Magnetic Oxides

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Lecture Outline

- Magnetic oxide overview
- Transition-metal ions and lattice sites (crystal fields)
- Electronic ground states (Hund vs Pauli)
- Spin-orbit-lattice effects (Jahn-Teller, $\lambda L \cdot S$, $T_1$)
- Magnetic order in oxide systems (superexchange)
- Signal propagation (RF and IR)
- Spin transport phenomena (polarons for CMR, HTS)
- Other magnetic oxides (orthoferrites, ferroics, dilute systems)
## Technology Overview

<table>
<thead>
<tr>
<th>Properties</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractory ($T_{melt} \rightarrow 2000 , ^\circ C$)</td>
<td>Permanent magnets</td>
</tr>
<tr>
<td>Chemically stable</td>
<td>Magnetic recording</td>
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<tr>
<td>Physically rugged</td>
<td>AC magnets</td>
</tr>
<tr>
<td>Film (not so) friendly</td>
<td>RF control devices</td>
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<tr>
<td>Frequency tunable by $\varepsilon$ and $\mu$</td>
<td>Microwave absorbers</td>
</tr>
<tr>
<td>Broad range $4\pi M_s$ ($10^2 - 10^4 , G$)</td>
<td>EPR and FMR (medical)</td>
</tr>
<tr>
<td>Curie $T_c \rightarrow 1000 , K$</td>
<td>Fiber optics</td>
</tr>
<tr>
<td>Resistivity $\rho &lt; 10^{-4} , \Omega\text{-cm}$</td>
<td>Superconductors</td>
</tr>
<tr>
<td>Well-studied</td>
<td>Magnetoresistance</td>
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<td></td>
<td>Spintronics</td>
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</tbody>
</table>
Periodic Table
Transition Element Models

Iron Group

3d

Argon

Active 3d shell

Lanthanide Group (Rare Earths)

4f

Xenon

Inert 4f shell
Hund’s Rule – $3d^n$ Series

|
|---|---|---|---|---|---|---|---|---|---|
| $m_i$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| −2 |   |   |   |   |   |   |   |   |   |   |
| −1 |   |   |   |   |   |   |   |   |   |   |
| 0  |   |   |   |   |   |   |   |   |   |   |
| +1 |   |   |   |   |   |   |   |   |   |   |
| +2 |   |   |   |   |   |   |   |   |   |   |
| $S = \Sigma m_s$ | 1/2 | 1 | 3/2 | 2 | 5/2 | 2 | 3/2 | 1 | 1/2 | 0 |
| $L = \Sigma m_i$ | 2 | 3 | 3 | 2 | 0 | 2 | 3 | 3 | 2 | 0 |

$\frac{2S+1}{2} L_J = 2D_{3/2} \quad 3F_2 \quad 4F_{3/2} \quad 5D_0 \quad 6S_{5/2} \quad 5D_4 \quad 4F_{9/2} \quad 3F_4 \quad 2D_{3/2} \quad 1S_0$

$J = L - S \quad \quad J = L + S$
Oxygen Lattice Sites

- **Tetrahedral Site** ($O_4$)
  - Metal cation
  - Oxygen anion

- **Octahedral Site** ($O_6$)

- **Simple Cubic Site** ($O_8$)

- **Perovskite A Site** ($O_{12}$)

- **Tetragonal Pyramid** $O_5$

- **Plane** $O_4$

- **Linear Chain** $O_2$

- **Trigonal Bipyramid** $O_5$
Octahedral-Site Distortions
d Orbitals in Octahedral Site

$\mathbf{e}_g$

$d_{xy}$  \( L_z = 0 \)

$\mathbf{t}_{2g}$

$d_{xy}$  \( L_z = 0 \)

$(1/2)(d_{yz} \pm id_{xz})$  \( L_z = \pm 1 \)

\[ e_g \quad +6Dq \]

\[ 3d \quad 10Dq \]

\[ t_{2g} \quad -4Dq \]

\[ E = 0 \]
Low-Spin State of Mn$^{3+}$ (3d$^4$)

High-spin configurations (Hund’s rule) that arise from Internal repulsion correspond to ferromagnetism in molecular antibonding states.

Low-spin configurations (Pauli principle) correspond to the condensation of antiferromagnetic spins in molecular bonding states.
One-Electron Models (Octahedral)
Jahn-Teller / Spin-Orbit Stabilizations
### Jahn-Teller / Spin-Orbit (cont’d)

<table>
<thead>
<tr>
<th>J-T</th>
<th>S-O</th>
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</thead>
<tbody>
<tr>
<td>Distortion creates <strong>singlet</strong> ground state</td>
<td>Distortion creates <strong>degenerate</strong> ground state</td>
</tr>
<tr>
<td>Orbit-lattice interaction</td>
<td>Spin-orbit-lattice interaction</td>
</tr>
<tr>
<td>Magnetostriction (independent of spin ordering)</td>
<td>Anisotropy and magnetostriction below Curie temperature (<strong>opposite</strong> sign to JT effect)</td>
</tr>
<tr>
<td>Weak spin-lattice interaction</td>
<td>Strong spin-lattice interaction</td>
</tr>
</tbody>
</table>
Exchange Diagrams

(a) Paramagnetism (dipole alignment)

(b) Direct ferromagnetism (spin polarization by Hund’s rule)

(c) Direct antiferromagnetism (exchange stabilization)

(d) Indirect antiferromagnetism (superexchange)
Bond Types

Ionic
(bound electrons)

Metallic
(collective electrons)

Metal-Oxide
(occupied hybrid orbitals)
Bonding and Spin Alignment

Magnetic Metals

- Collective (delocalized) d spins
- High density: $\sum e^2/r_{ij}$ repulsion, antibonding (Hund’s rule): FM
- Low density: nuclear attraction, bonding (Pauli pairing): AFM
- Direct exchange; band models

Magnetic Oxides

- Localized d spins in bonding states
- $\sum e^2/r_{ij} \sim 0$
- Electron-nuclear attraction, (Pauli pairing): AFM
- Superexchange; Anderson, Goodenough, Ballhausen
Combined Exchange Constant

\[\Delta E_{\text{ex}} = -2 \sum_{i>j} J_{ij} S_i \cdot S_j\]

\[J_{ij} = \sum_n \left( -J_{ij}^{n\text{super}} + J_{ij}^{n\text{direct}} + J_{ij}^{n\text{double}} \right)\]

\[\mathcal{H}_0 = -\left(\frac{\hbar^2}{2m}\right)(\nabla_a^2 + \nabla_b^2) - \frac{Z_a e^2}{r_{a1}} - \frac{Z_b e^2}{r_{b2}} - \frac{Z_a e^2}{r_{a2}} - \frac{Z_b e^2}{r_{b1}} + \frac{e^2}{r_{12}} + \frac{Z_a Z_b e^2}{r_{ab}}\]

\[\mathcal{H}_1 = \mathcal{H}_a + \mathcal{H}_b + \frac{e^2}{r_{12}}\]
Molecular Orbital Theory

One-Electron Perturbation Model

\[ \mathcal{H}_1 = \mathcal{H}_M + \mathcal{H}_L + \left( \frac{e^2}{r_{ij}} \sim 0 \right) \]
where \( \mathcal{H}_{M,L} = E_{M,L} \approx IP_{M,L} + LE_{M,L} \)
\( U_{ML} = E_M - E_L \)
overlap \( S_{ML} = \langle \varphi_M | \varphi_L \rangle \)
transfer \( b_{ML} = \langle \varphi_M | \mathcal{H} | \varphi_L \rangle \)

\[
\begin{bmatrix}
E_M - E & b_{ML} - E S_{ML} \\
b_{ML} - E S_{ML} & E_L - E
\end{bmatrix} = 0
\]

\[ E_{\pm} = \frac{1}{2} \left( E_M + E_L \pm \sqrt{U_{ML}^2 + b_{ML}^2} \right) \]

Energy-Level Occupancy (Aufbau)

\[ \varphi_- = \frac{1}{\sqrt{2 - 2 S_{ML}^2}} \left( c_L \varphi_M - c_M \varphi_L \right) \]
\[ \varphi_+ = \frac{1}{\sqrt{2 + 2 S_{ML}^2}} \left( c_M \varphi_M + c_L \varphi_L \right) \]
Bonding – Antibonding States
Goodenough-Kanamori Rules (180°)

VIRTUAL TRANSFER (two unpaired spins)
Half-filled ↔ half-filled orbitals
  Correlation superexchange, $J < 0$          ANTFERROMAGNETISM

REAL TRANSFER (one spin)
Filled ↔ half-filled ↔ empty orbitals
Hund’s rule exchange $U_{ex} > 0$
  Delocalization superexchange, $J > 0$          FERROMAGNETISM

SPIN TRANSPORT (special case of mixed-valence)
Filled ↔ half-filled ↔ empty orbitals
Polaron trap activation energy $U_p << b_p$
  Double exchange $J > 0$                      FERROMAGNETISM (ITINERANT)

TRANSPORT BY:
  A) THERMAL ACTIVATED MOBILITY (Verwey hopping, random)
  B) COVALENT TUNNELING (Holstein polarons, coherent)
G-K Diagrams

Correlation AFM

\[ \Delta E_{ex}^{corr} = b^2/2U \]

Delocalization FM

\[ \Delta E_{ex}^{deloc} = (b^2/2U)(U_{ex}/U) \]
\[ = b^2/2U_{ex} \]
\[ U >> U_{ex} \]
\[ U << U_{ex} \]

Polaron (double) FM

\[ \Delta E_{ex}^{pol} = U_p^2/4b_p \]
\[ b_p >> U_p \]
G-K Table (180° bonds)

<table>
<thead>
<tr>
<th></th>
<th>$t_{2g}$</th>
<th>$e_g$</th>
<th></th>
<th></th>
<th></th>
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</tr>
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<tbody>
<tr>
<td></td>
<td>d$^0$</td>
<td>d$^1$</td>
<td>d$^2$</td>
<td>d$^3$</td>
<td>d$^4$</td>
<td>d$^5$</td>
<td>d$^6$</td>
</tr>
<tr>
<td>d$^1$</td>
<td>S = 0</td>
<td>NEGL</td>
<td>W</td>
<td>W</td>
<td>~</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>d$^2$</td>
<td>W</td>
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<td>~</td>
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<tr>
<td>d$^3$</td>
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<td>M</td>
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<tr>
<td>d$^4$</td>
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<tr>
<td>d$^5$</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>S</td>
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<td>S</td>
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<tr>
<td>d$^6$</td>
<td>S</td>
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<tr>
<td>d$^7$</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>d$^8$</td>
<td>S</td>
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<tr>
<td>d$^9$</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>d$^{10}$</td>
<td>S = 0</td>
<td></td>
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$S$ = Strong  \hspace{1cm} W = Weak  \hspace{1cm} NEGL = Negligible  
M = Moderate  \hspace{1cm} \sim = Quasi-static
Magnetic Sublattices

**FERROMAGNETISM**

\[ N_{ij} > 0 \]

**ANTIFERROMAGNETISM**

\[ N_{ij} < 0 \]
\[ N_{ii} \text{ or } N_{jj} > 0 \]

**FERRIMAGNETISM**

\[ N_{ij} < 0 \]
\[ N_{ii}, N_{jj} < 0 \]
Ferrite Thermomagnetism

\[ M = M_B - M_B \]
Spinel Ferrites

Diagram showing the tetrahedral and octahedral sites in a spinel structure with angles and coordination numbers.

Graph showing the variation of certain ions with temperature.

Symbols and labels for coordination numbers and angles.

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Rare-Earth Garnets
Diluted $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG)

- tetrahedral-site dilution
- octahedral-site dilution
Circular Polarization

Electromagnetic wave

- Electric field
- Magnetic field

Left-Hand Circular Polarization (LHCP)

Right-Hand Circular Polarization (RHCP)
Faraday Rotation

- Circular components
- Faraday rotation angle

\[ \varphi_+ = -\beta_+ z \]
\[ \varphi_- = \beta_- z \]
Dipole Transitions

Larmor precession

Linearly polarized field comprising both circular modes $H_{xx}x \pm iH_y$

Circularly polarized $p_{x,y}$ electrons

$p_z$ forms oscillating dipole $ez$ ($L_z = 0$)

$p_{x,y}$ form rotating dipoles $e(x \pm iy)$ in $x$-$y$ plane ($L_z = \pm 1$)

Linearly polarized field comprising both circular modes $E_x \pm iE_y$

Zeeman splitting (partial)

$S_z$

$|e\rangle$

$|g\rangle$

$\omega_0$

$\Delta S_z = \pm 1$

Increasing $H$

Spin-orbit multiplet $p$-state splitting

$|e^{a,b}\rangle^2P$

$|g\rangle^2S$

$L_z$

$\Delta L_z = \pm 1$

$-1 \ (x - iy)$

$0 \ z$

$+1 \ (x + iy)$

$\omega_0^a$

$\omega_0^b$

$0$

$2\Delta$
Resonance Line Shapes

Permeability

\[ \mu', \mu'' \text{ (arbitrary units)} \]

\[ \omega_0 \text{ (arbitrary units)} \]

Permittivity

\[ \varepsilon_1 \text{ (arbitrary units)} \]

\[ \omega (\text{arbitrary units}) \]

Relative error
Bismuth Iron Garnet

[Diagram of Bi covalent bonds and energy levels for Fe_{oct} and Fe_{tet}]

\( Y_{2.75}Bi_{0.25}Fe_5O_{12} \)

- Fe_{tet} = 3.15 eV
- Fe_{tet} = 2.6 eV
- Fe_{tet} = 3.9 eV

\( \varepsilon_i \times 10^{-3} \)

\( \omega \text{ (eV)} \)

Theory

Experiment

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Faraday Rotation Isolators

High-Power Microwaves

1. High-power path (1-2)
2. Polarization filter
3. Samarium-cobalt magnet

Fiber-Optic Infrared

1. Optical fiber
2. BiYIG
3. GdGaG
4. Buffer layers for lattice match
5. Silicon or GaAs

SmCo magnet
G-K Diagrams

Correlation AFM

Delocalization FM

Polaron (double) FM
Brillouin-Weiss vs Applied $H$

\[ M(T) = M(0) \langle \cos \theta \rangle = M(0) B_S(a) \]

\[ a = \frac{m H_{\text{ex}}}{kT} = \frac{(g m_B S) N M}{kT} \]

\[ H_{\text{ex}} + H = N M + H = N M(0) B_S + H \]

\[ N = \left( \frac{z}{n} \right) \frac{2J}{g^2 m_B^2} \]

\[ T_C = \frac{2z}{3k} J S(S+1) \]

where \( z = \) number of neighbors
\( n = \) density of spins
Brillouin Function $H$ Sensitivity

![Graph showing Brillouin Function with temperature on the x-axis and $B_s$ on the y-axis. The graph includes a curve for $H = 0$ and another for $H = 10$ T, with a peak at $T_c$.](image)
Charge Transfer in J-T Ions

\[
\begin{align*}
\text{Mn}^{2+} & \quad \text{Mn}^{4+} & \quad \text{Mn}^{3+} & \quad \text{Cu}^{1+} & \quad \text{Cu}^{2+} & \quad \text{Cu}^{3+} \\
S = 5/2 & \quad S = 3/2 & \quad S = 2 & \quad S = 0 & \quad S = 1/2 & \quad S = 0 \\
\end{align*}
\]

\[
\begin{align*}
\text{e}_g & \quad \text{d}_{x^2-y^2} & \quad \text{d}_{z^2} \\
\end{align*}
\]

\[
\begin{align*}
\text{t}_{2g} & \quad \text{d}^5 & \quad \text{d}^3 & \quad \text{d}^4 & \quad \text{d}^{10} & \quad \text{d}^9 & \quad \text{d}^8 \\
\end{align*}
\]

Charge-Transfer Exchange
Ferromagnetic Spin Alignment

S = 0 Ions
Antiferromagnetic Frustration
CMR Theory

\[
\rho = \left[ n'_{\text{eff}} e^{\left(\frac{eD}{kT}\right)} \right]^{-1}
\]

\[
n'_{\text{eff}} = n_{\text{eff}} \left[ \mathcal{B}_S \exp(-E^0_{\text{hop}}/kT) + (1 - \mathcal{B}_S)(-E_{\text{hop}}/kT) \right]
\]

\[
E_{\text{hop}} = E^0_{\text{hop}} + E^{\text{ex}}_{\text{hop}} \left[ 1 - \mathcal{B}_S(T, H) \right]
\]
CMR Curves vs $T, H$
CMR Data Fitting

La$_{0.77}$Ca$_{0.23}$MnO$_3$

- Theory (Average S)
- $H = 0$
- $\bullet = 1T$
- $\boldsymbol{\nabla} = 3T$
- $\boldsymbol{\triangle} = 5T$
- $\bigcirc = 14T$

$(Data \, of \, Li \, et \, al.)$

$T_C = 270 \, K$

$\rho \, (m\Omega \, cm)$

Temperature (K)
Metallic Perovskites

\[ (\text{La}^{3+}_{1-x}\text{Sr}^{2+}_x)[\text{Mn}^{3+}_{1-x}\text{Mn}^{4+}_x]\text{O}_3 \]

\[ (\text{La}^{3+}_{2-x}\text{Sr}^{2+}_x)[\text{Cu}^{2+}_{1-x}\text{Cu}^{3+}_x]\text{O}_4 \]

\[ \rho \sim T \exp\left(\frac{E_{\text{hop}}}{kT}\right) \]

\[ E_{\text{hop}} = E_{\text{hop}}^{\text{trap}} + E_{\text{hop}}^{\text{ex}} \]

\[ = E_{\text{hop}}^{\text{trap}} + zJS(S+1)(1-\cos\theta) \]

\[ \rho \sim T \exp\left(\frac{E_{\text{hop}}}{kT}\right) \]

\[ E_{\text{hop}} = E_{\text{hop}}^{\text{trap}}, \]

if \( S = 0 \) in Cu\(^{3+}\) and \( T > T_N \)
Polaron Rings

CHARGE BALANCE: \([A_{1-x}A^{x-}](B_{1-x}B^{+x})O_3\)

CHARGE TRANSFER: \(B \leftrightarrow B^+ + e^-\)
3d\(^8\) Low-Spin State
$d^8 \, S = 0$ Stabilization vs Axial Field
Spin Frustration by $S = 0 \text{Cu}^{3+}$ Ions
Polaron Tunneling vs Hopping

Quantum Tunneling  

Thermal Hopping

\[ b_p \sim \frac{1}{\tau_p} \] (inverse of polaron lifetime)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
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<tbody>
<tr>
<td>( b_{\text{pol}} &gt; E_{\text{hop}} )</td>
<td>large polarons in broad bands; spontaneous conduction by covalent transfer</td>
</tr>
<tr>
<td>( b_{\text{pol}} \leq E_{\text{hop}} )</td>
<td>small polarons in thermally narrowed bands; local conduction among equivalent neighbors</td>
</tr>
<tr>
<td>( b_{\text{pol}} \ll E_{\text{hop}} )</td>
<td>hopping electrons from deep in traps; random conduction by thermal activation</td>
</tr>
</tbody>
</table>
Polaron Mobility

\[ b_{\text{pol}} > E_{\text{hop}} \]

\[ b_{\text{pol}} = b \exp[-\gamma \coth(\Theta_D/2T)] \]

\[ \mu_{\text{pol}} \sim eD/kT \]

\[ b_{\text{pol}} < E_{\text{hop}} \]

\[ b_{\text{pol}} \approx b \exp[-\gamma(2T/\Theta_D)] \]

\[ \mu_{\text{hop}} \sim (eD/kT)\exp(-E_{\text{hop}}/kT) \]
Zero-Spin Transfer Combinations

d\textsuperscript{10} \quad d\textsuperscript{9} \quad d\textsuperscript{8} \quad d\textsuperscript{7} \quad d\textsuperscript{6} \quad d\textsuperscript{5}

\textit{e\textsubscript{g}}
- d\textsubscript{z2}
- d\textsubscript{x2-y2}

\textit{t\textsubscript{2g}}
- d\textsubscript{yz}
- d\textsubscript{xz}
- d\textsubscript{xy}

10Dq
$T_c, T_N = 0$ Condition
$T_c$ Fitting of Theory to Data

![Graph showing fitting of theory to data for different compounds and experimental data points.](image-url)
$T_c$ vs $x$, $\beta$ Predictions

$E_{\text{hop}} = 4$ meV

$x_f = 0.035$

$\beta = 0$, $0.25$, $0.5$, $0.75$, $1.0$, $0.33$

CET THEORY
Unconventional Magnetic Oxides

- **Magnetic Perovskites (Orthoferrites):** $(\text{RE})^3+\text{Fe}^3+\text{O}_3 \rightarrow 0.5$-degree canted AFM sublattices produce net $4\pi M \sim 10^2$ G, $T_C > 550$ K

- **Double Perovskite Ferrites:** $\text{A}^{3+}_2\text{Fe}^{(3+n)+}\text{M}^{(3–n)+}\text{O}_6 \rightarrow$ charge-ordered cation form magnetically unbalanced sublattices and produce higher $4\pi M$, $T_C > 300$ K. Polarized spin transport can be expected

- **Double Perovskite Ferromagnet:** $\text{A}^{3+}_2\text{Mn}^{4+}\text{Ni}^{2+}\text{O}_6 \rightarrow$ charge-ordered ferromagnetism by delocalization exchange produces ferromagnetism with semiconducting properties near 300 K. Classic example of Goodenough-Kanamori rules.

- **Magnetolectric (Piezomagnetic) Perovskite:** $\text{Bi}^{3+}\text{Fe}^3+\text{O}_3$ films offer basis for combined ferroelectric/piezoelectric/ferromagnetic properties at $T > 600$ K

- **Dilute Magnetic Oxides:** Substitutional combinations of Fe and Cu in $\text{In}_2\text{O}_3$ films produce both ferromagnetism and n-type semiconduction at $T \rightarrow 600$ K