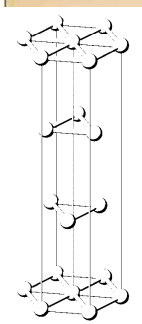
Symmetry and the Landau Theory of Phase Transitions: Application to Trigonal Spin Interactions in Magnetoelectric $CuFeO_2$ and $HoMnO_3$.



1. **Magnetoelectrics and Multiferroics.**
2. **Landau theory of phase transitions and symmetry.**
3. **Spin density and the Non-Local Free Energy.**
4. **Frustrated $CuFeO_2$: Magnetoelectricity and trigonal symmetry.**
5. **Frustrated $HoMnO_3$: Ho-Mn coupling and trigonal symmetry.**

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MUN PHYSICS

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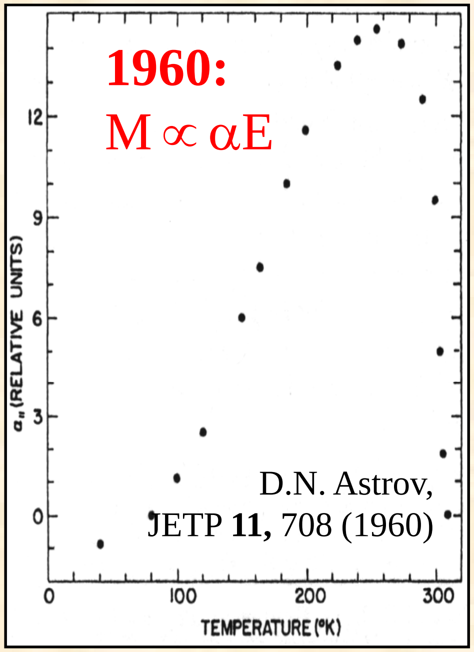
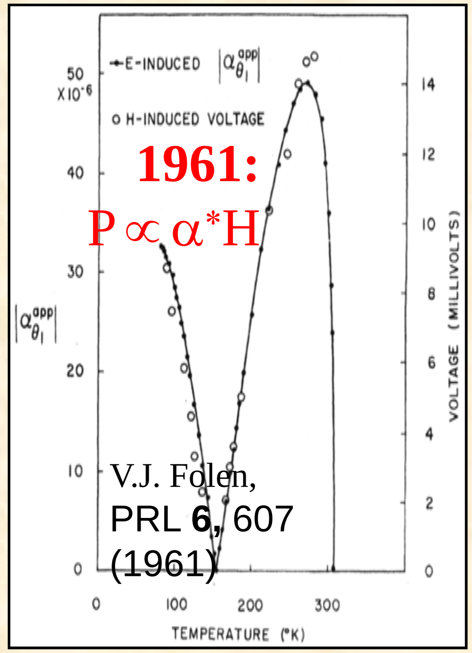
Magnetoelectric Effect: The early days. Cr_2O_3 (a simple AF)

- applied uniform electric field **E** induces a *uniform* magnetization **M**
- applied uniform magnetic field **H** induces a *uniform* electric polarization **P**





Early measurements found only a very small effect: ~ 10^{-3} V/(cmOe) ~ $5/10^6$ of AF spins reverse.

α = response function

$$M_i = \chi^m_{ij} H_j + \frac{1}{\mu_0 c}\alpha_{ji} E_j \qquad P_i = \epsilon_0 \chi^e_{ij} E_j + \frac{1}{c}\alpha^*_{ij} H_j$$

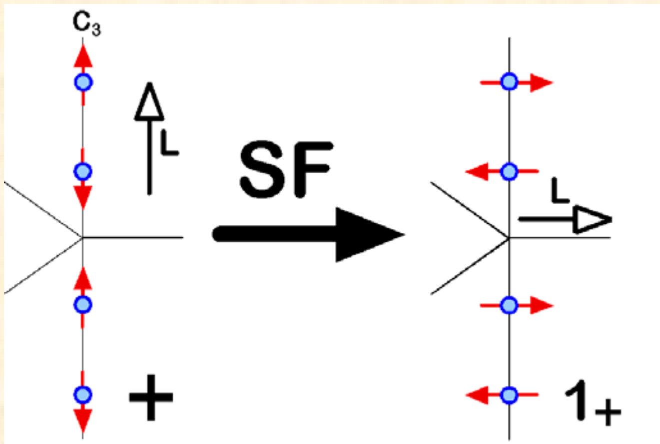
Courtesy of M. Fiebig

Magnetic Phase Diagram of Cr_2O_3.

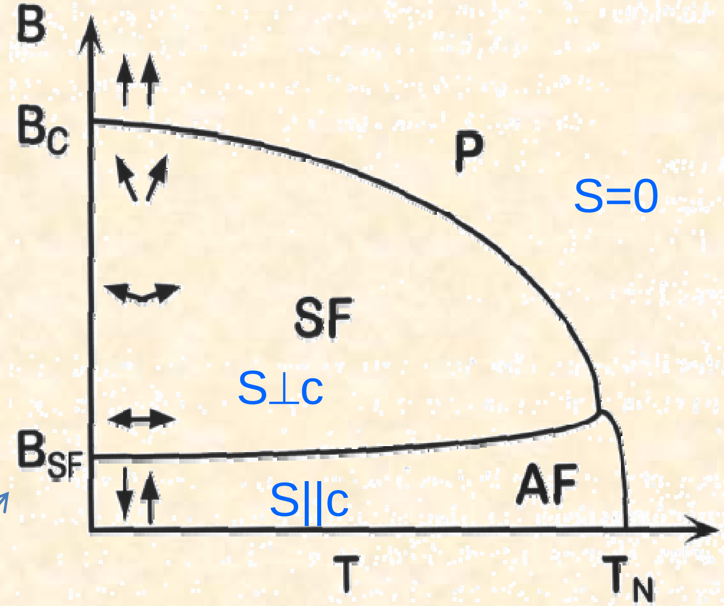
- ***Spin-Flop transition in an unfrustrated <u>uniaxial</u> AF.***

Period-2 spin structure: **Q**=½**G**

H



Rhombohedral crystal symmetry



Simple H-T phase diagram of an axial antiferromagnet.

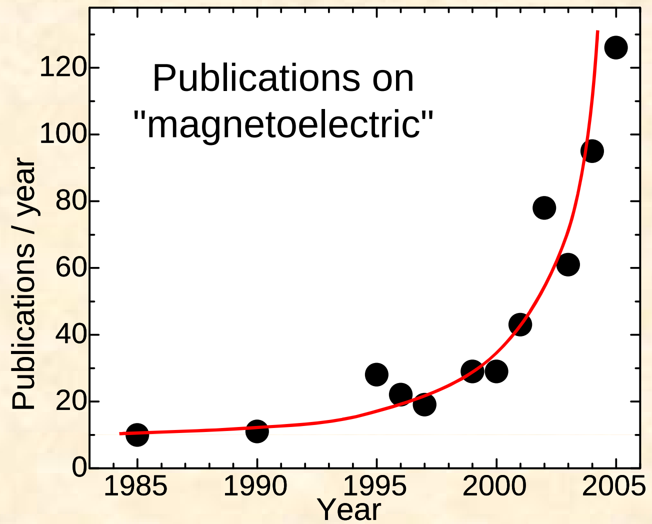
Critical field is proportional to anisotropy strength $-D(S_z)^2$

D>0: axial

D<0: planar

“Revival of the Magnetoelectric Effect”

M. Fiebig, J. Phys. D 38, R123 (2005)



1894 — First discussion of an intrinsic correlation between magnetic and electric properties

P. Curie, J. de Physique (3rd Series) **3,** 393 (1894)

"Les conditions de symétrie nos permettons d'imaginer qu'un corps à molécule dissymétrique se polarise peut-être magnétiquement lorsqu'on le place dans un champ électrique.

1926 — Introduction of the term "magnetoelectric" for these correlations

P. Debye, Z. Phys. **36,** 300 (1926)

Title: *Bemerkung zu einigen neuen Versuchen über einen magneto-elektrischen Richteffekt*

1957 — Magnetoelectric effect only in time-asymmetric (i.e. magnetically ordered) media!

L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960)

"The magnetoelectric effect is odd with respect to time reversal and vanishes in materials without magnetic structure"

1959 — Magnetoelectric effect predicted for antiferromagnetic Cr_2O_3

I. E. Dzyaloshinskii, J. Exptl. Teor. Fiz. **37,** 881 (1959); Sov. Phys.—JETP **10,** 628 (1959)

"We should like to show here that among the well known antiferromagnetic substances there is one, namely Cr_2O_3, where the magnetoelectric effect should occur from symmetry considerations."

1960/61 — First observation in Cr_2O_3

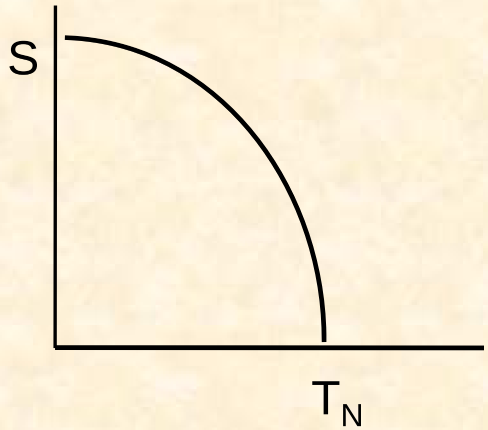
E → M: D. N. Astrov, J. Exptl. Teor. Fiz. 38, 984 (1960); Sov. Phys.—JETP **11,** 708 (1960)

H → P: V. J. Folen, G. T. Rado, and E. W. Stalder, Phys. Rev. Lett. **6,** 607 (1961)

Landau Theory of Magnetic Phase Transitions.

• Description of long-range ordered spin configurations near a phase transition T_N:

$\mathbf{S}$=0, $T>T_N$ and $\mathbf{S}\neq 0$, $T<T_N$.



• Express free energy as a Taylor expansion in powers of S near T_N.

• Variational principle. *F[**S**]* is a minimum at the equilibrium spin configuration:

$$\frac{\delta F}{\delta \mathbf{S}} = 0$$

Free energy must be invariant with respect to all symmetries, including crystal symmetry.

e.g., *time reversal symmetry* S→-S and H→-H

Only even powers of S

$$F = AS^2 + \tfrac{1}{2}BS^4 + \ldots$$

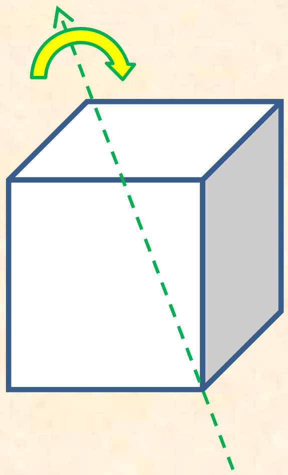
$A=a(T-T_N)$, B=constant, C=constant,…

Minimization gives:

$S^2 = 0$, $T>T_N$

$S^2 = (a/B)(T_N-T)$, $T<T_N$

Crystal Symmetry: Example Cubic



Free energy must be invariant w.r.t. the Generators of point group: **C_{31}, C_{2m}**

Point Group Symmetry operations:

e.g. C_{31} = 3-fold rotation about diagonal: $S_x \to S_y \to S_z$

C_{2x} = 2-fold about x-axis: $S_x \to S_x$, $S_y \to -S_y$, $S_z \to -S_z$

Example: General term at second order:

$$F_2 = \sum_{\alpha\beta} A_{\alpha\beta} S_\alpha S_\beta = A_{xx} S_x S_x + A_{yy} S_y S_y + A_{zz} S_z S_z + A_{xy} S_x S_y + A_{xz} S_x S_z + A_{yz} S_y S_z$$

C_{31}: $F_2 \to A_{xx} S_y S_y + A_{yy} S_z S_z + A_{zz} S_x S_x + A_{xy} S_y S_z + A_{xz} S_y S_x + A_{yz} S_z S_x$

Thus: $A_{xx}=A_{yy}=A_{zz}\equiv A$, $A_{xy}=A_{xz}=A_{yz}\equiv A'$

Cubic Crystal Symmetry

- C_{2x} leads to A'=0, giving: $F_2 = A(S \cdot S)$ $\Rightarrow$ Isotropic (like exchange)

- Demanding that the most general *4th-order term* $\sum B_{\alpha\beta\gamma\delta} S_\alpha S_\beta S_\gamma S_\delta$ be invariant w.r.t. point-group generators leads to:

$$F_4 = \tfrac{1}{2} B(S \cdot S)^2 + E(S_x^4 + S_y^4 + S_z^4)$$ Cubic

Anisotropy

*E>0: **S** || <111> (Ni)*

*E<0: **S** || <100> (Fe)*

- *Crystals with cubic symmetry have moments in either <111> or <100> directions.*

Fundamental Assumptions

1. *If a term in the free energy is allowed by symmetry, it must exist (may be very small).*

2. *All terms which are independently invariant have independent coefficients.*

Spin Density description of magnetic states

$$\mathbf{s}(\mathbf{r}) = \sum_q \mathbf{S}_q e^{i\mathbf{q}\cdot\mathbf{r}} = \mathbf{m} + \mathbf{S}_\mathbf{Q} e^{i\mathbf{Q}\cdot\mathbf{r}} + \mathbf{S}^*_\mathbf{Q} e^{-i\mathbf{Q}\cdot\mathbf{r}} + \ldots$$

uniform magnetization ~ H

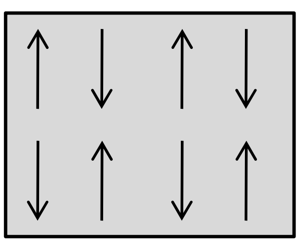
Order parameters = polarization vectors

Define real vectors S_1 and S_2:

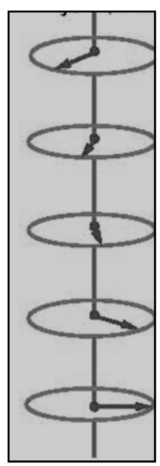
$$\mathbf{S}_Q = \mathbf{S}_1 + i\mathbf{S}_2$$

$\mathbf{s}(\mathbf{r}) = \mathbf{m} + 2\mathbf{S}_1\cos(\mathbf{Q}\cdot\mathbf{r}) - 2\mathbf{S}_2\sin(\mathbf{Q}\cdot\mathbf{r}) + \ldots$

Square lattice *simple AF:*
$\mathbf{Q}=(\pi/a)\mathbf{x}+(\pi/a)\mathbf{y} = \mathbf{G}/2$
$\mathbf{S}_1=S\mathbf{y}$, $\mathbf{S}_2=0$



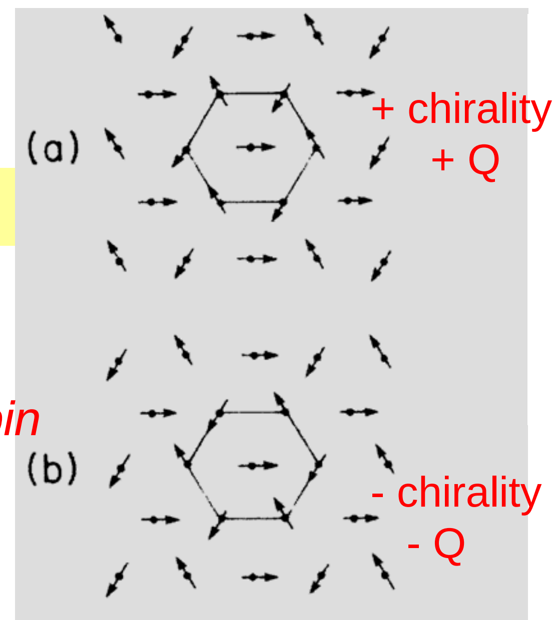
Helical with $\mathbf{S}\perp\mathbf{Q}$:
$\mathbf{Q}=Q\mathbf{z}$ [*incommensurate* $\mathbf{Q}\neq(n/m)\mathbf{G}$]
$\mathbf{S}_1=S\mathbf{x}$, $\mathbf{S}_2=S\mathbf{y}$



$\mathbf{S}_1\perp\mathbf{S}_2$, $S_1=S_2$

Frustrated Antiferromagnets = non-colinear spin order

Triangular Lattice *120^0 spin structure:*
Helical with $\mathbf{S}$ in plane of $\mathbf{Q}$:
$\mathbf{Q}=\pm(4\pi/3a)\mathbf{x}=\mathbf{G}/3$
$\mathbf{S}_1=S\mathbf{x}$, $\mathbf{S}_2=S\mathbf{y}$



Non-Local Formulation of the Free Energy

Consider a general expression of the free energy:

$$F[s(r)] = \int dr dr' A_{\alpha\beta}(r,r') s_\alpha(r) s_\beta(r') + \int dr_1 dr_2 dr_3 dr_4 B_{\alpha\beta\gamma\delta}(r_1,r_2;r_3,r_4) s_\alpha(r_1) s_\beta(r_2) s_\gamma(r_3) s_\delta(r_4) + \ldots$$

Apply symmetry requirements for system of interest:

$$F = F_{isotropic} + F_{anisotropic}$$

$$F_{iso}[s(r)] = \int dr dr' A(r-r') \mathbf{s}(r)\cdot\mathbf{s}(r') + \int dr_1 dr_2 dr_3 dr_4 B(r_1,r_2;r_3,r_4) \mathbf{s}(r_1)\cdot\mathbf{s}(r_2) \mathbf{s}(r_3)\cdot\mathbf{s}(r_4) + \ldots$$

Isotropic terms to 4th order

$$A(\mathbf{r}) = aT\delta(\mathbf{r}) + J(\mathbf{r})$$

temperature

Usual spin-spin *Exchange* integral

Second-order isotropic terms

$$\mathbf{s}(\mathbf{r}) = \sum_q \mathbf{S}_q e^{i\mathbf{q}\cdot\mathbf{r}} = \mathbf{m} + \mathbf{S}_\mathbf{Q} e^{i\mathbf{Q}\cdot\mathbf{r}} + \mathbf{S}_\mathbf{Q}^* e^{-i\mathbf{Q}\cdot\mathbf{r}} + \ldots$$

$F = F(\mathbf{Q}, \mathbf{m}, \mathbf{S})$

$F_2 = A_0 m^2 + A_\mathbf{Q} S^2$

$A_\mathbf{Q} = aT + J_\mathbf{Q}$

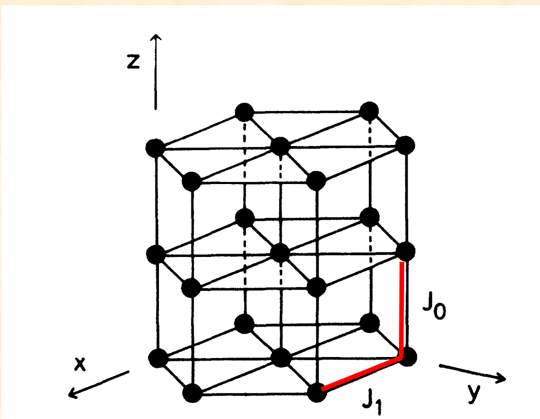
$A_0 = aT + J_0$

$$J_\mathbf{Q} = \frac{1}{N} \sum_\mathbf{R} J(R) e^{i\mathbf{Q}\cdot\mathbf{R}}$$

R = lattice vector

First ordered phase as T is lowered from paramagnetic (S=0) state has wave vector ***Q*** *which maximizes* $T_N = -J_\mathbf{Q}/a$.

<u>Example</u>: near-neighbor sites on a simple hexagonal lattice



$$\mathbf{R} = \pm c\mathbf{z}; \pm a\mathbf{x} \pm (a\mathbf{x} \pm (\sqrt{3}/2) a\mathbf{y})$$

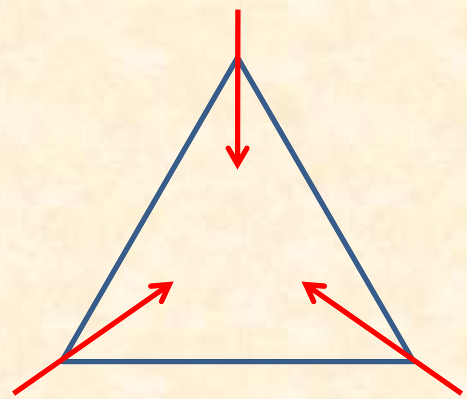
$J_\mathbf{Q} = 2J_0 \cos(q_z) + 2J_1 f_1$

$f_1 = \cos(q_x) + 2\cos(q_x/2)\cos(q_y)$

$$q_x = aQ_x, q_y = (\sqrt{3}/2) aQ_y, q_z = cQ_z$$

For J_1 antiferromagnetic, $J_\mathbf{Q}$ is maximized by

$q_x = 4\pi/3$, $q_y = 0$: 120^0 spin structure.



Fourth-order isotropic terms

$$F_s^{(4)} = B_1(\mathbf{S}\cdot\mathbf{S}^*)^2 + \tfrac{1}{2}B_2\,|\mathbf{S}\cdot\mathbf{S}|^2 + \tfrac{1}{4}B_3[(\mathbf{S}\cdot\mathbf{S})^2 + (\mathbf{S}^*\cdot\mathbf{S}^*)^2]\Delta_{4\mathbf{Q},\mathbf{G}_1} + B_4(\mathbf{S}\cdot\mathbf{S}^*)[\mathbf{S}\cdot\mathbf{S} + \mathbf{S}^*\cdot\mathbf{S}^*]\Delta_{2\mathbf{Q},\mathbf{G}_1}$$

Umklapp terms stabilize ***commensurate*** spin structures

$$\frac{1}{N}\sum_{\mathbf{R}} e^{i\mathbf{Q}\cdot\mathbf{R}} = \Delta_{\mathbf{Q},\mathbf{G}}$$

R = lattice vector
G = reciprocal lattice vector

$$B_1 = B_{\mathbf{Q},-\mathbf{Q},\mathbf{Q},-\mathbf{Q}}\,,\quad B_2 = B_{\mathbf{Q},\mathbf{Q},-\mathbf{Q},-\mathbf{Q}}\,,\quad B_3 = B_{\mathbf{Q},\mathbf{Q},\mathbf{Q},\mathbf{Q}}\,,\quad B_4 = B_{-\mathbf{Q},\mathbf{Q},\mathbf{Q},\mathbf{Q}}\,,$$

- Four independent 4th-order coefficients of isotropic terms.
- *Usually taken to be independent constants.*

$$B_{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4} = \Delta_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4,\mathbf{G}}\left[\frac{V}{N}\right]^3 \sum_{\mathbf{R}_1\mathbf{R}_2\mathbf{R}_3} B(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)e^{i(\mathbf{q}_1\cdot\mathbf{R}_1+\mathbf{q}_2\cdot\mathbf{R}_2+\mathbf{q}_3\cdot\mathbf{R}_3)}$$

$$\mathbf{S} = \mathbf{S}_1 + i\mathbf{S}_2$$

<u>Example:</u> $B_2|\mathbf{S}\cdot\mathbf{S}|^2 = B_2\{(S_1^2 - S_2^2)^2 + 4(\mathbf{S}_1\cdot\mathbf{S}_2)^2\}$ is minimized by

for $B_2>0$, $S_1^2=S_2^2$ and $\mathbf{S}_1 \perp \mathbf{S}_2$: *Helical* spin polarization.

for $B_2<0$, $\mathbf{S}_1 || \mathbf{S}_2$: *Linear* spin polarization.

Phase Diagram of a Simple AF: Spin-Flop

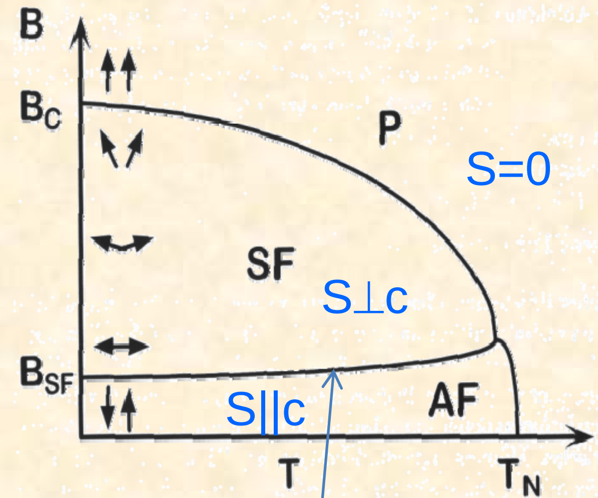
Example: rhombohedral symmetry giving axial anisotropy along **z** (Cr_2O_3).

- Applied magnetic field **H**||**z** induces **m||z||c**.
- NN AF exchange interactions along **z** give Q=½G.

$S = S_Q$

$$F(\mathbf{Q}, \mathbf{m}, \mathbf{S}) = \tfrac{1}{2}A_0 m^2 + A_{\mathbf{Q}} S^2 + -D|S_z|^2 + B_1 S^4$$

$$+ \tfrac{1}{2}B_2|\mathbf{S}\cdot\mathbf{S}|^2 + \tfrac{1}{4}B_3 m^4 + B_4|\mathbf{m}\cdot\mathbf{S}|^2 + \tfrac{1}{2}B_5 m^2 S^2 - \mathbf{m}\cdot\mathbf{H}$$



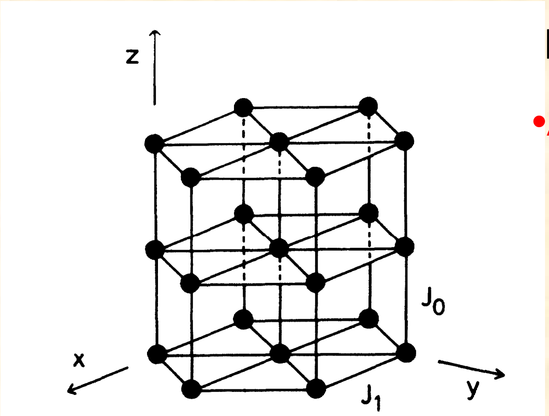
First-order *spin-flop* transition when $B_4 m^2 = D$.

•*Competition* between crystal-field and magnetic-field induced anisotropy: $(B_4 m^2 - D) S_z^2$

•Phase diagram is determined by minimizing F(**Q**, **m**, **S**)

Phase Diagram of a Geometrically Frustrated AF: $CsNiCl_3$

• Ni^{2+} (S=1, L=3) on simple hexagonal lattice (AA stacked triangular layers)



NN AF interactions J_0 and J_1: $\mathbf{Q}=\mathbf{G}_{||}/2 + \mathbf{G}_{\perp}/3$

$\boldsymbol{S}_2\sin(\boldsymbol{Q}\bullet\boldsymbol{r})\neq 0$

•Anisotropy is weakly axial.

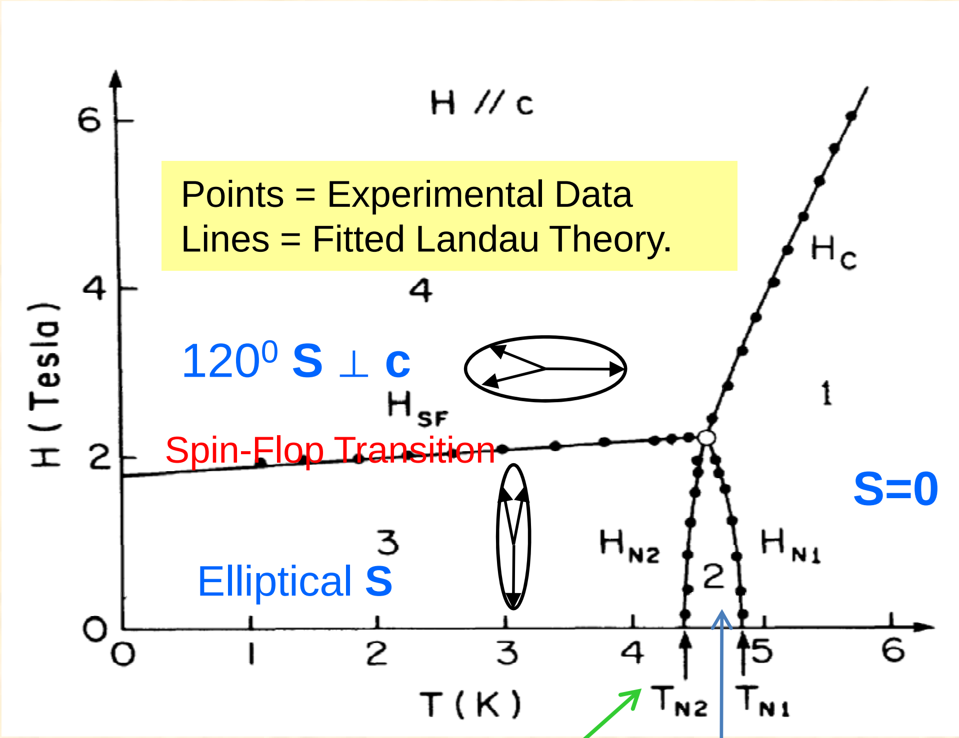
$\mathbf{s}(\mathbf{r}) = \mathbf{m} + 2\mathbf{S}_1\cos(\mathbf{Q}\cdot\mathbf{r}) - 2\mathbf{S}_2\sin(\mathbf{Q}\cdot\mathbf{r})$

Free energy is the same as with simple AF

$F(\mathbf{Q}, \mathbf{m}, \mathbf{S}) = \frac{1}{2}A_0m^2 + A_{\mathbf{Q}}S^2 + -D|S_z|^2$

$+ B_1S^4 + \frac{1}{2}B_2|\mathbf{S}\cdot\mathbf{S}|^2 + \frac{1}{4}B_3m^4 + B_4|\mathbf{m}\cdot\mathbf{S}|^2$

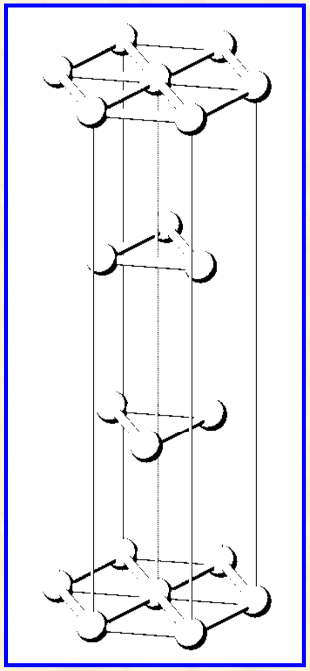
$+ \frac{1}{2}B_5m^2S^2 - \mathbf{m}\cdot\mathbf{H}$



Linear **S** || **c**

Transition at T_{N2} due to competition between D-term (collinear) and B_2-term (non-collinear).

$CuFeO_2$ *P* ***induced*** by non-collinear spin state at H≠0.



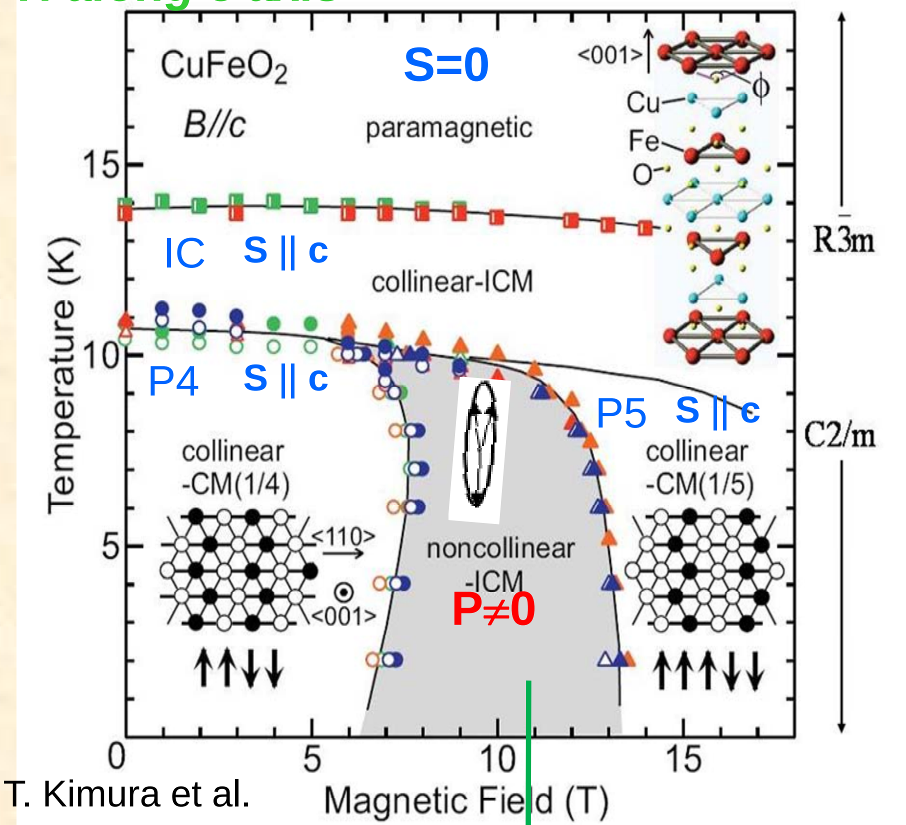
Cu^{+} → nonmagnetic
Fe^{3+} (^{6}S state) → **S** = 5/2, **L**=0

Space Group $R\bar{3}m$

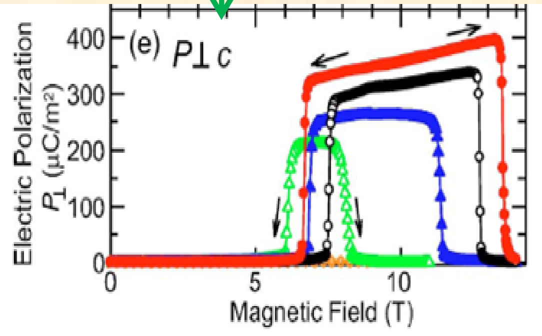
WEAK AXIAL ANISOTROPY

ABC stacked triangular layers.

H along c axis



T. Kimura et al.



Phase diagram exhibits spin states:

- IC collinear (H=0 and H≠0)
- P4 collinear (H=0 and H≠0)
- IC non-collinear (H≠0)
- P5 collinear (H≠0)
- P3 collinear (H≠0) ,…

ME Coupling from Anti-symmetric Exchange: Spin Structures.

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

Magnetoelectric effect by antisymmetric exchange

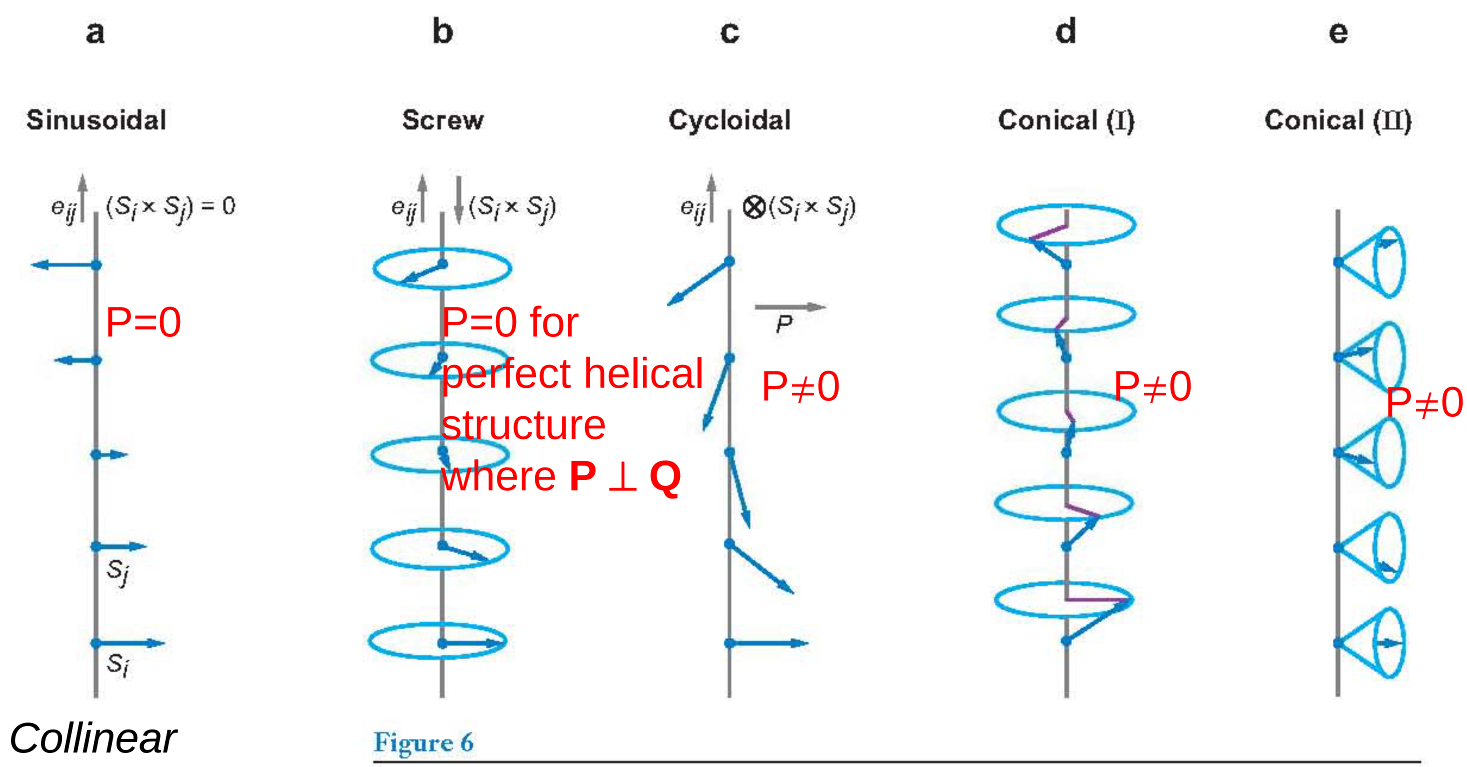


Figure 6

Schematic illustrations of types of magnetic structure with a long wavelength. (*a*) Sinusoidal, (*b*) screw, (*c*) cycloidal, and (*d*,*e*) conical structures. Geometric configurations of the unit vector connecting the neighboring magnetic moments at i and j sites $\vec{e}_{ij}$ and the vector spin chirality $(\vec{S}_i \times \vec{S}_j)$ are also shown for the respective structures.

T. Kimura, Ann. Rev. Mater. Res. **37**, 387 (2007).

Trigonal Anisotropy.

Spin Hamiltonian and Free Energy must be invariant wrt generators of crystal space group.

Space Group Generators

$CuFeO_2$ ($R\bar{3}m$): $\{C_3|000\}$, I, $\{\sigma_{d1}|000\}$ 3-fold rotation about **c**.

$HoMnO_3$ ($P6_3mc$): $\{C_6|00½\}$, $\{\sigma_{v1}|000\}$ 6-fold rotation about **c** *with a translation*.

• General 2nd order term $\sum A_{\alpha\beta} S_\alpha S_\beta$ leads to terms $D(S_{iz})^2$ and $J_z S_{iz} S_{jz}$.

• At 4th order $\sum B_{\alpha\beta\gamma\delta} S_\alpha S_\beta S_\gamma S_\delta$ can get a ***trigonal anisotropy*** term involving <u>all three vector components</u>:

$$K\{S_z S_y[3S_x^2 - S_x^2]\}$$

See, e.g., R.A. Cowley and J. Jensen, J. Phys. Condens. Matter **4**, 9673 (1992)

<u>Applications:</u>

•$CuFeO_2$. Single-site (Fe) form induces canting in Noncolinear IC phase $\longrightarrow P \neq 0$.

• $HoMnO_3$. Mn-Ho coupling leads to successive Mn reorientation transitions.

Magnetoelectic Coupling in $CuFeO_2$

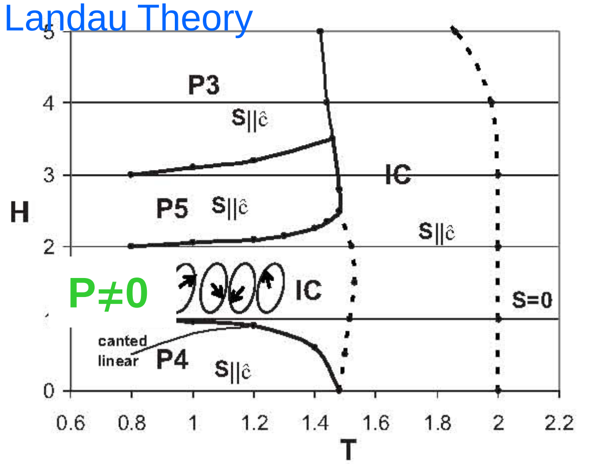
$$\mathcal{H}_C = \frac{1}{2}\sum_{ij} C(\mathbf{r}_{ij})(\mathbf{P}_{ij}\times\mathbf{e}_{ij})\cdot(\mathbf{s}_i\times\mathbf{s}_j)_z, \longrightarrow \mathcal{H}_{CP} = -\frac{1}{8A_P}\sum_{\alpha}\sum_{\langle ij\rangle}[C(\mathbf{r}_{ij})e_{ij}^{\alpha}(\mathbf{s}_i\times\mathbf{s}_j)\cdot\hat{\mathbf{z}}]^2,$$

Biquadratic antisymmetric exchange

$F_P = ½A_pP^2$

$$\mathbf{s}(\mathbf{r}) = \sum_q \mathbf{S}_q e^{i\mathbf{q}\cdot\mathbf{r}} = \mathbf{m} + \mathbf{S}_Q e^{i\mathbf{Q}\cdot\mathbf{r}} + \mathbf{S}_Q^* e^{-i\mathbf{Q}\cdot\mathbf{r}} + \ldots$$

Landau Theory



$$P_x = -(i/A_p)C_x(\boldsymbol{S}\times\boldsymbol{S}^*)_z$$

$$P_y = -(i/A_p)C_y(\boldsymbol{S}\times\boldsymbol{S}^*)_z$$

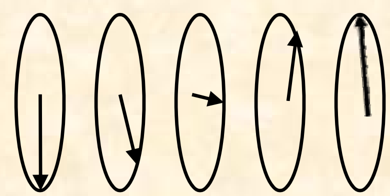
$\sim (\boldsymbol{S}_1 x \boldsymbol{S}_2)_z \sim (S_{1x}S_{2y} - S_{1y}S_{2x})$

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

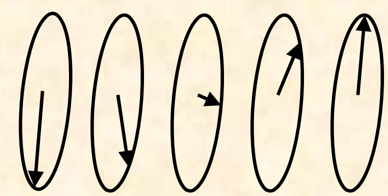
Canting (S not perpendicular to Q) stabilized by Trigonal Anisotropy

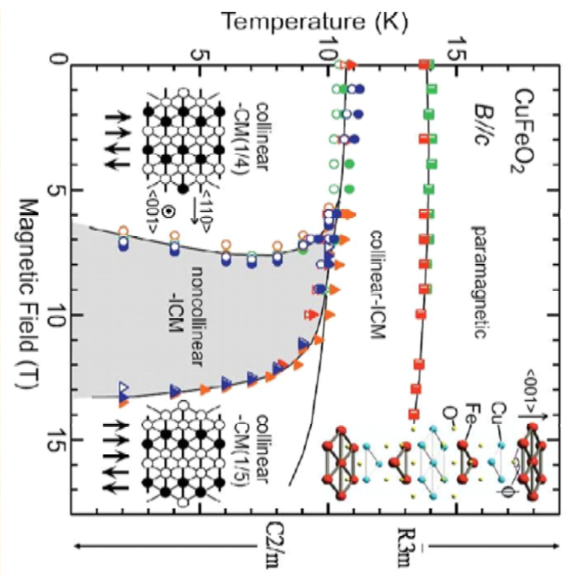
$K\{S_zS_y[3S_x^2 - S_x^2]\}$

P=0 for proper helix



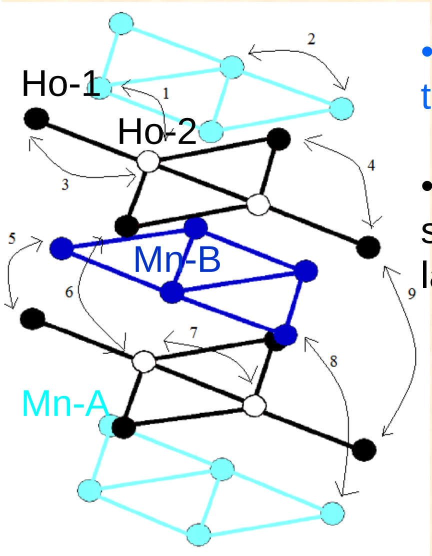
P≠0 for *canted* helix





$HoMnO_3$

P <u>*coexists*</u> with magnetic order : ***P***≠0, T_c=900K. ***S*** ≠ 0 T_N=75K.

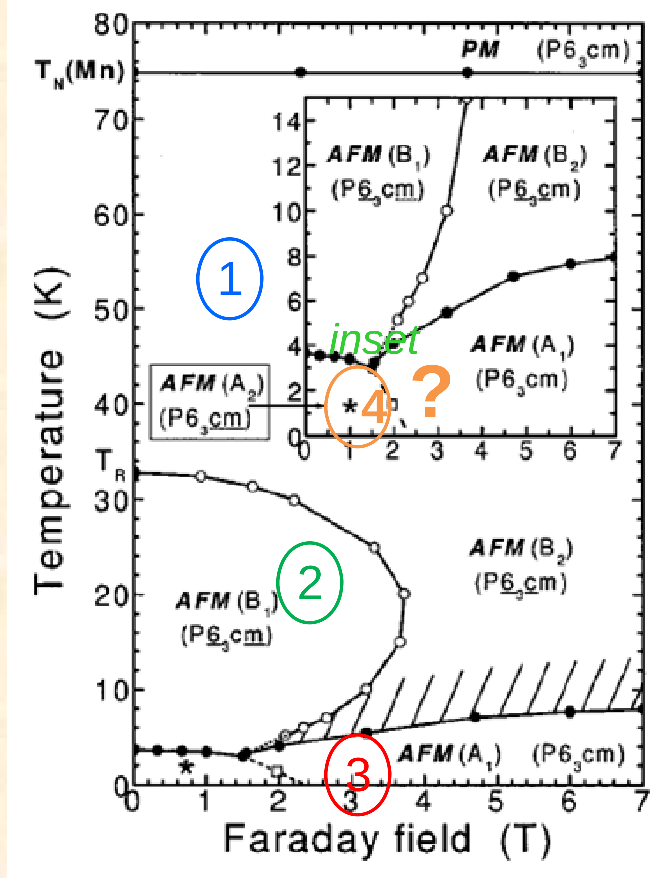


•Mn *AB* stacking of triangular layers.

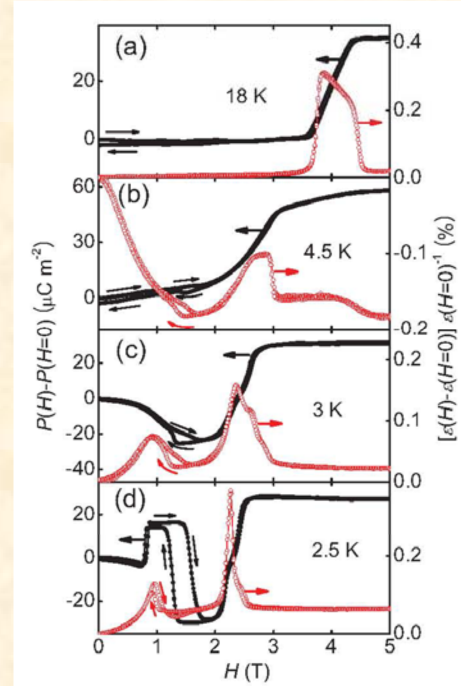
•Ho(1) and Ho(2) *AA* stacking of triangular layers.

$S_{Mn} \perp c$.

H_o ions can also order at low T: S_{Ho} || c



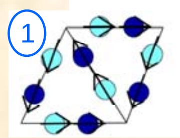
H modifies P

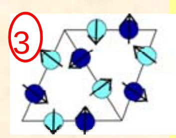


$S_{Ho} \perp S_{Mn}$

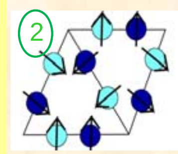
Exchange coupling:

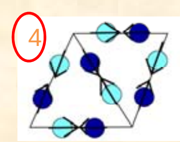
$S_{Mn} \cdot S_{Ho} = 0$





1. S_{Mn-A} || S_{Mn-B} ⊥ **a**
2. S_{Mn-A} || S_{Mn-B} || **a**
3. S_{Mn-A} || $-S_{Mn-B}$ || **a**
4. S_{Mn-A} || $-S_{Mn-B}$ ⊥ **a**





Mn form P3 120^0 in-plane spin structure.

Ho^{3+} → **S**=2, **L**=6
Mn^{3+} → **S**=2, **L**=2

Fiebig et al, J. App. Phys., 91 8867 (2002)

$HoMnO_3$: Mn Spins Only.

$$\mathcal{H} = \sum_{\langle ij \rangle} J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j - D\sum_i (S_i^z)^2 + E\sum[(S_i^x + iS_i^y)^6 + (S_i^x - iS_i^y)^6] + \bullet\bullet\bullet$$

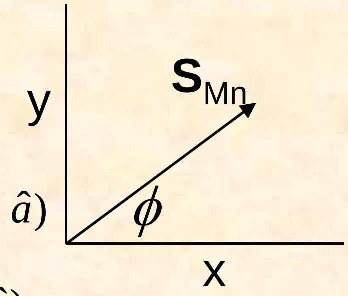
Hexagonal symmetry

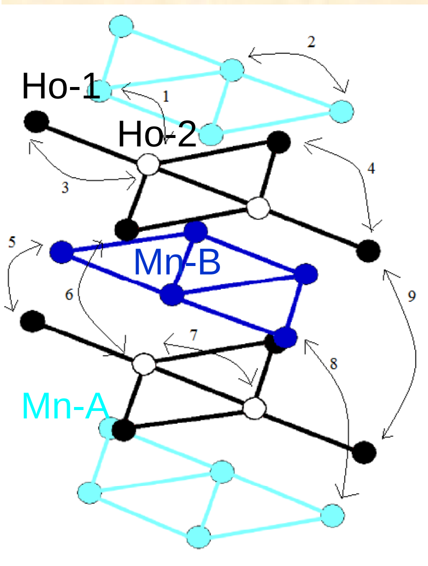
D<0: **S**⊥c

$$ES^6 \cos 6\phi$$

- J = NN AF exchange in triangular planes.
- J' = NN AF (or F) exchange between triangular planes (Mn_A-Mn_B)

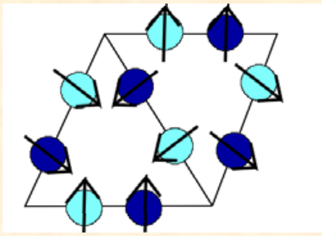
- E>0, $\phi = (2n+1)\frac{\pi}{6}$ $(S_{Mn} \perp \hat{a})$
- E<0, $\phi = n\frac{\pi}{3}$ $(S_{Mn} // \hat{a})$





Model Hamiltonian yields <u>all four</u> Mn spin configurations, depending on given signs of J' and E.

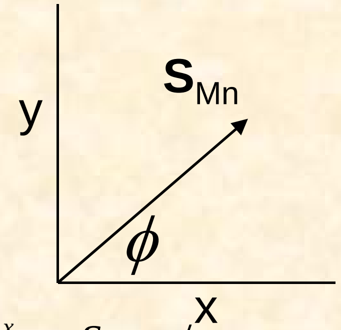
1. $S_{Mn\text{-}A} \parallel S_{Mn\text{-}B} \perp a$
2. $S_{Mn\text{-}A} \parallel S_{Mn\text{-}B} \parallel a$
3. $S_{Mn\text{-}A} \parallel -S_{Mn\text{-}B} \parallel a$
4. $S_{Mn\text{-}A} \parallel -S_{Mn\text{-}B} \perp a$



Ho-Mn Trigonal Coupling

•*Transitions between the four Mn spin states do not occur without coupling to* $\boldsymbol{S}_{Ho}$.

• Usual exchange interaction is zero $\boldsymbol{S}_{Mn}\bullet\boldsymbol{S}_{Ho} = 0$ since $\boldsymbol{S}_{Mn} \perp \boldsymbol{S}_{Ho}$



$S^{x}_{Mn} = S\cos\phi$

• ***Consider Trigonal anisotropy***

$$K\sum S^{z}_{Ho}S^{y}_{Mn}[3{S^{x}_{Mn}}^{2} - {S^{y}_{Mn}}^{2}]$$

$\sim KS_{Ho}(S_{Mn})^3\cos(3\phi)$

K>0, $\phi = (2n+1)\frac{\pi}{3}$

K<0, $\phi = n\frac{2\pi}{3}$

• $P6_3mc$ symmetry allows for this interaction if *either* (but not both) Mn *or* Ho have an AF interlayer configuration (screw axis $\{C_6^+|00½\}$).

• ***Provides a competition with Ecos6ϕ to drive re-orientation transitions involving ϕ - with simultaneous coupling to Holmium ions.***

A Simple Landau Model with Ho-Mn Coupling: H=0

$$F = AS^2 + A_o S_o^2 + \frac{1}{2}BS^4 + \frac{1}{2}B_o S_o^4 + B_1 S^2 S_o^2 + \frac{1}{3}CS^6 + KS_o S^3 cos3\phi + ES^6 cos6\phi$$

$A_0=a(T-T_0)$

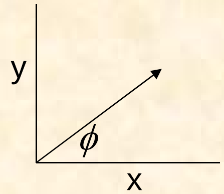
$A=a(T-T_N)$

$S=S_{Mn}$, $S_0=S_{Ho}$

$S_0 \sim S^3 cos3\phi$

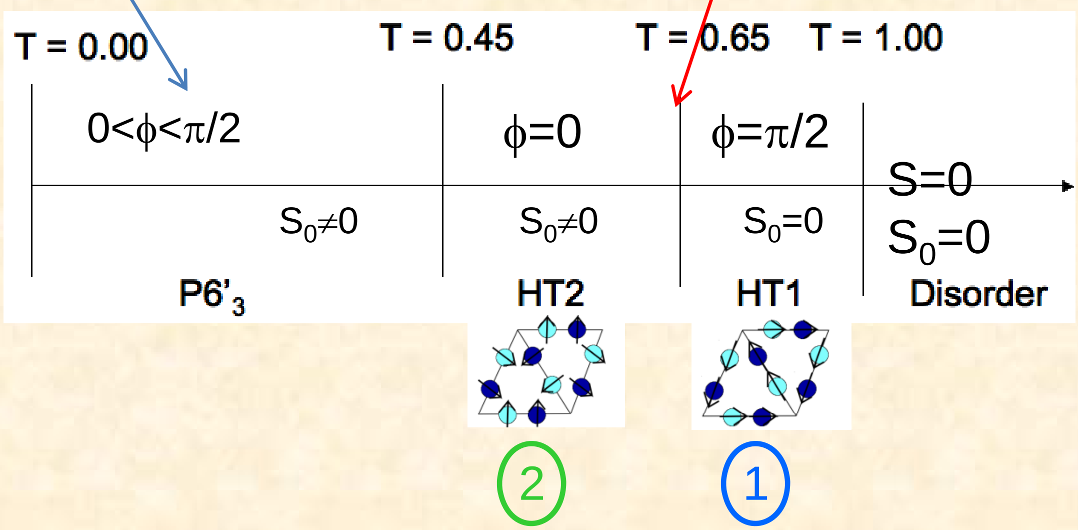
Ho order is incipient to Mn order.
This is observed experimentally.

H=0 only (so far).

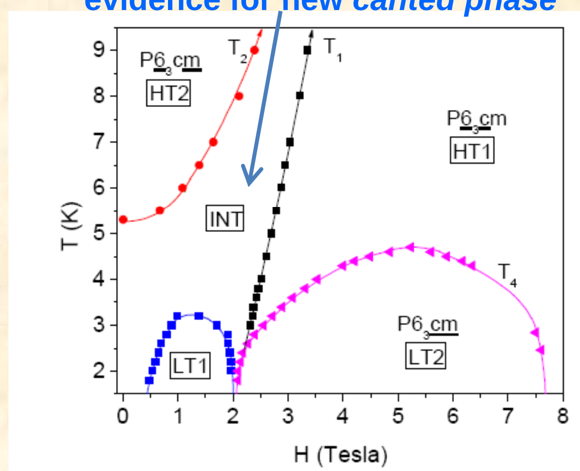


Canted Phase:
***S_{Mn}** oriented between x and y*

Phase transition: Simultaneous Mn-moment reorientation and Ho-moment ordering.



$HoMnO_3$: Experimental evidence for new *canted phase*



Yen et. Al, J. Mat. Res., 22 8 2163 (2007)

Thin Films of $HoMnO_3$

Magnetic phase transitions similar to bulk.

APPLIED PHYSICS LETTERS **90**, 012502 (2007)

Growth and multiferroic properties of hexagonal $HoMnO_3$ films

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(Received 30 September 2006; accepted 27 November 2006; published online 2 January 2007)

Hexagonal, twin-free $HoMnO_3$ (0001) films of 25–240 nm thickness were grown epitaxially on $Y_2O_3:ZrO_2$(111) substrates using pulsed laser deposition. Ferroelectric polar order and Mn^{3+} antiferromagnetism were observed by optical second harmonic generation. Magnetization data reveal Ho^{3+} ordering which is, with subtle deviations, similar to that of bulk crystals. However, three phase transitions below 6 K and thermal hysteresis of magnetization at $T < 42$ K were detected.

Other Thin-Film Applications of Magnetic Symmetry and Spin Order: Exchange Bias Antiferromagnet $IrMn_3$.

JOURNAL OF APPLIED PHYSICS VOLUME 86, NUMBER 7 1 OCTOBER 1999

Magnetic neutron scattering study of ordered Mn_3Ir

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Used widely in GMR and TMR spin valves.
Thin films perpendicular to <111>.

$IrMn_3$ = fcc = ABC stacked *triangular layers* along <111>

Bulk T_N = 960 K

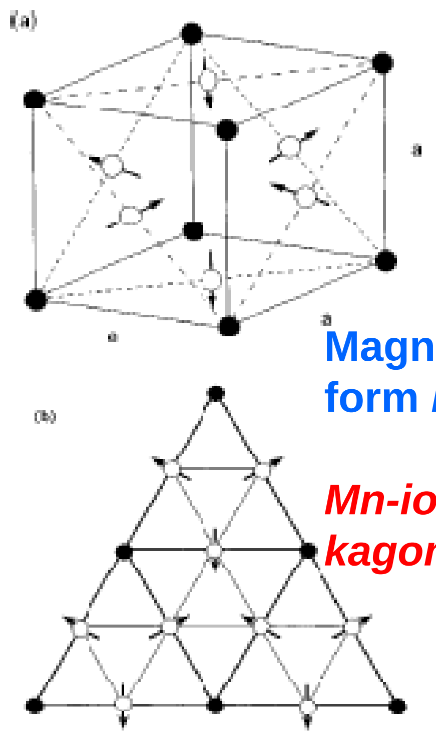
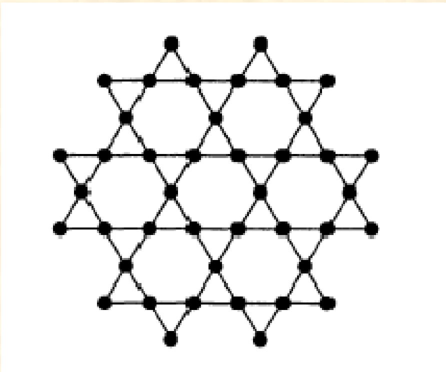


FIG. 3. (a) Antiferromagnetic structure and (b) the corresponding (111) surface spin structure for Mn_3Ir. Open and solid circles represent Mn and Ir atoms, respectively.

Magnetic Mn-ions (open circles) form *kagome* lattice.

Mn-ions in Mn_3Ir = ABC stacked kagome lattice.



How does spin order due to frustration in the Mn-ion kagome lattice impact its exchange bias properties ?

Collaborators:

http://www.mun.ca/physics/

Guy Quirion, Oleg Petrenko, Mariathas Tagore, Stephen Condran.

•***Understanding the complex spin ordering in magnetoelectric antiferromagnetics is key to revealing the relationship between spin and electric degrees of freedom.***

• ***Non-local Landau-type free energy constructed from rigorous symmetry requirements provides a useful foundation for the marriage of microscopic and phenomenological descriptions of multi-phase systems resulting from lots of frustration.***

S. Condran and M.L. Plumer, A model of magnetic order in hexagonal $HoMnO_3$, J. Phys.: Condens. Matter, Fast Track Commun. 22, 162201-1,5 (2010).

G. Quirion, M.L. Plumer, O.A. Petrenko, G. Balakrishnan, and C. Proust, Magnetic phase diagram of magnetoelectric $CuFeO_2$ in high magnetic fields, Phys. Rev. B 80, 064420-1,5 (2009).

G. Quirion, M.J. Tagore, M.L. Plumer and O. Petrenko, Magnetoelastic coupling in $CuFeO_2$, J. Phys.: Conf. Ser. 145, 012070-1,4 (2009).

M.L. Plumer, Nonlocal Landau theory of the magnetic phase diagram of highly frustrated magnetoelectric CuFeO2, Phys. Rev. B 78, 094402-1,8 (2008).

G. Quirion, M.J. Tagore, M.L. Plumer and O.A. Petrenko, Evidence of soft modes in magnetoelectric $CuFeO_2$: Ultrasonic velocity measurements and Landau theory, Phys. Rev. B. 77, 094111-1,7 (2008).

M.L. Plumer, Biquadratic antisymmetric exchange and the magnetic phase diagram of magnetoelectric $CuFeO_2$, Phys. Rev. B. 76, 144411-1,6 (2007).

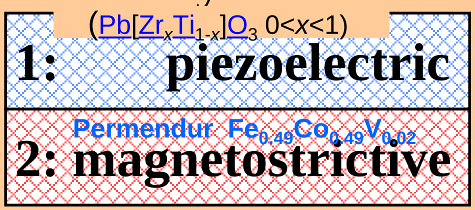
BACK-UP SLIDES

Modern Magnetoelectric Multiferroics

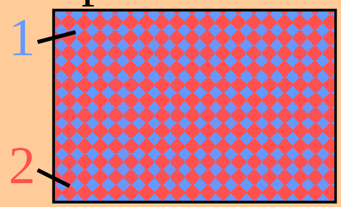
Courtesy of M. Fiebig

Composite materials
for device application

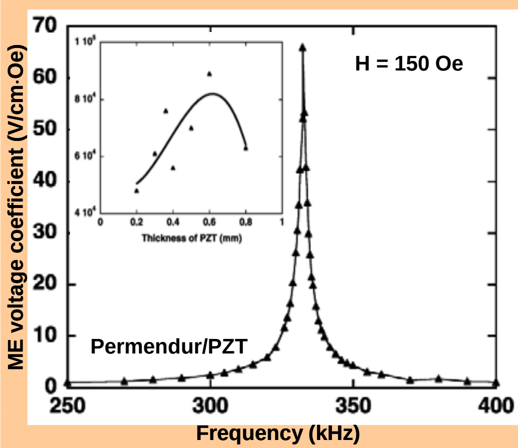
layered



particulate



$$\text{ME effect} = \frac{\text{electrical}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}$$



Effects up to 90 kV/cm·Oe

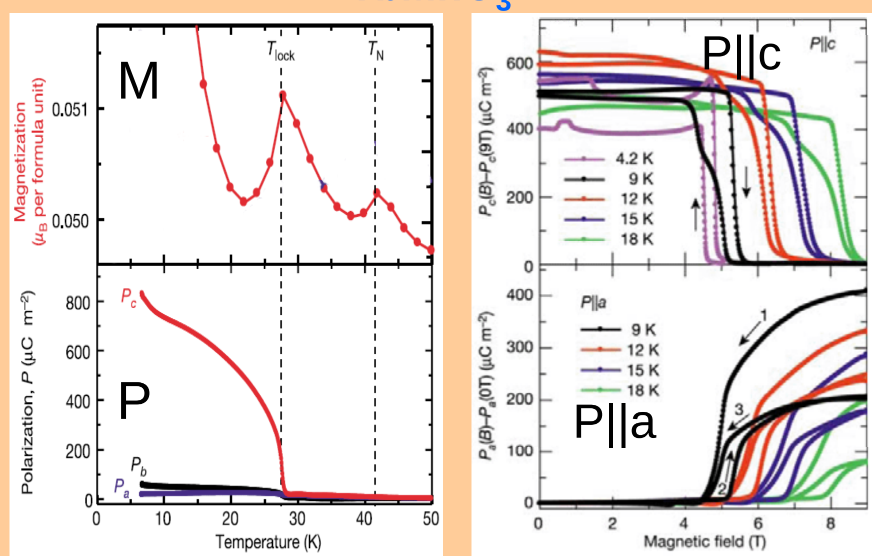
($10^{3...5}$ ×single-phase effect)

U. Laletsin et al., Appl. Phys. A **78**, 33 (2004)

Intrinsic multiferroics
for basic research (and devices)

- Small absolute magnetoelectric coefficient but novel physics
- "Gigantic" ME effect if magnetic field sets ferroelectric properties:

$TbMnO_3$



T. Kimura et al., Nature **426**, 55 (2003)

230 Space Groups and their Generators

Bradley and Cracknell:

The Mathematical Theory of the Symmetry in Solids.

Hexagonal Symmetry:

$$F_2 = A(S \cdot S) - D(S_z)^2$$

$$F_4 = \tfrac{1}{2}B(S \cdot S)^2 + E_1 S_z^4 + E_2 S_z^2 (S_x^2 + S_y^2)$$

Anisotropy

S||c or S⊥c

$HoMnO_3$ → 186

$CsNiCl_3$ → 194

International number	International symbol	Schönflies symbol	Generating elements	t_0
181	$P6_422$	$\Gamma_h D_6^5$	$\{C_6^+ \mid 00\tfrac{2}{3}\}, \{C'_{21} \mid 000\}$	0
182	$P6_322$	$\Gamma_h D_6^6$	$\{C_6^+ \mid 00\tfrac{1}{2}\}, \{C'_{21} \mid 000\}$, $\{C_6^+ \mid 00\tfrac{1}{2}\}, \{C''_{21} \mid 000\}$	*
183	$P6mm$	$\Gamma_h C_{6v}^1$	$\{C_6^+ \mid 000\}, \{\sigma_{v1} \mid 000\}$	0
184	$P6cc$	$\Gamma_h C_{6v}^2$	$\{C_6^+ \mid 000\}, \{\sigma_{v1} \mid 00\tfrac{1}{2}\}$	0
185	$P6_3cm$	$\Gamma_h C_{6v}^3$	$\{C_6^+ \mid 00\tfrac{1}{2}\}, \{\sigma_{v1} \mid 00\tfrac{1}{2}\}$	0
186	$P6_3mc$	$\Gamma_h C_{6v}^4$	$\{C_6^+ \mid 00\tfrac{1}{2}\}, \{\sigma_{v1} \mid 000\}$	0
187	$P\bar{6}m2$	$\Gamma_h D_{3h}^1$	$\{S_3^+ \mid 000\}, \{\sigma_{v1} \mid 000\}$	0
188	$P\bar{6}c2$	$\Gamma_h D_{3h}^2$	$\{S_3^+ \mid 000\}, \{\sigma_{v1} \mid 00\tfrac{1}{2}\}$, $\{S_3^+ \mid 00\tfrac{1}{2}\}, \{\sigma_{v1} \mid 00\tfrac{1}{2}\}$	$\tfrac{1}{4}t_3$
189	$P\bar{6}2m$	$\Gamma_h D_{3h}^3$	$\{S_3^+ \mid 000\}, \{\sigma_{d1} \mid 000\}$	0
190	$P\bar{6}2c$	$\Gamma_h D_{3h}^4$	$\{S_3^+ \mid 000\}, \{\sigma_{d1} \mid 00\tfrac{1}{2}\}$, $\{S_3^+ \mid 00\tfrac{1}{2}\}, \{\sigma_{d1} \mid 00\tfrac{1}{2}\}$	$\tfrac{1}{4}t_3$
191	$P6/mmm$	$\Gamma_h D_{6h}^1$	$\{C_6^+ \mid 000\}, \{C'_{21} \mid 000\}, \{I \mid 000\}$	0
192	$P6/mcc$	$\Gamma_h D_{6h}^2$	$\{C_6^+ \mid 000\}, \{C'_{21} \mid 00\tfrac{1}{2}\}, \{I \mid 000\}$	0
193	$P6_3/mcm$	$\Gamma_h D_{6h}^3$	$\{C_6^+ \mid 00\tfrac{1}{2}\}, \{C'_{21} \mid 000\}, \{I \mid 000\}$	0
194	$P6_3/mmc$	$\Gamma_h D_{6h}^4$	$\{C_6^+ \mid 00\tfrac{1}{2}\}, \{C'_{21} \mid 00\tfrac{1}{2}\}, \{I \mid 000\}$	0
195	$P23$	$\Gamma_c T^1$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$	0
196	$F23$	$\Gamma_c^f T^2$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$	0
197	$I23$	$\Gamma_c^v T^3$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$	0
198	$P2_13$	$\Gamma_c T^4$	$\{C_{2z} \mid \tfrac{1}{2}0\tfrac{1}{2}\}, \{C_{2x} \mid \tfrac{1}{2}\tfrac{1}{2}0\}, \{C_{31}^+ \mid 000\}$	0
199	$I2_13$	$\Gamma_c^v T^5$	$\{C_{2z} \mid \tfrac{1}{2}0\tfrac{1}{2}\}, \{C_{2x} \mid \tfrac{1}{2}\tfrac{1}{2}0\}, \{C_{31}^+ \mid 000\}$	0
200	$Pm3$	$\Gamma_c T_h^1$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$, $\{I \mid 000\}$	0
201	$Pn3$	$\Gamma_c T_h^2$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$, $\{I \mid \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}$	0
202	$Fm3$	$\Gamma_c^f T_h^3$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$, $\{I \mid 000\}$	0
203	$Fd3$	$\Gamma_c^f T_h^4$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$, $\{I \mid \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}\}$	0
204	$Im3$	$\Gamma_c^v T_h^5$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{31}^+ \mid 000\}$, $\{I \mid 000\}$	0
205	$Pa3$	$\Gamma_c T_h^6$	$\{C_{2z} \mid \tfrac{1}{2}0\tfrac{1}{2}\}, \{C_{2x} \mid \tfrac{1}{2}\tfrac{1}{2}0\}, \{C_{31}^+ \mid 000\}$, $\{I \mid 000\}$	0
206	$Ia3$	$\Gamma_c^v T_h^7$	$\{C_{2z} \mid \tfrac{1}{2}0\tfrac{1}{2}\}, \{C_{2x} \mid \tfrac{1}{2}\tfrac{1}{2}0\}, \{C_{31}^+ \mid 000\}$, $\{I \mid 000\}$	0
207	$P432$	$\Gamma_c O^1$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{2a} \mid 000\}$, $\{C_{31}^+ \mid 000\}$	0
208	$P4_232$	$\Gamma_c O^2$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{2a} \mid \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}$, $\{C_{31}^+ \mid 000\}$	0
209	$F432$	$\Gamma_c^f O^3$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{2a} \mid 000\}$, $\{C_{31}^+ \mid 000\}$	0
210	$F4_132$	$\Gamma_c^f O^4$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{2a} \mid \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}\}$, $\{C_{31}^+ \mid 000\}$	0
211	$I432$	$\Gamma_c^v O^5$	$\{C_{2z} \mid 000\}, \{C_{2x} \mid 000\}, \{C_{2a} \mid 000\}$, $\{C_{31}^+ \mid 000\}$	0
212	$P4_332$	$\Gamma_c O^6$	$\{C_{2z} \mid \tfrac{1}{2}0\tfrac{1}{2}\}, \{C_{2x} \mid \tfrac{1}{2}\tfrac{1}{2}0\}, \{C_{2a} \mid \tfrac{1}{4}\tfrac{3}{4}\tfrac{3}{4}\}$, $\{C_{31}^+ \mid 000\}$	0

Conclusions

- ***$CuFeO_2$*** magnetic phase diagram : *ABC stacked triangular layers*
  - *- biquadratic symmetric exchange (magnetoelastic coupling) stabilizes collinear states*
  - *- biquadratic antisymmetric exchange (magnetoelectric coupling) stabilizes non-collinear state*
  - *- trigonal anisotropy leads to canting and $P \neq 0$*

- ***$HoMnO_3$*** magnetic phase diagram : *AB stacked triangular layers*
  - *- only commensurate P3 phases*
  - *- four main Mn states determined by 6^{th}-order anisotropy and inter-layer coupling*
  - *- trigonal anisotropy gives interaction between Mn and Ho and drives a series of transitions*

•*Understanding the complex spin ordering in magnetoelectric antiferromagnetics is key to revealing the relationship between spin and electric degrees of freedom.*

• *Non-local Landau-type free energy constructed from rigorous symmetry requirements provides a useful foundation for the marriage of microscopic and phenomenological descriptions of multi-phase systems resulting from lots of frustration.*

$CuFeO_2$: Magnetoelectricity and Noncollinearity

Why does *noncollinear* state exist and why is $P \neq 0$ only in that phase ?

• Consider coupling between spin, electric polarization and position vectors: ***S, P, r.***

• Inversion symmetry $\mathbf{r} \to -\mathbf{r}$, $\mathbf{r} \leftrightarrow \mathbf{r}'$, $\mathbf{P} \to -\mathbf{P}$ and other $R\bar{3}m$ crystal symmetry requirements (space group generators $\{S_6^+|000\}$, $\{\sigma_{d1}|000\}$) leads to:

$$F_C = \frac{1}{2V^2} \int d\mathbf{r} d\mathbf{r}' C(\boldsymbol{\tau}) [\mathbf{P}(\boldsymbol{\tau}) \times \hat{\boldsymbol{\tau}}] \cdot [\mathbf{s}(\mathbf{r}) \times \mathbf{s}(\mathbf{r}')]_z$$

$\tau = \mathbf{r} - \mathbf{r}'$

z component

• Add polarization energy ~ P^2:

$$F_P = \frac{A_p}{2V^2} \int d\mathbf{r} d\mathbf{r}' \mathbf{P}^2(\tau)$$

• Integrate out ***P*** (minimize wrt ***P***):

$$F_{CP} = -\frac{1}{8V^2 A_P} \sum_{\alpha} \int d\mathbf{r} d\mathbf{r}' \{C(\boldsymbol{\tau}) \hat{\tau}^{\alpha} [\mathbf{s}(\mathbf{r}) \times \mathbf{s}(\mathbf{r}')] \cdot \hat{\mathbf{z}}\}^2,$$

Biquadratic anti-symmetric exchange.

Non-local Landau Free Energy for $CuFeO_2$

$$F = F_2 + F_4 + F_6 + F_z + F_{CP} + F_K - \boldsymbol{m}\cdot\boldsymbol{H}$$

Isotropic (includes biquadratic symmetric exchange).

Biquadratic anti-symmetric exchange

Trigonal anisotropy (3-fold rotation axis)

$$F_K = \frac{K}{2V}\int d\mathbf{r}\, s_z(\mathbf{r}) s_y(\mathbf{r})[3s_x^2(\mathbf{r}) - s_y^2(\mathbf{r})].$$

Favors canted spin structures

Axial exchange anisotropy:

$$F_z = \frac{1}{2V^2}\int d\mathbf{r}\, d\mathbf{r}' J_z(\mathbf{r}-\mathbf{r}') s_z(\mathbf{r}) s_z(\mathbf{r}').$$

- Insert spin density and evaluate. $\mathbf{s}(\mathbf{r}) = \sum_{j\mathbf{q}} \mathbf{S}_{j\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} = \mathbf{m} + \mathbf{S}_j e^{i\mathbf{Q}\cdot\mathbf{r}} + \mathbf{S}_j^* \mathbf{e}^{-i\mathbf{Q}\cdot\mathbf{r}} + \ldots$

- Three triangular layers: *j= A, B, C.*

$$\boldsymbol{r} = \boldsymbol{R} + \boldsymbol{w}_j$$

$$w_A = 0, w_B = \frac{1}{3}ax + \frac{1}{3}by + \frac{1}{3}cz, w_C = \frac{1}{3}ax - \frac{1}{3}by - \frac{1}{3}cz$$

$$\mathbf{S}_A = \mathbf{S}e^{i\gamma}, \quad \mathbf{S}_B = \mathbf{S}_C = \mathbf{S}e^{i(\gamma-\phi)}.$$

$$\hat{s} = \hat{s}_1 + i\hat{s}_2$$

Ansatz: phase difference only.

Second-order Isotropic Terms

$$F_2 = \tfrac{1}{2} A_0 m^2 + A_Q S^2$$

$S^2 = \mathbf{S} \cdot \mathbf{S}^*$, $\quad A_Q = aT + J_Q$

J_2-J_3 phase diagram

CuFeO$_2$

$J_2 \sim 0.3/J_1$
$J_3 \sim 0.3/J_1$

BIG !

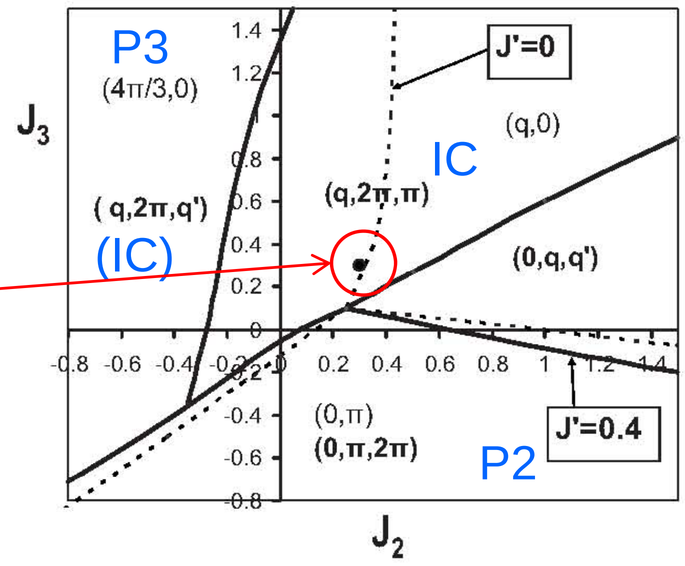


FIG. 1. Sketch of the J_2-J_3 phase diagram based on minimization of the exchange integral $J_{\mathbf{q}}$ with $J_1=1$. Broken curves correspond to the case $J'=0$ and solid curves to $J'=0.4$. Solid circle indicates values used in the present model; $J_2=J_3=0.3$ and $J'=0.4$.

$$q_x = aQ_x, q_y = bQ_y, q_z = cQ_z$$

$$b = (\sqrt{3}/2)a$$

•Wave vector is determined by minimizing J_Q *and Umklapp* terms (later).

$$J_Q = \frac{1}{N} \sum_R J(R) e^{iQ \cdot R}$$

• 1st, 2nd, 3rd neighbor in-plane exchange coupling J_1, J_2, J_3 *plus* inter-plane exchange J'.

$$J_Q = 2f(\mathbf{q}, \phi)$$

$$f(\mathbf{q},\phi) = J_1 f_1(\mathbf{q}) + J_2 f_2(\mathbf{q}) + J_3 f_3(\mathbf{q}) + \frac{1}{3} J' f'(\mathbf{q})(1 + 2\cos\phi), \quad (20)$$

where[37]

$$f_1 = \cos q_x + 2\cos\frac{1}{2}q_x \cos q_y,$$

$$f_2 = \cos 2q_y + 2\cos\frac{3}{2}q_x \cos q_y,$$

$$f_3 = \cos 2q_x + 2\cos q_x \cos 2q_y,$$

$$f' = \cos\left(\frac{2}{3}q_x - \frac{1}{3}q_z\right) + 2\cos\frac{1}{2}q_x \cos\left(\frac{1}{3}q_y + \frac{1}{3}q_z\right), \quad (21)$$

Fourth- and Sixth-order Isotropic Terms

Fourth Order

$$F_{4,R} = B_1 S^4 + \frac{1}{2} B_2 |\mathbf{S}\cdot\mathbf{S}|^2 + \frac{1}{4} B_3 m^4 + 2B_4 |\mathbf{m}\cdot\mathbf{S}|^2 + B_5 m^2 S^2, \quad (23)$$

'Regular' terms: $B_4<0$: *magnetoelastic coupling (?) favors S || H || c.*

$$F_{4,3} = B_{4,3}[(\mathbf{m}\cdot\mathbf{S})(\mathbf{S}\cdot\mathbf{S})e^{3i\gamma} + \text{c.c.}]\Delta_{3\mathbf{Q},\mathbf{G}}, \quad (24)$$

Field-induced Umklapp term: Stabilizes collinear P3 structures. $\mathbf{Q} = \frac{1}{3}\mathbf{G}$

$$F_{4,4} = \frac{1}{4} B_{4,4}[(\mathbf{S}\cdot\mathbf{S})^2 e^{4i\gamma} + \text{c.c.}]\Delta_{4\mathbf{Q},\mathbf{G}}. \quad (25)$$

Zero field Umklapp term: Stabilizes collinear P4 structures $\mathbf{Q} = \frac{1}{4}\mathbf{G}$

- *Umklapp terms favor collinear structures.*
- *Odd-order Umklapp terms are generated by an applied field and favor **S** || **H**.*

Sixth Order

- *more Regular and Umklapp terms (3Q=G, 4Q=G, 5Q=G, 6Q=G)*

$CuFeO_2$: Super Frustration

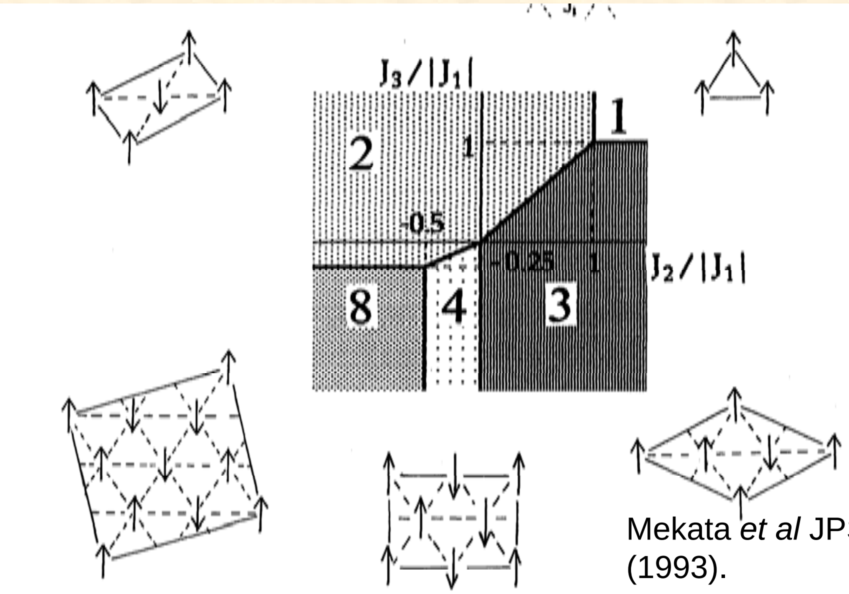
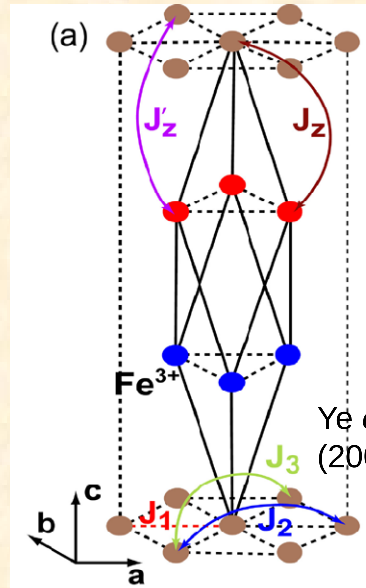


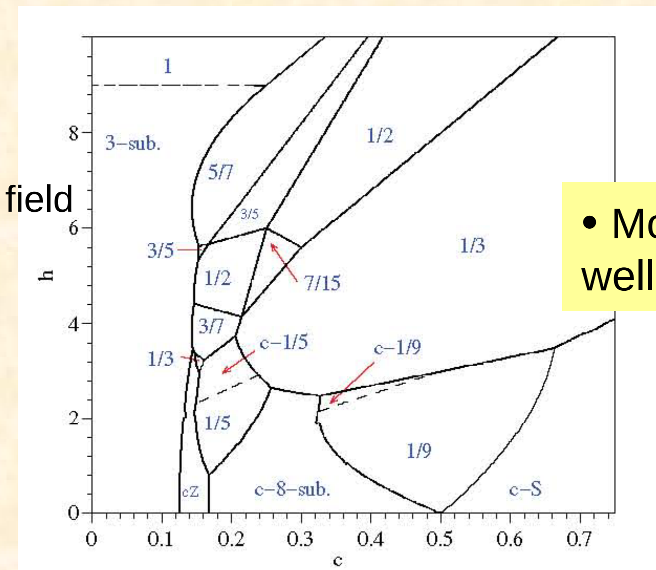
Fig. 11. Magnetic phase diagram of Ising spin triangular lattice antiferromagnet at 0 K.

Mekata *et al* JPSJ **62**, 474 (1993).

• Early Ising model with up to 3rd neighbor exchange interactions (J_1, J_2, J_3) on a 2D triangular lattice reveals a multitude of commensurate phases (P2, P3, P4, P8)



Ye *et al* PRL **99**, 157201 (2007).



c=biquadratic exchange

• More recent models include inter-layer interactions (weak) as well as biquadratic exchange (Wang and Vishwanath, PRL (2008)).

• *None of these predict the noncollinear (field-induced) phase that yields spin-induced $P \neq 0$.*

$HoMnO_3$: Mn Spins Only. LLG.

$$\mathcal{H} = \sum_{\langle ij \rangle} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - D\sum_i (S_i^z)^2 + E\sum[(S_i^x + iS_i^y)^6 + (S_i^x - iS_i^y)^6] + \bullet\bullet\bullet$$

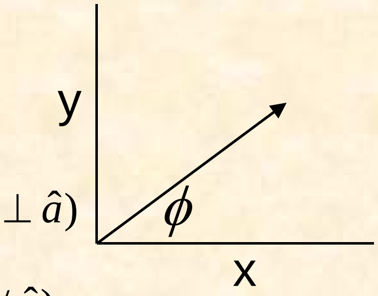
Hexagonal symmetry

D<0: **S**⊥c

$$ES^6 \sin 6\phi$$

- J = NN AF exchange in triangular planes.
- J' = NN AF (or F) exchange between triangular planes (Mn_A-Mn_B)

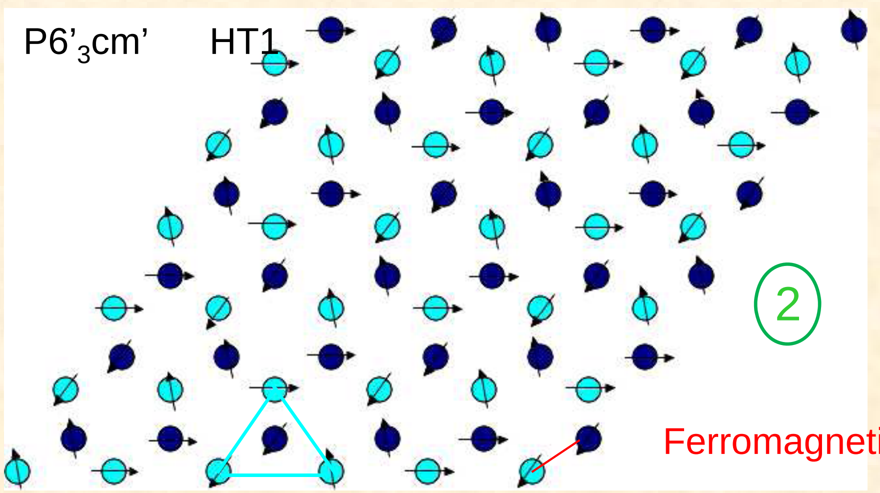
- E>0, $\phi = (2n+1)\frac{\pi}{6}$ $(S_{Mn} \perp \hat{a})$
- E<0, $\phi = n\frac{\pi}{3}$ $(S_{Mn} // \hat{a})$



•Determine equilibrium spin structures using the **Landau Lifshitz Gilbert** equation:

$$\frac{d\boldsymbol{S}(t)}{dt} = -\frac{\gamma}{1+\alpha^2}(\boldsymbol{S} \times \boldsymbol{H}_{eff}) - \frac{\alpha\gamma}{1+\alpha^2}(\boldsymbol{S} \times (\boldsymbol{S} \times \boldsymbol{H}_{eff}))$$

$$H_{eff} = -\frac{\partial E}{\partial \vec{S}}$$



Ferromagnetic between planes and ***S*** **|| a**

Model Hamiltonian yields <u>all four</u> Mn spin configurations, depending on signs of J' and E.

LLG: Finite-Temperature Effects

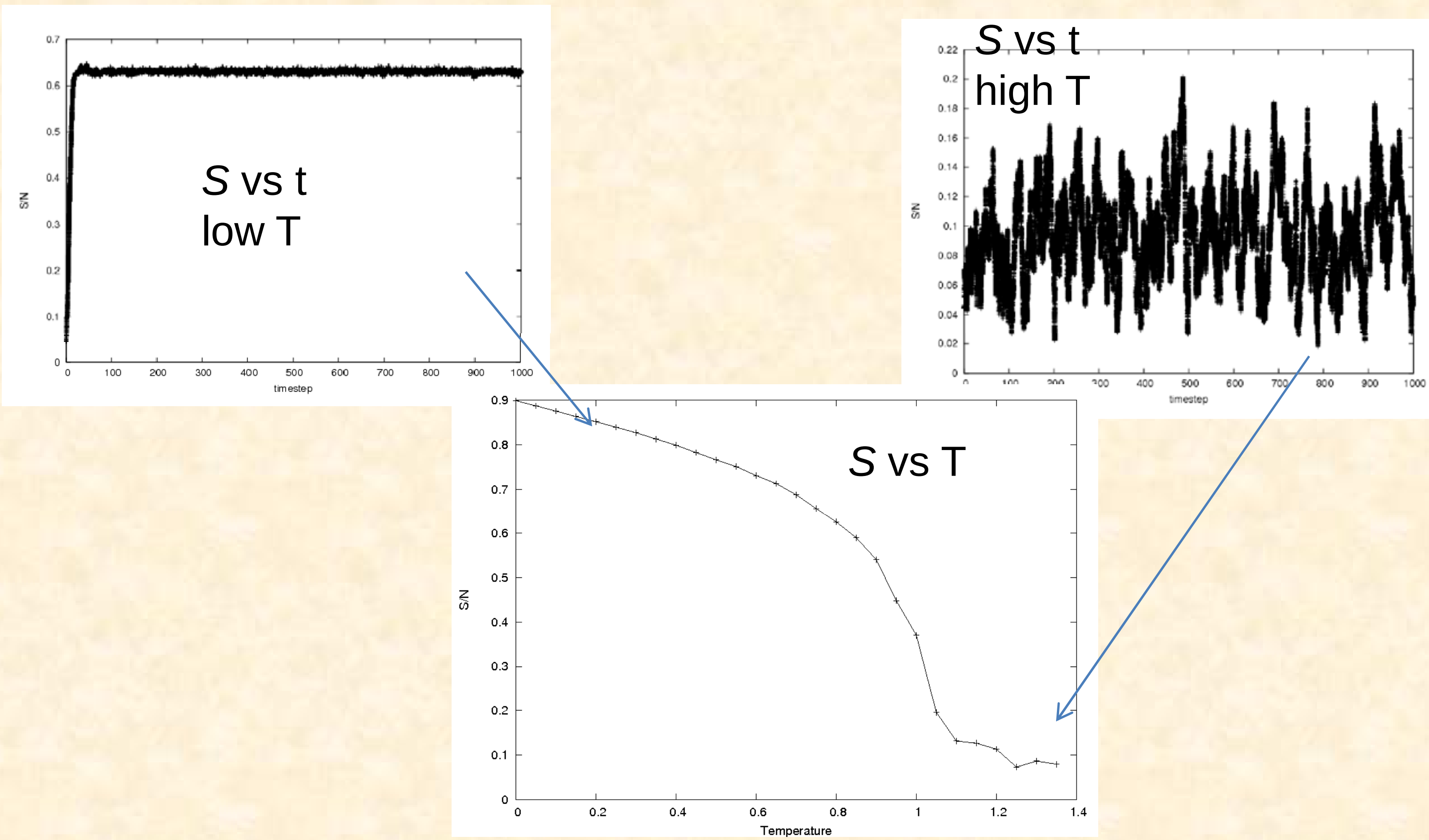
Add stochastic field term via Langevin dynamics.

$$\vec{S}(t+\Delta t) = \vec{S}(t) - \frac{\Delta t \gamma}{1+\alpha^2}\left[\vec{S}\times\vec{H}_{\text{eff}} + \alpha\vec{S}\times(\vec{S}\times\vec{H}_{\text{eff}})\right] - \sqrt{\Delta t}\vec{S}\times\vec{\eta}$$

Euler algorithm

$$\eta = \sqrt{4\beta k_B T}$$

$$\beta = \frac{\alpha\gamma}{1+\alpha^2}$$



Magnetoelectric and Multiferroic Device Applications

• *Magnetic vector field sensor using magnetoelectric thin-film composites,*
E. Quandt *et al*, IEEE Trans. Magn. 41, 3667 (2005).

• *Magnetoelectric switching of exchange bias,*
P. Borisov *et a*l, PRL 94, 117203 (2005).

• *Room temperature exchange bias and spin valves based on $BiFeO_3$ / $SrRuO_3$ / $SrTiO_3$ /Si (001) heterostructures,*
L.W. Martin *et al.* APL 91, 172513 (2007).

• *Spintronics with multiferroics,*
H. Bea *et al*., JPCM 20, 434221 (2008).

• *Demonstration of magnetoelectric read head of multiferroic heterojunctions,*
Y. Zhang *et al*. APL 92, 152510 (2008).

• *Multiferroics and magnetolectrics: thin films and nanostructures,*
L.W. Martin *et al*, JPCM 20, 434220 (2008).

Molecular Field Theory Derivation of the Landau Free Energy

Use Mean-Field Theory: $\mathcal{H}_{MF} = -\sum_{i,\alpha} h_i^\alpha \langle S_i^\alpha \rangle$ with $h_i^\alpha = \sum J_{ij}^{\alpha\beta} \langle S_j^\beta \rangle$

$\langle S_i^\alpha \rangle = \frac{h_i^\alpha}{h_i} \frac{\sum m e^{h_i m / k_B T}}{\sum e^{h_i m / k_B T}}$ m = -*J*, -*J*+1, ….*J*-1,*J* where *J* is the total angular momentum

- Formulate free energy from variational principle:

F ≤ $F_0 + \langle \mathcal{H} - \mathcal{H}_{MF} \rangle$ and $F_0 = \mathrm{tr}[w_{MF}\mathcal{H}_{MF}] + (k_B T)\mathrm{tr}[w_{MF}\mathbf{Ln}(w_{MF})]$

$$w_{MF} = \frac{e^{-\mathcal{H}_{MF}/k_B T}}{tr(e^{-\mathcal{H}_{MF}/k_B T})}$$

- Expand in powers of $\langle S_i \rangle$: *F = E - TS*

$$F = \sum J_{ij}^{\alpha\beta} \langle S_i^\alpha \rangle \langle S_j^\beta \rangle + T\{a \sum \langle S_i^\alpha \rangle^2 + b \sum \langle S_i^\alpha \rangle^2 \langle S_j^\beta \rangle^2 + \dots$$

Entropy - All isotropic

⇒ Same as *Phenomenological Non-local Landau Free Energy, but with* $B_1 = B_2 = B_3 = \dots = bT$ ($\cong bT_N$ = *constant)*

$$a = \frac{3J}{J+1}$$

$$b = \frac{1}{45} \frac{(2J+1)^4 - 1}{(2J)^4}$$

P. Bak and J. von Boehm, Phys. Rev. B **21,** 5297 1980.

Magnetoelastic Coupling

• Consider dependence of exchange integral on inter-ion separation:

$$J(\mathbf{r}'-\mathbf{r})=J(\mathbf{r}_0'-\mathbf{r}_0)+[\mathbf{u}(\mathbf{r}_0')-\mathbf{u}(\mathbf{r}_0)]\cdot\nabla J(\mathbf{r}_0)+\cdots$$

• Define τ=r-r' and introduce *strain tensor* $e_{\alpha\beta}=e_i$ (i=1-6, Voigt notation)

$$J(\boldsymbol{\tau})\cong J(\boldsymbol{\tau}_0)+e_iK_i(\boldsymbol{\tau}_0)$$

$$K_{\alpha\beta}(\tau_0)=\frac{1}{2}\left[\frac{\partial J}{\partial r_\alpha}\tau_\beta+\frac{\partial J}{\partial r_\beta}\tau_\alpha\right]_0$$

• Add elastic energy to this exchange-striction term:

$$F_e=(\tfrac{1}{2}j^2/V^2)\int d\mathbf{r}\int d\mathbf{r}'K_i(\boldsymbol{\tau})e_i\mathbf{s}(\mathbf{r})\cdot\mathbf{s}(\mathbf{r}')+\tfrac{1}{2}\upsilon C_{ij}e_ie_j$$

quadratic in s(r)

Elastic constants

• $\delta F[s(r),e_i]/\delta e_i=0$ yields impact of magnetic phase changes on elastic properties:

$$e_i=(-\tfrac{1}{2}j^2/\upsilon V^2)\int d\mathbf{r}\int d\mathbf{r}'s_{ij}K_j(\boldsymbol{\tau})\mathbf{s}(\mathbf{r})\cdot\mathbf{s}(\mathbf{r}')$$

$s_{ij}=[\mathbf{C}^{-1}]_{ij}$ compliance matrix

Magnetic Phase Diagram of $CuFeO_2$

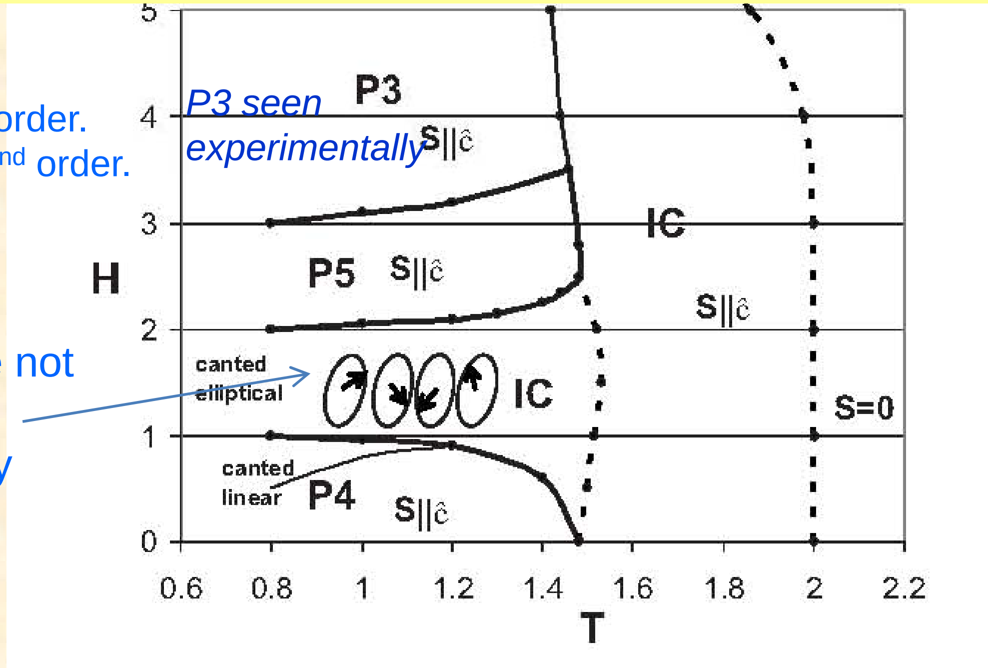
- Numerical minimization of Free Energy F=F(**m,S,Q**) .

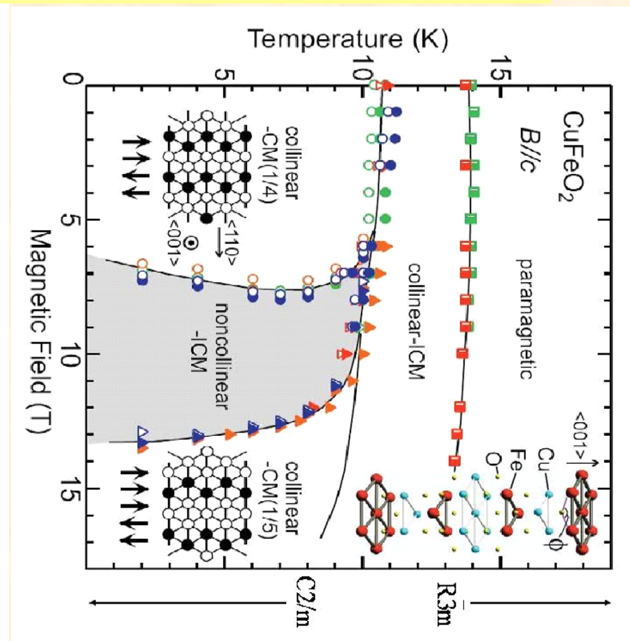
- Lots of fitting parameters: J_1, J_2, J_3, J', B_1, B_2, …C_1, C_2, … *Not a simple model*

***Qualitative and quantitative features of the phase diagram are reproduced*.**

•Solid lines=1st order.
•Broken lines=2nd order.

Canted phase not verified experimentally





- *Multitude of phases very close in energy due to many competing interactions.*

- *Small changes in T or H can induce phase changes.*

Biquadratic Exchange (Symmetric)

- Insert this e_i back into F[s(r),e_i] to get F[s(r)]:

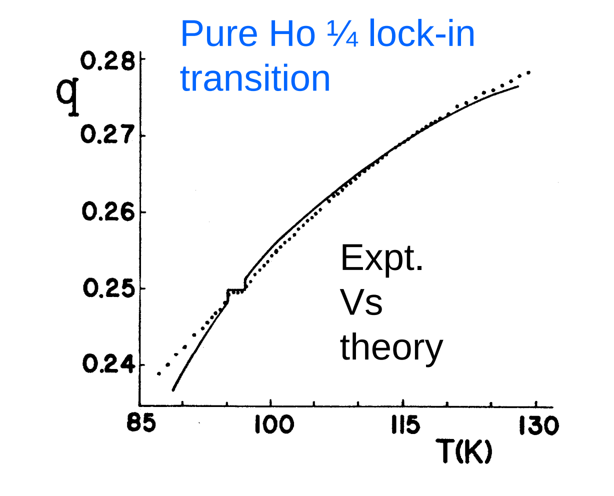
$$F_K = (-\tfrac{1}{8} j^4 / c V^4) \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 K_i(\mathbf{r}_1 - \mathbf{r}_2) s_{ij} K_j(\mathbf{r}_3 - \mathbf{r}_4)[\mathbf{s}(\mathbf{r}_1)\cdot\mathbf{s}(\mathbf{r}_2)][\mathbf{s}(\mathbf{r}_3)\cdot\mathbf{s}(\mathbf{r}_4)]$$

Biquadratic exchange from magnetoelastic coupling

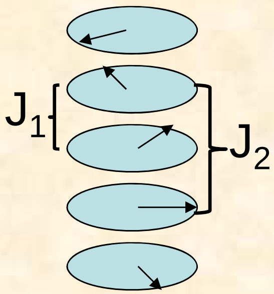
•Magnetoelastic coupling is one mechanism for $B_1 \neq B_2 \neq B_3 \neq \ldots$

•Also from higher-order (Pauli-exclusion) exchange and overlap of atomic wave functions.

•*Typically favors collinear* $\boldsymbol{S}_i \parallel \boldsymbol{S}_j$ *and* $\boldsymbol{Q}=\boldsymbol{G}/4$ *(period-4) spin configurations.*



Holmium: *IC* wavevector due to competition between NN and NNN exchange

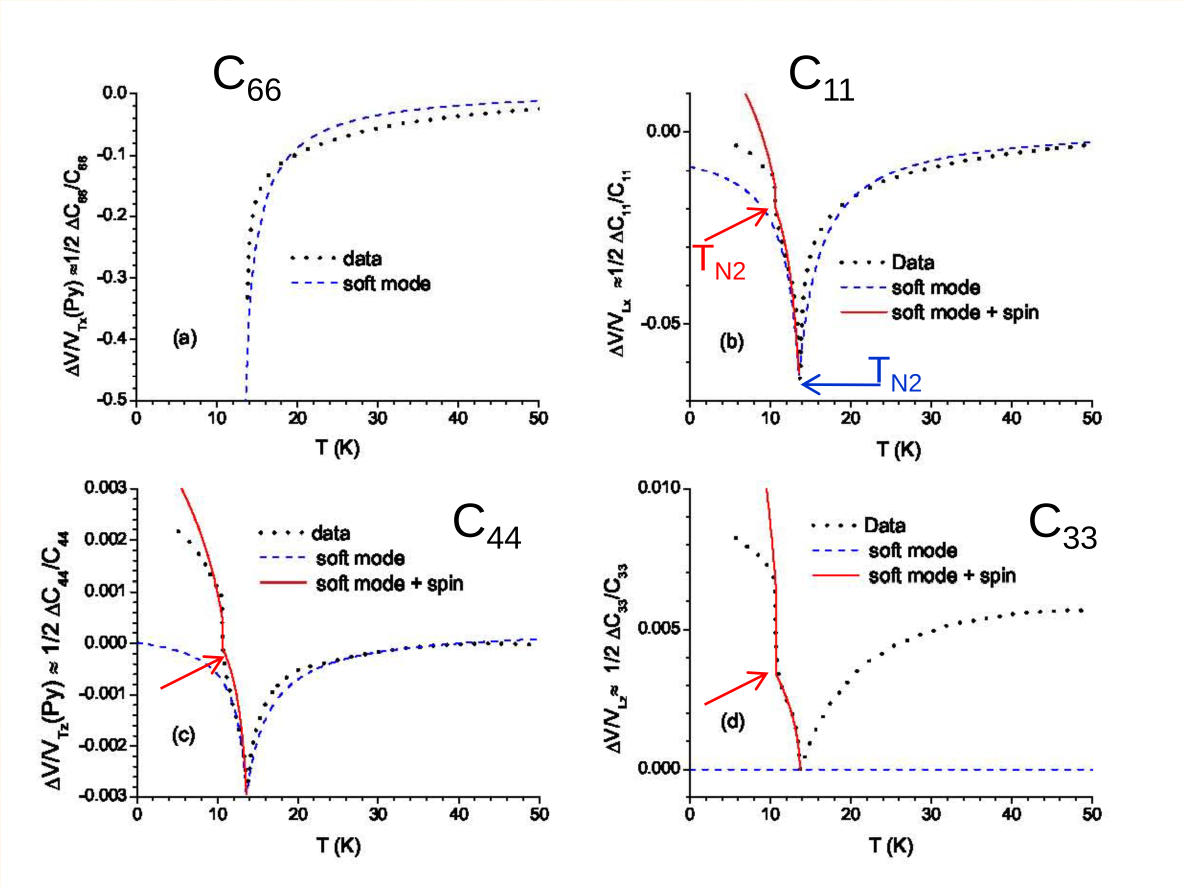


$\cos Q = -J_1/(4J_2)$

Magnetoelastic Coupling in $CuFeO_2$ (H=0)

G. Quirion *et al (2008).*

- **Very strong in this compound.**



$T_{N1} \Rightarrow$ Para – IC

$T_{N2} \Rightarrow$ IC – P4

- Simultaneous magnetic and structural transitions at T_{N1}=14K.

- Landau free energy including magnetoelastic coupling (red) gives better fit to ultrasound data, especially C_{33}.

S || **z** at H=0

$$
\begin{aligned}
F_{Se} \;=\;& \beta_1 S_z^2(e_1+e_2) + \beta_3 S_z^2 e_3 + \gamma_1(2e_1^2+2e_2^2+e_6^2)S_z^2 + \gamma_2(4e_1e_2-e_6^2)S_z^2 \\
+\;& \gamma_3 e_3^2 S_z^2 + \gamma_4(e_4^2+e_5^2)S_z^2 + \gamma_5((e_1-e_2)e_4+e_5e_6)S_z^2\;,
\end{aligned}
$$

Very High Field: Guy's new ultrasound data.