$ can be estimated. The spatial resolution is about 3 mm, which is convenient for IN11.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Counts/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam on, no Cd mask</td>
<td>30052</td>
</tr>
<tr>
<td>Beam on, with Cd mask</td>
<td>0.27</td>
</tr>
<tr>
<td>Beam off, with Cd mask</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 1: Gamma sensitivity test.

This value was measured using Cd apertures of different sizes placed in front of the detector. The overall system (detector and electronics) effective dead time, which is about 300 ns, determines the loss of counting events, which becomes important at high input flux. Due to the pulse recognition algorithm, the dead time in first approximation is not determined by the coincidence window (i.e. twice the length of the DL) but by the width of the analog pulses. The result is a higher efficiency of the detector at high count rate, as the pile up is strongly reduced and does not corrupt the spectrum. At present the count rate is limited by the speed of the VME processor to the order of 300 kcps. Figure 2 shows that there is no saturation up to 200 kcps, (the curve stays perfectly linear).

Figure 3 shows an example of spin echo data taken with a standard sample (graphite). It shows the value of the two-dimensional information. Getting the spin echo phase pattern over the whole detector solid angle allows for a more efficient instrument tuning, because it provides information about the character of the field integral inhomogeneity that might be present. The instrumental resolution is effectively increased, which is especially important at high precession current (long Fourier time). Finally, in magnetic scattering experiments the data can be corrected for subtle effects, which are due to the broad $q$ resolution, in a much more reliable way.

4. Conclusion
The results obtained during the installation of the detector show that it is possible to register spin echo data in two spatial dimensions using a delay line based neutron detector. It is a fast, compact, easy-to-install and solid data acquisition device and state of the art in its category. The single arm option of IN11 will be significantly improved by this detector system.

References
How to achieve high intensity in NSE spectroscopy?

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Neutron Spin Echo Spectroscopy (NSE) allows us to reach high energy resolution in the $10^{-5}$ range while keeping the high intensity advantage of a beam which is only 10 – 20 % monochromatic. A further enhancement of the data collection rate has been achieved at the SPAN spectrometer at BENSC, HMI, by substantially increasing the detector solid angle and the efficiency of beam delivery. We developed a novel precession field configuration with cylindrical symmetry, which for the first time enables simultaneous NSE measurements over the whole range of scattering angles accessible by a spectrometer, typically from -150° to 150°.

1. Introduction
Since the commissioning of ILL in the early seventies, neutron sources did not further improve and it was the better use of neutrons, i.e. a better neutron economy, that lead to the considerable increase in neutron intensities achieved in the last years. The development has been twofold: improvement of neutron optics and increase of the total solid angle for simultaneous measurements. The tremendous progresses made in the development of novel neutron optical devices based on supermirrors allow for a most efficient beam delivery and are of particular importance when it comes to polarized neutrons. Simultaneous measurements over a large angular range are a straightforward way to improve data acquisition for most of the neutron scattering techniques. When it comes to neutron spin echo (NSE), however, the tight conditions for the homogeneity ($10^{-4}$–$10^{-5}$) of the magnetic precession field integral, or of the neutron flight path in RNSE, along all neutron trajectories make simultaneous measurements over a wide angular range difficult.

Fig. 1: Schematic view of SPAN from the top with the NSE precession coils ($\phi$ 1 m, $\phi$ 3 m and $\phi$ 4.8 m) and the choppers used for the TOF measurements. The double chopper is removed in the NSE configuration.
The novel spectrometer SPAN at BENSC (HMI)[1,2] marks a considerable development towards higher neutron intensity in NSE spectroscopy both by its improved neutron optics and by its novel magnetic field configuration, which for the first time enables simultaneous NSE measurements over a wide angular range. The magnetic field of SPAN is created by the three pairs of coils with diameters of 1 m, 3 m and 4.8 m respectively shown in Fig. 1.

All scattering angles are open and accessible to NSE, typically from –150° to 150° deg. In the case of SPAN, geometrical restrictions due to the shielding of neighboring neutron guides reduce the angular range from –30° to 150° deg as shown in fig.1.

2. NSE configuration
The set-up of SPAN has a vertical symmetry axis, which crosses the horizontal scattering plane at the sample position and leads to the required symmetry of the magnetic field. In each pair of coils the electric currents are antiparallel to each other and the resulting magnetic field is horizontal in the scattering plane. A slight asymmetry in the currents of the smallest coils, with a diameter of 1 m, produces a weak vertical field around the sample, which maintains the required axial symmetry of the magnetic field configuration.

A neutron wavelength band \( \Delta \lambda / \lambda \sim 15 \% \) FWHM is selected by a mechanical velocity selector. The \( \pi/2 \) flippers, which mark the beginning and the end of NSE precessions, are positioned at 2.5 m from the sample and the maximum magnetic field integral reaches 0.06 T m, i.e., \( \sim 1/3 \) that of IN11. This somehow reduced energy resolution, which amounts to 80 neV at a wavelength of 9 Å, is exclusively due to the limited electric power of the coils and power supplies of this very first realization of “wide angle NSE” and not to any intrinsic magnetic field inhomogeneities. The intrinsic limit of the coil configuration is evaluated to be beyond 2-3 times the actual one.

At SPAN NSE is routinely done with two detector banks simultaneously. In summer 2001 the third detector bank will be commissioned for NSE and the angular opening for NSE or polarization analysis measurements will reach 32°. Fig. 2 shows typical NSE spectra collected simultaneously with two banks on a reference quartz sample at 6.5 Å. The magnetic field integral was 0.03 T m and the scattering angles were 94 ± 4 deg and 130 ± 5 deg, respectively. These spectra illustrate particularly well the advantages of the SPAN configuration: (a) the resolution does not change significantly with the scattering angle, (b) the echo phase shift between neighboring detectors and also between detector banks can be reduced to a minimum and last but not least (c) broad bands of scattering angles can be accessed simulta-

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Fig. 2: NSE spectra of a reference quartz sample collected simultaneously at 94 ± 4 deg and 130 ± 5 deg respectively. The wavelength was 6.5 Å and the magnetic field integral was equal to 0.03 T m.
neously by NSE, not only some discrete Q-values. For investigations, where the dynamics varies slowly with Q, detector binning can be easily introduced to improve data quality and reduce counting time. On the other side, every detector can be considered separately leading to a detailed analysis of the Q-dependence of the dynamics, when this is required.

The open configuration of the set-up allows for time-of-flight (TOF) measurements and SPAN can also be run as a medium resolution TOF spectrometer. In the TOF configuration a double chopper made out of two counter-rotating discs is positioned next to the sample and it is used together with the other two choppers and the velocity selector as shown in fig. 1. TOF measurements can be done with or without polarization analysis. The TOF resolution typically amounts to 0.1 meV FWHM at 7 Å.

The combination of NSE and TOF leads to the particularly large dynamic energy transfer range of more than four orders of magnitude, which is required in the studies of the dynamics of systems with a broad distribution of relaxation times, such as glasses and spin-glasses, or of systems with strongly q-dependent relaxation rates, such as ferromagnets near their critical temperature $T_c$ [3,4].

### 3. Neutron Optics

The neutron optical elements of SPAN (polarizing neutron guide and polarization analyzing devices) are designed for a particularly large wavelength range, which extents from 2.5 Å up to 10 Å, i.e. from the thermal to the cold neutron spectrum. SPAN is located at an end position of a beam-splitter polarizing guide [iii], which as usually in NSE spectrometers does not penetrate into the NSE precession area and ends at 2.8 m from the sample. The beam has particularly large dimensions: a width of 58 mm and a height of 100 mm and illuminates a typical sample area of 40 mm × 40 mm. The vertical divergence reaches ±1.2° for both the incoming and scattered beams. NSE measurements with such a large beam cross section and relaxed vertical collimation are made possible by the use of NSE Fresnel correction coils [4], which decouple the resolution from the beam collimation and allow the high NSE resolution to be reached without the cost of a high collimation. The high homogeneity of the magnetic field of SPAN would allow for an even higher vertical divergence of at least ±1.5°.

The analysers of SPAN are remanent supermirrors [5] which are magnetized with a short magnetic field pulse, preserve their magnetization and perform in the stray magnetic field of the main coils whithout any additional field. In order to cover the totality of the wavelength range provided by the guide without suffering severe intensity losses at the lowest wavelengths, the coating of the mirrors has a critical angle, which is 2.5 times the critical angle of Ni.

The neutron optics at SPAN overcomes the drawback of the medium flux reactor source and the spectrometer offers at $\lambda = 4.5$ Å about the same data acquisition rate per detector as IN11C at ILL.

At the lowest wavelength of 2.5 Å, $Q_{max}$ reaches 4.8, which opens up new possibilities in probing coherent dynamics in the high Q range, where localized motions should occur. That high Q values have never been accessible by any other NSE spectrometer before and have up to now only been reached by the combined thermal TAS-NSE spectrometers TASSE-IN20 at ILL and PONTA at ISSP-JAERI [vi].

The novel design of SPAN opens up for the first time the possibility to collect NSE spectra simultaneously over a wide detector solid angle reaching 0.27 strad for an acceptable vertical beam divergence of ±1.5°. SPAN, in full operation at BENSC, is being further developed steadily. It is planned to enhance beam delivery with the installation of a novel guide with low loss a ballistic design [vii] and a final converging part. The SPAN geometry would also allow for adding optional IN11 type solenoids to achieve higher energy resolution in a reduced angular range of about $2° \times 2°$ and 1 m long solenoid sections are available for add on.

### References

A new IN11 with an almost 35 times higher counting rate than that of IN11C

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IN11C, the wide-angle option of the neutron spin echo (NSE) spectrometer IN11 has been successfully operating since 1997, offering a counting rate which is 20 times higher than that of IN11A. We now propose to further improve this counting rate by completely reconstructing IN11, which would lead to an intensity gain of more than one order of magnitude compared to IN11C and would also improve the energy resolution. The new instrument would require an experimental zone of about 80 m² and an end position at a new neutron guide. The design would be similar to that of SPAN at HMI, Berlin, with the largest possible detector solid angle. The incident neutron wavelength and monochromatization would be selected by TOF, which would also allow for performing inelastic TOF spectroscopy with polarisation analysis.

At present, two “classical” Neutron Spin Echo (NSE) spectrometers exist at the ILL: IN11 [1] and IN15 [2]. This is well justified because they cover different ranges in Fourier time \( t \) and momentum transfer \( Q \) and on average they are oversubscribed by a factor of two. The differences between IN11 and IN15 are due to the wavelength ranges: \( 4 \lambda \leq \lambda \leq 12 \AA \) for IN11, and \( 8 \AA \leq \lambda \leq 25 \AA \) for IN15, respectively. IN15 was put into operation in 1997 and has taken over almost all low-\( q \) experiments, because these nowadays often require Fourier times of up to \( t = 200 \) ns, which cannot be reached at IN11. On the other hand, the long wavelength neutrons naturally limit the \( Q \) range accessible to IN15, and IN11 is still indispensable for experiments on polymers and glass dynamics at \( Q \geq 0.5 \) Å⁻¹.

IN15 with its long Fourier times marked a substantial improvement in NSE spectroscopy. Another development option consists of increasing the detector solid angle over which NSE measurements can be performed simultaneously and thus increase the NSE counting rate. However, the NSE homogeneity requirements for the magnetic fields created by long solenoids give an upper limit for the detector solid angle. IN11C, the multidector option of IN11, offers an angular range of 30° for simultaneous NSE measurements and represents the solution to the detector solid angle problem at the position, where IN11 is located [3]. The success of IN11C is due to its high counting rate, which is 20 times higher than that of IN11A. The drawback is in the energy resolution, which cannot reach that of IN11A, because the precession field of IN11C cannot be made as homogeneous as that of IN11A.

A novel concept in NSE instrumentation has been successfully realised with the spectrometer SPAN at BENSC (HMI, Berlin) [4], which allows for significantly increasing the detector solid angle, far beyond that of IN11C. The novelty consists in the precession field, which is created by two flat solenoids with vertical axes and antiparallel currents. The neutrons precess between the two solenoids in the horizontal scattering plane, where the magnetic field is horizontal and all scattering angles, typically from \(-150^\circ\) to \(150^\circ\), are accessible at the same time. This arrangement of coils has a real cylinder symmetry, which makes the precession field far more homogeneous than that of IN11C.

NSE spectrometers use velocity selectors for selecting the incoming wavelength. Such a selector should also be an option for the new instrument. As a further development, however, we propose to equip the instrument with a flexible chopper system and select the neutron wavelength by the time-of-flight (TOF) technique. The recent developments at IN15 [5] showed that it is technically possible to combine NSE and TOF and that this combination brings a higher flexibility in choosing the \( Q \) resolution and an increased NSE dynamic range. The TOF option should considerably increase the potential and flexibility of the instrument. In the NSE mode it would allow for matching the \( \lambda \) band and monochromatisation to the requirements of each experiment and, without NSE, it would enable inelastic TOF experiments combined with polarisation analysis, similarly to SPAN. The design of the TOF set-up (number and configuration of the choppers) should be fixed after detailed calculations.

Large intensity gains are expected from the installation of a new neutron guide system. The improved neutron optics of the spectrometer would also allow for extending the minimum useable wavelength down to \( \lambda = 2.5 \) Å, which is about at the cross-over between cold and thermal spectra. At this wavelength the \( Q \) range will extend up to \( Q = 4.5 \) Å⁻¹, where localized motions should occur.

The new guide of the spectrometer should be a ballistic one [6]. Details, like the geometry of the cold source, guide noses etc. have still to be worked out. The intensity gain with respect to the existing IN11 guide (3 cm × 3 cm cross section, Ni coating) should come from the much larger cross section and the larger transmitted divergence, which would give a substantial gain at short wavelengths. The guide entrance window, next to the cold source, could have a height of 20 cm and a width of 6 cm. The first part of the guide would be a diverging section that expands the width of the beam up to 12 cm, by using m=2 supermirrors.
at the sides and m=3 supermirrors at the top and bottom. The part with constant cross section would use m=3 supermirrors at the top and bottom and m=1.5 supermirrors at the sides. In the NSE mode the guide cannot extend into the precession field area and it should end at a distance of about 3.5 m from the sample. If in the NSE mode for resolution reasons the guide exit has to be reduced down to 10 cm × 10 cm to match the size of the detectors, the expected intensity gain over IN11C would be roughly a factor of 9, with a small decrease at the very shortest wavelength, as shown in figure 1. For polarisation analysis measurements and other configurations, where the NSE resolution would not be important, the whole beam should be used, with a height 20 cm, a vertical divergence of 3 times Ni and a width of 12 cm combined with a horizontal divergence of 1.5 times Ni. In these configurations a converging section (“collector”) could be introduced to focus the beam to the sample, which would lead to further intensity gains, mainly at long wavelengths. The considerable intensity gains should allow for studying relaxation phenomena at Q = 0.5 Å⁻¹, i.e. in the interatomic correlations range, where the scattered intensity is weak and the experiments are difficult.

We consider building 4 detector banks, with an opening angle of 30° per bank. This should further increase the intensity gain over IN11C by a factor of 4. The comparison applies to the velocity selector version of the new spectrometer, but should also be valid for the TOF version under the condition that the TOF monochromatisation matches that of the velocity selector.

Experiments at IN11 call for Fourier times of up to t = 20 ns at Q=1.5 Å⁻¹. At a scattering angle of 150° the wavelength should be 8.1 Å and the field integral should reach 2 10⁵ G cm. At SPAN the field integral reaches 6 10⁴ G cm and an increase by a factor 2-3 seems technically possible. The gain with respect to IN11C, where a reasonable echo resolution cannot be obtained above 2 10⁴ G cm, would be of a factor 6–9. The sample–detector distance of the new spectrometer will be 3.5–4 m, giving an outer diameter of the experimental zone of 8-9 m and a surface area of about 80 m². The final dimensions should be fixed after detailed magnetic field calculations.

With the new NSE spectrometer the gain in performance, compared to the existing IN11C, would be considerable: (a) in the total detector counting rate, which should increased by a factor of 30 – 35 depending on the wavelength, (b) in a 6 – 9 times better energy resolution due to a more homogeneous precession field, (c) in an extended Q range of up to Q = 4.5 Å⁻¹ and (d) in a variable Q resolution. The scientific interest for such an instrument at the ILL would be significant and this should justify the costs.

**Fig. 1:** Result of a Monte Carlo simulation showing the neutron gain factor at the sample, as it is expected by using a neutron guide with a cross section of 10 cm × 10 cm and coating as specified in the text, instead of the 3 cm × 3 cm of the IN11 guide. The calculation assumed quite substantial intensity losses in the long supermirror guide. The divergence is m=3 vertically and m=1.5 horizontally. The distance between the guide exit and the sample is 3.5 m. The minimum wavelength of the new instrument should reach λ_{min} = 2.5 Å, compared to λ_{min} = 4 Å for IN11

**References**

The specific features of neutron reflection and transmission through layered magnetic nanostructures are discussed. The possibility of using layered magnetic nanostructures as elements or combinations of the elements of the spin-echo spectrometer is demonstrated.

1. Introduction

The spin-echo spectrometer making use of neutron spin precession in the magnetic field (NSE) was suggested by Mezei to measure energy transfer to/from the neutron \[1\]. The basis for this method is the measurement of the change in the phase shift between the waves of two spin states of the neutron in the magnetic field, \( \delta \Delta \phi \), that arises due to change in the neutron energy at scattering. In the NSE spectrometer the phase shift depends on the product of the magnetic field strength \( H \) by the size of the magnetic field region \( L \) where spin precession occurs (further referred to as a phase shifting region of the spin-echo spectrometer). In \[2\] there is proposed a resonance spin-echo spectrometer (NRSE) in which the wave vector difference of two spin states arises in the inside region of the resonance coil where a permanent and an oscillating magnetic field act together. The wave vector shift induces the phase shift in the region between the resonance coils (the phase shifting region). Pynn \[3\] related \( \Delta \phi \) to the scattering angle and showed that the spin-echo technique can be used to measure elastic neutron scattering. Rekveldt \[4\] extended the use of phase precession to measurements of the scattering angle at diffraction, small angle scattering, and in reflectometric experiments. In \[5\], a three-layer structure whose margin layers are one-dimensional lattices of sublayers and whose middle layer is homogeneous and provides the phase shift of the neutron wave is suggested. This paper discusses some new applications of layered structures as different components of the spin-echo spectrometer.

2. Physical substantiation and realization

The elements of the spin-echo spectrometer that change the neutron beam polarization in some or other way are a polarizer, \( \pi/2 \) and \( \pi \) rotators of polarization (PR), wave phase shifter (WPS), and a polarization analyzer \[1\]. The element responsible for the sensitivity of the spectrometer is the WPS. Let us investigate a WPS-1 operating in the reflection mode. From Eq. (1) we obtain that the derivative of \( \Delta \phi \) with respect to \( E_r \) is

\[
\frac{\delta \Delta \phi}{\delta E_r} = \frac{\delta \phi^+}{\delta E_r} - \frac{\delta \phi^-}{\delta E_r} = \left( \frac{l_+}{k_+^2} - \frac{l_-}{k_-^2} \right) \times \frac{\alpha^2}{2}
\]

From Eq. (2) it is seen that since \( k_+^2 \) and \( k_-^2 \) decrease with decreasing \( E_r \), the \( \delta \Delta \phi / \delta E_r \) increases. Decreasing \( E_r \) we come to the region of total reflection \( (E_r = U_{\pm} \mu B) \). Let us consider WPS-1 that is a three-layer structure with the first magnetic layer, second nonmagnetic layer with a low potential, and the third nonmagnetic layer but with a large potential of interaction. Further we suppose that external magnetic field strength is directed along the magnetization of the first layer. We are mainly interested in the region of \( E_r \) variation, that is limited by the energy of the potential interaction of the neutron with a minus spin state in the magnetic layer \( U^- \) on one side and by the energy of

\[
\Delta \phi = \phi^+ - \phi^- = \kappa^+ l_+ - \kappa^- l_-
\]

Fig. 1: The dependence of the phase shift \( \Delta \phi \) on \( E_r \) for the structure Fe(20nm)/Bi(200nm)/Cu(3000nm)/Si(substrate).
the potential nuclear interaction \(U_j\) in the third layer on the other side (\(U_- < E < U_+\)), in which the reflection coefficients \(R^-\) and \(R^+\) are close to unity. In place of Eq. (2) the new realationship can be then written

\[
\delta \Delta \phi / \delta E = l_z [N^- \delta k_z / \delta E - N^+ \delta k_z / \delta E]
\]

(3)

where \(N^+ = (1+|r|^2)\) is the average number of neutron transmissions through layer 2, \(r\) is reflection amplitude from first layer, \(l_z\) is thickness of layer 2 along the axis \(Z\).

Figure 1 illustrates the results of the calculation of the dependence \(\Delta \phi, (E)\) for the structure \(Fe(20nm)/Bi(200nm)/Cu(3000nm)/Si(substrate)\). In the discussed case, \(\phi^+\) is the phase of the reflection amplitude \(r^+ = |r|^2 \times \exp(i \phi^+)\). It is seen that \(\Delta \phi^+\) is a periodic function. At the same time, the negative derivative sections mainly correspond to changes in the phase \(\phi^+\) while the positive derivative sections mainly correspond to changes in the phase \(\phi^-\). The positive derivative is larger in absolute value than the negative derivative. This is due to the effect of resonance enhancement of the phase derivative that takes place when the resonance condition holds

\[2 \phi^+ + \Delta \phi^+ = n \pi, \text{ where } n = 0, 1, 2, \ldots\]

(4)

where \(\phi_{1-3}\) are the phases of the reflection amplitudes of the neutron in the middle layer from the third and the first layers, respectively.

For the investigated structure the negative derivative of the reflection amplitude \(\delta \phi / \delta E\) over the interval \(E = 127 \pm 158\) neV is equal in absolute value to \(\delta \phi / \delta E = 0.17\) rad/neV while the positive derivative over the interval \(159 \pm 161\) neV equals \(\delta \phi / \delta E = 1.5\) rad/neV, i.e. is 9 times larger.

Next, let us investigate a WPS-2 operating in the transmission mode. It also has three layers the first and the third of which have a finite thickness \(d\) and are magnetic. Again we suppose that external magnetic field strength is directed along the magnetization direction.

The optical potential of the middle layer \(U_2\) is taken to be smaller than the minus spin state potential of the magnetic layers: \(U_- < U_0 < U_+\). Let us investigate neutrons with the energy \(E\) satisfying the condition \(U_- - E < E < U_0 + U_+\).

Figure 2 depicts the results of the calculation of the structure \(Fe(20nm)/Bi(200nm)/Fe(20nm)/Fe(20nm)/Si\) in the magnetic field 100 Oe. It is seen that the transmission coefficient of the plus spin state \(t^+\) has a resonance behavior reaching unity at \(E = 100, 130, 165\) neV. The transmission coefficient \(t^-\) of the minus spin state is somewhat smaller than the transmission coefficient of the plus spin state due to reflection. Nevertheless, changing the parameters of the structure it is easy to realize the necessary condition \(t^- > t^+\). For example, the phase shift derivative at \(E = 100\) neV equals 6.5 rad/neV, which is close to the value of the phase shift derivative in WPS-1 by the order of magnitude.

Let us study the possibility of realization of the \(\pi/2\) polarization rotator (PR). It is clear that in the neutron transmission geometry a magnetic layer with magnetization lying in its plane and directed perpendicular to the external magnetic field strength can be used as a \(\pi/2\) or \(\pi\) PR. Of interest is the fact that in the reflection geometry, a magnetic layer can be a \(\pi/2\) and even \(\pi\) PR. Figure 3 illustrates the wavelength dependence of \(R^-\) and \(R^+\) for a 150 nm iron layer on a silicon substrate at a neutron beam glancing angle of 3 mrad. To realize a \(\pi/2\) PR in the reflection geometry, the condition \(R^- = R^+\) must be met. It is seen that this condition is satisfied for a set of wavelengths and at \(\lambda = 3.17\) Å the corresponding reflection coefficients are maximum and are equal to 0.5. In the case of cobalt that has a smaller nuclear potential than iron it is possible to realize a \(\pi\) PR. Figure 4 presents the wavelength dependence of \(R^-\) and of the reflected beam polarization \(P = (R^-/R^+)\) for a 150 nm cobalt layer on a silicon substrate.
substrate and a glancing angle of 1 mrad. It is seen that the curves both have an oscillating behavior and the polarization may become negative reaching, for example, a minimum of −0.998 at $\lambda=3.79$ Å. Actually, a layered structure itself can be a spin-echo spectrometer (if not to mention the polarizer and the polarization analyzer that are always necessary). Let us investigate the structure $\text{Fe(100nm)/Bi(X)/Fe(200nm)/Bi(20000nm)/Fe(100nm)/Si}$ comprising three magnetic Fe layers and two nonmagnetic Bi layers. Let the magnetization of the iron layers equal to the saturation magnetization $21.6 \text{ k Oe}$ lie in the plane and be directed perpendicular to an external magnetic field equal to say $1 \text{ k Oe}$. Figure 5 shows the dependence of the transmission $T^+$ and $T^-$ on the thickness $X$ of the bismuth layer for the neutrons with the wavelength $1.53 \text{ Å}$ and the glancing angle $10$ mrad. It is seen that the dependence is periodic and its period is $\Delta X=8500 \text{ nm}$. Change in the thickness $X$ is equivalent to change in the precession phase $\Delta \varphi_p=\gamma H \Delta X/(\sin(\theta))$ in the layer. It is easy to calculate that as it must be expected, $\Delta \varphi_p=2\pi$.

**References**

Analytical approach to dynamic neutron polarisation*

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Although the concept of so-called ‘dynamical’ neutron polarisation has been proposed more than 20 years ago, which promised to build a loss-free polariser for pulsed polychromatic neutron beams, until now no efforts were undertaken to work out its details. We have performed both analytical and numerical simulations to proof the feasibility of this method and to determine the achievable degree of polarisation under realistic conditions.

1. Introduction

About two decades ago the radically new concept of ‘dynamical’ neutron polarisation was proposed [1] which should allow to polarise a beam of slow neutrons without losing - at least in principle - even a single particle. It is based upon the spin-dependent energy splitting of monochromatic neutrons transmitted through a NMR-like arrangement of crossed static and oscillating magnetic fields, which causes different interaction times of the two opposite spin states with a subsequent static precession field. If this Larmor precession is stopped at a position where these two states are oriented parallel to a given direction, all neutrons are in the same spin state. Recently it was demonstrated experimentally that for ultra-cold neutrons even the inevitable interaction time difference with the resonance field is sufficient to cause such a polarisation effect [2], a phenomenon predicted already by [3]. For pulsed beams the method should be applicable even to polychromatic neutrons if one exploits the spatial dispersion of the particles in combination with suitably chosen variation of either the splitting or the precession field with time. Here we present the first results of analytic calculations of the required space and time dependence of the fields involved, which go far beyond the simple iterative approach described in Ref. [1].

2. Idealised model of ‘dynamical’ polarisation

Generating a pulse of polychromatic neutrons at time $t=0$ at position $x=0$ we let them pass a neutron guide of length $L$ before they enter a spin-dependent NMR-like velocity splitting system of length $a$. This system imposes a spin-dependent change of velocity $\pm \Delta \upsilon(t) < \upsilon$ to each particle [1]. As a consequence, spin ‘$\uparrow$’ and spin ‘$\downarrow$’ neutrons leave the device not at the time $t = (L+a)/\upsilon$, as they would if the splitting device is turned off, but at different times $t_\uparrow$ and $t_\downarrow$, respectively. At $x = x_1 := L+a$ the neutrons encounter a 90°-spin rotator coil, which initiates Larmor precession in the homogeneous field of a magnet of length $l$ mounted at (see Fig. 1). Precession is stopped by another 90°-turner placed at $x = x_2 := L+a+l$ at the times $T_\uparrow$ and $T_\downarrow$, respectively. At this point, the key-idea to understand this kind of ‘dynamical’ polariser is, that due to the different velocities of the two spin states leaving the splitting system, ‘$\downarrow$’-neutrons spend slightly more time within the precession region than ‘$\uparrow$’-neutrons. If this excess time interval equals exactly half a precession period, after leaving the

(*) We thank the Austron society for financial support.

Fig. 1: Schematic sketch of a dynamical polarisation set up at a pulsed neutron source (not to scale).
second 90°-spin turner all neutrons are either in 'up' or 'down' spin state (depending on the chosen orientation of the field within the spin turner at the moment when the neutron enters). Thus the beam has been completely polarised without loosing even a single neutron, however, on the cost of a tiny energy difference between the two spin eigenstates.

How to modify the magnetic fields that this dynamic polarization condition is satisfied? With \( \omega(t',\mathbf{u}) = \gamma B(t',\mathbf{u}) \), where \( \gamma = 2\mu_0 h = -1.83 \times 10^7 \text{s}^{-1} \) is the gyromagnetic ratio of the neutron and \( \mu \) its magnetic moment, a mathematical formulation of the problem looks like

\[
\frac{d}{d\tau}(\omega(t',\mathbf{u})) = \varphi(\mathbf{u}) \quad \text{and} \quad \pi + \frac{d}{d\tau}(\omega(t',\mathbf{u})) = \varphi(\mathbf{u}) \quad \forall \mathbf{u}
\]  

(1),

where, under the reasonable assumption \( \Delta \mathbf{u} < \mathbf{u} \),

\[
t_{\omega} = \frac{x}{\mathbf{u}} \pm \Delta t_{\omega} \quad \Delta t_{\omega} = \frac{1}{\mathbf{u}^2} \int d\Delta \mathbf{u}(x,\mathbf{u})
\]  

(2)

\[
t_{\mathbf{u}} = \frac{x}{\mathbf{u}} \pm \Delta t_{\mathbf{u}} \quad \Delta t_{\mathbf{u}} = \Delta t_{\omega} \pm (x-x_1) \frac{\Delta \mathbf{u}(x,\mathbf{u})}{\mathbf{u}^2}
\]  

(3)

From Eq. (1) it follows that the final rotation-angle for the 'down' spin state at any moment of time has to be equal to the angular orientation of the flipping-axis of the second turner. Otherwise the magnetic moment wouldn't be turned back along the field direction. A similar condition must be met for the 'ups', with the only difference, that those are initially advanced by half a round. Since we want to polarise a polychromatic beam, these two conditions must be fulfilled for all velocities. Under the idealisations of (a) infinitely short pulse-length (\( \rightarrow \) perfect velocity-dispersion), (b) negligible beam divergence, (c) perfect radial field homogeneity, (d) negligible thickness of 90°-spin turners, we did an extensive analytical calculation based on a separation-ansatz \( \omega(t',\mathbf{u}) = \omega(t')b(x'(t')) \) for the magnetic fields, which yields up to \( O(\Delta \mathbf{u}/\mathbf{u})^3 \):

\[
\omega(t') = \frac{\omega_1}{l_{\omega}} + \frac{\omega_2}{l_{\omega}} \frac{\pi}{2} \left( \frac{k-2}{2} \frac{k+1}{2} \right) dx b(x') \frac{x^2}{x^2}
\]  

(4)

\[
\varphi(t') = \varphi(t') + \frac{\varphi_1}{l_{\omega}} + \frac{\varphi_2}{l_{\omega}} \frac{\pi}{2} \left( \frac{k-2}{2} \frac{k+1}{2} \right) dx b(x') \frac{x^2}{x^2}
\]  

(5)

where the splitting system must fulfil the relation

\[
g = \frac{x}{\mathbf{u}} \Delta \mathbf{u}(x,\mathbf{u}) \cdot dx \Delta \mathbf{u}(x,\mathbf{u}) = \frac{1}{l_{\omega}} \frac{\mathbf{u}}{\mathbf{u}^2}
\]  

(6)

\( \hat{x}, \hat{u} \) and \( \hat{t}_{\omega} \) indicate normalised variables with respect to \( L, \mathbf{u} \) and \( t_{\omega} = L/\hat{t}_{\omega} \), where \( \mathbf{u} \) is the most abound neutron velocity. Typically \( C_\omega \) is of the form

\[
C_\omega = \frac{F_{\text{max}}}{\mu B_{\text{split}}} \times f(\text{geometry},k)
\]  

(7)

We are free to choose the exponent \( k \) among all real numbers. Clever choices for \( k \) are:

- \( k = 1 \) → Continuous operation of the velocity splitting system.
- \( k = -1 \) → Fixed rotation axis of the second 90° turner.
- \( k = -2 \) → Time-independent precession field.

3. Stability of the solution under realistic conditions

If the assumptions (a)-(d) hold, a degree of polarisation of 1 can be achieved. In practice, however, they can be fulfilled only approximately. Therefore, for errors of type (a)-(c) a stability analysis was performed both analytically and numerically with excellent accordance. Error type (d) had to be treated purely numerically. As a typical result, Fig. 2 shows the achievable effective polarization degree as a function of the minimal neutron wave length (\( \approx \) maximal velocity) for two different source pulse durations \( \tau \) for a Maxwellian spectrum of a cold moderator \( (T = 25 \text{ K}) \). It is obvious that the method fails if \( \tau \) is of the order of the time difference caused by the resonance RF splitting system. Therefore, to cope with this problem, a maximal splitting field \( B_{\text{split}} = 40 \text{T} \) (produced in reality by 4 consecutive superconducting 10 T stages separated by low-field spinflippers !) and a large incident flight path \( L = 60 \text{ m} \) were assumed. Since it is technically not possible to cycle such a high splitting field rapidly enough, one is urged to choose case \( k = 1 \) from the above mentioned three possibilities (which are all equivalent with respect to the finally achievable degree of polarisation). Finite beam divergence turned out to be no problem, as long as the fields are radially homogeneous across the beam. However, homogeneity itself imposes quite a serious condition: \( \Delta B/B = 10^{-4} \) should be maintained in the precession system. Like in standard NMR experiments the required homogeneity of the much higher field of the splitting system depends on the chosen relative resonance width. Since in the case \( k = 1 \) the rotation axis of the second 90° turner is not constant but varies with time at typical frequencies in the

Fig. 2: Achievable degree of polarisation versus minimal neutron wavelength for a pulsed source with 25 K moderator temperature for two different lengths of the primary neutron pulses. The analytical results were obtained under the idealised assumption of infinitely thin spin turn devices, whereas the numerical values were obtained for a realistic thickness of 1 cm. Time dependence of the precession field and the orientation 90°-spin turner were chosen according to the parameter \( k=1 \) (see text).
kHz range, it is necessary to keep its thickness $d$ as low as possible in order to avoid disturbing transmission time effects. Our numerical simulations have shown that even a comfortable value $d = 1$ cm is sufficiently small to cause no significant deterioration of the achievable polarisation degree (see Fig. 2).

References
Collecting Images and Processing Images for Tomography – a Test Bed for Future Data Flow Control at ILL

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A new high flux and large area thermal neutron beam is ready to supply the future radiography/tomography station IRIS at the ILL-Grenoble. The flux of $2.9 \times 10^8$ neutrons cm$^{-2}$ s$^{-1}$ and the use of modern image sensors, scintillator technologies, fast data acquisition and online reconstruction will open new frontiers in real time radiography and rapid tomography. It will take advantage the new RISC velocity engine generation and the processor farm architecture already used at the ILL. Here we describe the future architecture of the IRIS electronics and computing. IRIS will be ready for first test experiments in summer 2001. Its design and performance will be presented in a different paper.

The emerging field of neutron radiography and tomography [1] competes with other techniques like X-ray tomography [2], NMR techniques [3] or positron based techniques [4]. Certain unique neutron properties, as their isotope-specific interaction with matter, open wide perspectives in non-destructive imaging. The ILL wants to complement existing neutron facilities by a radiography and tomography station with sub-ms time resolution, dedicated for fast processes in bulky samples like car engines or turbines.

1. The detector of IRIS and its impact on the processor architecture

The thermal neutron flux measured at the ILL H9 beam exit is $5 \times 10^7$ cm$^{-2}$ s$^{-1}$ and will be $2.9 \times 10^8$ cm$^{-2}$ s$^{-1}$ at the sample position of the radiography/tomography station IRIS (ILL Radiographic Imaging Station), 2.5 m downstream of the H9 exit window. This compares to $1 \times 10^7$ cm$^{-2}$ s$^{-1}$ at the SINQ tomography station [5] and to $1.6 \times 10^8$ cm$^{-2}$ s$^{-1}$ at ANTARES [6], the future station at the FRM-II. The high flux at IRIS opens new perspectives for fast neutron tomography and dynamic radiography. It also implies a fast data acquisition system coupled with a high speed reconstruction farm. With an L/D ratio (distance from source / diameter of source) of about 100, IRIS will be suited for applications with medium spatial resolution.

The best candidates for detectors at the new ILL-radiography and tomography station are large area scintillators viewed by CCD cameras. For IRIS we use a 20cm $\times$ 20cm scintillator plate [7] of 1 mm thickness and 80% detection efficiency, being imaged on a CCD with 512$^2$ pixels. The readout time of the CCD is still a limiting factor for a rapid data taking.

The efficiency of light transmission from the scintillator to the camera is inverse-proportional to the square of the magnification m of the optics. The IRIS detector with $m=25$ collects about $10^4$ of the photons emitted from the scintillator plate. Thus the number of electrons on the CCD per detected neutron will be about 1 to 5. Taking the lower bound and accounting for a mean beam attenuation of 2 in the sample, we can expect $2.3 \times 10^5$ photons/s and per pixel on the CCD.

With a CCD depth of 12 bits, the array is saturated within 16 ms. This time should be compared to the readout time of 70 ms for the CCD in mind. Viewing the scintillator by of 4-10 cameras will bridge the dead time from individual cameras.

By combining a scintillator for thermal neutrons with one for fast neutrons, the pictures from both radiations can be recorded simultaneously by different cameras, if colour-selective optics are used. The loss in spatial resolution due to the large thickness of the fast neutron scintillator (25 mm) may partly be compensated by stereographic imaging, reconstructing each event in 3D. The information from both pictures can be used for better characterization of the sample materials.

The use of an image intensifier (with typical light-multiplication factor 10$^3$) allows rapid gating for time dependent processes. The technology of liquid crystal polymer light shutters developed by Philips Optics may also be applied for that purpose. Estimates show that changes in the macroscopic total cross section of about 0.04cm$^{-1}$ within one individual pixel of 1 mm$^2$ inside a sample can be detected within 1 ms. For tomography, the data acquisition system needs synchronization with the rotation table, and for dynamic radiography the process itself gates the light shutter. For periodic processes, a large enhancement of image contrast in reached in this way.

2. Electronics and Computing

Present ILL instrumentation is based on VME real time processing fitted with PCI Mezzanine Cards (PMC). Many CCD handling PMCs exist on the market as professional broadcasting makes a large use of VME systems. Another option is our present GPIO-PMC [8] device, used at the ILL for axis control, flipping logic and data acquisition, which fits for the readout of one CCD.
A 512² pixel CCD with 15 frames per seconds yields 4 Mpixels/s. The PCI bus, used on our VME processors has a bandwidth of 30 Mpixels/s (with a camera depth of 16 bits). The PowerPC 750 may peek, add and poke data in its 2 Mbytes memory in a parallel way. This operation is done in 1.3 ns. The pixel bandwidth of the accumulation of frames with 32 bits depth lies around 750 Mpixels/s.

For each processor may handle the data of seven cameras. This real-time architecture is already used on the D17b reflectometer for its large delay line detector.

As for the instrument software, IDL is an ideal candidate. It processes large amount of pictures and is used for tomography at SINQ and the Al-reactor. IDL is also the main data treatment platform at the ILL. Furthermore, IDL has been merged to MAD, the ILL instrument control program. Any hardware devices as motors, choppers and detector commands are available within IDL. MADIDL is a perfect candidate for instrument control and is used for example in automatic alignment procedures or handling 3D data. Present tomographic reconstruction is in the range of one hour. The use of VME real-time processors may decrease the reconstruction time. A pre-study of a reconstruction of the data from a 512² CCD camera has already been achieved at the ILL. The back projection requires 512² additions for 180 frames. The convolution with a Shepp-Logan or Ramlak wavelet has also been introduced. The required total number of floating point operations lies around 50 gigaflops. If we consider using only a fourth of the 5.3 gigaflops top performance of the PowerPC 750, an object could be reconstructed within 40 seconds. The next step is to distribute the process on several VME processors. Such a processor farm could lower the reconstruction to ca. 5 seconds.

For a multi CCD structure, the reconstruction farm would ease the processor farm could lower the reconstruction to ca. 5 seconds. Such a project is an ideal breeding ground for new instrumental techniques. Robotics, large and flexible arrays of detection, online reconstruction and virtual reality displays, could then migrate on other instruments.

4. Future aspects of detectors based on scintillator

Due to their gamma sensitivity, scintillating detectors are only sporadically used at the ILL. Scintillators with high n- and low γ-detection efficiency, high optical transparency and high light output/event have been produced at different places (e.g. ISIS), mainly in view of applications for pulsed neutron sources. γ-discrimination for scintillator based detectors is commonly done via pulse shape analysis of the signal from the PM, coupled to the scintillator. A similar procedure might be possible for image intensifiers, by analyzing the shape of the drop in the HV. Other scintillator techniques could be envisaged: the advent of scintillating fibers doped with neutron absorbers opens new perspectives for thermal and hot neutrons, as the production of scintillating face plates of mm- to cm-thickness with high detection efficiency and high spatial resolution seems possible in this way. Furthermore, in the near future, X-ray films in medical applications will be replaced by large area diode arrays with higher efficiency and comparable resolution, thus reducing the irradiation dose. Their use in neutron detection will also be studied.

5. Conclusion

Building a tomography station at the ILL is an exciting project. The state of the art electronics for detector and data acquisition today fits with the requirements of a first version of such an instrument. Such a project is an ideal breeding ground for new instrumental techniques. Robotics, large and flexible arrays of detection, online reconstruction and virtual reality displays, could then migrate on other instruments.
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D19: A fast new monochromatic diffractometer for chemistry, physics and the biosciences

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The proposed new large detector array to replace the banana detector currently used on instrument D19 at the Institut Laue Langevin will produce a gain of a factor of up to 25 in solid angle. This paper emphasises the huge gains that will follow from this development for both single crystal work and for fibre diffraction studies of biological and industrial polymers. Such gains offer exciting new opportunities in chemistry, physics and biology as well as the obvious gains in terms of data quality, experiment throughput and cost effective use of valuable neutron beam time.

1. Background

The existing D19 detector is a thin “banana” shaped device that has an angular aperture of $4^\circ \times 64^\circ$. Despite being located on a thermal beam at one of the best neutron sources in the world, the diffracted neutrons are sadly under-exploited. The reason for this is the limited size of the detector. A simple example from a typical fibre diffraction experiment demonstrates this point and is shown in Figure 1. At any given instant in time during such an experiment, fewer than 5% of the diffracted neutrons are detected. The case for the major upgrade planned on the D19 diffractometer has been given in detail by Forsyth & Mason [1]. The installation of a new detector system will result in a gain of a factor of ~25 in effective detecting solid angle. This will be a very significant step forward and one that will open up entirely new project areas in single crystal and fibre diffraction. In addition to new problems that cannot be tackled using the current system, the new instrument will become much more competitive in existing areas for which there is strong demand to carry out projects of high scientific interest.

2. Crystallography

Approximately half of D19's time is used for studies of single crystals: D19 is the instrument of choice (worldwide) to obtain accurate neutron data when the unit cell is large and/or when the samples are small. Usually the aim of these experiments is to find accurate positional and anisotropic displacement parameters for atoms not found with adequate precision by X-rays. Proposals that are consistently rated highly by the peer-review sub-committees of the ILL Scientific Council demonstrate that there is a strong demand from users with large inorganic or organic systems and relatively small crystals. Such experiments push D19 in its current configuration to the limit and the limited size of the detector occasionally leads to disappointing results (eg structural refinements with only isotropic displacement parameters\(^{(1)}\)). The new detector will result in the creation of a fast monochromatic instrument for high-resolution neutron crystallography and neutron fibre diffraction. It will be possible to study very much smaller samples, samples with much larger unit cells, and to carry out multiple pressure or multiple temperature experiments. As a high resolution monochromatic instrument, well matched for relatively large unit cells, the new D19 will complement admirably the scope of existing ILL instrumentation for small and large molecule crystallography. In crystallography, major new scientific opportunities are anticipated in structural studies of weak inter-

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\((1)\) A recent experiment at 20K on D19 by Wolfram Saenger and Olaf Nizm on a new cyclodextrin (called “CA10” with 10 glucose residues in a large ring to form a boat-shaped molecule, and complexing many water molecules), using a very small undeuterated crystal of only 0.14 mm³, unit cell 4874 Å, is a good example of what is and is not possible on the present D19. All water molecules could be refined, and the disorder of one of the important hydroxyl positions could be seen. But with only 2558 unique reflections measured in 20 days of beam time, only about 620 parameters could be refined. Other such difficult experiments are either not proposed, or fail. With better detectors, a full anisotropic refinement would be possible in much less time, leading to more reliable chemical conclusions. Note that the basic structure had been determined from synchrotron X-rays, but that the users judged, correctly in this case, that neutron diffraction would give key new information.
molecular interactions, fundamental studies of bonding, analytical investigations of organometallic complexes and catalysis, and protein crystallography (Fig. 2).

3. Fibre Diffraction

D19 is currently the only instrument in the world that is capable of carrying out high-angle neutron fibre diffraction measurements, and its work in this area has been very favourably reviewed (see for example a recent review by Stubbs [3] which specifically tags publications arising from D19 work as of special interest and outstanding interest; see also review by Niimura [4]). Such studies have provided important information on the location of water molecules or of hydrogen atoms in biological polymers such as DNA [5,6] (water is a key determinant of DNA structure), cellulose [7,8] (hydrogen bonding plays a vital role in determining its unique physical properties – see figure 3), hyaluronic acid [9], and filamentous viruses[10]. More recently work has started in collaboration with industry on the use of neutron fibre diffraction in the investigation of the physical properties of industrial polymers such as the poly aryl ether ketone compounds (eg PEEK, PEKK and related high-performance thermoplastics), analogues of Nylon 66, and Kevlar®[11]. The expanding interest in structural studies of biological and industrial polymers (as evidenced by current trends in X-ray diffraction work) and the key aspects of hydration and hydrogen bonding (totally inaccessible to X-ray fibre diffraction but nonetheless having a vital bearing on biological function or physical properties), are opening up important new opportunities for neutron fibre diffraction. The new D19 instrument will mean that for the first time detailed measurements will be possible of continuous diffraction(2) from polymer molecules. Such diffraction predominates in diffraction studies of many filamentous viruses, drug-DNA and protein-DNA complexes. It is also a key aspect of changes in ordering that occur during structural transitions. The new instrument will also mean that it will be possible to use D19 to study samples that have hitherto been far too small to study using neutrons.

4. The New Instrument – technical details

The design of the new detector bank, (shown in figure 4) is modular so that in the event of the failure of one detector module, replacement will be straightforward without disruption to the user programme. Having made a careful assessment of the requirements for D19 experiments and having carried out a number of detailed tests [12], gas detectors were chosen because many D19 applications require rapid step-scans that are only possible with fast electronic readout. Gas detectors also have low background and stable devices with high gas pressures can be made. The technical aspects have been covered in detailed studies at the ILL of an 8 detector version of this design [1]. The present D19 detector (4° x 64°) will be replaced by an array of twelve identical 2-dimensional PSDs. Each module will have a detection area of 192 x 192 mm, a resolution of 3mm, and a detection efficiency of 60%. The twelve detectors will be mounted on a curved surface with the option of 60cm or 90cm radii of curvature. The option of the larger maximum radius is included to enhance the ratio of signal to incoherent background for samples containing a large

(2) This type of diffraction occurs where molecules that are lined up in a parallel array (as in a fibre) have an essentially random axial relationship to one another and do not form a completely crystalline system. The consequence is that in all reciprocal lattice zones apart from the one that corresponds to the “birds eye view” along the axes of the filaments, the intensity that would normally be concentrated into strong crystalline reflections is spread out along layer lines in reciprocal space, giving continuous diffraction that on a point for point basis is much weaker by perhaps an order of magnitude. The data are however very well defined and offer a wealth of information that is not limited to localised regions of reciprocal space at reciprocal lattice points.
percentage of hydrogen atoms. When the incoherent background is small enough, the distance from the sample can be reduced to 60cm, in order to increase the number of reflections striking the detectors. The projected gain in measuring efficiency over the present D19 is a factor of up to 25. At the 60cm position, just one new square detector will be twice as efficient as the present very narrow detector because edge effects will be small.

5. Conclusion
The D19 upgrade described here will have an enormous impact on neutron crystallography and neutron fibre diffraction studies available to users of the ILL. New applications of the instrument will extend throughout disciplines in chemistry, physics, the life sciences and materials science, with huge improvements in data collection efficiency and data quality in each of these areas. These predictions have been clearly justified in recent tests during which a prototype module of the type planned for the new array has been tested on single crystal and fibrous samples.

References
Panel discussions
Panel Discussion on Science at the ILL

Panel Members:
Paul Attfield, Cambridge • Juan Colmenero, San Sebastian • Thomas Brückel, Jülich • Norman Ramsey, Harvard • Christian Vettier, ILL • Christophe Kratky, Graz • Peter Timmins, ILL • Sasha Belushkin, Dubna • Yasuo Endoh, Sendai • Jacques Martino, Saclay

The Panel Discussion was organised around scientific topics each of which were briefly presented by a specialist and then opened for discussion by the panel and the audience. The discussion was chaired by C. Vettier, Associate Director of ILL and Head of Science Division, who introduced the speakers and opened the debate.

Introducing the debate with the question “Where should we put the emphasis for the use of neutrons in scientific research at the ILL?”, he appealed to users in the audience to give their point of view and so contribute to identifying the directions ILL should take.

N. Ramsey, nuclear physics
For this field, about 80% of the experiments are not intensity limited, but for 20% of them intensity of the neutron beam is a limiting factor which is why the experiments are done at ILL. ILL provides the most intense neutron beams and we do the rest. This is especially true for ultra-cold neutrons where we need an improved cold source and are developing a better storage bottle with total reflection from the walls, but also with superfluid liquid helium in there at the same time which offers many advantages. We are looking for factors of 100 increase in intensity with this set-up which would be quite significant.

Th. Brückel, Chairman of the Scientific Council, solid state magnetism
In his role as Chairman of the Scientific Council, Th. Brückel pointed out that neutrons serve a wide range of disciplines from biology to nuclear physics and are now routinely used in magnetism, chemistry, and soft condensed matter studies. This is why the Scientific Council has supported the upgrade of the workhorse instruments for these fields which are the high count-rate instruments in powder diffraction and small-angle neutron scattering. There are however fields where neutrons are not used to their full potential and one of these is life sciences, so the scientific council strongly supports the decision of the ILL management to establish an in-house research group on biology to increase the visibility of the ILL to the life-sciences community.

In his own field, magnetism, T. Brückel mentioned the high-level of activity, and a major challenge being that of strongly correlated electronic systems where current theories were unable to predict whether the simple transition metal oxides were insulating or metallic, showing our lack of understanding here. Materials where electronic correlations play an important role include High Tc superconductors, GMR materials, heavy Fermions, and in all these materials polarisation analysis plays a very important role and should become a routine tool. This is possible at the ILL because of the high flux available and also because many of the developments, such as supermirrors, cryopad, He and Heusler crystals had been made here. T. Brückel strongly recommended that ILL invest heavily in this area because it has all the advantages to become a unique centre for polarised neutron research.

Y. Endoh, working in similar fields, fully supported developments in this field where neutrons were very important because of the interplay of charge, spin, electronic orbitals and lattices. Neutrons could not cover everything however, and to do the best science, neutrons should be combined with other modern techniques such as synchrotron radiation. C. Vettier asked if this meant that neutron techniques were not modern. Th. Brückel replied that the cryopad which had been developed here for 3-dimensional polarisation analysis was certainly a very modern technique. A. Furrer noted that High Tc superconductors were not homogenous and local probe techniques were needed to characterise them.

P. Attfield, neutron powder diffraction
P. Attfield gave a brief review of the diffractometers at ILL before concentrating on the powder diffraction instruments. D2B really will be a super instrument. D20 is now working very well amid feelings of relief and exhilaration. D1A is shared between strain and powder diffraction. The neutron powder technique is both simple and versatile, being adapted to practically all types of inorganic crystalline samples and sample environments. The most common data analysis technique, Rietveld profile analysis is now straightforward and fast. Neutron powder diffraction analysis is however perceived not to perform well for hydrogenous, molecular materials. In X-ray powder diffraction this technique is gaining ground for smaller molecules where structures are being solved quite routinely. For neutrons this is more difficult, but the problem should be addressed using whatever techniques can be applied, such as a second monochrometer to remove the inelastic part of the incoherent scattering. The challenge is therefore to look into whether neutron powder diffraction can be applied
with greater success to organic materials and whether ILL could take the lead in such developments. Asked whether this question was just about tools or whether there was some new physics to be done, P. Attfield replied that improvements in resolution or intensity inevitably lead to the observation of new physics, chemistry or biology. A good example was that of charge-ordered structural refinements in transition-metal oxides which were now being solved at ILL due to the performance of D2B. Improvements were being made continuously and resulted in new scientific areas being studied.

**Juan Colmenero, complex molecular systems**

J. Colmenero noted that the topic of soft condensed matter had been nicely presented by D. Richter. The main conclusion was the need for more intensity, e.g., for kinetic studies and time-resolved small-angle scattering. For soft condensed matter, disordered systems and glasses, which have a broad range of lengths and timescales, this implied a broad range of $Q$ and frequencies extending over many orders of magnitude, difficult to cover with neutrons. When compared with other techniques, neutrons covered the most important range, but it would be nice to be able to extend the resolution and the $Q$-range and also obtain more intensity. A. Rennie pointed out that flux was important, but instrument stability was sometimes more important as had been demonstrated with D4. He also pointed out that the ILL should be taking the lead in extending timescales down for real-time and stroboscopical experiments in cases where neutrons were needed. J. Suck said that more measurements were being made on derivatives in temperature, pressure, etc. so stability was becoming more important.

**Sasha Belushkin**

A. Belushkin asked whether ILL was doing all it could for the wider external science communities, the chemists, biologists, condensed matter physicists, etc. for whom neutron scattering was crucial, rather than for the more technique-minded neutron scattering community who might be more interested in technical aspects such as intensity or resolution. The real question was whether these external communities were happy that we were doing our best for them.

C. Kratky replied that he had only done one neutron scattering experiment, but had followed ILL for many years. He noted that neutrons have very nice properties and had been well appreciated for 25 years. Even so, taking the statistics from a biomedical database, one publication in 20,000 involved neutrons and one in 200,000 related to protein crystallography. Although ILL has 2-3 instruments dedicated to this area, problems that were suited to being solved with neutrons were in fact being solved using NMR, X-ray crystallography, or EXAFS. To create greater awareness of neutrons in this field, ILL needs to set up its own internal research programme rather than build new instruments. G. Zaccai was cited as setting a good example of how to increase the profile for neutrons in biology.

**Peter Timmins (replacing John Helliwell), structural biology**

P. Timmins reported on a project which was not explicitly in the Roadmap or the Millennium Programme. He described a partnership for structural biology being established between ILL, ESRF and EMBL. The project was to pool resources to construct a joint building for structural biology, including laboratories, shared equipment and a deuteration laboratory. Synergy for ILL would be generated through an in-house activity within a biological environment involving greater numbers of people working together in the same field.

C. Kratky strongly supported this idea, but noted that the neutron community would have to assert itself. It would help generate a lot of publications in NMR. P. Timmins replied that the project would be partly financed with the help of the NMR community through grants from various funding agencies.

R. Cywinski commented that this was similar to the FAME project to provide an environment for the engineering community for both neutron and synchrotron radiation. This was positive progress which showed that we were approaching a critical threshold of external users who use a range of techniques, including neutrons, to pursue their activity.

P. Timmins noted that there was a tendency to equate structural biology with protein crystallography. Although neutrons could not compete with X-rays in the field of protein crystallography, a whole range of neutron techniques were being used for other biological studies. These included crystallography, fibre diffraction, reflectometry, small-angle scattering and inelastic scattering, and progress had to be made in all these areas rather than trying to compete in the more limited area of protein crystallography.

**J. Martino, particle and nuclear physics**

J. Martino introduced the topic by mentioning a paper in the session on industrial use, that of the transmutation of nuclear waste which could become important for nuclear waste incineration. ILL could play an important role because it is one of few reactors with epithermal neutrons available.

The two main instruments at ILL for elementary particle physics were PF1 and PF2. For these, a factor of 3-4 increase in intensity could be very valuable. Recent progress for ultra-cold neutrons in the superfluid $^3$He bottle had been quite encouraging and will probably lead to breakthroughs.

For the gamma spectrometer, GAMS, developments with planar crystals had now reached their theoretical limit, so further development required the use of curved crystals which were now being implemented. This would give the increased the solid angle but more work was needed to reach the same energy resolution as with planar geometry.

J. Martino explained that with the fission product spectrometer Lohengrin, the ILL had a unique instrument for the study of radioactive exotic nuclei which are created at ILL by thermal-neutron induced fission. The fission products can be studied efficiently at ILL, especially those with a short lifetime of the order
of microseconds and play a major role in supernova explosions. To develop this field further, the new miniball instrument of the millenium program, with a large solid angle is very much needed to increase sensitivity. Rick Casten supported this view. GAMS and Lohengrin were totally unique, the best in the world by a large margin and were continuously upgraded. They had played a major role in nuclear structure studies for 25 years. C. Vettier stressed that the ILL wanted to maintain the diversity of its research and its management were fully aware of the importance of this field.

C. Vettier closed the meeting by saying that the symposium had been made possible firstly thanks to the Roadmap that Dirk Dubbers had written and secondly because of the commitment from ILL staff to make it a success. Finally, because ILL was good at making instruments for science, we had good ones now and would have even better ones in the future.

He thanked everyone who contributed to the symposium.

Albert Wright
Panel Discussion on the Organisation of the ILL

Panel Members:
Robert Comès, LURE, Paris • Robert Cywinski, Univ. of Leeds • Dirk Dubbers, ILL Grenoble • Marc Fontana, Univ. of Parma • Albert Furrer, PSI-SINQ and ETH, Zurich • Françoise Leclercq, CNRS, Lille • Michael Steiner, HMI, Berlin

The Panel Discussion was organised around a number of topics to which the panel and audience were invited to contribute. The topics covered the way the ILL is used by different groups, external relations with users and other institutions, and the quality and evaluation of research. The discussion was chaired by D. Dubbers, Director of ILL.

The Use of ILL

Equal versus privileged access
This session covered fast access, block allocation and director’s discretion time.

R. Cywinski pointed out that in neutron scattering there is a need for rapid sample characterisation and urgent investigations on newly discovered materials, especially using powder diffraction. D. Dubbers noted that ILL has recognised this need and for a trial period a fast access scheme has been introduced giving access every three months to certain SANS and diffraction instruments. D. Richter suggested that such tests could be made more appropriately at medium flux national sources via co-operation agreements. D. Dubbers replied that ILL would look into cooperating with medium flux sources for rapid characterisation.

On block allocation, M. Steiner called for long-term access for thesis students and for training young scientists who needed planned access within a long-term programme. The national sources do a good job in this area, but ILL could also help here. A. Furrer commented that SINQ has introduced a system for block allocation for a trial period and after two years, 2/3 of beamtime is allocated on a long-term basis (2 years) leaving 1/3 for short-term proposals. Both long-term and short-term proposals are evaluated according to their scientific merits on a competitive basis. This considerably reduces administration and allows evaluation to be made over a longer period. A. J. Leadbetter agreed that this could be a good system, but the difficulty was in achieving the right balance between long-term and short-term allocation. The latter should be higher than one third of the allocated beamtime.

Public versus private use
This session covered CRG instruments and their private use.

D. Dubbers explained that 25% of instruments at ILL were CRG instruments and that 17% of all ILL beamtime was used privately on these CRG instruments. R. Comès noted that the CRG system had developed from the previous special instrument policy, which in some ways had advantages. However, the CRG policy has lead to continuous improvements on CRG instruments through external funding. Also, CRGs are better than unused beamlines. The danger is that individual CRGs run by independent groups could be developed into more general instruments covering a range of different techniques so that they were no longer optimised for any specific purpose. Beamtime allocation between private and general use was question of balance which should not exceed about 20%.

D. Dubbers pointed out that CRG private use is projected to remain at a constant level in the Road Map and some test positions are still available to try out bright ideas. R. Cywinski reminded the panel that CRGs are fully discussed in the Scientific Council and the Instrument Subcommittee, whose aim is to optimise their performance and make sure that the CRGs are not sub-standard instruments. Furthermore, CRGs provide a means for additional participation by countries that are unable to increase their general contribution to the budget, thus bringing added value to the ILL. D. Richter fully agreed, adding that some CRGs are unique world-class instruments that provide real added value for ILL through the efforts of highly-motivated university groups.

Scientific versus industrial Use
This session covered confidential and peer reviewed use of ILL by commercial companies.

R. Cywinski emphasised the tremendous importance of this activity which demonstrates the technological value of neutron scattering to politicians and public funding organisations. A. Wright and the Industrial Liaison Group were to be commended on their achievements in attracting industry for confidential research. D. Dubbers presented figures for confidential industrial use over the last five years, showing strong growth in recent years. Latest figures for industrial use were: confidential commercial use, 0.5%; direct proposals with industrial participation, 3%; indirect proposals with hidden industrial interest, 10-30% depending on evaluation. More transparency was needed on industrial interest in peer review experiments because ILL could use this information to advantage. R. Comès noted that this was not easy to obtain since university groups preferred to keep information about industrial contracts confidential.

External versus in-house use
This topic covers the amount of time ILL scientists spend on own research compared to their service functions for external scientists and overlaps with their collaboration in the research of visiting groups. A. Furrer presented the results of an ENSA enquiry.
among users about what makes a neutron scattering centre attractive to them. The highest ratings were given for: the quality of instruments, sample environment and the scientific environment. The latter point was strongly dependent on the involvement of instrument scientists in developing their own fields of research. A high neutron flux and the reliability of the source were also important. D. Dubbers showed the high level of beamtime allocated for competitive research and the small amount (~1%) allocated to in-house use (proposals from ILL scientists only). M. Steiner argued that in-house use and own research were essential for motivating scientists to get optimum performance from the instruments. Some of this was organised through collaboration with external users. ILL scientists needed to build their own research profile so as to become known in specific scientific disciplines independently of instrumental and technical considerations. In addition, every research institute needed to be recognised for its own research. F. Leclercq pointed out that ILL needs stable scientists who have their own scientific life and who collaborate with users and scientists from other neutron sources. This means more permanent jobs at ILL. J. Suck noted that ILL scientists submitted fewer in-house proposals than in the past. It was pointed out from the audience that these were human resources issues that needed to be resolved to attract the best scientists by offering good opportunities at ILL which would be valuable for further career development in public or private research. R. Scherm agreed that ILL scientists needed to do more of their own research. He suggested that ILL introduce sabbatical leave or rotating Senior Scientists positions for two-year periods. This was widely applauded by the audience. In the past ILL scientists spent too much time on service duties, and this needed to be changed. B. Ferago questioned who would do the service work if ILL scientists did more of their own research. R. Scherm accepted the relevance of the question, adding that the only solution would be to appoint more scientists. There followed a general discussion about the role of PhD students. ILL scientists could do more own research with the help of PhD students. D. Dubbers noted that ILL has about 30 PhD students and would like to have more.

**Quality of research**

**Selection of proposals**

M. Fontana and M. Steiner noted that good proposal selection is vital for high-quality research which in turn is essential to ensure continued public funding. The user base also needed to be broadened into new fields. It was however difficult for inexperienced users to get beamtime. This could be addressed by collaborating and cooperating with medium-flux sources to enable new users to get experience. At ILL, selection on the basis of pure quality was justified given the ILL’s status as the world’s leading neutron scattering centre, but when coupled with pressure for beamtime, this meant that inexperienced users were likely to be rejected. To counter this, subcommittees should be extended to include non-neutron users.

R. Cywinski asked that rejection notices be more informative so that inexperienced proposers could learn from them. In the past, college secretaries passed on this information to get new users started, but this is less true now and needs to be reactivated.

D. Dubbers said that ILL would act on this. M. Steiner noted that unusual, but worthy proposals could easily be rejected by the current system. A. Rennie noted that some good proposals might have a high risk of failure, but this should not be a reason to exclude difficult but exciting experiments. It was pointed out by F. Leclercq that the system did not allow for repeat experiments to confirm experimental results. B. Dorner noted that competing teams were either given joint time to collaborate or separate allocations.

C. Kratky remarked that only half the experiments lead to publication. Did this mean that the others are repeats or do half of experiments fail? D. Dubbers replied that the publication rate was a good figure and probably should not be higher than it is now.

**Should the organisation of science be a democratic process?**

M. Steiner suggested that the question be posed differently. It was not about voting, but about organising and selecting research topics from the bottom up. K. Schreckenbach said that the democratic process should support minority scientific domains and exotic proposals outside the fashionable trends. Individuals may have bright ideas that we fail to integrate into the system, so they get dropped. D. Dubbers admitted that when a consensus among colleagues was required to adopt a new idea, then the idea could not be too revolutionary.

Because of the lively debate, D. Dubbers said that the organisation and science panel topics along with the discussion of the Roadmap would be put on the web to get more feedback.

D. Dubbers thanked the panel and the audience for a very lively and frank discussion and closed the session.

Due to the limited time, the following topics programmed for discussion could not be treated in depth:

- Evaluation of work performed
- How to avoid self reproduction
- External relations:
  - with ILL users,
  - with other neutron sources: co-operation versus competition,
  - with neighbouring institutions,
  - with learned societies.

*Albert Wright*
Introduction
The Industrial Liaison and Consulting Group of the ILL (ILCG) held a closed meeting for invited participants from industry and applied research laboratories to consider the feasibility and advantages of setting up a network of scientists and industrialists interested in using neutrons for applied research. The objectives, operating principles and provisional programme of ANNet (Applied Neutron Network) were established.

Participants
ILCG members:
A. Wright (ANNet Chairman), P. Lindner (ANNet Administrator), P. Convert, T. Pirling.

External members:

Background
A. Wright welcomed the participants and gave a brief presentation of how applied and industrial research had been integrated into the context of research activities at ILL. Each year more than 700 experiments selected by scientific review committees are carried out by about 1500 scientists. About 20% of these are non-commercial experiments related to applied or industrial research. Sales of beamtime for confidential use by industry represent less than 1% of instrument use, mostly for strain imaging and small-angle neutron scattering.

P. Lindner presented the historical development of applied and industrial research at ILL. The Industrial Liaison and Consulting Group (ILCG) at the ILL was set up in 1998 to facilitate and co-ordinate the access of applied and industrial research using neutrons at the ILL. It promotes the use of neutrons for applied and industrial research at ILL through communications, presentations and workshops and organises access for commercial industrial users. Since the typical industrial customer usually lacks the neutron expertise to carry out the experiment successfully, this is usually provided either by ILL scientists or more frequently by scientists from the neutron user community. The interaction of these three communities; Industry, Neutron users and ILL scientists forms the basis for the creation of the Applied Neutron Network.

Objectives of ANNet
The main objective of ANNet was defined in the following broad terms: To facilitate the development of applied and industrial neutron research at ILL.

The term applied and industrial neutron research includes both non-confidential, peer-reviewed experiments channelled through the Scientific Co-ordination Office of the ILL and commercial, confidential industrial experiments channelled through the ILCG. Three scientific communities will interact in ANNet:
1. Academic research scientists from universities, engineering schools and applied research laboratories, often with dual expertise in neutron techniques and specific scientific domains.
2. Industrial research scientists and engineers.
3. Neutron scientists from ILL.

To reach its objective, ANNet will address the following points:
1. Facilitating communications between the three communities defined above.
2. Informing industry and applied laboratories about neutron facilities available at the ILL and expertise available from the user community.
3. Creating a wider knowledge base for neutrons in industry and applied research laboratories.
4. Responding to the needs of industry and applied research laboratories within the framework of ILLs general mission (fundamental & applied research, non-military applications) and infrastructure.

ANNet membership
ANNet membership will comprise two levels, an advisory working party and ordinary members.

The ANNet working party is an advisory body and support group made up of scientists and engineers with strong links with industry and/or applied research laboratories and wide knowledge of the use of neutrons for applied research. Its role is to promote ANNet to industry and applied research laboratories and provide feedback to the ILCG on ANNet operations.

ANNet ordinary members are scientists and engineers from industry, applied research institutions, universities and neutron centres who believe in developing applied research using neutrons. Many of them have dual expertise in both neutron techniques and specific scientific domains. Confronting expert scientists with an extensive range of scientific and neutron skills with real industrial research programmes should provide a new dynamism for the development of applied and industrial research using neutrons.

Administration, communications and operations
ANNet will be financed and administered by the Industrial Liaison Officer through the ILCG. It will be operated by the ILCG, who will constitute and animate special interest groups involving all
three communities of scientists and engineers. Expert groups will be able to communicate their expertise and experience to industrial members. The latter will be able to identify and locate the expertise they require for specific problems or future research programmes. They will also have the opportunity to meet with or communicate selected programmes to interested expert groups via the ANNet hub with appropriate discretion. A web site will be set up to promote ANNet and act as a medium for discussion and communication. Through its members, ANNet will also organise a programme of events throughout the year to promote and communicate applied neutron research.

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