Multiferroism: introduction

This also holds for **multiferroic compounds** with several degrees of freedom (charge, spin, orbit, lattice…)
They are often prone to magnetic frustration leading to complex (T, P, H, E) phase diagram and complex (chiral) magnetic orders that can sustain ferroelectricity

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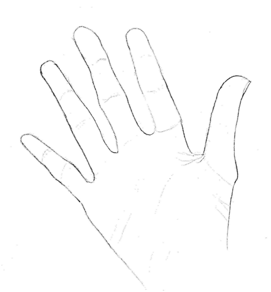
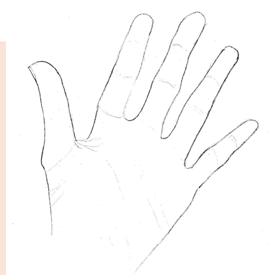
Definitions of chirality



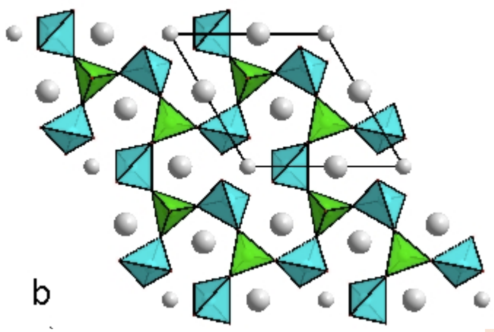


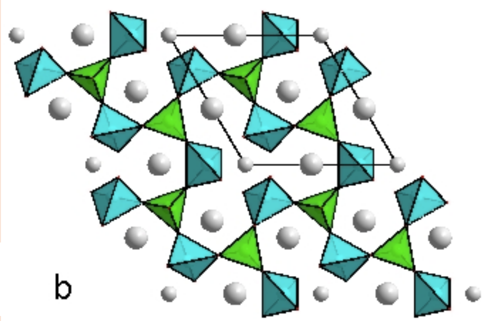
- **Casual** -> Chirality is what distinguishes a phenomenon from its materialization in a mirror

- **Math.** -> object whose symmetry group does not contain any negative isometries (inversion centers, mirrors)

- **Structural chirality** :

non-centrosymmetric crystal whose point group does not contain improper symmetry elements





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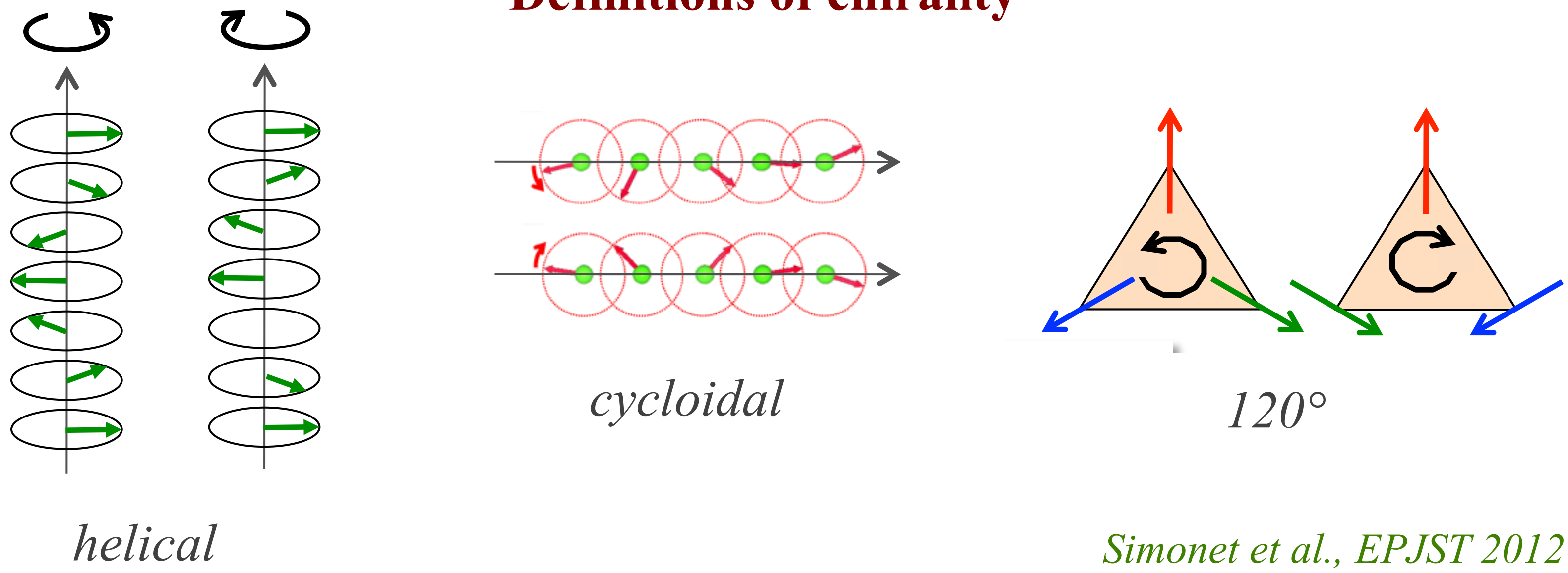
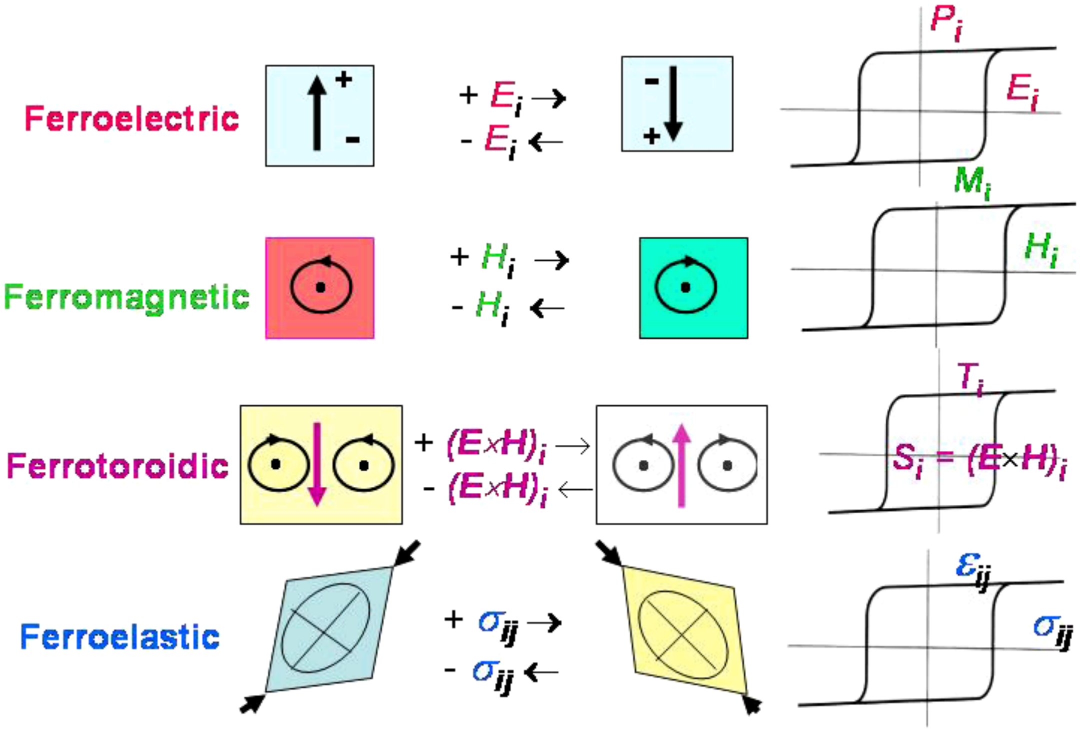


Simonet et al., EPJST 2012

- **Magnetic chirality** -> sense of rotation of non collinear spins along an orientated line, defined by a **chirality vector or spin current** $\propto \vec{S}_i \times \vec{S}_j$

Multiferroism: introduction

Multiferroics : coexistence of at least two (anti)ferroic orders
among : ferroelasticity, ferromagnetism, ferroelectricity, and ferrotoroidicity

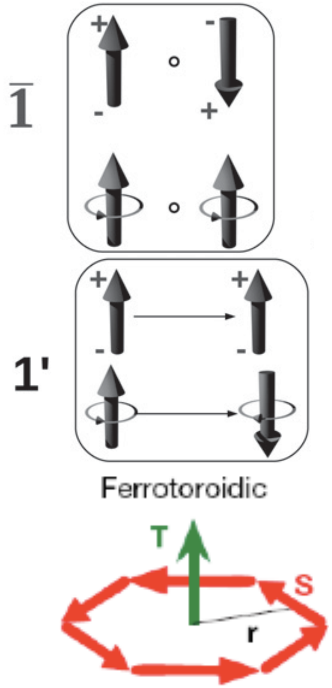


breaks spatial inversion

breaks time reversal

breaks spatial inversion
& time reversal

invariant upon both
spatial inversion & time reversal



Hysteresis cycle, presence of switchable domains

Multiferroism: introduction

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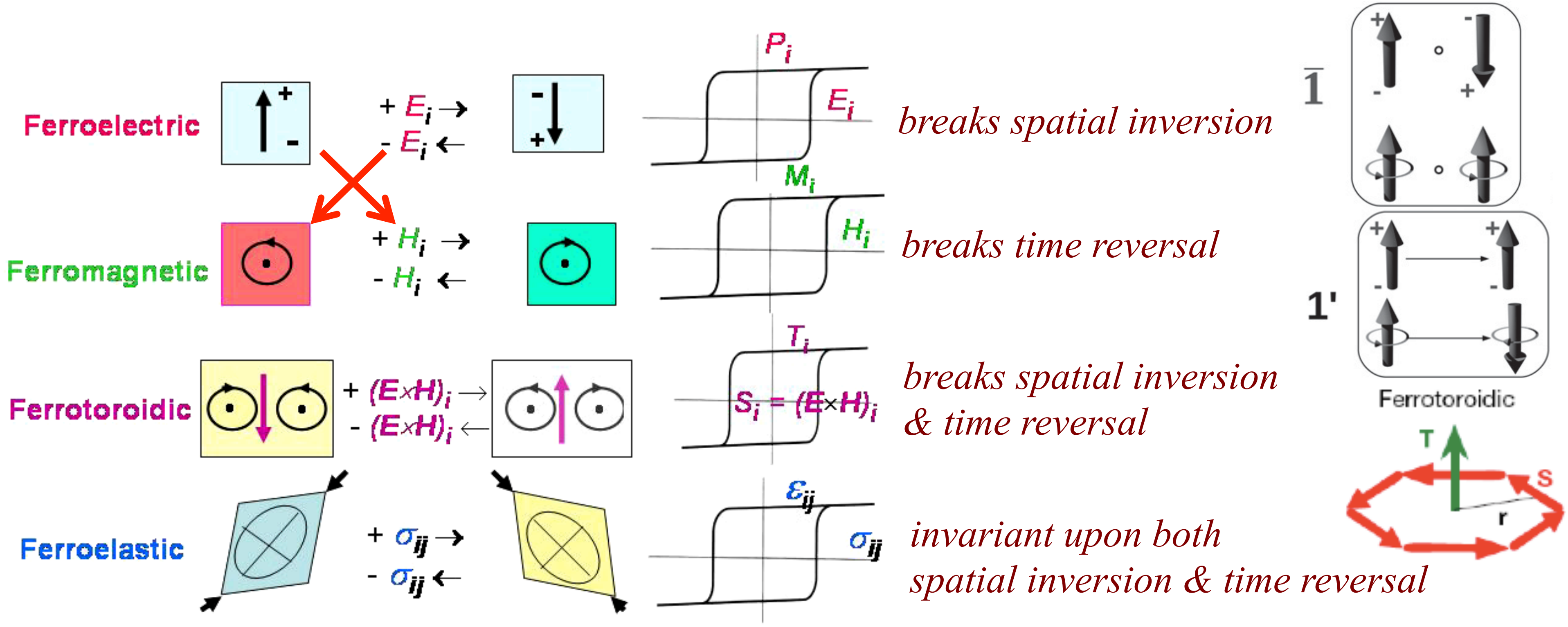


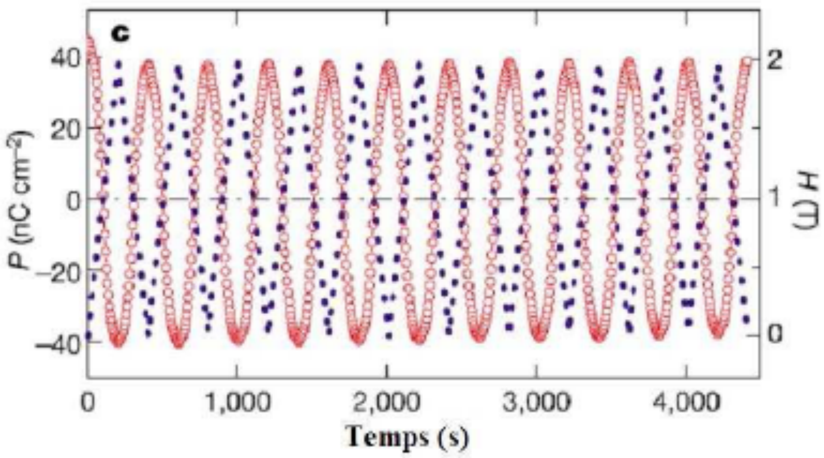
Cross couplings, ex. **Magnetoelectric coupling**: M induced by E and P induced by H

Multiferroism: introduction

Importance of the ME coupling for the applications (spintronics, magnonics)

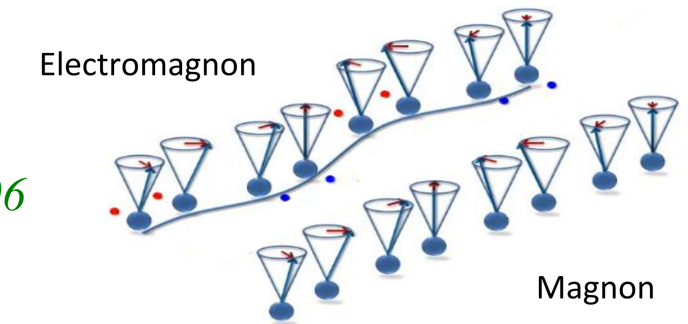
→Magnetoelectric switching
Manipulation of domains M/P by E, H

$TbMn_2O_5$
Hur Nature 2004



→Manipulation of hybrid excitations by E/H

Pimenov et al.
Nat. Phys. 2006



Multiferroism: introduction

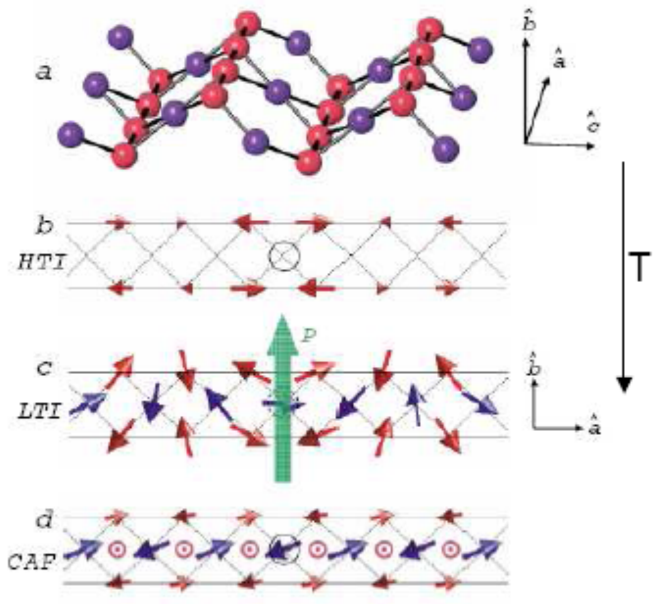
Classification of multiferroics

Type I multiferroics : $T_E \neq T_M$ Ex. $BiMnO_3$, $BiFeO_3$, $Ni_3B_7O_{13}I$

Type II multiferroics : $T_E = T_M$: Common origin

magnetic frustration
→complex magnetic orders
→loss of spatial inversion, small electric polarization
→strong ME coupling between the order parameters

Ex. $Ni_3V_2O_8$, $TbMn_2O_5$, $MnWO_4$, $TbMnO_3$, $RbFe(MoO_4)_2$



$Ni_3V_2O_8$
Lawes PRL 2005

Multiferroism: about symmetries and chirality

Importance of symmetries

Type II multiferroics: Magnetic order responsible for loss of inversion centre, necessary condition for ferroelectricity

Prediction of type and directions of ferroic orders and associated domains, and of the ME tensor symmetry

Magneto-electric type	Type of ordering: Magnetic	Type of ordering: Electric	Permitted terms of stored free enthalpy	Shubnikov point groups: V_s not permitted	Shubnikov point groups: V_s permitted	Number of Shubnikov groups	
FE IV	D	P	E EHH	1′, 21′, m1′, mm21′, 41′, 4mm1′, 31′, 3m1′, 61′, 6mm1′		10	
FE III	M̄	P	E HEE EHH	6′, 6′mm′		2	31
FE II	M̄	P	E EH HEE EHH	4′, 4′mm′	mm2, 4mm, 3m, 6mm	6	
FE I/FM I	M	P	E H EH HEE EHH	m′m′2, 3m′, 4m′m′, 6m′m′	1, 2, 3, 4, 6, m, 2′, m′, mm′2′	13	49
FM II	M	P̄	H EH HEE EHH	4̄, 4̄2′m′	2′2′2, 42′2′, 32′, 62′2′	6	
FM III	M	P̄	H HEE EHH	6̄, 6̄m′2′		2	31
FM IV	M	O	H HEE	1̄, 2/m, 2′/m′, m′m′m, 4/m, 4/mm′m′, 3̄, 3̄m′, 6/m, 6/mm′m′		10	
AA I	M̄	P̄	EH HEE EHH	222, 422, 4̄2m, 4′22′, 4̄′2m′, 32, 622, 6̄′m′2, 23, 4̄′3m′	4̄′, 4̄′2′m, 6̄′, 6̄′m2′	14	
AA II	M̄	P̄	HEE EHH	6̄m2, 6′2′2		2	122
AA III	M̄	P̄	EH	m′m′m′, 4′/m′, 4′/m′m′m, 4/m′m′m′, 3̄′m′, 6/m′m′m′, 432, m′3, m′3m′	1̄′, 2/m′, 2′/m, mmm′, 4/m′, 4/m′mm, 3̄′, 3̄′m, 6/m′, 6/m′mm	19	
AA IV	M̄	O	HEE	mmm, 4′/m, 4/mmm, 4′/mmm′, 6/mmm, 3̄m, 6′/m′, 6′/m′m′m, m3, m3m′		10	
AA IV	M̄	P̄	HEE	4′32′		1	
AA V	M̄	P̄	EHH	4̄3m		1	
AA V	D	P̄	EHH	2221′, 4̄1′, 4221′, 4̄2m1′, 6221′, 321′, 6̄1′, 6̄m21′, 231′, 4̄3m1′		10	73
AA VI	M̄	O		m3m		1	
AA VI	D	P̄		4321′		1	
AA VI	M̄	P̄		6′/m, 6′/mm′m, m′3m		3	
AA VI	D	O		1̄1′, 2/m1′, mmm1′, 4/m1′, 4/mmm1′, 3̄1′, 3̄m1′, 6/m1′, 6/mmm1′, m31′, m3m1′		11	

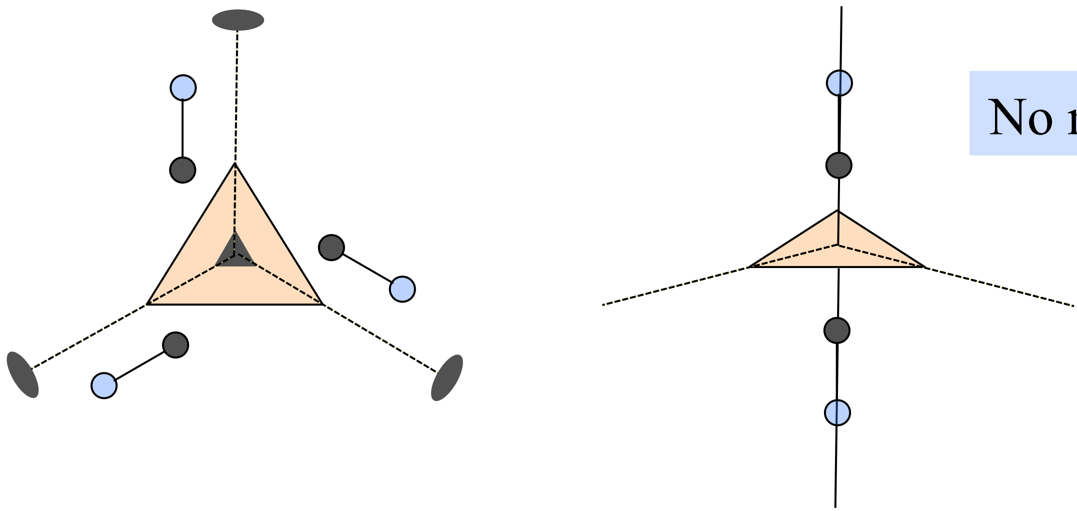
Ex. classification of magnetic point groups
H. Schmidt,
Int. J. Magn. 1973

Magneto-electric type	Type of ordering: Magnetic	Type of ordering: Electric	Permitted terms of Stored free enthalpy	Shubnikov point groups: V_s not permitted	Shubnikov point groups: V_s permitted	Number of Shubnikov groups			
FE IV	D	P	E EHH	1', 21', m1', mm21', 41', 4mm1', 31', 3m1', 61', 6mm1'		10			
FE III	$\bar{M}$	P	E HEE EHH	6', 6'mm'		2	31		
FE II	$\bar{M}$	P	E EH HEE EHH	4', 4'mm'	mm2, 4mm, 3m, 6mm	6			
FE I/FM I	M	P	E H EH HEE EHH	m'm'2, 3m', 4m'm', 6m'm'	1, 2, 3, 4, 6, m, 2', m', mm'2'	13		49	
FM II	M	$\bar{P}$	H EH HEE EHH	$\bar{4}$, $\bar{4}$2'm'	2'2'2, 42'2', 32', 62'2'	6			
FM III	M	$\bar{P}$	H HEE EHH	$\bar{6}$, $\bar{6}$m'2'		2	31		
FM IV	M	O	H HEE	$\bar{1}$, 2/m, 2'/m', m'm'm, 4/m, 4/mm'm', $\bar{3}$, $\bar{3}$m', 6/m, 6/mm'm'		10			
AA I	$\bar{M}$	$\bar{P}$	EH, HEE, EHH	32 2m, 4'22', $\bar{4}$'2m', m'2, 23, $\bar{4}$'3m'	$\bar{4}$', $\bar{4}$'2'm, $\bar{6}$', $\bar{6}$'m2'	14			
AA II	$\bar{M}$	$\bar{P}$	HEE EHH	$\bar{6}$m2, 6'2'2		2			122
AA III	$\bar{M}$	$\bar{P}$	EH	m'm'm', 4'/m', 4'/m'm'm, 4/m'm'm', $\bar{3}$'m', 6/m'm'm', 432, m'3, m'3m'	$\bar{1}$', 2/m', 2'/m, mmm', 4/m', 4/m'mm, $\bar{3}$', $\bar{3}$'m, 6/m', 6/m'mm	19			
AA IV	$\bar{M}$	O	HEE	mmm, 4'/m, 4/mmm, 4'/mmm', 6/mmm, $\bar{3}$m, 6'/m', 6'/m'm'm, m3, m3m'		10			
	$\bar{M}$	P		4'32'		1			
AA V	$\bar{M}$	$\bar{P}$	EHH	$\bar{4}$3m		1			
	D	$\bar{P}$		2221', $\bar{4}$1', 4221', $\bar{4}$2m1', 6221', 321', $\bar{6}$1', $\bar{6}$m21', 231', $\bar{4}$3m1'		10	73		
AA VI	$\bar{M}$	O		m3m		1			
	D	P		4321'		1			
	$\bar{M}$	$\bar{P}$		6'/m, 6'/mm'm, m'3m		3			
	D	O		$\bar{1}$1', 2/m1', mmm1', 4/m1', 4/mmm1', $\bar{3}$1', $\bar{3}$m1', 6/m1', 6/mmm1', m31', m3m1'		11			

Multiferroism: about symmetries and chirality

Importance of symmetries

An example "with the hands":
32 (*D*3) point group (one 3-fold axis and three 2-fold axis)



No macroscopic electric polarization

Multiferroism: about symmetries and chirality

Importance of symmetries

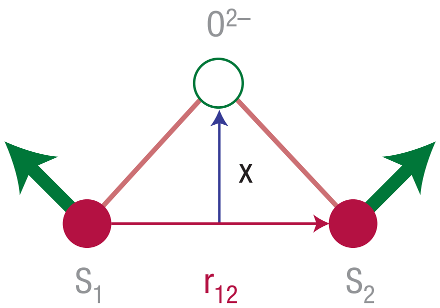
microscopic mechanisms of electronic and/or magnetostrictive origins
➔ Electric polarization

Example ferroelectricity induced by magnetic cycloid

Dzyaloshinskii-Moryia interaction

$$\vec{D}_{ij}.(\vec{S}_i \times \vec{S}_j)$$

$$\vec{D}_{ij} \propto \lambda \vec{x} \times \vec{r}_{ij}$$



Katsura et al. PRL (2005)
Sergienko et al. PRB (2006)
Cheong et al. Nat. Mat. (2007)

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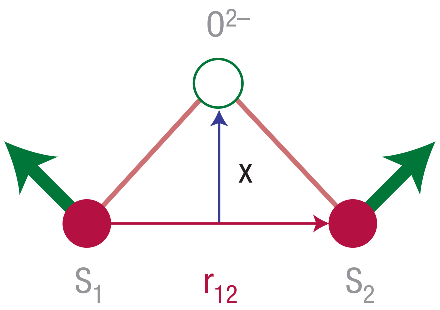
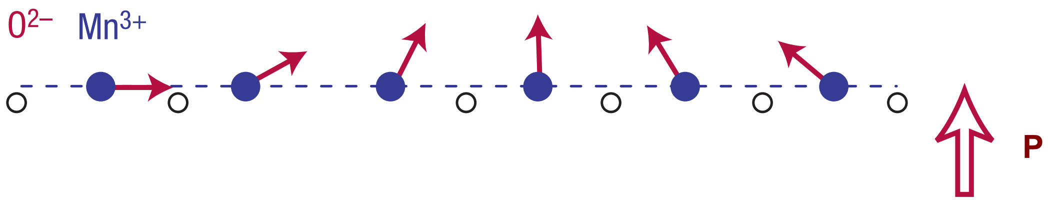


$$\vec{P} \propto \vec{r}_{ij} \times (\vec{S}_i \times \vec{S}_j)$$



Katsura et al. PRL (2005)
Sergienko et al. PRB (2006)
Mostovoy, PRL.(2006)

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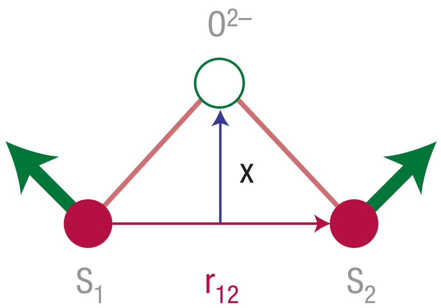
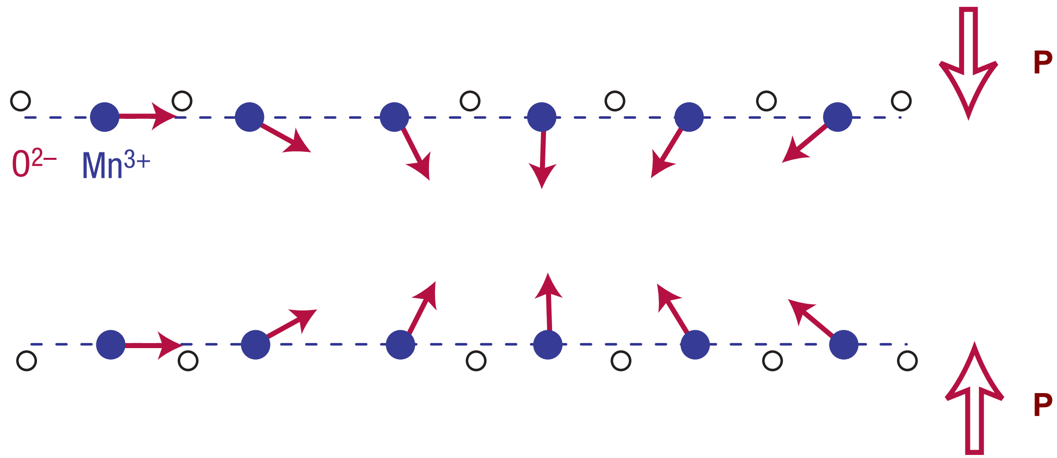




Katsura et al. PRL (2005)
Sergienko et al. PRB (2006)
Cheong et al. Nat. Mat. (2007)

Magnetic chirality/electric polarization domains

Multiferroism: about symmetries and chirality

Various way to probe the chiral scattering with polarized neutrons

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \langle N_{\mathbf{Q}} \cdot N_{\mathbf{Q}}^{\dagger}\rangle_{\omega} + \langle \mathbf{M}_{\perp\mathbf{Q}} \cdot \mathbf{M}_{\perp\mathbf{Q}}^{\dagger}\rangle_{\omega}$$
$$- i\mathbf{P}_0 \cdot \langle \mathbf{M}_{\perp\mathbf{Q}} \wedge \mathbf{M}_{\perp\mathbf{Q}}^{\dagger}\rangle_{\omega}$$
$$+ \mathbf{P}_0 \cdot \left[\langle N_{\mathbf{Q}}^{\dagger} \cdot \mathbf{M}_{\perp\mathbf{Q}}\rangle_{\omega} + \langle \mathbf{M}_{\perp\mathbf{Q}}^{\dagger} \cdot N_{\mathbf{Q}}\rangle_{\omega}\right]$$

Blume-Maleyev equations

Unpolarized neutrons

nuclear-magnetic terms

$$\mathbf{P}_f \frac{d^2\sigma}{d\Omega\, dE_f} = \mathbf{P}_0 \cdot \langle N_{\mathbf{Q}} \cdot N_{\mathbf{Q}}^{\dagger}\rangle_{\omega} - \mathbf{P}_0 \cdot \langle \mathbf{M}_{\perp\mathbf{Q}}^{\dagger} \cdot \mathbf{M}_{\perp\mathbf{Q}}\rangle_{\omega}$$
$$+ \langle N_{\mathbf{Q}}^{\dagger} \cdot \mathbf{M}_{\perp\mathbf{Q}}\rangle_{\omega} + \langle \mathbf{M}_{\perp\mathbf{Q}}^{\dagger} \cdot N_{\mathbf{Q}}\rangle_{\omega}$$
$$+ i\langle \mathbf{M}_{\perp\mathbf{Q}} \wedge \mathbf{M}_{\perp\mathbf{Q}}^{\dagger}\rangle_{\omega}$$
$$+ \langle \mathbf{M}_{\perp\mathbf{Q}}^{\dagger} \cdot (\mathbf{P}_0 \cdot \mathbf{M}_{\perp\mathbf{Q}})\rangle_{\omega} + \langle (\mathbf{P}_0 \cdot \mathbf{M}_{\perp\mathbf{Q}}^{\dagger}) \cdot \mathbf{M}_{\perp\mathbf{Q}}\rangle_{\omega}$$
$$+ i\mathbf{P}_0 \wedge \left[\langle \mathbf{M}_{\perp\mathbf{Q}}^{\dagger} \cdot N_{\mathbf{Q}}\rangle_{\omega} - \langle N_{\mathbf{Q}}^{\dagger} \cdot \mathbf{M}_{\perp\mathbf{Q}}\rangle_{\omega}\right]$$

P_0 initial polarization
P_f final polarization

Information about correlations between ≠ spin components: *chiral term*

Multiferroism: about symmetries and chirality

Various way to probe the chiral scattering with polarized neutrons

- Select spin state and direction of incident neutron ↑↓, no polarization analysis

- Analyze polarization of scattered beam in the same direction as incident polarization:
  longitudinal polarization analysis

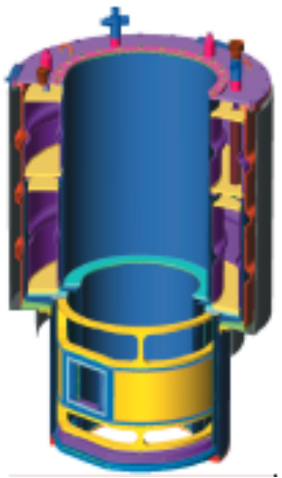
- Analyze polarization of scattered beam in any direction:
  spherical polarization analysis (CRYOPAD)

Polarization matrix P

final polarization

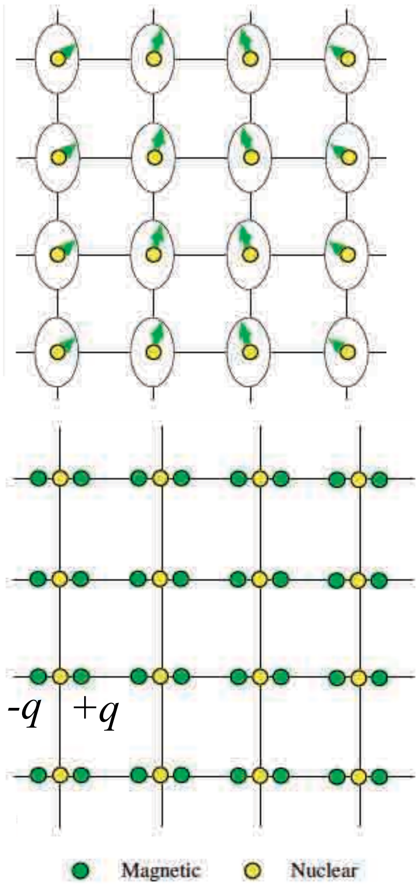
incident polarization

$$\begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix}$$



Multiferroism: examples

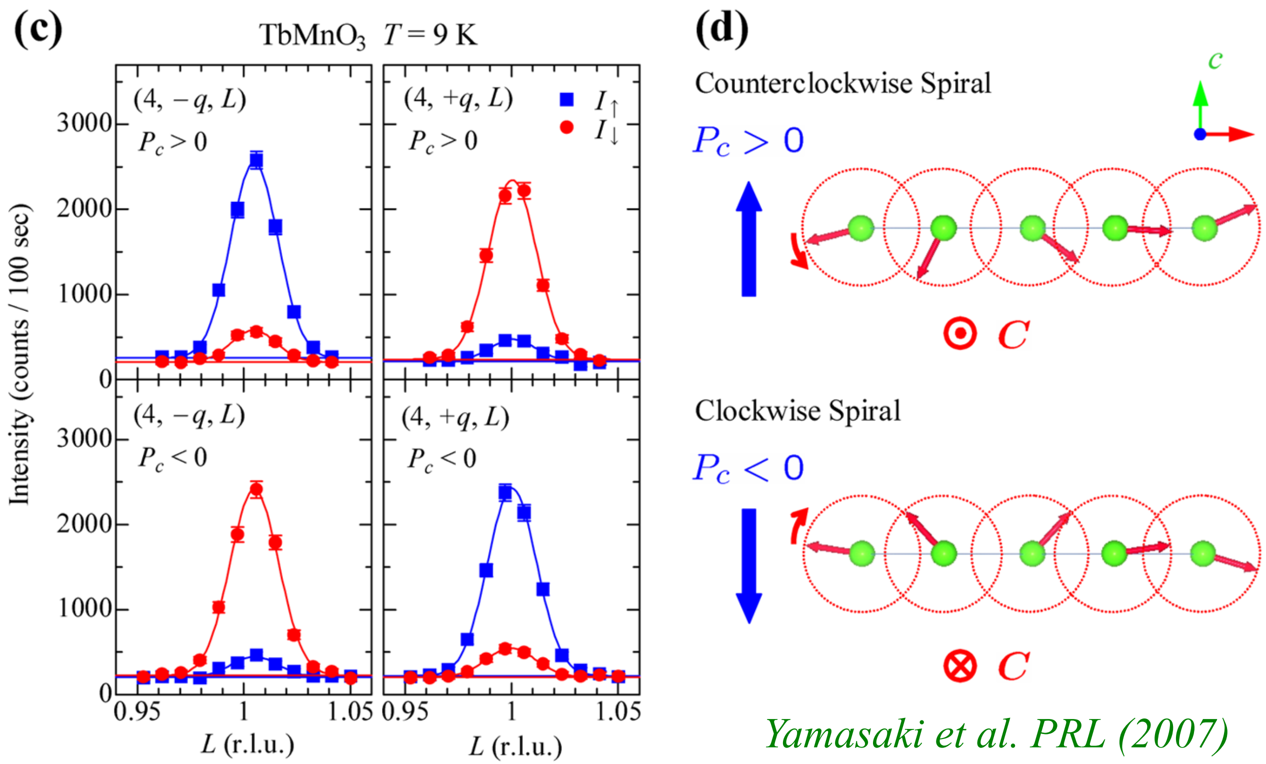
Ex: $TbMnO_3$: electric control of chirality in a magnetic cycloid



Use of polarized neutrons, no polarization analysis

$$\frac{d\sigma_M}{d\Omega}(\vec{Q} = \vec{H} \pm \vec{q}) \propto [1 + \cos^2\beta \mp 2\epsilon \cos\beta(\vec{P}_0.\hat{\vec{Q}})]\delta(\vec{Q} - \vec{H} \mp \vec{q})$$

± 1 chirality



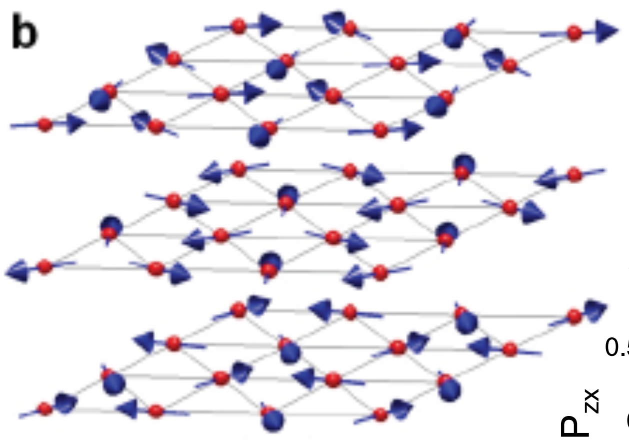
Yamasaki et al. PRL (2007)

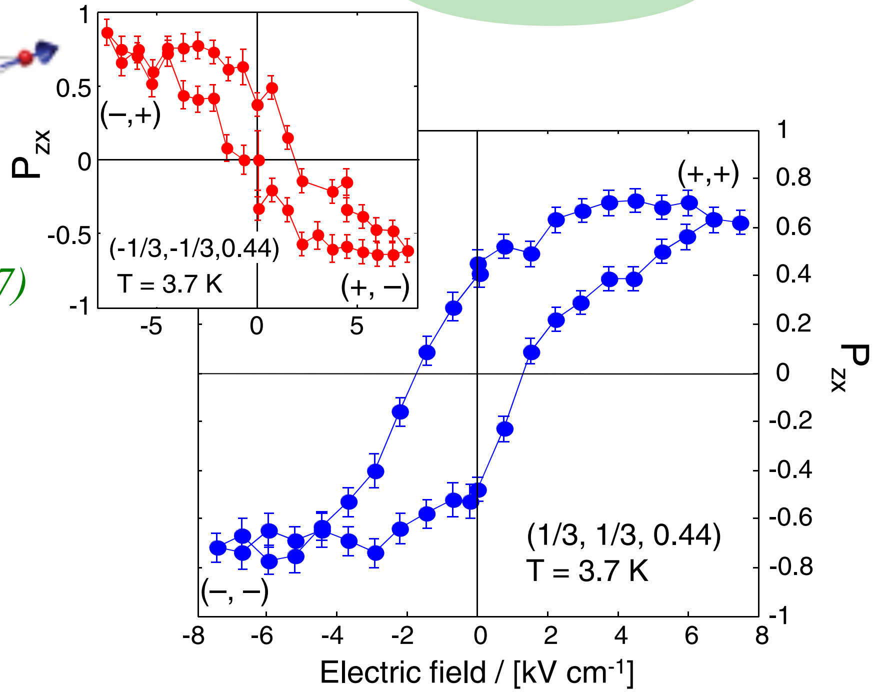
Multiferroism: examples

Ex: $RbFe(MoO_4)_2$: electrical control of triangular + helical chiralities

Use of spherical polarimetry

$$\begin{pmatrix} \frac{-M_{ch}+P_0(\sigma_N-\sigma_M^y-\sigma_M^z)}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0M_{ch}} & \frac{R_y+I_zP_0}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0M_{ch}} & \frac{R_z-I_yP_0}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0M_{ch}} \\ \frac{-M_{ch}-I_zP_0}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0R_y} & \frac{R_y+P_0(\sigma_N+\sigma_M^y-\sigma_M^z)}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0R_y} & \frac{R_z+P_0M_{yz}}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0R_y} \\ \frac{-M_{ch}+I_yP_0}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0R_z} & \frac{R_y+P_0M_{yz}}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0R_z} & \frac{R_z+P_0(\sigma_N-\sigma_M^y+\sigma_M^z)}{\sigma_N+\sigma_M^y+\sigma_M^z+P_0R_z} \end{pmatrix}$$





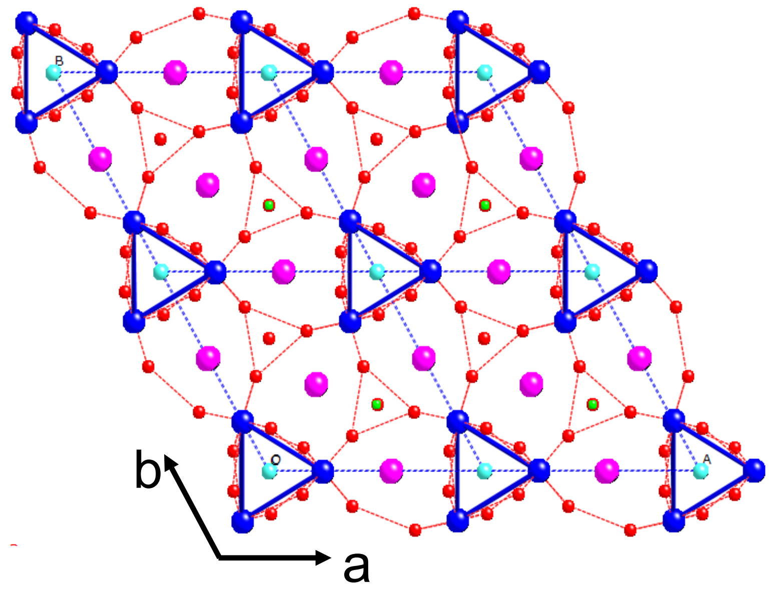
Kenzelmann et al. PRL (2007)
Hearmon et al. PRL (2012)

Multiferroism: examples

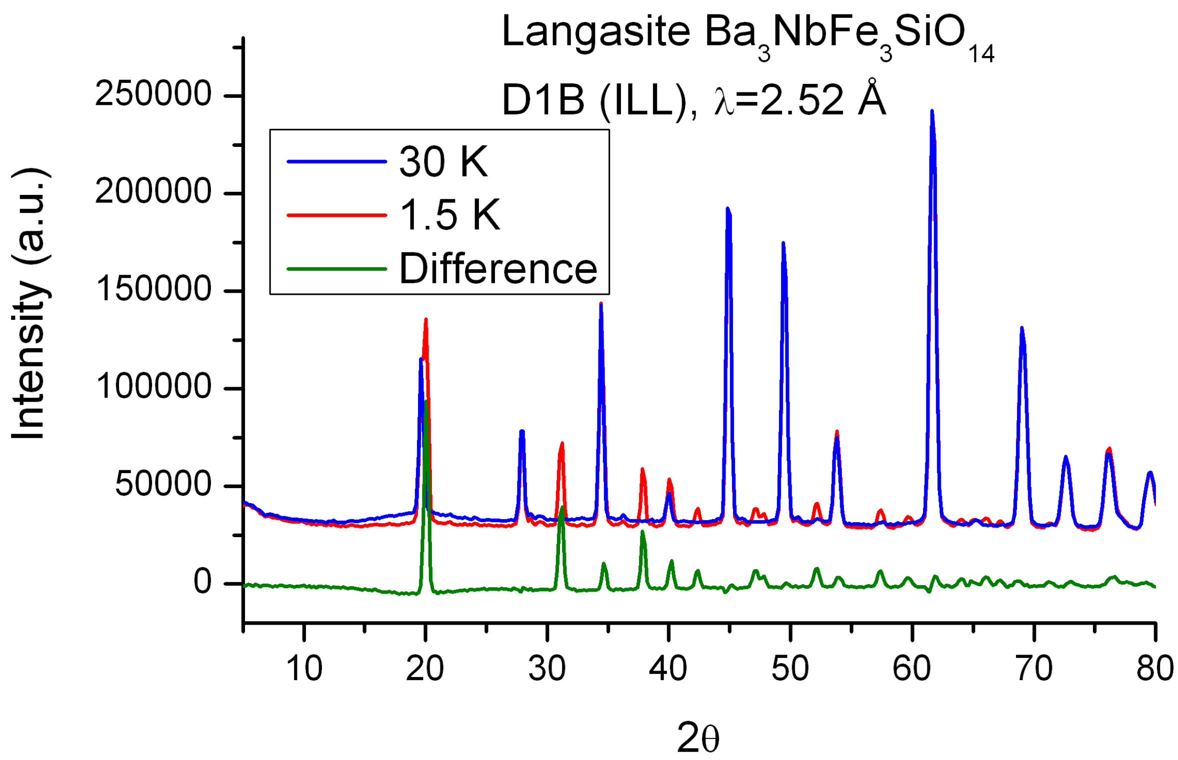
Ex: $Ba_3NbFe_3Si_2O_{14}$: trigonal space group P321
Non-centrosymmetric (chiral) structure

Powder neutron diffraction

Magnetic transition at T_N=28 K
Propagation vector q=(0, 0, ≈1/7)

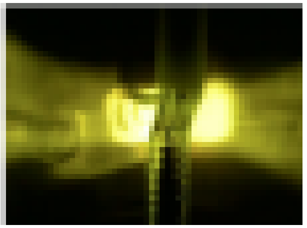


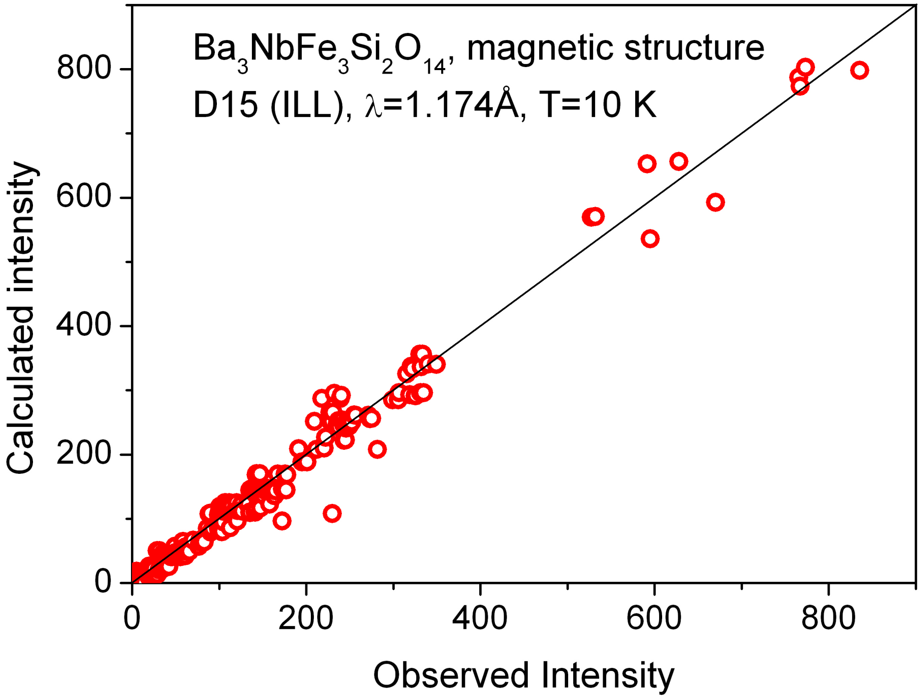
triangular lattice of Fe^{3+} triangles, S=5/2

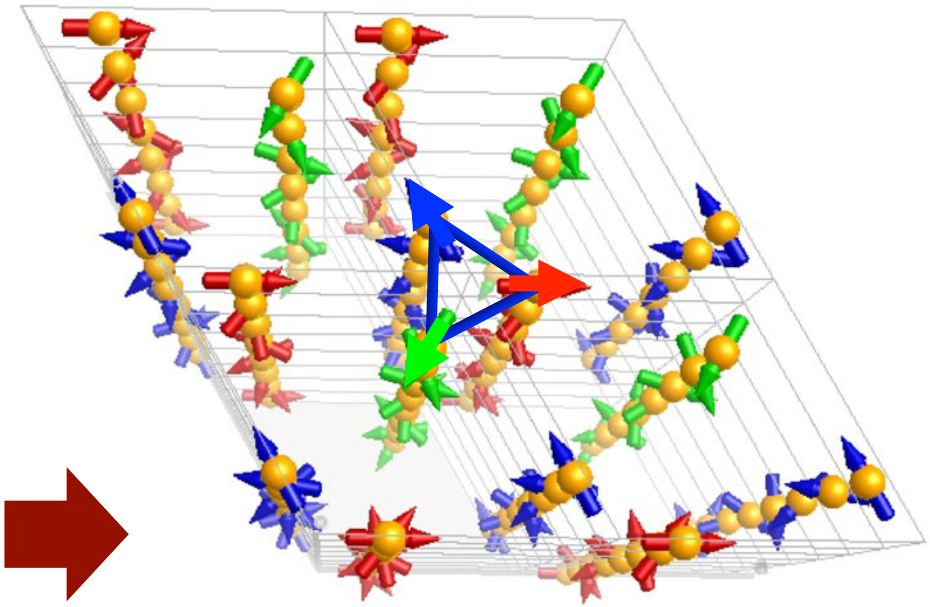


Multiferroism: examples

Single-crystal neutron diffraction: complex magnetic structure







120° moments on triangles in (a, b) plane

Helices propagating along c with period ≈7c

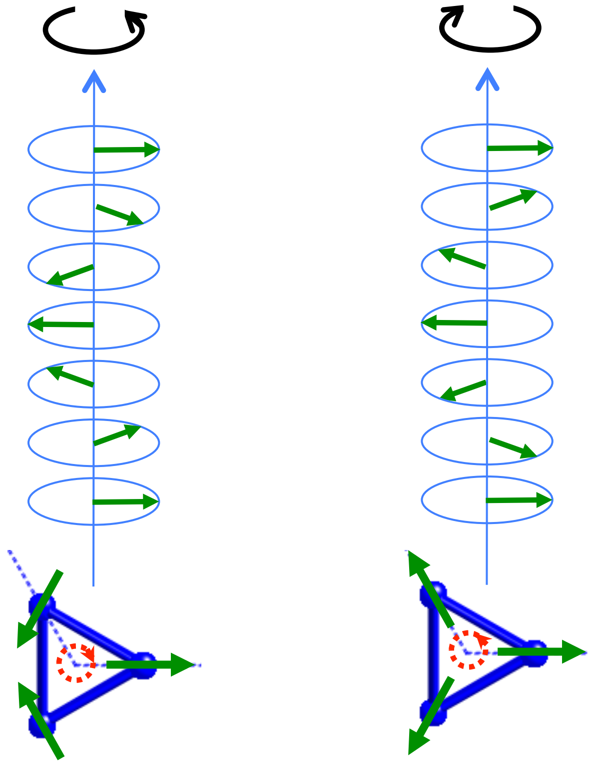
Marty et al., PRL 2008

Multiferroism: examples

Static Chirality

2 chiralities associated to helices
and triangular arrangements

Unpolarized neutron single-crystal diffraction
➔2 possible magnetic structures



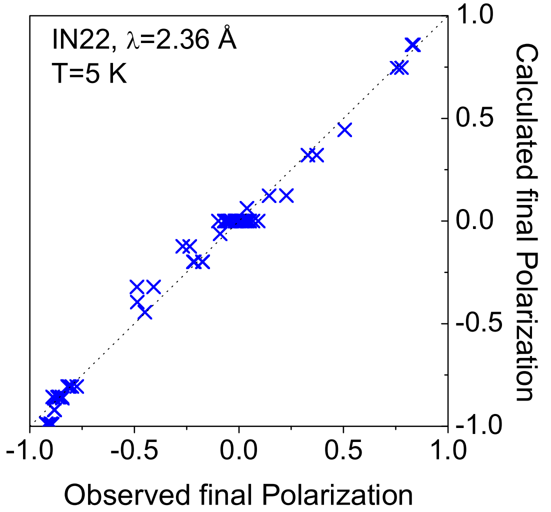
Multiferroism: examples

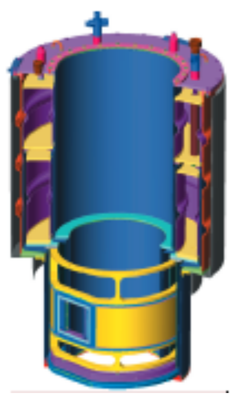
Static Chirality

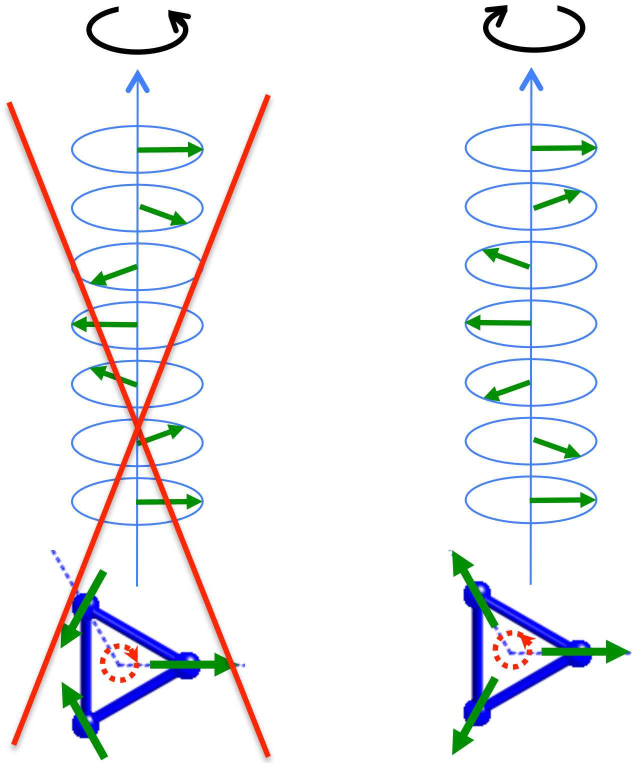
2 chiralities associated to helices and triangular arrangements

Unpolarized neutron single-crystal diffraction
➔2 possible magnetic structures

Spherical polarization analysis with CRYOPAD
➔A single possibility is selected



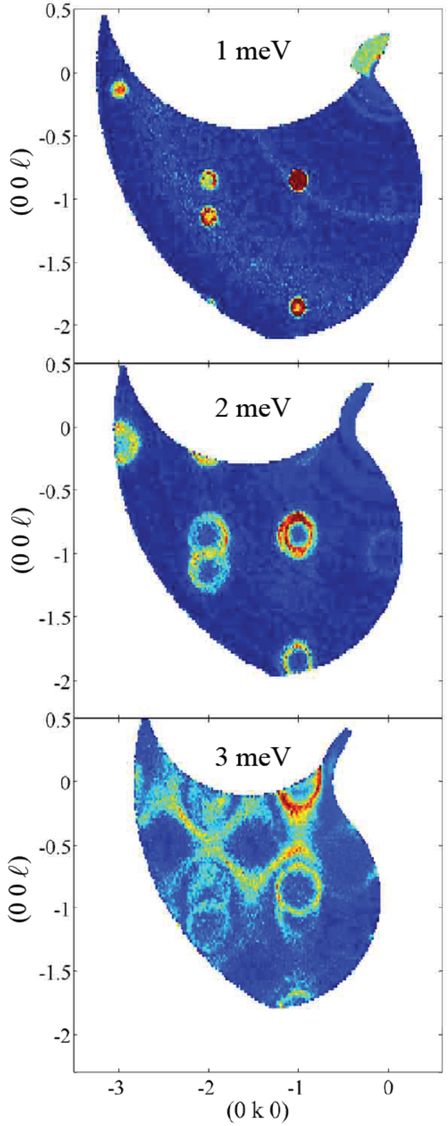




➔Single domain chiral structure

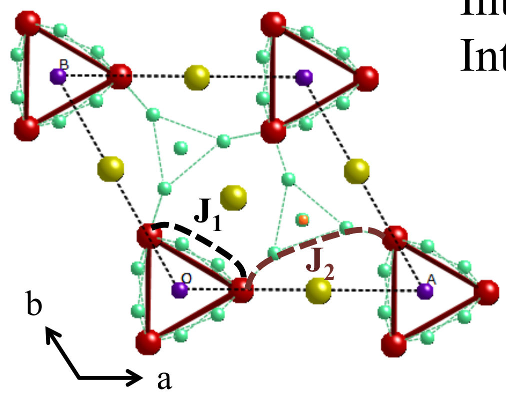
Multiferroism: examples

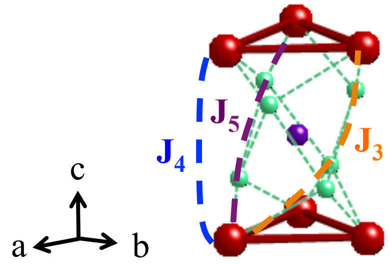
Experiment

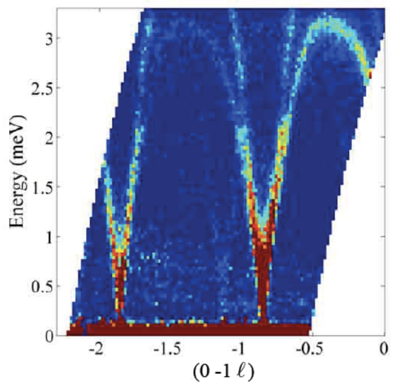


**Inelastic neutron scattering:
spin waves and GS Hamiltonian**

Intra-plane interactions ➔120°arrangement
Inter-plane interactions ➔helix

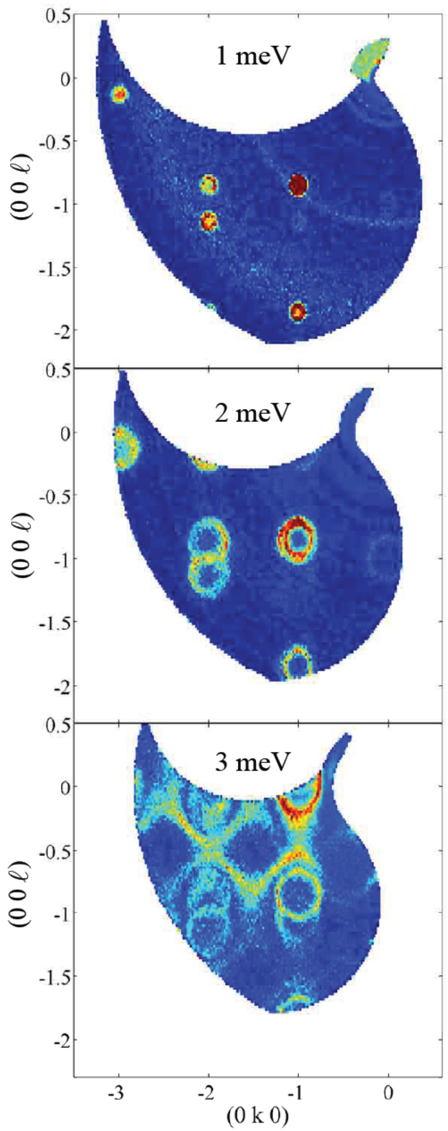






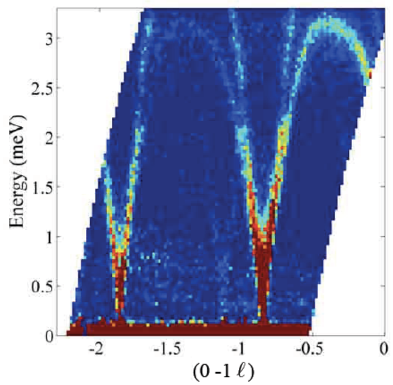
Multiferroism: examples

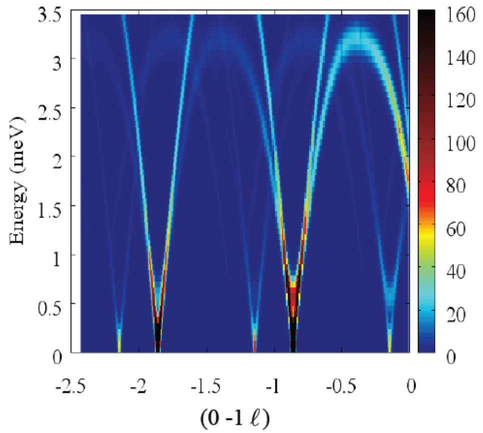
Experiment



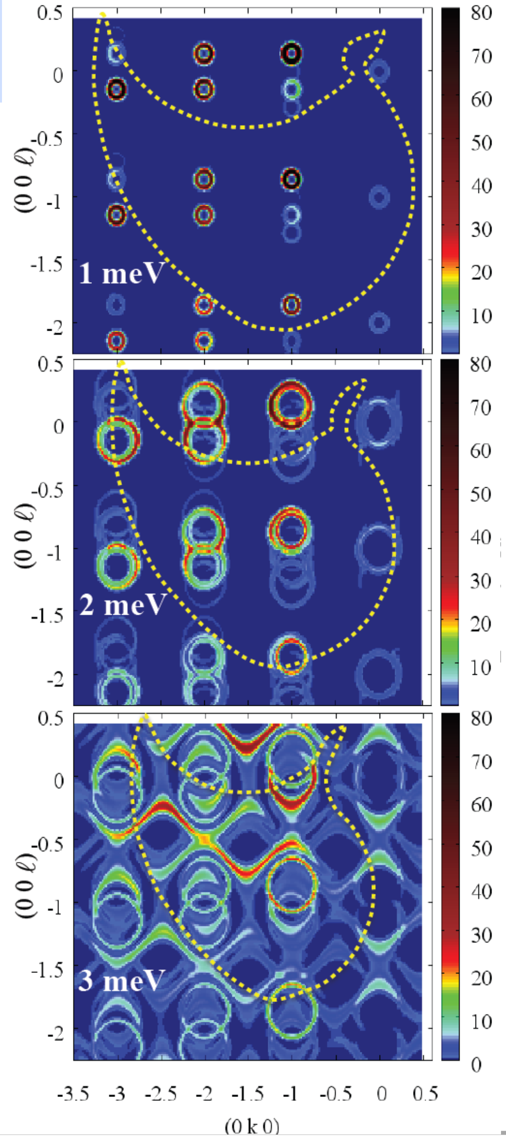
Inelastic neutron scattering: spin waves and GS Hamiltonian

Model:	J_1=0.85 meV
	J_2=0.24 meV
	J_3=0.053 meV
	J_4=0.017 meV
	J_5=0.24 meV
	DM+SI anisotropy





Calculation



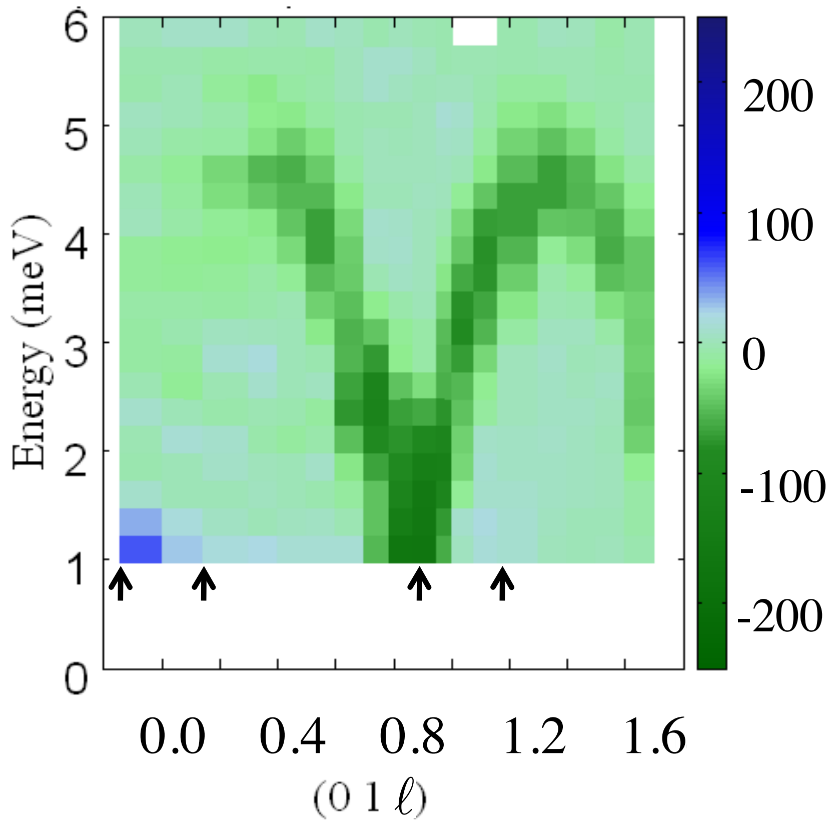
Loire et al. PRL 2011

Multiferroism: examples

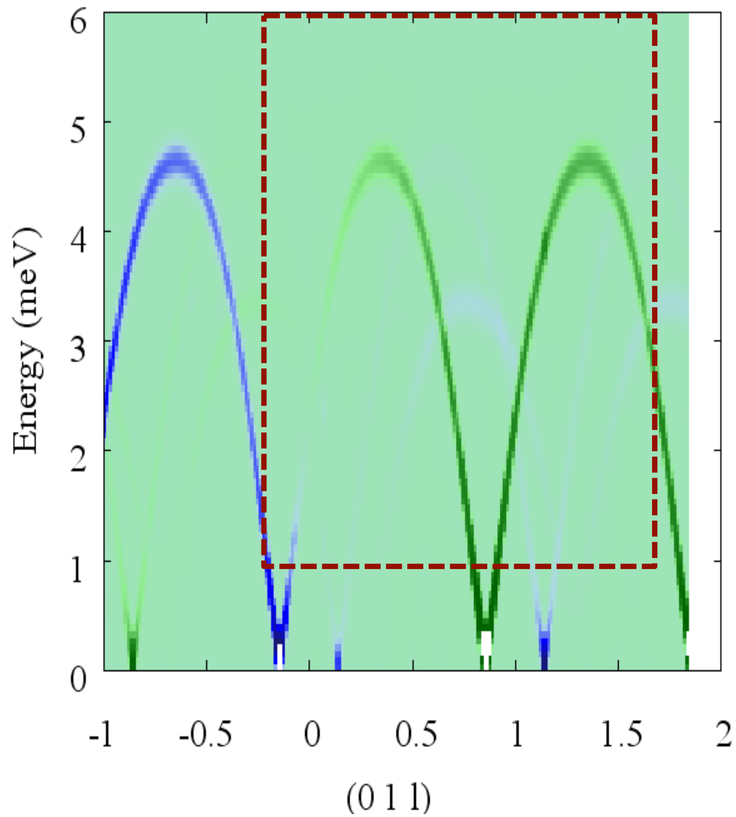
Dynamical Chirality

Fully chiral spin wave branch measured by longitudinal polarization analysis

Experiment



Calculation



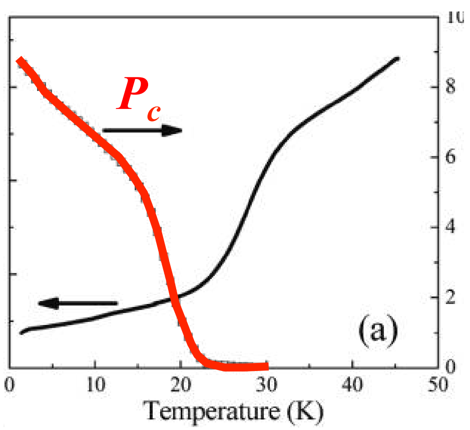
Dynamical fingerprint of the ground state magnetic chirality

Loire et al. PRL 2011

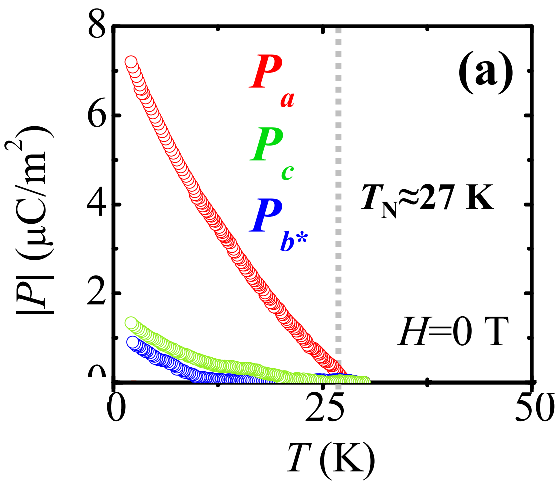
Multiferroism: examples

Multiferroicity?

Zhou et al. Chem. Mater. 2009



Lee et al. APL 2014



weak P // a or // c?

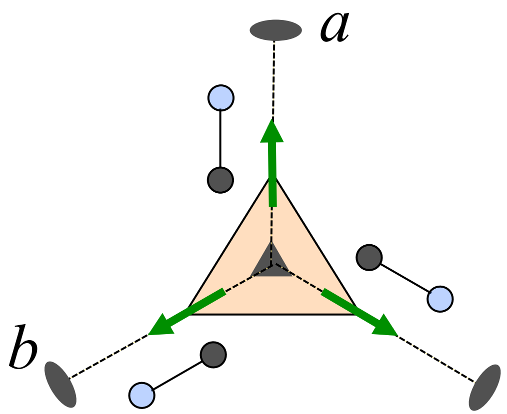
Multiferroism: examples

Multiferroicity?

Forbidden satellites along the (0,0,l) direction:

$$\vec{F}_M(0,0,\ell \pm q) = pf(|\vec{Q}|) \sum_{\nu=1,3} [\frac{\mu\hat{u} \pm i\mu\hat{v}}{2}] e^{\mp i\Phi_\nu} \; e^{i2\pi\frac{(\ell \pm q)}{2}}$$

$$= pf(|\vec{Q}|)[\frac{\mu\hat{u} \pm i\mu\hat{v}}{2}] e^{i2\pi\frac{(\ell \pm q)}{2}} (1 + e^{\mp i\frac{2\pi}{3}} + e^{\mp i\frac{4\pi}{3}}) = 0$$



Multiferroism: examples

Multiferroicity?

Forbidden satellites along the (0,0,l) direction

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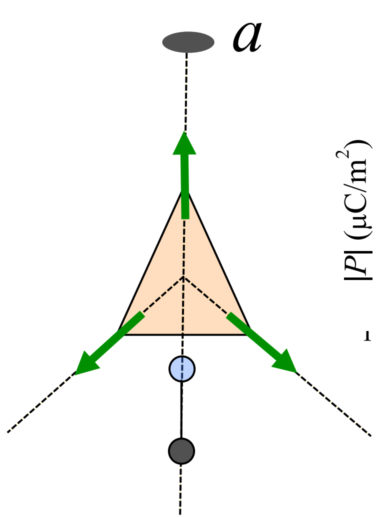
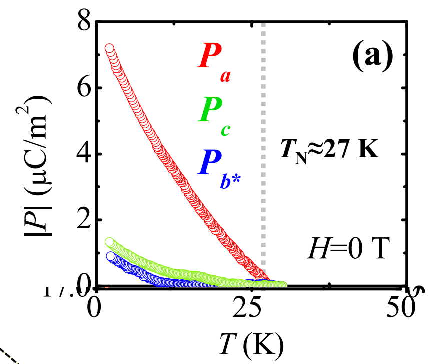
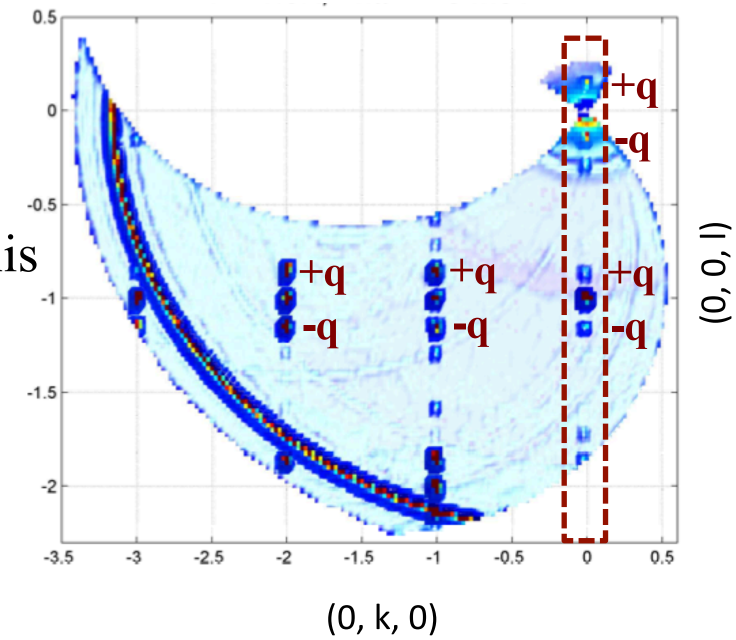
➔deviation from the 120° arrangement: loss of 3-fold axis





(b,c*) scattering plane*
IN5, λ = 4Å, T=1.6 K
Zero energy cut



Chaix et al. submitted

➔ polarization along the 2-fold axis *a*

Complexity is beautiful!

Thank you for your attention

Acknowledgments :
J. Robert, E. Lhotel, R. Ballou, E. Lefrançois