Landau Theory of the Magnetic Phase Diagram of Magnetoelectric CuFeO$_2$

1. Magnetoelectrics and Multiferroics.
2. Landau theory of phase transitions and Symmetry.
4. Frustrated CuFeO$_2$: Phase diagram and magnetoelastic coupling.

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Magnetoelectric Effect: The early days.

- applied uniform electric field $\mathbf{E}$ induces a uniform magnetization $\mathbf{M}$
- applied uniform magnetic field $\mathbf{H}$ induces a uniform electric polarization $\mathbf{P}$

$\text{Cr}_2\text{O}_3$ (a simple AF)

**1960:**

$\mathbf{M} \propto \alpha \mathbf{E}$

D.N. Astrov, *JETP* 11, 708 (1960)

**1961:**

$\mathbf{P} \propto \alpha^* \mathbf{H}$

V.J. Folen, *PRL* 6, 607 (1961)

Early measurements found only a very small effect: $\sim 10^{-3} \text{V/(cmOe)}$

$\sim 5/10^6$ of AF spins reverse.

$\alpha = \text{response function}$

\[
\begin{align*}
\mathbf{M}_i &= \chi_{ij}^m H_j + \frac{1}{\mu_0 c} \alpha_{ji} E_j \\
\mathbf{P}_i &= \varepsilon_0 \chi_{ij}^e E_j + \frac{1}{c} \alpha_{ij}^* H_j
\end{align*}
\]

Courtesy of M. Fiebig
Multiferroics: Everything’s related to everything else

Variables: P, M, ε

Fields: E, H, σ

Response functions: χ_E, d, χ_M, S, α

“Revival of the Magnetoelectric Effect”

Publications on "magnetoelectric"

![Graph showing the number of publications per year from 1985 to 2005.]

- Y-axis: Publications / year
- X-axis: Year
- Data points and trend line showing an increase in publications over time.
Modern Magnetoelectric Multiferroics

Courtesy of M. Fiebig

**Composite materials**
for device application

1: piezoelectric

- Permendur \( \text{Fe}_{0.49}\text{Co}_{0.49}\text{V}_{0.02}\)

2: magnetostrictive

\( (\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3, 0<x<1) \)

**Intrinsic multiferroics**
for basic research (and devices)

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

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

*Effects up to 90 kV/cm·Oe (10^3...^5 \times single-phase effect)*


Magnetic Phase Diagram of Cr$_2$O$_3$.

- Spin-Flop transition in an unfrustrated uniaxial AF.

*Period-2 spin structure: $Q = \frac{1}{2}G$*

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
CuFeO$_2$ and HoMnO$_3$: *Frustrated Triangular Antiferromagnets*

**CuFeO$_2$:** $P$ *induced* by non-collinear spin state at $H\neq 0$ ($T_N=14K$).

**HoMnO$_3$:** $P$ *coexists* with magnetic order: $P\neq 0$, $T_c=900K$. $S \neq 0$ $T_N=75K$. $H$ modifies $P$.

Both have very complex H-T magnetic phase diagrams: *More later!*

N. Hur et al.

T. Kimura et al.
Microscopic Origins of Magnetoelectric Coupling.

Electric field induces magnetic ion displacements $r \Rightarrow$ modifies crystal field and overlapping wave functions.

Interaction between the lattice and magnetism is crucial (*magnetoelastic coupling*).

- Single-ion anisotropy $\sim r_i (S_i^z)^2$
- Symmetric exchange $\sim r_{ij} (S_i^\alpha S_j^\beta + S_j^\beta S_i^\alpha)$
- Antisymmetric exchange $\sim r_{ij} (S_i^\alpha S_j^\beta - S_j^\beta S_i^\alpha)$
- Dipolar interactions $\sim S_i \cdot S_j/r_{ij}^3 - 3(S_i \cdot r_{ij})(S_j \cdot r_{ij}).r_{ij}^5$
- Zeeman energy $\sim H^\alpha g(r_i)^{\alpha\beta} S^\beta$


Dzyaloshinski-Moriya Interaction

\[ D(r_{ij}) \cdot (S_i \times S_j) \]
ME Coupling from Anti-symmetric Exchange: Spin Structures.

\[ P \propto r_{ij} \times (S_i \times S_j) \]

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 \( \vec{r}_{ij} \) and the vector spin chirality \((\vec{S}_i \times \vec{S}_j)\) are also shown for the respective structures.

Landau Theory of Magnetic Phase Transitions.

- Description of long-range ordered spin configurations near a phase transition $T_N$:
  $S=0$, $T>T_N$ and $S\neq 0$, $T<T_N$.

- 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:

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

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

**Only even powers of $S$**

$$F = AS^2 + \frac{1}{2} BS^4 + \frac{1}{3} CS^6 + ...$$

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

**Minimization gives:**

<table>
<thead>
<tr>
<th>$S^2 = 0$</th>
<th>$T&gt;T_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^2 = (a/B)(T_N-T)$</td>
<td>$T&lt;T_N$</td>
</tr>
</tbody>
</table>

E.g., time reversal symmetry $S\rightarrow-S$ and $H\rightarrow-H$. 
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:

- **\( C_{31} = 3\)-fold rotation about diagonal:** \( S_x \rightarrow S_y \rightarrow S_z \)
- **\( C_{2x} = 2\)-fold about x-axis:** \( S_x \rightarrow S_x, S_y \rightarrow -S_y, S_z \rightarrow -S_z \)

Example: General term at second order:

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

\[
C_{31} \rightarrow A_{xx} S_y S_y + A_{yy} S_z S_z + A_{zz} S_x S_x + A_{xy} S_y S_z + A_{xz} S_y S_x + A_{yz} S_z S_x
\]

Thus: \( A_{xx} = A_{yy} = A_{zz} \equiv A, \quad A_{xy} = A_{xz} = A_{yz} \equiv A' \)
Cubic Crystal Symmetry

• $C_{21}$ 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:

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

Cubic)

Anisotropy

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

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

• Crystals with cubic symmetry have moments in either $<111>$ or $<100>$ directions.
Impact of Symmetry

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

• All terms which are independently invariant have independent coefficients.
230 Space Groups and their Generators

Bradley and Cracknell:


**Hexagonal Symmetry:**

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

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

**Anisotropy**

\[ S \parallel c \text{ or } S \perp c \]
Spin Density description of magnetic states

\[ s(r) = \sum_q S_q e^{i q \cdot r} = m + S_c e^{i Q \cdot r} + S^*_c e^{-i Q \cdot r} + \ldots \]

Define real vectors \( S_1 \) and \( S_2 \):

\[ S_Q = S_1 + iS_2 \]

\( s(r) = m + 2S_1 \cos(Q \cdot r) - 2S_2 \sin(Q \cdot r) + \ldots \)

Order parameters

Uniform magnetization ~ \( H \)

Triangular Lattice 120° spin structure:

Helical with \( S \) in plane of \( Q \):
\[ Q = \pm (4\pi/3a)x = G/3 \]
\[ S_1 = S_x, S_2 = S_y \]

Square lattice simple AF:
\[ Q = (\pi/a)x + (\pi/a)y = G/2 \]
\[ S_1 = S_y, S_2 = 0 \]

Helical with \( S \perp Q \):
\[ Q = Qz \ [\text{incommensurate } Q = (n/m)G] \]
\[ S_1 = S_x, S_2 = S_y \]

Frustrated Antiferromagnets

+ chirality + \( Q \)

- chirality - \( Q \)
Non-Local Formulation of the Free Energy

Consider a general expression of the free energy:

\[
F[s(r)] = \int drdr' A_{\alpha\beta}(r-r')s_\alpha(r)s_\beta(r') + \int dr_1dr_2dr_3dr_4 B_{\alpha\beta\gamma\delta}(r_1,r_2;r_3,r_4) s_\alpha(r_1)s_\beta(r_2)s_\gamma(r_3)s_\delta(r_4) + \ldots
\]

Apply symmetry requirements for system of interest:

\[
F = F_{\text{isotropic}} + F_{\text{anisotropic}}
\]

\[
F_{\text{iso}}[s(r)] = \int drdr' A(r-r')s(r) \cdot s(r') + \int dr_1dr_2dr_3dr_4 B(r_1,r_2;r_3,r_4) s(r_1) \cdot s(r_2) s(r_3) \cdot s(r_4) + \ldots
\]

Isotropic terms to 4\textsuperscript{th} order

\[A(r) = aT\delta(r) + J(r)\]

temperature

Usual spin-spin \textit{Exchange} integral
Second-order isotropic terms

\[ s(r) = \sum_q S_q e^{i\mathbf{q} \cdot \mathbf{r}} = m + S_q e^{i\mathbf{Q} \cdot \mathbf{r}} + S_q^* e^{-i\mathbf{Q} \cdot \mathbf{r}} + \ldots \]

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

\[ F_2 = A_0 m^2 + A_Q S^2 \]

\[ A_Q = aT + J_Q \]

\[ A_0 = aT + J_0 \]

\[ J_Q = \frac{1}{N} \sum \mathbf{r} \cdot \mathbf{J}(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} \]

\[ \mathbf{R} = \text{lattice vector} \]

First order state as \( T \) is lowered has wave vector \( \mathbf{Q} \) which maximizes \( T_N = -\frac{J_Q}{a} \).

Example: near-neighbor sites on a simple hexagonal lattice

\[ \mathbf{R} = \pm c \mathbf{z} \pm a \mathbf{x} \pm (a \mathbf{x} \pm \sqrt{3} a \mathbf{y}) \]

\[ J_Q = 2J_0 \cos(q_z) + 2J_1 f_1 \]

\[ f_1 = \cos(q_x) + 2 \cos(q_x/2) \cos(q_y) \]

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

For \( J_1 \) antiferromagnetic, \( J_Q \) is maximized by

\[ q_x = 4\pi/3, q_y = 0: 120^\circ \text{ spin structure.} \]
Fourth-order isotropic terms

\[ F_4^{(4)} = B_1 (\mathbf{S} \cdot \mathbf{S})^2 + \frac{1}{2} B_2 |\mathbf{S} \cdot \mathbf{S}|^2 + \frac{1}{4} B_3 [(\mathbf{S} \cdot \mathbf{S})^2 + (\mathbf{S}^* \cdot \mathbf{S}^*)^2] \Delta_{4Q, G_1} + B_4 (\mathbf{S} \cdot \mathbf{S}^*)[\mathbf{S} \cdot \mathbf{S} + \mathbf{S}^* \cdot \mathbf{S}^*] \Delta_{2Q, G_1} \]

Umklapp terms

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

\( \mathbf{R} = \) lattice vector
\( \mathbf{G} = \) reciprocal lattice vector

- Four independent 4\(^{th}\)-order coefficients of isotropic terms.
- Usually taken to be independent constants.

\[ B_1 = B_{Q, -Q, -Q, -Q}, \quad B_2 = B_{Q, Q, -Q, -Q}, \quad B_3 = B_{Q, Q, Q, Q}, \quad B_4 = B \sum_{Q, Q, Q} \]

\[ B_{q_1, q_2, q_3, q_4} = \Delta_{q_1 + q_2 + q_3 + q_4, G} \left( \frac{V}{N} \right)^3 \sum_{R_1 R_2 R_3} B(R_1, R_2, R_3) e^{i(q_1 \cdot R_1 + q_2 \cdot R_2 + q_3 \cdot R_3)} \]

\[ \mathbf{S} = \mathbf{S}_1 + i\mathbf{S}_2 \]

Example: \( B_2 |\mathbf{S} \cdot \mathbf{S}|^2 = B_2 \{(\mathbf{S}_1^2 - \mathbf{S}_2^2)^2 + 4(\mathbf{S}_1 \cdot \mathbf{S}_2)^2\} \) is minimized by

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

for \( B_2 < 0 \), \( \mathbf{S}_1 \parallel \mathbf{S}_2 \): *Linear* spin polarization.
Molecular Field Theory Derivation of the Landau Free Energy

Use Mean-Field Theory:
\[ H_{MF} = - \sum_{i,\alpha} h_i^\alpha \langle S_i^\alpha \rangle \]
with
\[ h_i^\alpha = \sum_{\beta} J_{ij}^{\alpha\beta} \langle S_j^\beta \rangle \]

\[ \langle S_i^\alpha \rangle = \frac{h_i^\alpha}{\sum_{\alpha} m e^{h_i^{\alpha m}/k_B T}} \]
where \( m = -J, -J+1, \ldots, J-1, J \) and \( J \) is the total angular momentum.

- Formulate free energy from variational principle:

\[ F \leq F_0 + \langle H - H_{MF} \rangle \quad \text{and} \quad F_0 = \text{tr}[w_{MF} H_{MF}] + (k_B T) \text{tr}[w_{MF} \text{Ln}(w_{MF})] \]

\[ w_{MF} = \frac{e^{-H_{MF}/k_B T}}{\text{tr}(e^{-H_{MF}/k_B T})} \]

- Expand in powers of \( \langle S_i \rangle \):

\[ F = E - TS \]

\[ F = \sum_{i} J_{ij}^{\alpha\beta} \langle S_i^\alpha \rangle \langle S_j^\beta \rangle + T \left\{ a \sum \langle S_i^\alpha \rangle^2 + b \sum \langle S_i^\alpha \rangle^2 \langle S_j^\beta \rangle^2 \right\} + \ldots \]

\( \text{All isotropic} \)

⇒ As Non-local Landau Free Energy, but with \( B_1 = B_2 = B_3 = \ldots = bT \) (\( \cong bT_N = \text{constant} \))

\[ a = \frac{3J}{J+1} \]
\[ b = \frac{1}{45} \frac{(2J+1)^4 - 1}{(2J)^4} \]

Magneetoelastic Coupling

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

\[ J(r' - r) = J(r'_0 - r_0) + [u(r'_0) - u(r_0)] \cdot \nabla J(r_0) + \cdots \]

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

\[ J(\tau) \equiv J(\tau_0) + e_i K_i(\tau) \]

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

• Add elastic energy to this exchange-striction term:

\[ F_e = \left( \frac{1}{2} j^2 / V^2 \right) \int dr \int dr' K_i(\tau) e_i s(r) \cdot s(r') + \frac{1}{2} \nu C_{ij} e_i e_j \]

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:

\[ e_i = \left( - \frac{1}{2} j^2 / \nu V^2 \right) \int dr \int dr' s_{ij} K_j(\tau) s(r) \cdot s(r') \]

\[ s_{ij} = \left[ C^{-1} \right]_{ij} \text{ compliance matrix} \]
Biquadratic Exchange (Symmetric)

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

$$F_K = (-\frac{1}{8} j^4/\alpha V^4) \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 K_i(r_1 - r_2) s_{ij} K_j(r_3 - r_4)[s(r_1) \cdot s(r_2)][s(r_3) \cdot s(r_4)]$$

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 (usual) exchange and overlap of atomic wave functions.

• Typically favors collinear $S_i \parallel S_j$ and $Q = G/4$ (period-4) spin configurations.

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

$$\cos Q = -J_1/(4J_2)$$
Phase Diagram of a Simple AF: Spin-Flop

Example: rhombohedral symmetry giving axial anisotropy along z (Cr₂O₃).

- Applied magnetic field $H\parallel z$ induces $m\parallel z\parallel c$.
- NN AF exchange interactions along $z$ give $Q=\frac{1}{2}G$.

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

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

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

- Phase diagram is determined by minimizing $F(Q, m, S)$

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

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**Graphical Elements**

- Axis labels and phase boundaries indicate the transition regions and magnetic states.
- Arrows indicate the direction of magnetic field and spin orientation changes.
Phase Diagram of a Geometrically Frustrated AF: CsNiCl$_3$

- Ni$^{2+}$ (S=1, L=3) on simple hexagonal lattice with NN AF interactions $J_0$ and $J_1$:

\[ Q = \frac{G}{2} + \frac{G'}{3} \]

\[ S_2 \sin(Q \cdot r) \neq 0 \]

- Anisotropy is weakly axial.

\[ s(r) = m + 2S_1 \cos(Q \cdot r) - 2S_2 \sin(Q \cdot r) \]

Free energy is the same as with simple AF

\[ F(Q, m, S) = \frac{1}{2}A_0 m^2 + A_Q S^2 + -D|S_z|^2 + B_1 S^4 + \frac{1}{2}B_2 |S \cdot S|^2 + \frac{1}{4}B_3 m^4 + B_4 |m \cdot S|^2 + \frac{1}{2}B_5 m^2 S^2 - m \cdot H \]

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

Points = Experimental Data
Lines = Fitted Landau Theory.

120$^\circ$ $S \perp c$

Spin-Flop Transition

Elliptical $S$

Linear $S \parallel c$
CuFeO$_2$

Cu$^+$ → nonmagnetic
Fe$^{3+}$ (6S state) → $S = 5/2$

Space Group R$\bar{3}$m

3-fold rotation c-axis. rhombohedral

$\text{ABC stacked triangular layers.}$

$a = 3.03$ Å $c = 17.09$ Å

$L = 0$. No spin-orbit coupling.
Usual source of anisotropy is absent.

If anisotropy is weak, why no spin-flop?

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),...
**CuFeO$_2$: Super Frustration**

- Early Ising model with up to 3$^{rd}$ neighbor exchange interactions (J$_1$, J$_2$, J$_3$) on a 2D triangular lattice reveals a multitude of commensurate phases (P2, P3, P4, P8).

![Magnetic phase diagram of Ising spin triangular lattice antiferromagnet at 0 K.](image)

- 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 $P \neq 0$.
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 $r \rightarrow -r$, $r \leftrightarrow r'$, $P \rightarrow -P$ and other $R3m$ crystal symmetry requirements (space group generators $\{S_{6}^{+}|000\}$, $\{\sigma_{d1}|000\}$) leads to:

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

- Add polarization energy $\sim P^2$:

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

- Integrate out $P$ (minimize wrt $P$):

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

*Biquadratic anti-symmetric exchange.*
Non-local Landau Free Energy for CuFeO$_2$

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

Isotropic (includes biquadratic symmetric exchange).

Biquadratic anti-symmetric exchange

Trigonal anisotropy (3-fold rotation axis)

Axial exchange anisotropy:

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

Favors canted spin structures

- Insert spin density and evaluate.
  $$ s(\mathbf{r}) = \sum_{j, q} S_j q^{iQ \cdot \mathbf{r}} = m + S_j e^{iQ \cdot r} + S_j^* e^{-iQ \cdot r} + ... $$

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

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

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

Ansatz: phase difference only.

$$ S_A = S e^{i\gamma}, \quad S_B = S e^{i(\gamma - \phi)}, \quad S_C = S e^{i(\gamma + \phi)} $$

$\mathbf{s} = \mathbf{s}_1 + i \mathbf{s}_2$
Second-order Isotropic Terms

\[ F_2 = \frac{1}{2} A_0 m^2 + A_Q S^2 \]

\[ S^2 = S \cdot S^*, \quad A_Q = a T + J_Q \]

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

1st, 2nd, 3rd neighbor in-plane exchange coupling \( J_1, J_2, J_3 \) plus inter-plane exchange \( J' \). \( J_Q = 2f(q, \phi) \)

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

where

\[
J_1 = \cos q_x + 2 \cos \frac{1}{2} q_x \cos q_y, \quad (21)
\]

\[
f_2 = \cos 2q_y + 2 \cos \frac{3}{2} q_x \cos q_y, \quad (21)
\]

\[
f_3 = \cos 2q_x + 2 \cos q_x \cos 2q_y, \quad (21)
\]

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

\( q_x = a Q_x, q_y = b Q_y, q_z = c Q_z, \)

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

FIG. 1. Sketch of the \( J_2-J_3 \) phase diagram based on minimization of the exchange integral \( J_q \) 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 \( J' = 0.4 \).

CuFeO\(_2\)

\( J_2 \sim 0.3/J_1 \)

\( J_3 \sim 0.3/J_1 \)

BIG!
### Fourth- and Sixth-order Isotropic Terms

#### Fourth Order

\[ F_{4,2} = B_1 S^4 + \frac{1}{2} B_2 |S \cdot S|^2 + \frac{1}{4} B_3 m^4 + 2 B_4 |m \cdot S|^2 + B_5 m^2 S^2 , \]

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

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

\[ Q = \frac{1}{3} G \]

- **Field-induced Umklapp term:** Stabilizes P3 structures.
- **Zero field Umklapp term:** Stabilizes P4 structures

- *Umklapp terms favor collinear structures (e.g., \( S \parallel H \)).*
- *Odd-order Umklapp terms are generated by an applied field and favor \( S \parallel H \).*

#### Sixth Order

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

\[ Q = \frac{1}{4} G \]
Magnetoelectric Coupling

\[ F_C = i(C_x P_x + C_y P_y) \hat{z} \cdot (\mathbf{S} \times \mathbf{S}^*), \]

\[ F_P = \frac{1}{2} A_p P^2 \]

- **Wave-vector dependent coefficients**
  - \( C_x \) and \( C_y \) favor IC structures

\[ C_x = -\frac{4}{3} b \left\{ C_1 \cos \frac{1}{2} q_z \sin q_y - \frac{1}{3} C' \left[ \sin \left( \frac{1}{3} q_z - \frac{2}{3} q_y \right) \right. \right. \]
\[ \left. \left. - \sin \left( \frac{1}{3} q_z + \frac{1}{3} q_y \right) \cos \frac{1}{2} q_z \right] (1 + 2 \cos \phi) \right\}, \]

\[ C_y = \frac{2}{3} a \left\{ C_1 \left[ \sin q_z + \sin \frac{1}{2} q_z \cos q_y \right] \right. \]
\[ \left. + C' \sin \frac{1}{2} q_z \cos \left( \frac{1}{3} q_z + \frac{1}{3} q_y \right) (1 + 2 \cos \phi) \right\}. \]

\[ P_x = -(i / A_p) C_x (\mathbf{S} \times \mathbf{S}^*)_z \]
\[ P_y = -(i / A_p) C_y (\mathbf{S} \times \mathbf{S}^*)_z \]

\(~ (S_1 x S_2)_z \sim (S_{1x} S_{2y} - S_{1y} S_{2x})\)

\[ P \propto r_i \times (S_i \times S_j) \]

\[ P = 0 \text{ for proper helix} \]
\[ P \neq 0 \text{ for canted helix} \]

\[ F_K = K \left\{ [3(S_x^*)^2 S_y S_z - S_z S_y (S_y^*)^2] + 2S_z S_x^* (3|S_x|^2 - |S_y|^2) \right\} + \text{c.c.} \]
Magnetic Phase Diagram of CuFeO$_2$

- Numerical minimization of Free Energy $F=F(m,S,Q)$.
- Lots of fitting parameters: $J_1, J_2, J_3, J', B_1, B_2, \ldots C_1, C_2, \ldots$ 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.
Magnetoelastic Coupling in CuFeO$_2$ (H=0)


- 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 $C_{33}$.

$S \parallel z$ at H=0

\[
F_{Se} = \beta_1 S_z^2 (e_1 + e_2) + \beta_3 S_z e_3 + \gamma_1 (2e_1^2 + 2e_2^2 + e_6^2) S_z^2 + \gamma_2 (4e_1 e_2 - e_6^2) S_z^2 \\
+ \gamma_3 e_3^2 S_z^2 + \gamma_4 (e_4^2 + e_5^2) S_z^2 + \gamma_5 ((e_1 - e_2)e_4 + e_5 e_6) S_z^2 ,
\]
HoMnO$_3$ with Stephen Condran (MSc 2009)

- **Mn** form P3 120° in-plane spin structure.  
  \[ S_{\text{Mn}} \perp c. \]

- Mn AB stacking of triangular layers.

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

- Ho ions can also order: \( S_{\text{Ho}} \parallel c \) at low T

**Ferro interplane**

- \( S_{\text{Mn-A}} \parallel S_{\text{Mn-B}} \perp a \)

- \( S_{\text{Mn-A}} \parallel S_{\text{Mn-B}} \parallel a \)

**Anti-Ferro interplane**

- \( S_{\text{Mn-A}} \parallel -S_{\text{Mn-B}} \parallel a \)

- \( S_{\text{Mn-A}} \parallel -S_{\text{Mn-B}} \perp a \)

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

**Hexagonal symmetry**

- \( J = \) NN AF exchange in triangular planes.
- \( J' = \) NN AF (or F) exchange between triangular planes (Mn\(_A\)-Mn\(_B\))
- \( E > 0, \phi = (2n+1)\frac{\pi}{6} \) (\( S_{Mn} \perp \hat{a} \))
- \( E < 0, \phi = \frac{n\pi}{3} \) (\( S_{Mn} \parallel \hat{a} \))

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

\[
\frac{d\mathbf{S}(t)}{dt} = -\gamma \left( \frac{\mathbf{S} \times \mathbf{H}_{\text{eff}}}{1 + \alpha^2} - \frac{\alpha \gamma}{1 + \alpha^2} \left( \mathbf{S} \times (\mathbf{S} \times \mathbf{H}_{\text{eff}}) \right) \right)
\]

\[ \mathbf{H}_{\text{eff}} = -\frac{\partial E}{\partial \mathbf{S}} \]

Model Hamiltonian yields all four Mn spin configurations, depending on signs of \( J' \) and \( E \).

Ferromagnetic between planes and \( \mathbf{S} \parallel \mathbf{a} \)
**Ho-Mn Trigonal Coupling**

- *Transitions* between the four Mn spin states do not occur without coupling to $S_{Ho}$.

- Usual exchange interaction $S_i \cdot S_j = 0$ since $S_{Mn} \perp S_{Ho}$

- **Consider Trigonal anisotropy**

\[
K \sum S^z_{Ho} S^y_{Mn} \left[ 3 S^x_{Mn} - S^y_{Mn} \right] = 2K S^z_{Ho} S^3_{Mn} \sin 3\phi \\
K > 0, \quad \phi = (2n + 1) \frac{\pi}{3} \\
K < 0, \quad \phi = n \frac{2\pi}{3} \\
S^x_{Mn} = S \cos \phi
\]

- P6$_3$mc 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 $E \cos 6\phi$ to drive re-orientation transitions involving $\phi$ - with simultaneous coupling to Holmium ions.**
A Simple Landau Model with Ho-Mn Coupling: H=0

\[ F = A S^2 + A_0 S_0^2 + \frac{1}{2} B S^4 + \frac{1}{2} B_0 S_0^4 + B_1 S^2 S_0^2 + \frac{1}{3} C S^6 + K S_0 S^3 \cos 3\phi + E S^6 \cos 6\phi \]

- \( A_0 = a(T-T_0) \)
- \( A = a(T-T_N) \)

\[ S=S_{Mn}, \quad S_0=S_{Ho} \]

\[ S_0 \sim S^3 \cos 3\phi \]

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

**Canted Phase:**
- \( S_{Mn} \) oriented between x and y

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

**Table:**

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<tr>
<th>( T )</th>
<th>0.00</th>
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<td>( S_0 \neq 0 )</td>
<td>( S_0 = 0 )</td>
<td>( S_0 = 0 )</td>
<td></td>
</tr>
<tr>
<td>( 0 &lt; \phi &lt; \pi/2 )</td>
<td>( \phi = 0 )</td>
<td>( \phi = \pi/2 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- P6'₃
- HT2
- HT1
- Disorder

\( H=0 \) only (so far).
HoMnO$_3$: Experimental evidence for new canted phase

Conclusions

- **CuFeO$_2$** magnetic phase diagram: *ABC stacked triangular layers*
  - biquadratic *symmetric* exchange (magnetoelastic coupling) stabilizes collinear states
  - biquadratic *antisymmetric* exchange (magnetoelastic 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.**
Collaborators:
Guy Quirion, Oleg Petrenko, Mariathas Tagore, Stephen Condran.

http://www.mun.ca/physics/
BACK-UP SLIDES
Add stochastic field term via Langevin dynamics.

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

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,

- Magnetoelectric switching of exchange bias,

- Room temperature exchange bias and spin valves based on $\text{BiFeO}_3$/$\text{SrRuO}_3$/$\text{SrTiO}_3$/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 magnetoelectrics: thin films and nanostructures,


“Revival of the Magnetoelectric Effect”

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

1959 — Magnetoelectric effect predicted for antiferromagnetic Cr₂O₃
"We should like to show here that among the well known antiferromagnetic substances there is one, namely Cr₂O₃, where the magnetoelectric effect should occur from symmetry considerations."

1960/61 — First observation in Cr₂O₃