**Competing Ferroic Orders**
The magnetoelectric effect

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**Module Outline (Extremely tentative)**

1. **Overview and Background**
   - Ferro ordering, the magnetoelectric effect
   - Complex oxides basics: Types of insulators (i.e., ZSA classifications), Coordination chemistry

2. **Structure and Ferroelectricity**
   - Basics of space groups
   - Soft mode theory, lattice dynamics, group theoretic methods
   - Competing lattice instabilities
   - microscopic mechanisms, improper FE
   - Modern theory of polarization (Berry Phase)

3. **Magnetism**
   - Basics, exchange interactions, superexchange, Dzyaloshinskii-Moria
   - How spins couple to the lattice! Phenomenology and microscopics (spin-phonon, spin-lattice, etc)
   - Competing magnetic orders

4. **Lets start putting things together**
   - Phase competition: magnetic and polar orders and colossal magnetoelectric responses
   - Magnetic order induced ferroelectricity
   - Ferroelectric induced ferromagnetism, switching magnetism 180° with an electric field aren’t these forbidden by some symmetry? NO!

5. **Finish up loose ends and recent papers I wish I understood better**
   - Toroidal moments
**Ab initio** Yes a play on what I do.

➢ What does my title mean?

"ferro" derived from the Latin "ferrum" → Iron

- Iron is the sixth most abundant element in the Universe
- While it makes up about 5% of the Earth’s crust, the Earth’s core is believed to consist largely of an iron-nickel alloy constituting 35% of the mass of the Earth as a whole.
- Iron is consequently the most abundant element on Earth, but only the fourth most abundant element in the Earth’s crust.
- Most of the iron in the crust is found combined with oxygen as iron oxide minerals such as hematite and magnetite.


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**Ferromagnetism**

Ordering of spins → spontaneous magnetization

\[ M \equiv \sum_i \langle S_i \rangle \neq 0 \]

Spontaneous time-reversal, \( R \), symmetry breaking

\[ \mathcal{F}(M) = \alpha M^2 + \beta M^4 - MH \]

Symmetry properties \( M(-t) = -M(t) \)

- Time inversion \( R \) \( t \rightarrow -t \)
- Space inversion \( I \) \( t \rightarrow -r \)
- Mirror reflection \( m \)

M and H are Axial vectors
**Ferroelectricity**

Spontaneous polarization \( \rightarrow \) Dipole moment per unit volume

Ordering of polar mode

\( P_\alpha \approx \sum \Gamma_{\alpha,\beta}^{*} \langle u_{\beta}; i \rangle \neq 0 \)

Spontaneous space-inversion, \( I \), symmetry breaking

Symmetry properties \( P(-x) = -P(x) \)

**AntiFerromagnetism**

\( q \neq 0 \), Ordering of spins

\( M \equiv \sum_i \langle S_i \rangle = 0 \)

e.g., two sublattice spin system

\( L = S_1 - S_2 \)

Symmetry properties

\( L(-t) = -L(t) ; L(-x) = \pm L(x) \)

Does the AFM ordering of spins spontaneously break time-reversal, \( R \), symmetry breaking?

First, what does the question mean?

Does the point group of the space group contain \( R \)?

\( \mathcal{F}(M) = \alpha M^2 + \beta M^4 - L H_q \)

Depends on details of crystallographic structure!

Cant ignore structure!!

i.e., LATTICE + BASIS (don’t just pick your favorite sublattice and ignore the rest!!!)
**AntiFerromagnetism**

Symmetry properties $L(-t) = -L(t)$; $L(-x) = \pm L(x)$

e.g., two sublattice spin system (in the ordered phase)

$$L = S_1 - S_2$$

Example 1: two spins sit in the same unit cell in the paramagnetic phase,
Yes! $R$ is not a symmetry element.

Example 2: two spins sit in different unit cells in the paramagnetic phase,
No! the space group contains $\{R|\tau\}$ ⇒ the point group, $\tau \rightarrow 0$ contains $\{R|0\}$.

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**Ab initio**

Yes a play on what I do.

➢ What does my title mean?

Def: Linear magnetoelectric effect

Landau and Lifshitz, “Electrodynamics of continuous media”

Dzyaloshinskii, JETP 1957; Astrov JETP 1960 → Cr$_2$O$_3$

Hans Schmid, Geneva; Smolenskii USSR

Requirements: 1) broken space-inversion symmetry
2) broken time-reversal symmetry

\[
\mathcal{F} = \mathcal{F}_0 + P_s E + M_s H + \epsilon E^2 + \mu H^2 + \gamma EH
\]

\[
P = \left. \frac{\partial \mathcal{F}}{\partial E} \right|_{E=0} = P_s + \gamma H
\]

\[
M = \left. \frac{\partial \mathcal{F}}{\partial H} \right|_{H=0} = M_s + \gamma E
\]

$\gamma$ = linear magnetoelectric coefficient
Crystal structure of $\text{Cr}_2\text{O}_3$

\[ \text{AFM order parameter} \quad T_N = 306\text{K} \]

\[ \text{L} = M_1 - M_2 + M_3 - M_4 \quad \text{L}_z \neq 0 \]

Symmetries of paramagnetic phase

<table>
<thead>
<tr>
<th></th>
<th>$I$</th>
<th>$2_x$</th>
<th>$3_z$</th>
</tr>
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<tbody>
<tr>
<td>$L_z$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
</tr>
<tr>
<td>$E_z$</td>
<td>$-$</td>
<td>$-$</td>
<td>$+$</td>
</tr>
<tr>
<td>$H_z$</td>
<td>$+$</td>
<td>$-$</td>
<td>$+$</td>
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</tbody>
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Point group $\overline{3}m$

- $1, \ 3(2\perp), \ \pm 3_z$
- $\overline{1}, \ 3(m\perp), \ \pm \overline{3}_z$

Invariants:

\[ \lambda L_z E_z H_z = \alpha_{\parallel} E_z H_z \]

\[ L_z (E_x H_x + E_y H_y) = \alpha_{\parallel}, \alpha_{\perp} \propto L_z \]
**Basic Training 2009– Lecture 01**

Cr₂O₃  

**magnetic point group**

$$3'm'$$

Symmetries of low-T phase:  

$$1, 3(2_\perp), ± 3_z, 1'/3, 3(m'_\perp), ± 3'z$$

<table>
<thead>
<tr>
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<th>$$I'$$</th>
<th>$$2_x$$</th>
<th>$$3_z$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$$E_x$$</td>
<td>$$\begin{pmatrix} -1 &amp; 0 \ 0 &amp; -1 \end{pmatrix}$$</td>
<td>$$\begin{pmatrix} 1 &amp; 0 \ 0 &amp; -1 \end{pmatrix}$$</td>
<td>$$R_{2\pi/3}$$</td>
</tr>
<tr>
<td>$$E_z$$</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
</tbody>
</table>

Inversion combined with time reversal:

$$I' = IT$$

120°-rotation

$$R_{2\pi/3} = \frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$$

**Invariants:**

$$F_{me} = -\alpha_\parallel E_z H_z - \alpha_\perp (E_x H_x + E_y H_y)$$

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**Linear magnetoelectric effect**

From Max Mostovoy

$$\text{Cr}_2\text{O}_3$$

I. E. Dzyaloshinskii JETP 10 628 (1959),  
D. N. Astrov, JETP 11 708 (1960)

$$P = \chi_e E + \alpha H$$

$$M = \alpha E + \chi_m H$$

From Max Mostovoy

**Cr₂O₃**

I. E. Dzyaloshinskii JETP 10 628 (1959),  
D. N. Astrov, JETP 11 708 (1960)

$$P = \chi_e E + \alpha H$$

$$M = \alpha E + \chi_m H$$

G.T. Rado PRL 13 335 (1964)
Next time

ME revisited, and basic oxide physics

• ME effect revisited: Toroidal moments
• Complex oxides basics: Types of insulators (i.e., ZSA classifications), Coordination chemistry