Competing Ferroic Orders
The magnetoelectric effect

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Basic Training 2009– Lecture 04

Basic Training in Condensed Matter Theory 2009
Module Outline

1. Overview and Background
   • Ferro ordering, the magnetoelectric effect

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

3. 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)

4. Magnetism
   • Basics, exchange interactions, superexchange, Dzyaloshinskii-Moria
   • How spins couple to the lattice! Phenomenology and microscopics (spin-phonon, spin-lattice, etc)
   • Competing magnetic orders
   • Systems: ZnCr2O4, EuTiO3, SeCuO4, TeCuO4
Magnetism and how it couples to the lattice

Isotropic Exchange

- Tuning AFM ⇔ FM
  - The Goodenough-Kanamori rules

- Spin-phonon coupling
  - ZnCr$_2$O$_4$ → spin-induced phonon anisotropy
  - EuTiO$_3$ → magneto-capacitance

Dzyaloshinskii-Moria Exchange

- Spin-lattice coupling
  - Weak ferromagnetism Fe$_2$O$_3$
  - Spin spiral Lifshitz invariant
Magnetic properties of localized systems

Magnetism arises from an incomplete shell

\( \text{Eu}_2\text{O}_3 \)

Eu: \( 4f^7 \ 5d^0 \ 6s^2 \)
\( \rightarrow \) Eu\(^{3+} \): \( 4f^6 \ 5d^0 \ 6s^0 \)

Question: is \( \text{Eu}_2\text{O}_3 \) magnetic?

What do I mean by magnetic? For now I mean, Does a magnetic field couple to the fairly large \( S=3\mu_B \), NO! why?

Well magnetic field couples to \( J=|S-L| \)

Hund’s Rules
1) Max \( S =3 \)
2) Max \( L =3 \)
3) \( J=|S-L| \) \( =0 \) less than half filled (\( J=|S+L| \) if more ...)

But is it magnetic? Yes!

\[ \chi = \frac{N}{V} \left( 2\mu_B^2 \sum_n \left| \langle 0 | L_z + gS_z | 0 \rangle \right|^2 \frac{E_n - E_0}{e^2 m \mu_0} - \frac{e^2 m \mu_0}{6m_e} \sum_{i=1}^Z \langle r_i^2 \rangle \right) \]

Van Vleck Paramagnetism
diamagnetism

Both terms, small and temperature independent \( (\chi_{VV} \sim 1/\Delta) \)
Magnetic properties of localized systems

Currie Weiss

Susceptibility

$$\chi \propto \frac{1}{T - \theta_{CW}}$$

$$\chi^{-1}$$

$$\Theta_{CW} = T_c$$

$T_N$

$$E = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \sum_i \mathbf{S}_i \cdot \mathbf{H}$$

Magnetic exchange interactions

$$k_B \theta_{CW} = \frac{2}{3} \sum_n J_n z_n S(S + 1)$$

Mean-field
Properties of common Antiferromagnets
Effect of strong magnetic field (AFM)

- Susceptibility below $T_N$ and Spin flop
  - Hard vs easy axis
**Origin of easy/hard axis**

- **Spin-orbit interaction**  \[ \lambda \vec{L} \cdot \vec{S} \]

1. Single-ion anisotropy

   - Crystal field couple to charge density
   - Charge density couple to spin

2. Anisotropic exchange coupling

   - Different energy
General form of spin-spin coupling

\[ H = \vec{S}_1 \cdot \vec{J} \cdot \vec{S}_2 \]

\[ H = J \vec{S}_1 \cdot \vec{S}_2 + \vec{D} \cdot (\vec{S}_1 \times \vec{S}_2) \]

Isotropic symmetric exchange \((l=0)\)

Dzyaloshinskii-Moriya Antisymmetric exchange \((l=1)\)

+ \(k_x S_{1x} S_{2x}\) + \(k_y S_{1y} S_{2y}\) + \(k_z S_{1z} S_{2z}\)

Anisotropic symmetric exchange \((l=2)\)

D and K both spin-orbit effects

\[ D \sim \lambda J \approx (\Delta g/g)J \]

\[ k \sim \lambda^2 J \approx (\Delta g/g)^2 J \]
Dzyaloshinskii-Moriya

Relativistic correction to Anderson's superexchange

\[ E = |J| \langle S_i \cdot S_j \rangle + \sum D_{ij} \langle S_i \times S_j \rangle \]

- Collinear AFM: \( D = 0 \)
- Spin canting: \( D \neq 0 \)

Direction of canting determined by the sign of \( D \)
Weak ferromagnetism vs ME effect

$\Cr_2\O_3$

$3^+_z$

$L = M_1 - M_2 + M_3 - M_4$

$\Fe_2\O_3$

$3^+_z$

$L = M_1 + M_2 - M_3 - M_4$

Neel temperature ~500K
Morin temp ~260K

Invaria
**Exchange: Background**

Hund’s rule ➞ like FM

Covalent bond ➞ like AFM
**Exchange: Background**

**Direct exchange**

- If they are the same orbital ➞ **AFM**
- If they are the different orbital ➞ **FM**

**Superexchange**

90° **SE**

- 90° Hund’s rule
- J_H coupling on the anion

**Diagram:**

- **Left:** TM-d → O → TM-d
- **Right:** 90° SE
Exchange: Background

NiO

Competing interactions
1. Strong AFM Ni-O-Ni 180°
2. Weaker FM 90° SE
Exchange: Background

Arbitrary angle

\[ J = J_{90} \sin^2 \theta + J_{180} \cos^2 \theta \]

Empirically 135°
ACr2X4: Cubic Spinel Structure

Cr$^{3+}$: 3d$^3$ 4s$^0$

Superexchange pathways

$\varepsilon_g \quad \rightarrow \quad S=3/2$

$\varepsilon_{2g} \uparrow$

What is Moment?
$\mu \sim S = 3/2$

Why ->
orbital dof quenched
ACr2X4: Cubic Spinel Structure

- Network of edge sharing octahedra
Background: Spinels

ACr$_2$X$_4$

• A = Zn, Cd, Hg
• X = O, S, Se

Cr$^{3+}$: 3d$^3$ 4s$^0$

e$_g$  

\[ \begin{array}{c}
\uparrow \\
t_{2g}
\end{array} \]

\[ \Rightarrow \text{S} = \frac{3}{2} \]

\[
\begin{array}{c|c|c}
\text{a (Å)} & \text{Theory} & \text{Exp.} \\
\hline
\text{CdCr}_2\text{S}_4 & 10.12 & 10.24 \\
\text{CdCr}_2\text{Se}_4 & 10.63 & 10.74 \\
\text{HgCr}_2\text{Se}_4 & 10.65 & 10.74 \\
\text{ZnCr}_2\text{O}_4 & 8.26 & 8.31 \\
\text{CdCr}_2\text{O}_4 & 8.54 & 8.59 \\
\end{array}
\]

Ferromagnetic Insulators

\[ T_c \sim 100K, \quad T_\Theta \sim 200K \]

Anti-ferromagnetic Insulators

\[ T_N \sim 10K, \quad T_\Theta \sim 100K \]
Exchange interactions

- Direct Cr-Cr exchange $\rightarrow$ AFM
- $90^\circ$ Cr-O-Cr SE $\rightarrow$ FM

AFM $\rightarrow$ FM

- a) as lattice constant increases
- b) as electronegativity of anion decreases

![Diagram showing exchange interactions]

- Direct exchange cation-cation
- $90^\circ$ superexchange
Huge spin-phonon coupling

AFM-ZnCr$_2$O$_4$

Symmetry lowering at $T_n$

$O_h \rightarrow D_{4h}$

Cubic to tetragonal

Phonon splitting at $T_n$

$T_{1u} \rightarrow A_{2u} \oplus E_u$

$$\omega_{AFM} = \omega_{PM} + \lambda \langle S_i \cdot S_j \rangle$$

Exp: $\lambda = 6$-$10$ cm$^{-1}$

$T_n = 12.5K$
**Spin-phonon coupling**

**Phonon modulated exchange interaction**

Baltensperger and Helman, Helvetica physica acta 1968.

\[
\mathcal{E} = \mathcal{E}_0 + \mathcal{E}_{\text{phonon}} + \mathcal{E}_{\text{spin}}
\]

\[
\mathcal{E}_{\text{ph}} = \frac{1}{2} \omega_0^2 u^2
\]

\[
\mathcal{E}_{\text{sp}} = -\sum J_{ij} \langle S_i \cdot S_j \rangle
\]

\[
J(u) \approx J(0) + \frac{1}{2} \frac{\partial^2 J}{\partial u^2} \langle S_i \cdot S_j \rangle \cdot u^2
\]

\[
\Rightarrow \quad \omega^2 \propto \omega_0^2 - \frac{\partial^2 J}{\partial u^2} \langle S_i \cdot S_j \rangle
\]

- renormalized phonon
- bare phonon
- magnetic contribution

*Example: can understand large spin-phonon coupling in ZnCr$_2$O$_4*

Spin-phonon coupling

Phonon modulated exchange interaction
Baltensperger and Helman, Helvetica physica acta 1968.

\[ E = E_0 + E_{\text{phonons}} + E_{\text{spin}} \]

\[ E_{\text{ph}} = \frac{1}{2} \sum_{\eta \eta'} C_{\eta, \eta'} f_{\eta} f_{\eta'} \]

\[ E_{\text{spin}} = - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \]

\[ J(f_\eta)_{ij} \approx J(0)_{ij} + \frac{\partial J_{ij}}{\partial f_\eta} f_\eta + \frac{1}{2} \frac{\partial^2 J_{ij}}{\partial f_\eta \partial f_{\eta'}} f_\eta f_{\eta'} \]

\[ \tilde{C}_{\eta, \eta'} = C_{\eta, \eta'} - \sum_{ij} \frac{\partial^2 J_{ij}}{\partial f_\eta \partial f_{\eta'}} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \]

e.g. can understand large spin-phonon coupling in ZnCr$_2$O$_4$

to lowest order in $S_i S_j$
**Origin of large anisotropy**

$f_3$ has significant anisotropy in force constant matrix

$f_3$: One set of T1u Partner functions

Direct-exchange length scale, $\alpha^{-1}$

Exp: $\alpha=8.9$ Å$^{-1}$

Theory: $\alpha=9.05$ Å$^{-1}$

$$J_d(R_c) \approx J_d e^{-\alpha \Delta R_c}$$
Bulk Eu$^{2+}$Ti$^{4+}$O$_3$: Ground state antiferromagnetic paraelectric

- $r$(Eu$^{2+}$) $\sim r$(Sr$^{2+}$); Cubic perovskite
- Eu$^{2+} \rightarrow J=S=7/2$; $T_n \sim 5.5$K, G-type AFM
**Perovskites and the Period Table**

Perovskites $ABX_3$

Substitutions on A, B or both

$(A_{1-x}A'_{x})(B_{1-y}B'_{y})O_3$

Random distribution or ordered
Phonon anomaly at $T_c$

FM- CdCr$_2$S$_4$

Symmetry lowering at $T_c$
$O_h \rightarrow O_h$
Cubic to cubic (ignoring LS)

No phonon splitting at $T_c$
$T_{1u} \rightarrow T_{1u}$

$$\omega_{FM} = \omega_{PM} + \lambda \langle S_i \cdot S_j \rangle$$

Effect of magnetic ordering on phonon parameters for infrared active modes in ferromagnetic spinel CdCr$_2$S$_4$

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