

Observation of Spin-chiral Domains in Multiferroic Hexaferrites by Scanning Resonant X-ray Microdiffraction

- Study of Magnetoelectric Effects due to Multi-spin Variables -

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Collaborators

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Spring-8, RIKEN Y. Tanaka, S. Shin (Scanning Resonant X-ray diffraction)

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ISSP, Univ. of Tokyo M. Soda (Neutron diffraction)

Outline

1. Introduction: Magnetoelectric effect & multi-spin variables

2. Room-temperature magnetoelectrics possibly by spin spiral

Hexaferrites $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ with the Z-type structure

**3. Observation of Spin-chiral Domains in Multiferroic Hexaferrites
by Scanning Resonant X-ray**

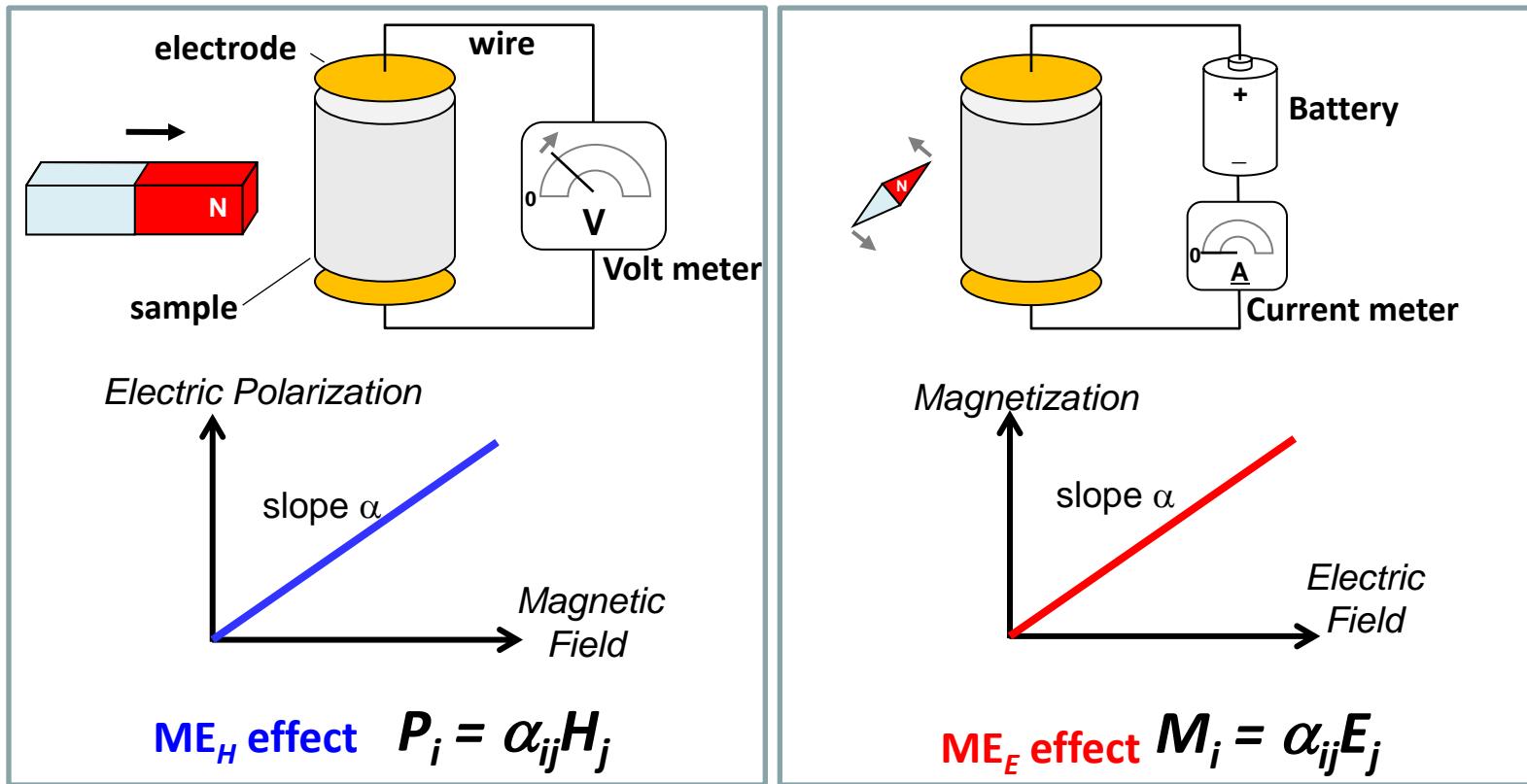
Hexaferrites $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ with the Y-type structure

4. Magnetoelectric effect observed in a magnetically-disordered system

XY-like spin-glass $(\text{Ni},\text{Mn})\text{TiO}_3$ with the ilmenite structure

Magnetoelectric (ME) effect

Magnetoelectric effect \Rightarrow Induction of **Polarization** by **Magnetic fields** (ME_H) or **Magnetization** by **Electric fields** (ME_E)



P. Curie [1894]

First proposal of the ME effect on symmetry grounds.

Landau & Lifshitz [1957] Shows that the ME effect should exist in magnetic crystals.

Dzyaloshinskii [1959] Shows that the AF Cr_2O_3 has a magnetic symmetry which allows the effect.

Astrov [1960] First successful observation of the effect in a Cr_2O_3 crystal.

Symmetry aspect is useful to explain the ME effect.

$$M_i = \alpha_{ij} E_j$$

Since E is a polar 1st rank tensor & M is an axial 1st rank tensor,
the ME effect is an axial 2nd rank tensor which transforms as follows.

In tensor form, $M'_i = \pm|a|a_{ij}M_j = \pm|a|a_{ij}\alpha_{jk}E_k$

In matrix form,

$$(M') = \pm|a| (a) (M) = \pm|a| (a) (\alpha) (E)$$

$$= \pm|a| (a) (\alpha)(a)_t (E') = (\alpha') (E') \Rightarrow (\alpha') = \pm|a| (a)(\alpha)(a)_t$$

e.g. inversion operation $\bar{1}$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

$$= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The ME effect vanishes for all symmetry groups containing time reversal symmetry (1').

$$(\alpha') = (-1)(+1)(+1)(\alpha)(+1) = (-\alpha) = (\alpha) = 0$$

The ME effect also disappears for ordinary inversion symmetry ($\bar{1}$) operations.

$$(\alpha') = (+1)(-1)(-1)(\alpha)(-1) = (-\alpha) = (\alpha) = 0$$

For space inversion accompanied by time inversion ($\bar{1}'$), the ME effect is permitted.

$$(\alpha') = (-1)(-1)(-1)(\alpha)(-1) = (\alpha) = (\alpha)$$

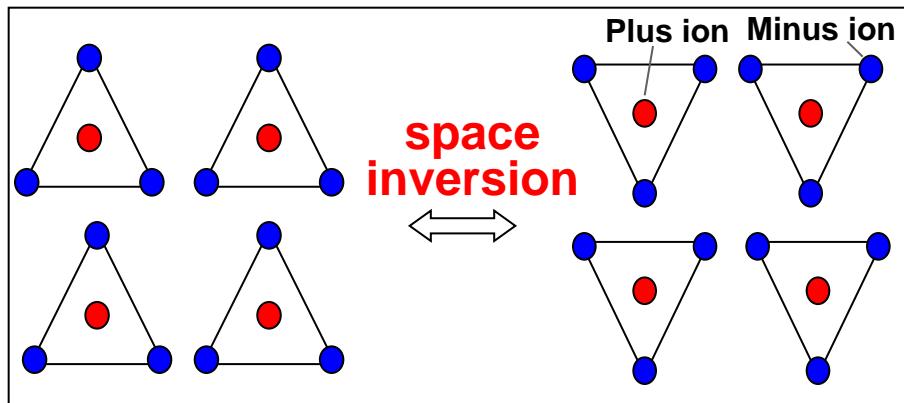
Requirements
of the linear ME effect



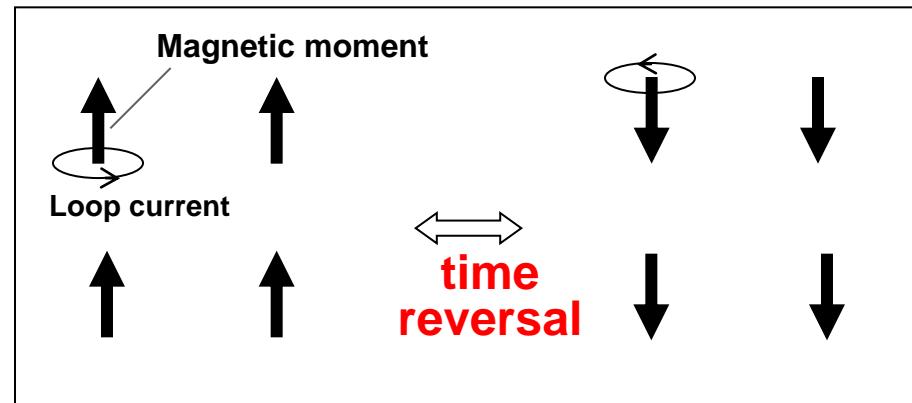
Both space inversion symmetry
& time reversal symmetry must be broken.

Constraints on appearance of linear ME effect

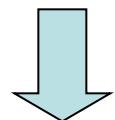
—Breaking of Space Inversion & Time reversal symmetries—



e.g., ferroelectrics

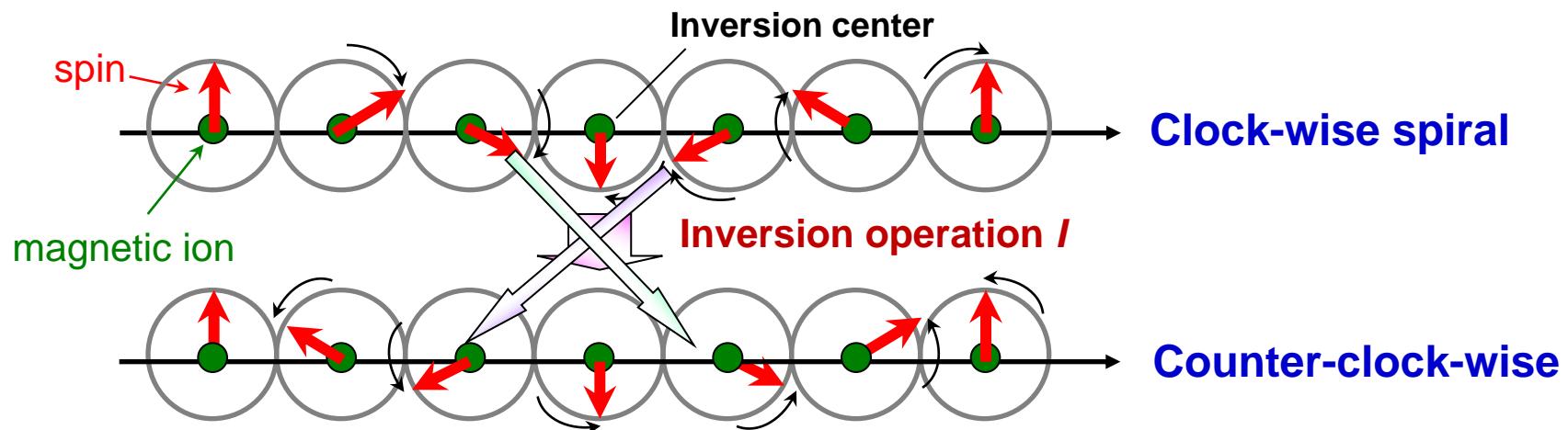


e.g., ferromagnets



Multiferroics

Broken of space inversion symmetry in spiral spin systems

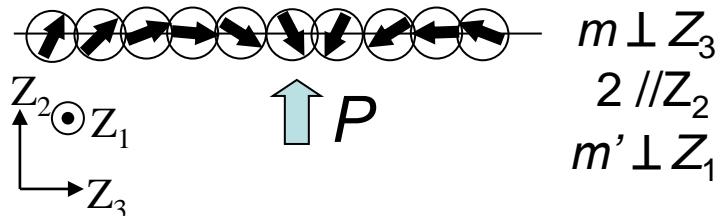


The CW & CCW spiral structures are inverted by I to each other.
However, these two spiral structures are not identical.

Thus, the inversion symmetry is broken by a spiral spin order.

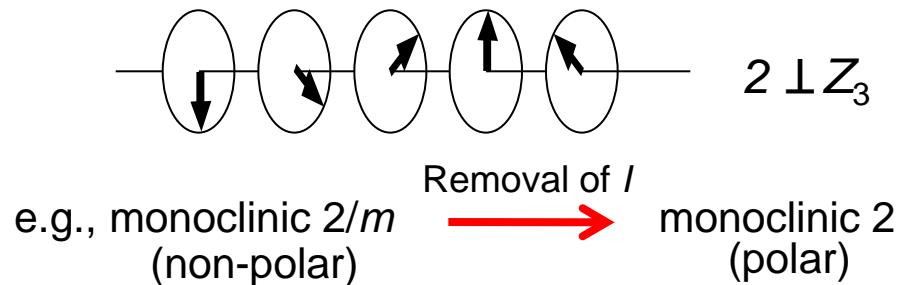
To make system ferroelectric,

1. Cycloidal spiral structure



2. Screw spiral structure

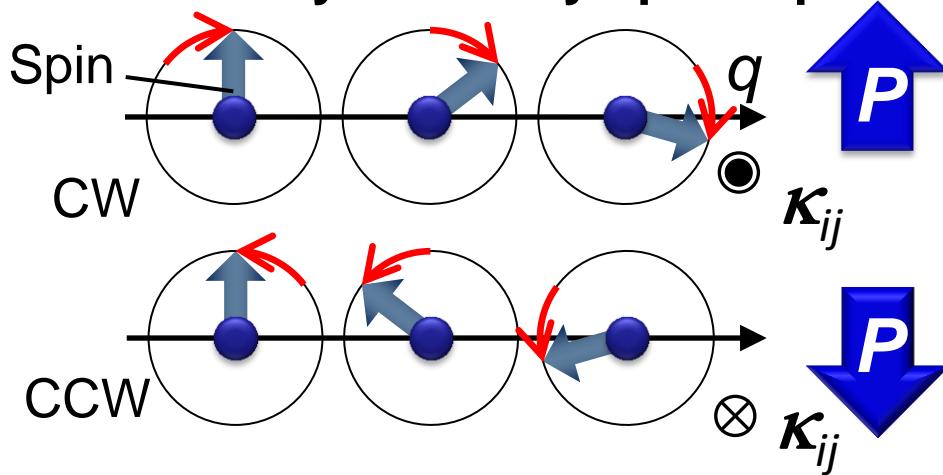
+ low crystal symmetry



An example of multi-spin variables which induces ME coupling

- Vector spin chirality -

- Ferroelectricity driven by spiral spin order



Y. Yamasaki et al.,
PRL 98, 147204 (2007).

Vector spin chirality

$$\kappa_{ij} \equiv \mathbf{S}_i \times \mathbf{S}_j$$

Spin-current (or Inverse DM) interaction

$$p_{ij} \propto \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$$

Katsura et al., PRL (2005); Sergienko & Dagotto PRB (2006)

✓ Polarization $P \Leftrightarrow$ Chirality κ_{ij}

Vector spin chirality can be detected as electric polarization P through ME coupling.

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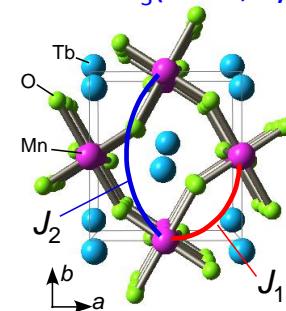
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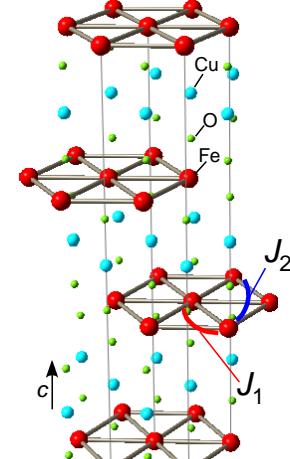
List of spin-spiral-driven ferroelectrics

Compound	Crystal structure	Magnetic ion	Proposed spin structure	Temperature range (K)	Ref.
$RMnO_3$ ($R=Tb$, etc.)	O (mmm) [perovskite]	Mn^{3+} S=2	cycloidal	≤ 28	Kimura et al. (2003)
$Ni_3V_2O_8$	O (mmm)	Ni^{2+} S=1	cycloidal	3.9~6.3	Lawes et al. (2005)
$(Ba,Sr)_2M_2Fe_{12}O_{22}$	R (-3m) [haxaferrite]	Fe^{3+} S=5/2	screw, L-conical ($B=0$) T-conical ($B>0$)	≤ 110	Kimura et al. (2005)
$CuFeO_2$	R -3m [delafossite]	Fe^{3+} S=5/2	collinear($B=0$) screw ($B>0$)	≤ 11	Kimura et al. (2005)
$CoCr_2O_4$	C ($m3m$) [spinel]	Co^{2+} Cr^{3+} S=3/2 S=3/2	T-conical	≤ 26	Yamasaki et al. (2006)
$MnWO_4$	M ($2/m$) [wulfenite]	Mn^{2+} S=5/2	cycloidal	7~12.5	Taniguchi et al. (2006)
$RbFe(MoO_4)_2$	R (-3m)	Fe^{3+} S=5/2	screw	≤ 3.8	Kenzelmann et al. (2006)
$LiCu_2O_2$	O (mmm)	Cu^{2+} S=1/2	cycloidal	≤ 23	Park et al. (2007)
$LiCuVO_4$	O (mmm)	Cu^{2+} S=1/2	cycloidal	≤ 2.4	Naito et al. (2007)
CuO	M ($2/m$) [tenorite]	Cu^{2+} S=1/2	cycloidal + screw	212~230	Kimura et al. (2008)
$ACrO_2$ ($A=Ag, Cu$)	R (-3m) [delafossite]	Cr^{3+} S=3/2	screw	≤ 24	Seki et al. (2008)
$FeVO_4$	Tri (-1)	Fe^{3+} S=5/2	cycloidal	≤ 16	Daoud-Aladine et al. (2009)
$CuCl_2$	M ($2/m$) [distorted CdI ₂]	Mn^{2+} S=5/2	cycloidal	≤ 24	Seki et al. (2010)

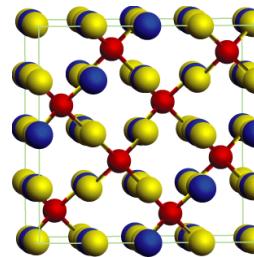
Perovskite
 $RMnO_3$ ($R=Tb, Dy$)



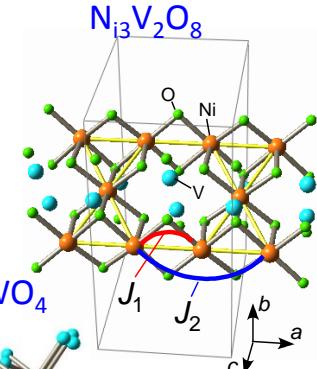
Delafossite
 $Cu(Fe,Cr)O_2$



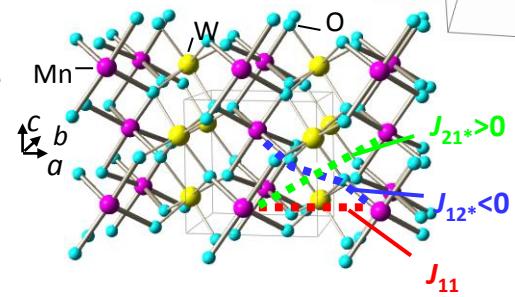
Spinel $CoCr_2O_4$



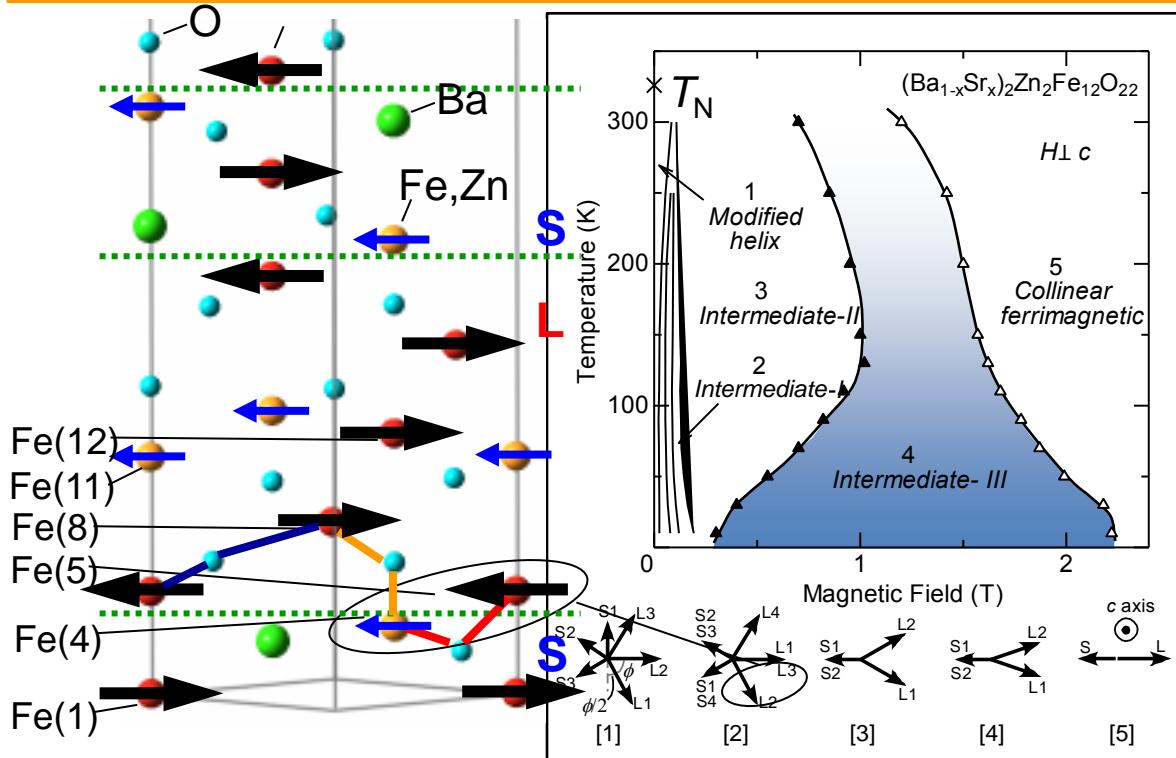
Kagome staircase
 $Ni_3V_2O_8$



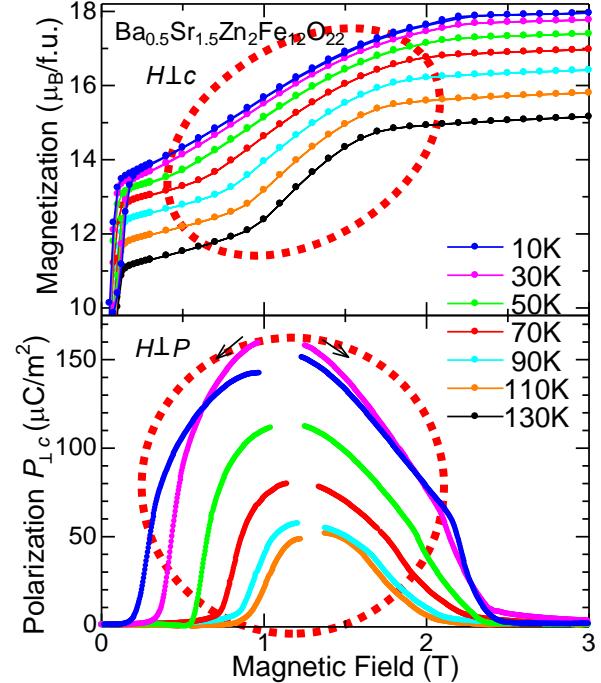
Wulfenite $MnWO_4$



High- T multiferriocs - Y-type hexaferrite $(\text{Ba},\text{Sr})_2(\text{Zn},\text{Mg})_2\text{Fe}_{12}\text{O}_{22}$ -



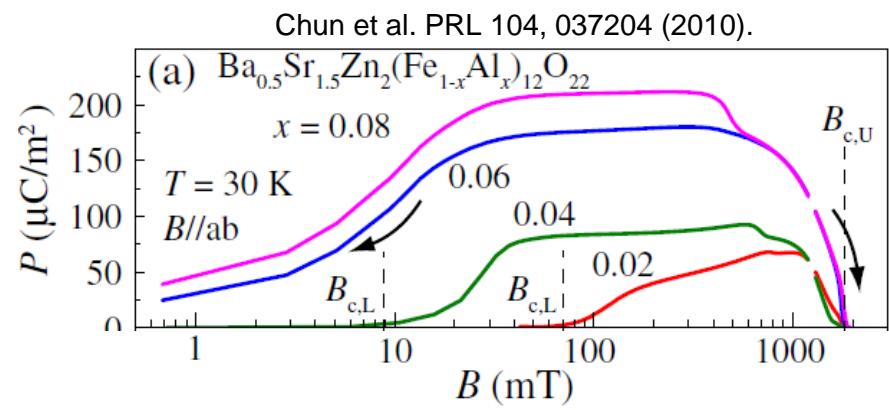
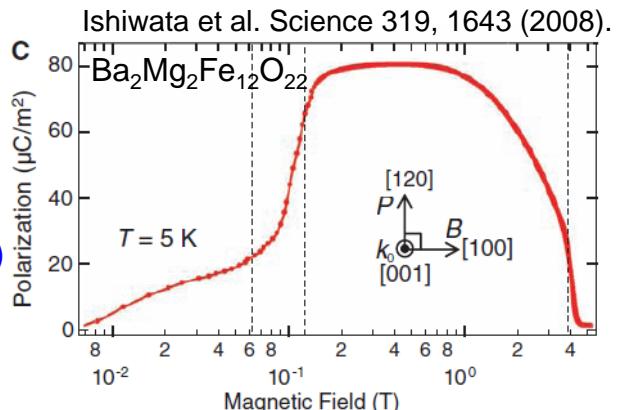
Kimura et al., PRL 94, 137201 (2005)



Ferroelectric intermediate-III phase survives up to near room temperature.

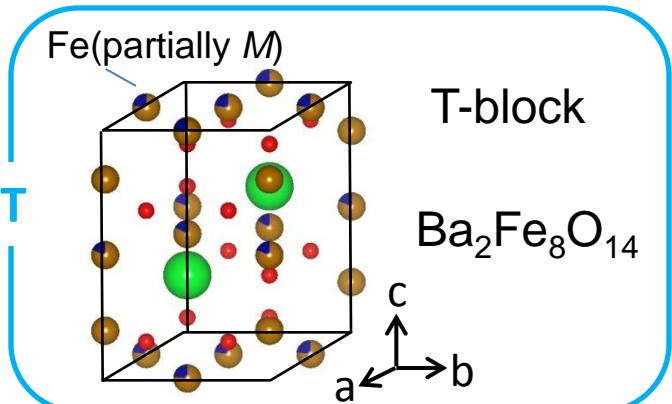
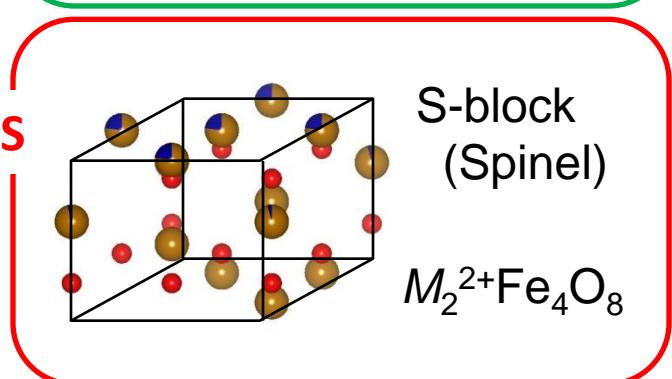
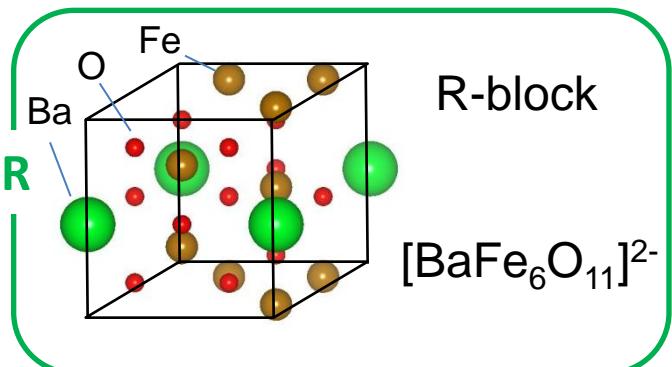
However, suppression of resistivity does not allow experimental observation of polarization above $\sim 110\text{K}$.

ME effect
at low H ($\sim \text{mT}$)
but only at low T
($\sim 30\text{K}$)



Classification of hexagonal ferrites

- Stacking sequence composed of 3 types of blocks-



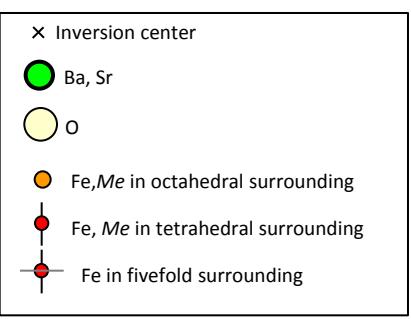
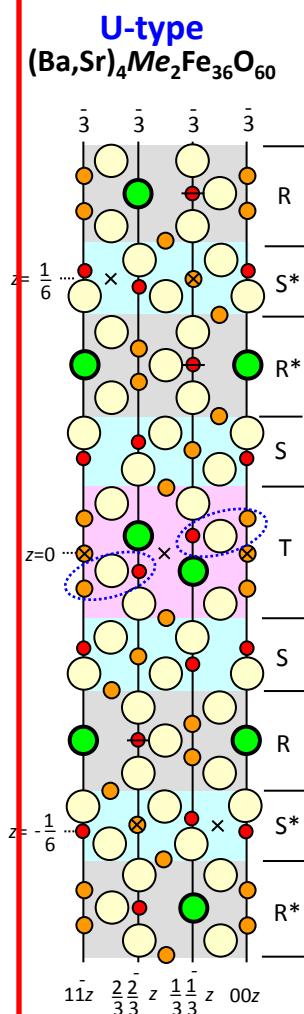
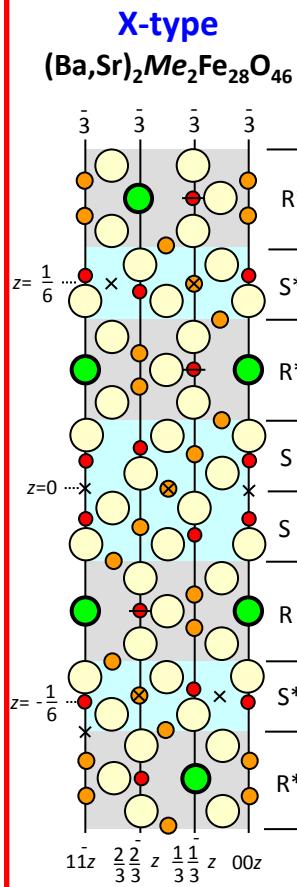
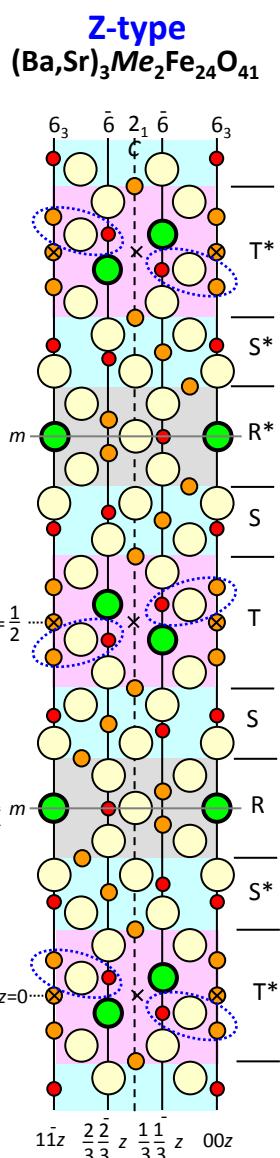
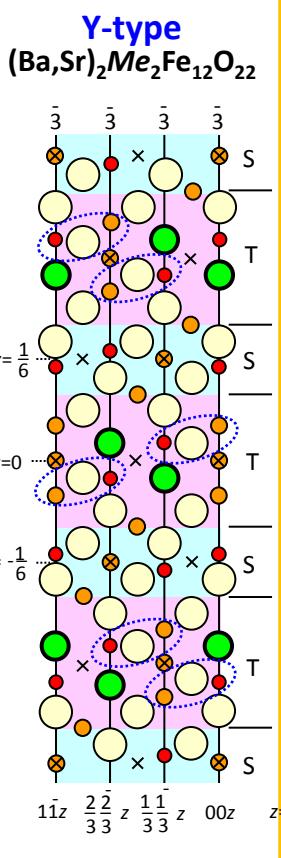
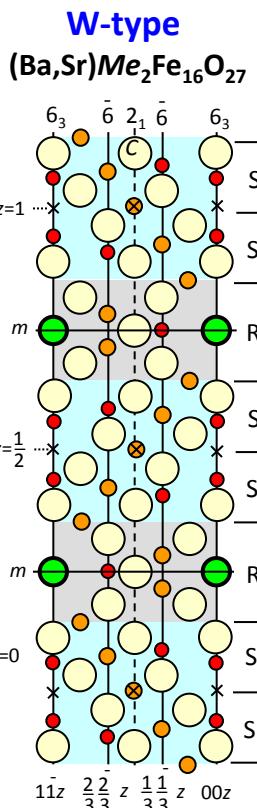
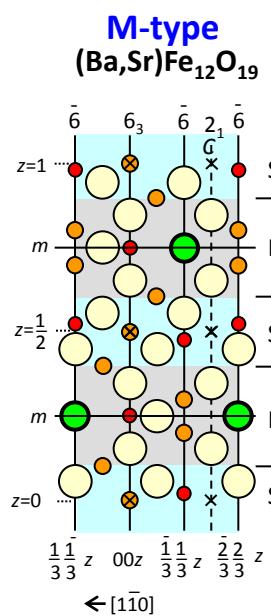
J. Smit & H.P.J. Wijn, Ferrite (Philips' Technical Library, 1959)

	Chem. form.	stacking	c(Å)	S.G.
M	$BaFe_{12}O_{19}$	RSR^*S^*	23.19	$P6_3/mmc$
W	$BaM_2Fe_{16}O_{27}$	$RS_2R^*S^*_2$	32.84	$P6_3/mmc$
Y	$Ba_2M_2Fe_{12}O_{22}$	$(TS)_3$	43.56	$R-3/m$
Z	$Ba_3M_2Fe_{24}O_{41}$	$RSTS R^*S^*T^*S^*$	52.3	$P6_3/mmc$
X	$Ba_2M_2Fe_{28}O_{46}$	$(RSR^*S^*)_3$	84.11	$R-3/m$
U	$Ba_4M_2Fe_{36}O_{60}$	$(RSR^*S^*TS^*)_3$	113	$R-3/m$

M-type
(magnetoplumbite)
 $BaFe_{12}O_{19}$
($c=23.19\text{ \AA}$)



Crystal structures of 6 main types of hexaferrites



Former studies on magnetism of Z-type hexaferrites

Noncollinear Magnetic Structures in Hexagonal Ferrites of the $\text{Ba}_{3-x}\text{Sr}_{3-x}\text{Zn}_2\text{Fe}_{24}\text{O}_{41}$ (Z) System

M. I. NAMTALISHVILI, O. P. ALESHKO-OZHEVSKII, AND I. I. YAMZIN

Crystallography Institute, USSR Academy of Sciences

Submitted July 26, 1971

Zh. Eksp. Teor. Fiz. 62, 701–709 (February, 1972)

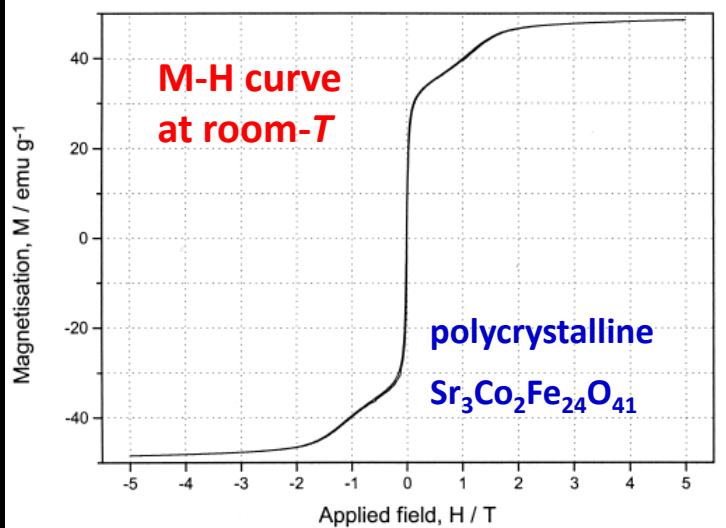


Zh. Eksp. Teor. Fiz.
62, 701 (1972)

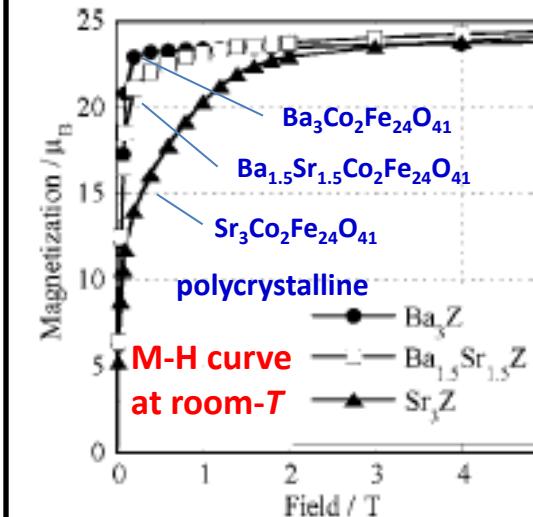
Single crystals are investigated at temperatures from 78°K up to the Curie point for values $x=2.4, 2.0, 1.5, 0$. The neutron diffraction pattern is explained on the basis of angular magnetic structures which combine spin collinearity within certain blocks of the unit cell and noncollinearity of their summary magnetic moments. Noncollinearity is observed in crystals in which a significant part of the ions are replaced by strontium. With increase of strontium concentration and lowering of temperature, a deviation of the spins from the hexagonal axis occurs and the angle between directions of the summary magnetic moments of the blocks increases. Moreover, spin modulation at temperatures below 110–120°K arises. The noncollinearity is ascribed to violation in the exchange interaction scheme on localization of zinc ions in crystallographic positions at the block boundaries.

Noncollinear
spin structure?

Pullar et al., Mater. Res. Bull. 36, 1531 (2001).



Takada et al., JAP 100, 043904 (2006).

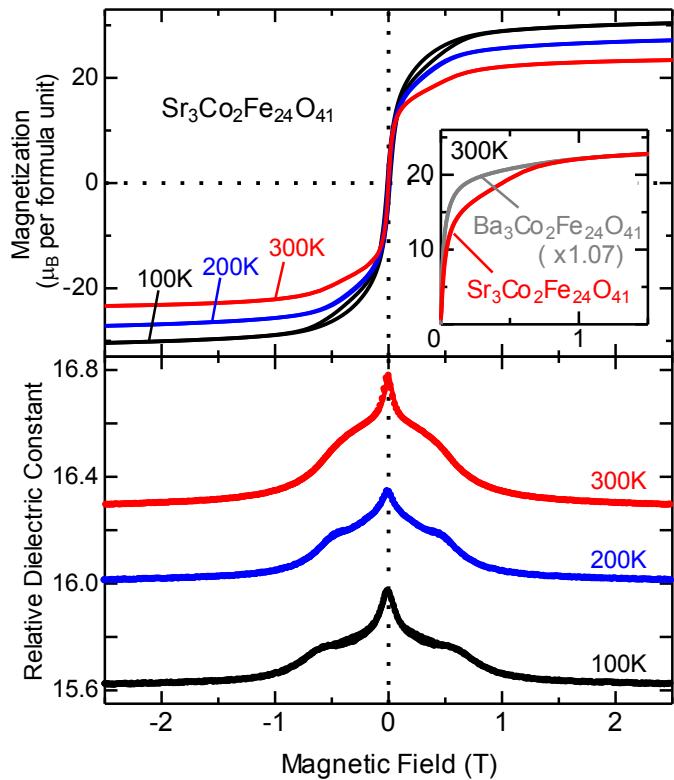


M of $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ increases in a stepwise fashion.

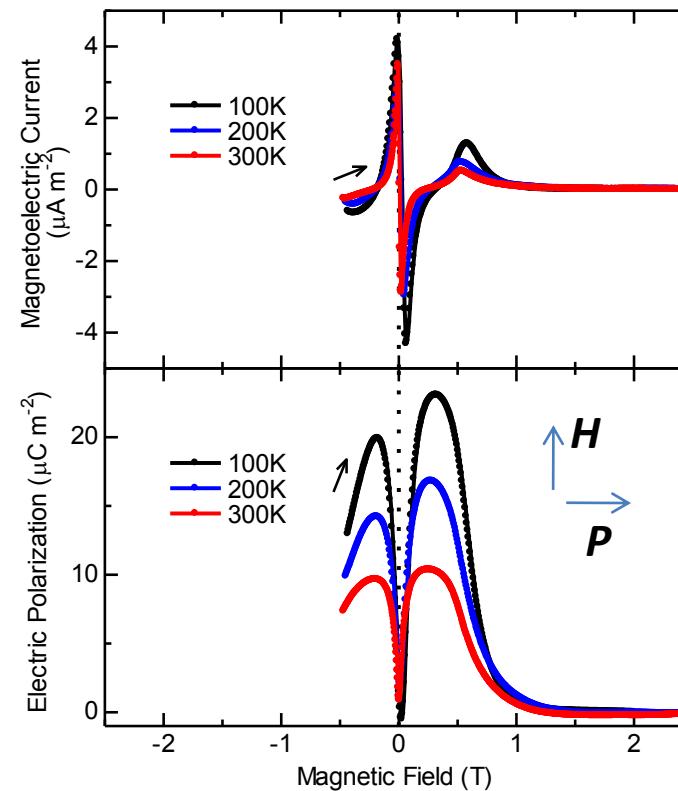
→ Similar to magnetoelectric Y-type hexaferrites

Magnetic & magnetoelectric properties of Z-type $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$

polycrystalline ceramics sintered in oxygen.



Kitagawa et al., Nature Mater. 9, 797 (2010).



ME_H effects are observed at a wide T range including room temperature.

*ME coefficient defined as $\alpha = \mu_0 dP/dB$

The α exceeds 1×10^{-10} s/m below 0.04T and reached a maximum $\sim 2.5 \times 10^{-10}$ s/m at 0.003T.

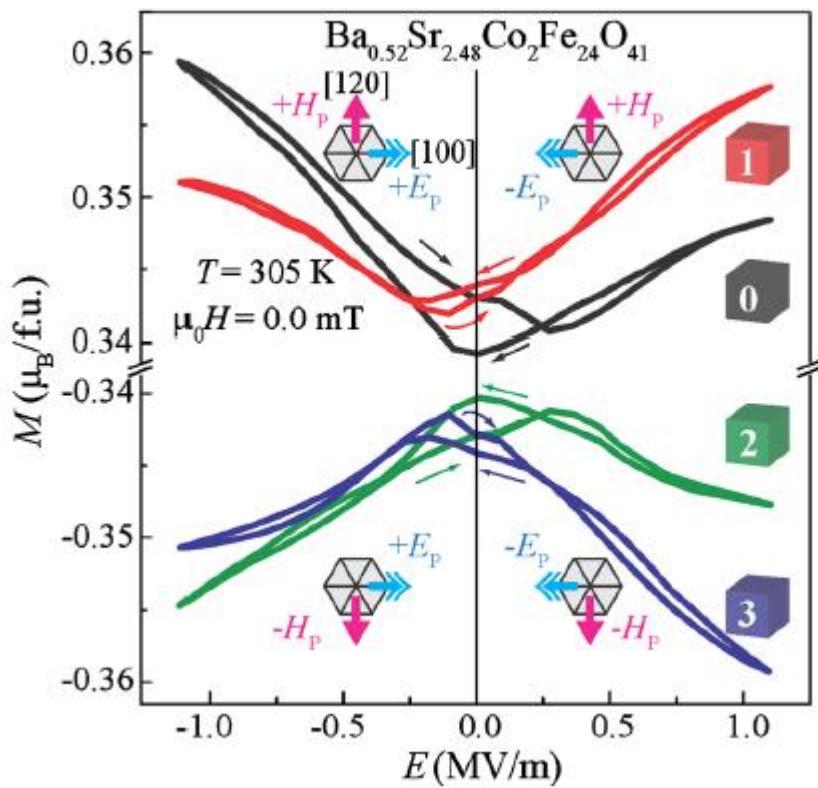
(c.f. α in Cr_2O_3 : 4×10^{-12} s/m; α in Z-type single crystal: 3×10^{-9} s/m by Chun et al. PRL 108, 177201 (2012)

Recently, ME_E effects are also observed at room temperature. \Rightarrow

Electric control of Magnetism in Z-type hexaferrites

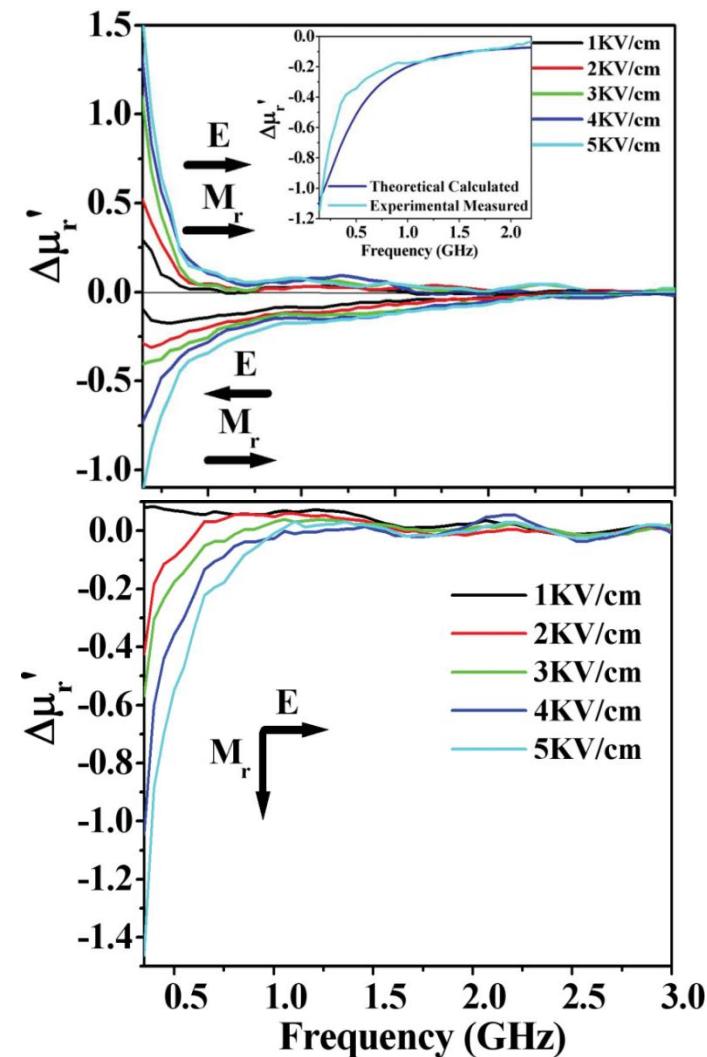
Change in Magnetization by E

Chun et al. Phys. Rev. Lett. 108, 177201 (2012)



Change in magnetic permeability at GHz range by E

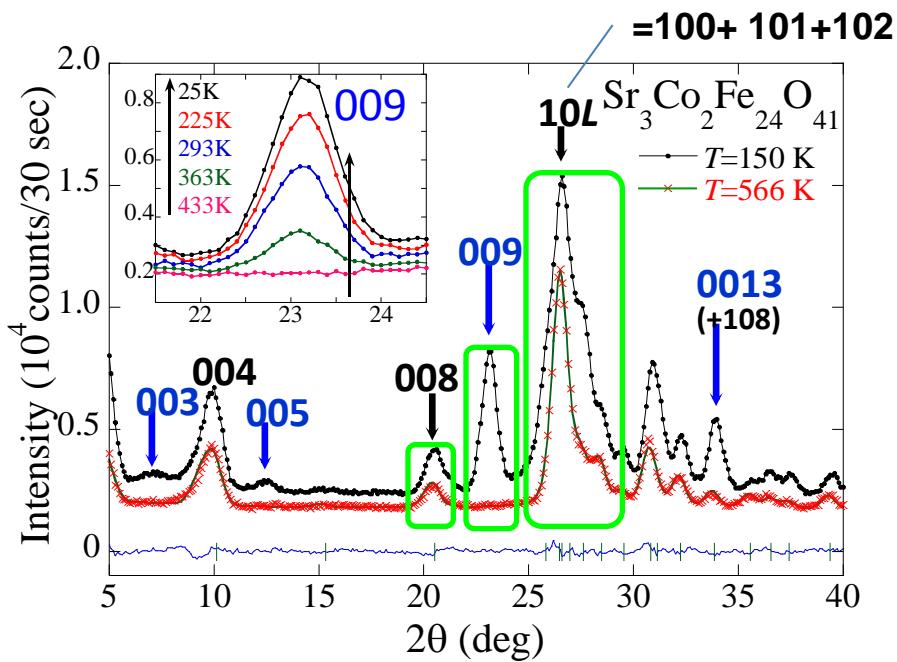
Ebnabbasi et al. Phys. Rev. B 86, 024430 (2012)



Understanding of the origin of the ME effect of Z-type $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$

Neutron powder diffraction (at JRR-3 of JAEA, Tokai, Japan)

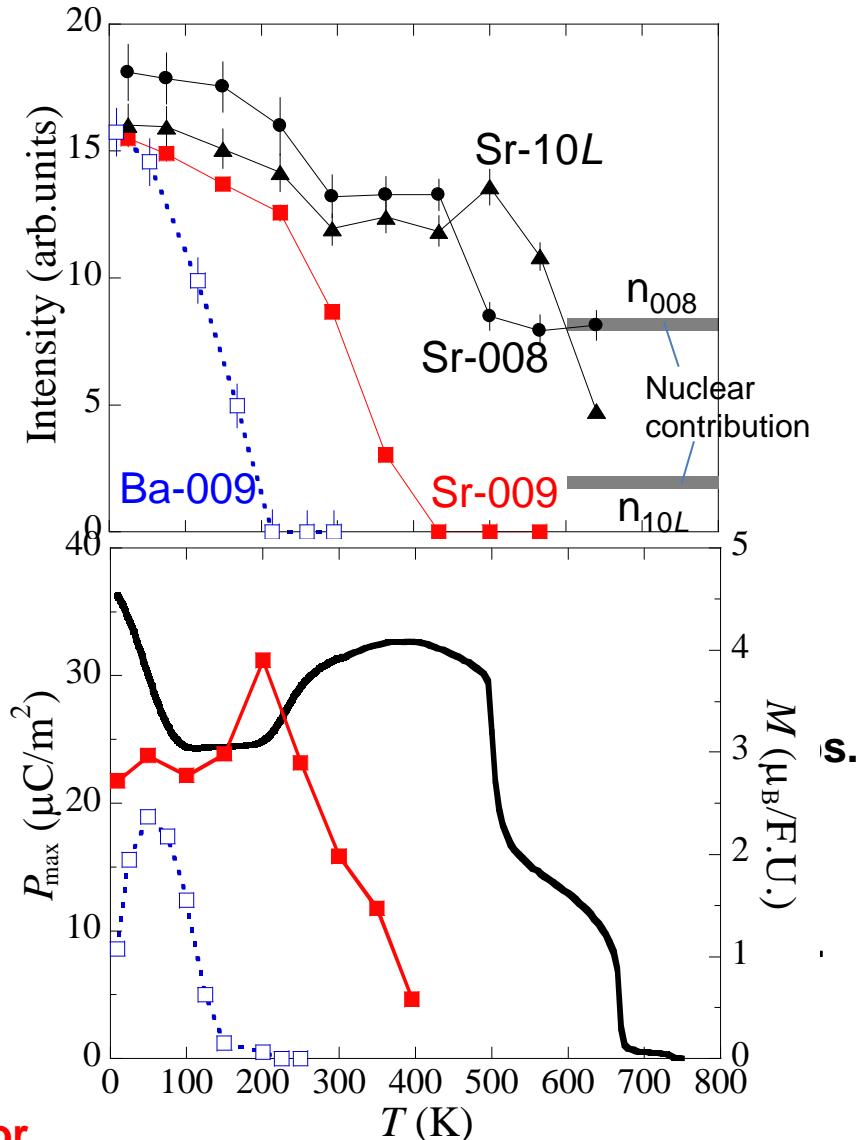
Soda et al., PRL 106, 087201 (2011).



*Below ~670K, a ferrimagnetic ordering where

*Below ~500K, the moments rotate toward the a

*Below ~400K, a new magnetic order $[(0,0,1_0)]$ b

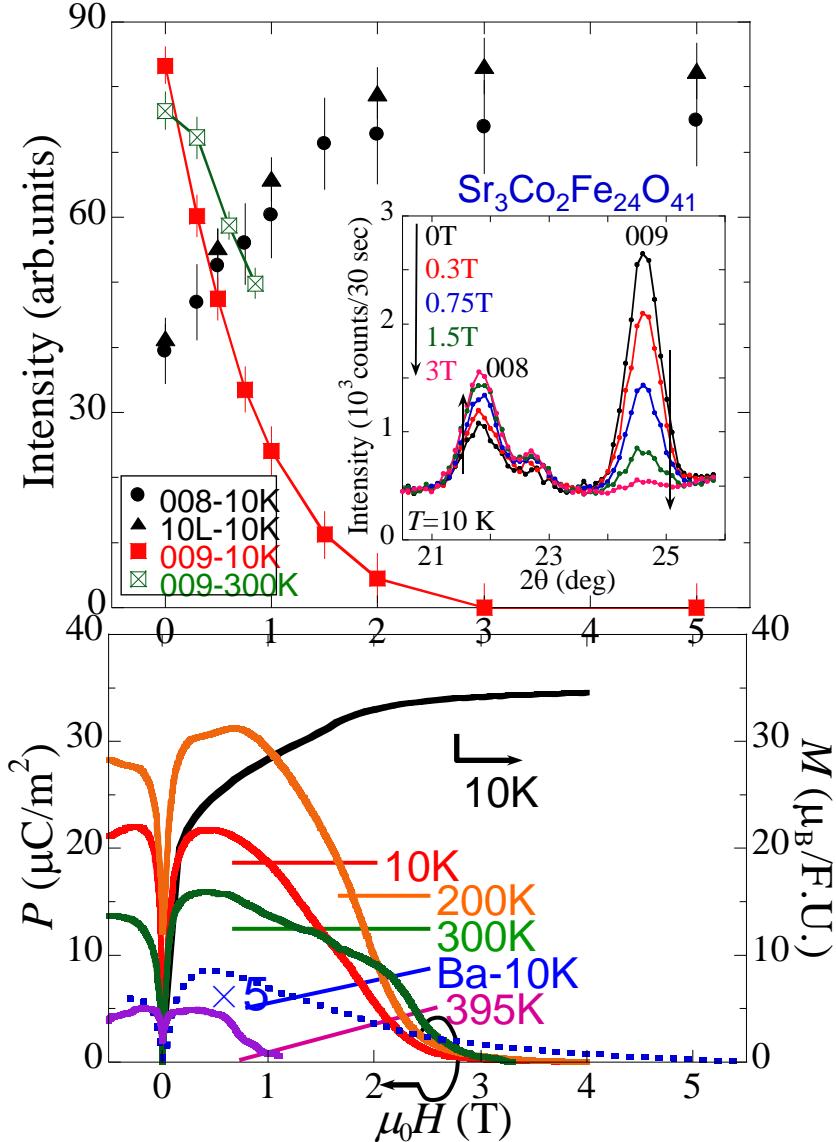


The magnetic order with $(0,0,1)$ propagation vector

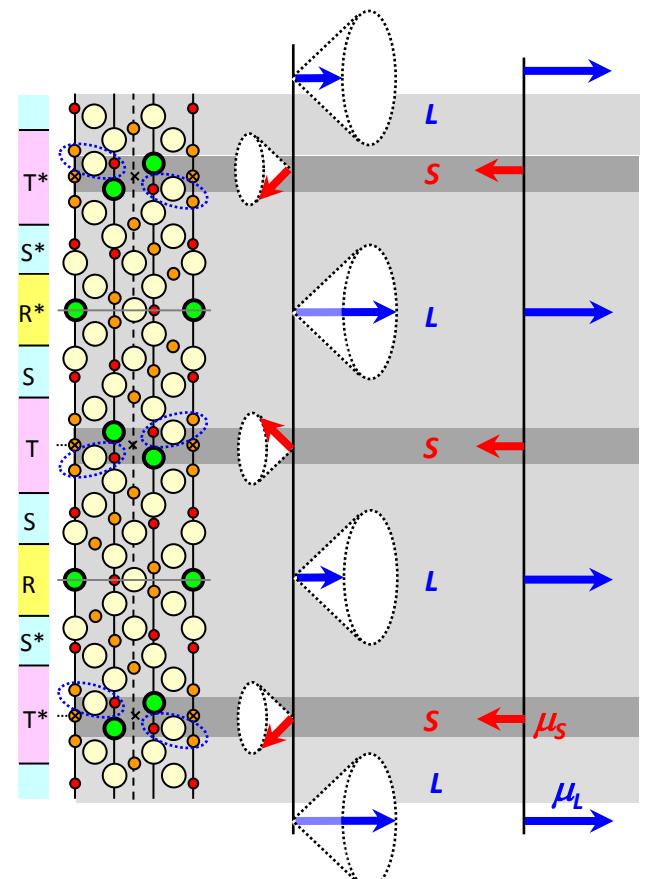
has intimate connection with the room-temperature ME effect in $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$.

Origin of magnetoelectric effect –Neutron diffraction, H -dependence-

Soda et al., PRL 106, 087201 (2011).



Proposed spin structure related to ME effect
in Z-type $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$

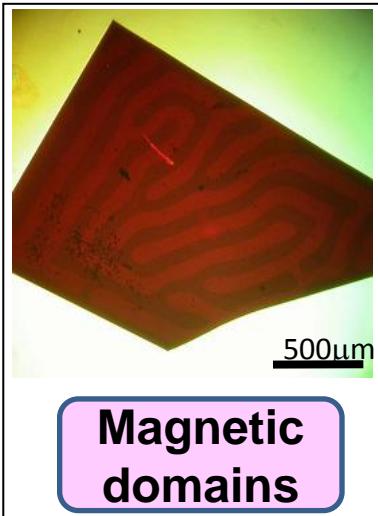


In analogy with Y-type hexaferrites, the r.t. ME effect can be understood in terms of P induced by a transverse conical spin structure through the inverse DM mechanism.

Domain structures in ferroic solids

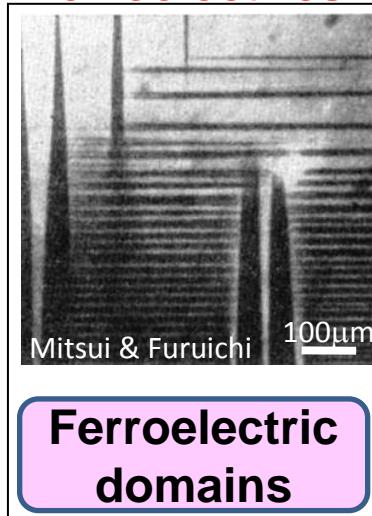
Formation of domain structures by phase transitions in solids

ferromagnet



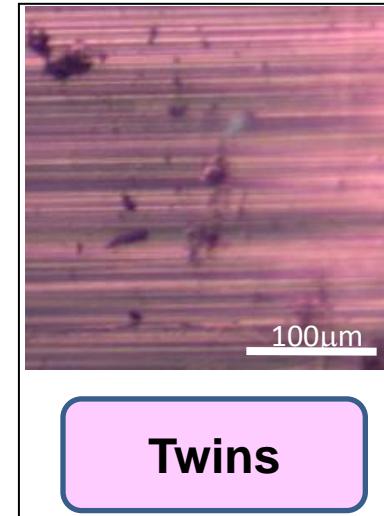
Magnetic
domains

ferroelectrics



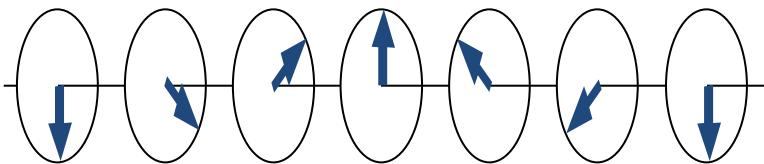
Ferroelectric
domains

ferroelastics

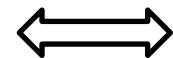


Twins

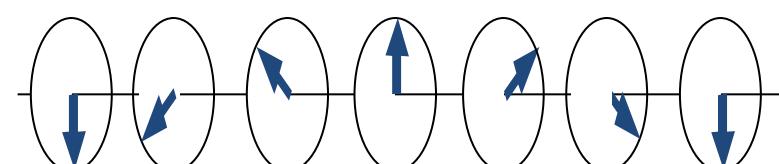
Left-handed spin-helicity (0)



E and/or *H*



Right-handed spin-helicity (1)



**Observation of spiral-spin domains in spiral magnets*

by scanning resonant x-ray microdiffraction

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Imaging spiral magnetic domains in Ho by circularly polarized Bragg diffraction

J.C. Lang et al., J. Appl. Phys. 95, 6537 (2004).

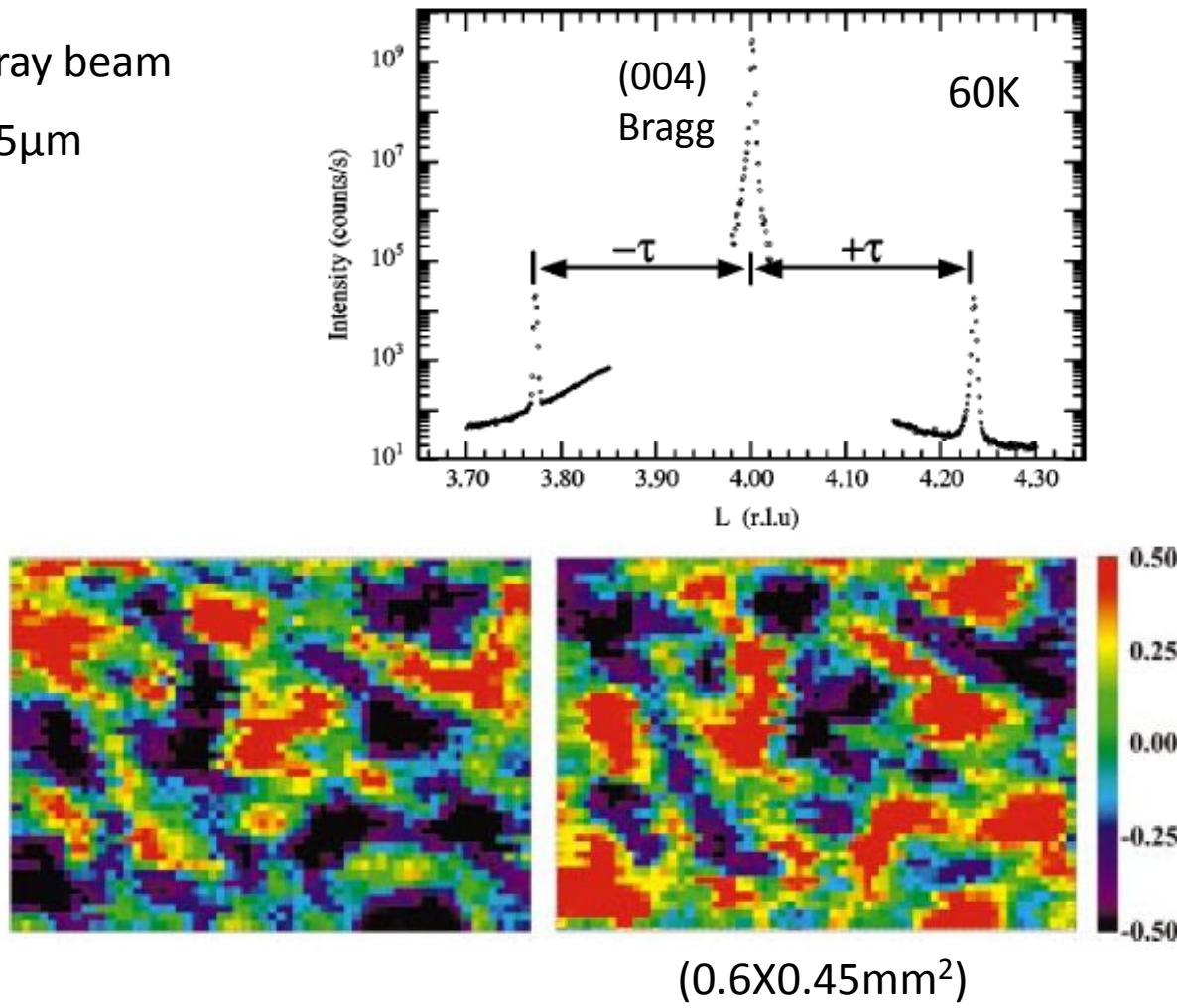
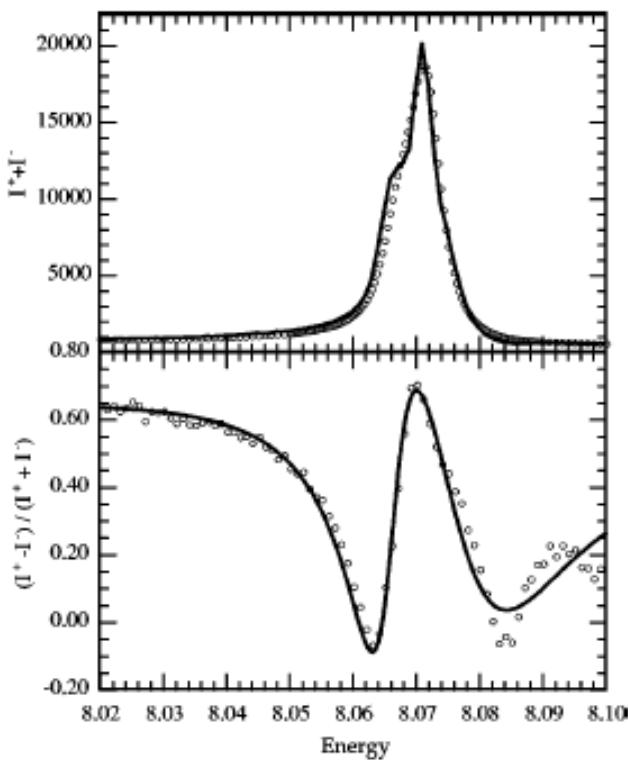
Ho metal

[spiral magnetic order with $(0,0, L \pm \tau)$ below $T_N = 133\text{K}$]

X-ray energy $E \sim 8.071\text{ eV}$ ($\sim \text{Ho } L_3\text{-edge } 2p \rightarrow 5d$)

Size of circularly polarized x-ray beam

$25\text{ }\mu\text{m} \times 25\mu\text{m}$



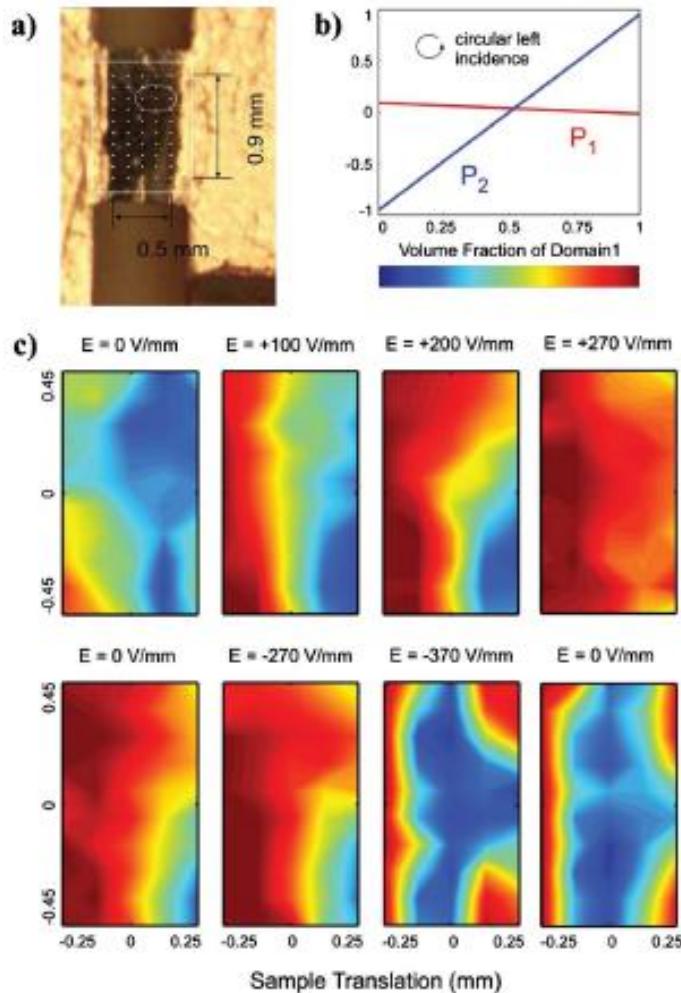
Imaging spiral magnetic domains in multiferroics by circularly polarized X-ray

$\text{Ni}_3\text{V}_2\text{O}_8$

Fabrizi, Phys. Rev. B **82**, 024434 (2010).

Nonresonant X-ray

Beam size $\approx 380 \times 250 \mu\text{m}^2$

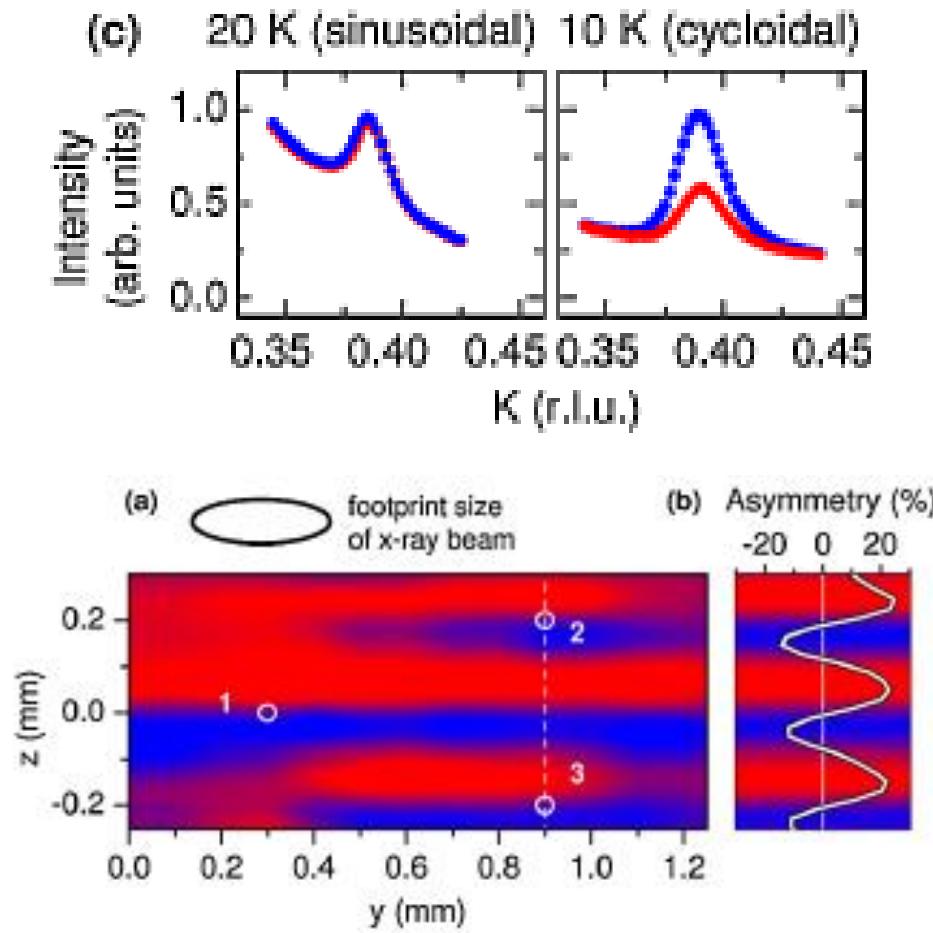


DyMnO_3

Schierle, Phys. Rev. Lett. **105**, 167207 (2010).

X-ray energy : Dy M_5 -edge

Beam size $\approx 300 \times 100 \mu\text{m}^2$



Imaging spin-chiral domains in Y-type $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ by circularly polarized X-ray

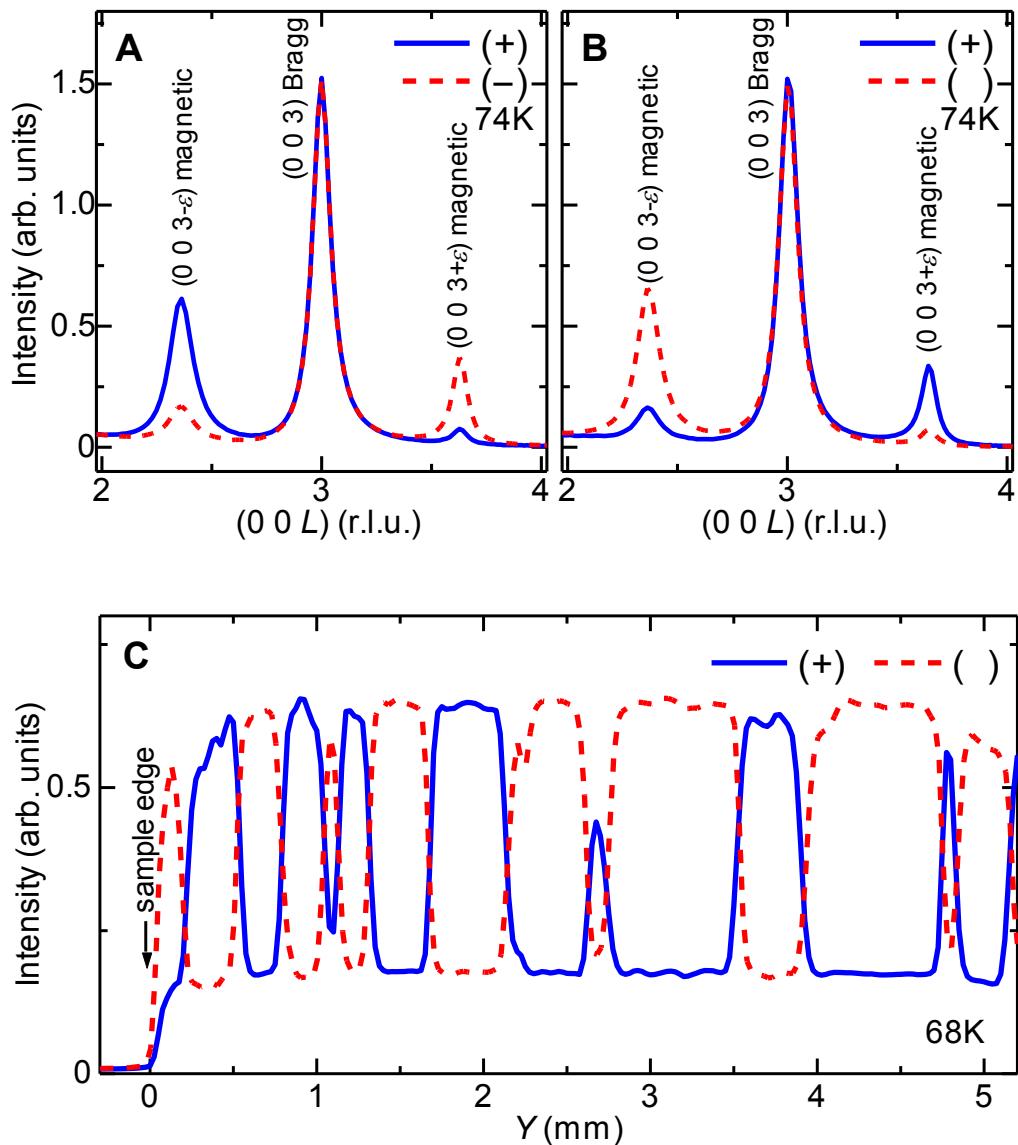
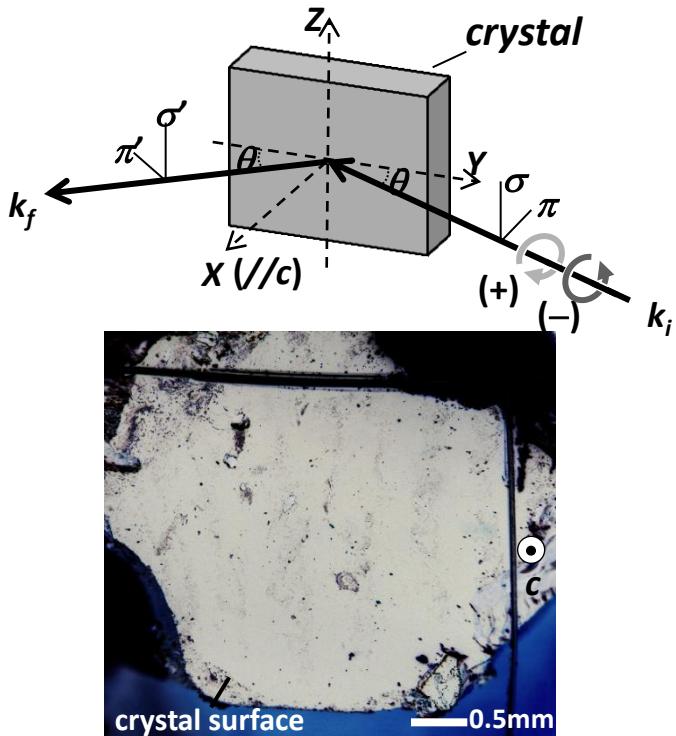
Sample Y-type $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ $T_N \sim 310$ K magnetic satellite $(0,0,3n \pm \varepsilon)$, c –axis length ~ 43 Å

Experimental conditions (@BL17SU, Spring-8)

Incident x-ray energy 710 eV ($\lambda \sim 17$ Å)
[at Fe L_3 edge ($2p \rightarrow 3d$)]

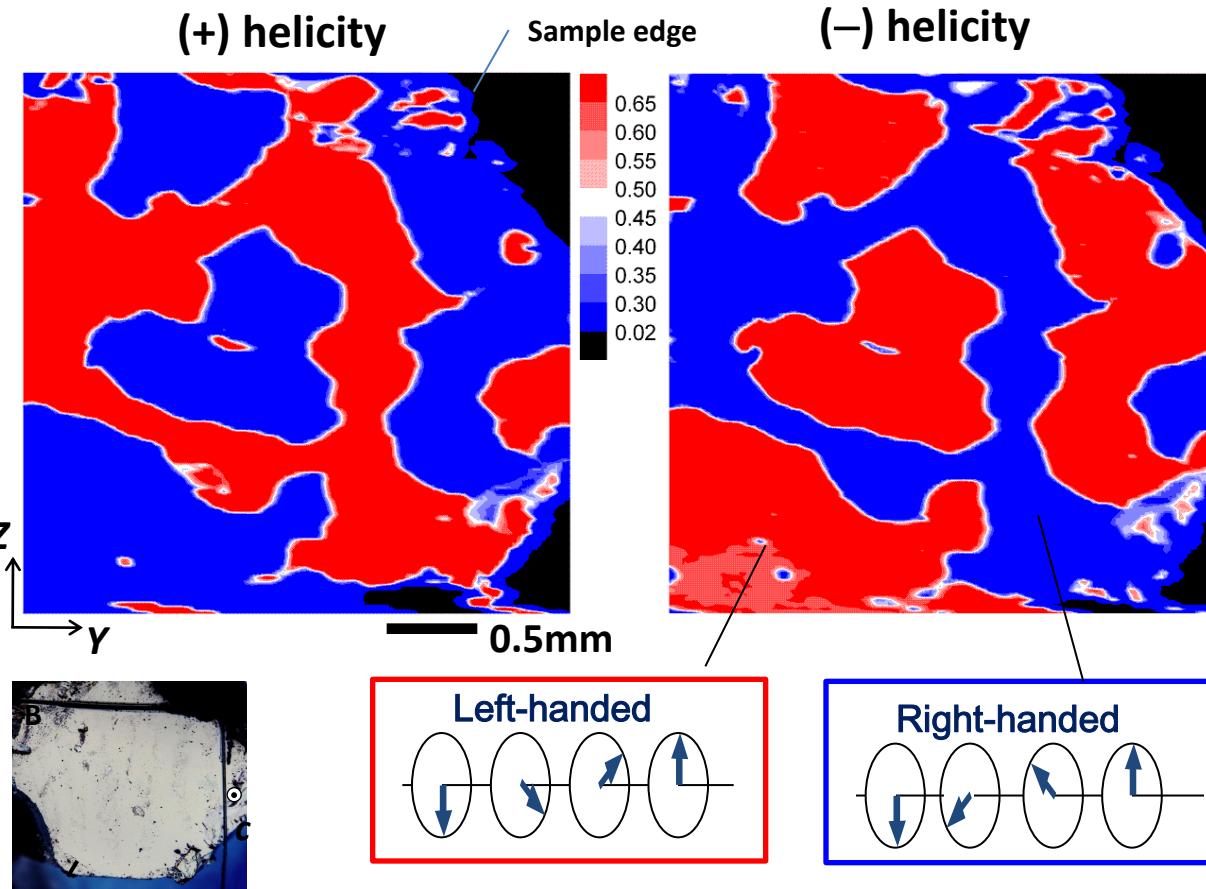
Beam size $\sim 30 \times 15 \mu\text{m}^2$
with a 25 μm step

Penetration depth ~ 40 nm

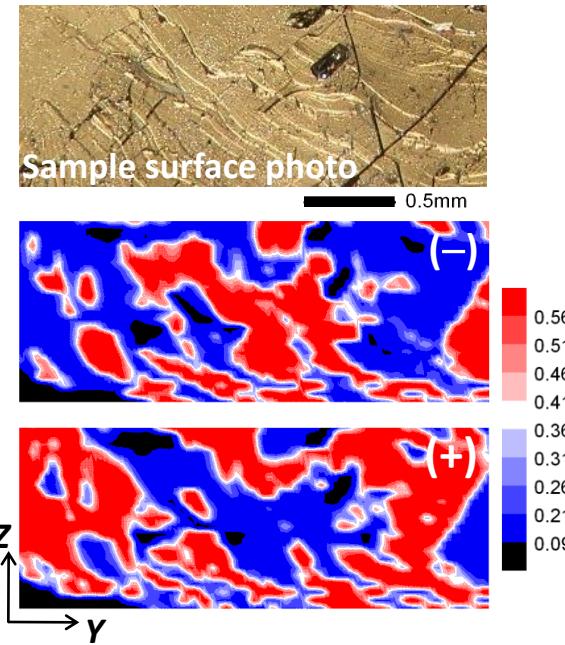


Spatial images of spin-chiral domain structure in $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ at 68 K

Y. Hiraoka et al., PRB 84, 064418 (2011).



c.f. Data of a crystal with a rough surface



*Red and blue regions correspond to either a left- or right-handed spin-chiral monodomain.

*The observed domains are irregular in shape with a size on a **submillimeter** scale.

*There is a tendency that the domain boundaries are clamped at surface defects.

*The observed domains were apparently smaller in size than those on a smooth surface.

Outline

1. Introduction: Magnetoelectric effect & multi-spin variables

2. Room-temperature magnetoelectrics possibly by spin spiral

Hexaferrites $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ with the Z-type structure

**3. Observation of Spin-chiral Domains in Multiferroic Hexaferrites
by Scanning Resonant X-ray**

Hexaferrites $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ with the Y-type structure

4. Magnetoelectric effect observed in a magnetically-disordered system

XY-like spin-glass $(\text{Ni},\text{Mn})\text{TiO}_3$ with the ilmenite structure

Theoretically, multi-spin variables can be nonzero even in the absence of long-range magnetic order.

Chiral spin liquid phase in helimagnets

F. Cinti et al., PRL 100, 057203 (2008);
PRB 83, 174414 (2011).

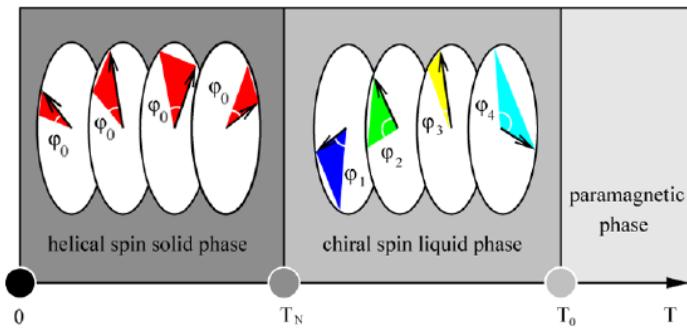


FIG. 1 (color online). Schematic representation of Villain's conjecture. In the chiral spin liquid phase, corkscrews all turning clockwise (or all anticlockwise) with in general $\varphi_i \neq \varphi_j$. In the helical spin solid phase, same angle value φ_0 for all spins.

Spin-chirality decoupling in spin-glass system

H. Kawamura, PRL 68, 3785 (2011);
J. Phys. Condens. Matter 23, 164210 (2011).

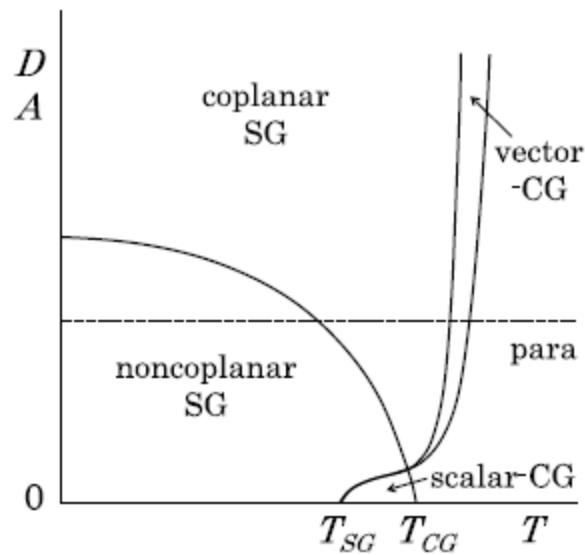


Figure 1. Phase diagram of the XY -like SG with an easy-plane-type uniaxial magnetic anisotropy in the uniaxial anisotropy versus the temperature plane. T_{CG} and T_{SG} represent the chiral-glass and the spin-glass transition temperatures of the fully isotropic Heisenberg system.

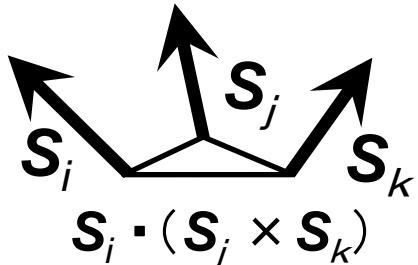
→ **It is possible that ME materials are found in magnetically-disordered phases.**

Spin chirality in spin glass system

A chirality driven mechanism for spin-glass transitions

H. Kawamura, PRL 68, (1992) 3785.

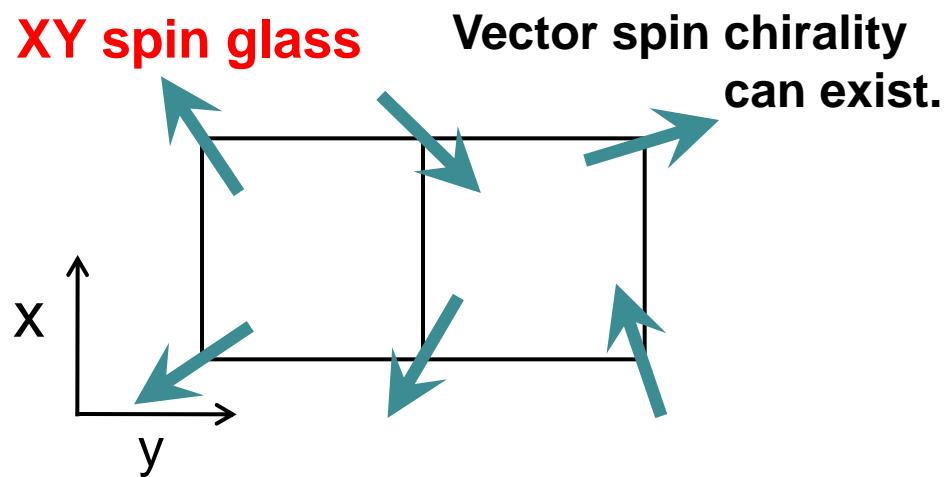
Heisenberg spin glass



Anomalous Hall effect
due to scalar spin chirality

T. Taniguchi, et al., PRL 93, (2004) 246605.

XY spin glass



H. Kawamura, J. Phys. Cond. Matter 23, 164210 (2011).

Can we detect vector spin chirality
in spin glass system though magnetoelectric coupling?

Example compounds showing insulating & XY-like spin glass state



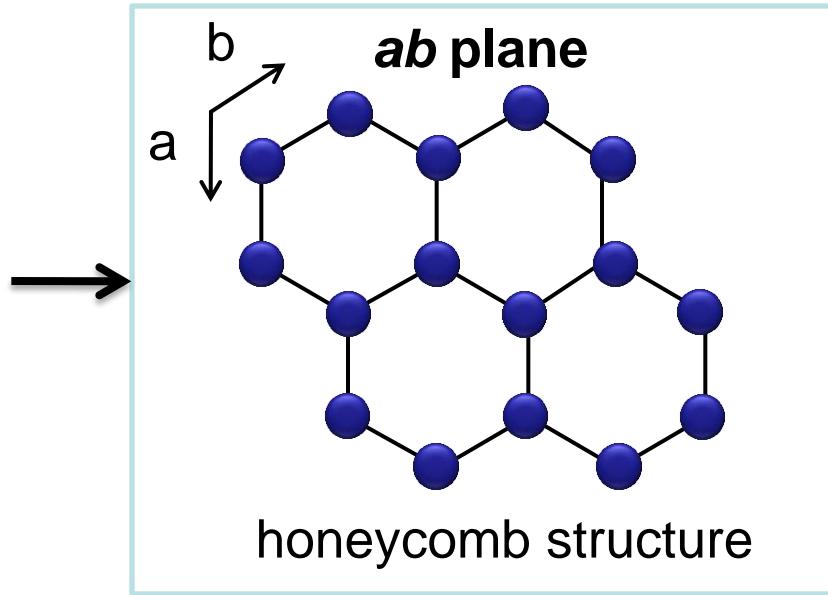
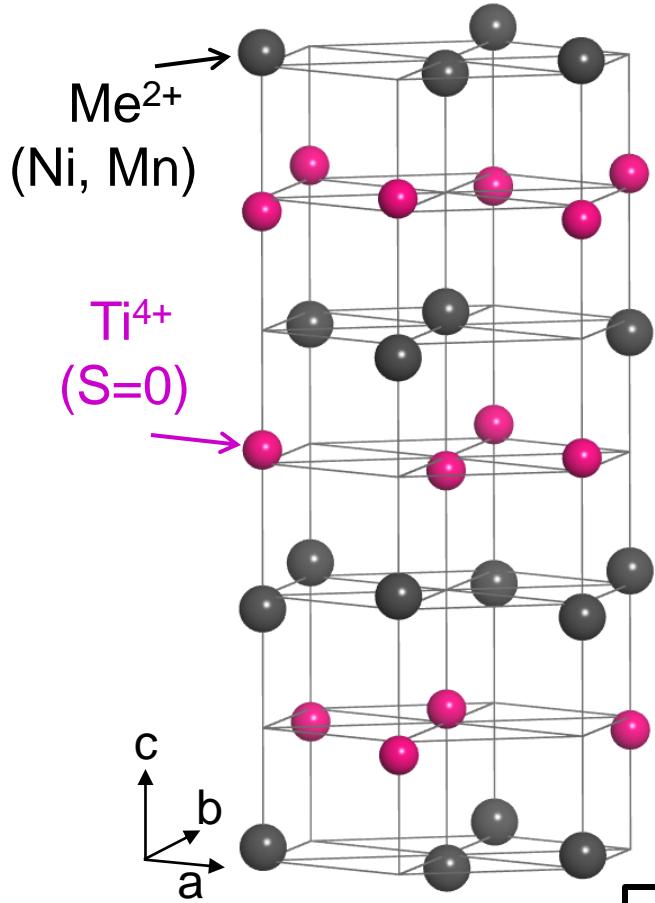
K. Katsumata et al., PRB 25, 428 (1982).



A. Ito et al., JMMM 104, 1637 (1992).

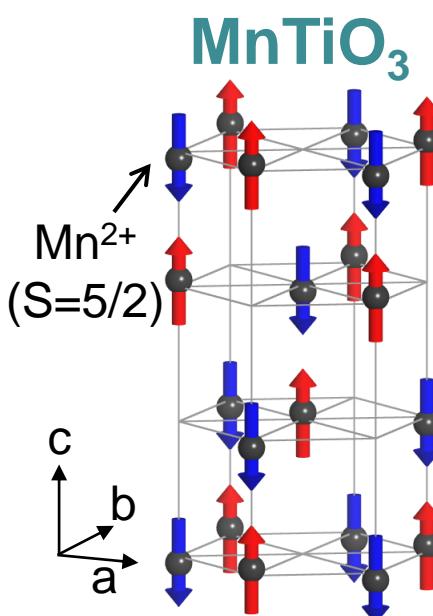
Crystal structure of $\text{Ni}_x\text{Mn}_{1-x}\text{TiO}_3$

ilmenite structure



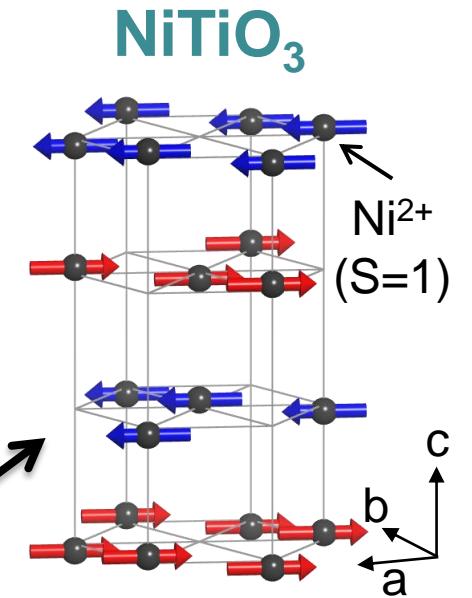
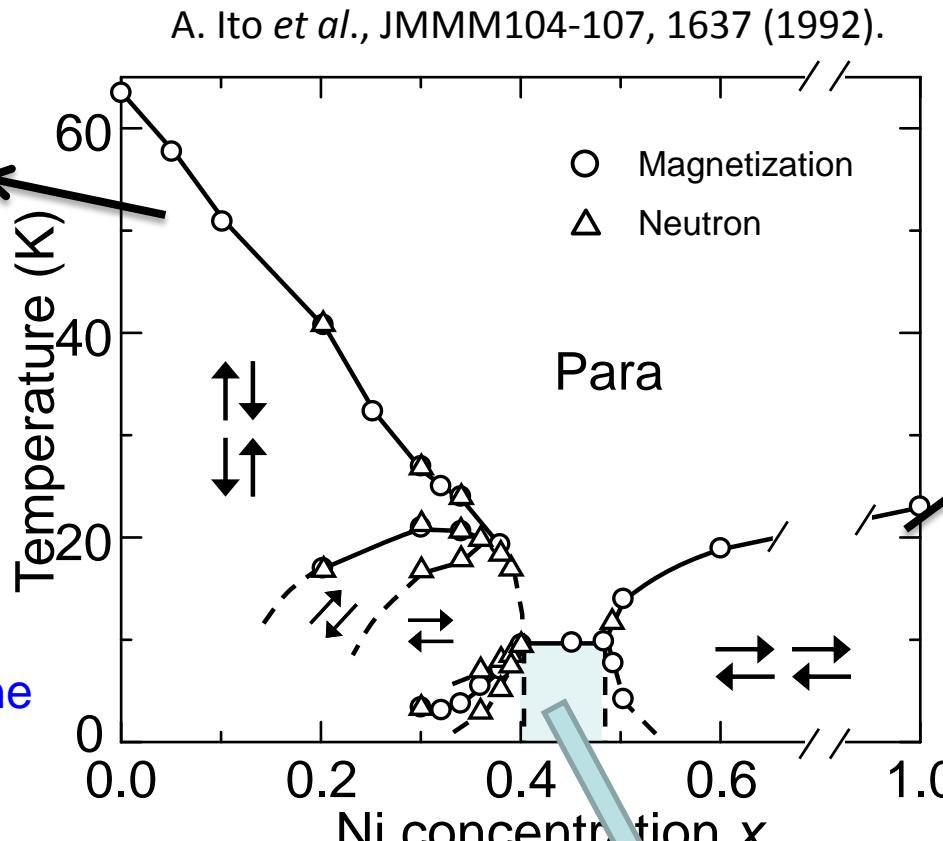
- Alternating stack of Me^{2+} & Ti^{4+}
- Only Me (Ni, Mn) ions are magnetic.
- Space group $\bar{R}\bar{3}$ → centrosymmetric

Magnetic phase diagram of $\text{Ni}_x\text{Mn}_{1-x}\text{TiO}_3$



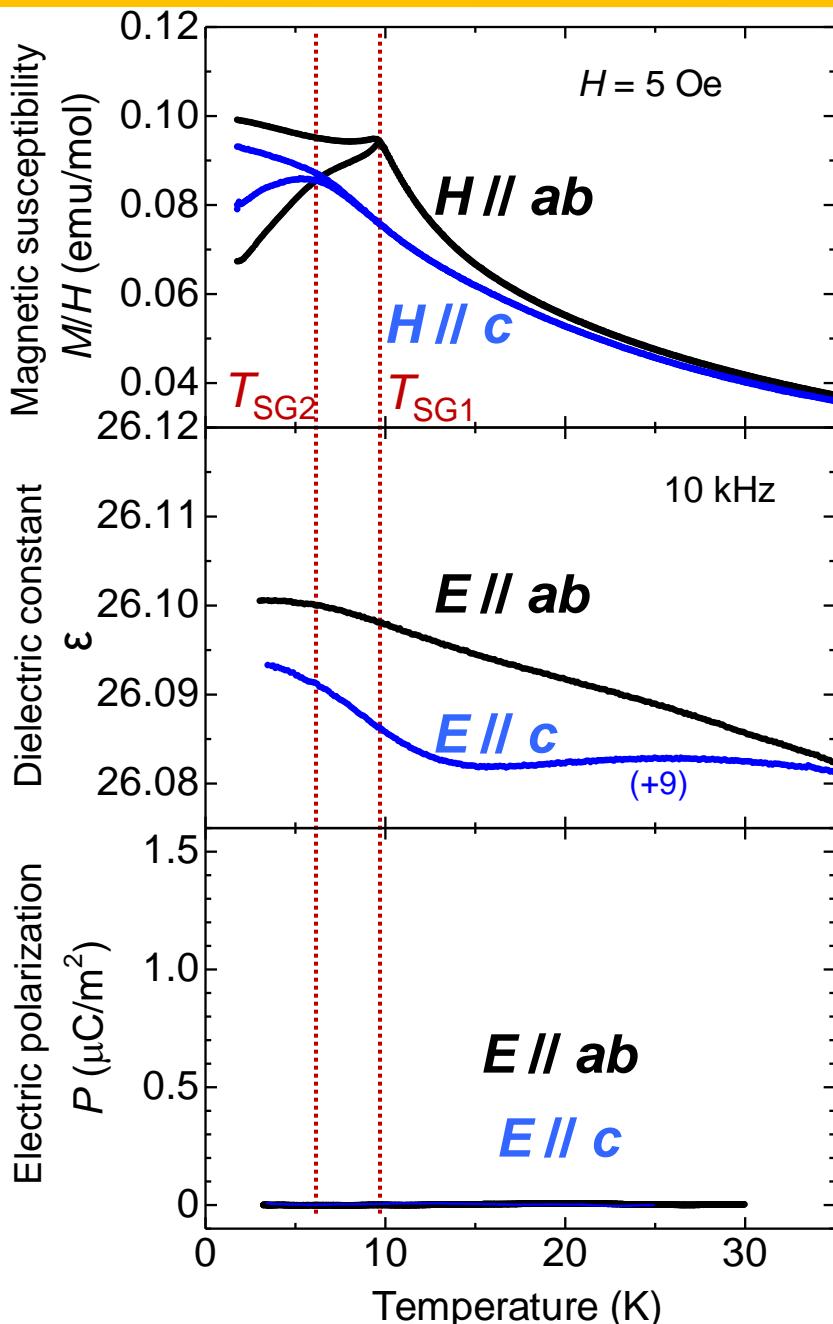
G. Shirane *et al.*,
JPSJ 14, 1352 (1959).

- $\text{Ni}_{1-x}\text{Mn}_x\text{TiO}_3$
Both exchange interaction & magnetic anisotropy are randomly frustrated.



\rightarrow **Ni = 0.4~0.5 shows spin glass phase with weak inplane anisotropy.**

Magnetic & dielectric properties at zero magnetic fields



$\text{Ni}_{0.42}\text{Mn}_{0.58}\text{TiO}_3$

Magnetic susceptibility

Anomalies at $T_{\text{SG}1} \sim 9.5 \text{ K}$
 $T_{\text{SG}2} \sim 6.0 \text{ K}$

Spin glass transition

[consistent with previous study]

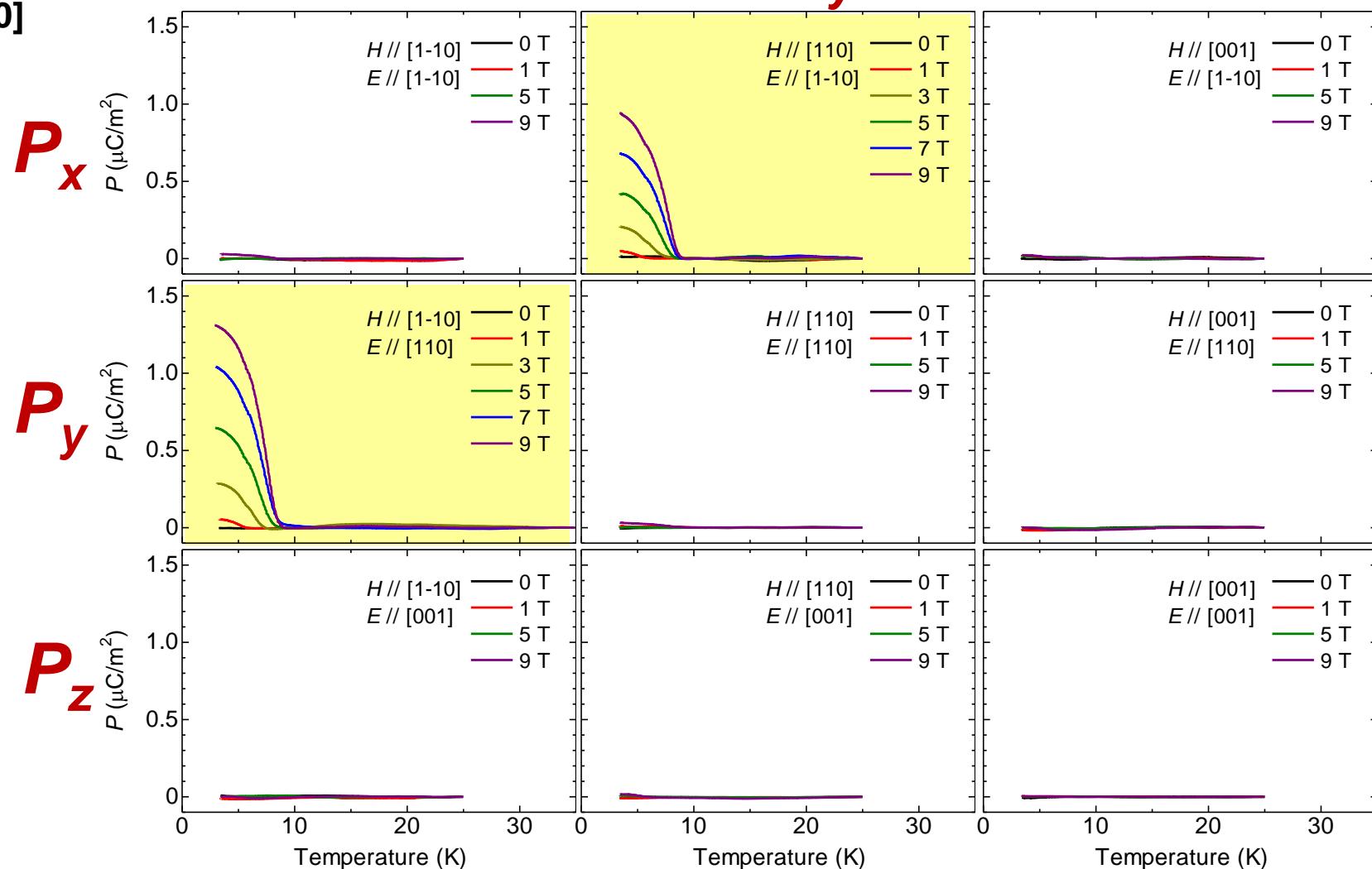
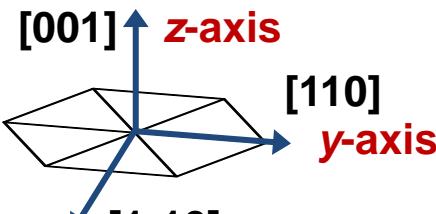
H. Kawano et al., JPSJ 62, 2575 (1993)]

Dielectric properties

No anomaly at $T_{\text{SG}1}$ & $T_{\text{SG}2}$

No correlation between
magnetic & dielectric
properties was observed.

Magnetic field effect on electric polarization in $\text{Ni}_{0.42}\text{Mn}_{0.58}\text{TiO}_3$



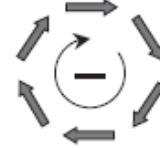
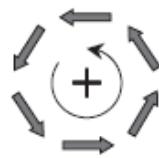
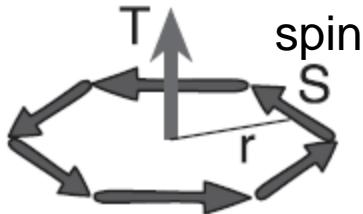
Yamaguchi et al., PRL 108, 057203 (2012).

Antisymmetric ME effect induced by toroidal moment

Toroidal ordering induces ME effect

Toroidal moment T

ordered arrangement of magnetic vortices

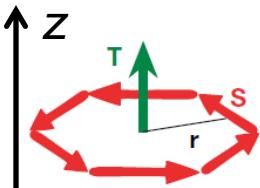


$$T \sim \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{S}_{\alpha}$$

Space inversion I	Time reversal T
Invariant	change
Invariant	 Scalar spin chirality $S_i \cdot (S_j \times S_k)$
change	 Vector spin chirality $S_i \times S_j$

Free energy expression including toroidal moment T

H. Schmid, J. Phys. Condens. Matter 20, 434203, 2008



$$F = -P^s_i E_i - M^s_i H_i - T^s_i (\mathbf{E} \times \mathbf{H})_i \cdots - \alpha_{ij} E_i H_j \cdots$$

consider $T = (0, 0, T_z)$

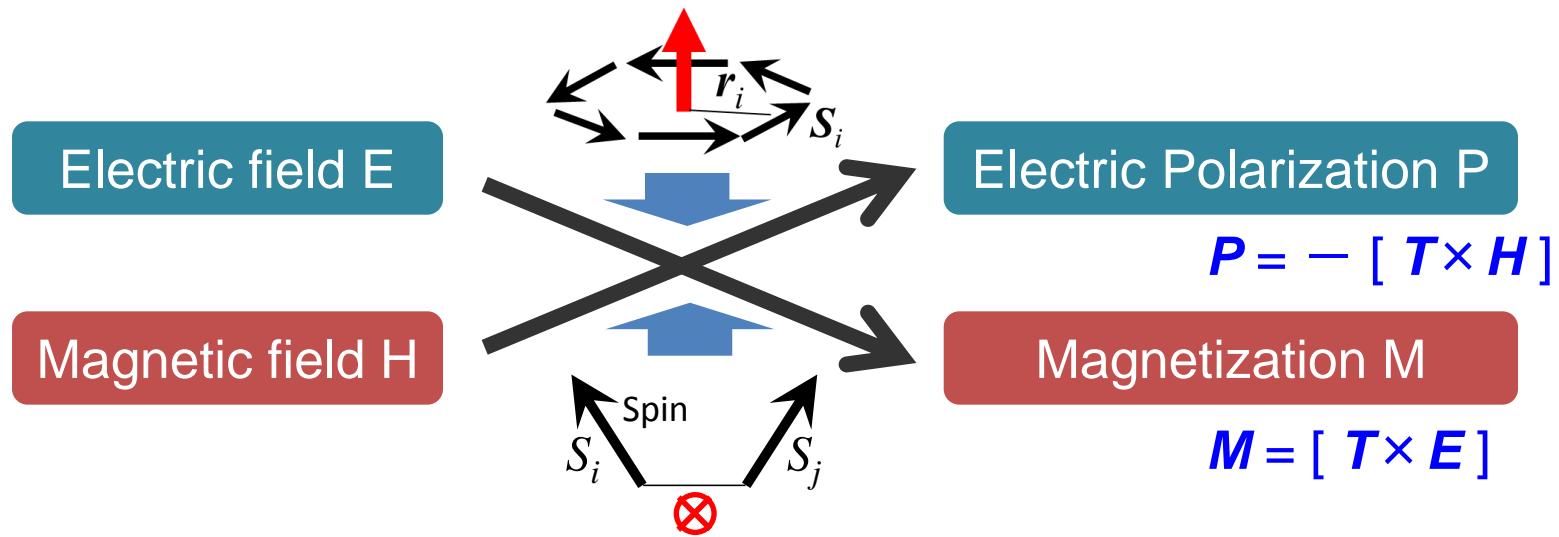
$$F = -P^s_i E_i - M^s_i H_i - T_z (E_x H_y - E_y H_x) \cdots - \alpha_{ij} E_i H_j \cdots$$

$$P_x = -\frac{\partial F}{\partial E_x} = P^s_x + \mathbf{T}_z \mathbf{H}_y \cdots + \alpha_{xj} H_j \cdots$$

$$P_y = -\frac{\partial F}{\partial E_y} = P^s_y - \mathbf{T}_z \mathbf{H}_x \cdots + \alpha_{yj} H_j \cdots$$

off-diagonal & antisymmetric magnetoelectric effect

Summary - Study of Magnetoelectric Effects due to Multi-spin Variables -



*Room-temperature magnetoelectrics possibly by spin spiral

Hexaferrites $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ with the Z-type structure

*Observation of spin-chiral domains in multiferroic hexaferrites
by scanning resonant x-ray microdiffraction

Hexaferrites $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ with the Y-type structure

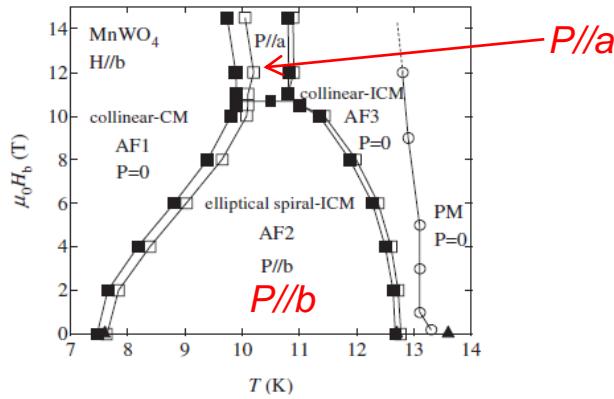
*Magnetoelectric effect observed in a magnetically-disordered system

XY-like spin-glass $(\text{Ni},\text{Mn})\text{TiO}_3$ with the ilmenite structure

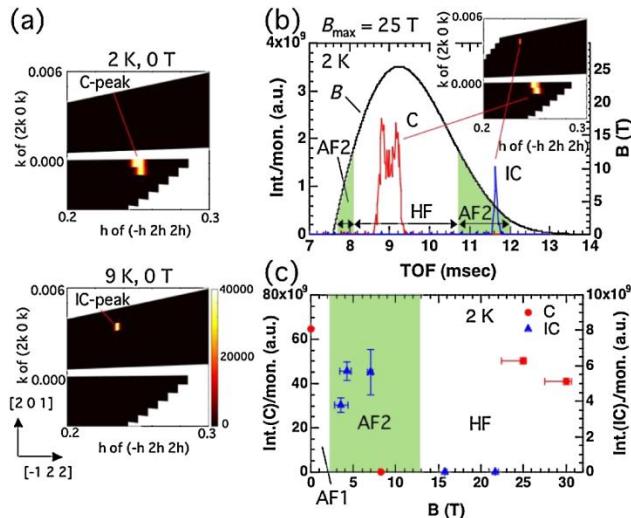
Proposed work for synchrotron and neutron applications of high magnetic fields on multiferroics

MnWO₄ Spin-spiral multiferroic with *P*2/c monoclinic structure
 $Q_{mag} = (-0.214, 1/2, 0.457)$

Taniguchii et al. PRL 97, 097203 (2006)



Nojiri et al. PRL 106, 237202 (2011)



CuO Spin-spiral multiferroic with *C*2/c monoclinic structure

Kimura et al., Nature Mater. 7, 291 (2008)

$Q_{mag} = (0.506, 0, -0.483)$

To be appeared in PRL

Magnetic Phase Diagram of CuO via High-Resolution Ultrasonic Velocity Measurements

R. Villarreal,¹ G. Quirion,¹ M. L. Plumer,¹ M. Poirier,² T. Usui,³ and T. Kimura³

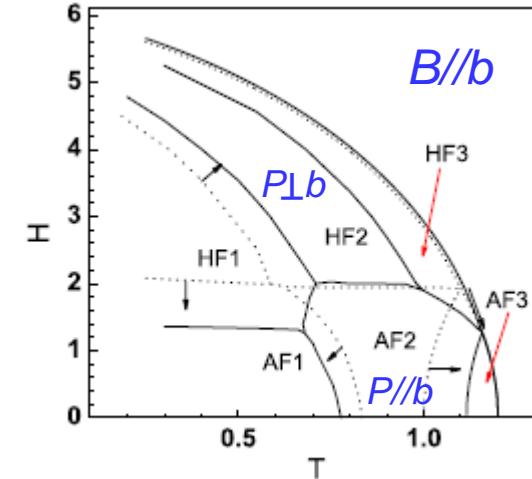
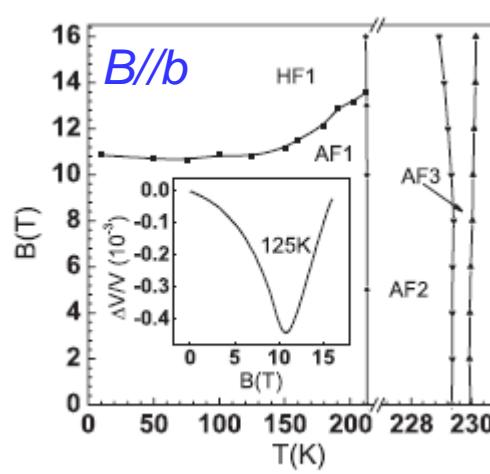
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(Received 22 May 2012; revised manuscript received 27 July 2012)

Experiment



Landau-type free energy analysis suggests
a polarization flopped phase is induced by *B*.