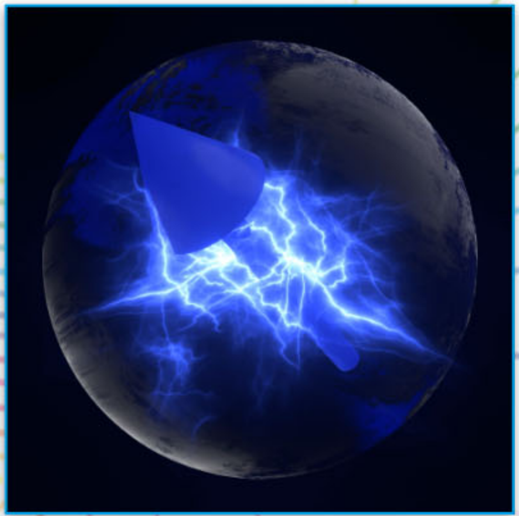
Spherical Neutron Polarimetry

A pioneering ILL technique and its unique contribution to multiferroics research



Navid Qureshi

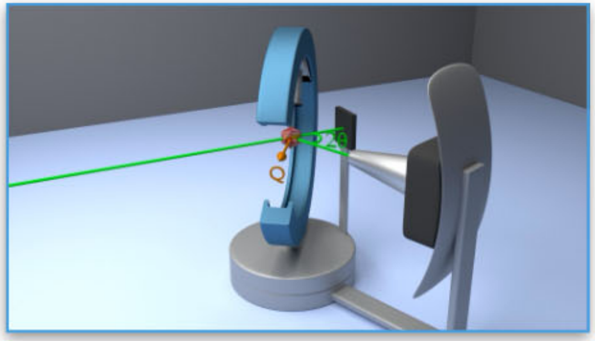
Outline

Content of the presentation

- Introduction to SNP
- The **Cryo**genic **P**olarisation **A**nalysis **D**evice
- Key contributions to magnetoelectric and multiferroic systems
- Conclusions

Introduction to SNP

Motivation



THE PROBLEM

Unpolarised neutrons only give access to the modulus of the magnetic interaction vector $\mathbf{M}_\perp$ via the observed intensity $I \sim \mathbf{M}_\perp \mathbf{M}_\perp^* = |M_\perp|^2$.

$$\mathbf{M}_\perp(\mathbf{Q}) = \hat{\mathbf{Q}} \times (\mathbf{M} \times \hat{\mathbf{Q}}) \qquad \mathbf{M}(\mathbf{Q}) = \sum_j \mathbf{S}_j f_j(\mathbf{Q}) \exp(i\mathbf{Q}\mathbf{r}_j)$$

THE RAY OF HOPE

In 1963 Blume and Maleev independently publish their equations relating the final neutron polarisation to generalised cross sections.

Blume (1963) Phys. Rev. **130** 1670

Maleev et al. (1963) Sov. Phys. Solid State. **4** 2533

THE DREAM

Be able to measure all the terms in these equations precisely.

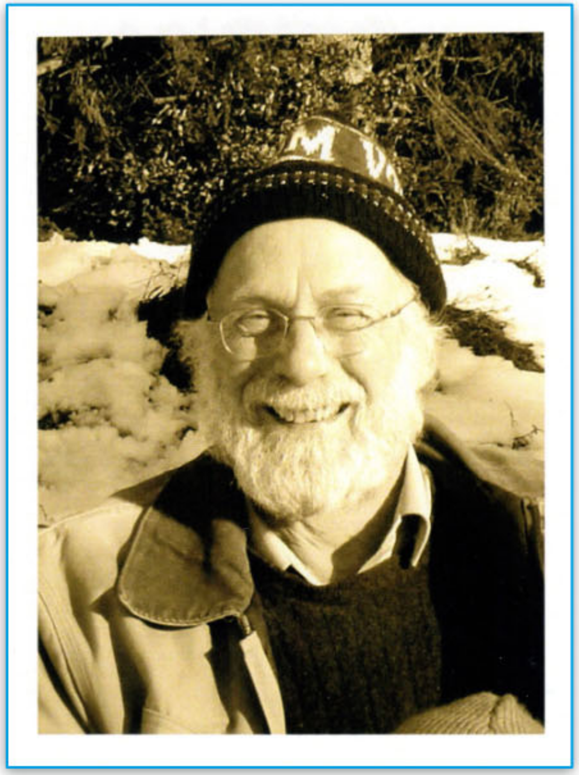
Introduction to SNP

The dream come true

THANK YOU FRANCIS !!!

- Polarising neutron beams with Heusler alloy
- Cryoflipper (no wavelength and stray field dependency)
- **Cryo**genic **P**olarisation **A**nalysis **D**evice for SNP

  (with major contributions by S. Pujol and P. J. Brown)
- ^{3}He spin filter cell and pumping station



Introduction to SNP

Milestones (by Francis Tasset)

- 1963 Blume and Maleev independently publish the equations
- 1969 Riste, Moon and Koehler analyse polarisation
- 1973 Alperin demonstrates that 3D polarisation analysis is possible
- 1976 FT's sabbatical at ORNL working on superconducting Nb
- 1977 FT's cryoflipper based on superconducting screens
- 1988 First Cryopad taking advantage of Meissner shields
- 1993 FT introduces the term "Spherical Neutron Polarimetry"
- 1995 Cryopad II
- 1998 SNP is finally accepted and adopted by the experts
- 2002 Cryopad III (first project of ILL Millennium Programme)

$$\begin{aligned}\mathbf{P}'I = {} & \mathbf{P}(N^2 - \mathbf{M}_\perp \mathbf{M}_\perp^*) \\ & + 2\Re[\mathbf{M}_\perp(\mathbf{P} \cdot \mathbf{M}_\perp^*)] \\ & + 2\Re(N^* \mathbf{M}_\perp) \\ & + \mathbf{P} \times 2\Im(N^* \mathbf{M}_\perp) \\ & - \Im(\mathbf{M}_\perp \times \mathbf{M}_\perp^*)\end{aligned}$$

$$\begin{aligned}I = {} & N^2 + \mathbf{M}_\perp \mathbf{M}_\perp^* \\ & + 2\Re(\mathbf{P} \cdot N^* \mathbf{M}_\perp) \\ & + \mathbf{P} \cdot \Im(\mathbf{M}_\perp \times \mathbf{M}_\perp^*)\end{aligned}$$

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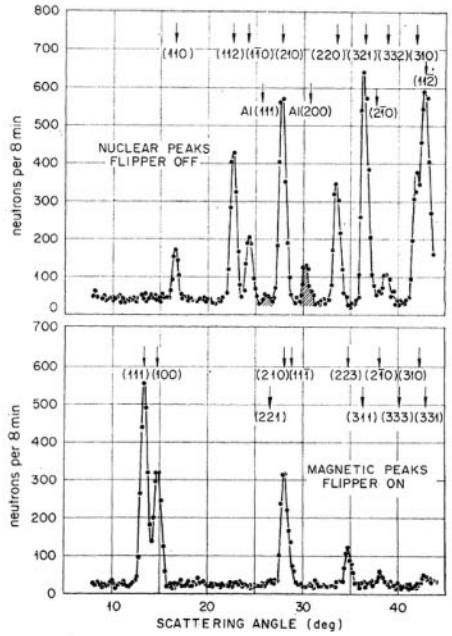

Moon et al. (1969) Phys. Rev. **181** 920

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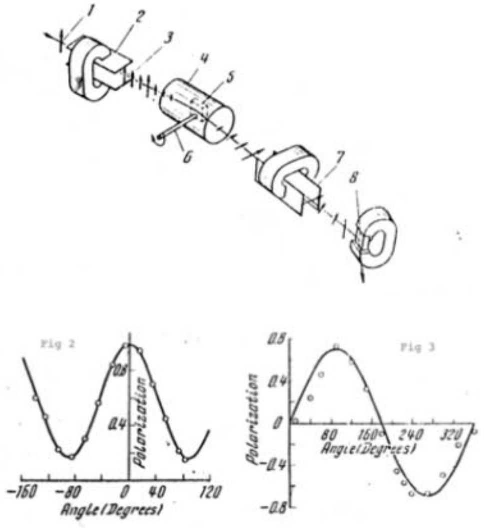

Alperin (1973) International Conference on Magnetism, Moscow, ed., Proc. ICM-73

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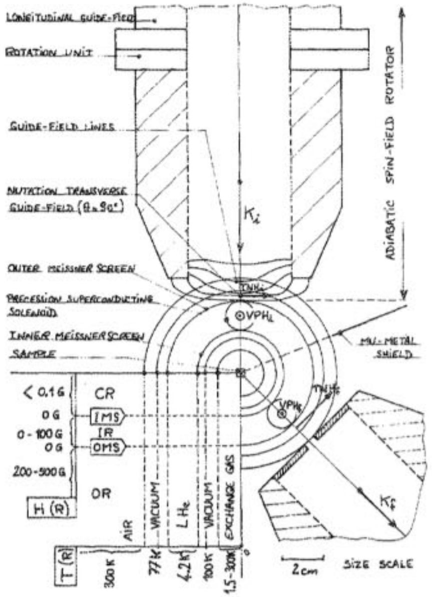
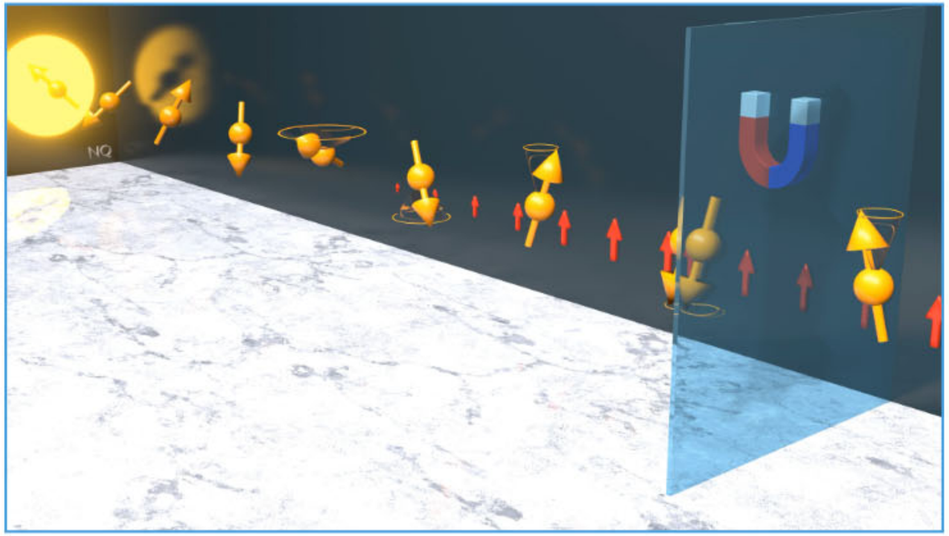


F.Tasset et al. (1988) J. Appl. Phys. **63** 3606

The Cryopad

Manipulation of polarised neutron beams

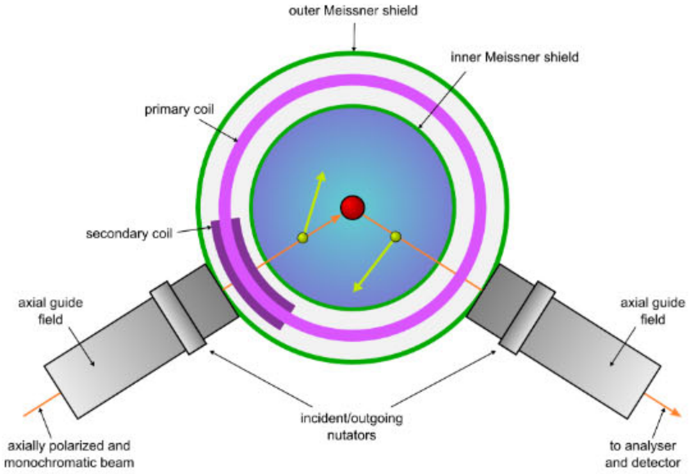


Francis Tasset's polarisation lab

The Cryopad

Manipulation of polarised neutron beams

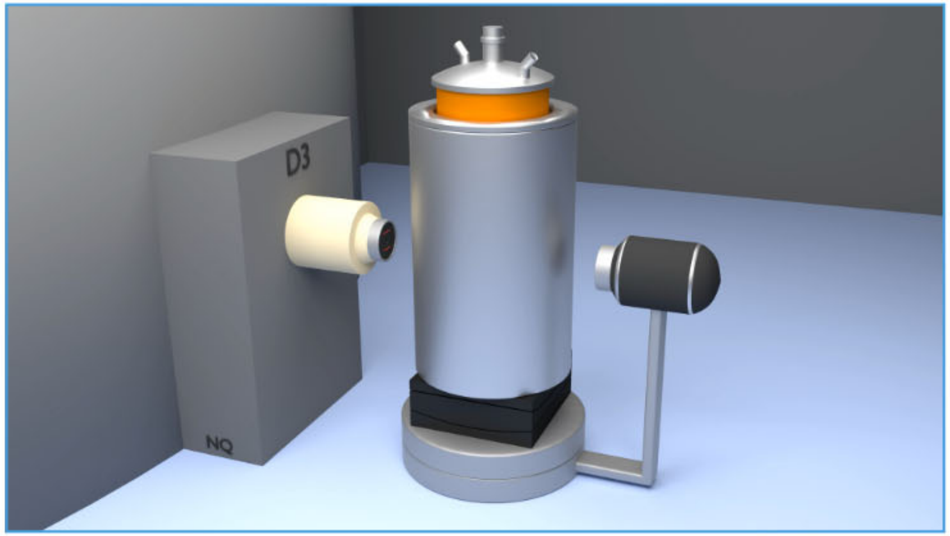
top view



mounted on D3

The Cryopad

Making magic happen



Local coordination system:

x || **Q**
z vertical
y completes right-handed set

$$\mathbf{M}_{\perp,x} = 0$$

$$\mathbf{P}_i \parallel x \qquad \mathbf{P}_f \parallel y$$

$$P_{f,i} = P_{yx} = \frac{n^+ - n^-}{n^+ + n^-}$$

The Cryopad

The polarisation matrix

Final neutron polarisation is related to initial one by $\mathbf{P}_f = \mathcal{P}\mathbf{P}_i + \mathbf{P}'$

rotational part

created/annihilated polarisation

$$\mathbf{P}_{f,i} = \begin{pmatrix} p_{fx}\frac{p_{ix}(N^2-M_\perp^2)-J_{yz}}{I_x} & p_{fx}\frac{-p_{iy}J_{nz}-J_{yz}}{I_y} & p_{fx}\frac{p_{iz}J_{ny}-J_{yz}}{I_z} \\ p_{fy}\frac{p_{ix}J_{nz}+R_{ny}}{I_x} & p_{fy}\frac{p_{iy}(N^2+M_{\perp y}^2-M_{\perp z}^2)+R_{ny}}{I_y} & p_{fy}\frac{p_{iz}R_{yz}+R_{ny}}{I_z} \\ p_{fz}\frac{-p_{ix}J_{ny}+R_{nz}}{I_x} & p_{fz}\frac{p_{iy}R_{yz}+R_{nz}}{I_y} & p_{fz}\frac{p_{iz}(N^2-M_{\perp y}^2+M_{\perp z}^2)+R_{nz}}{I_z} \end{pmatrix}$$

Easily distinguish nuclear, magnetic, chiral and interference terms.

$$I_x = N^2 + M_\perp^2 + p_{ix}J_{yz} \quad R_{yz} = 2\Re(M_{\perp y}M_{\perp z}^*) \quad R_{nz} = 2\Re(NM_{\perp z}^*)$$
$$I_y = N^2 + M_\perp^2 + p_{iy}R_{ny} \quad J_{yz} = 2\Im(M_{\perp y}M_{\perp z}^*) \quad J_{ny} = 2\Im(NM_{\perp y}^*)$$
$$I_z = N^2 + M_\perp^2 + p_{iz}R_{nz}$$

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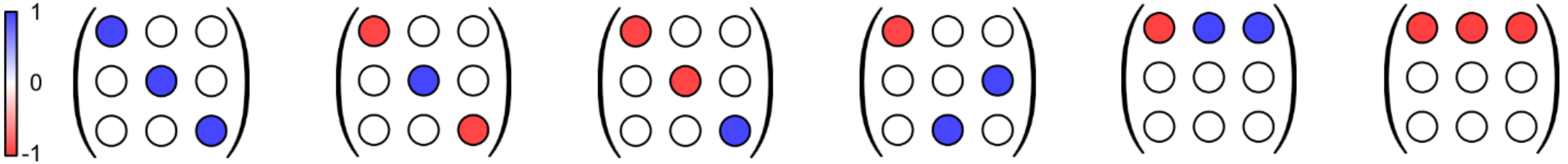


nuclear

purely magnetic $M_{\perp z} = 0$

purely magnetic $M_{\perp y} = 0$

purely magnetic $M_{\perp y} = M_{\perp z}$

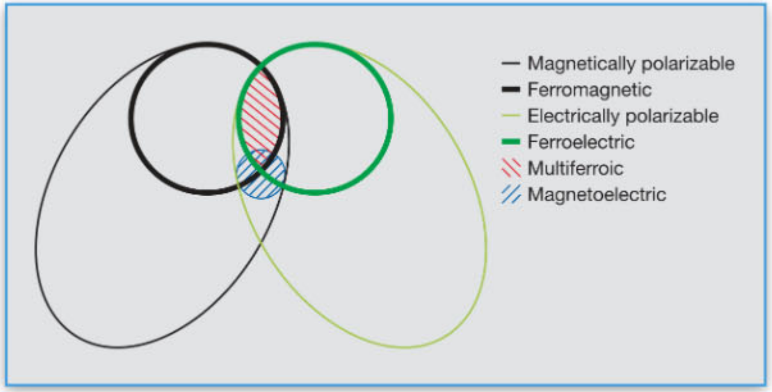
left-handed helix $iM_{\perp y} = M_{\perp z}$

right-handed helix $iM_{\perp y} = -M_{\perp z}$

Examples

Magnetoelectric and multiferroic materials

- Magnetoelectric effect predicted by P. Curie in 1894
- Crosstalk between magnetisation and electric polarisation
- Multiferroics possess at least two (anti)ferroic orders
- Used as magnetic field sensors and transducers
- Immense potential for non-volatile data storage applications (faster and consumes less energy)
- spin-transfer torque: ~ 10 fJ
- capacitive ME device: ~ 1 aJ (10^4 less)



Eerenstein et al. (2006) Nature **442** 759

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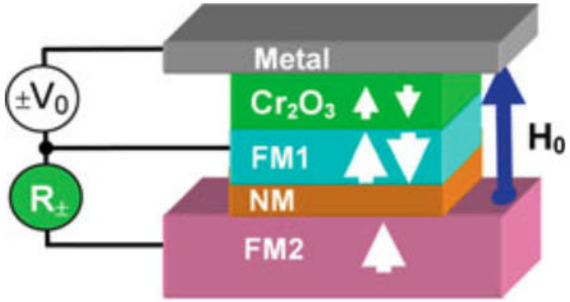
Magnetic Random Access Memory



Kleemann and Binek (2013)
Multiferroic and magnetoelectric materials

Examples

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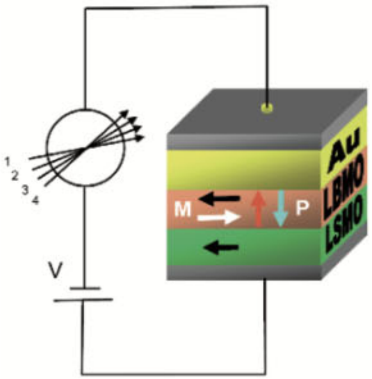
4-bit logic



Kleemann and Borisov (2013)
Multiferroic and magnetoelectric materials for spintronics

Examples

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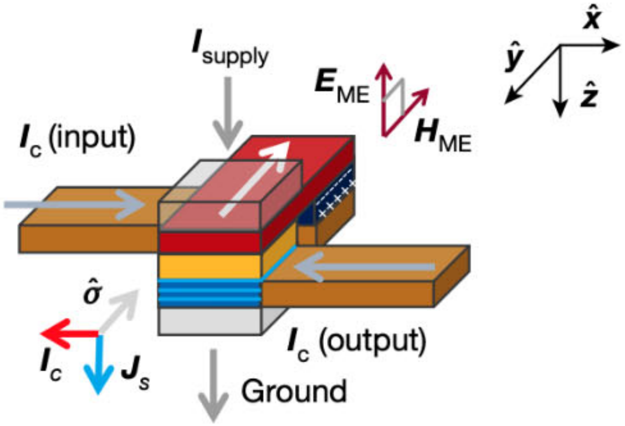
MESO logic device, Intel (MagnetoElectricSpinOrbit)



Manipatruni et al. (2019) Nature **565** 35

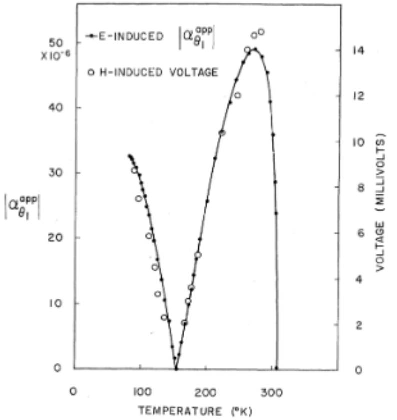
Examples

Cr_2O_3 - the prototype magnetoelectric

- Predicted by Dzyaloshinskii in 1960
- First observation of linear magnetoelectric effect
- $P_i = \alpha_{ij} H_j$ or $M_i = \alpha_{ji} E_j$
- Corundum structure, space group $R\bar{3}c$, T_N = 307 K
- Magnetic symmetry ($\bar{3}'m'$) breaks spatial and time-inversion

Astrov (1960) Sov. Phys. JETP **11** 708

FIG. 2



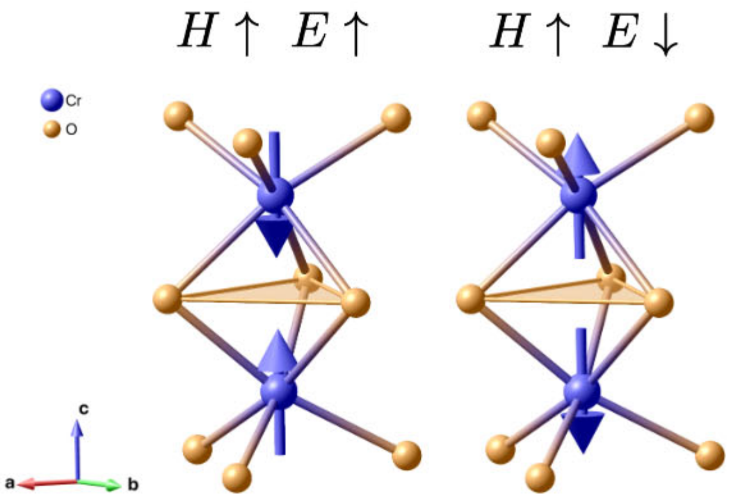
Rado and Folen (1961) Phys. Rev. Lett **7** 310

Examples

Cr_2O_3 - sign of magnetoelectric coefficient

- Problem: presence of 180° magnetic domains
- Annealing under field achieves domain selection
- Domains indistinguishable with unpolarised neutrons
- SNP can tell the difference!
- *b* vertical, (-1 0 2): P_i || *z r*otates towards +/- *x*
- information about sign of magnetoelectric coefficient

Brown, Forsyth and Tasset (1998) J. Phys.: Condens. Matter. **10** 663



Examples

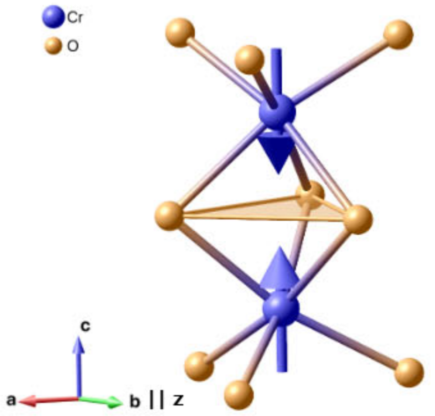
Cr_2O_3 - sign of magnetoelectric coefficient

$$\mathbf{P}_{f,i} = \begin{pmatrix} p_{fx}\frac{\cancel{p_{ix}(N^2-M_{\perp}^2}) \cancel{-J_{yz}}}{I_x} & p_{fx}\frac{\cancel{-p_{iy}J_{nz}-J_{yz}}}{I_y} & p_{fx}\frac{p_{iz}J_{ny}\cancel{-J_{yz}}}{I_z} \\ p_{fy}\frac{\cancel{p_{ix}J_{nz}}+\cancel{R_{ny}}}{I_x} & p_{fy}\frac{p_{iy}(N^2+M_{\perp y}^2-\cancel{M_{\perp z}^2})\cancel{+R_{ny}}}{I_y} & p_{fy}\frac{\cancel{p_{iz}R_{yz}}+\cancel{R_{ny}}}{I_z} \\ p_{fz}\frac{-p_{ix}J_{ny}+\cancel{R_{nz}}}{I_x} & p_{fz}\frac{\cancel{p_{iy}R_{yz}+R_{nz}}}{I_y} & p_{fz}\frac{\cancel{p_{iz}(N^2-M_{\perp y}^2}\cancel{+M_{\perp z}^2})+\cancel{R_{nz}}}{I_z} \end{pmatrix}$$

- *b* || *z*, moments along *c* —> no *z* component
- (-1 0 2) at room temperature: $N \approx M_{\perp y}$
- $\Im(N) = 0 \quad \Re(M_{\perp}) = 0$ —> No real interference terms

Brown, Forsyth and Tasset (1998) J. Phys.: Condens. Matter. **10** 663

$$R_{ny} = 2\Re(NM_{\perp y}^*) \quad J_{ny} = 2\Im(NM_{\perp y}^*)$$



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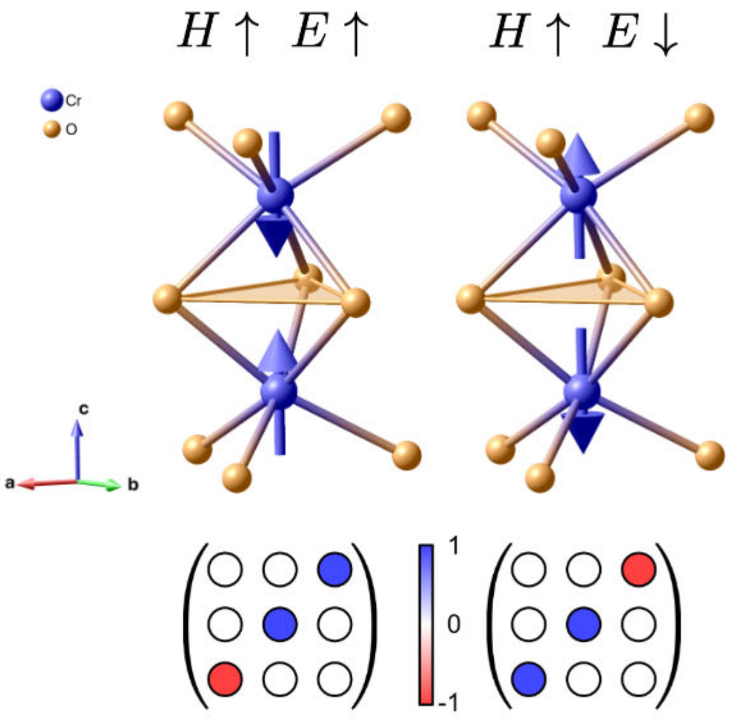
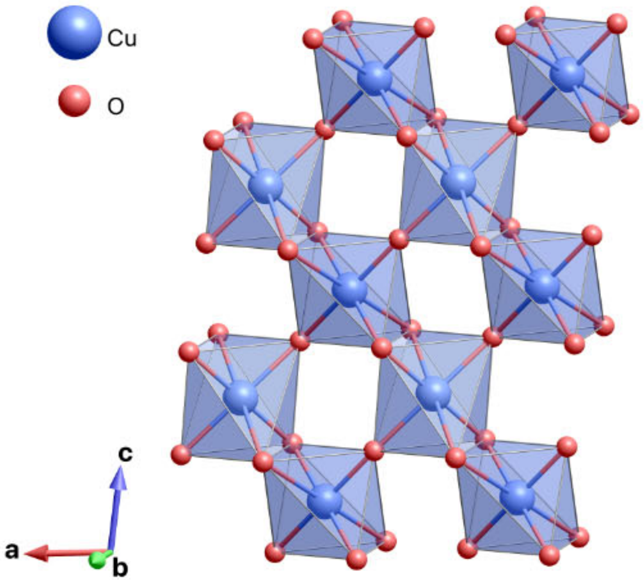


Examples

CuO - a high-T multiferroic

- so far the only known binary multiferroic compound
- monoclinic space group *C2/c*
- spiral magnetic ordering induces electric polarisation at 230 K
- DFT + MC: applying pressure drives multiferroic state towards RT
- recently confirmed by neutron diffraction under pressure



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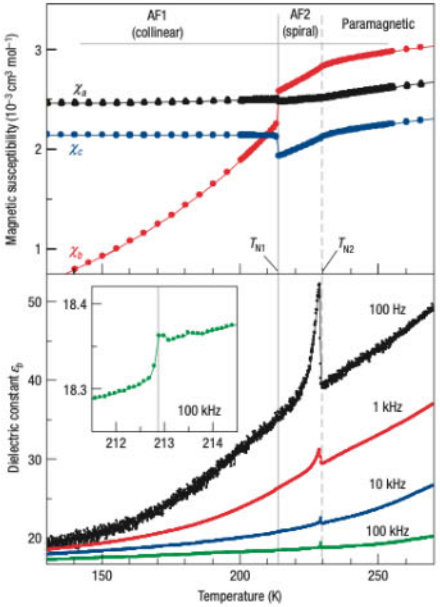

Kimura et al. (2008) *Nat. Mater.* **7** 291

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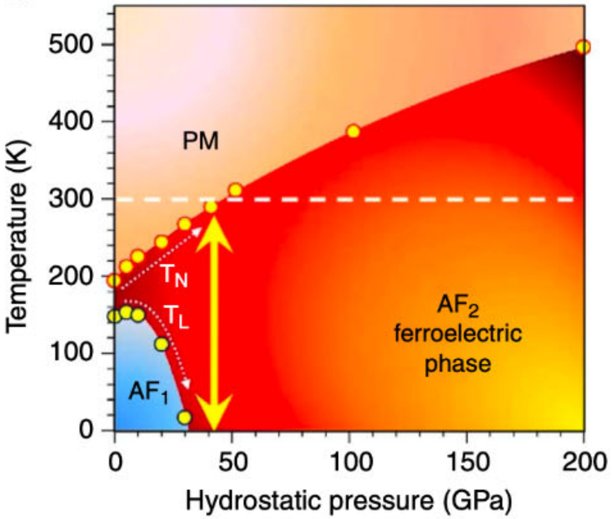

Rocquefelte et al. (2013) *Nat. Mater.* **4** 2511

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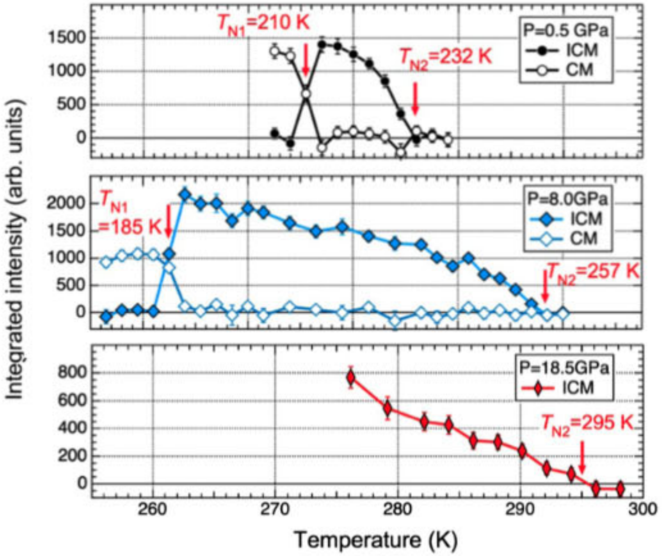
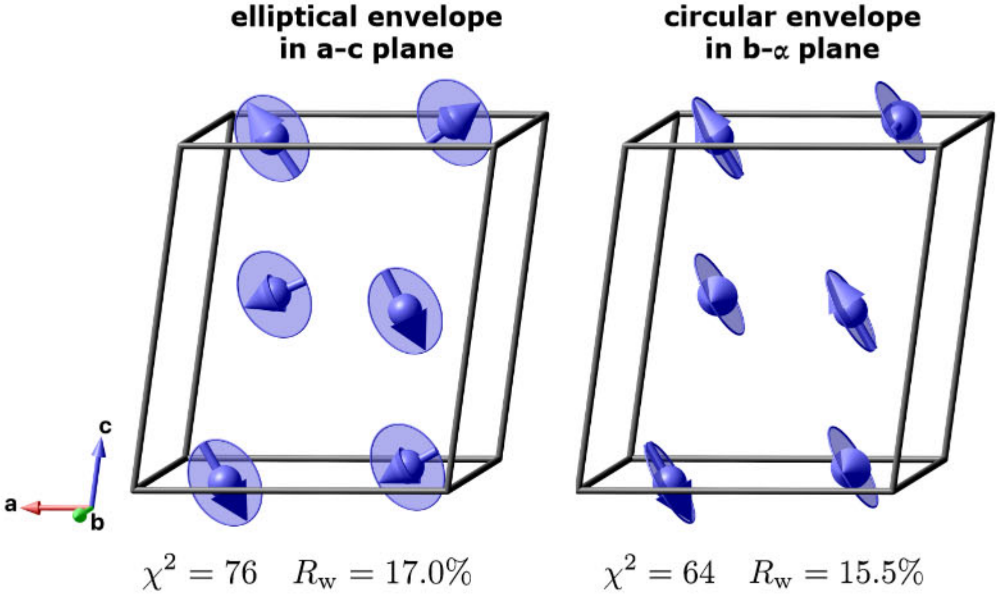


Terada et al. (2022) *Phys. Rev. Lett.* **129** 217601

Examples

CuO - a high-T multiferroic

- CuO is a building block of high-T_C cuprates
- magnetism in CuO —> hole pairing mechanism?
- unpolarised neutrons: model ambiguity



$\chi^2 = 76 \quad R_\mathrm{w} = 17.0\%$ $\qquad$ $\chi^2 = 64 \quad R_\mathrm{w} = 15.5\%$

Forsyth, Brown et al. (1988) J. Phys. C: Solid State Phys **21** 2917

Brown, ..., Forsyth, ... and Tasset (1991) J. Phys.: Condens. Matter. **3** 4281

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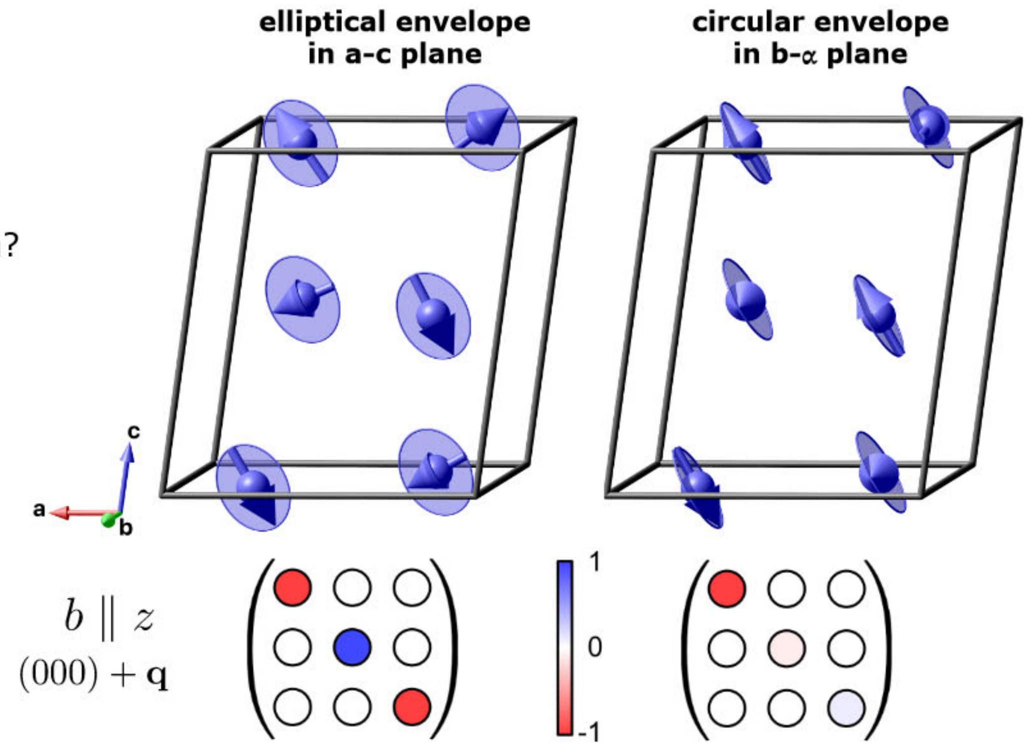
- magnetism in CuO —> hole pairing mechanism?
- unpolarised neutrons: model ambiguity
- correct model determined by SNP
- superior to unpolarised neutrons especially for weak reflections and non-collinear structures



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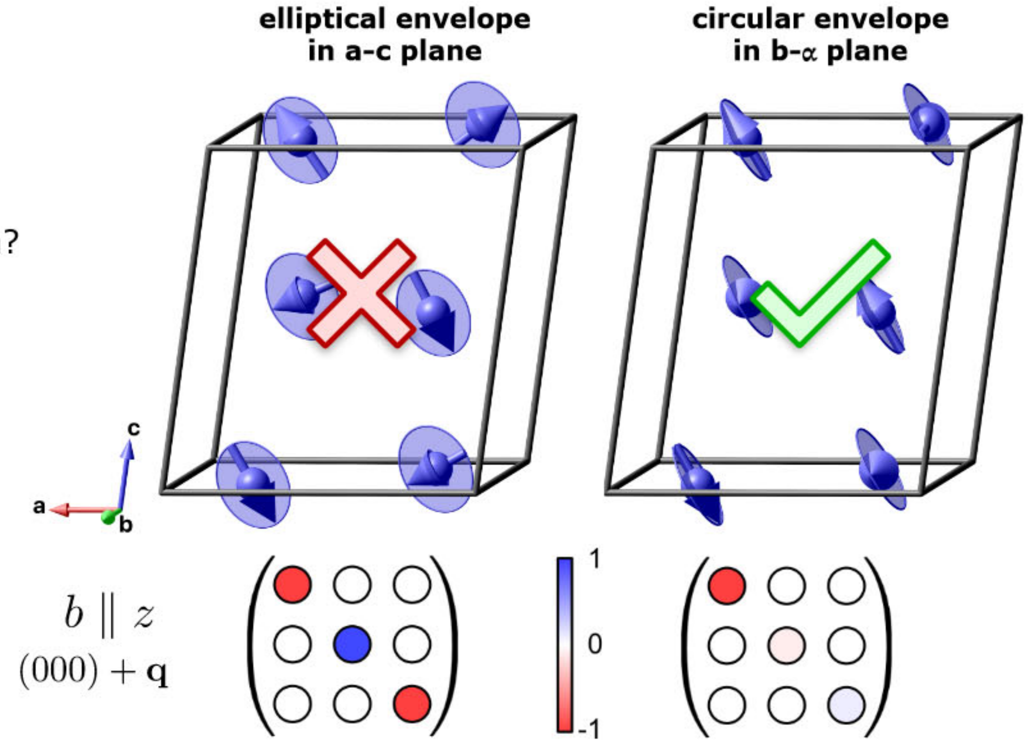
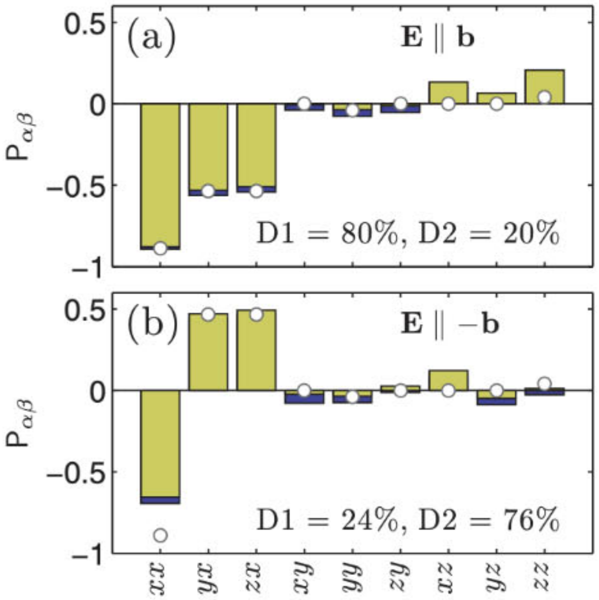


Examples

CuO - switching behaviour

- strong coupling between magnetic order and electric polarisation
- electric field control of chiral domains
- magnetic chirality is inaccessible with unpolarised neutrons
- SNP can tell the difference



Babkevich et al. (2012) Phys. Rev.B **85** 134428

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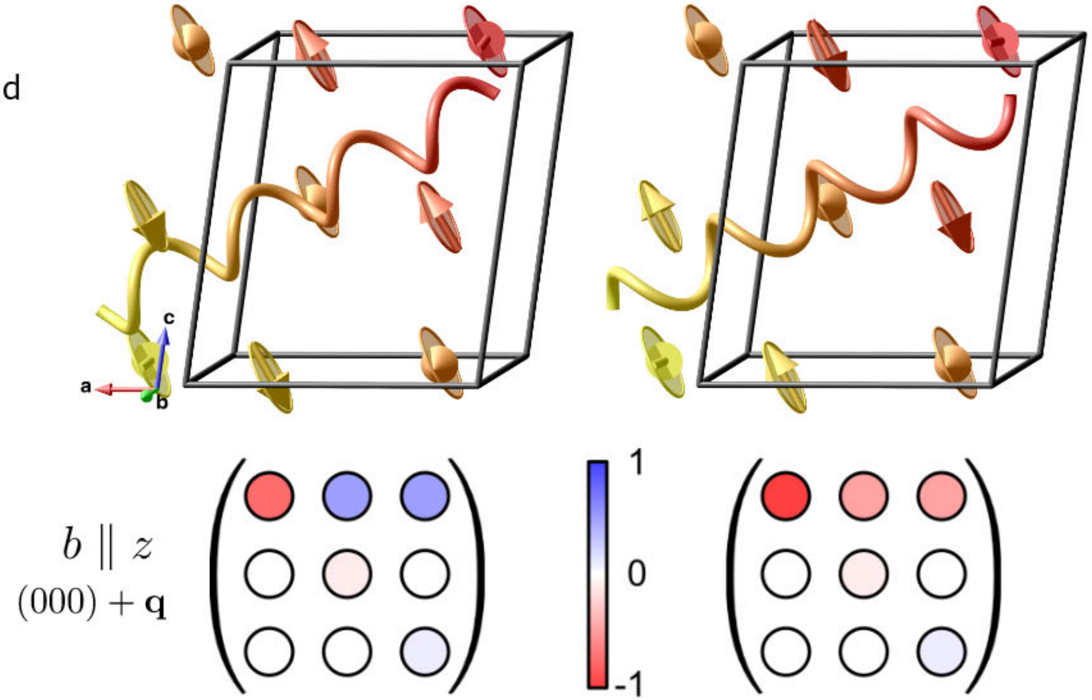
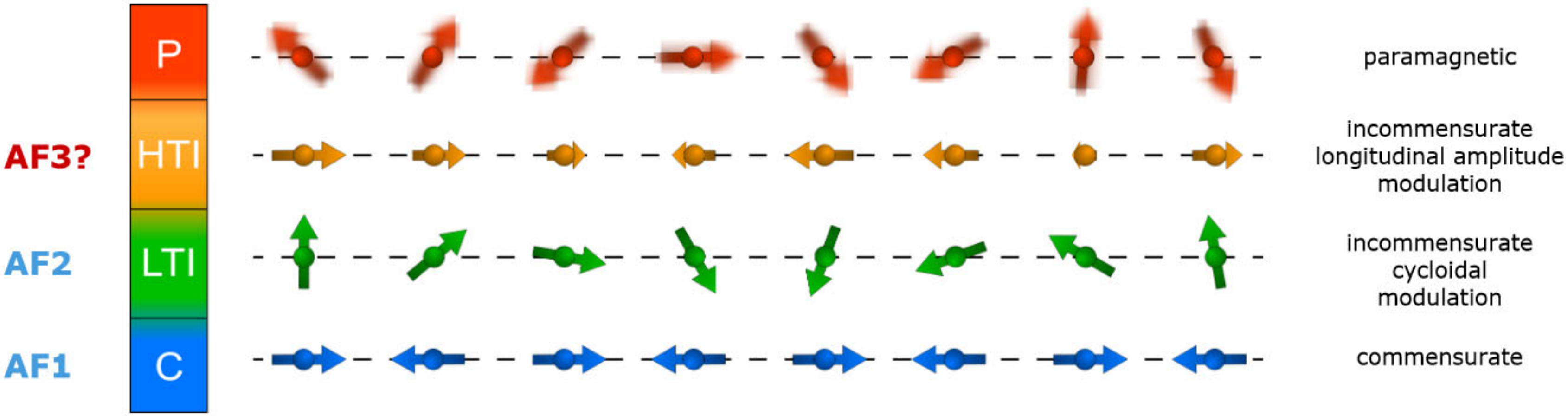


Examples

CuO - search for the AF3 phase

usual sequence of magnetic phases in multiferroics (e.g. $TbMnO_3$, $Ni_3V_2O_8$):



paramagnetic

incommensurate
longitudinal amplitude
modulation

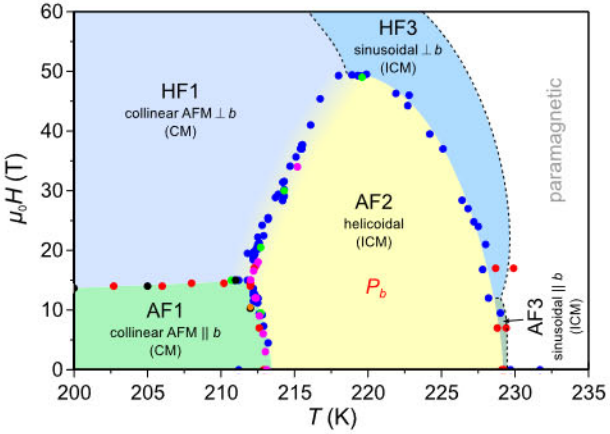
incommensurate
cycloidal
modulation

commensurate

Examples

CuO - search for the AF3 phase

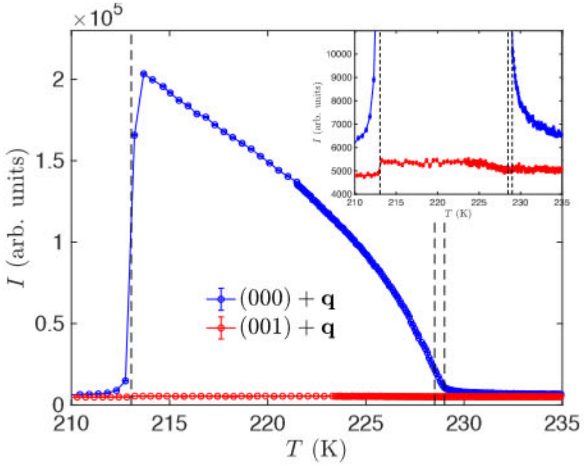
macroscopic methods



0.5 K stability range!

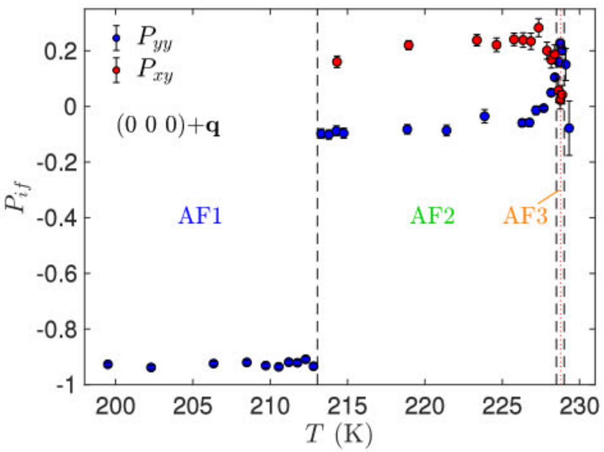
Wang, Qureshi et al. (2016) *Nat. Commun.* **7** 10295

unpolarised neutrons



No anomalies in I(T)

SNP on P_{yy} and P_{xy} elements



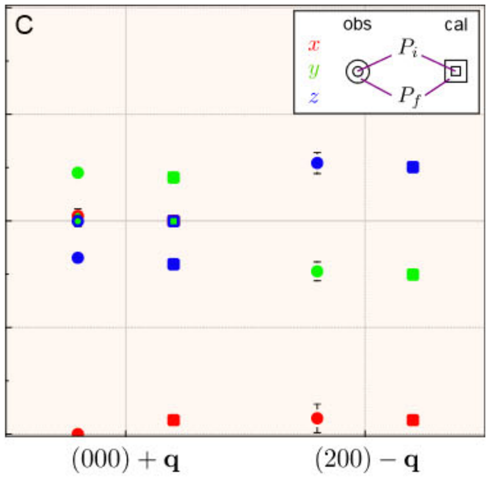
Microscopic proof of AF3!

Qureshi et al. (2020) Sci. Adv. **6** eaay7661

Examples

CuO - search for the AF3 phase

observed vs. calculated

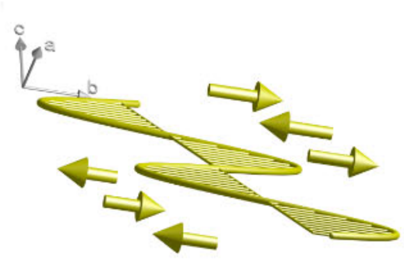


analysed with

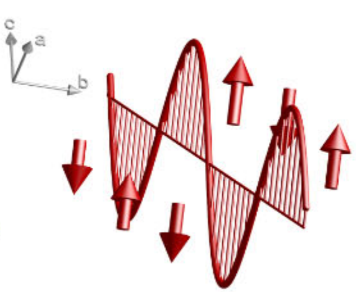
MAG2POL
Navid Qureshi, ILL 2016 - 2023

Qureshi (2019) J. Appl. Cryst. **52** 175

phase coexistence



SDW μ || b



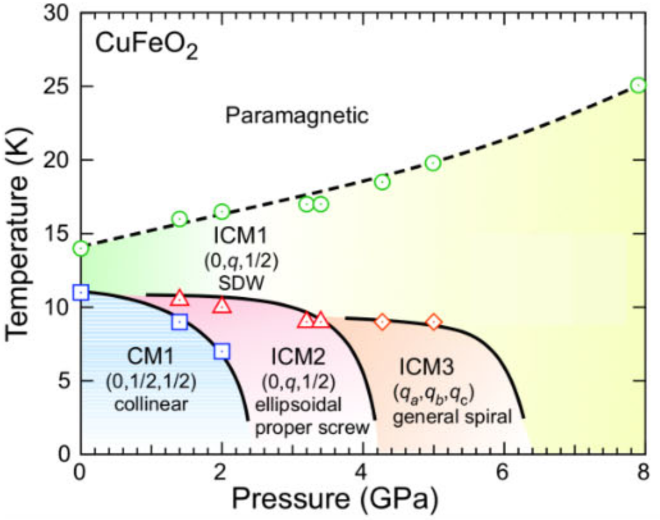
SDW μ || α

Examples

$CuFeO_2$ - pressure-induced multiferroicity

Complex p-T phase diagram

including collinear spin-density waves and non-collinear spiral structures

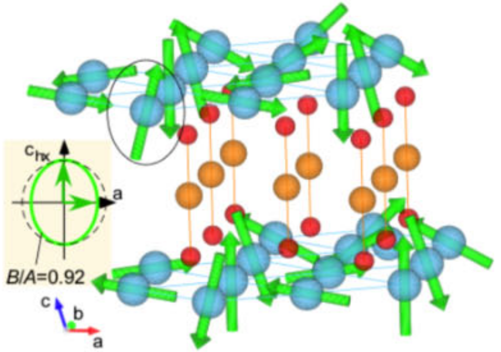


Lack of information

Limited number of observations (integrated intensities) did not allow to reveal:

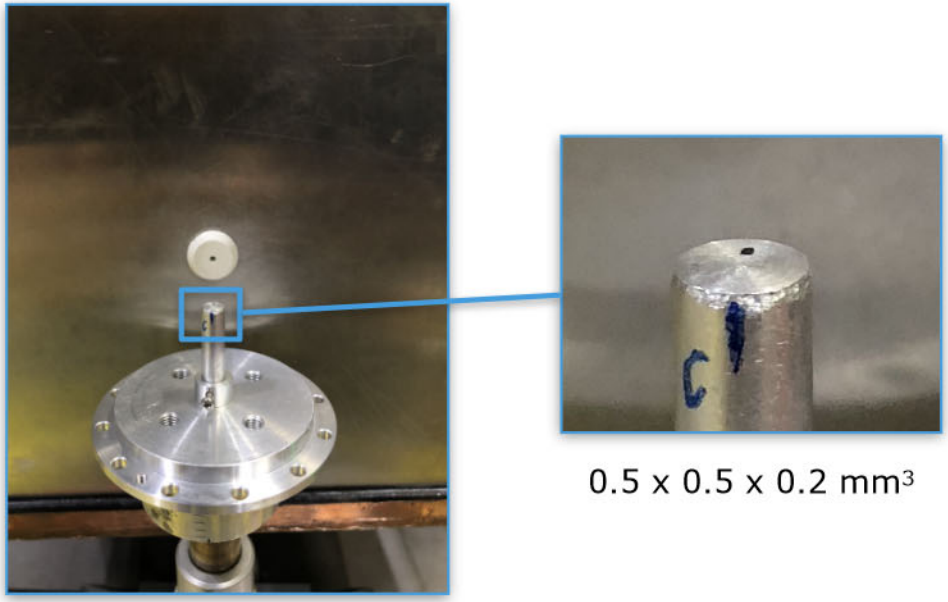
Terada et al. (2014) Phys. Rev. B **83** 220403(R)

- stability region of ICM1
- ellipsoidicity ratio of ICM2
- magnetic structure of ICM3



Examples

$CuFeO_2$ - pressure-induced multiferroicity



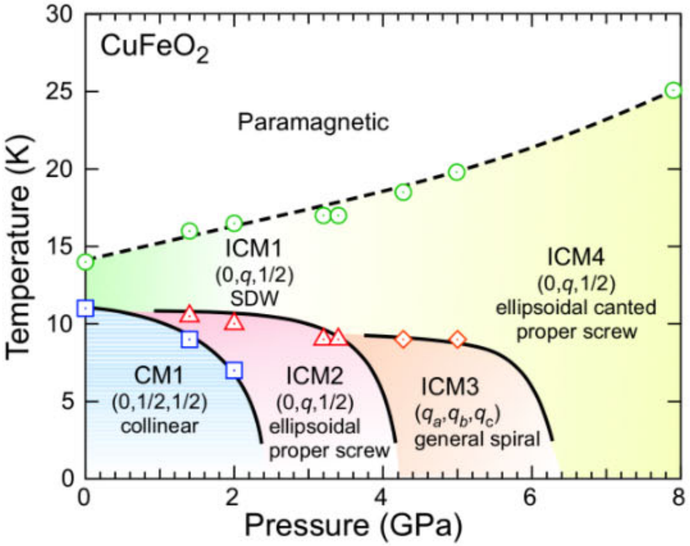
0.5 x 0.5 x 0.2 mm^3

non-magnetic pressure cell (up to 10 GPa)

Examples

CuFeO₂ - pressure-induced multiferroicity

- SNP under pressure: It's possible!!!
- Determined 5 complex magnetic structures at 3 different pressures in 7 days with a 0.05 mm^3 sample
- SNP is an excellent approach to study novel pressure-induced phenomena associated with complex magnetic order



Terada, Qureshi et al. (2018) Nat. Commun. **9** 4368

Conclusions

SNP and the future

- SNP is a powerful technique without alternatives for certain scientific challenges
- Magnetic domain sensitivity makes it the ideal probe for switching behaviour of smart materials
- Weak signals (small moments, small samples, thin films) are no problem as long as different from background
- Importance for future spintronic candidates, but also emerging field of twistronics (2D materials, few-layer limit)

Conclusions

SNP and the future

- SNP is a powerful technique without alternatives for certain scientific challenges
- Magnetic domain sensitivity makes it the ideal probe for switching behaviour of smart materials
- Weak signals (small moments, small samples, thin films) are no problem as long as different from background
- Importance for future spintronic candidates, but also emerging field of twistronics (2D materials, few-layer limit)
- D3 at 50%: overload of 5.9 (!) in College 5B in current proposal round
- We need D3 at 100% in order not to miss out on excellent science!

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