Spherical neutron polarimetry (SNP) as a powerful method for precise magnetic structure determination

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Outline

- Introduction

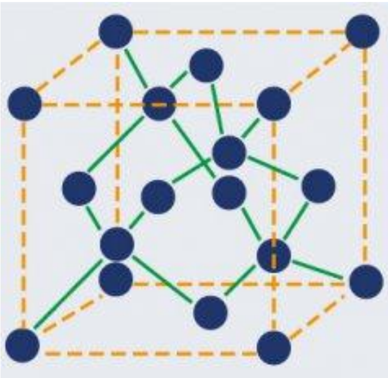
- Basics of SNP
  - Fundamental equations for SNP
  - The experimental strategy

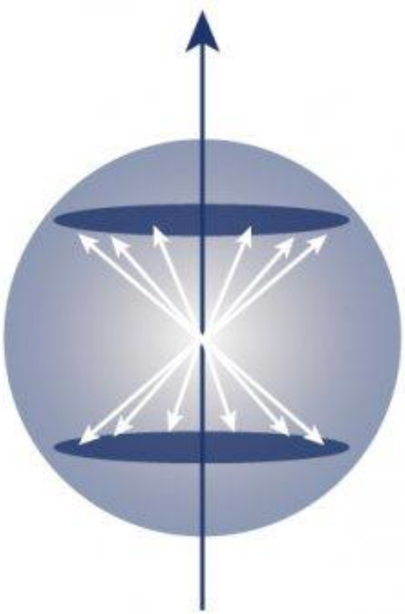
- Experimental setup for SNP on POLI
  - Cryopad
  - Instrument layout POLI

- Magnetic structure from SNP, AFM domains
  - Multiferroic $Ba_2CoGe_2O_7$

- Summary

Introduction





- **Electrically neutral:** Neutrons carry no electric charge and therefore do not interact with the electron shell of the atom, but interact with atomic nuclei, instead. Thus, neutrons can penetrate deep into matter.

- **Sensitive for atomic structures:** The wavelength of thermal neutrons is of the same order of magnitude as interatomic distances in solids, therefore neutrons are ideal for determining interatomic arrangements in condensed matter.

- **Magnetically sensitive:** Neutrons have a magnetic moment which is approximately 2.000 times smaller than the magnetic moment associated with the spin of an electron. However, it is sufficiently large to give raise to an interaction with the magnetic field from unpaired electrons in a sample. Therefore, neutrons are an excellent probe to investigate magnetic properties of materials.

Introduction to SNP

• SNP uses vector characteristic of the neutron polarisation;

• SNP is performed in zero field so the polarisation does not precess, rotation as well as change of the polarisation due to interaction with the sample are analysed;

•SNP distinguishes polarisation rotation from depolarisation;

•Determination of the direction of the magnetic interaction vector;

• Applications:

- Unique solution of complex magnetic structures (collinear or non-collinear AFM, incommensurate structures, direct evidence of chirality)

- Studies of magneto-electric domains;

- Determination of anti-ferromagnetic form factors;

It is based on the fundamental Blume-Maleev ecuations:

P. J. Brown, Spherical Neutron Polarimetry, Ch. 5 "Neutron Scattering From Magnetic Materials, ed. T. Chatterji, Elsevier, 2005

Blume – Maleev equations

Equation 19 from M Blume, *Phys. Rev.* **130** 1670 (1963)

$$
\begin{aligned}
\tfrac{1}{2}\mathbf{P}_f \frac{d\sigma}{d\Omega'} = {} & \tfrac{1}{2}\mathbf{P}\Big|\sum_{\mathbf{n}} e^{i\mathbf{K}\cdot\mathbf{n}}\Big|^2 |F_N(\mathbf{K})|^2 - \tfrac{1}{2}\mathbf{P}N\sum_j \left(\tfrac{1}{3}\langle\{a_j{}^2\}\rangle - \tfrac{1}{3}\langle\{a_j\}^2\rangle + \langle\{a_j\}\rangle^2\right) + \frac{1}{2}\left(\frac{\gamma e^2}{mc^2}\right)\sum_{\mathbf{n}j,\mathbf{n}'j'} \exp[i\mathbf{K}\cdot(\mathbf{R}_{\mathbf{n}j}-\mathbf{R}_{\mathbf{n}'j'})] \\
& \times\Big(\langle\{a_{j'}\}\rangle S_{\mathbf{n}j} f_{\mathbf{n}j}(\mathbf{K})\mathbf{q}_{\mathbf{n}j} + \langle\{a_j\}\rangle S_{\mathbf{n}'j'} f_{\mathbf{n}'j'}{}^*(\mathbf{K})\mathbf{q}_{\mathbf{n}'j'} - i\langle\{a_{j'}\}\rangle S_{\mathbf{n}j} f_{\mathbf{n}j}(\mathbf{K})(\mathbf{P}\times\mathbf{q}_{\mathbf{n}j}) \\
& + i\langle\{a_j\}\rangle S_{\mathbf{n}'j'} f_{\mathbf{n}'j'}{}^*(\mathbf{K})(\mathbf{P}\times\mathbf{q}_{\mathbf{n}'j'})\Big) + \frac{1}{2}\left(\frac{\gamma e^2}{mc^2}\right)^2 \sum_{\mathbf{n}j,\mathbf{n}'j'} \exp[i\mathbf{K}\cdot(\mathbf{R}_{\mathbf{n}j}-\mathbf{R}_{\mathbf{n}'j'})] S_{\mathbf{n}'j'} S_{\mathbf{n}j} f_{\mathbf{n}'j'}{}^*(\mathbf{K}) f_{\mathbf{n}j}(\mathbf{K}) \\
& \times\Big(-i(\mathbf{q}_{\mathbf{n}'j'}\times\mathbf{q}_{\mathbf{n}j}) + \mathbf{q}_{\mathbf{n}'j'}(\mathbf{P}\cdot\mathbf{q}_{\mathbf{n}j}) + (\mathbf{P}\cdot\mathbf{q}_{\mathbf{n}'j'})\mathbf{q}_{\mathbf{n}j} - \mathbf{P}(\mathbf{q}_{\mathbf{n}'j'}\cdot\mathbf{q}_{\mathbf{n}j})\Big).
\end{aligned}
$$

At almost the same time, essentially the same equations were elaborated by Serge Maleev.

S.V. Maleev, V.G. Bar'yaktar and R.A. Suris, *Sov. Phys. - Solid State* **4** 2533 (1963)

The Idea of SNP is to be able to measure all the terms in these equations precisely

The Blume-Maleev Equations written in terms of Structure Factors

The scattered polarisation $\mathbf{P}'$ and scattered intensity I for incident polarisation $\mathbf{P}$ can be written as:

$$
\begin{aligned}
\mathbf{P}'I \quad = \quad & \mathbf{P}(|N(\mathbf{k})|^2 - \mathbf{M}_\perp(\mathbf{k}) \cdot \mathbf{M}_\perp^*(\mathbf{k})) \quad \text{part parallel to } \mathbf{P} \\
& + 2\Re[\mathbf{M}_\perp(\mathbf{P} \cdot \mathbf{M}_\perp^*(\mathbf{k}))] \\
& + 2\Re[\mathbf{M}_\perp(\mathbf{k}) N^*(\mathbf{k})] \quad \text{part parallel to } \mathbf{M}_\perp \\
& + \mathbf{P} \times 2\Im(\mathbf{M}_\perp N^*(\mathbf{k})) \quad \text{part perpendicular to } \mathbf{P} \text{ and } \mathbf{M}_\perp \\
& - \Im\mathbf{M}_\perp(\mathbf{k}) \times \mathbf{M}_\perp^*(\mathbf{k})) \quad \text{part parallel to } \mathbf{k}
\end{aligned}
$$

$$
\begin{aligned}
I \quad = \quad & |N(\mathbf{k})|^2 + \mathbf{M}_\perp(\mathbf{k}) \cdot \mathbf{M}_\perp^*(\mathbf{k}) \quad \text{polarisation independent part} \\
& + 2\Re(\mathbf{P} \cdot \mathbf{M}_\perp(\mathbf{k}) N^*(\mathbf{k})) \\
& + \mathbf{P} \cdot \Im(\mathbf{M}_\perp(\mathbf{k}) \times \mathbf{M}_\perp^*(\mathbf{k})) \quad \text{polarisation dependent parts}
\end{aligned}
$$

(P. J. Brown, Spherical Neutron Polarimetry, Ch. 5 “Neutron Scattering From Magnetic Materials, ed. T. Chatterji (2005))

The polarisation tensor

The *Polarisation axes* are defined with:

- x parallel to the scattering vector $\mathbf{k}$.
- z perpendicular to the scattering plane (vertical)
- y completing the right handed cartesian set

With this choice of axes there are no components of the magnetic interaction vector $\mathbf{M}_\perp(\mathbf{k})$ parallel to x.

The Blume Maleev equations can be written in tensor form

$$\mathbf{P}' = \mathsf{P}\mathbf{P} + \mathbf{P}'' \quad \text{or in components} \quad P_i' = \mathsf{P}_{ij}P_j + P_i''$$

$\mathbf{P}''$ is the polarisation created in the scattering process.

The polarisation tensor

The polarisation tensor on polarisation axes becomes:

$$\mathbf{P} = \begin{pmatrix} (N^2 - M^2)/I_x & J_{nz}/I_x & J_{ny}/I_x \\ -J_{nz}/I_y & (N^2 - M^2 + R_{yy})/I_y & R_{yz}/I_y \\ -J_{ny}/I_z & R_{zy}/I_z & (N^2 - M^2 + R_{zz})/I_z \end{pmatrix}$$

And the polarisation created is

$$\mathbf{P}'' = \begin{pmatrix} -J_{yz}/I \\ R_{ny}/I \\ R_{nz}/I \end{pmatrix} \qquad \begin{aligned} I_x &= M^2 + N^2 + P_x J_{yz} \\ I_y &= M^2 + N^2 + P_y R_{ny} \\ I_z &= M^2 + N^2 + P_z R_{nz} \\ I &= M^2 + N^2 + P_x J_{yz} + P_y R_{ny} + P_z R_{nz} \end{aligned}$$

$$\begin{aligned} N^2 &= N(\mathbf{k})N^*(\mathbf{k}) \\ R_{ij} &= 2\Re(M_{\perp i}(\mathbf{k})M_{\perp j}{}^*(\mathbf{k})) \\ J_{ij} &= 2\Im(M_{\perp i}(\mathbf{k})M_{\perp j}{}^*(\mathbf{k})) \end{aligned} \qquad \begin{aligned} M^2 &= \mathbf{M}_\perp(\mathbf{k}) \cdot \mathbf{M}_\perp(\mathbf{k}) \\ R_{ni} &= 2\Re(N(\mathbf{k})M_{\perp i}{}^*(\mathbf{k})) \\ J_{ni} &= 2\Im(N(\mathbf{k})M_{\perp i}{}^*(\mathbf{k})) \end{aligned}$$

The experimental strategy: Polarisation Matrix

The usual experimental strategy is to measure the scattered polarisation $\mathbf{P}'$ with the incident polarisation $\mathbf{P}$ parallel to polarisation x, y, z in turn.
This determines the polarisation matrix.

The *polarisation matrix* P_{ij} is the experimentally measurable quantity related to the polarisation tensor.
The matrix element P_{ij} gives the ith component of scattered polarisation when the incident polarisation is in the jth direction.

$$P_{ij} = \left\langle \frac{\mathsf{P}_{ij} P_j + P_i''}{P_j} \right\rangle_{\text{domains}}$$

Off-diagonal terms in the polarisation matrix correspond to rotation of the polarisation direction.

They are of two kinds.

1. P_{yz} and P_{zy} which depend upon $R_{yz} = 2\Re(M_{\perp y}(\mathbf{k})M_{\perp z}{}^{*}(\mathbf{k}))$
   They can be reduced to zero by choosing either the y or z axis parallel to $\mathbf{M}_{\perp}$.

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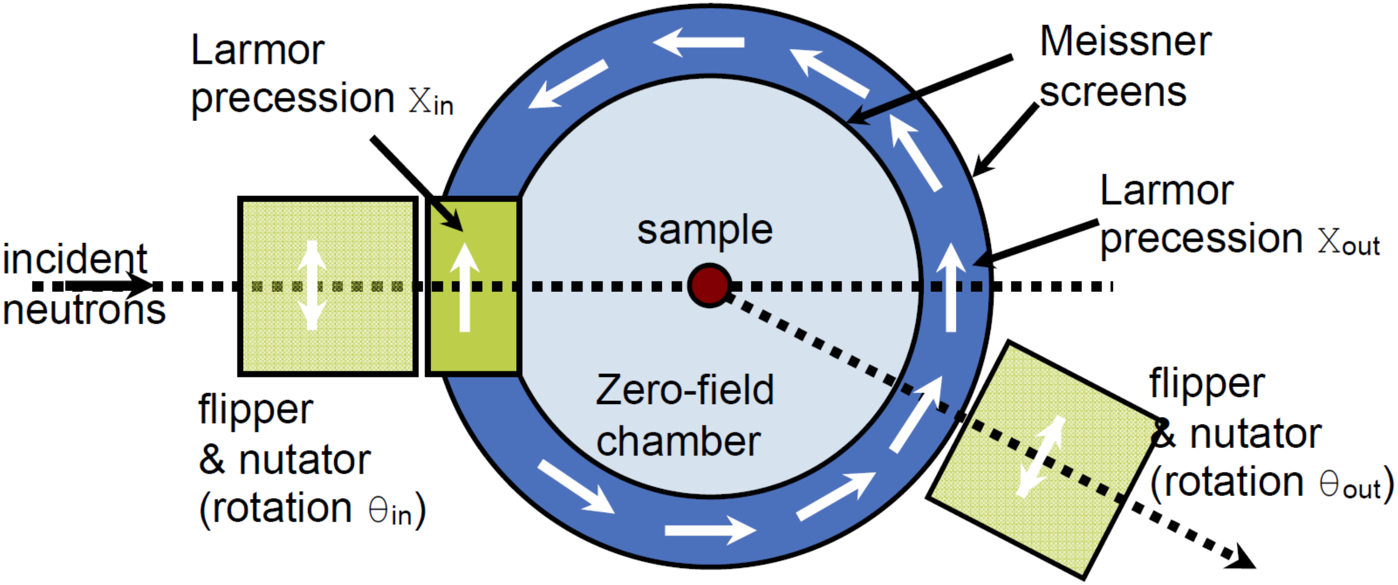
They can be reduced to zero by choosing either the y or z axis parallel to $\mathbf{M}_\perp$.

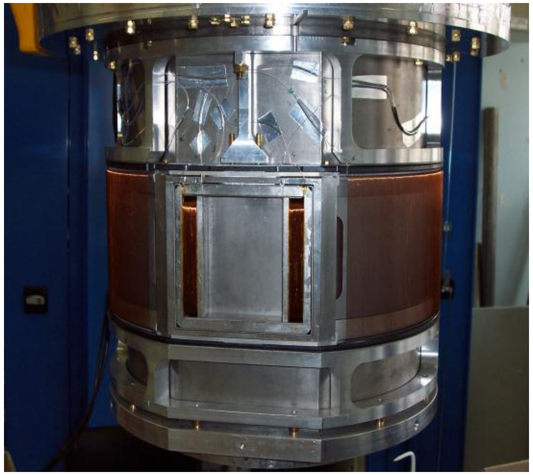
2. Elements P_{xy}, P_{xz}, P_{yx} and P_{zx} which represent rotations towards, or away from, the scattering vector.
They depend on $\Im(\mathbf{M}_\perp N^*)$ and are always present when nuclear and magnetic scattering occur together with a phase difference which is neither 0 or π.

The experimental strategy: Cryopad

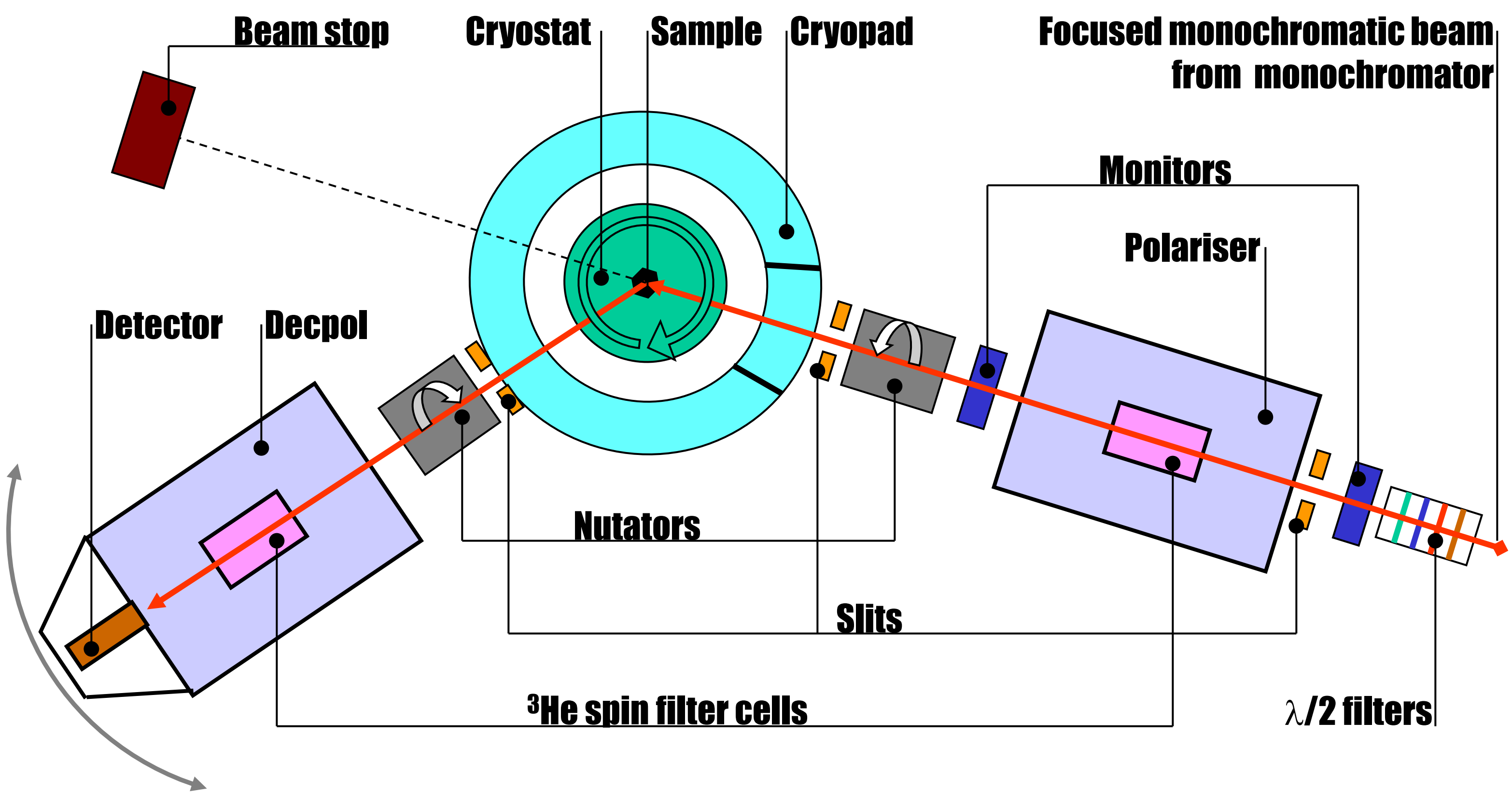


F. Tasset et al., Physica B 267}268 (1999) 69

$$\frac{n^+ - n^-}{n^+ + n^-} = P' \cdot A$$

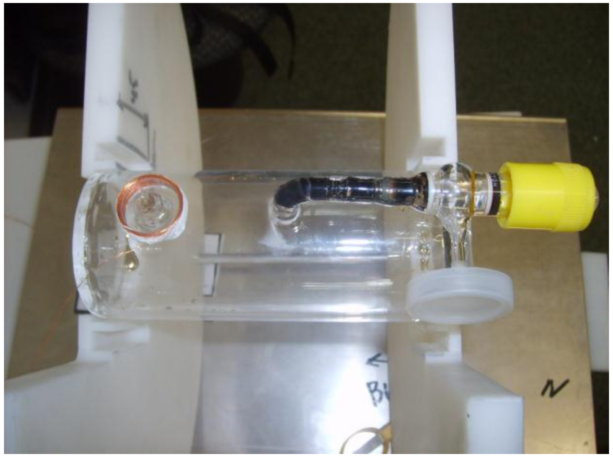


SNP on POLI

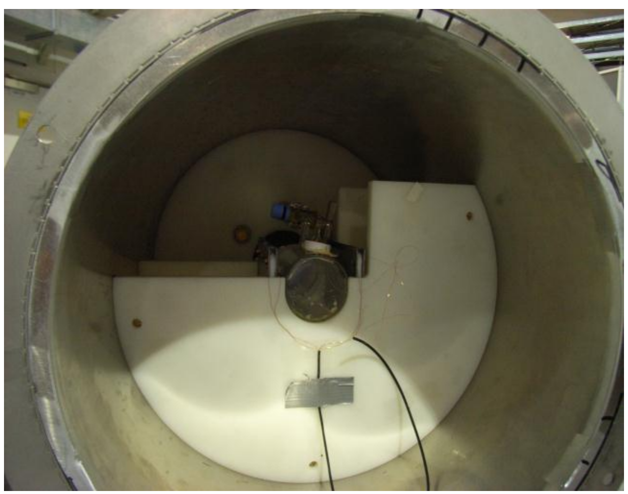


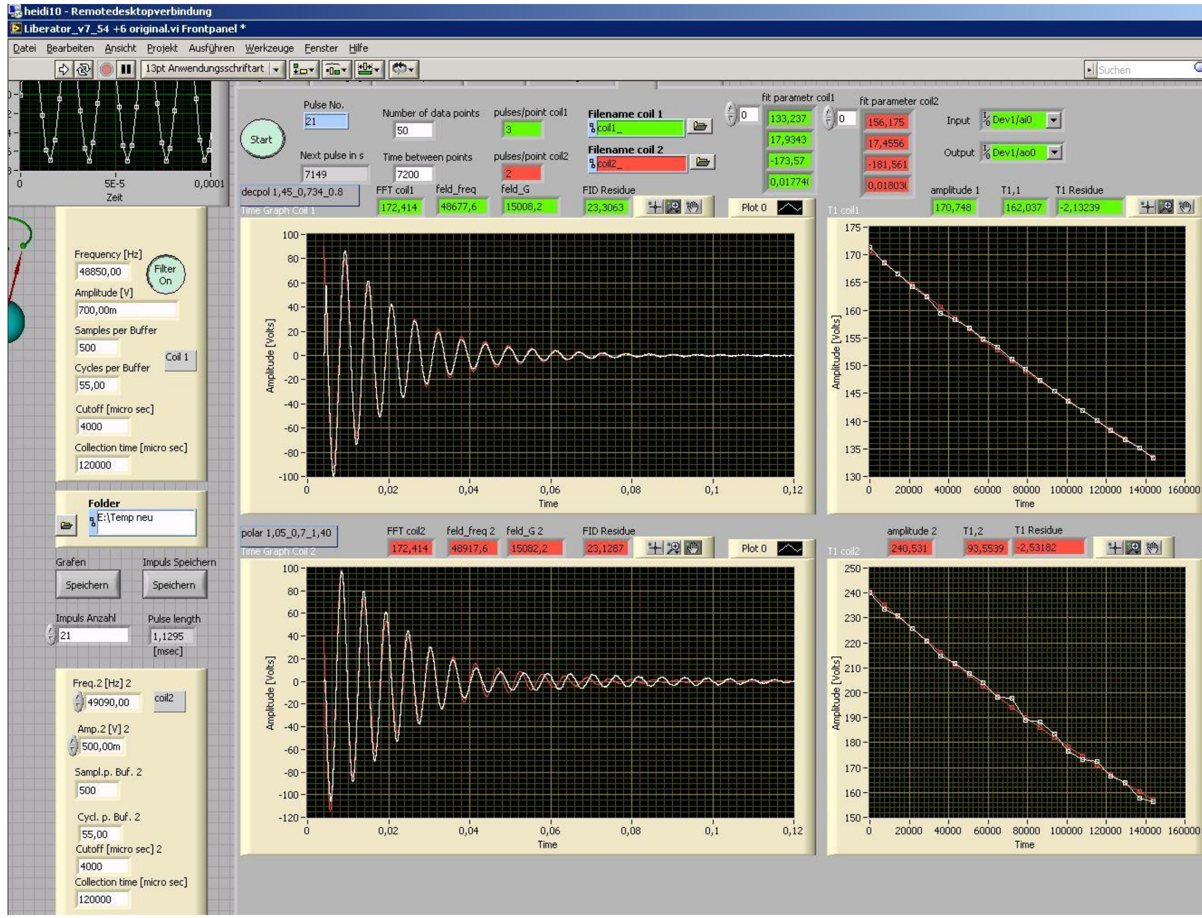
POLI is using ^{3}He spin filter both to create and to analyse neutron polarisation

Corrections for time-dependent polarisation



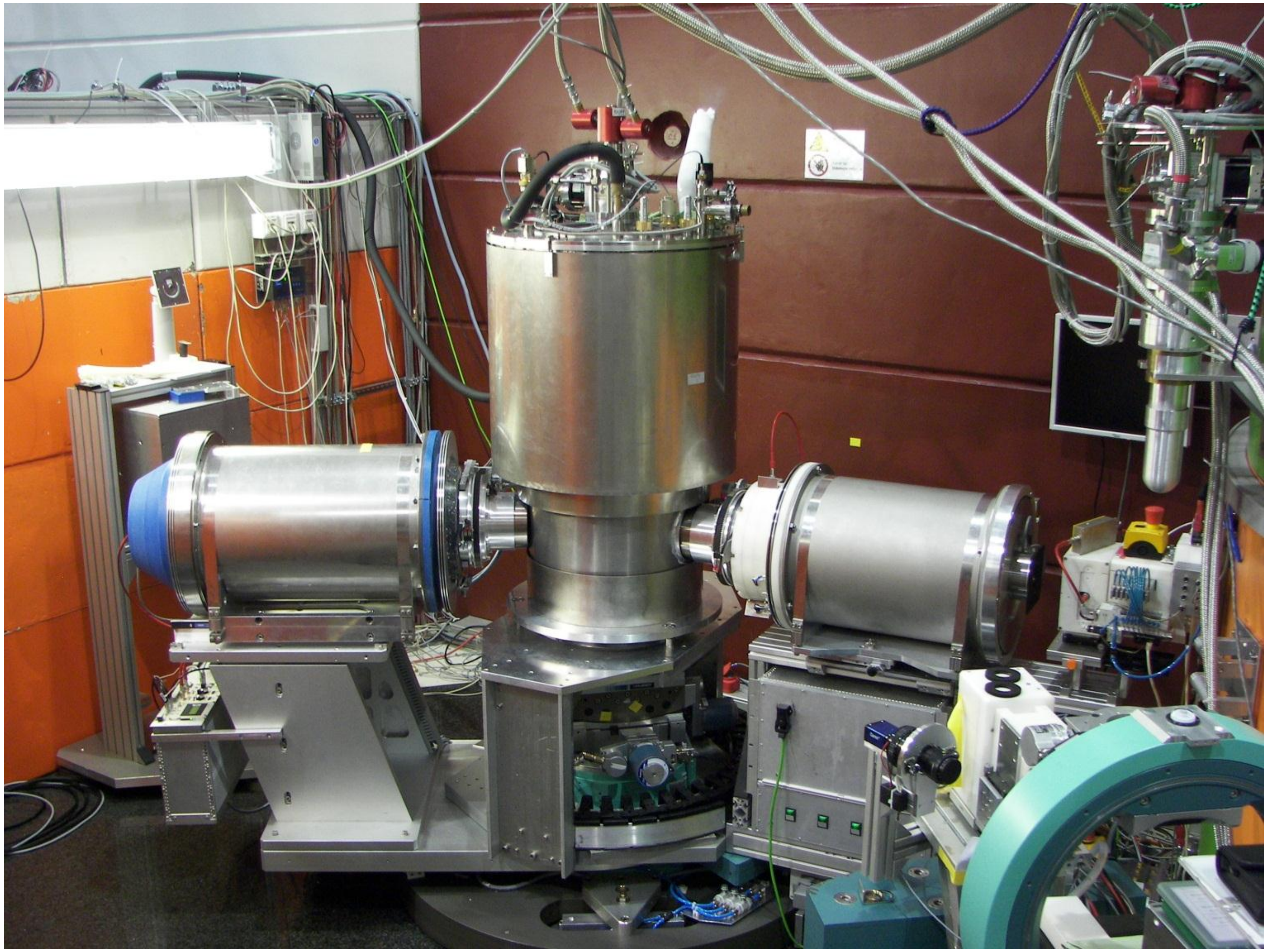
^{3}He filled spin filter cell





Independent in-situ measurement of the T_1 in the polariser and analyser during the scattering experiment using the LabView NMR monitor

SNP on POLI



V. Hutanu et al., J. Phys.: Conf. Ser. 294 012012 (2011)
V. Hutanu et al., Phys. Rev. B 89, 064403 (2014)

SNP on POLI with Cryopad is available for users since 2011,

until now 11 experiments (7 ext.+ 4 int.)

2 Bachelor thesis,

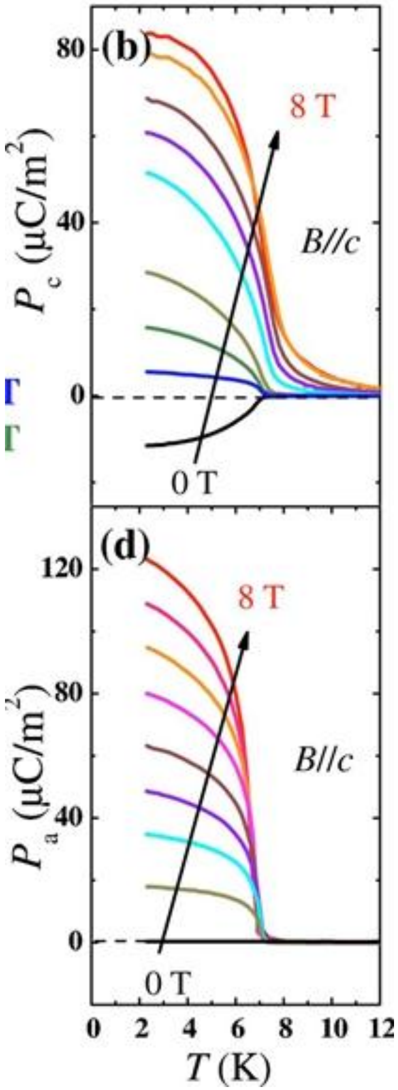
1 Diploma thesis,

1 PhD thesis,

4 Instrumental papers,

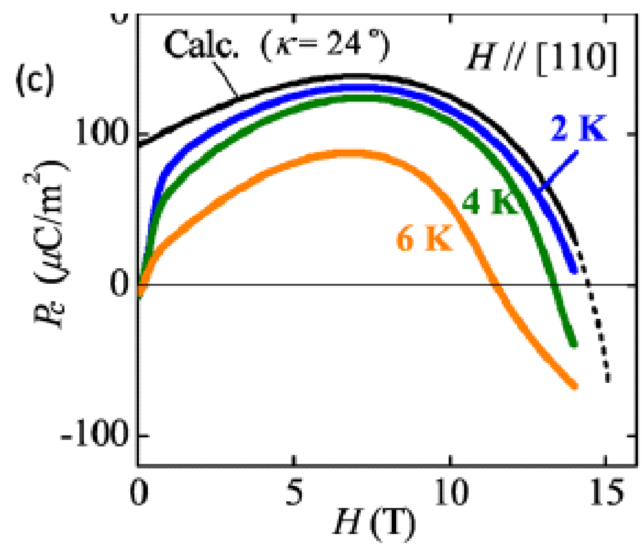
1 Scientific paper published , another 2 in preparation.

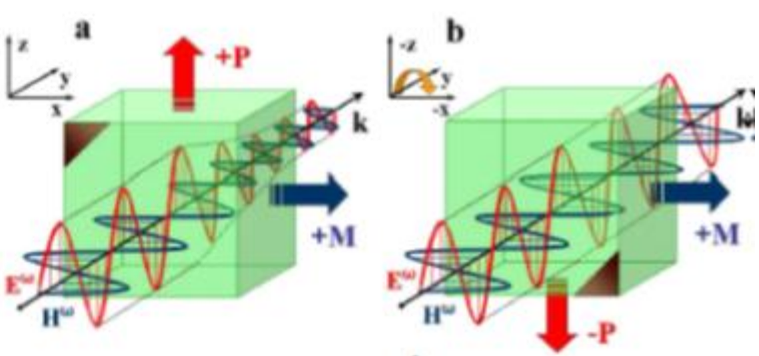
SNP application example: multiferroic $Ba_2CoGe_2O_7$



A smooth rotation of the EP with the magnetic field rather than a sudden flip, is quite unique and cannot be explained by well-accepted spin-current model or by an exchange striction mechanism conventional for other multiferroics.

H. Murakawa et al., Phys. Rev. Lett. (2010)





I. Kézsmárki et al. PRL 2011

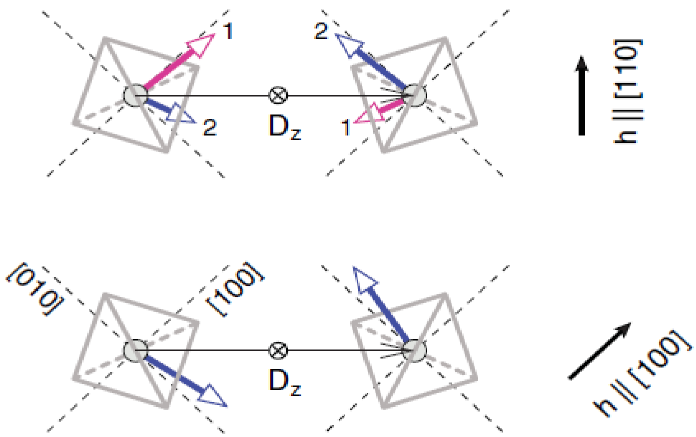
A novel spin-dependent hybridization mechanism with a metal-ligand hybridization modified by local spin configurations through spin-orbit coupling.

Giant directional dichroism of terahertz light in resonance with magnetic excitations (electromagnons) .

H.T. Yi et al., Appl. Phys. Lett. (2008)

Two different DM interactions along [1-10] and [001] ?

SNP application example: multiferroic $Ba_2CoGe_2O_7$



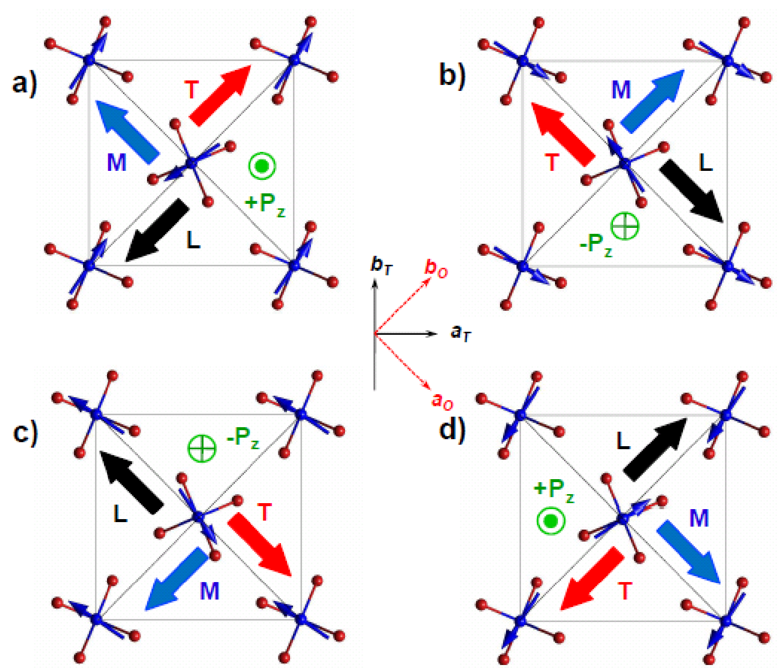
J. Romhanyi et al., Phys. Rev. B. 84, 224419 (2011)

Similar spin-dependent hybridization model, but adding in the Hamiltonian an exchange anysotropy and antiferroelectric polarization-polarization term. Mean field calculations.

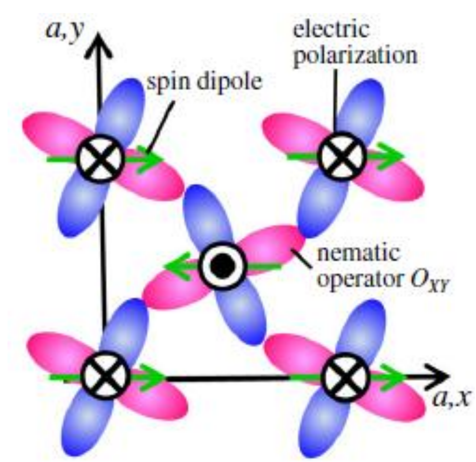
P. Toledano, at al. Phys. Rev. B **84**,094421 (2011)

Spontaneous toroidal moment, collinear to antiferromagnetic vector L = s_1-s_1 along a-plane.

$$\vec{T} = \hat{\nu}(\vec{M} \times \vec{P})$$



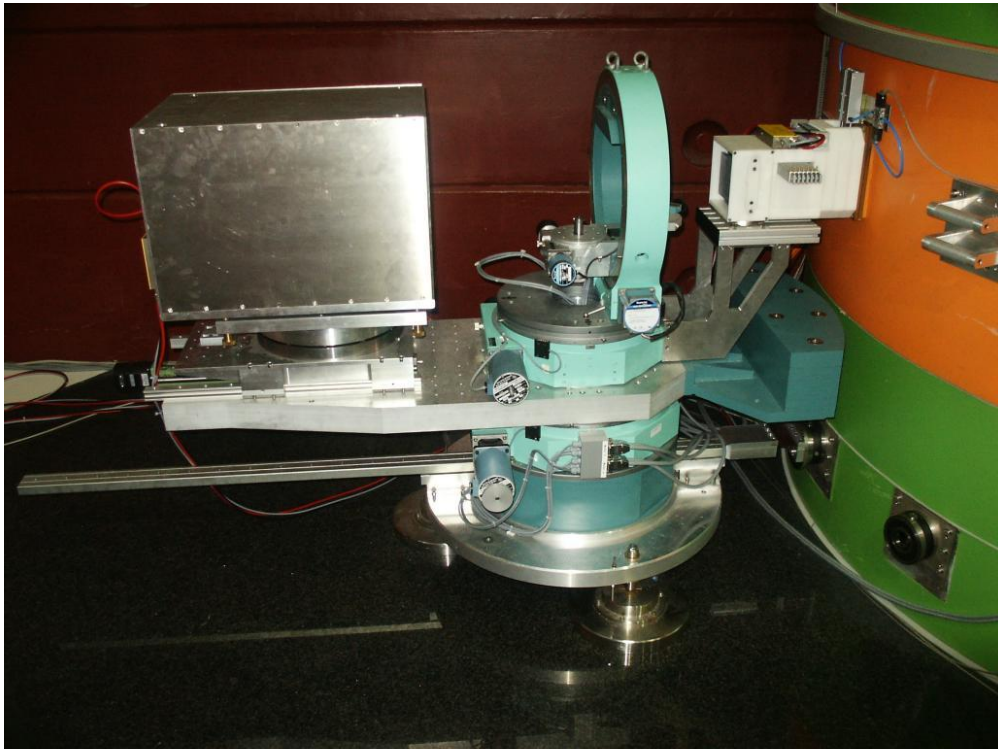
Spin-nematic interaction
M. Soda et al. PRL 2014

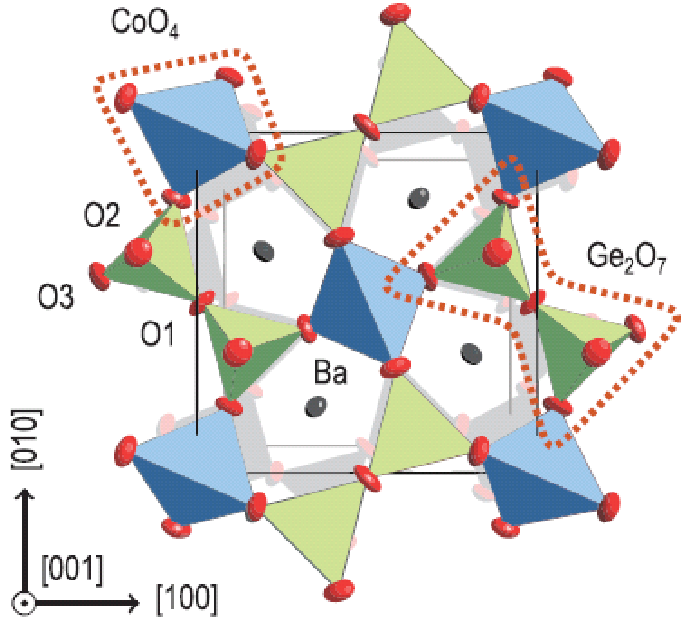


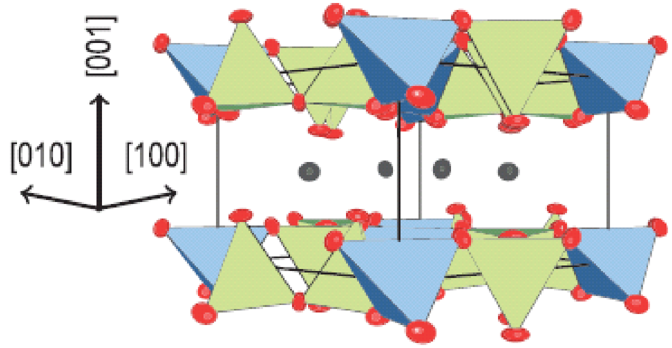
Crystal structure of $Ba_2CoGe_2O_7$

Single Crystal diffraction at RT and 90 K with synchrotron at BM01A station SNBL, ESRF Grenoble (Nr. 113, $P\text{-}42_1m$)

V. Hutanu et al., Phys Rev. B **84**, 212101 (2011).



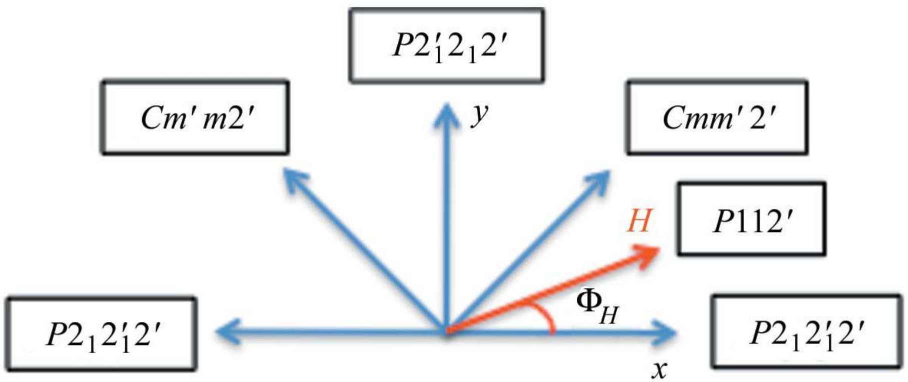




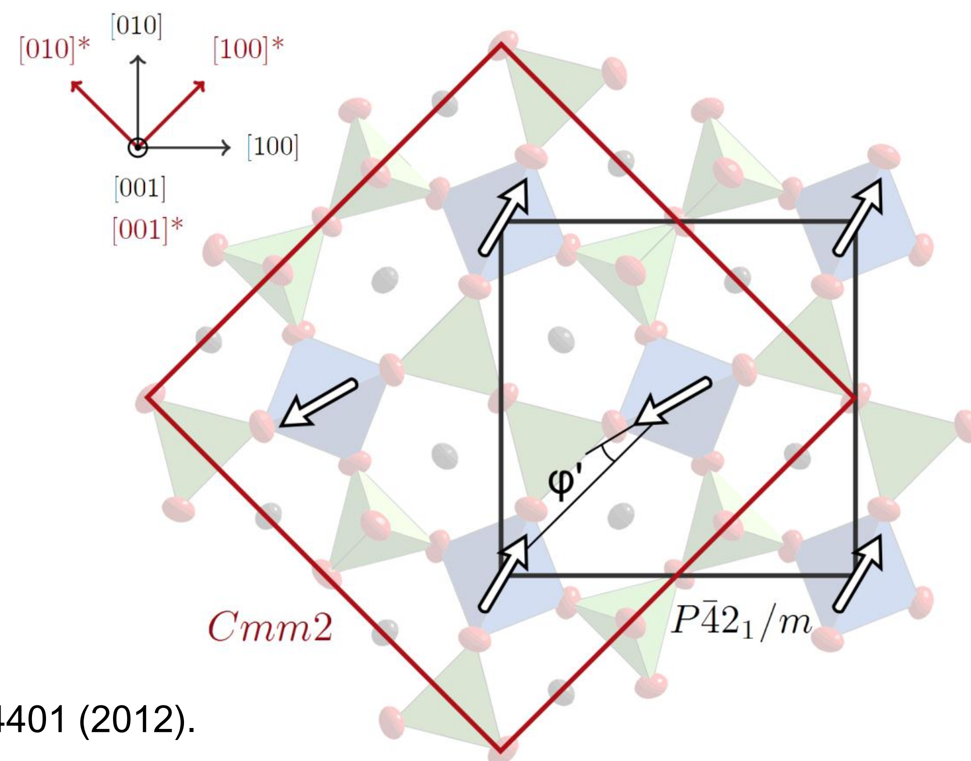
Single Crystal diffraction at 10 K and 2 K at SCND HEiDi
No phase transition at low temparature, lower simmetry orthorhombic *Cmm2* (Nr.35)

Magnetic structure of Ba2CoGe2O7

J.M. Perez-Mato, et al. Acta Cryst. A**67**, 264 (2011)



Different magnetic domains dependent on magnetic. moment direction



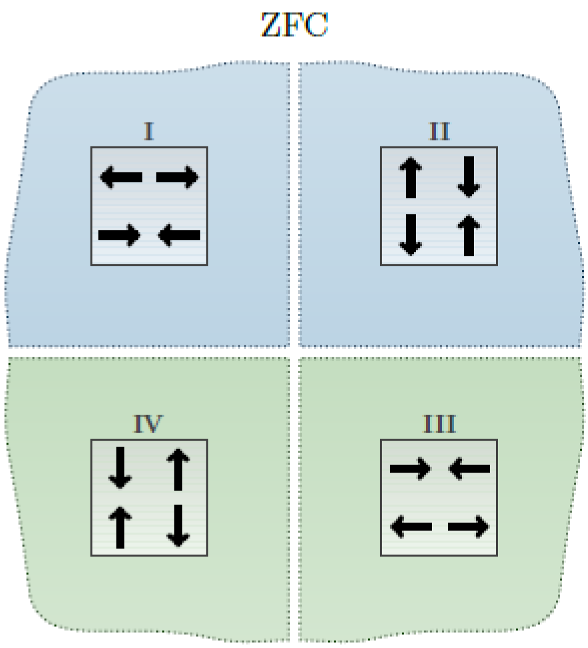
M = 2.9 ± 0.1 μB , FM along c,

φ' ≈ 8° ± 7° ???

Equivalent AFM domains do not permit the unique solution ??

V. Hutanu, A. Sazonov et. al Phys. Rev. B 86, 104401 (2012).

Example $Ba_2CoGe_2O_7$



$$\begin{bmatrix} xx & 0 & 0 \\ 0 & yy & 0 \\ 0 & 0 & zz \end{bmatrix}$$

Same ratio all domains

$$\begin{bmatrix} xx & 0 & a \\ 0 & yy & 0 \\ -a & 0 & zz \end{bmatrix}$$

Only domains type I ,II

$$\begin{bmatrix} xx & 0 & 0 \\ 0 & yy & b \\ 0 & b & zz \end{bmatrix}$$

Domains type I ,IV

$$\begin{bmatrix} xx & c & 0 \\ -c & yy & 0 \\ 0 & 0 & zz \end{bmatrix}$$

Domains type I ,III

$$\begin{bmatrix} xx & -c & 0 \\ c & yy & 0 \\ 0 & 0 & zz \end{bmatrix}$$

Domains type II ,IV

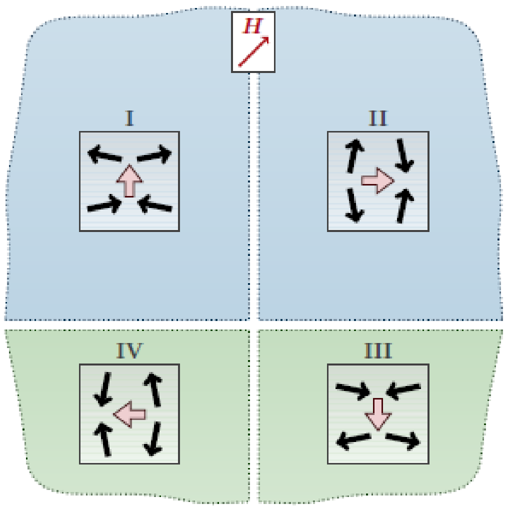
Example $Ba_2CoGe_2O_7$

	$\mathcal{P}_{ij}$	ZFC x'	ZFC y'	ZFC z'
Observed	x'	0.73(1)	0.01(2)	−0.06(4)
	y'	0.07(6)	0.76(2)	0.04(4)
	z'	0.04(2)	0.04(1)	0.76(4)
Calc100	x'	0.78	−0.01	−0.05
	y'	0.01	0.88	0.00
	z'	0.05	0.00	0.89
Calc110	x'	0.89	0.00	−0.03
	y'	0.00	0.94	0.00
	z'	0.03	0.00	0.95

Not cleare separation between the models in ZFC case

SNP application example: multiferroic $Ba_2CoGe_2O_7$

FC, $B \parallel [110]$

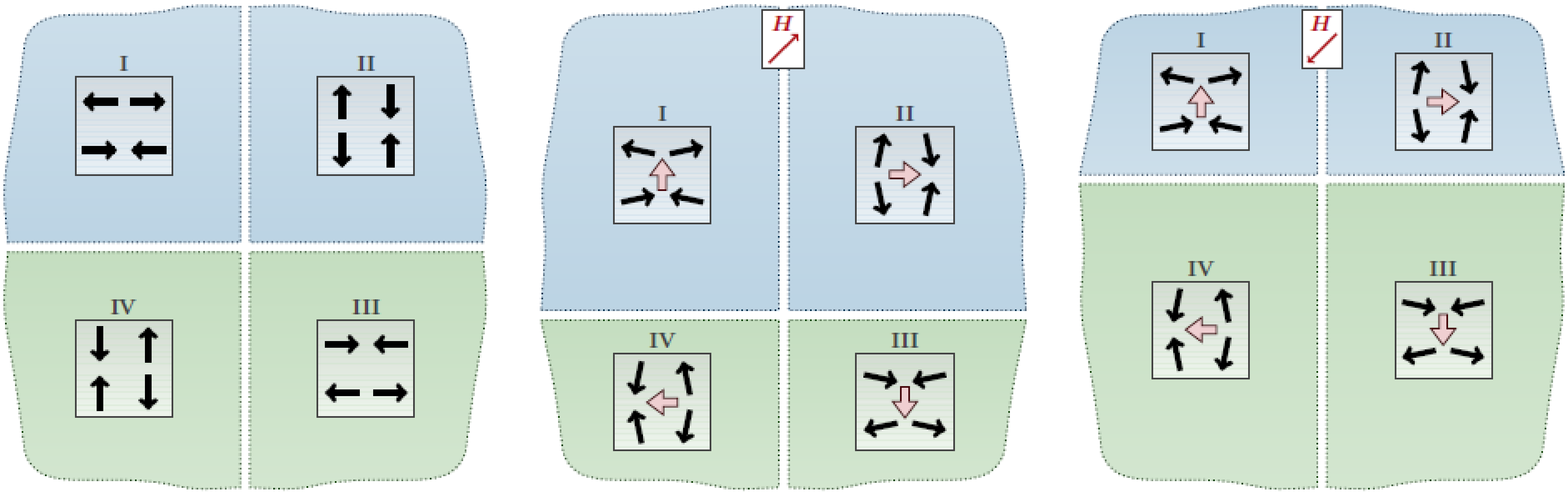


Field: 20 mT

	FC, $B \parallel [110]$		
	x'	y'	z'
Obs.	0.74(1)	0.03(2)	$\boxed{0.30(2)}$
	0.00(3)	0.82(2)	−0.02(6)
	$\boxed{-0.29(1)}$	0.00(3)	0.79(2)
(100)	0.78	0.01	0.22
	−0.01	0.88	0.00
	−0.22	0.00	0.89
(110)	0.89	0.00	0.17
	0.00	0.94	0.00
	−0.17	0.00	0.95

SNP application example: multiferroic $Ba_2CoGe_2O_7$

ZFC | FC, $B \parallel [110]$ | FC, $B \parallel [\bar{1}\bar{1}0]$



ZFC:

I	II	III	IV
28(3)%	24(3)%	21(3)%	27(3)%

FC, $B \parallel [110]$:

I	II	III	IV
37(4)%	38(4)%	12(3)%	13(3)%

FC, $B \parallel [\bar{1}\bar{1}0]$:

I	II	III	IV
11(3)%	13(3)%	36(4)%	40(4)%

Statistic distribution for the ZFC sample

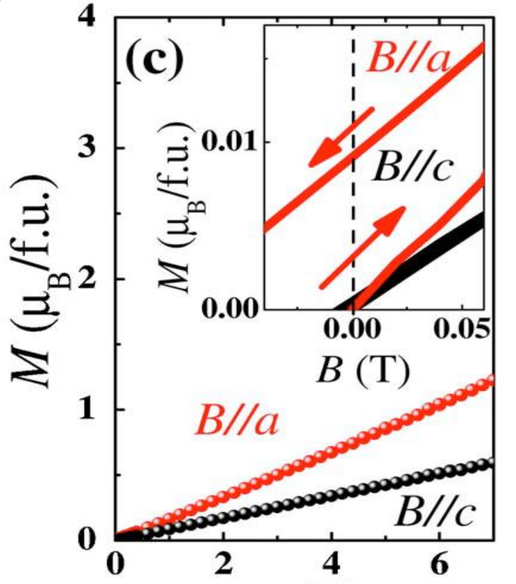
Symmetric picture (no preferential domain), same energies

Reversible ratio by field reverce,

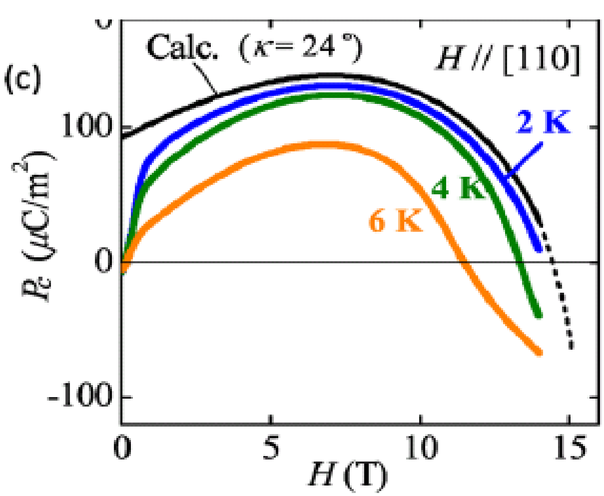
No memory effect after heating at 15 K

V. Hutanu, A. Sazonov et. al Phys. Rev. B 89, 64403 (2014)

SNP application example: multiferroic $Ba_2CoGe_2O_7$



Yi et al. Appl. Phys. Lett 2008



- Linear dependence domain ratio – field.

Field necessary to create double domain structure could be estimated: 40 mT.

-This is in disagreement with the hybridisation model of Murakawa (PRL 2010), where deviation at 1 T has been atributed to the domain formations.

- No dependence on the electric field direction along c toroidal moment (Toledano, PRB 2011)

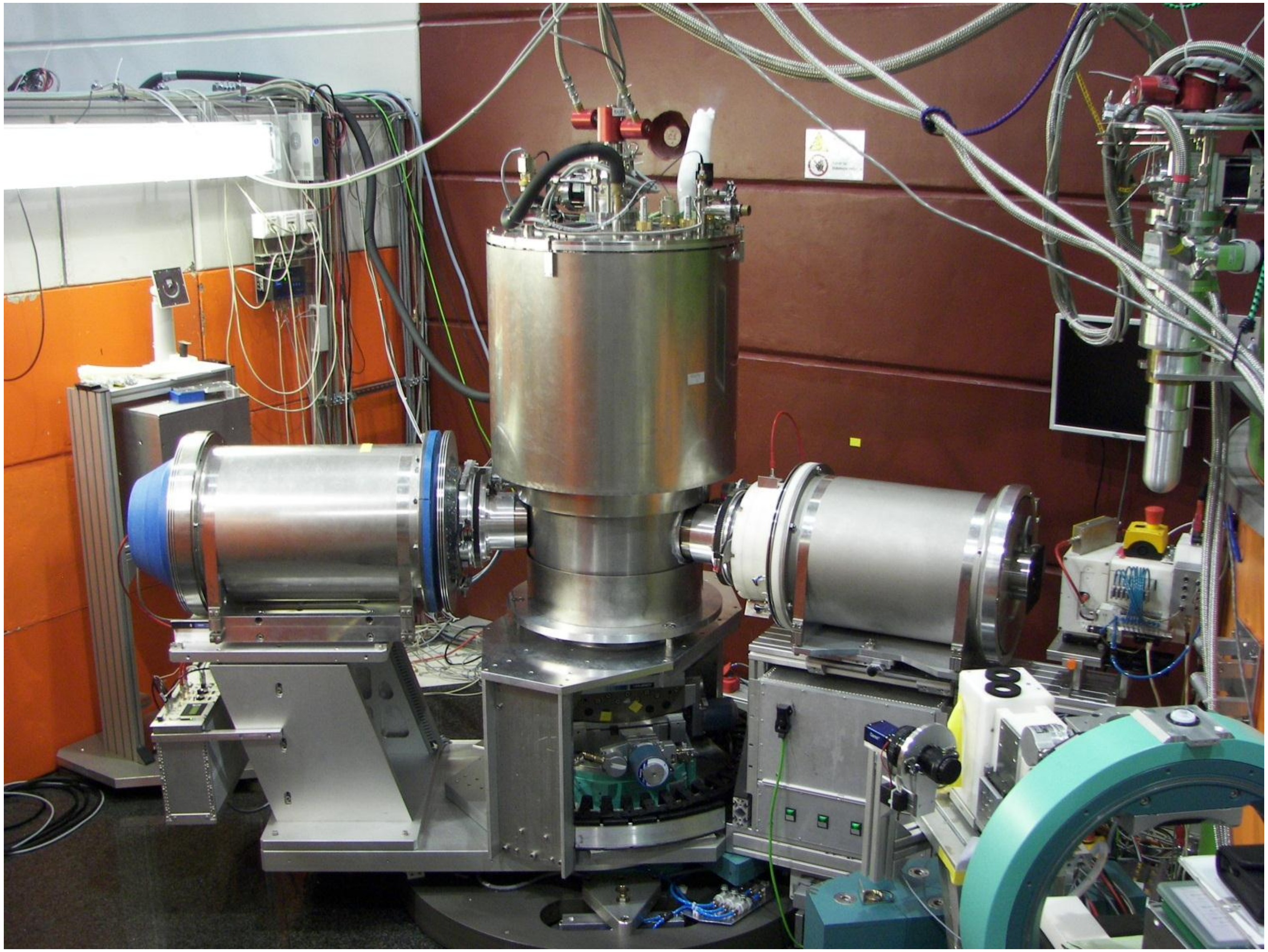
-Our results do not support the nematic interaction model of Soda (PRL 2014), neither on spin orientation, no on domain flop

-Best agreement to the Romhanyi (PRB 2011) model of hybridisation and antiferroilectric coupling

Conclusions

- SNP using third generation polarimeter Cryopad and new ^{3}He spin filter polariser and analyser has been recently implemented on instrument POLI at MLZ Garching Germany.
- This technique allowds a precise determining of the magnetic order in the ground state of the complex AFM structures. Also other types of structure like helical, spin dencity wave etc. can be determined.
- Different types of the magnetic domains in the sample (configuration, orientation, chiral, etc.) can be distinguesched, domain ratio determined and domain dynamics in dependance on external stimuli (e.g. electric and magnetic field) studied.
- Collinear magnetic AFM order with the main moment pointing along (100) direction in orthorombic cell has been found in multiferroic $Ba_2CoGe_2O_7$.
- This result is in agreement to the Romhanyi (PRB 2011) model of hybridisation and antiferroilectric coupling between 2D layers.
- Last, but most important …….

You are welcome to use it



POLI with Cryopad (SNP) are available for external users