Orbital Anisotropy in Multiferroic Systems: X-ray Absorption & Magnetic Circular Dichroism

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Multiferroic

Coexistence of Magnetism and Ferroelectricity
Magnetoelectric Effects


Ferromagnetic
H-field switching M

Magnetic Storage Devices

Ferroelectric
E-field switching P

Sensors
FeRAM

Multiple-state Memories

H, E-field switching M, P
Magnetoelectric effects in Multiferroic Materials

- Electrical Polarization Reversal by Magnetic field

**TbMn$_2$O$_5$**


**CoCr$_2$O$_4$**

- PRL (2006) Tokura’s group

Electron Spectroscopy Laboratory
Multiferroic and Magnetoelectric Materials

Orbital Anisotropy vs. Multiferroic

**Magnetism (Spin)**
Internal Coordinates

Orbital Angular Momentum

**Electricity (Polarization)**
Real Coordinates

- **Dzyloshinskii-Moriya (DM) Interaction**
  - Spin-Orbit coupling (derived from Relativistic Dirac equation)
    \[ H_{\text{SO}} = \sum_i \zeta(\vec{r}_i)\vec{l}_i \cdot \vec{s}_i = \lambda \vec{L} \cdot \vec{S} \]
  - Effective local spin Hamiltonian
    \[ H_{\text{eff}} = \langle \Gamma' \gamma' | H_{\text{SO}} + H_{\text{SO}} \frac{1}{E - H_{\text{SO}}} H_{\text{SO}} | \Gamma \gamma \rangle \]
    \[ = \lambda \sum_\mu L_\mu S_\mu - \sum_{\Gamma' \gamma'} |\langle \Gamma' \gamma' | \lambda \vec{L} \cdot \vec{S} | \Gamma \gamma \rangle|^2 \frac{1}{E_{\Gamma' \gamma'} - E_{\Gamma \gamma}} \]
    \[ = \lambda \sum_\mu L_\mu S_\mu - \lambda^2 \sum_{\mu\nu} \Lambda_{\mu\nu} S_\mu S_\nu \]
    \[ H_{DM} = \sum_{i,j} \vec{D}(\lambda) \cdot \vec{s}_i \times \vec{s}_j \]

Magnetic Anisotropy
Orient local spin axis

DM Interaction
Anisotropic Superexchange
Orbital Anisotropy vs. Multiferroic

- **Ferroelectricity (Polarization)**
  - Break of Central-Symmetry
  - \( L \neq 0 \)
  - Orbital Anisotropy

- **Multiferroic (Spin & Polarization)**
  - \( L \neq 0 \)
  - Orbital Anisotropy
  - L·S coupling
  - Magnetic Anisotropy

\[ \vec{P} = 0 \]
\[ \vec{L} = 0 \]

Central Symmetry
Ferroelectric

\[ \vec{P} = P\hat{\mathbf{z}} \]
\[ L_z = 0 \]
\[ L_{xy} \neq 0 \]

In normal cases\( \vec{P} \perp \vec{M} \)

**Orbital Anisotropy is an essential factor in Multiferroic!!**
Soft X-ray Absorption Spectroscopy (XAS)

-a Powerful tool determining the Ground State Symmetry

**Dipole Selection rule**

- $3d$ Transition Metal $L_{2,3}$-edge: $2p \rightarrow 3d$
- $4f$ Rare Earth $M_{4,5}$-edge: $3d \rightarrow 3f$
- O K-edge: $1s \rightarrow 2p$
- Etc.

Two Particle Excitation Spectral Function
(Quasi-one Particle Excitation Spectrum)

$$\rho \propto \left| \langle \Psi_f^{N*} | \phi_v^\dagger \phi_c | \Psi_G^N \rangle \right|^2 \delta (h\nu - (E_f - E_G))$$

Importance of Atomic Multiplets
Finger Print of Ground State Symmetry

O K-edge XAS: Show Conduction Bands
Different multiplet structure for different valence states

Multiplet Calculations of Mn $L_{2,3}$-edge XAS for Different Valence States

F.M.F. de Groot et al, PRB (1990)
Finger Print of the Ground States

Ground State Valence

Ground State Symmetry (Spin State)

Multiplet structure vs ionic multiplet with crystal field

V $2p^63d^2 \rightarrow 2p^53d^3$

Mn $2p^63d^5 \rightarrow 2p^53d^6$

Co $2p^63d^7 \rightarrow 2p^53d^8$

Multiplet structure: determined by $2p^53d^{n+1}$ configuration depends on the valence, crystal field, spin state
O 1s XAS in TMOs (Conduction band)

Due to TM 3d – O 2p Hybridization

- $e_g$
- $t_{2g}$

Cu$^{2+}(d^9)$, Ni$^{2+}(d^8)$

Co$^{2+}(d^7)$, Fe$^{2+}(d^6)$, Mn$^{2+}(d^5)$

Cr$^{3+}(d^3)$, V$^{3+}(d^2)$, Ti$^{3+}(d^1)$
# XAS Measurement Modes

<table>
<thead>
<tr>
<th>Measurement Mode</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Transmission yield</strong></td>
<td>- Direct measurement</td>
</tr>
<tr>
<td></td>
<td>- Sample thickness limit (≤1000Å)</td>
</tr>
<tr>
<td></td>
<td>: due to large absorption cross section in soft x-ray region</td>
</tr>
<tr>
<td><strong>Total electron yield</strong></td>
<td>- Indirect measurement</td>
</tr>
<tr>
<td></td>
<td>- Rather surface sensitivity</td>
</tr>
<tr>
<td></td>
<td>: Small probing depth (≈50Å)</td>
</tr>
<tr>
<td><strong>Fluorescence yield</strong></td>
<td>- Indirect measurement</td>
</tr>
<tr>
<td></td>
<td>- Self-absorption problem</td>
</tr>
<tr>
<td></td>
<td>: Difficult at 3$d$ transition metal $L$-edge, 4$f$ rare-earh $M$-edge</td>
</tr>
</tbody>
</table>
Direct Measurements on Orbital Anisotropy & Momentum

-XAS using linearly polarized light on a system with geometrical Anisotropy

Orbital Anisotropy/Directional Lattice distortion

- Selective Dipole selection rule depending on the Orbital Symmetry
  i.e. Polarization vector $E \parallel c$ vs $E \perp c$
  ⇒ Information on the Orbital states and anisotropy

Chen et al. PRL (1992)
Orbital Selection in Polarization dependent XAS

*d*-orbitals under $O_h$ crystal field

None-zero transition matrix elements in TM $L$-edge; $2p \rightarrow 3d$

$3d$: $xy$, $yz$, $zx$, $x^2-y^2$, $2z^2-x^2-y^2$ ($3z^2-r^2$)

$E \parallel x$

$E \parallel y$

$E \parallel z$

$2p$: $p_x$, $p_y$, $p_z$

O $2p$ – TM $3d$ orbital bondings

O $K$-edge; $1s \rightarrow 2p$ ($p_x$, $p_y$, $p_z$)

$zx(yz)$: $p_z$, $p_x$ ($p_y$)

$xy$: $p_x$, $p_y$

$3z^2-r^2$: $p_z$, (weak $p_x$, $p_y$)

$x^2-y^2$: $p_x$, $p_y$
Element specific Orbital and Spin Moments

**Sum rule:**

\[
M_L \propto \sigma_+ - \sigma_- \equiv \Delta \sigma \\
M_S \propto \left( 2 \Delta \sigma_{L_3} - 4 \Delta \sigma_{L_2} \right) \times (1 + \alpha)
\]

\[
\sigma_\pm \equiv \int \mu_\pm \\
\Delta \sigma_{L_3} = p \\
\Delta \sigma_{L_2} = p - q
\]

\[
m_o = \frac{2q}{9p - 6q}
\]

Chen et al. PRL (1995)
Multiferroic Systems under Research

- **GaFeO$_3$ (Polar Ferrimagnet – Piezo-electric)**
  Fe$^{3+}$ ($d^5$) ions: half-full, $L = 0$ (?)

- **BiFeO$_3$ (Antiferromagnet-Huge Ferroelectricity)**
  Fe$^{3+}$ ($d^5$) half-full: Orbital Anisotropy and Magnetization/ Stain effect in films

- **YMnO$_3$ (Antiferromagnet - Ferroelectricity)**
  Mn$^{3+}$ ($d^4$) in hexagonal: Orbital Anisotropy and origin of ferroelectricity

- **LuFe$_2$O$_4$ (Ferrimagnet– Ferroelectric)**
  Fe$^{2+}$ ($d^6$) – Fe$^{3+}$ ($d^5$) Mixed valence in hexagonal, charge-ordering
  Huge Coercivity ($H_C > 10$ T)
I. Polar Ferrimagnet GaFeO$_3$

Kim et al. PRL (2006)
**Magnetoelectric phenomena in GaFeO\textsubscript{3}**

**Ferrimagnetic + Piezoelectric**

X-ray nonreciplocal dichroism (XNDD)  
Kubota et al., PRL (2004)

Optical Magnetoelectric Effect  
Jung et al., PRL (2004)

**What is the mechanism?**

**Mostly Phenomenological Studies**  
Need microscopic information.
GaFeO$_3$  $Fe^{3+}$ ($d^5$) half-full

- Polar-Ferrimagnet (Ferrimagnet + Piezoelectric)

  $T_C = 200K \sim 300K$ (depends on Growth)

  $M = 0.6 \sim 0.9 \mu_B/Fe$ (due to the site disorder)

  4 different Cation sites (Ga1, Fe1, Ga2, Fe2)
  - Ga1: Tetrahedral sites
  - Ga2, Fe1, Fe2: Octahedral Sites

  c : Magnetic easy axis (chain direction)
  a : Interchain direction
  b : piezo direction

  Fe fraction on Cation site
  - $f_{Ga1} = 0$ (Ga$^{3+}$ only)
  - $f_{Fe1} = 0.825$ (Down-spin)
  - $f_{Ga2} = 0.35$ (Up-spin)
  - $f_{Fe2} = 0.825$ (Up-spin)

  $\Rightarrow M = 0.86 \mu_B/Fe$

*Double HCP Closed-Pack (Orthorhombic)*
Gilleo’s Classic Model for $Ga_{2-x}Fe_xO_3$

- Expected $Fe^{3+}$ fractional distributions on 4 different cation sites

Gilleo Classic Model for $Ga_{2-x}Fe_xO_3$

i) $f_{Ga_1} = 0$

ii) $f_{Fe_1} = f_{Fe_2} = 3x/7 + 0.8$ (1 for $x = 1.4$)

iii) $f_{Ga_2} = 8x/7 - 0.8$ (0 for $x = 0.7$)

- $GaFeO_3$ ($x = 1$)

  $Ga_1$ ($T_{3d}$): $f_{Ga_1} = 0$ ($Ga^{3+}$ only)
  $Fe_1$ ($O_h$): $f_{Fe_1} = 0.825$ (Down-spin)
  $Ga_2$ ($O_h$): $f_{Ga_2} = 0.35$ (Up-spin)
  $Fe_2$ ($O_h$): $f_{Fe_2} = 0.825$ (Up-spin)

  $\mu = 0.86 \mu_B/Fe$

It is important to check whether $f_{Ga_1} \approx 0$
GaFeO$_3$ crystal in this study

- Grown by Flux method
- $M(5K) = 0.87\mu_B/Fe$
- Agree to the expected Cation site Fe fraction
- $T_C \sim 250K$
- $c$ : easy axis (Strong Magnetic Anisotropy)
- $b$ : hardest axis

**Diagram:**
- Very slim hysteresis curve along c-axis

**Graph:**
- Magnetization vs. Temperature
- $H/c$ vs. Magnetic Field
Fe L$_{2,3}$-edge XAS and XMCD

-XAS line shape is nearly identical to that of $\alpha$-Fe$_2$O$_3$ ($O_h$ Fe$^{3+}$ only)
-MCD line shape indicates almost no Fe$^{3+}$($T_d$)
($\gamma$-Fe$_2$O$_3$: Fe$_{3/4}^T$O$_{5/4}$O$_3$)

Fe$^{3+}$ fraction at Ga1($T_d$) site is negligible
Fe $L_{2,3}$-edge XMCD

$M_O/M_S \sim 0.046$

$M_O \sim 0.23 \mu_B$ for $S = 5/2$ (5 $\mu_B$)

Large Orbital Magnetic Moment

(d$^5$ at $O_h/T_{3d}$: $M_O \approx 0$)

Very large Titling of lattice

Anisotropic Bonding with O 2p states
Origin of Large Orbital Moments and Magnetic Anisotropy

Crystal Off-Centered Movements

Off-centering Movements $\Rightarrow$ Parity Symm. Breaking $\Rightarrow$ Non-vanishing $L$

- Movements in $ab$-direction and largest $b$-direction
  - Fe1: mainly $b$-direction $\Rightarrow L$ along $a$ and $c$
  - Fe2: along $a$ & $b$-direction $\Rightarrow L$ along $c$

Largest $L$ along $c$ $\Rightarrow$ easy axis : $c$
hardest axis : $b$

$E_{MC} \sim -\zeta \Delta L \cdot S$
Crystal Field under Trigonal Symmetry ($D_{3d}$)

- $e_g$: Toward Ligands
- $e_g \sigma$: In XY-Plane (crystal $ca$-plane)
- $e_g \pi$: Along Z-direction (crystal $b$-direction)
- $t_{2g}$
- $a_{1g}$: Along Z-direction (crystal $b$-direction)

$O_h$, $D_{3d}$

3K: + or – depends on the trigonal tilting
O K-edge XAS (Fe 3d state conduction band)

Additional Atomic movements

\[ \begin{align*}
  e_g & \quad e_g^\sigma \\
  t_{2g} & \quad e_g^\pi \\
  a_{1g} & \quad e_g \sim 0.04eV \\
  \sim 0.4eV & \quad \sim 1.4eV
\end{align*} \]

Anisotropic Bonding with O 2p

\[ \text{Largest Hybrid. along } b\text{-axis} \]

the Orbital Momentum

& Magnetoelectric Effect
**Conclusions & Summary**

- **Fe$^{3+}$ fraction** at the tetrahedral Ga1 site is **negligible**, consistent with Gilleo’s classic model.

- A large **orbital moment** ($M_O/M_S \sim 0.05$) is obtained from XMCD.

- The large orbital moment results from **off-centering atomic movements**, which explains the **magnetic anisotropy**.

- O K-edge XAS shows a strong polarization dependence of Fe 3d states; **Orbital Anisotropy ➔ Orbital Moment**

- Magnetoelectric effects is probably due to the **anisotropic bonding and the orbital anisotropy**.
II. Hexagonal Manganite YMnO$_3$

Cho et al. PRL (2007)
Crystal structure of Manganites ReMnO$_3$

Small ionic radius $\Rightarrow$ Hexagonal
$Re = Y, Ho, Er, Tm, Yb, Lu$

Large ionic radius $\Rightarrow$ Orthorhombic
$Re = La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Bi$
Hexagonal Manganites ReMnO$_3$

Acta Cryst 16, 957(1963)

**Table 1. Unit cell parameters of several hexagonal rare-earth orthomanganites of the LuMnO$_3$ type**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a_0$ (Å)</th>
<th>$c_0$ (Å)</th>
<th>$c/a$</th>
<th>$T_C$</th>
<th>Spont. Pol (P/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YMnO$_3$</td>
<td>6.125*</td>
<td>11.41*</td>
<td>1.862*</td>
<td>~ 1000K</td>
<td>5.5 μC/cm$^2$</td>
</tr>
<tr>
<td>HoMnO$_3$</td>
<td>6.136</td>
<td>11.42</td>
<td>1.861</td>
<td>~ 1000K</td>
<td>5.6 μC/cm$^2$</td>
</tr>
<tr>
<td>ErMnO$_3$</td>
<td>6.115</td>
<td>11.41</td>
<td>1.866</td>
<td>~ 900K</td>
<td>5.6 μC/cm$^2$</td>
</tr>
<tr>
<td>TmMnO$_3$</td>
<td>6.062</td>
<td>11.40</td>
<td>1.881</td>
<td>~ 600K</td>
<td>5.6 μC/cm$^2$</td>
</tr>
<tr>
<td>YbMnO$_3$</td>
<td>6.062</td>
<td>11.40</td>
<td>1.881</td>
<td>~ 1100K</td>
<td></td>
</tr>
<tr>
<td>LuMnO$_3$</td>
<td>6.042</td>
<td>11.37</td>
<td>1.882</td>
<td>~ 600K</td>
<td></td>
</tr>
</tbody>
</table>

Magnetic order: **Antiferromagnetic (A-type) ($T_N \sim 80$K)**

Geometrically spin frustration

- Coexistence of Ferroelectricity & Anti-ferromagnetism
  - “Multiferroicity” *(Structure driven Multiferroic)*

With High ferroelectric $T_C$ vs Low Magnetic $T_N$
Mechanisms of Ferroelectric Distortions

In general, short-range inter-atomic repulsion and lattice energy obstructs a ferroelectric distortion.

Need a stabilizing mechanism with soft phonon modes

- Prototype ferroelectricity: the so-called “$d^0$-ness” (e.g. BaTiO$_3$)
  Off-center movement of Ti in TiO$_6$ lowers the energy through the Ti 3d-O 2p enhanced hybridization (rehybridization).

- PbTiO$_3$ or BiMnO$_3$: Lone pair of Pb$^{2+}$ or Bi$^{3+}$ (6s$^2$)
  => Ferroelectric Distortion

- TbMnO$_3$: Spin frustration of sinusoidal AFM ordering
Ferroelectricity of YMnO$_3$?

- Mn$^{3+}$ (3$d^4$); In-Planar Spins (AFM) $\Rightarrow$ Not $d^0$-ness
- Unlike Bi$^{3+}$ in BiMnO$_3$, Y$^{3+}$ ion; no lone pair of electrons.
- Hexagonal Unit Cell -- $d_{z^2}^0$-ness due to the peculiar Crystal field (D$_{3h}$) $\Rightarrow$ Directional Mn $d^0$– ness
  - Filippetti et al. PRB 65, 195120 (2002)

Cubic

$\begin{align*}
\text{Jahn-Teller} & \\
\uparrow t_{2g} & \quad \uparrow e_g \\
\uparrow x^2-y^2 & \quad \uparrow z^2 \\
\uparrow z^2 & \quad \uparrow x^2-y^2/xy \\
\uparrow xy & \quad \uparrow yz/zx \\
\end{align*}$

Hexagonal

$\begin{align*}
\text{MnO}_5 \\
\text{Bi-pyramid} \\
\text{NO } t_{2g}-e_g \text{ thing!!} \\
\text{NOT a Jahn-Teller but an extreme limit of JT.}
\end{align*}$
**Ferroelectric distortions in YMnO₃**

- Actual ferroelectric displacements at rather Y sites, not Mn sites.
- Y considered to be almost purely ionic (no re-hybridization).
  - **Suggest electro-static dipole-dipole interaction (no anomalous dynamic charge)**
    (B.B. van Aken et al. Nature Mat. 3 164 (2004))
- Y sites truly ionic?
- What is the origin of the ferroelectric distortion in YMnO₃?

**Figure 3** Schematic of a MnO₆ polyhedron with Y layers above and below. 
(a, b) The calculated atomic positions of the centrosymmetric (a) and ferroelectric structures (b). The numbers give the bond lengths in Å. The arrows indicate atomic displacements with respect to the centrosymmetric structure.

O K-edge Polarized XAS

- Strong Hybridization for both Mn 3d and Y 4d
- Strong Anisotropy for both Mn 3d and Y 4d

Strong covalency (strong hybridization)
Large transferred O 2p holes in Y 4d

Against ionic Y

Is it “Y d⁰-ness”?
**Born Effective Charge** $Z^*$ (Dynamical Charge)

: responsible for the electric polarization $P$

- can be several times larger than the static charge

\[ e.g. \text{ BaTiO}_3 : Z^*_\text{Ti} \approx +7.5 \quad \text{vs} \quad Z_\text{Ti} \approx +2.5 \]
\[ Z^*_\text{O} || \approx -6 \quad \text{vs} \quad Z_\text{O} \approx -1.5 \]

\[ \text{Dynamical charge} = \text{Static charge} + \text{Dynamical contribution} \]

\[ \text{Cf) Anomalous contribution:} \quad Z^*(u) - \langle Z(u) \rangle \]

- For interatomic displacement $u$ : dipole moment $p(u) = uZ(u)$

\[ Z^*(u) = \frac{\partial p(u)}{\partial u} = Z(u) + u \frac{\partial Z(u)}{\partial u} \]

\[ \text{Change of polarization : displacement current} \]

\[ \text{Dynamical charge} = \text{Static charge} + \text{Dynamical contribution} \]

- Harrison’s bond orbital model (simple tight binding estimation) in 1\textsuperscript{st} order

\[ p- d \text { hybridization strength} \quad V \sim d^{-7/2}, \quad Z(u) = Z_{\text{ionic}} - \Delta Z \quad (\sim V_{\text{eff}}^2/(\epsilon_d - \epsilon_p) \sim d^{-7}) \]

\[ u \frac{\delta Z(u)}{\delta u} = u \frac{\delta (\Delta Z)}{\delta u} = -7 \times (\Delta Z) \quad (\times 2) \quad \text{Very large dynamic contribution (anomalous)} \]

Dynamic contribution propor. to Transferred Charge ($\Delta Z$)!!
Local Structure of $\text{MnO}_5$ and $\text{YO}_8$

Off-centering Movements of Y-ions

- Hybridization change along c
  
  $\text{YMnO}_3$:
  $O_p-Y^1-O_p : 70\%, O_p-Y^2-O_p : 35\%$

- Average hybridization change
  
  $Y^1-O : 8\%, Y^2-O : 4\%$
  
  ($\text{BaTiO}_3 : \text{Ti-O} : 5\%$)

- $\text{Y d}^{0}$-ness lower the energy through the rehybridization due to the ferroelectric distortion as in $\text{BaTiO}_3$ ($\text{Ti d}^{0}$-ness)!
Polarization Dependent Mn L-edge and O K-edge XAS

Hexagonal vs. Orthorhombic Manganites

(a) Mn $L_{2,3}$-edge

- Hexagonal
- $E//ab$
- $E//c$

(b) O K-edge

- Hexagonal
- Dy 5d
- Mn 3d
- DyMnO$_3$
- LaMnO$_3$
- DyMnO$_3$

Intensity (Arb. Units)

Photon Energy (eV)
Summary & Conclusions

• Orbital and Bonding Anisotropy not only in Mn 3d but also in Y 4d

• Strong Y 4d-O 2p Hybridization
  ➔ Transferred charge to Y 4d is even larger than that to Mn 3d.

• Large ferroelectric off-center displacements in Y-O ions in polar. direction
  ➔ even larger than those in BaTiO₃.

• Large hybridization enhancement (Rehybridization) of Y 4d-O 2p
  ➔ comparable to Ti 3d-O 2p in BaTiO₃
  ➔ large anomalous contribution on Born effective charges of Y and Oₚ

• Y d⁰-ness with rehybridization is responsible for the ferroelectric instability.

• Re d⁰-ness is extended to the ferroelectricity of hexagonal ReMnO₃
III. Giant Coercive Ferrimagnet LuFe$_2$O$_4$
LuFe$_2$O$_4$ – Ferrimagnet + Ferroelectric, Huge coercivity ($H_C > 10$ T)

- **RFe$_2$O$_4$ family**
  Rhombohedral structure (R-3m)$^*$
  Fe$^{2+}$(d$^6$) and Fe$^{3+}$(d$^5$) mixed valence

- **Bipyramidal local symmetry** ($D_{3h}$)

- **Hexagonal bi-layered structure**
  Triangular Network $\rightarrow$ Frustration (charge & spin)
  Polar charge ordering $\rightarrow$ Ferroelectricity$^+$

\[ a = 3.44 \text{ Å} \]
\[ c = 25.25 \text{ Å} \]

† N. Ikeda et al., Nature 436 1136 (2005)
Physical Phenomenon of LuFe$_2$O$_4$

- Large coercivity & strange saturate magnetic moment

M : $\sim 2.9 \mu_B$  
$H_C > 10T$ @ 4.2K

J. Iida et al., JPSJ 62 1723

Charge and Spin Ordering

Y. Yamada et al., JPSJ 66 3733

Ferrimagnetic Ordering

2D – CDW

330 K

P = 28 $\mu$C/cm$^2$

M. A. Subramanian et al., Adv. Mat. 18 1737

The charge ordering are strongly correlated with magnetic ordering.
Charge and Spin Ordering of LuFe$_2$O$_4$

- $(\frac{1}{3}, \frac{1}{3}, L+0.5)$ charge ordering
- slightly incommensurate
- $(0.030, 0.030, 1.5) : 3D$ CDW

Y. Yamada et al., JPSJ 66 3733 (1997)

- $(\frac{1}{3}, \frac{1}{3}, 0)$ magnetic spin ordering
- slightly incommensurate $(\delta, \delta, 0)$
- $\delta = 0.027$
- basically $(\frac{1}{3}, \frac{1}{3}, l)$ rod

J. Iida et al., JPSJ 62 1723 (1993)
A. D. Christianson et al., PRL 100 107601(2008)
Frustration of Charge and Spin orderings in LuFe$_2$O$_4$

- The triangular lattice causes the charge frustration.

![Diagram showing charge frustration]

- The triangular lattice causes spin frustration.

![Diagram showing spin frustration]


- (1/3 1/3) spin ordering cannot be determined uniquely.
Issues related to the Orbital Anisotropy in LuFe$_2$O$_4$

• Orbital Occupation and Energy levels under the D$_{3h}$ symmetry

Fe$^{2+}$ (d$^6$)

\[
\begin{align*}
\text{a}_1g \; (3z^2-r^2) & \quad \uparrow \\
\text{e}'' \; (x^2-y^2/xy) & \quad \uparrow \\
\text{e}' \; (yz/zx) & \quad \uparrow \\
\end{align*}
\]

or

\[
\begin{align*}
\text{a}_1g \; (3z^2-r^2) & \quad \uparrow \\
\text{e}' \; (yz/zx) & \quad \uparrow \\
\text{e}'' \; (x^2-y^2/xy) & \quad \uparrow \\
\end{align*}
\]

-GGA + U Band Calculation (Xiang et al., PRL. 98 246403 (2007)) without Charge Ordering: e'' ($x^2-y^2/xy$) is the lowest.

-Under the assumption of the lowest e'' ($x^2-y^2/xy$).

(Nagano et al., PRL. 99 217202 (2007))

(1/3,1/3, l) CO produced in Monte Carlo Simulation
But Spin order inconsistent with the neutron results.
Mössbauer suggests three different Fe$^{3+}$ sites.

Three Fe$^{3+}$ ions have different magnetic response.

Suggested Magnetic Configurations

<table>
<thead>
<tr>
<th></th>
<th>Fe$^{2+}$</th>
<th>Fe$^{3+}$</th>
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<tbody>
<tr>
<td></td>
<td>P</td>
<td>C</td>
</tr>
<tr>
<td>velocity (mm/s)</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>H$<em>{M</em>{obs}}$ (kOe)</td>
<td>↓</td>
<td>↓</td>
</tr>
</tbody>
</table>

Magnetic Moment

\[
\left( 4\mu_B \times 3 + 5\mu_B \right) / 3 = 2.33\; \mu_B \ll M_{obs} \sim 2.9\; \mu_B
\]

Others

- What is the origin of the large magnetic anisotropy and coersivity?
- Orbital anisotropy?
XMCD measurement

- Ferrimagnetic spin ordering
- Large unquenched orbital moment \( \sim 0.8 \mu_B/\text{f.u.} \)

\[
\begin{align*}
M_{\text{Fe}^{2+}} \text{ AF } M_{\text{Fe}^{3+}} & \quad M_{\text{Fe}^{2+}} : \uparrow \uparrow \uparrow \\
M_{\text{total}} / M_{\text{Fe}^{2+}} & \quad M_{\text{Fe}^{3+}} : \uparrow \downarrow \downarrow \\
\end{align*}
\]

\[
m_o = \frac{2q}{9p - 6q} = 0.35 \pm 0.05
\]

Assume Ionic Spins

\[
m_s = \frac{(3 \times 4\mu_B - 5\mu_B)}{3} = 2.3\mu_B / \text{f.u.}
\]

\[
m_o = m_s \times 0.35 \approx 0.8\mu_B / \text{f.u.}
\]

\[
m_{\text{tot}} \approx 3.1\mu_B / \text{f.u.} \quad (M \sim 2.9\mu_B)
\]
Linear Dichroism

- Linear dichroism shows that the $x^2-y^2$ and $xy$ orbitals are unoccupied.

\[ a_{1g} (3z^2-r^2) \]
\[ e'' (x^2-y^2/xy) \]
\[ e' (yz/zx) \]

Not

\[ a_{1g} (3z^2-r^2) \]
\[ e' (yz/zx) \]
\[ e'' (x^2-y^2/xy) \]

Against the GGA + U band calculation results. Need the band calculation with CO.
O $K$-edge Spectrum

- $zx, yz$ is the lowest state again in Fe sites
- degenerated $zx, yz$ levels $\Rightarrow$ origin of $M_O$

![Graph showing XAS intensity against photon energy with labels for $Fe^{2+}$ and $Fe^{3+}$ and MO levels](image-url)
Hybridization and dissolution of Orbital mixing

C$_{3v}$ crystal field
(the level structure is similar to that of Nagano et al. and Naka et al.)

$A_{1g} \{3z^2-r^2\}$

$E_g''' \{-a(yz)+b(xy) , a(zx)+b(x^2-y^2)\}$

$E_g'' \{a(yz)+b(xy) , -a(zx)+b(x^2-y^2)\}$

(b=0.783 and a=0.622)

hybridization

full multiplet CI calculation (Fe$^{2+}$)

Fe$^{2+}$ (d$^6$)

$E_g$ u ($3z^2-r^2$) 0.994 0.104 $A_{1g}$

$E_g$ v ($x^2-y^2$) 0.994 0.107 $E_g'$

$T_{2g}$ a (yz) 0.994 0.501 $E_g''$

$T_{2g}$ b (zx) 0.994 0.501 $E_g''$

$T_{2g}$ c (xy) 0.994 0.107 $E_g''$

($m_s=1.83$ $m_0=0.81$)

Large orbital moment
But …

• The calculation reproduce the overall XMCD spectral line.

• MCD line shape shows an unexpected low energy side-peak.

• There seem to be distinguishable Fe$^{2+}$ and Fe$^{3+}$ sites.
Polar Charge Ordering in LuFe$_2$O$_4$

- Two Different sites for both Fe$^{2+}$ and Fe$^{3+}$
  - 1Fe$^{2+}$ : 2Fe$^{3+}$ (Fe$^{3+}$ rich)
  - 2Fe$^{2+}$ : 1Fe$^{3+}$ (Fe$^{2+}$ rich)
  - Different Madelung potentials
  - Different Charge environments

- Ferroelectric or Antiferroelectric

(1/3 1/3 3/2) charge ordering is consistent with the anti-ferroelectric ordering.$^a$

$^{a}$ M. Angst et al., arXiv:0807.3527v2 (2008)
Madelung Potential Calculation

<table>
<thead>
<tr>
<th>$e\textbf{Å}^{-1}$</th>
<th>Antiferroelectric</th>
<th>Ferroelectric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$^{2+}$</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>Fe$^{2+}$ rich</td>
<td>-1.9426</td>
<td>-2.3908</td>
</tr>
<tr>
<td>Fe$^{3+}$ rich</td>
<td>-1.6995</td>
<td>-2.1476</td>
</tr>
<tr>
<td>Least Charge Fluctuation Gap</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Antiferroelectric charge order is more appropriate to explain the size of the 0.7 eV insulating gap of LuFe$_2$O$_4$.

(a. X. S. Xu et al., arXiv:0809.4483v1 (2008))
Two type of $\text{Fe}^{3+}$ spin ordering

- Two possible ferrimagnetic orderings
  - Take into account for different $\text{Fe}^{3+}$ & $\text{Fe}^{2+}$ sites

Three different $\text{Fe}^{3+}$ ions as observed in Mössbauer

- $\text{M}_{\text{Fe}^{2+}} : \uparrow \uparrow \uparrow$
- $\text{M}_{\text{Fe}^{3+}} : \uparrow \downarrow \downarrow$

### a.

- $1\text{Fe}^{2+} \uparrow : 1\text{Fe}^{3+} \downarrow : 1\text{Fe}^{3+} \uparrow$
- $2\text{Fe}^{2+} \uparrow : 1\text{Fe}^{3+} \downarrow$

### b.

- $1\text{Fe}^{2+} \uparrow : 2\text{Fe}^{3+} \downarrow$
- $2\text{Fe}^{2+} \uparrow : 1\text{Fe}^{3+} \uparrow$

### Graphs

- Intensity (Arb. Unit)
- Photon Energy (eV)
- MCD (x5, R-L)
- MCD (calculated)
XMCD and Calculation

- CI calculation successfully reproduce XMCD

- All of the Fe$^{2+}$ spins are parallel, two of the Fe$^{3+}$ spins are anti-parallel and the other one is opposite direction.
- (1/3 1/3 0) magnetic ordering
- Take into account for different Fe$^{2+}$ and Fe$^{3+}$ sites.
- Determine the spin configuration.

(a) Fe$^{3+}$ (b) Fe$^{2+}$
Summary

• Fe²⁺ possesses the large orbital moment.
  – Large crystalline anisotropy increases the coercivity with the collective freezing of magnetic domains
  – Origin of the giant magneto-electric effect
  – Explain the saturated magnetic moment $M \sim 2.9 \mu_B$

< calculated spin and orbital magnetic moment >

<table>
<thead>
<tr>
<th>$m_{\text{spin of Fe}^2+}$</th>
<th>$m_{\text{orbit of Fe}^2+}$</th>
<th>$m_{\text{spin of Fe}^3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.67 $\mu_B$</td>
<td>0.81 $\mu_B$</td>
<td>4.50 $\mu_B$</td>
</tr>
</tbody>
</table>

$M_{\text{spin}} = (3 \times 3.67 - 4.50)/3 = 2.17 \mu_B$

$M_{\text{total}} = (3 \times (3.67 + 0.81) - 4.50)/3 = 2.98 \mu_B$

$M_{\text{orbit}} / M_{\text{spin}} = 0.81 / 2.17 = 0.37$

$m_o / m_s \approx 0.35$ (measured ratio)

• Orbital occupation and level splittings

  $e'$ ($yz/zx$) lowest energy state orbital
  => contribute the large orbital moment of Fe²⁺

Fe³⁺

- $a_{1g} (3z^2-r^2)$
- $e'' (x^2-y^2/xy)$
- $e' (yz/zx)$

Fe²⁺

- $a_{1g} (3z^2-r^2)$
- $e'' (x^2-y^2/xy)$
- $e' (yz/zx)$