Large magnetodielectric and magnetoelastic coupling in various transition-metal oxides

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Outline of my talk

Large magnetodielectric coupling in $\text{EuTiO}_3$ and related compounds

Large magnetoelastic coupling in spinel vanadates and manganites
Coupling between various degrees of freedom

Electric field ($E$)

Polarization ($P$)

ferroelectricity

Charge degree of freedom

ferromagnetism

Spin degree of freedom

Magnetization ($M$)

Magnetic field ($H$)

crystal

ferroelasticity

Orbital degree of freedom

Distortion ($u$)

Stress ($X$)
Electrical resistance of metals varies with magnetic field
→ magnetoresistance (MR)

Capacitance (dielectric constant) of insulators varies with magnetic field
→ magnetocapacitance (MC)
FIG. 4. $\varepsilon(T)$ at 75 kHz near $T_M$ at (□) 0 T and (●) 5 T.

Perovskite EuTiO$_3$

Eu$^{2+}$(4f$^7$) and Ti$^{4+}$(3d$^0$)

• Similar with SrTiO$_3$ and BaTiO$_3$ both in terms of crystal and electronic structures

• Eu$^{2+} \rightarrow$ AF ordering at $T_N=5.5$K
Electron doping into the Ti $d$ state of EuTiO$_3$

AFM of Eu spins at 5.5 K $\rightarrow$ FM ordering at 8 K

\[ \text{Resistivity (\(\mu\Omega \text{ cm}\))} \]

\[ \text{Temperature (K)} \]

\[ x = 0 \]

\[ x > 0 \]

\[ \text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3 \]

\[ \text{Eu}_{0.9}\text{La}_{0.1}\text{TiO}_3 \]
Large dielectric constant in EuTiO$_3$.

Barrett’s formula:

\[ \varepsilon = A + \frac{C}{(T_1 / 2) \coth(T_1 / 2T) - T_0} \]

\[ T_1 = 162\text{K}, \quad T_0 = -25\text{K} \]

→ a quantum paraelectric state
Large magnetic-field dependence of dielectric constant

T. Katsufuji et al.
$\Delta \varepsilon = 7\%$ under 1.5 T
Dielectric constants decrease with AF ordering and increase when F aligned with magnetic field. The change of dielectric constants can be related to the pair correlation of neighboring Eu spins, $<S_i \cdot S_j>$.

→ Mean-field calculation

$<S_i \cdot S_j> = <S_i><S_j>$
Estimation of spin-spin interactions

\[ J_1 = -0.037 K \]
\[ J_2 = 0.069 K \]

\[ T_N = 5.5 \text{ K} \]
\[ \theta = 3.17 \text{ K} \]

EuTiO\textsubscript{3}

\[ \frac{1}{\chi} \text{ (mol/cm}^3\text{)} \]

1
2
3
4

Temperature (K)

0
10
20
30

\[ J_1 \quad J_2 \]

Eu

Ti

O
Spin pair correlation (calc.) and dielectric constants (exp.)

\[ \mathcal{E}(T, H) = \mathcal{E}_0(T) \left( 1 + \alpha \langle S_i \cdot S_j \rangle \right) \]

J. T. H. T. S. S. \( J_1 = 0.037 \text{ K} \)
J. T. H. T. S. S. \( J_2 = 0.069 \text{ K} \)

0 T
1 T
3 T
5 T
0 T
1 T
3 T
5 T
EuTiO\(_3\)

T. Katsufuji \textit{et al.}
Magnetic moment (calc. and exp.)

\( \langle S^z \rangle \) vs. \( T \) for different fields:
- \( 5 \) T
- \( 3 \) T
- \( 1 \) T
- \( 0.01 \) T

\( M \) vs. \( T \) for different fields:
- \( 5 \) T
- \( 3 \) T
- \( 1 \) T
- \( 0.01 \) T

**Calculation**:
- \( J_1 = ? \) .037 K
- \( J_2 = 0.069 \) K

**Experiment**:

T (K)

0 10 20 30
\[ \varepsilon(T, H) = \varepsilon_0(T) \left( 1 + \alpha \langle S_i \cdot S_j \rangle \right) \]

\[ \varepsilon(\omega) = \varepsilon_1(\omega) - i \varepsilon_2(\omega) = \varepsilon_\infty + \frac{4\pi N e^*}{\mu} \frac{\omega^2}{\omega_{ph}^2 - \omega^2} + i \Gamma \omega \]

\[ \omega_{ph} = \omega_0 - \Delta \langle S_i \cdot S_j \rangle \]

\[ \alpha = \frac{2\Delta}{\omega_0} \]

Ferromagnetic → softening
Anfiferromagnetic → hardening
If $\omega_0$ can be further lowered, $\alpha$ can be larger.

\[ \alpha = \frac{2\Delta}{\omega_0} \]
Dielectric constant is enhanced with Ba doping.
Magnetocapacitance is suppressed with Ba doping

T. Katsufuji et al.
Importance of dynamical fluctuation of electric dipole

Appearance of quasi-static ferroelectric domains

Ba doping $\rightarrow$ disorder

$$\alpha = \frac{2\Delta}{\omega_0}$$
Magnetocapacitance and spin fluctuation

\[ \varepsilon(T, H) = \varepsilon_0(T) \left( 1 + \alpha \langle S_i \cdot S_j \rangle \right) \]

\[ \frac{\varepsilon(T, H)}{\varepsilon(T, 0)} - 1 = \frac{1 + \alpha \langle S_i \cdot S_j \rangle_H}{1 + \alpha \langle S_i \cdot S_j \rangle_0} - 1 \]

In the paramagnetic phase, if spin fluctuation can be ignored,

\[ \langle S_i \cdot S_j \rangle_H = \langle M \rangle_H^2 \quad \langle S_i \cdot S_j \rangle_0 = 0 \]

\[ \therefore \frac{\varepsilon(H)}{\varepsilon(0)} - 1 = \alpha \langle M \rangle_H^2 \]

Magnetocapacitance should scale \( M^2 \) in the PM phase if spin fluctuation is negligible.
In EuTiO$_3$, $\varepsilon(T,5T)/\varepsilon(T,0T) - 1 \propto \langle M \rangle_{5T}^2$ holds true

Deviation of $\varepsilon(H)/\varepsilon(0) - 1$ from $\langle M \rangle_H^2$ indicates that $\langle S_i \cdot S_j \rangle_0$ cannot be ignored $\rightarrow$ spin fluctuation (AF or F)

$$\varepsilon(T,H)/\varepsilon(T,0) - 1 = \frac{1 + \alpha\langle S_i \cdot S_j \rangle_H}{1 + \alpha \langle S_i \cdot S_j \rangle_0} - 1$$

pyrochlore $R_2Ti_2O_7$ · geometrical spin frustration

$R=Ho$
Ferromagnetic interaction, Ising spin (spin ice)

$R=Gd$
Antiferromagnetic interaction, Heisenberg spin
$T$ dependence of dielectric constant in $R_2\text{Ti}_2\text{O}_7$
\( \text{Ho}_2\text{Ti}_2\text{O}_7 \)  
\( \varepsilon(H)/\varepsilon(0) - 1 < \alpha \langle M \rangle_H^2 \)  
\( \rightarrow \text{FM correlation} \)  
\( \langle S_i \cdot S_j \rangle_{0T} > 0 \)  

\( \varepsilon(H) \approx \varepsilon(0) \rightarrow \text{Locally ferromagnetic arrangement at low T (2in 2out)} \)

$\text{Gd}_2\text{Ti}_2\text{O}_7$ 

$\varepsilon(H)/\varepsilon(0) - 1 < \alpha \langle M \rangle_H^2$

$\rightarrow$ AF correlation 

$\langle S_i \cdot S_j \rangle_{0T} < 0$

Spinel $\text{ZnFe}_2\text{O}_4$

$S=5/2$ on the Fe site

Geometrical frustration $\rightarrow$ No long-range magnetic ordering


K. Kamazawa et al., PRB 68, 024412 (2003)
Temperature and magnetic-field dependence of $\varepsilon_1$

$$\varepsilon(H) / \varepsilon(0) - 1 < \alpha \left\langle M \right\rangle_H^2$$

→ AF correlation $\left\langle S_i \cdot S_j \right\rangle_{0T} < 0$

Crystal structure of hexagonal $RMnO_3$

Coexistence of Ferroelectricity along $c$ ($T_c>1000K$) and Magnetism ($T_N\sim70K$)

tilting of three MnO$_5$ bipyramids towards the oxygen at the center

trimer” formation of Mn ions
Critical decrease of in-plane dielectric constant at $T_N$

Evidence of strong magnetodielectric coupling

\[ \varepsilon = \varepsilon_0 \left( 1 + \alpha \langle S_i \cdot S_j \rangle \right) \]

No relation with ferroelectric moment along $c$

No magnetocapacitance due to a small magnetic susceptibility

To have a large magnetocapacitance...

You need both

Large magnetodielectric coupling

\[ \text{Large } \alpha \text{ in } \varepsilon = \varepsilon_0 \left( 1 + \alpha \langle S_i \cdot S_j \rangle \right) \]

and

Large magnetic susceptibility \( \chi \)
Enhancement of magnetic susceptibility with doping

Y. Aikawa and TK et al.,

T. Katsufuji et al.,
But doping suppresses the anomaly of $\varepsilon(T)$

Y. Aikawa and TK et al.,
Magnetocapacitance is not drastically enhanced with doping.

Y. Aikawa and TK et al.,
Summary of the first part

Large magnetocapacitance in EuTiO$_3$ was observed.

Spin pair correlation $\langle S_i \cdot S_j \rangle$ dominates the magnetodielectric coupling.

Information on spin fluctuation can be obtained by measuring magnetocapacitance and magnetization.

Both large magnetodielectric coupling and large magnetic susceptibility are necessary for large magnetocapacitance.
Localized $d$ electrons still have the freedom of which $d$ states to occupy.
Coupling between various degrees of freedom

- Electric field ($E$)
- Magnetic field ($H$)
- Stress ($X$)
- Spin degree of freedom
- Orbital degree of freedom
- Charge degree of freedom

- Polarization ($P$)
  - ferroelectricity
- Magnetization ($M$)
- Distortion ($u$)
- Stress ($X$)

ferromagnetism
ferroelasticity
Spinel MnV$_2$O$_4$

Mn$^{2+}$ (3d$^5$, without ODF)
V$^{3+}$ (3d$^2$, with ODF)

$A$ — tetrahedral site
$B$ — octahedral site

$S=5/2$  $S=1$
Why we love spinel structure AB$_2$O$_4$?

**Cubic symmetry**
- cf. Perovskite (GdFeO$_3$ distortion)

**Large transfer integral of the $t_{2g}$ orbital**
- at the B site (edge-shared BO$_6$)

**Two inequivalent sites (A & B) that can accommodate transition metals**
- → ferrimagnetic state

**If the valence of A is an odd number, the valence of B becomes half integer without any substitution**
- → charge ordering (ex. AlV$_2$O$_4$)

Y. Horibe et al., PRL 96, 086406 (2006)
Strain and magnetization in MnV$_2$O$_4$

Strain

Magnetization

MnV$_2$O$_4$ single crystal
$\Delta L \parallel [100]$

Cub.

Tetra.

Ferri

Spontaneous magnetization along the $c$ axis

Mn$^{2+}$

Ferrimagnetic ordering $=$ structural phase transition $=$ 57 K

Plumier et al., SSC 64, 53 (1987)

X-ray diffraction of MnV$_2$O$_4$ single crystal

MnV$_2$O$_4$

$T_N = 57$ K

$(440)_c$

$(404)_c = (224)_t$

$(440)_c = (400)_t$

$T_N = 57$ K

Cub.

Tetra.

Cub.

Tetra.

$a > c$

M

lattice constants (\(\AA\))

Intensity (arb. unit)

Temperature (K)

MnV$_2$O$_4$

Cub.

cooling

warming
Magnetic-field-induced structural phase transition in MnV\textsubscript{2}O\textsubscript{4}

$T$ dependence of strain

$H$ dependence of strain

T. Suzuki and TK et al.,
X-ray diffraction with $H$ and $M$ vs $H$

$T=59$ K $> T_N$

Paramag, Cubic

Ferrimag, Tetra

$M$ vs $H$

$M$ (emu/mol)

$H$ (T)

MnV$_2$O$_4$

single crystal

$T_H$

$56K$

$57K$

$58K$

$59K$

$60K$

$61K$

$62K$
Impurity doping: \( \text{Mn(V}_{1-x}\text{Al}_x)\text{O}_4 \rightarrow \) Structural anomaly disappears but Ferrimagnetic phase survives

\[
\begin{align*}
\text{Strain} & \quad \Delta L/L \ (\times 10^{-3}) \\
\text{Magnetization} & \quad M/H \ (\text{cm}^3/\text{mol}) \\
\end{align*}
\]

\( x=0.1 \)
\( x=0.05 \)
\( x=0 \)


Structural phase transition is a cooperative phenomenon
Domain alignment in MnV$_2$O$_4$ with $H$

$c$ axis is preferably oriented along $H$.

Large magnetostriction caused by the domain alignment.

Large magnetostriction caused by the domain alignment.
Magnetic-field dependence of strain and dielectric constant

Domain alignment + Anisotropy of dielectric constant

Dielectric constant

\[ \varepsilon \]

\[ T_N \]

MnV\textsubscript{2}O\textsubscript{4} polycrystal

\[ E//H \]

\[ E \perp H \]

Strain

\[ \Delta L/L \times 10^{-3} \]

\[ 5T (\Delta L \perp H) \]

\[ 0T \]

\[ 5T (\Delta L // H) \]

MnV\textsubscript{2}O\textsubscript{4}

Temperature (K)

Temperature (K)
Theoretical models of orbital ordering in spinel vanadates

Tsunetsugu-Motome
PRB 68, 060405 (2003)

Khomskii-Mizokawa
PRL 94, 156402 (2005)

Tchernyshyov
PRL 93, 157206 (2004)

t_{2g} orbital

cubic tetragonal

$d$-glide $a>c$

$z^x y^z x^y c$

$c f c$

$P 4_1 2_1 2$

$I 4_1 /a$

$I 4_1 /amd$

cf. ZnV$_2$O$_4$

no large single crystal is available
Orbital ordering of MnV$_2$O$_4$ by x-ray diffraction

<table>
<thead>
<tr>
<th></th>
<th>d-glide</th>
<th>fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsunetsugu-Motome($I4_1/a$)</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>Khomskii-Mizokowa($P4_12_12$)</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Tchernyshyov ($I4_1/amd$)</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

“Antiferro” orbital ordering

T. Suzuki and TK et al.,
Kugel-Khomskii interaction — interiomic spin-orbital interaction

If electrons exit at the same orbital, the total energy becomes lower if spins are aligned to the opposite direction

Orbital Ferro
Spin Antiferro

If electrons exit at the different orbitals, the total energy becomes lower if spins are aligned to the same direction

Orbital Antiferro
Spin Ferro

Hund energy
Origin of simultaneous spin/orbital ordering in MnV$_2$O$_4$

Ferrimagnetic ordering caused by the Mn-V antiferromagnetic interaction

\[ \text{Mn} \]

V$_2$ \[ \uparrow \] \[ \uparrow \] V$_1$

“Ferromagnetic” alignment of the V spins

favors the “antiferro-orbital” configuration between neighboring V sites through the Kugel-Khomskii interaction

Antiferro-orbital ordering (Tsunetsugu-Motome)

antiferromagnetic canting of the V spins for the ferro-orbital bond
Spinel FeV$_2$O$_4$

Fe$^{2+}$ (3d$^6$, with ODF)
V$^{3+}$ (3d$^2$, with ODF)

S=2
S=1
Crystal structure and magnetism in FeV$_2$O$_4$

Magnetization

Inverse $\chi$

Strain

FeV$_2$O$_4$

Ortho.

Tetra.

Cub.

Tetra.

Ortho.

Cub.

$L/T_n$

$L/L_c$ ($\times 10^{-3}$)

Temperature (K)

Magnetization ($\text{cm}^3/\text{mol}$)

Inverse $\chi$ ($\text{cm}^3/\text{mol}$)

Lattice const. (Å)

$c > a$

unique in FeV$_2$O$_4$

ZnV$_2$O$_4$

FeCr$_2$O$_4$

cf. M. Tanaka et al., JPSJ 21, 262 (1966)
Local distortion of FeO$_4$ tetrahedra and VO$_6$ octahedra

T. Katsufuji et al.,
“Colossal” magnetostriction in FeV$_2$O$_4$ ($\sim$1\%)
Long axes are preferably oriented along $H$.
Mechanism of successive structural phase transitions in FeV$_2$O$_4$

**HT Tetragonal(para) →** $a$ is the easy axis

Jahn-Teller distortion of FeO$_4$ = contraction along $c$ → energy of $z^2$ state becomes lower → spin exists in the $x^2$-$y^2$ state → $a$ axis becomes the easy axis

**Orbital-driven structural phase transition**

**LT Tetragonal(Ferri) →** $c$ is the easy axis

Orbital ordering of V → V spin is aligned along the $c$ axis → Fe spin is also along $c$ → spin exists in the $z^2$ state of Fe → FeO$_4$ is elongated along $c$ so that the energy of the $x^2$-$y^2$ state is lower

**Spin-driven structural phase transition**
Summary of successive structural phase transitions in FeV$_2$O$_4$

<table>
<thead>
<tr>
<th>$T &lt; T_N$</th>
<th>$T &gt; T_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LT tetragonal</strong></td>
<td><strong>HT tetragonal</strong></td>
</tr>
<tr>
<td><strong>Orthorhombic</strong></td>
<td><strong>Fe</strong> $z^2$ $z$ $x^2-y^2$</td>
</tr>
<tr>
<td>Fe $z^2$ $z$ $x^2-y^2$</td>
<td>$x^2-y^2$ Fe $z$</td>
</tr>
<tr>
<td>Ferrimagnetic ordering</td>
<td>$y_z$ $z_x$ $y_v$ $x_y$</td>
</tr>
</tbody>
</table>
Spinel $\text{Mn}_3\text{O}_4 \rightarrow \text{Mn}^{2+}\text{Mn}^{3+}_{2}\text{O}_4$

Mn$^{2+}$ (3d$^5$, no ODF)
Mn$^{3+}$ (3d$^4$, with ODF)

Structural phase transition (cubic $\rightarrow$ tetragonal) $> 1000$ K

Ferrimagnetic ordering at 43K
Spin structures in $\text{Mn}_3\text{O}_4=\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$

$T_N = 43 \text{ K} : \text{Yafet-Kittel (coplanar)}$

$T^{*}_1 = 39 \text{ K} : \text{Incommensurate (spiral)}$

$T^{*}_2 = 34 \text{ K} : \text{Cell-double (coplanar)}$

Anisotropy of magnetization in Mn$_3$O$_4$

Easy axis = (110)
Weak anisotropy along the $ab$ plane
c axis(001) is the strongly hard axis
Change of dielectric constant and strain with ferrimagnetic ordering in Mn$_3$O$_4$

Dielectric constant

Strain

$T^*_2=34$ K : Cell-double
$T^*_1=39$ K : Incommensurate
$T_N=43$ K : Yafet-Kittel
Magnetocapacitance in Mn$_3$O$_4$ along the $c$ axis

Magnetocapacitance and magnetostriction along the $ab$ plane

Difference of magnetocapacitance at different magnetic phases

\[ \Delta \varepsilon_1(H) \] vs Magnetic Field (T)

- **Cell-double**
  - \( E \parallel [100] \)
  - \( H \parallel [010] \)
  - \( \varepsilon_1(H) / \varepsilon_1(0) - 1 \)
  - Temperatures: 10 K, 5 K, 30 K, 34 K, 35 K

- **IC phase**
  - \( E \parallel [100] \)
  - \( H \parallel [100] \)
  - \( \varepsilon_1(H) / \varepsilon_1(0) - 1 \)
  - Temperatures: 36 K, 38 K, 41 K, 50 K

- **Yafet-Kittel**
  - \( E \parallel [100] \)
  - \( H \parallel [100] \)
  - \( \varepsilon_1(H) / \varepsilon_1(0) - 1 \)
  - Temperatures: 42 K, 50 K, 41 K, 38 K, 37 K
Similar $M(H)$ curves at different magnetic phases
Mechanism of magnetocapacitance in Mn$_3$O$_4$

Incommensurate phase

x$^2$ orbital and y$^2$ orbital are mixed with z$^2$ orbital by the inverse process of single-ion spin anisotropy

Origin of anisotropy

"z$^2$-$\delta x^2$" orbital

single-ion spin anisotropy

Mn$^{3+}$

Mn$^{2+}$

Mn$^{3+}$

Mn$^{3+}$
Summary of the second part

Simultaneous spin/orbital ordering by Kugel-Khomskii interaction in MnV$_2$O$_4$

Successive structural phase transitions by the competition and cooperation between Fe$^{2+}$ orbital and V$^{3+}$ orbital in FeV$_2$O$_4$

Magnetocapacitance by the inverse process of single-ion spin anisotropy in Mn$_3$O$_4$
References

EuTiO$_3$

R$_2$Ti$_2$O$_7$

ZnFe$_2$O$_4$

YMnO$_3$

MnV$_2$O$_4$

FeV$_2$O$_4$

Mn$_3$O$_4$