Neutron scattering investigations in extreme sample environments

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Extreme sample environments:

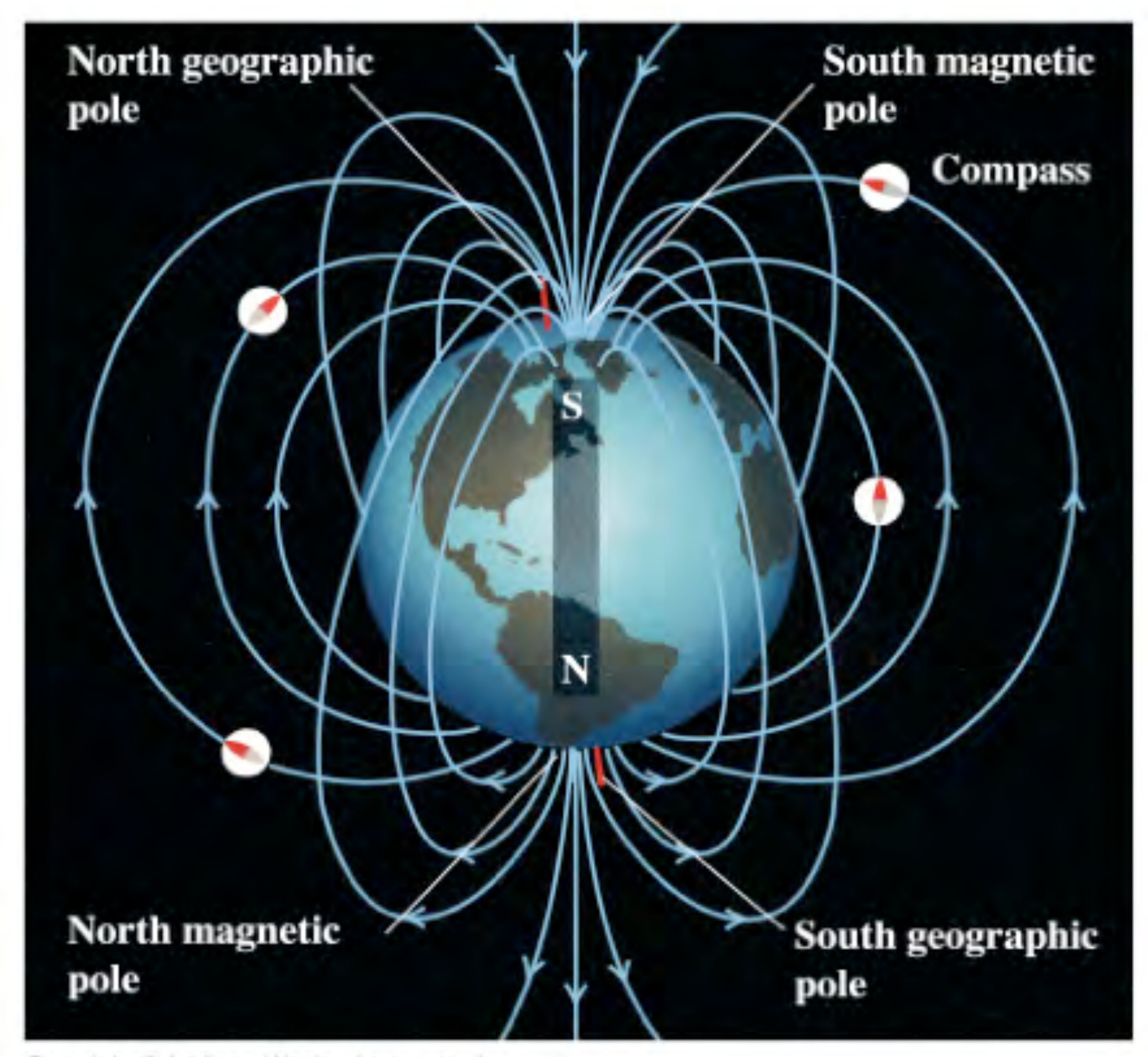
- *Low temperature*
- *High magnetic field*
- *High pressure*
- *Zero magnetic field*
- *Electric field*

Extreme conditions in our universe

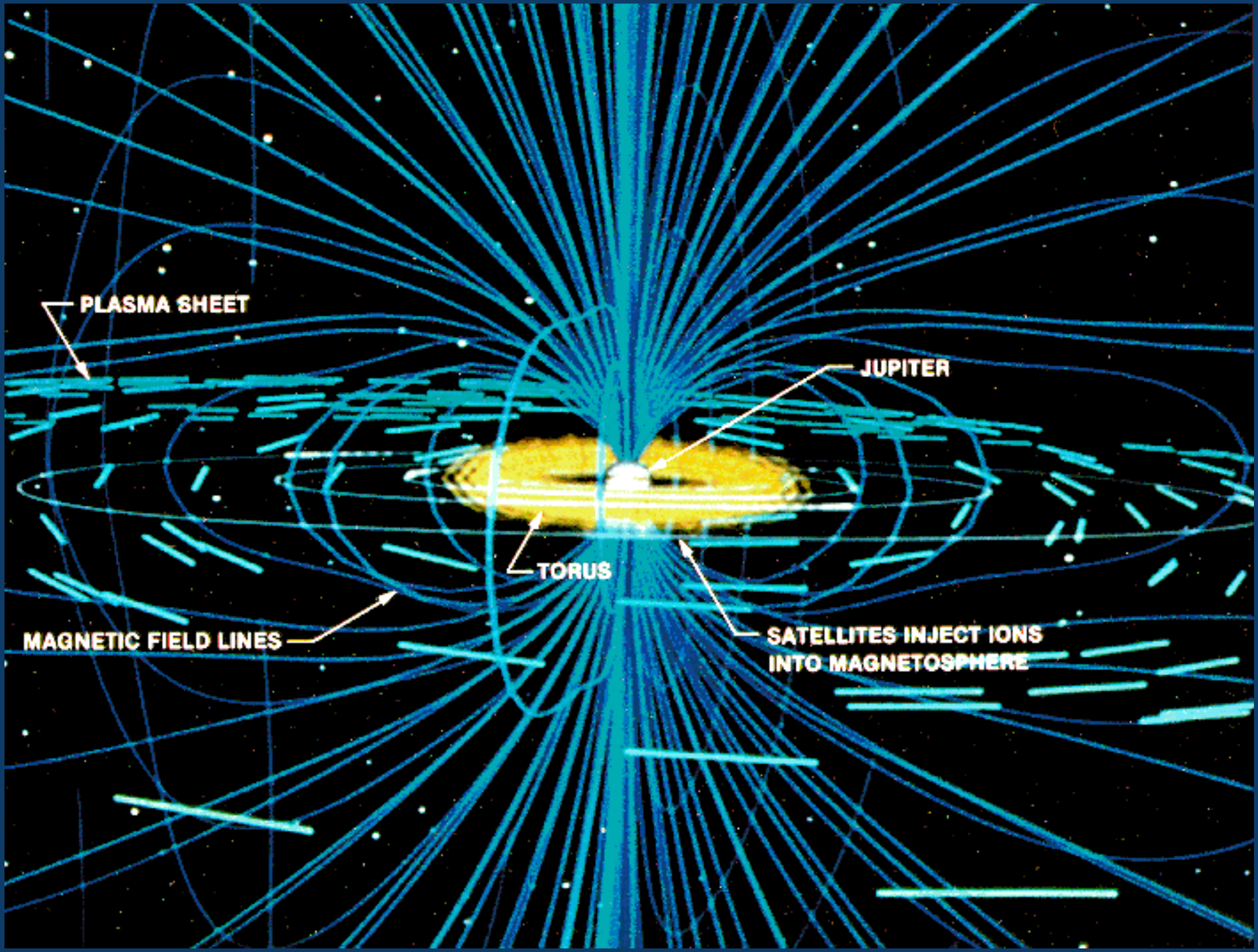
Pressure:	Centre of Earth	$P = 3.62$ Mbar
	Centre of Jupiter	$P = 100$ Mbar
	Centre of Sun	$P = 990$ Mbar
Magnetic field:	Surface of Earth	$H = 0.5$ G
	Surface of Jupiter	$H = 1$ T
	Surface of Sun	$H = 50\text{-}5000$ G
	Neutron Star	$H = 10^{10}$ T ?
Temperature:	Surface of Earth	$T = 288$ K
	Surface of Jupiter	$T = 160$ K
	Surface of Sun	$T = 5780$ K
	Core of Sun	$T = 16x10^{6}$ K
	Intergalactic space	$T = 2.73$ K

Coldest place in the universe is in the low temperature lab:
millikelvin? Easy! microkelvin, nanokelvin?

Earth's magnetic field



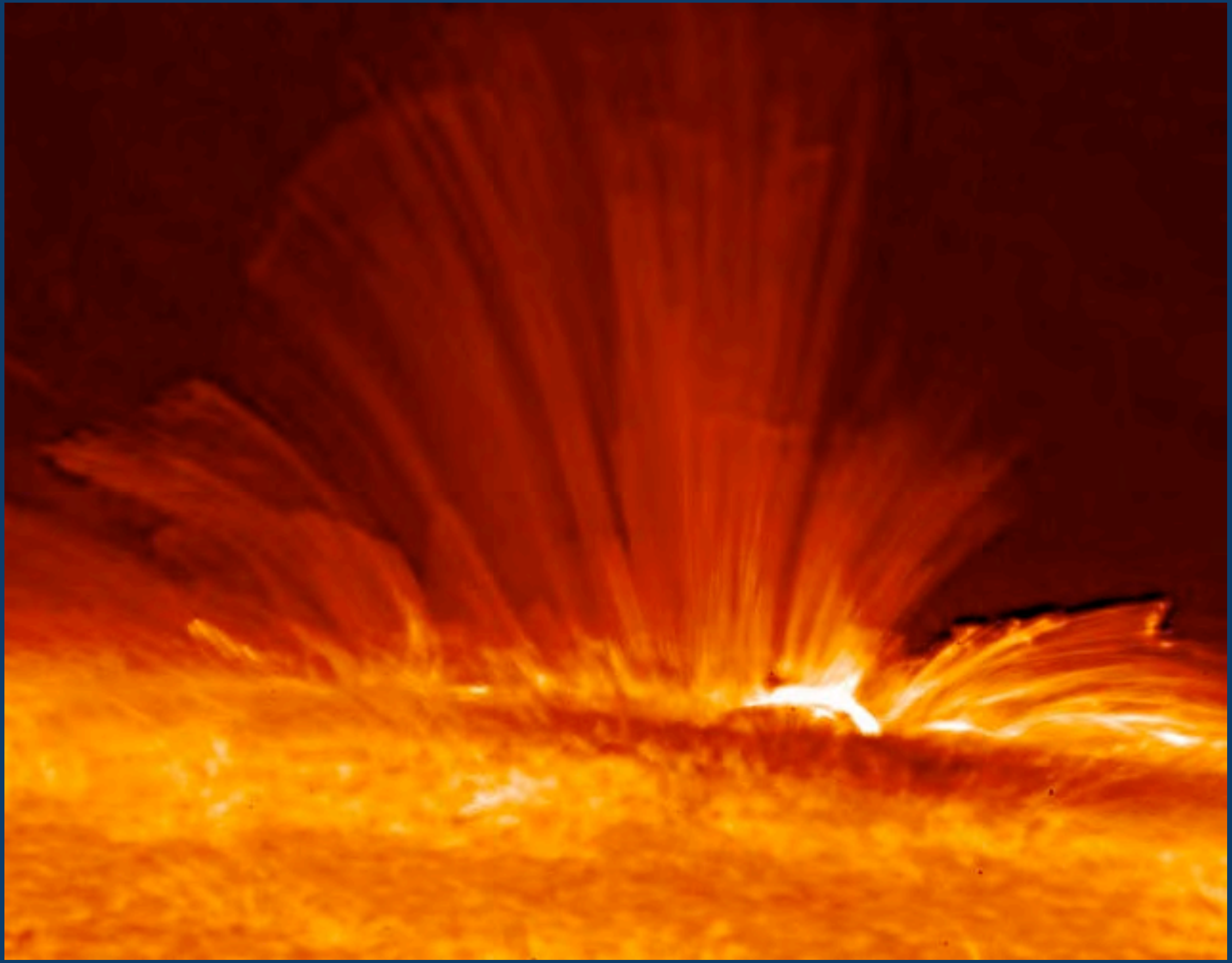
Magnetic field of Jupiter



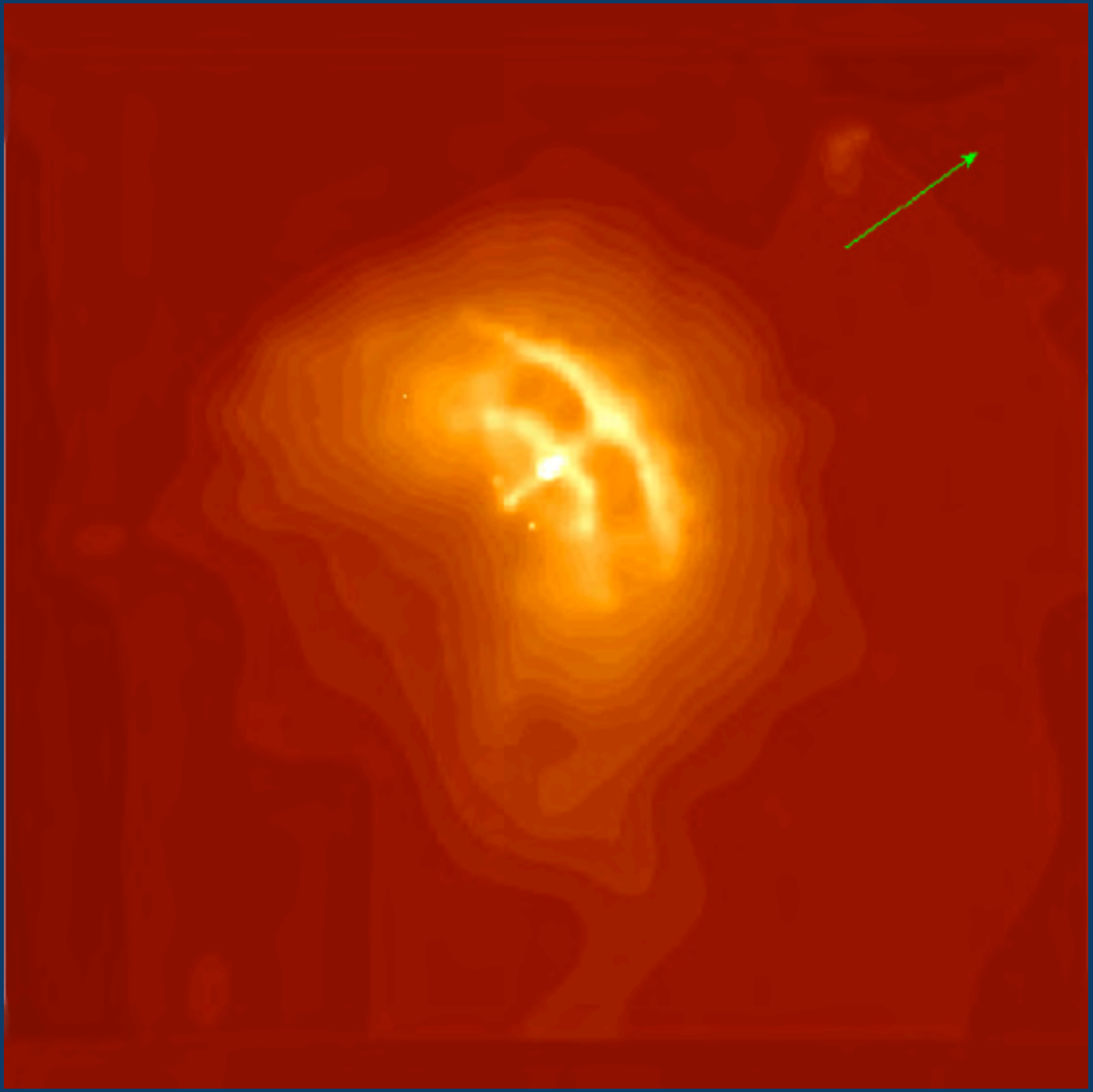
Solar cromosphere

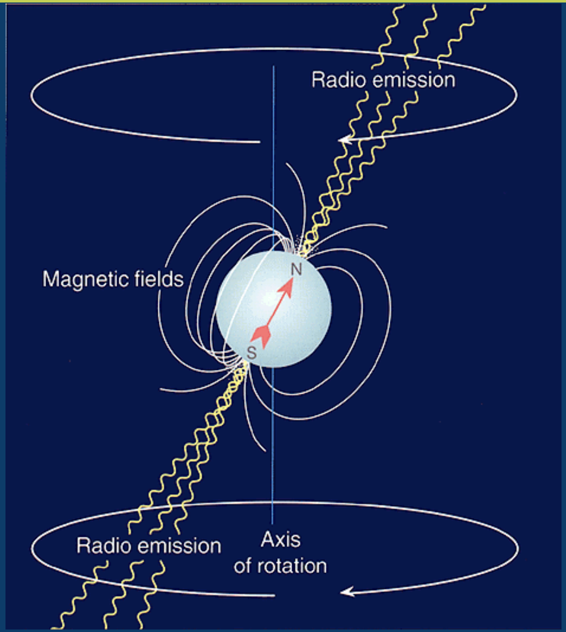
reveals the structure of the solar magnetic field rising vertically from a sunspot

HINODE



Vela Pulsar

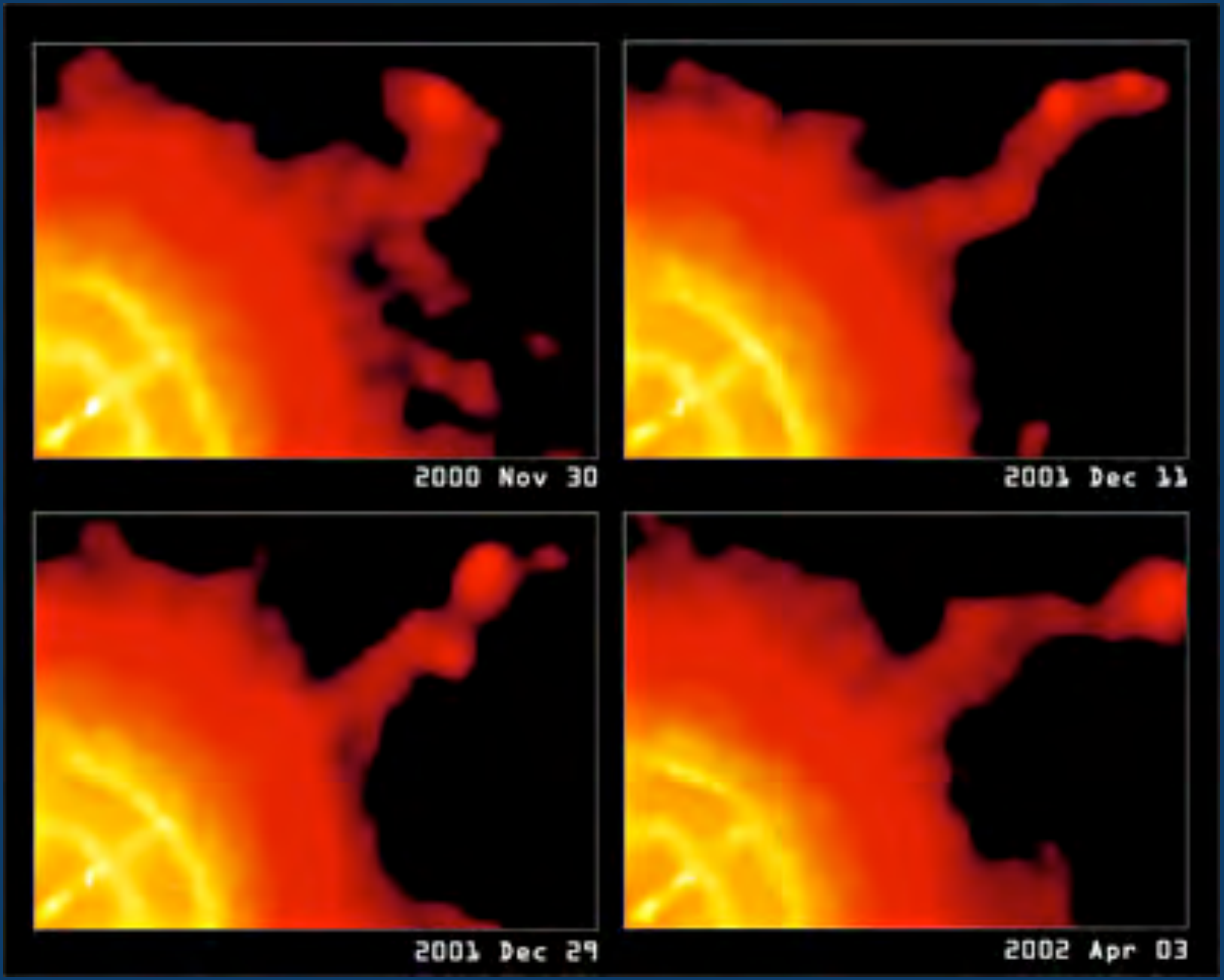




Chandra Reveals a Compact Nebula Created by a Shooting Neutron Star

The rings are thought to represent shock waves due to matter rushing away from the neutron star. More focused flows at the neutron star's polar regions produce the jets. The origin of this activity is thought to be enormous electric fields caused by the combination of the rapid rotation and intense magnetic fields of the neutron star.

Vela pulsar jet



Sample environment for neutron scattering experiments

- *Neutron, being a neutral particle, possesses a great penetrating power through engineering materials.*
- *The construction of sample environment is relatively easier for neutron experiments than for X-ray experiments.*

Low temperature

- *A vast majority of magnetic structures develop at a low temperature. Also many other interesting phenomena in condensed matter happen only at low temperatures.*

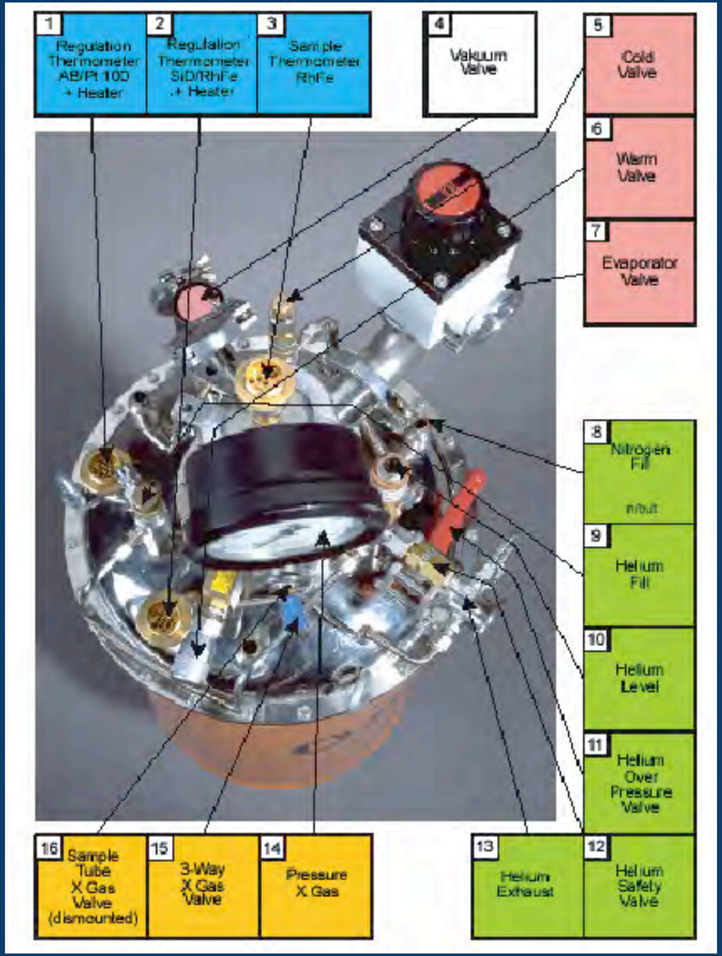
- *Neutron diffractometrs and spectrometers therefore must be equipped with cooling devices.*

Orange He cryostat

First developed at ILL

Side view

Top view

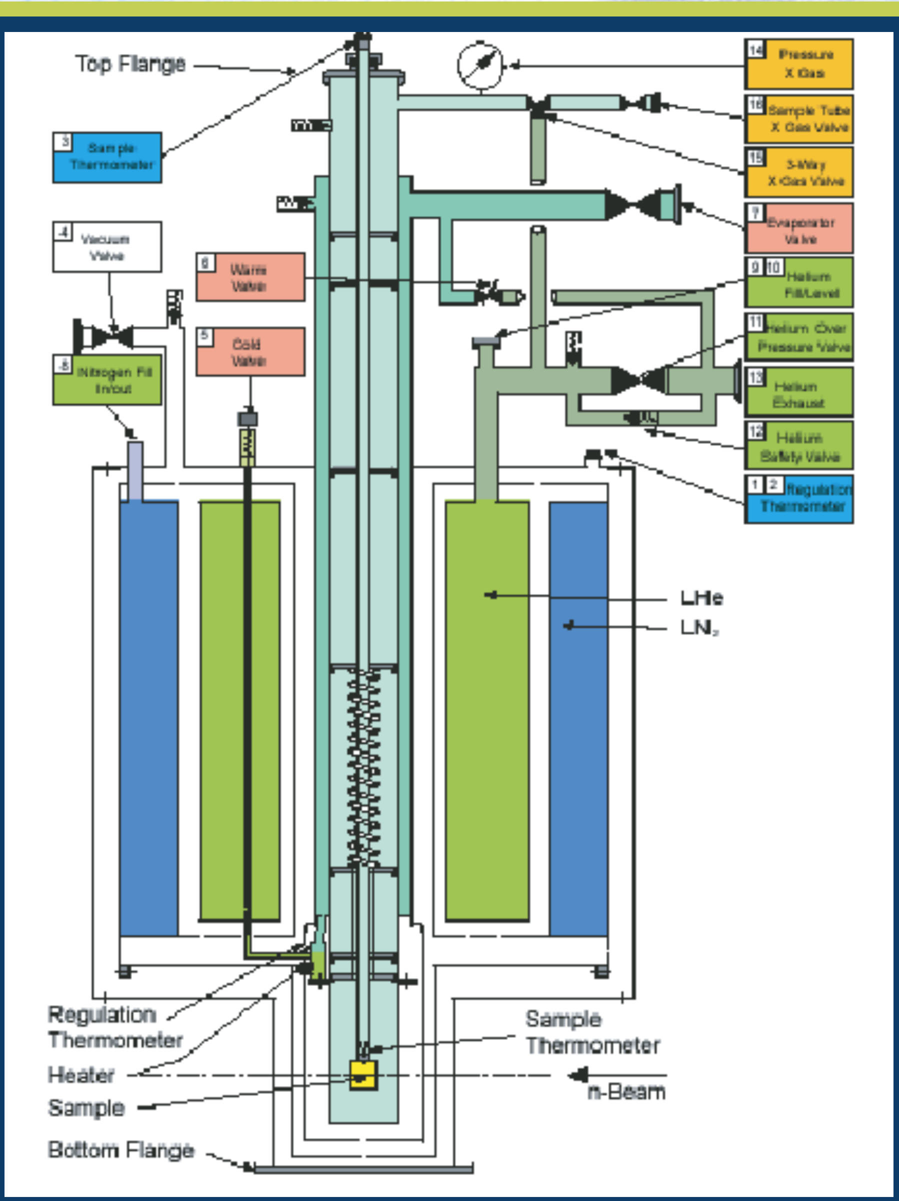


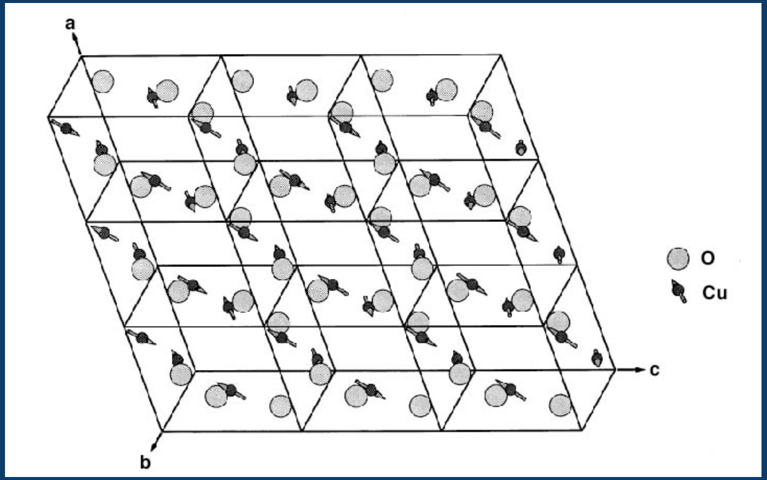
Temperature range:

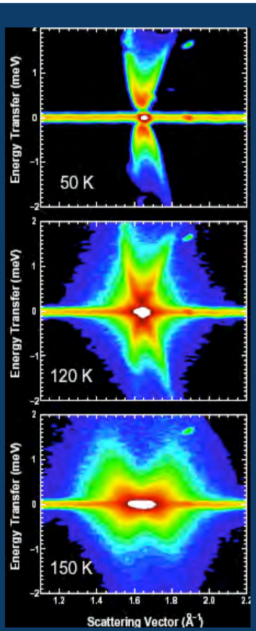
1.3 – 300 K

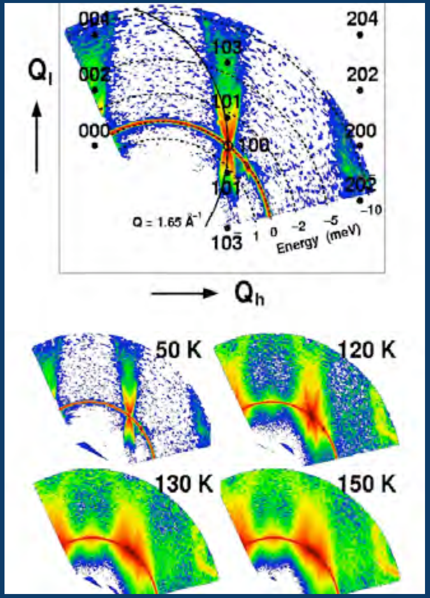
Great advantage: top loading, samples can be changed easily

A cross-section through a standard orange cryostat



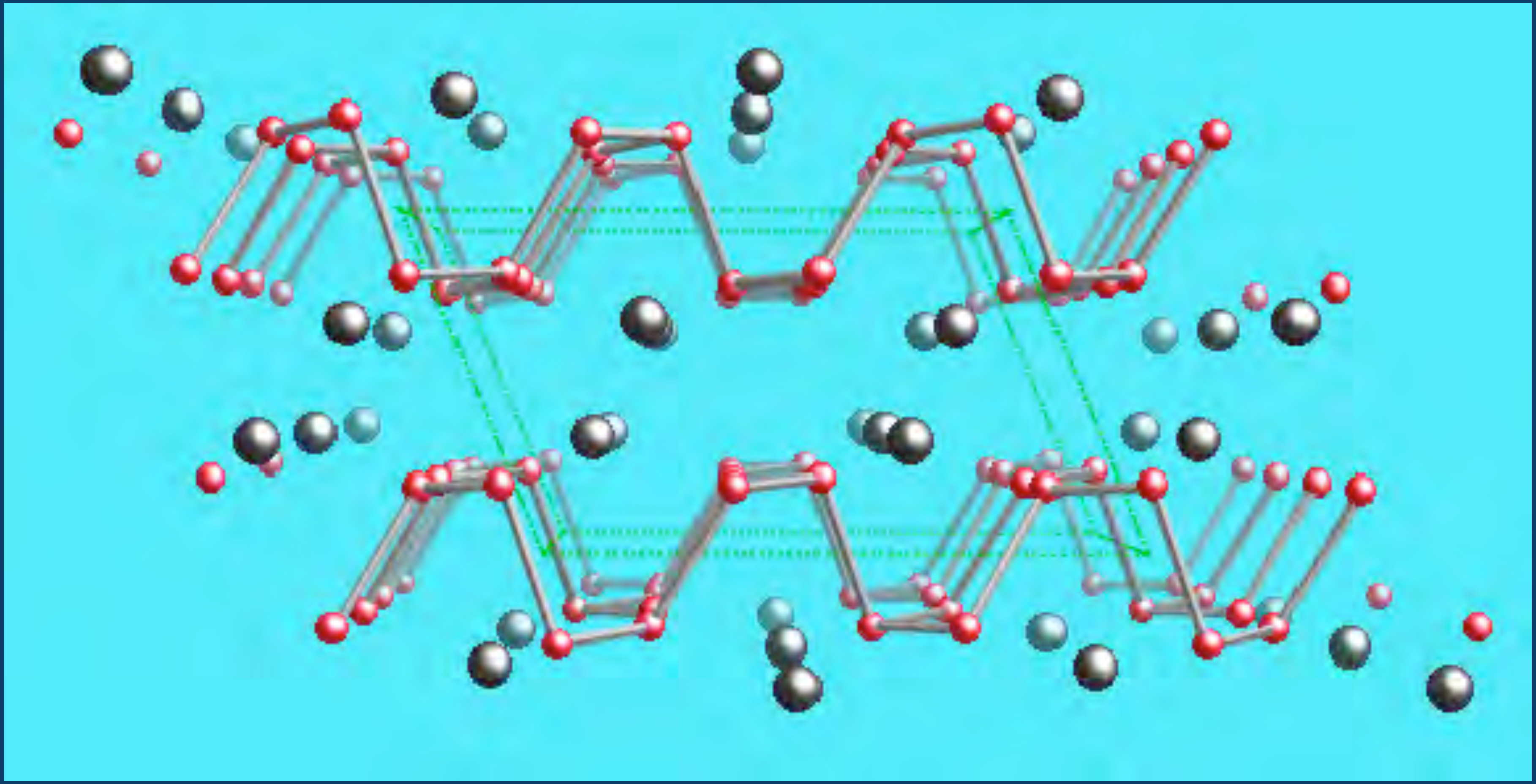






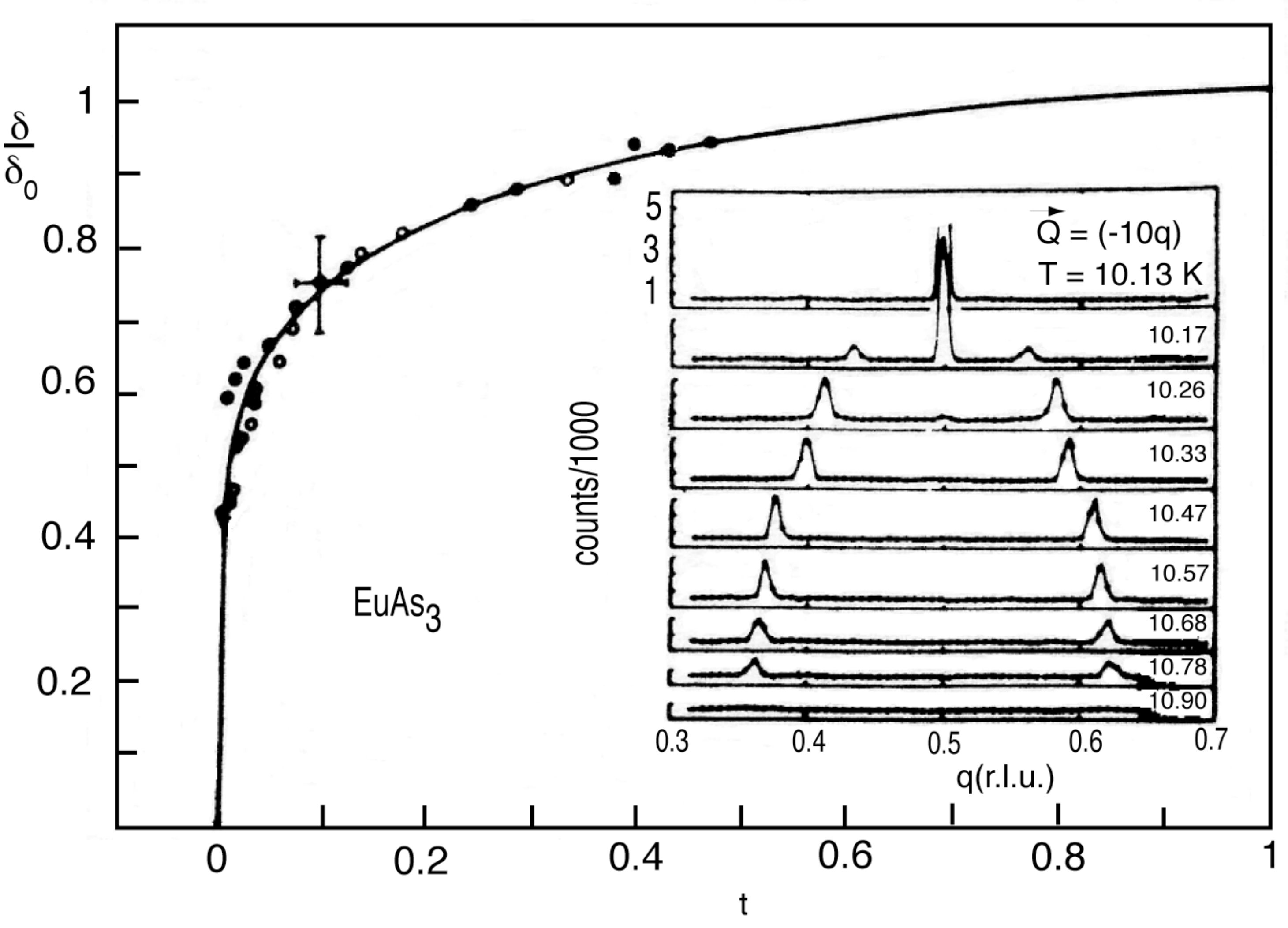
Semimetallic $EuAs_3$

Structure consists of polyanionic puckered layers of As atoms in which Eu atoms are sandwiched.



Commensurate-incommensurate lock-in phase transition in $EuAs_3$

*PRL **57**, 372 (1986)*



T_N = 11 K, T_L = 10.3 K
AF1 phase below T_L
IC phase: between T_N and T_L

Soliton-lattice model
No higher-order satellites

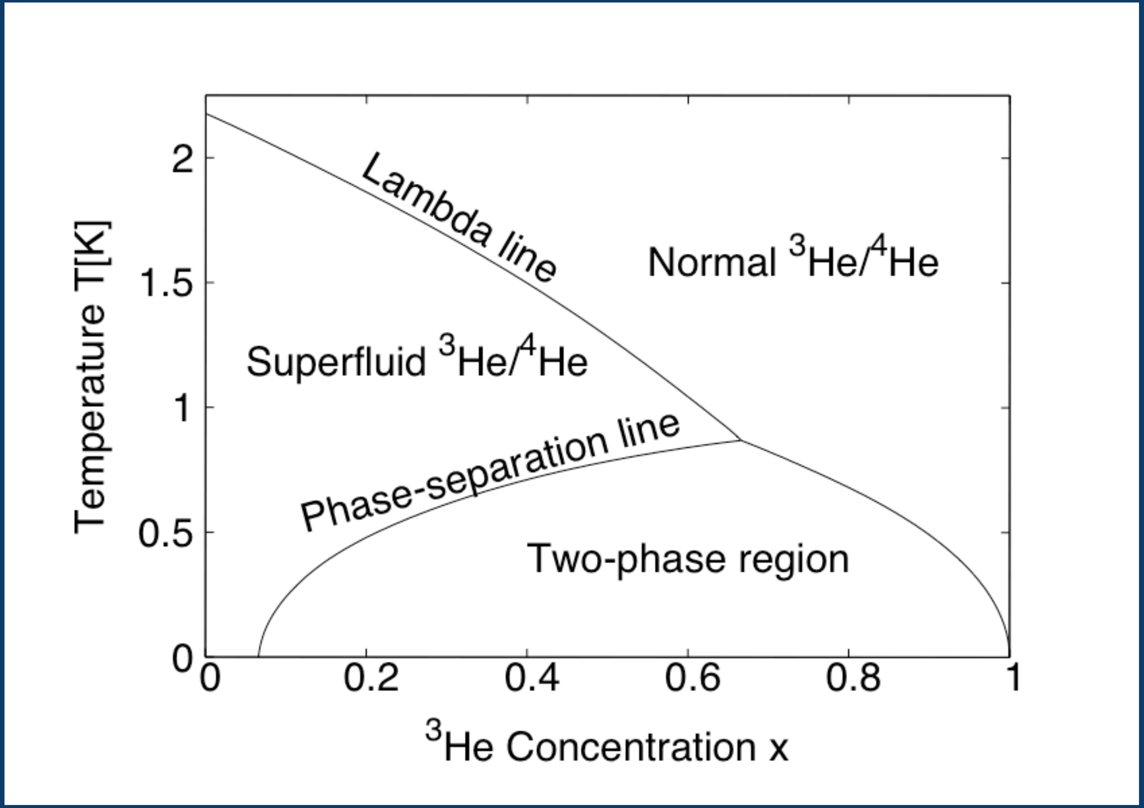
Millikelvin temperatures

- Temperatures down to about 300 mK can be obtained by evaporating ^3He (^3He cryostat).

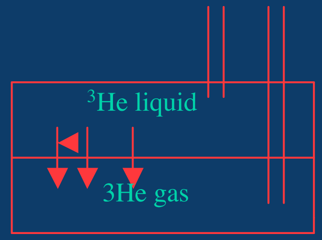
- Temperatures as low as 25 mK can be generated by using a mixture of ^3He and ^4He (dilution cryostat).

^{3}He-^{4}He phase diagram

- *The Bose liquid ^{4}He becomes superfluid at T_c = 2.177 K whereas the Fermi liquid ^{3}He becomes superfluid at Tc = 2.5 mK.*
- *Below T = 0.87 K the liquid separates into two distinct phases: ^{3}He-rich and ^{4}He-rich phases.*
- *^{3}He-rich liquid is lighter and floats on top of the heavier ^{4}He-rich liquid with a visible interface.*
- *If the liquid is cooled close to T = 0 the ^{3}He-rich phase becomes pure ^{3}He, but ^{4}He-rich phase does not become pure ^{4}He, but contains 6.54% ^{3}He (finite solubility).*



At temperatures much below 1 K dilute solution of ^{3}He in ^{4}He behaves like gaseous ^{3}He with a heavier effective mass.



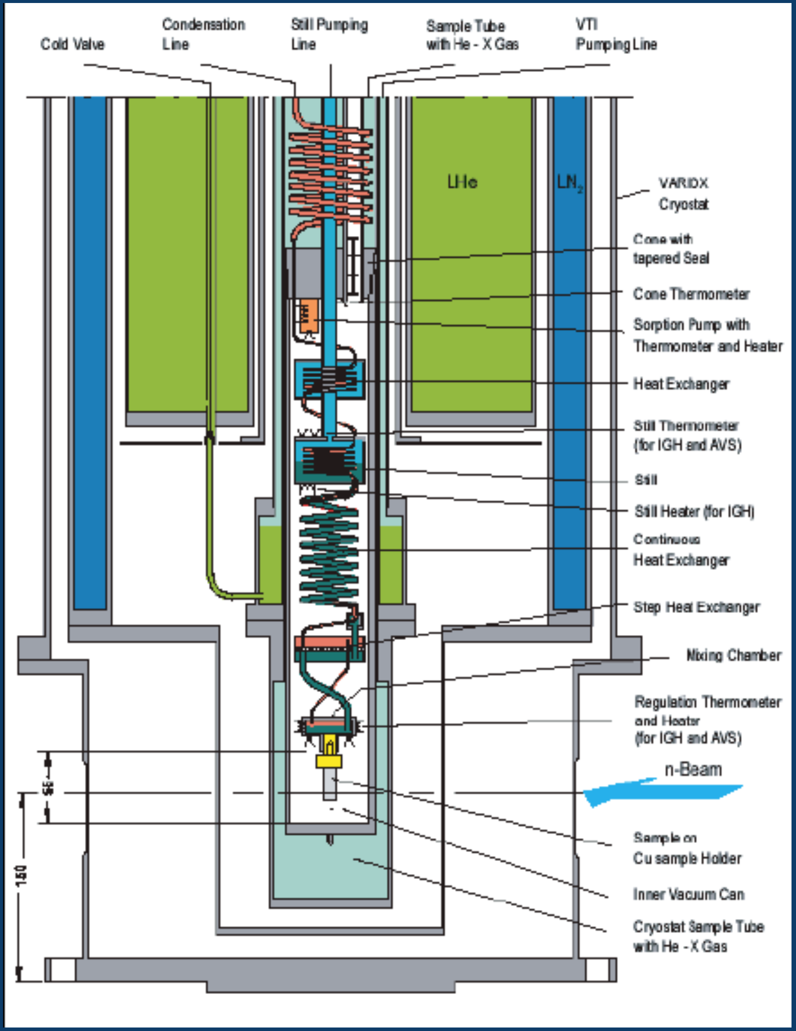
^{3}He atoms from the top liquid phase evaporate to the gas-like phase on bottom and generate cooling.

Oxford ^{3}He-^{4}He cryostat

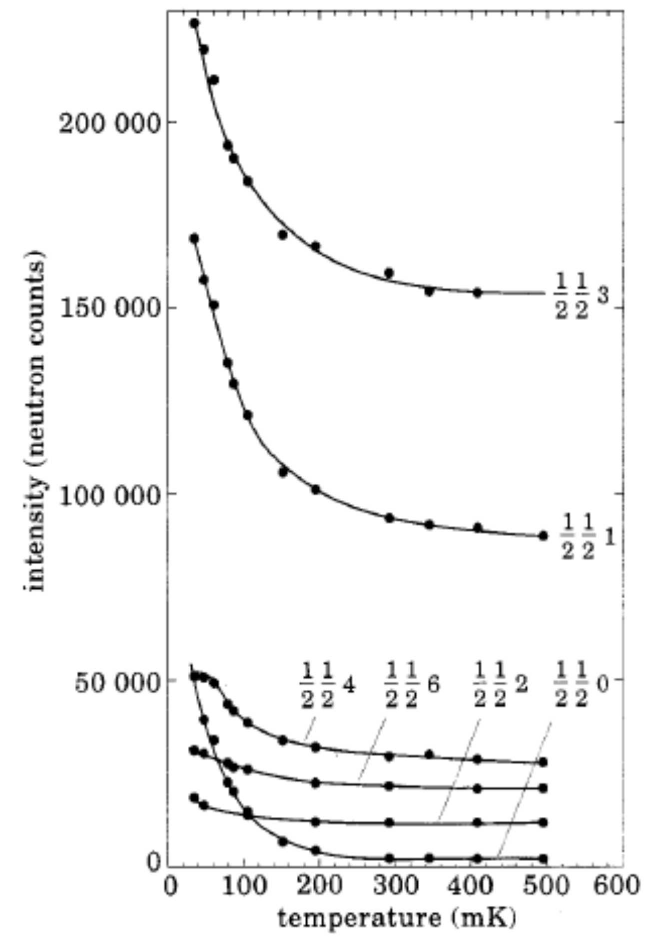
Developed at ILL, now commercialised

Side view

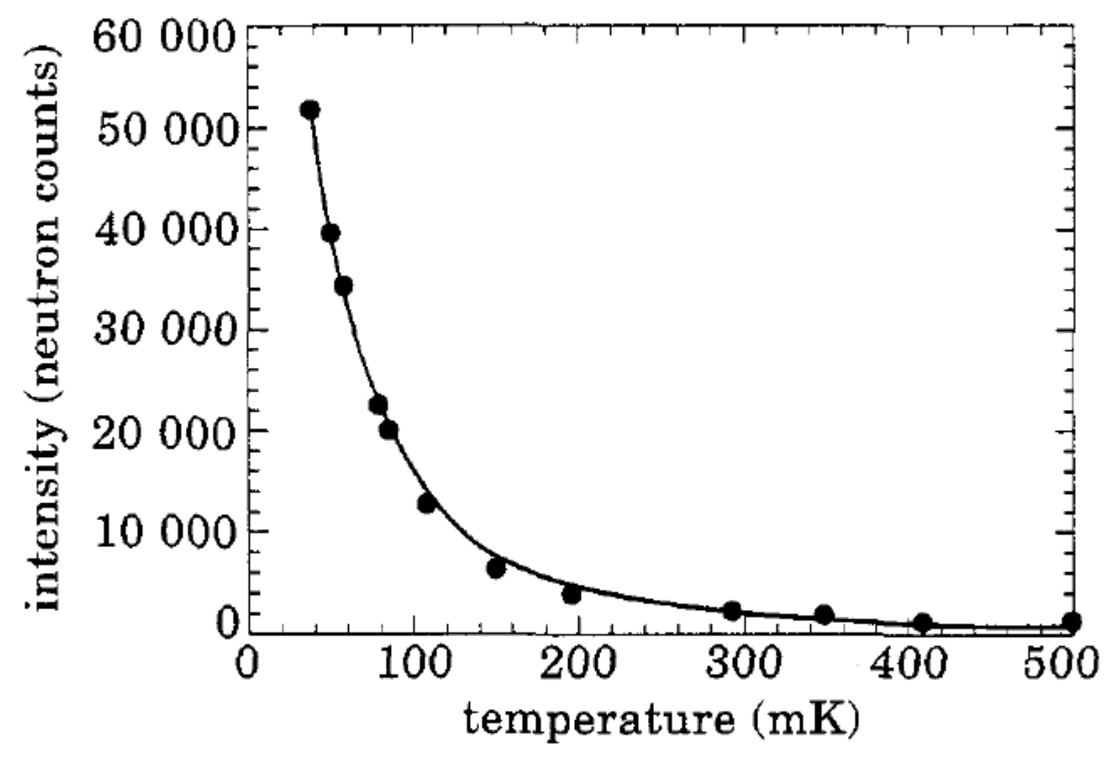
Cross section



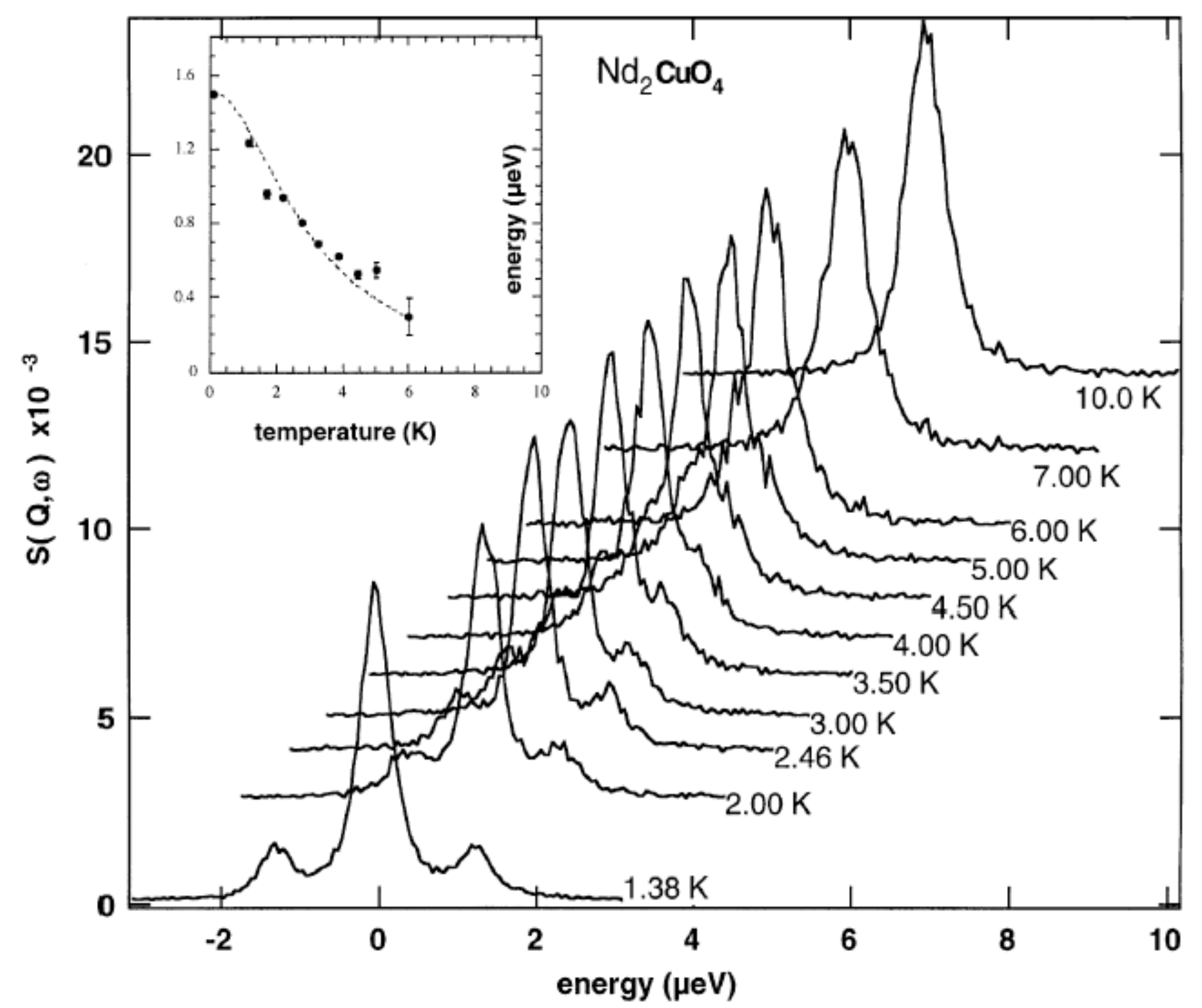
Hyperfine-induced nuclear ordering in Nd_2CuO_4



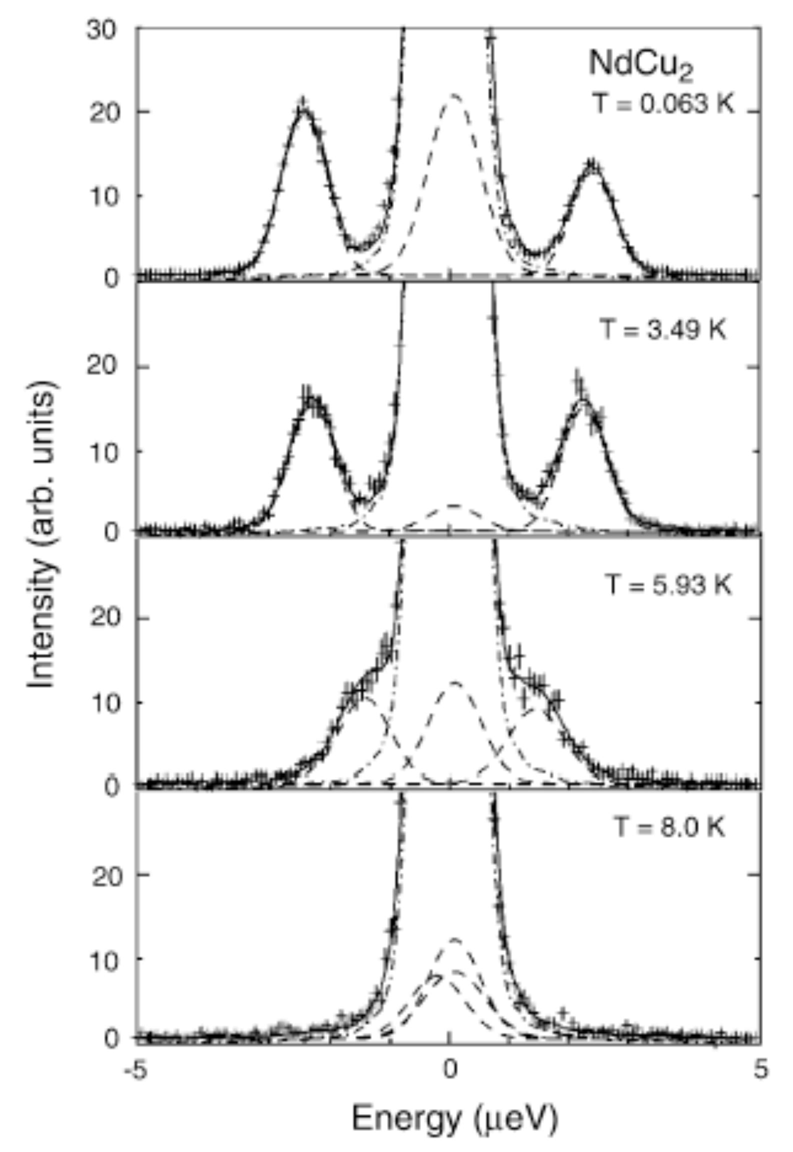
1/2,1/2,0 reflection

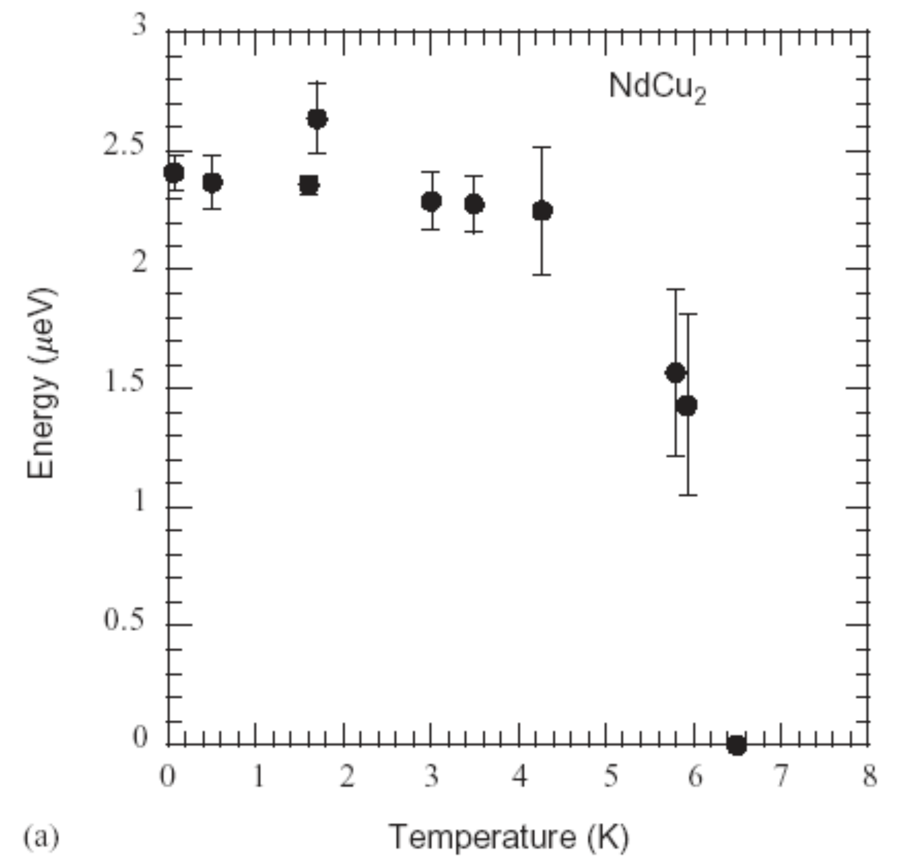


Nuclear spin excitations in Nd_2CuO_4

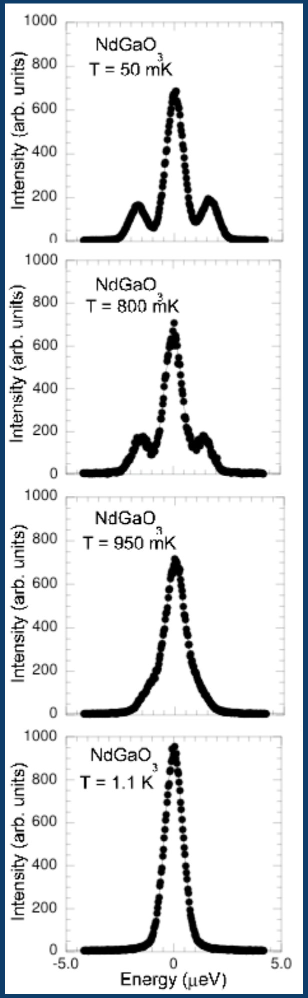


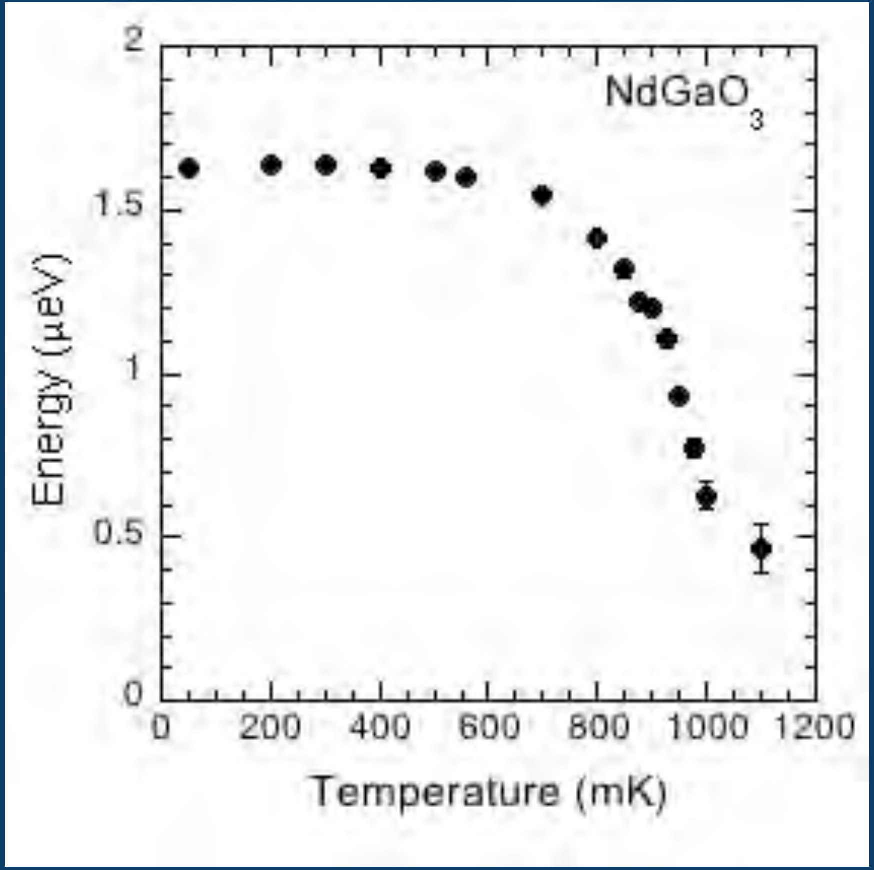
Low energy spin excitations in $NdCu_2$





Nuclear spin excitations in $NdGaO_3$





High magnetic field

- *Magnetic fields often influences the magnetic structures profoundly and causes field-induced phase transitions.*
- *Often these phase transitions occur at low temperatures and under high magnetic fields.*
- *So it is necessary to high magnetic fields and low temperatures simultaneously.*

Oxford 15 Tesla cryomagnet

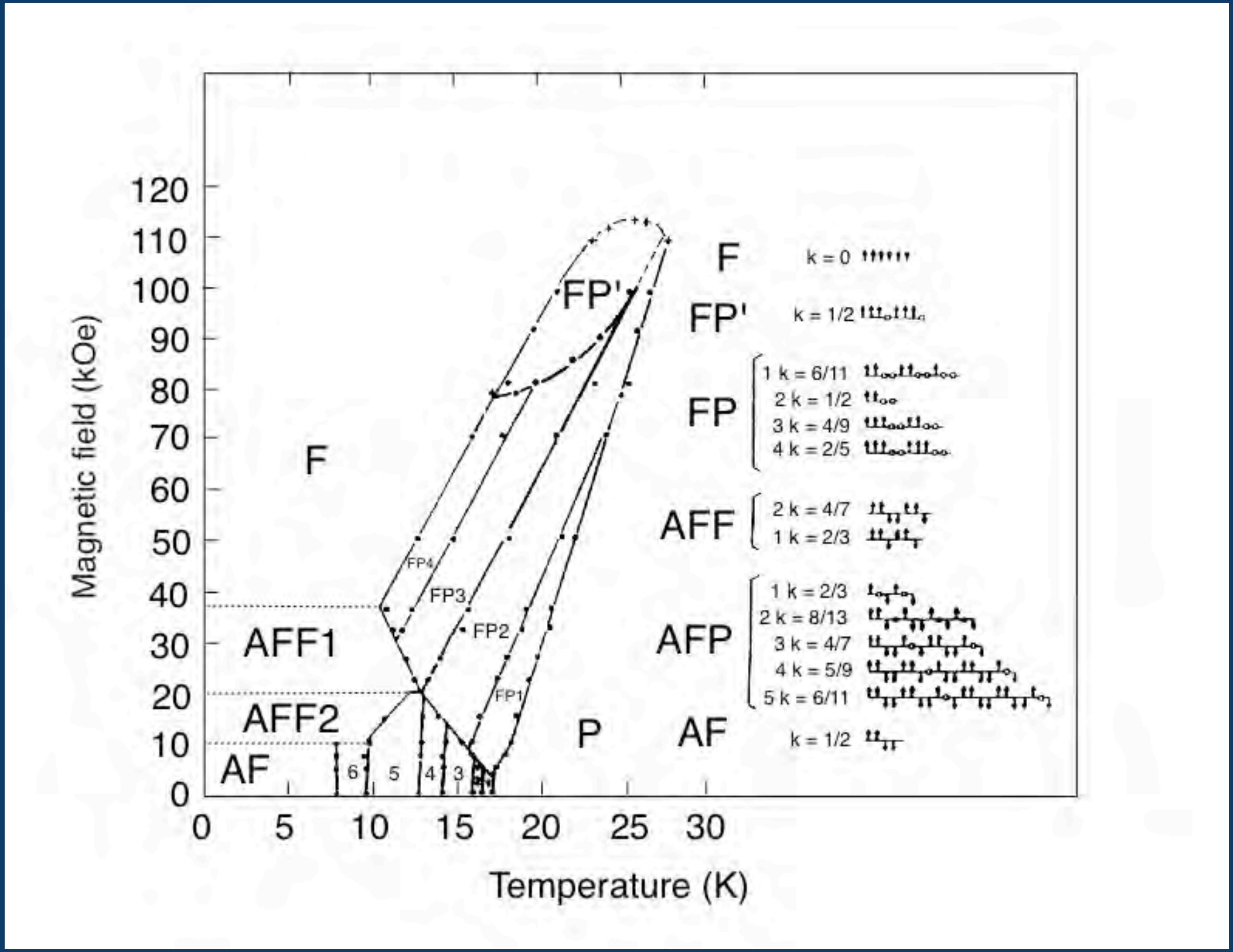
Developed at ILL and CENG, now commercialised

Side view

Top view

Kondo-lattice compound CeSb

(H-T) phase diagram of CeSb



The most complex magnetic phase diagram known so far: consists of sixteen phases.

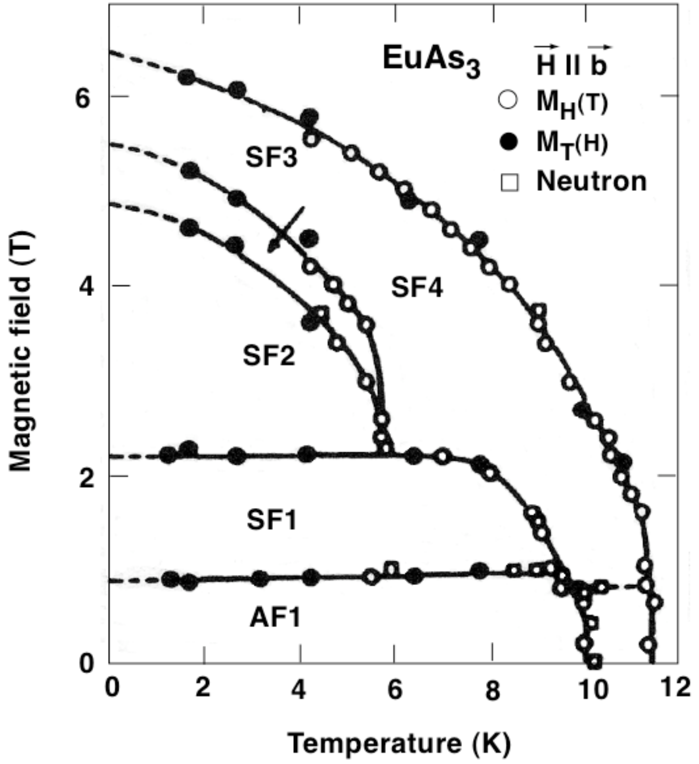
At H = 0 the low temperature Phase is the type-IA phase. The rest are modulated AFP phases containing paramagnetic planes.

The type-I phase is missing, but paramagnetic fluctuations corresponding to its wave vector has been observed.

Magnetic field effects on EuAs$_3$

(H-T) phase diagram

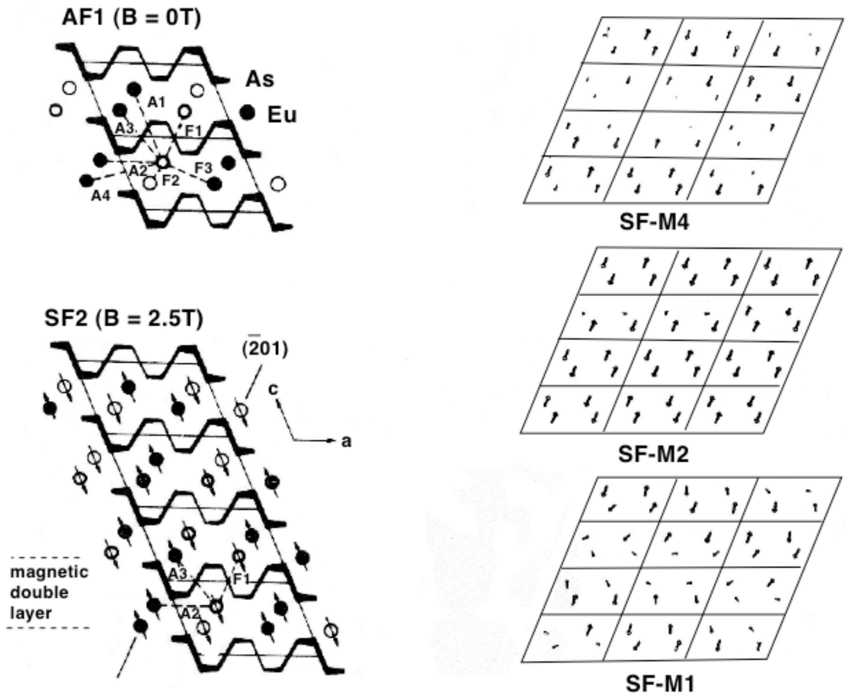
*PRB **41**, 4358 (1990)*



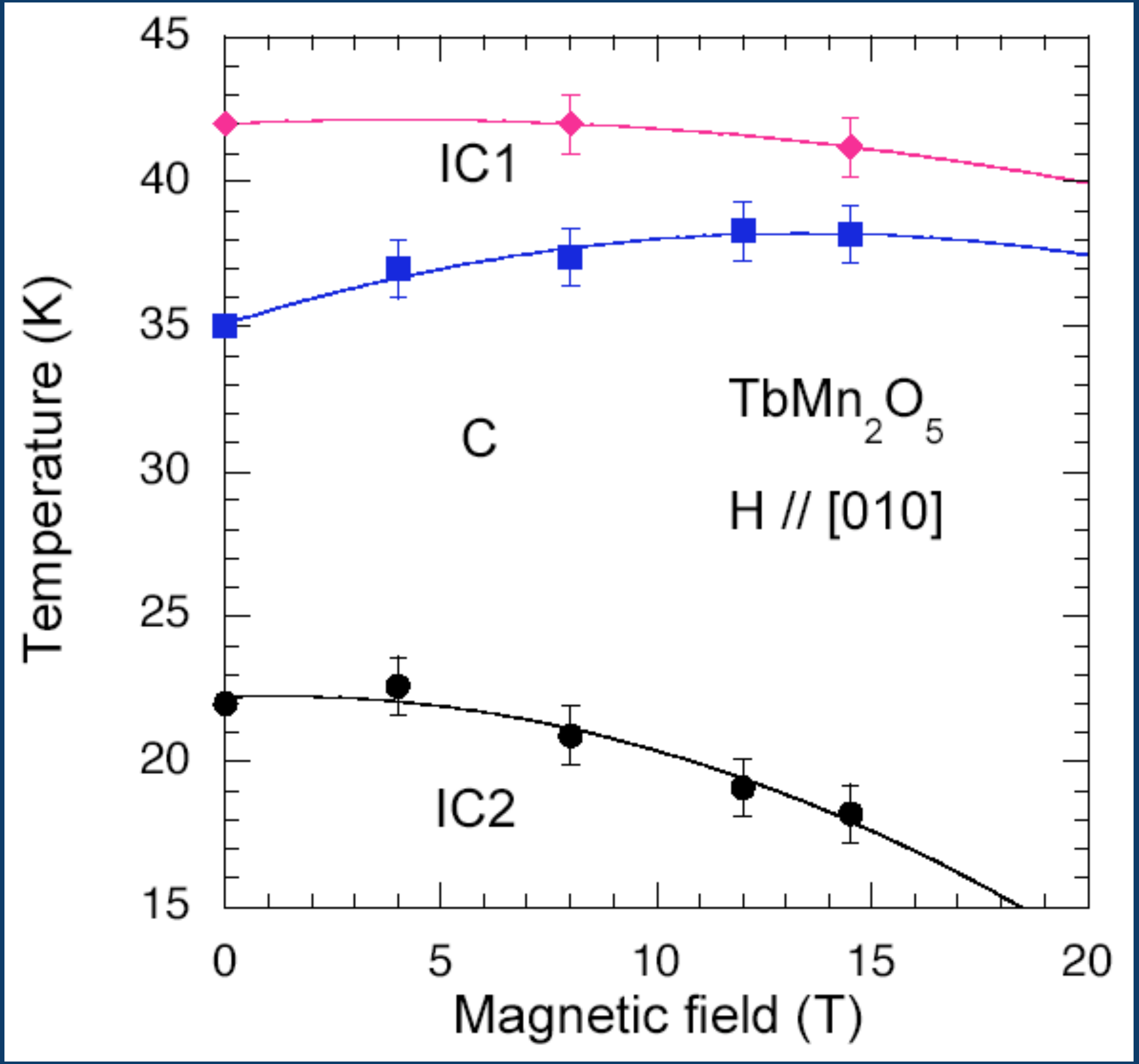
Magnetic structures

*PRB **37**, 269 (1988)*

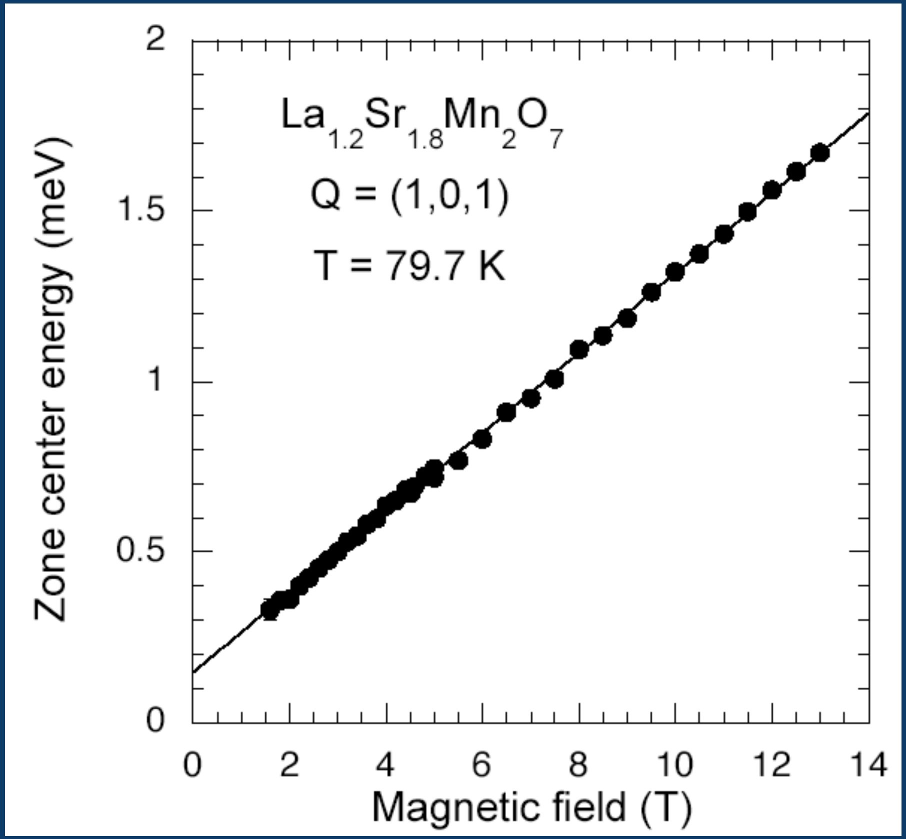
*PRB **38**, 350 (1988)*

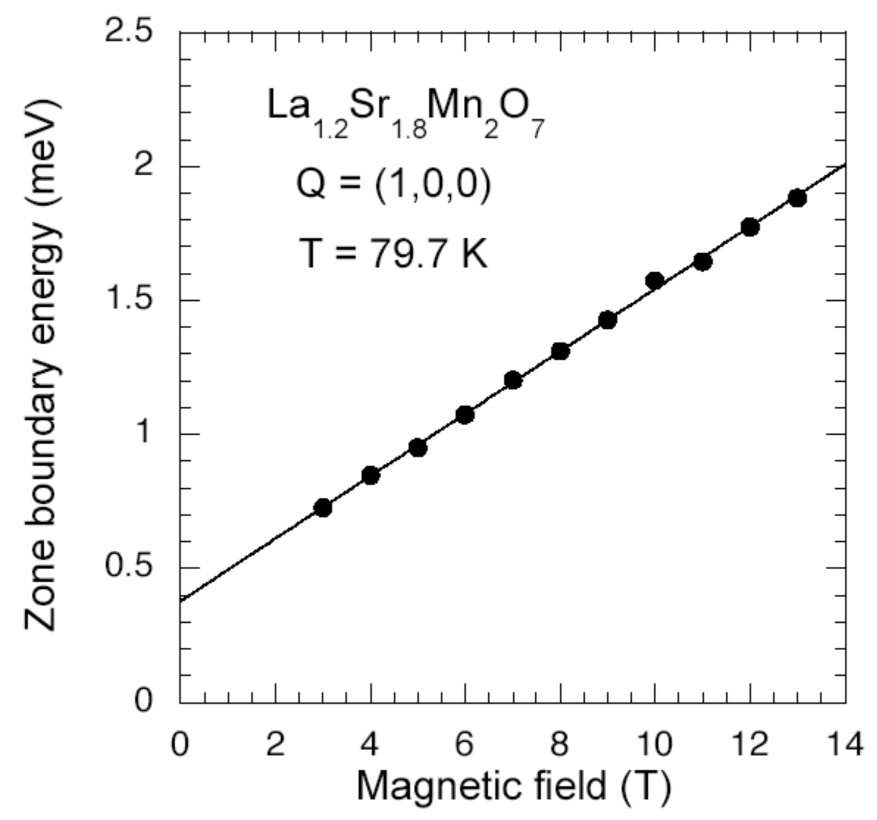


(H-T) phase diagram of multiferroic $TbMn_2O_5$



Field dependence of magnon energy



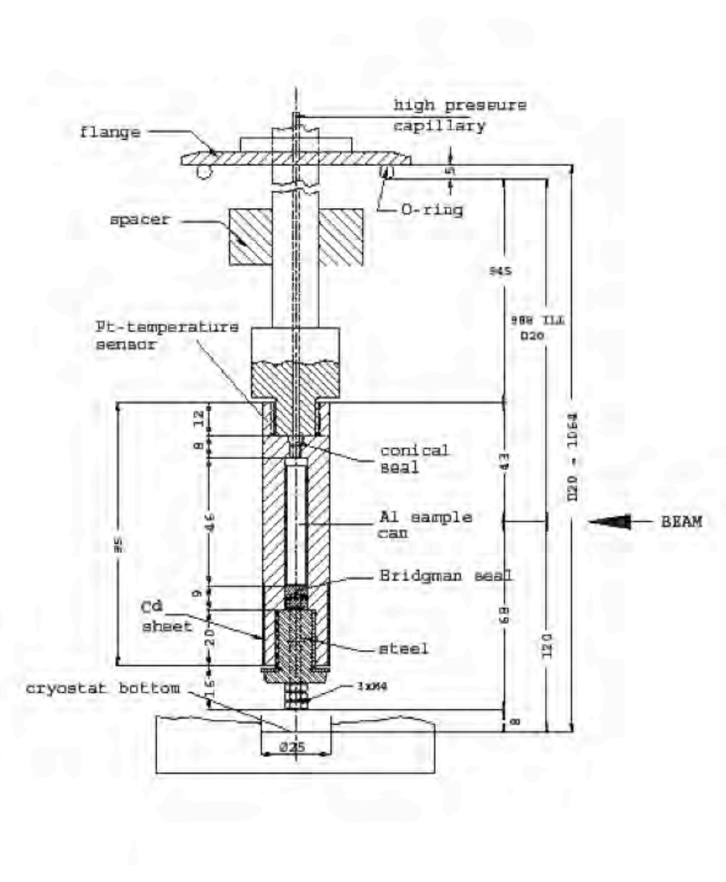


High pressure

- *High pressure causes reduction in volume and changes bond distances and bond angles causing modifications of orbital overlaps and hence exchange interactions.*

- *High pressure causes therefore drastic changes in properties of magnetic materials.*

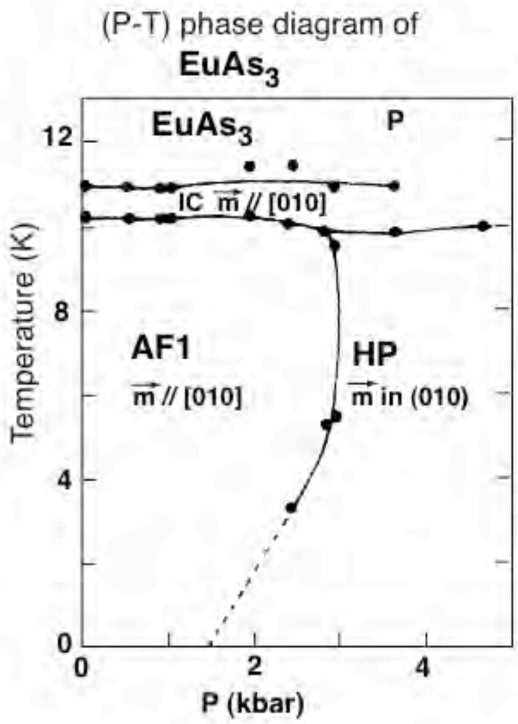
Gas Pressure Cell

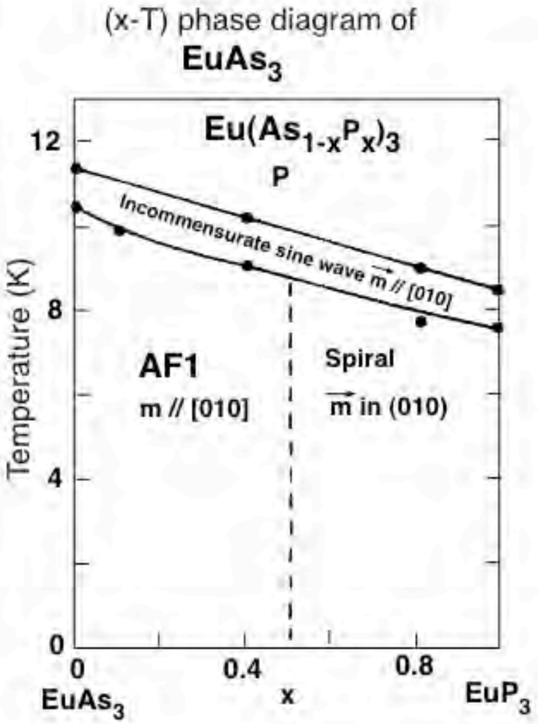


- *Pressure can be tunned easily*
- *Pressure is limited to 5 kbar*

Effects of pressure on the magnetic phases of $EuAs_3$

The similarity of the (P-T) and (x,T) phase diagrams suggests that the substitution of As by the smaller P atom generates chemical pressure

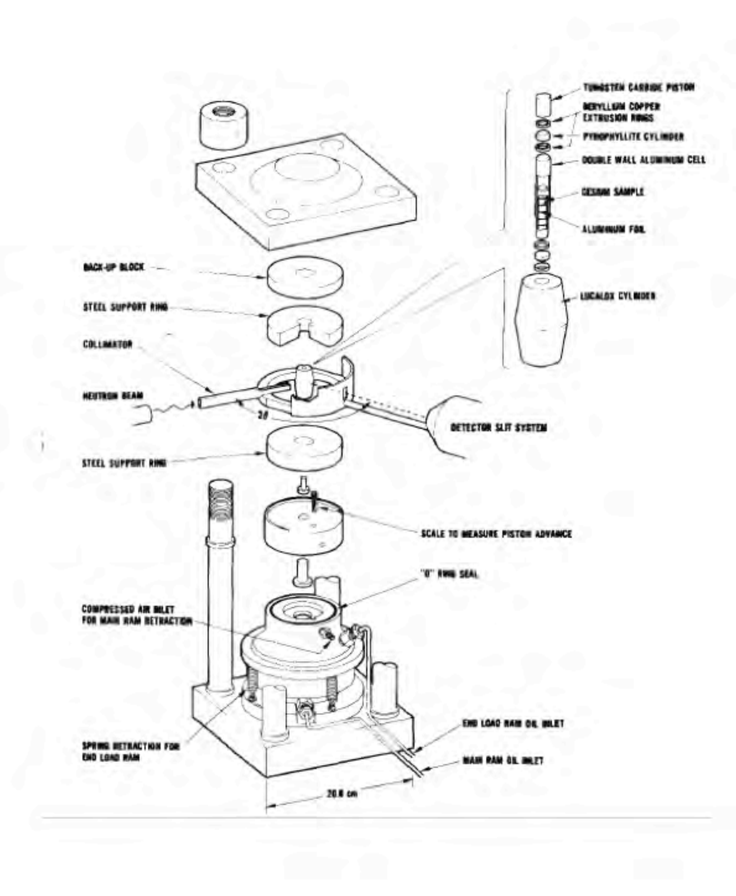

(P-T) phase diagram of $EuAs_3$

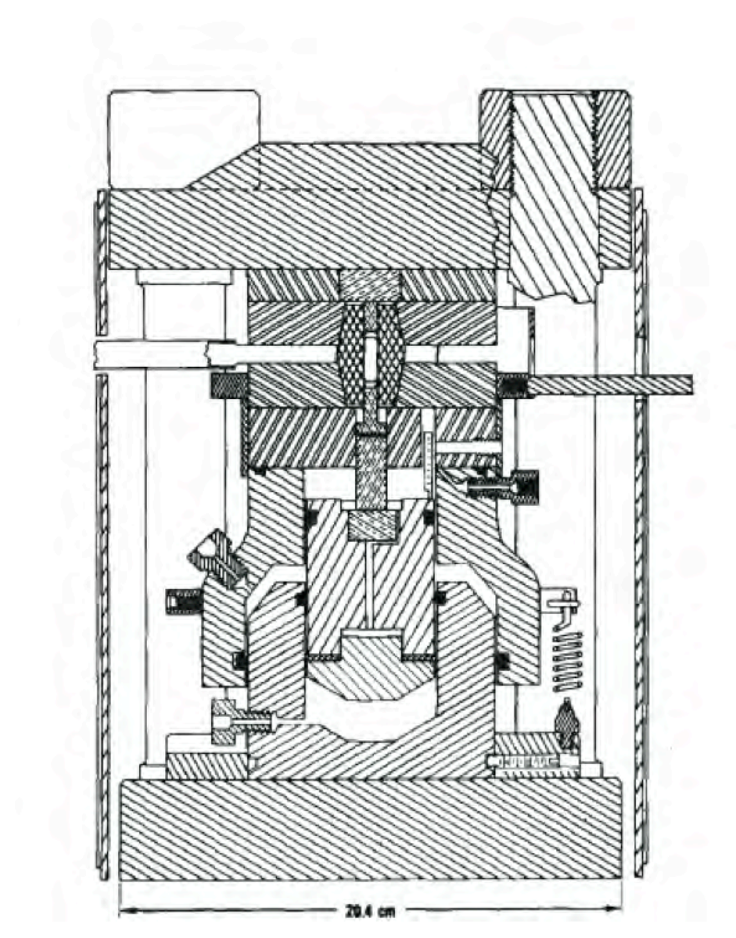

(x-T) phase diagram of $EuAs_3$

The ILL gas pressure cell was used

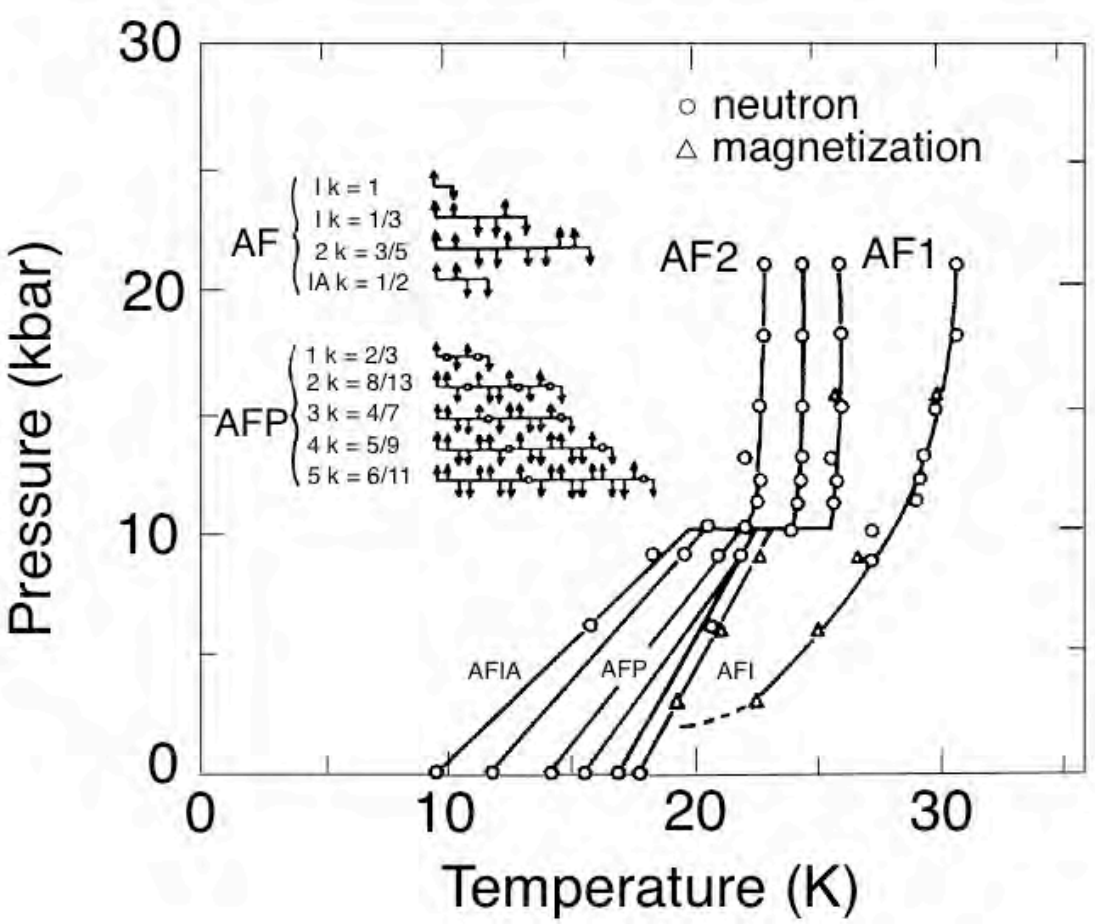
- ➨ *No AF1 phase at high P.*
- ➨ *A spiral phase is stabilized.*
- ➨ *(P,T) and (x,T) look similar*

McWhan Clamp pressure cell





Effect of pressure on the modulated magnetic phases of CeSb



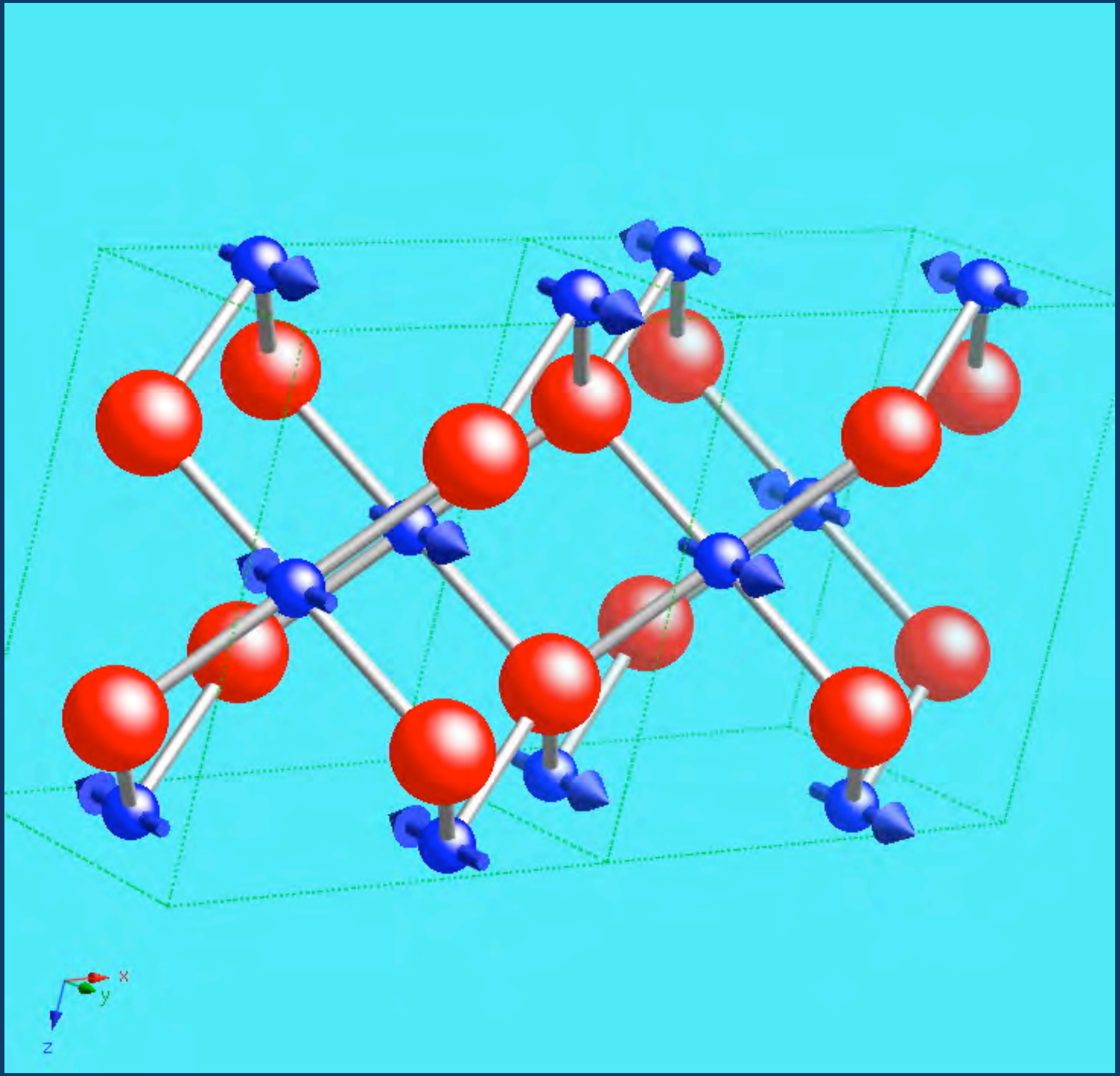
PRB **49**, 15096 (1994)

The ILL clamp pressure
cell was used.

Important results:

- Stabilization of type I AF phase.
- Disappearance of AFP phases**.**
- Type I and type IA at high pressure
- CeSb behaves like CeBi at high P.

Crystal and magnetic structure of CuO:

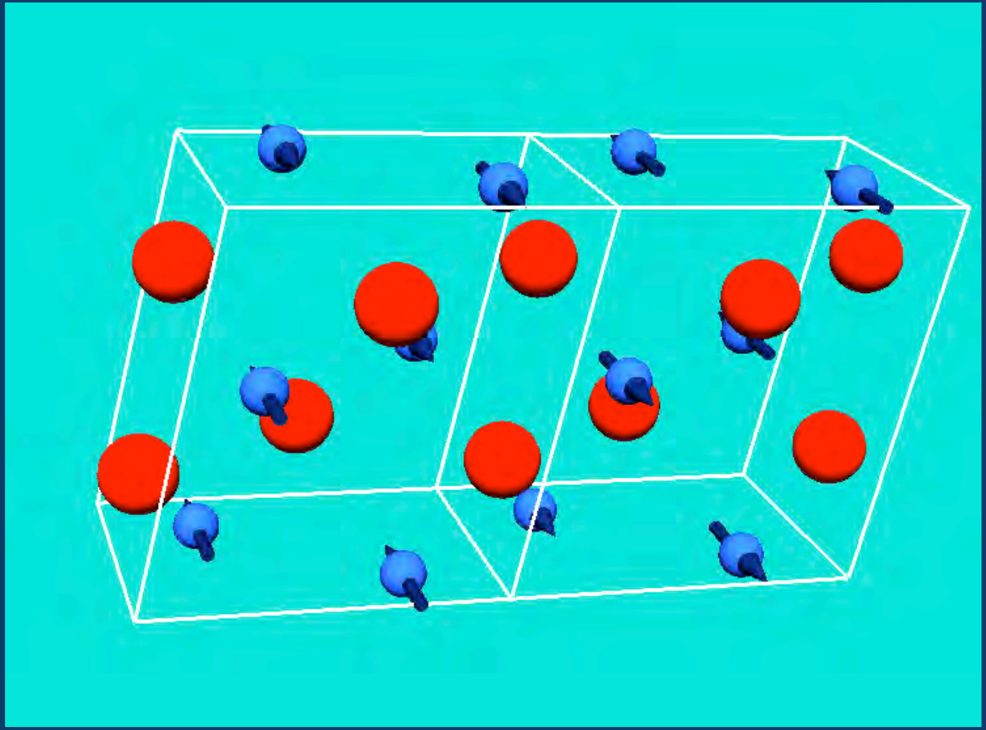


The structure consists of Cu^{2+} ions coordinated by O in approximate square planar arrangement. These planes share edges to form Cu-O-Cu chains.

Cu-Cu chains along [1,0,-1]: Cu-O-Cu bond angle is 146 deg. The strongest superexchange is expected within the chain direction.

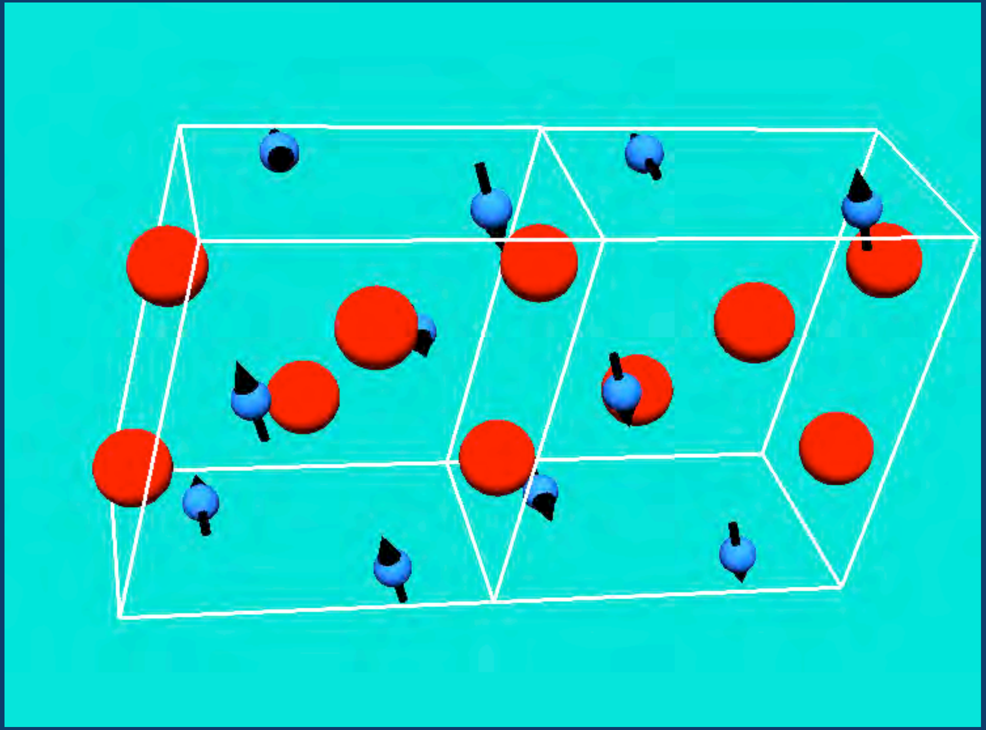
Magnetic structures of CuO

AF phase



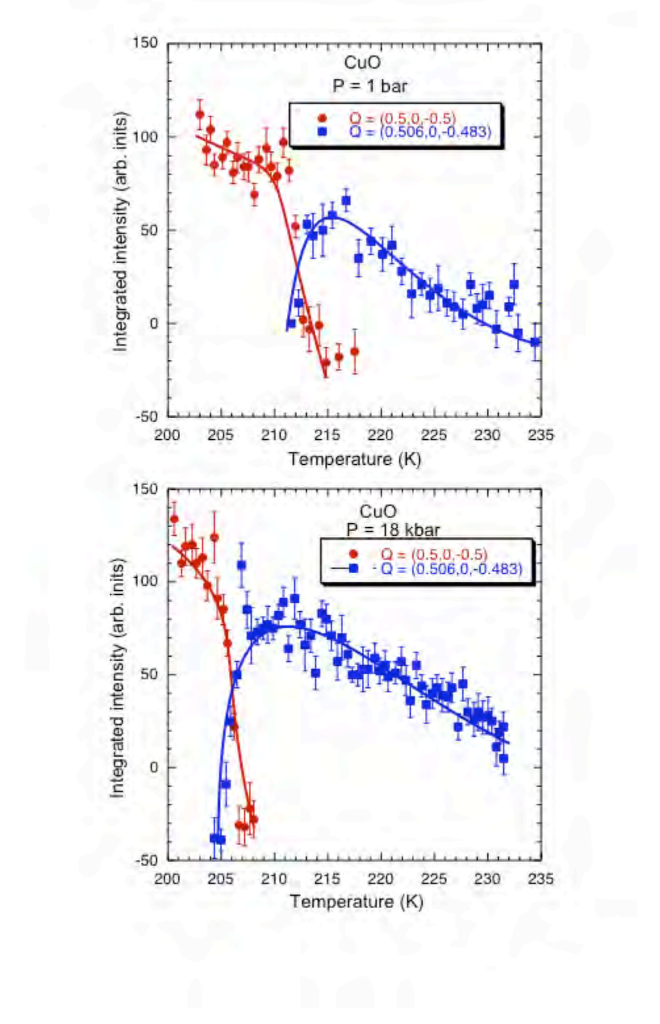
Spin frustration in the collinear arrangement

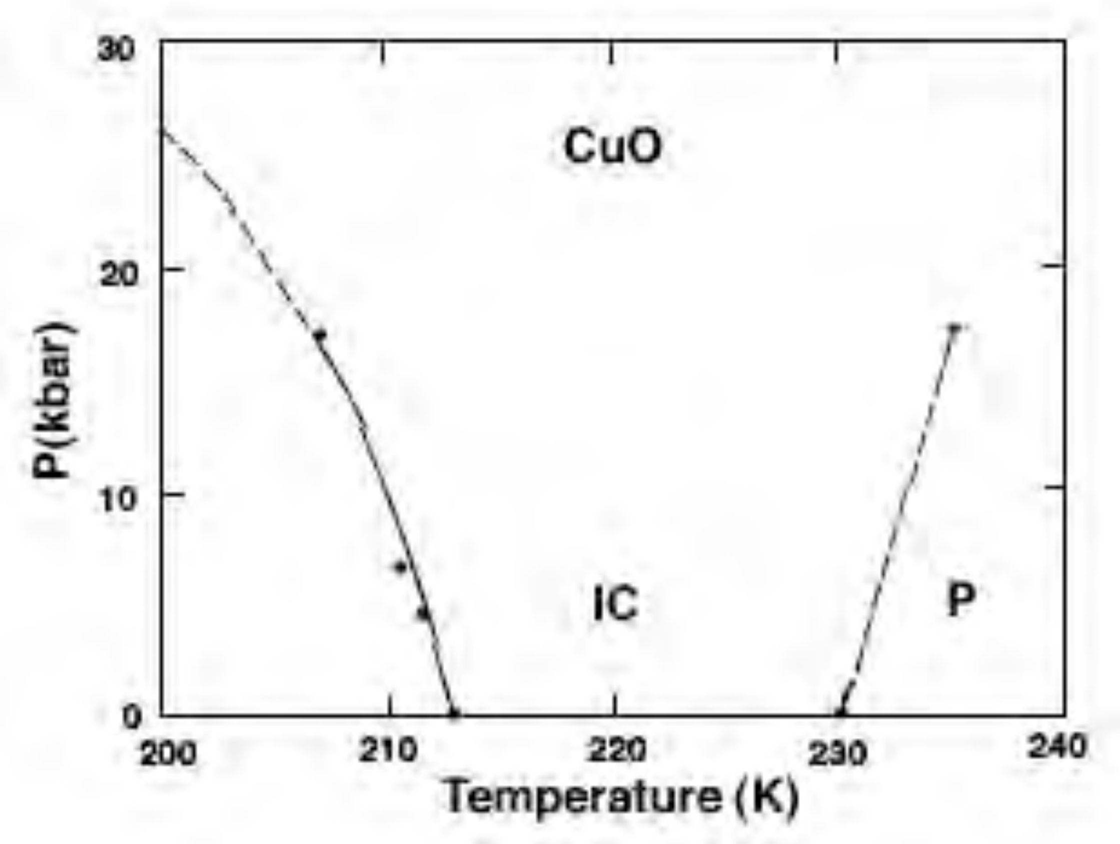
Incommensurate phase



Spin frustration is removed by non-collinear arrangement

Effect of pressure on the magnetic phases of CuO



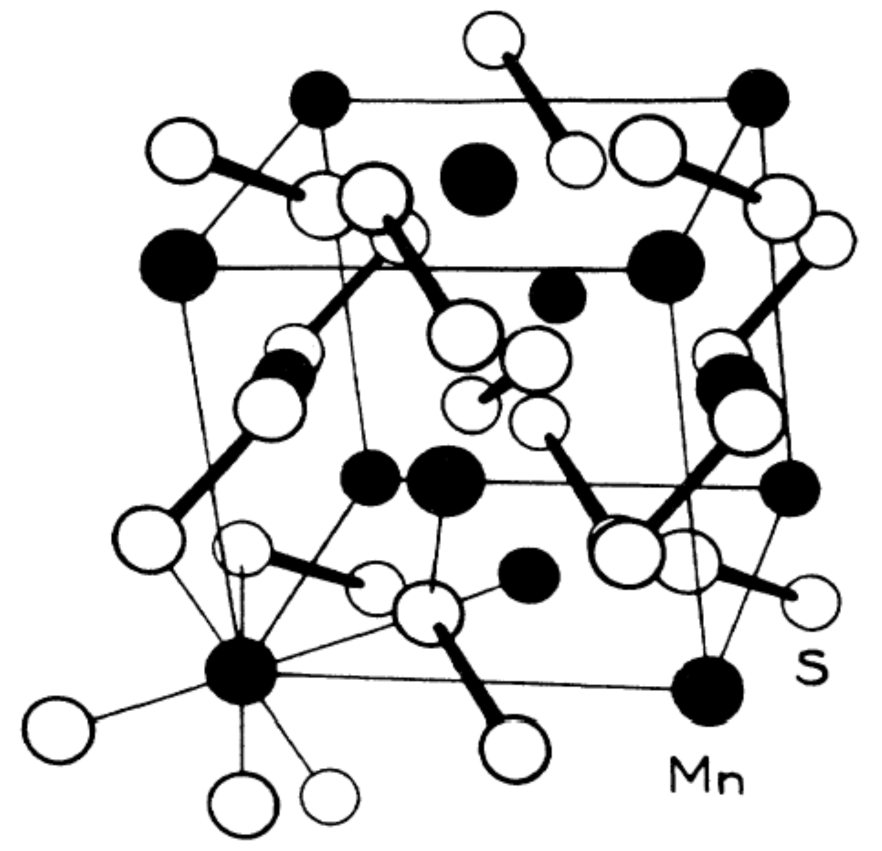


- *Stability range of the IC phase increases at high pressure. It is likely that the AF will be suppressed at pressure of about 100 kbar or so.*

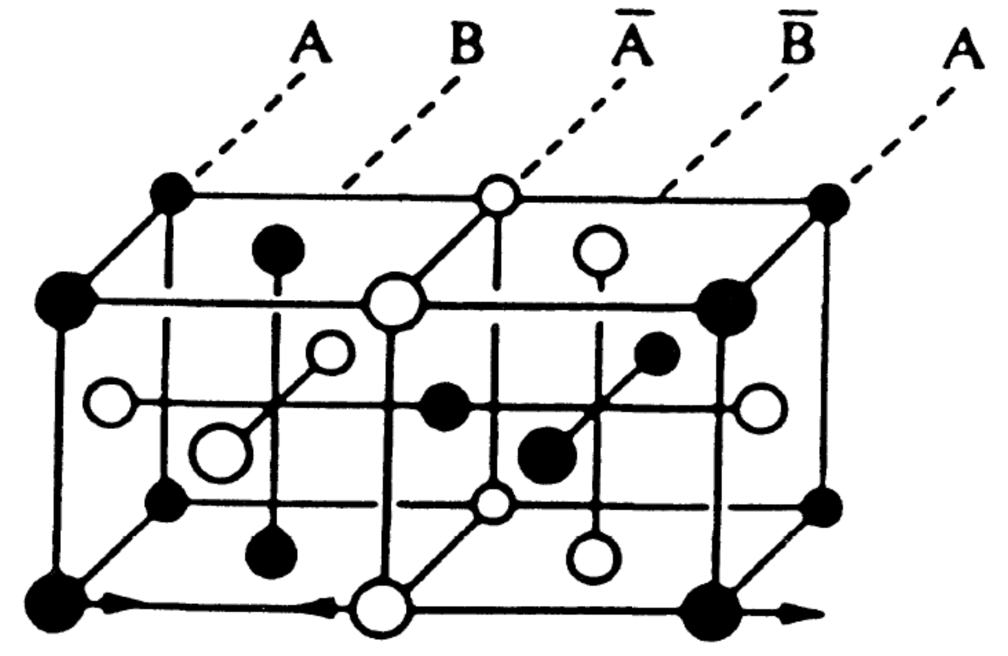
Frustrated AF MnS_2 on a fcc lattice

MnS_2 orders at T_N = 48.2 K with a type-III AF structure

Pyrite-type crystal structure

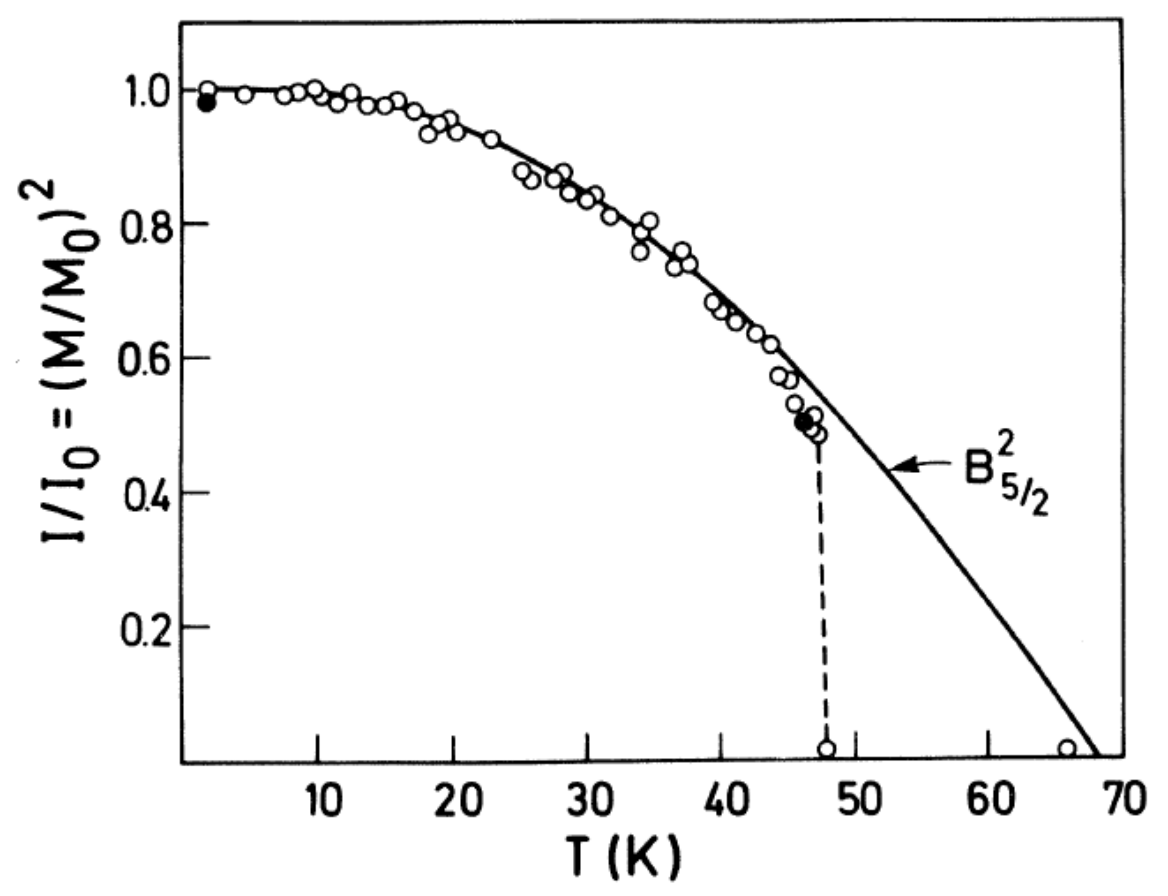


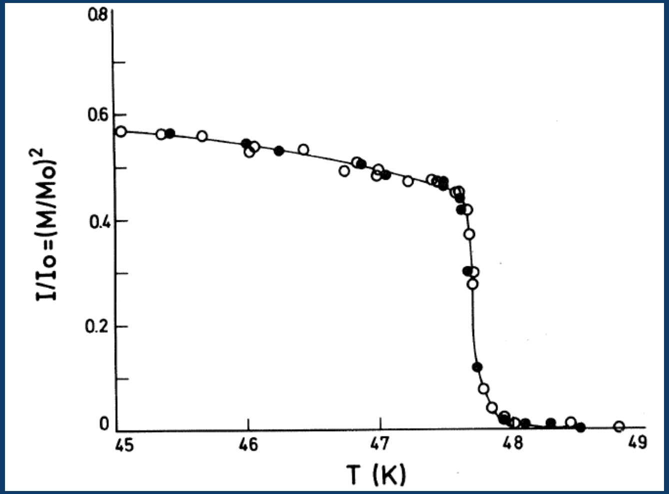
Type-III AF structure

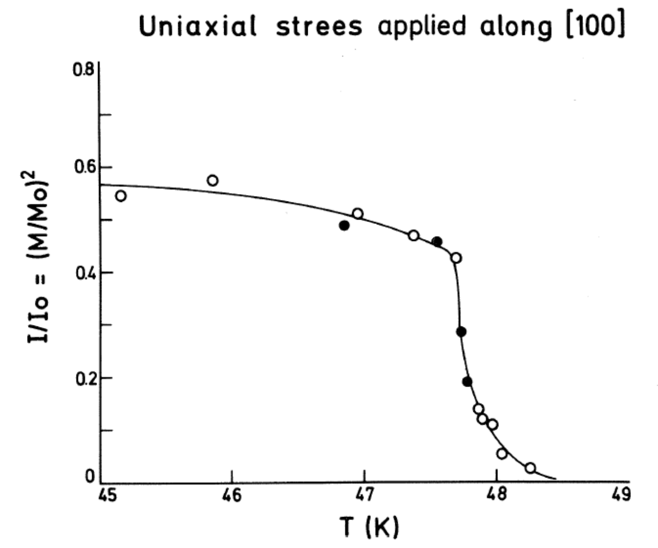


First-order phase transition in MnS_2

Temperature variation of the 1,1/2,0 reflection of MnS_2



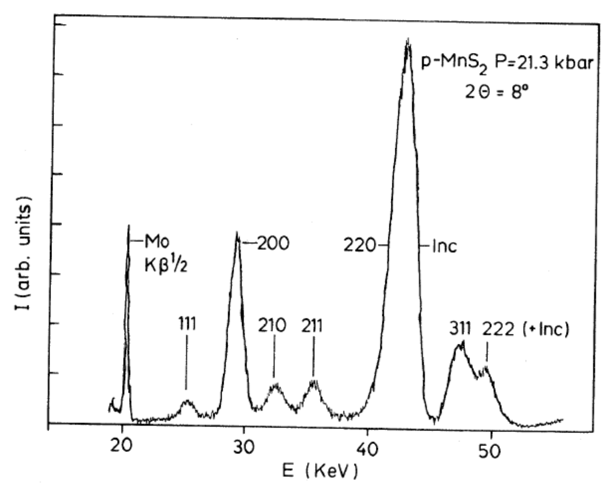


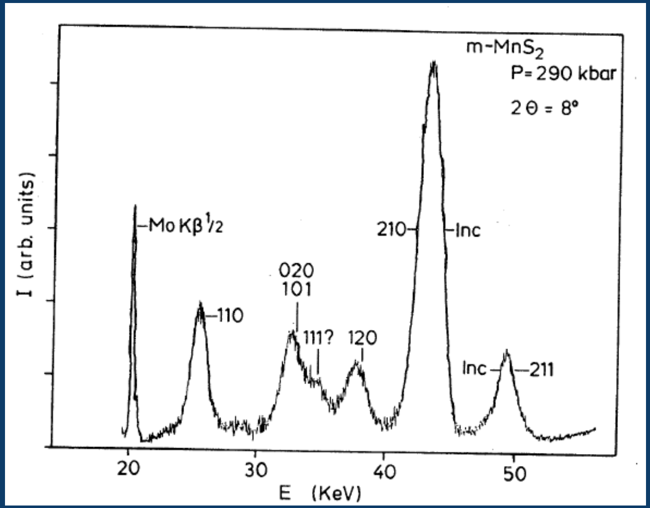

Uniaxial strees applied along [100]

High pressure X-ray diffraction on MnS$_2$

Laboratory X-ray diffraction

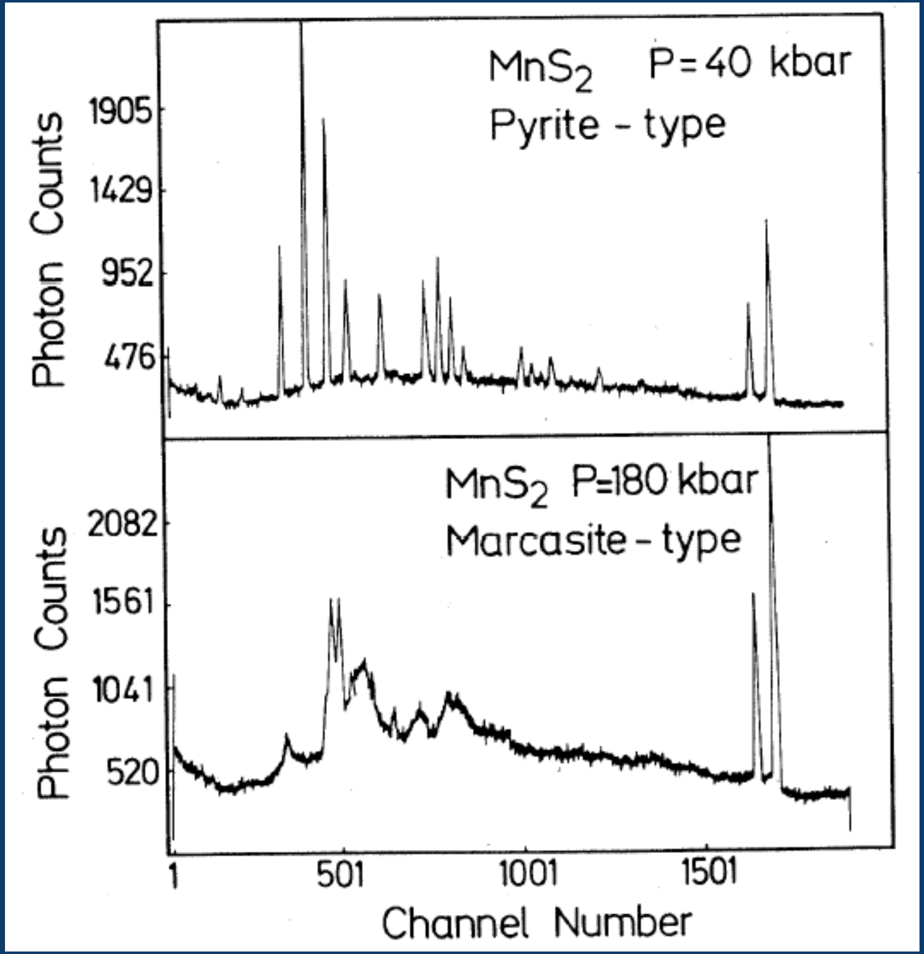
J. Phys. Chem. Solids **46**, 113 (1985)



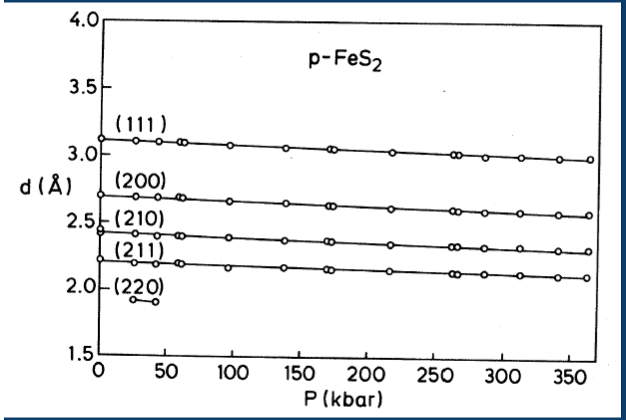


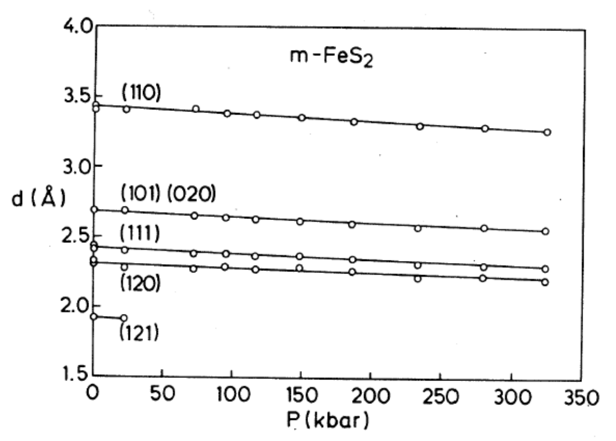
Synchrotron X-ray diffraction

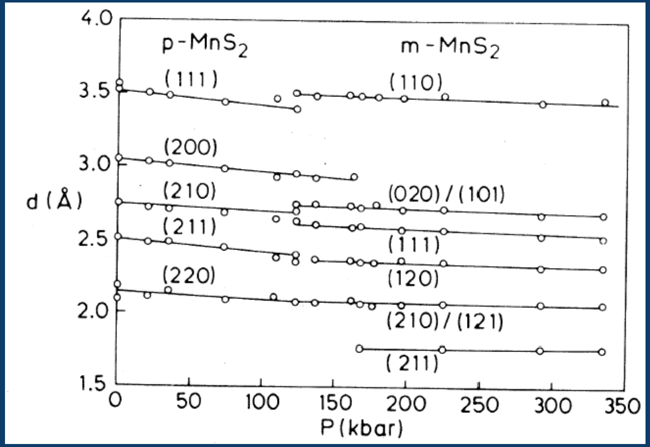
Physica **139&140B**, 305 (1986)

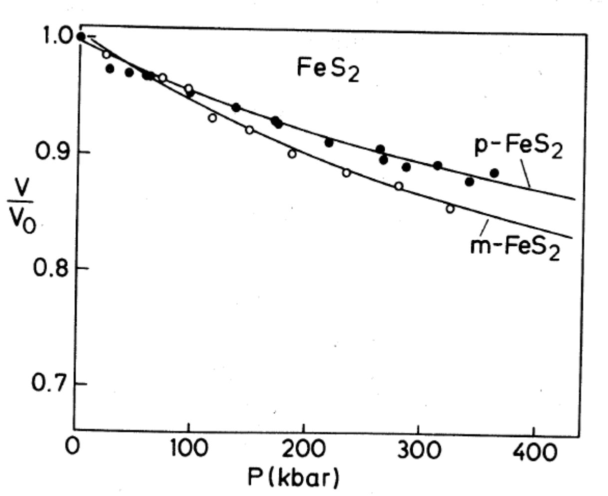


Pressure dependence of lattice spacing and volume

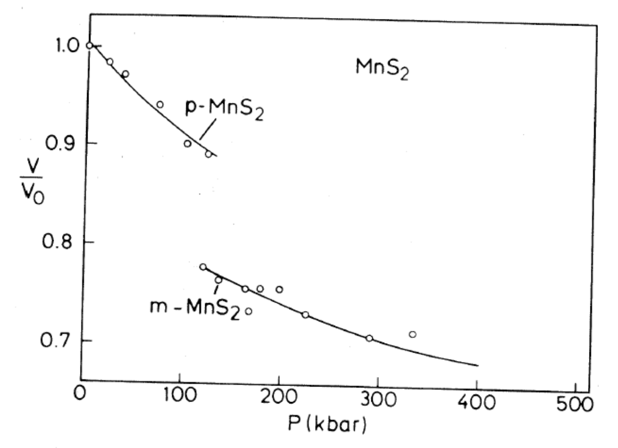








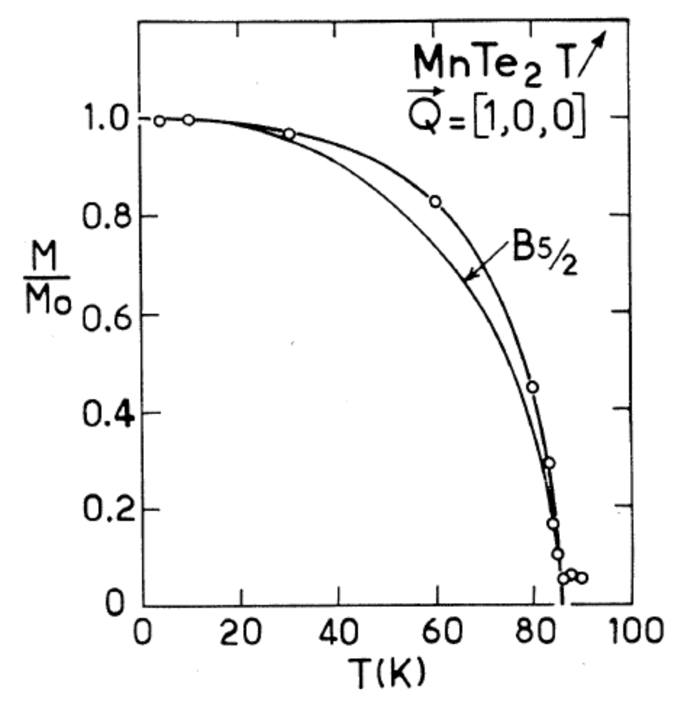
J. Phys. Chem. Solids **46**, 113 (1985)



Pyrite-marcasite transition with 15% volume contraction

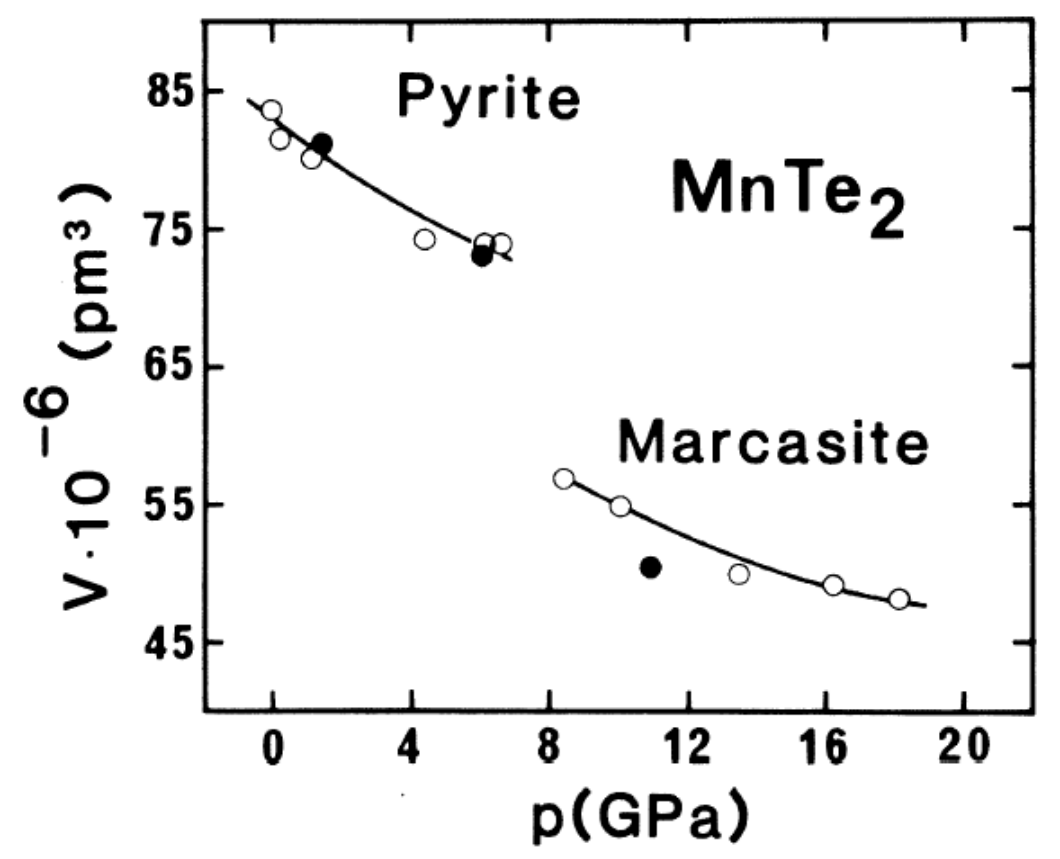
High pressure X-ray diffraction on $MnTe_2$

$MnTe_2$: type-I AF
$T_N = 87$ K



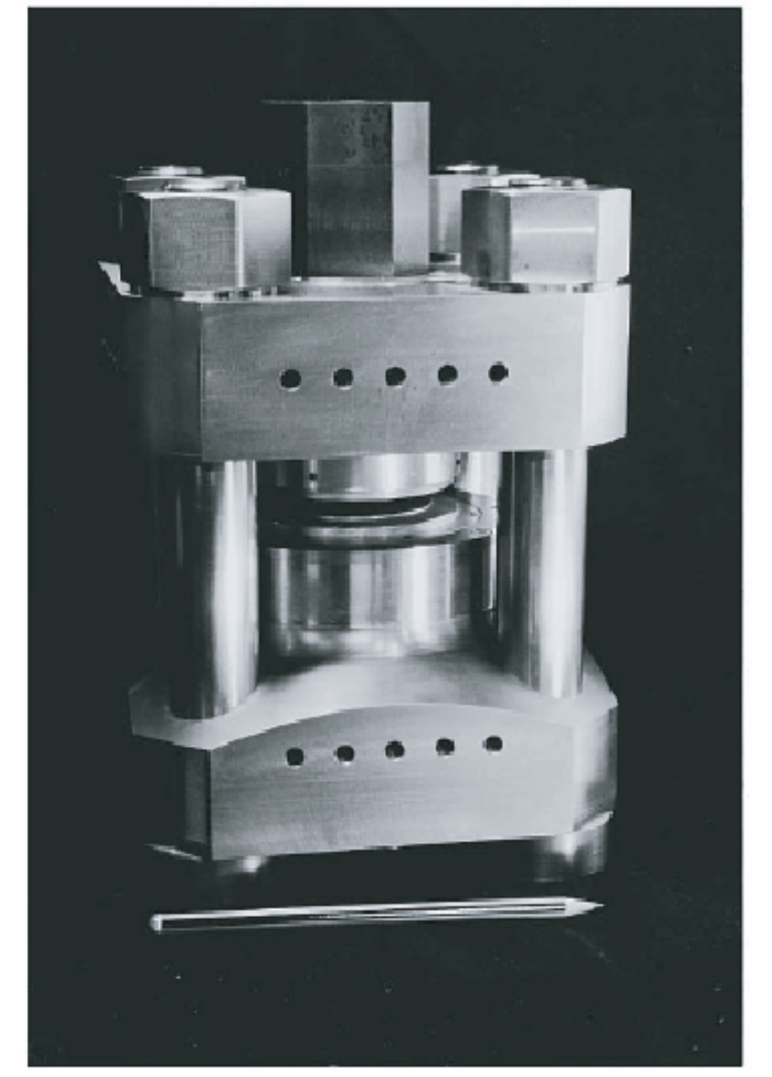
Phys. Lett. A **120**, 44 (1987).

Pressure-induced transition in$MnTe_2$

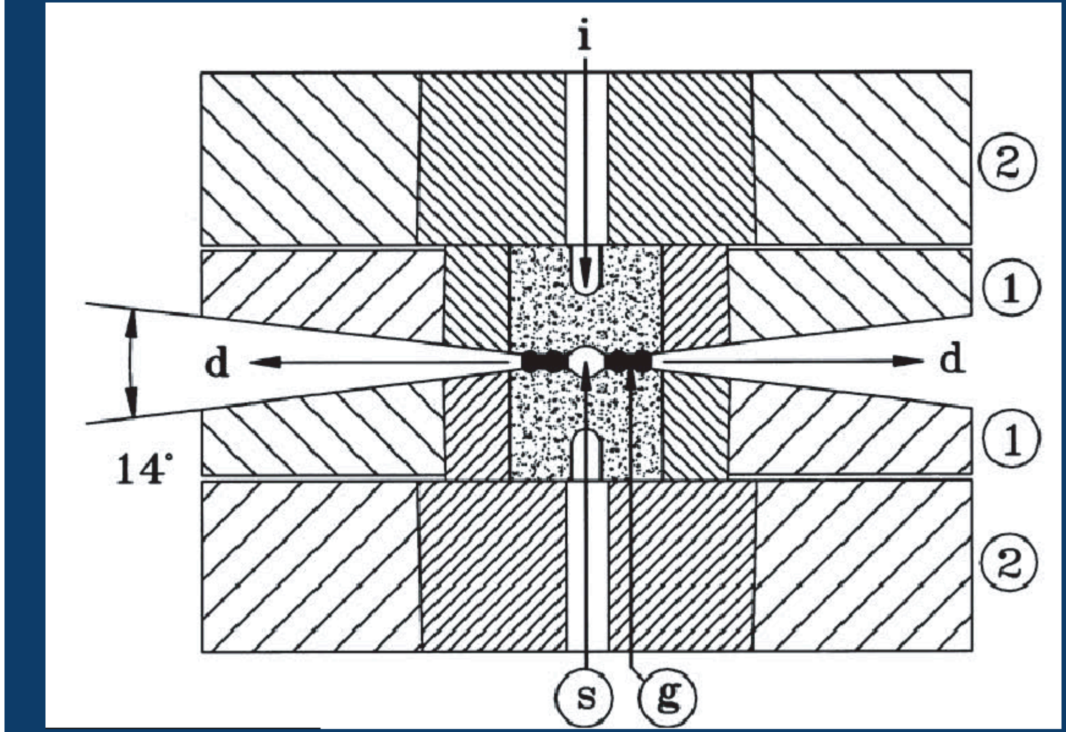


Phys. Lett. A **112**, 411 (1985).

Paris-Edinburgh high pressure cell



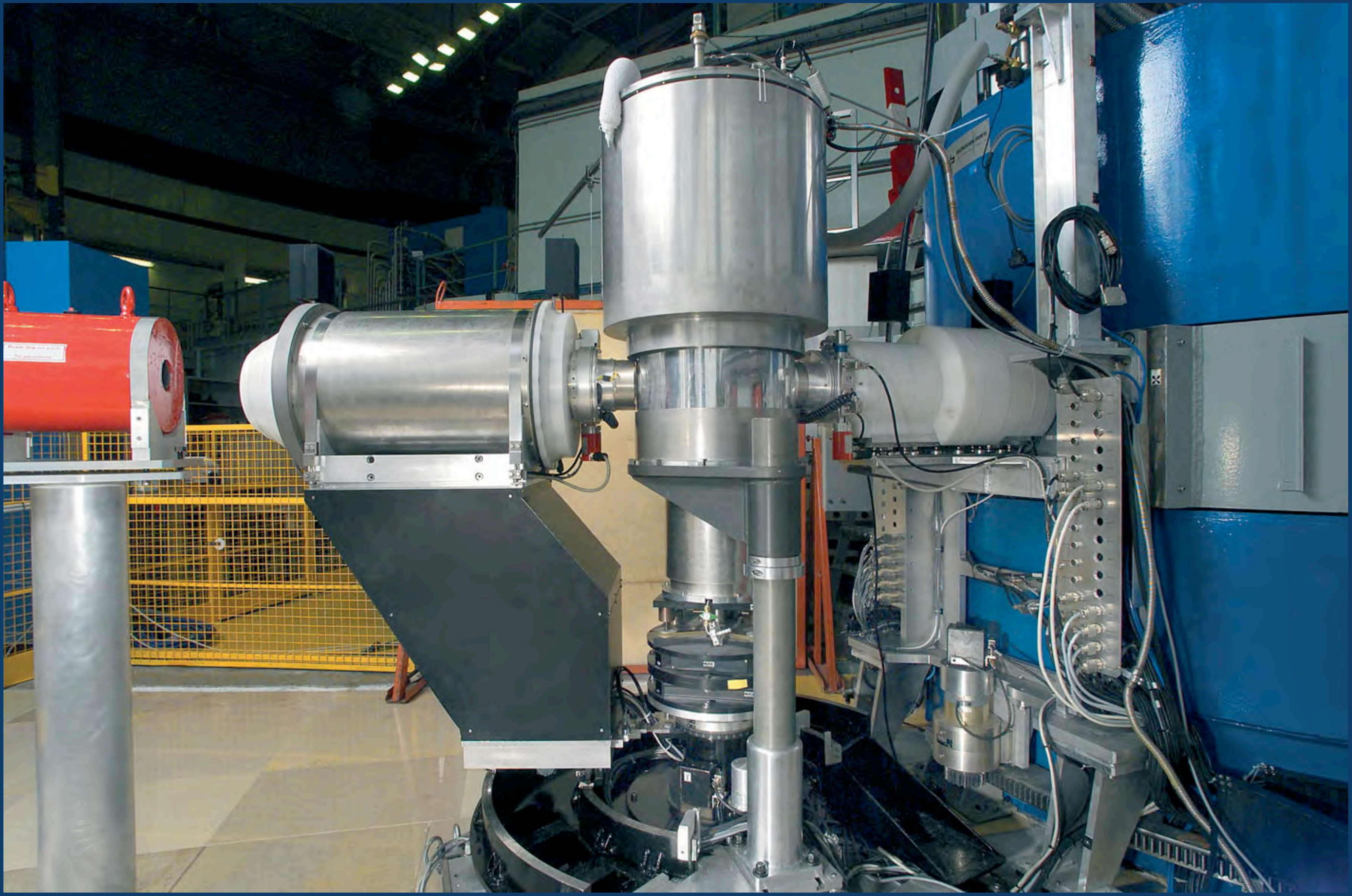
Pressure range:
1bar – 200 kbar at RT
1bar – 50 kar at 2 K



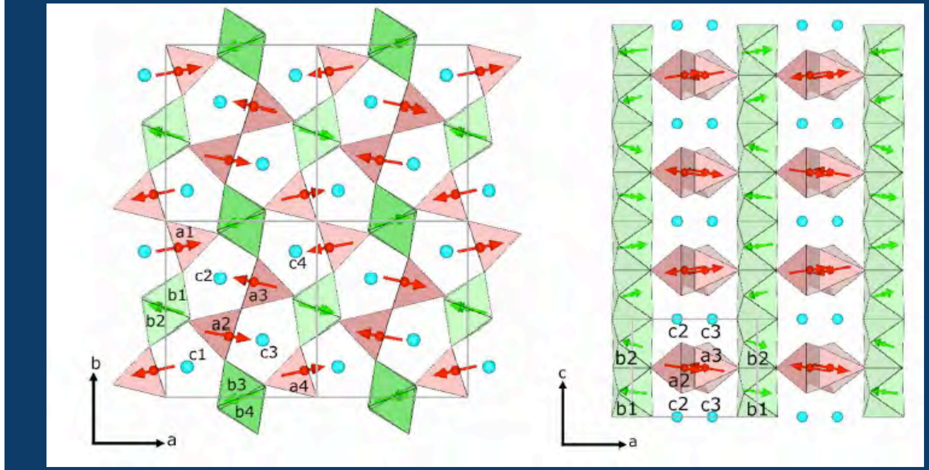
Zero magnetic field

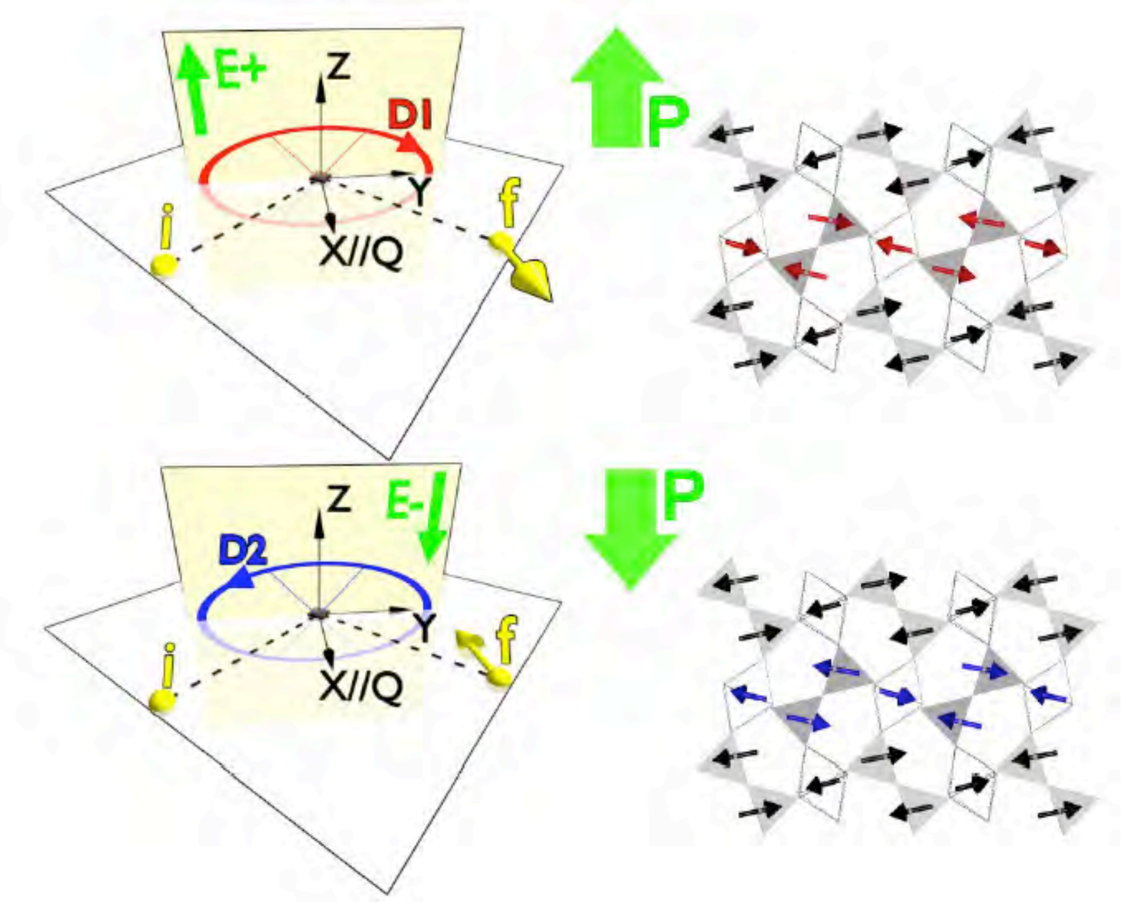
Electric field

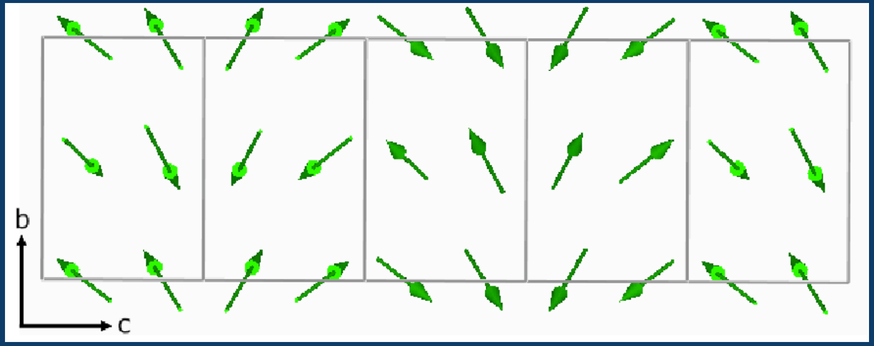
D3 with CRYOPAD



Electric field switching of AF domains in YMn_2O_5





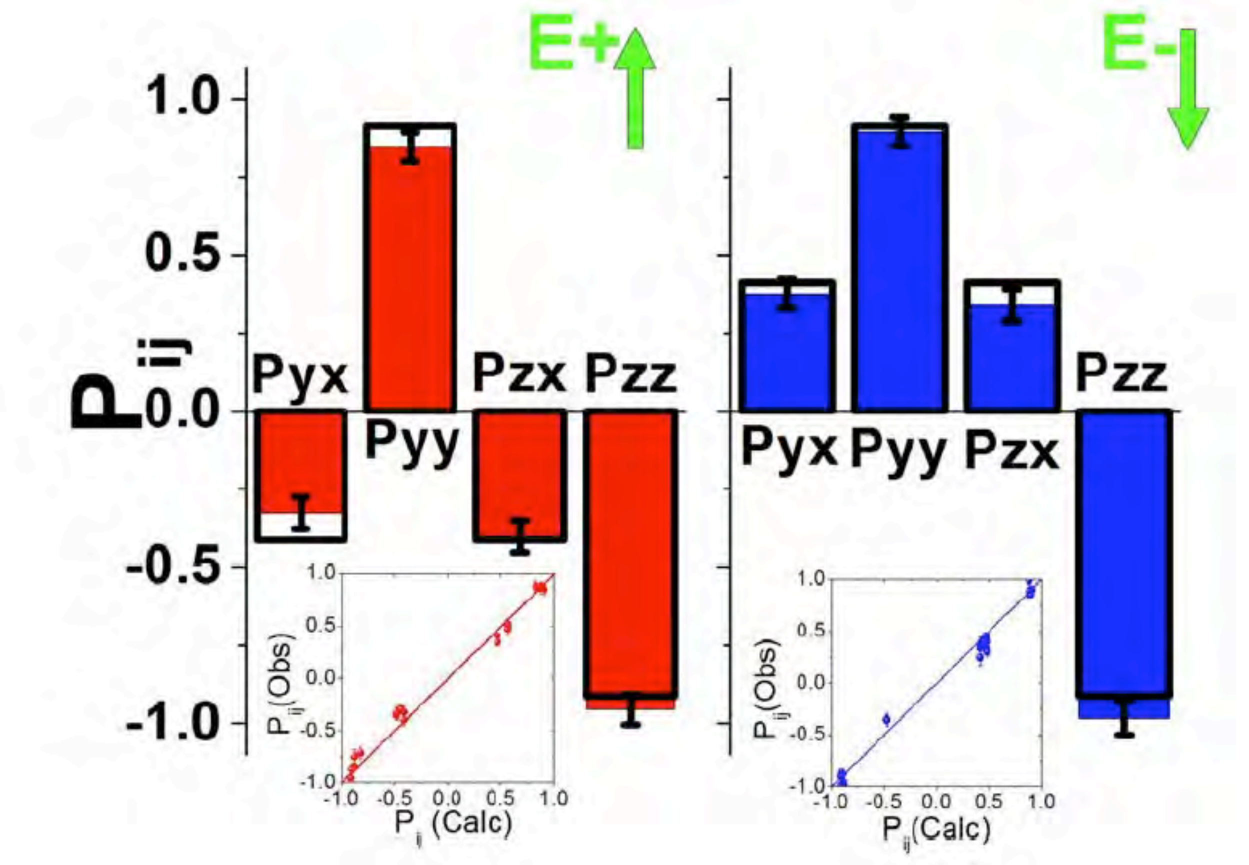


Magnetic exchange striction is mainly responsible of electric polarisation

Phys. Rev. Lett. (submitted)

Polarisation matrix elements

Q = (1/2,0,-5/4)   T = 25 K E = ± 2.2 kV/cm



$P_{ij} = (I^{ij}-I^{-ij})/ (I^{ij}+I^{-ij})$

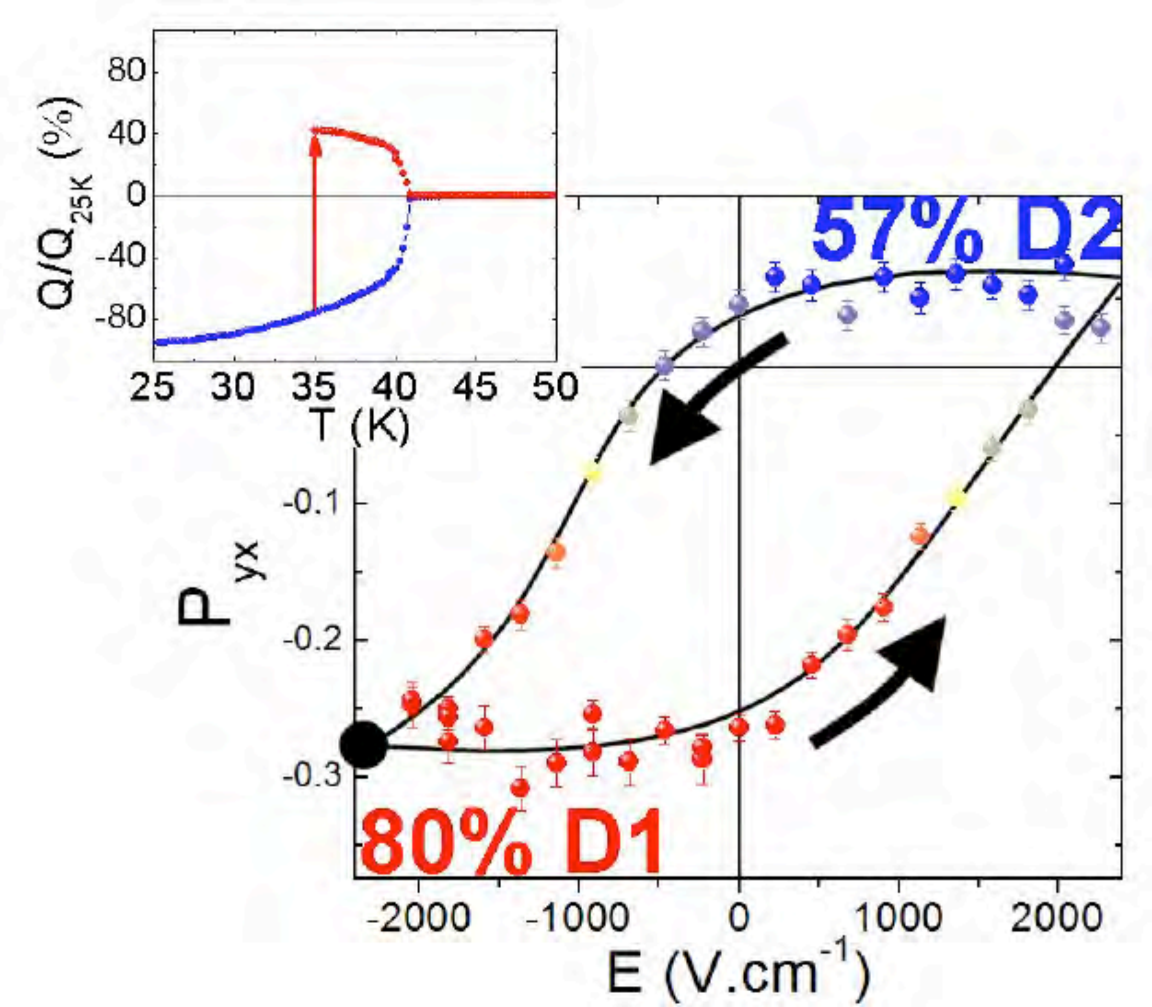
I^{ij} *: generalized cross-sections*

The indices i and j each refer to one of the three orthogonal directions defined by the experiment

Phys. Rev. Lett. (submitted)

Hysteresis loop measured on P_{yx}

$Q = (-1/2,0,-7/4)$ Field cooling $E = -2.2$ kV/cm



Conclusions

- *Neutron scattering is a very powerful condensed matter probe especially for structure and dynamics of magnetic materials.*

- *The realization of sample environment is relatively easier for neutron scattering than for X-ray scattering due to the transparency of neutrons through most engineering materials.*

- *Many outstanding new experiments can be done if the present limits can be extended by reasonably small amounts.*

Properties of some cryofluids

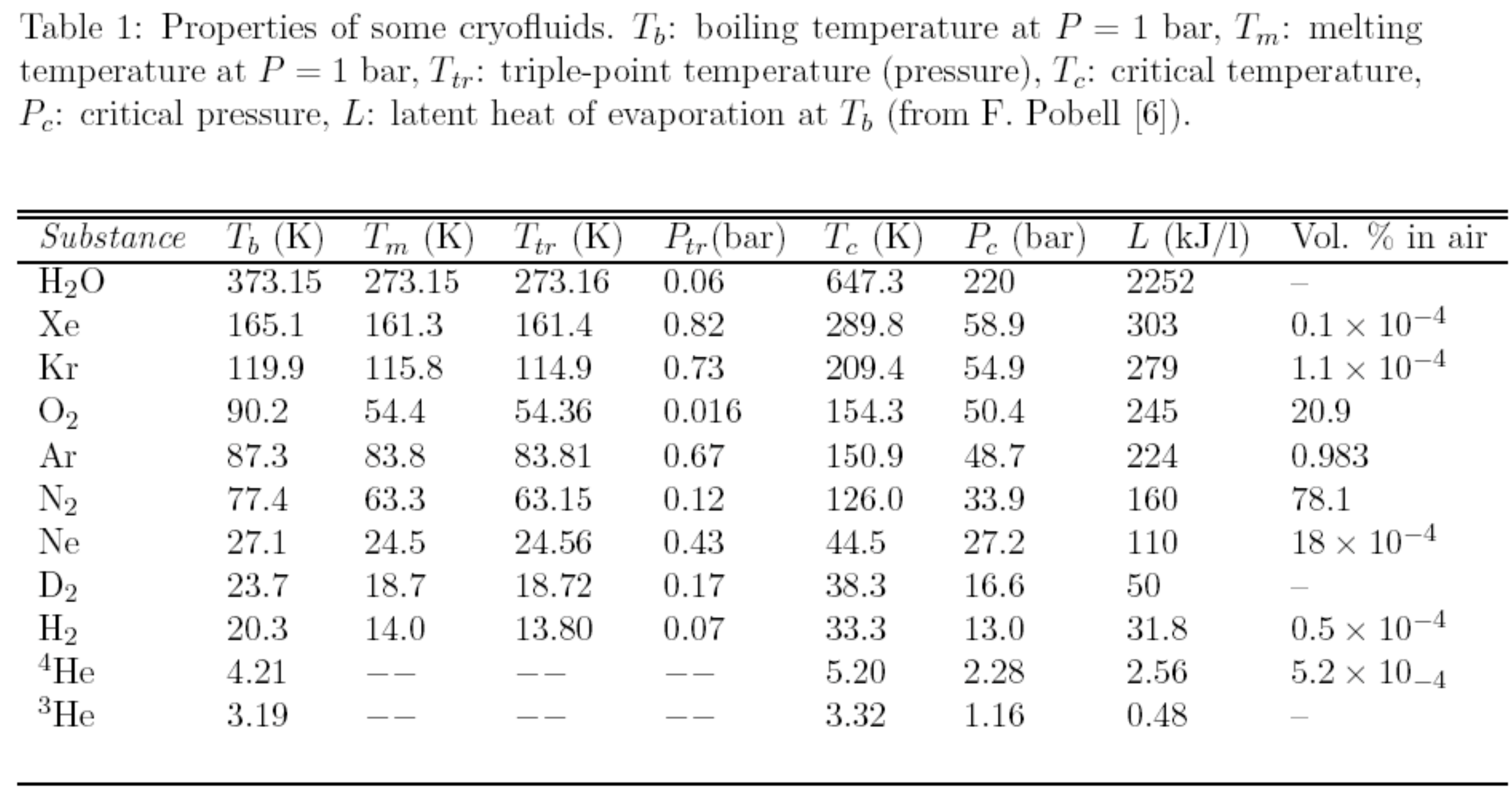


Table 1: Properties of some cryofluids. T_b: boiling temperature at $P = 1$ bar, T_m: melting temperature at $P = 1$ bar, T_{tr}: triple-point temperature (pressure), T_c: critical temperature, P_c: critical pressure, L: latent heat of evaporation at T_b (from F. Pobell [6]).

Substance	T_b (K)	T_m (K)	T_{tr} (K)	P_{tr}(bar)	T_c (K)	P_c (bar)	L (kJ/l)	Vol. % in air
H_2O	373.15	273.15	273.16	0.06	647.3	220	2252	–
Xe	165.1	161.3	161.4	0.82	289.8	58.9	303	0.1×10^{-4}
Kr	119.9	115.8	114.9	0.73	209.4	54.9	279	1.1×10^{-4}
O_2	90.2	54.4	54.36	0.016	154.3	50.4	245	20.9
Ar	87.3	83.8	83.81	0.67	150.9	48.7	224	0.983
N_2	77.4	63.3	63.15	0.12	126.0	33.9	160	78.1
Ne	27.1	24.5	24.56	0.43	44.5	27.2	110	18×10^{-4}
D_2	23.7	18.7	18.72	0.17	38.3	16.6	50	–
H_2	20.3	14.0	13.80	0.07	33.3	13.0	31.8	0.5×10^{-4}
^4He	4.21	– –	– –	– –	5.20	2.28	2.56	$5.2 \times 10_{-4}$
^3He	3.19	– –	– –	– –	3.32	1.16	0.48	–

Properties of cryofluids

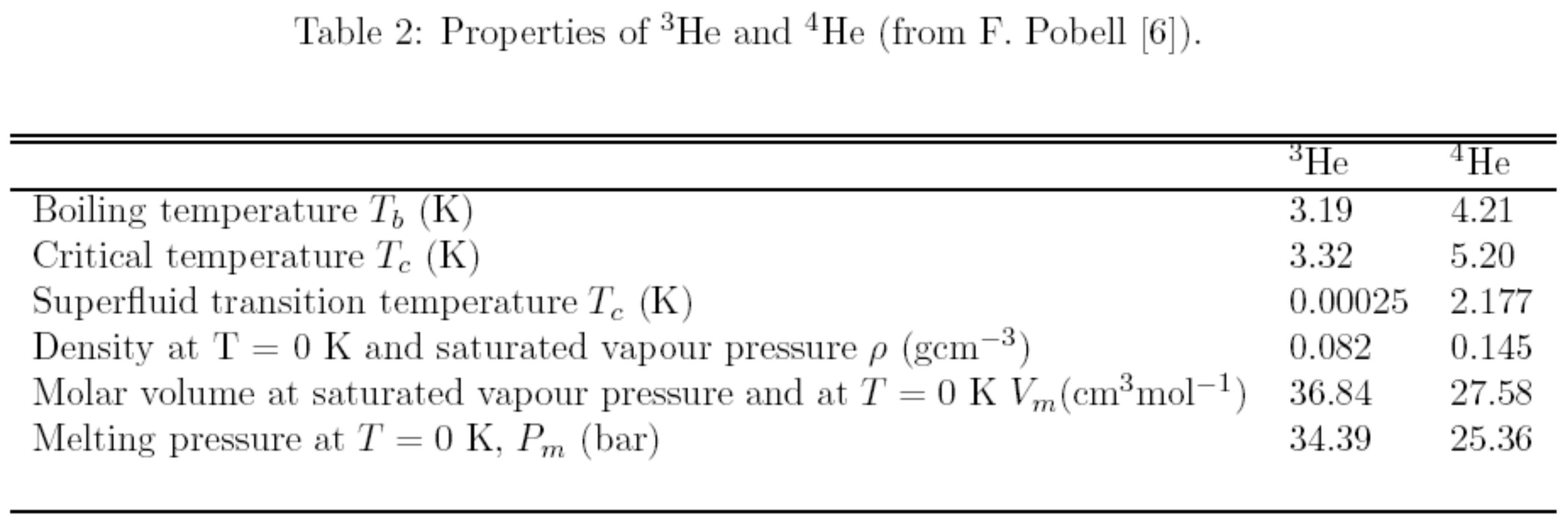


Table 2: Properties of ^{3}He and ^{4}He (from F. Pobell [6]).

	^{3}He	^{4}He
Boiling temperature T_b (K)	3.19	4.21
Critical temperature T_c (K)	3.32	5.20
Superfluid transition temperature T_c (K)	0.00025	2.177
Density at T = 0 K and saturated vapour pressure ρ (gcm^{-3})	0.082	0.145
Molar volume at saturated vapour pressure and at $T = 0$ K V_m(cm^{3}mol^{-1})	36.84	27.58
Melting pressure at $T = 0$ K, P_m (bar)	34.39	25.36

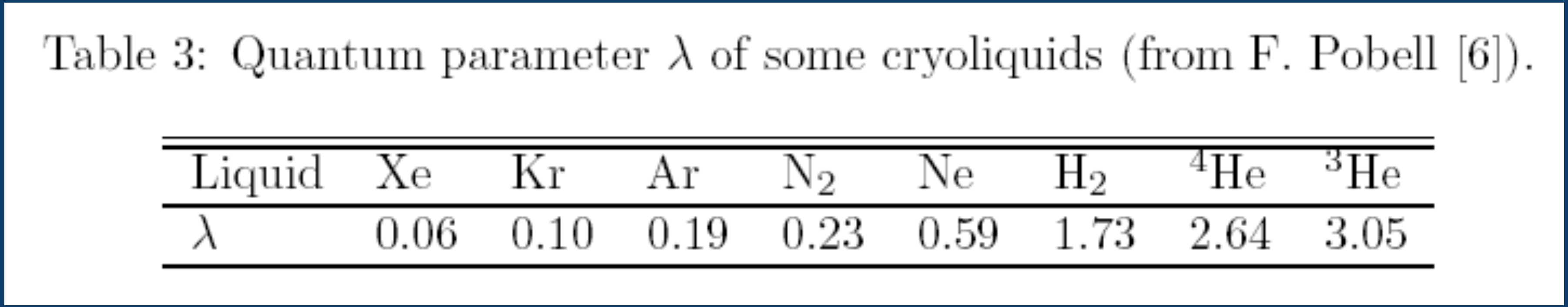


Table 3: Quantum parameter λ of some cryoliquids (from F. Pobell [6]).

Liquid	Xe	Kr	Ar	N_2	Ne	H_2	^{4}He	^{3}He
λ	0.06	0.10	0.19	0.23	0.59	1.73	2.64	3.05

High pressure, magnetism and modulated phases

- Modulated magnetic phases often arise due to the competing exchange interactions.
- Magnetic exchange interaction is a sensitive function of the bond distances and angles through orbital overlap.
- Pressure is known to modifies the bond distances and bond angles thereby causing modifications of exchange interactions.
- Pressure can modify the electronic structure such as p-f hybridization effects in rare-earth materials.
- The modulated magnetic phases and lock-in transitions are especially sensitive to pressure.

Modulated magnetic phases

Reciprocal lattice description:

F: $k_0 = (0,0,0)$

AF: $k_0=(1/2,1/2,1/2)$

Modulated: $k = k_0 + \delta$

Satellites $G = H + - k$

For reviews see:
Science 264, 226 (1994)
Int. J. Mod. Phys. B 7, 3225 (1993)

Book: Neutron scattering from magnetic materials
ed. T. Chatterji, Elsevier.(2006)

Microscopic origin of modulated phases:

- In general competing exchange interactions can lead to modulated phases: Axial next-nearest-neighbour-Ising (ANNNI) model
- A delicate balance between crystal-field splitting and strength of p-f hybridization: CeSb ($EuAs_3$)
- Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction: rare-earth metals
- Fermi surface nesting: Spin density wave (SDW) in Cr
- Dzyaloshinskii-Moriya anisotropic interaction: long period modulated phase in Mnsi

Magnetic properties of CuO

- The strongly correlated transition metal oxide CuO is closely related with the high temperature superconducting cuprate materials.
- The magnetic coupling between 3d Cu^{2+} spins through the Cu-O-Cu bond is believed to play an important role for super conductivity in high temperature superconductors.
- The application of pressure modifies significantly the Cu-O-Cu bond angle
- The strength and sign of the exchange interaction depends on the Cu-O-Cu bond angle through the orbital overlap

High spin - low spin transition in MnS_2

Experiment:

J. Phys. Chem. Solids **46**, 113 (1985); Physica **139&140B**, 305 (1986)

On the basis of volume contraction we suggested that the p-m transition in MnS_2 transition is accompanied by high spin - low spin (HS-LS) and most probably insulator-metal transition as well.

DFT +U calculations:

J. Phys.: Condens. Matter **15**, 979 (2003); PRB **73**, 115201 (2006)

HS-LS in MnS_2 has been predicted to occur around 110 - 160 kbar

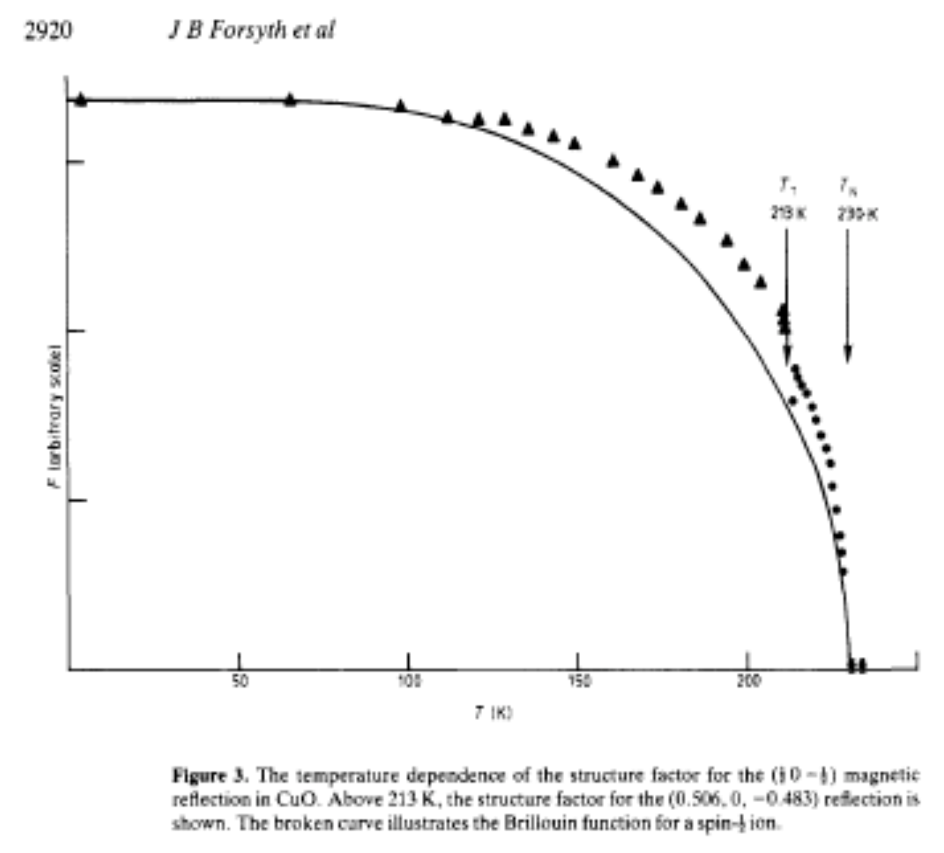
Mn^{2+}: d^5 high spin ($3t_{2g}$(up) $2e_g$(up), $S = 5/2$)
low spin (($3t_{2g}$(up) $2e_g$(down), $S = 1/2$)

Magnetic structures of CuO

Unpolarised neutron diffraction

Forsyth et al.,J. Phys. C 21, 2917 (1988)

Single crystal, unpolarized neutron diffraction

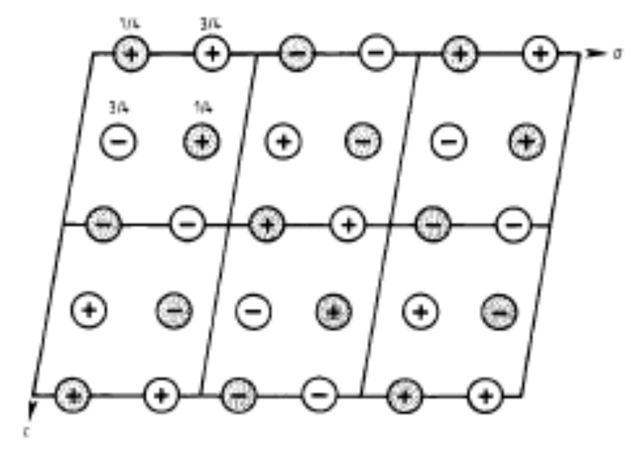


2920 *J B Forsyth et al*

Figure 3. The temperature dependence of the structure factor for the (½ 0 −½) magnetic reflection in CuO. Above 213 K, the structure factor for the (0.506, 0, −0.483) reflection is shown. The broken curve illustrates the Brillouin function for a spin-½ ion.

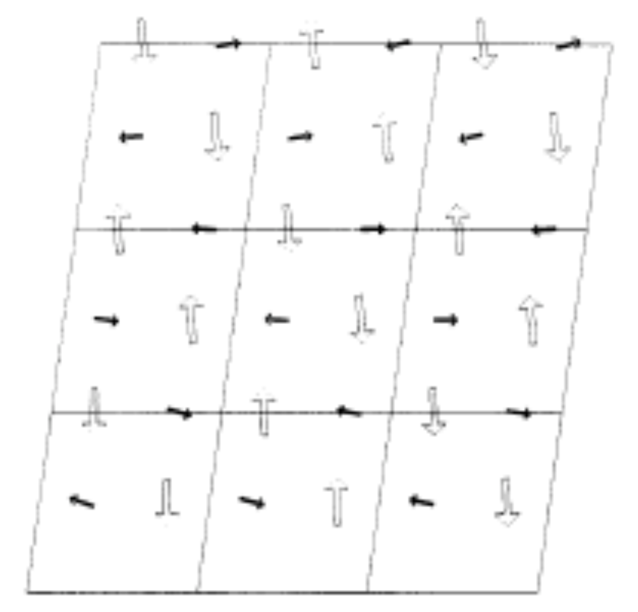
AF phase

m // b



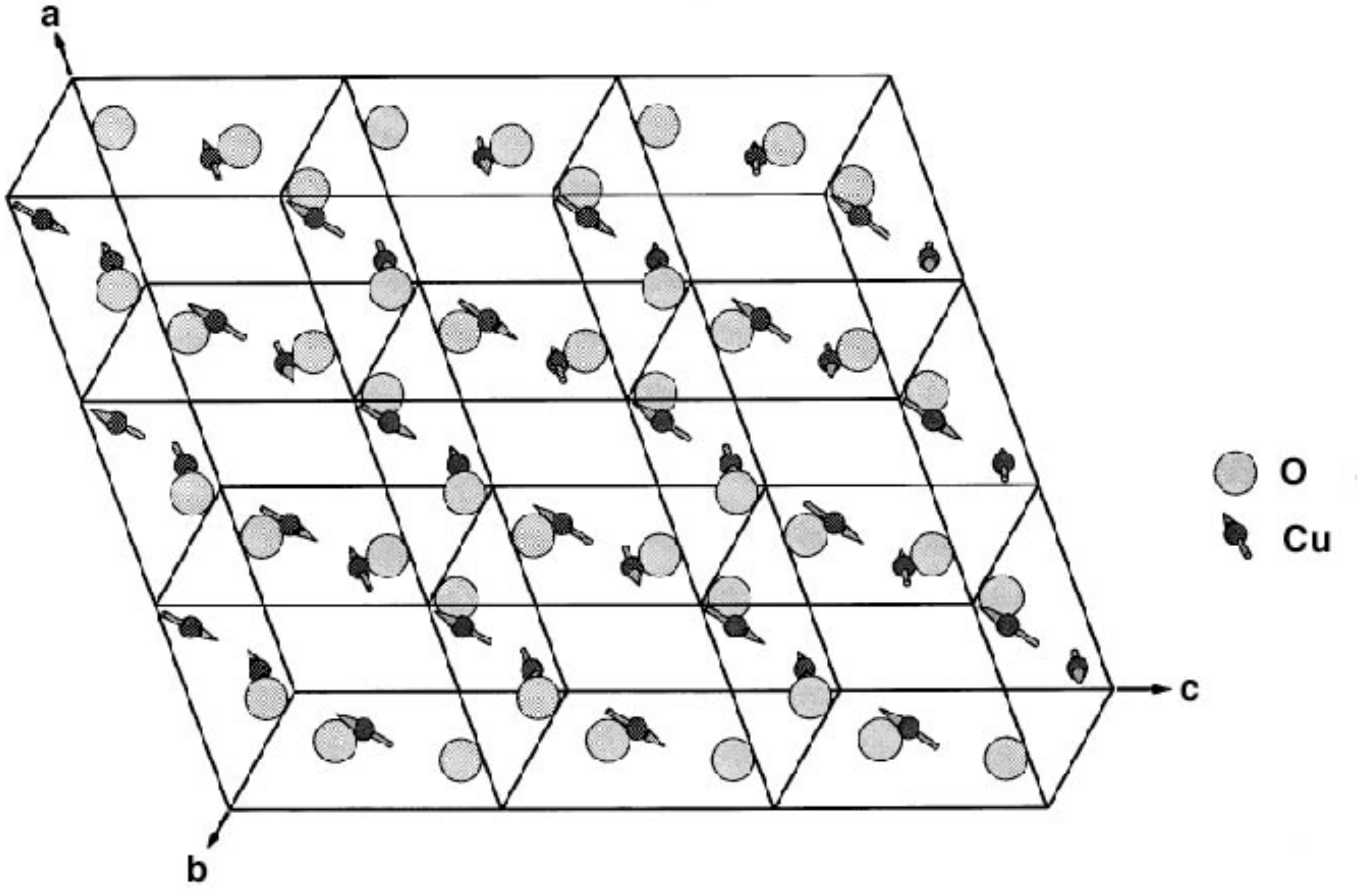
IC phase

m in (a-c) plane



Magnetic structures of CuO

Neutron polarimetry: Brown et al. J. Condens. Mat. 3, 4281 (1991)



Correction:
Spin component along b

Why we need higher pressure

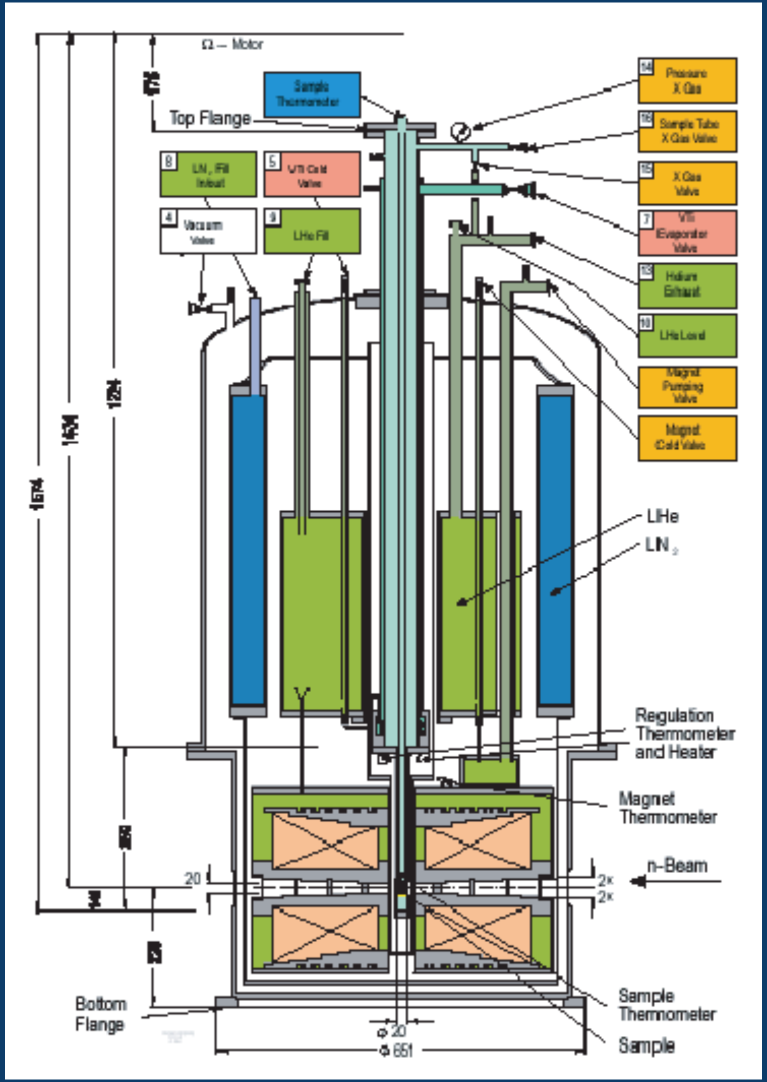
➨ Pressure modifies drastically the stabilities of the magnetic phases in rare-earth magnetic systems CeSb and EuAs3 because T_N and J are small.

➨The ordering temperature T_N and magnetic exchange interaction J of CuO is relatively high, so to cause drastic modifications of magnetic phases much higher pressures are needed.

➨The maximum pressure which could be generated at ILL for neutron diffraction experiments has increased significantly enabling us to do further high pressure experiments on CuO and other interesting electronic materials.

Cross-sections through the 15 Tesla cryomagnet

Horizontal cross section



Vertical cross section