Magnetoelectric Properties of Multiferroic $R\text{MnO}_3$

Thomas Lottermoser
Tsukuba, March 2004
Multiferroics and the Magnetoelectric Effect

Nonlinear Optics

Hexagonal Manganites

Experimental Results

Summary
Compounds with simultaneous (anti-)ferromagnetic, ferroelectric and/or ferroelastic ordering (Aizu 1969)

⇒ Multiferroics

1958 Idea of new compounds with coexisting magnetic and electric ordering by Smolenskii and Ioffe
1966 First experimental proof of a “multiferroic effect“ by Ascher et al.
1975 Suggestions for technical applications based on multiferroic properties by Wood and Austin
...

2000 “Why are there so few magnetic ferroelctrics?“ by Hill
Linear Magnetoelastic Effect

Polarization and magnetization of a medium:

\[ P_i = \epsilon_0 \chi_{ij}^e E_j \cdot M_i = \chi_{ij}^m H_j \]

Covariant relativistic formulation:

\[ \mu_0 c M^{\alpha \beta} = \frac{1}{2} \xi_{\mu \nu}^{\alpha \beta} F^{\mu \nu} \]

with:

\[ F^{\mu \nu} = \begin{pmatrix}
0 & -E_x & -E_y & -E_z \\
E_x & 0 & -cB_z & cB_y \\
E_y & cB_z & 0 & -cB_x \\
E_z & -cB_y & cB_x & 0
\end{pmatrix} \]

Relativistic equivalence of electric and magnetic fields requires "magneto-electric" cross-correlation (~ \( \alpha \)) in matter:

\[ P_i = \epsilon_0 \chi_{ij}^e E_j + \frac{1}{c} \alpha_{ij} H_j \]

\[ M_i = \chi_{ij}^m H_j + \frac{1}{\mu_0 c} \alpha_{ij} E_j \]

1960:

- Small effect (10^{-5})
- Limited choice of compounds
- Theoretically not well understood

2000:

- New materials with structural (heterostructures) or gigantic (multiferroic) magnetoelastic effects
- New theoretical concepts

Magnetoelectric Properties of Multiferroic \( RMnO_3 \)
Magnetoelectric Properties of Multiferroic $RMnO_3$

- Multiferroics and the Magnetoelectric Effect
- Nonlinear Optics
- Hexagonal Manganites
- Experimental Results
- Summary
In general: Multipole expansion of source term $\vec{S}$ for SHG:

$$\vec{S} = \mu_0 \frac{\partial^2 \vec{P}^{NL}}{\partial t^2} + \mu_0 \left( \nabla \times \frac{\partial \vec{M}^{NL}}{\partial t} \right) - \mu_0 \left( \nabla \frac{\partial^2 \vec{Q}^{NL}}{\partial t^2} \right)$$

⇒ Three nonlinear contributions:

- **Electric dipole (ED):**
  $$\vec{P}^{NL}(2\omega) \propto \hat{\chi}^{ED} : \vec{E}(\omega) \vec{E}(\omega)$$

- **Magnetic dipole (MD):**
  $$\vec{M}^{NL}(2\omega) \propto \hat{\chi}^{MD} : \vec{E}(\omega) \vec{E}(\omega)$$

- **Electric quadrupole (EQ):**
  $$\vec{Q}^{NL}(2\omega) \propto \hat{\chi}^{EQ} : \vec{E}(\omega) \vec{E}(\omega)$$

**SH source term**

$$S_i(2\omega) \propto \chi_{ijk} E_j(\omega) E_k(\omega)$$

**SH intensity**

$$I_{SH} \propto |S(c) + S(i)|^2$$

$$\propto |\chi(c) + A e^{i\psi} \chi(i)|^2 I^2(\omega)$$

$$= (\chi^2(c) + A^2 \chi^2(i)) + 2A \chi(c) \chi(i) \cos \psi) I^2(\omega)$$

always > 0  interference term

Amplitude A and phase $\psi$ can be controlled in the experiment.
Experimental Setup

Basic setup with a pulsed Nd:YAG - OPO laser system (3 ns, ≤100 Hz, 0.4 - 3.0 μm)
Phase Resolved SH Imaging

Achromatic beam imaging of sample onto reference crystal in phase measurements

Holographic interference of SH signal from sample and SH reference wave from quartz crystal → amplitude and phase of signal wave

Phase-Resolved SH Imaging (Results)

Visibility nearly 100%

Loss of spatial coherence fully compensated!

Advantages:

• Allows use of broadband laser sources with poor beam quality
• Large working distances (~1 m)
• More experimental freedom
• Improved image quality

SHG on Ferroelectric HoMnO₃ Domains

- 180° phase difference between SH contributions from opposite FEL domains
- 90° phase shift and drastic decrease of SH intensity in unpoled region
- Many samples exhibit asymmetry with respect to the direction of the poling field
- Multiferroics and the Magnetoelectric Effect
- Nonlinear Optics
- Hexagonal Manganites
- Experimental Results
- Summary
**Multiferroic Manganites $RMnO_3$**

First publications by Yakel and Bertaut on ferroelectric and antiferromagnetic properties in 1963

Dramatic increase of worldwide interest:
Groups in Canada, Germany, Japan, Korea, Netherlands, Russia, Spain, USA,...

Main topics:
- Crystallographic and magnetic structure
- Thin films and ferroelectric properties (→ application)
- Multiferroic/magnetoelectric properties

Hexagonal manganites $RMnO_3$ ($R = \text{Sc, Y, In, Ho, Er, Tm, Yb, Lu}$)

$T < T_C \approx 600-1000 \text{ K} \Rightarrow$ ferroelectric (FEL) + paramagnetic (PM)

$T < T_N \approx 70-130 \text{ K} \Rightarrow$ ferroelectric (FEL) + antiferromagnetic (AFM)

$T < T_{RE} \approx 5 \text{ K} \Rightarrow$ FM or AFM order of $R^{3+}$-spins for $R = \text{Ho - Yb}$
Crystallographic and Magnetic Structure

Ferroelectric phase transition:

Breaking of inversion symmetry $I$!

Order parameter: $P$

Antiferromagnetic phase transition of the Mn$^{3+}$ sublattice:

Breaking of time-reversal symmetry $T$, but not of inversion symmetry $I$!

Order parameter: $\ell$
Magnetic Structure and SHG Selection Rules

At least 8 different triangular in-plane spin structures with different magnetic symmetries and different selection rules for SHG:

**α structures:** SHG for $k\parallel z$ allowed

- $\alpha_x$ ($\varphi = 0^\circ$): $\chi_{xxx} = 0$, $\chi_{yyy} \neq 0$
- $\alpha_y$ ($\varphi = 90^\circ$): $\chi_{xxx} \neq 0$, $\chi_{yyy} = 0$
- $\alpha_\rho$ ($\varphi = 0\text{-}90^\circ$): $\chi_{xxx} \propto \sin \varphi$, $\chi_{yyy} \propto \cos \varphi$

**β structures:** SHG for $k\parallel z$ not allowed

- $\beta_x$, $\beta_y$, $\beta_\rho$: $\chi_{xxx} = 0$, $\chi_{yyy} = 0$

**Determine β structure from α-β transition**

- $\alpha_x \rightarrow \beta_y$: $\chi_{xxx} = 0$, $\chi_{yyy} \propto \cos \varphi$
- $\alpha_y \rightarrow \beta_x$: $\chi_{xxx} \propto \sin \varphi$, $\chi_{yyy} = 0$

Contrary to diffraction techniques: α and β models clearly distinguishable!
Magnetoelectric Properties of Multiferroic \( \text{RMnO}_3 \)

- Multiferroics and the Magnetoelectric Effect
- Nonlinear Optics
- Hexagonal Manganites
- Experimental Results
- Summary
The magnetic symmetry, *not* the R ion, determines the SH spectrum of $R\text{MnO}_3$.
Phase Coexistence and Spin Topography in ScMnO₃

Spin - angle topography

SH energy (eV)

SH intensity

P6₃cm

T = 1.5 K

|χ_{xxx}|²

|χ_{yyy}|²

P6₃cm

T = 1.5 K

P6₃

T = 1.5 K

Magnetic Symmetry of Hexagonal $RMnO_3$

Second harmonic generation is the only technique capable of the determination of this magnetic phase diagram!

$RMnO_3$

$\alpha_x \ (P\ 6_3\ cm)$

$\alpha_y \ (P\ 6_3\ cm)$

5.833 Å — In-plane lattice constant — 6.155 Å

Two-dimensional expansion of the SH susceptibility $\chi$ for electric and magnetic order parameters

$$\vec{P}^{NL}(2\omega) = \varepsilon_0 \left[ \hat{\chi}(0) + \hat{\chi}(\phi) + \hat{\chi}(\ell) + \hat{\chi}(\phi \ell) + \ldots \right] \vec{E}(\omega) \vec{E}(\omega)$$

$\chi(0)$: Paraelectric paramagnetic contribution — always allowed

$\chi(\mathcal{P})$: (Anti)ferroelectric contribution — allowed below

$\chi(\ell)$: (Anti)ferromagnetic contribution — the respective ordering temperature

$\chi(\mathcal{P}\ell)$: Ferroelectromagnetic contribution

- SHG allows simultaneous investigation of magnetic and electric structures
- Selective access to electric and magnetic sublattices
- Ferroelectromagnetic contribution reveals the magneto-electric interaction between the sublattices
# Symmetry analysis

<table>
<thead>
<tr>
<th>Ordered Sublattice</th>
<th>Space group</th>
<th>Parity - type symmetry operation</th>
<th>Order parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(para)</td>
<td>P\textsubscript{6_3/mmc}</td>
<td>I, T, IT</td>
<td>---</td>
</tr>
<tr>
<td>FEL</td>
<td>P\textsubscript{6_3cm}</td>
<td>T</td>
<td>( \mathcal{P} )</td>
</tr>
<tr>
<td>AFM</td>
<td>P\textsubscript{6_3/mcm}</td>
<td>I</td>
<td>( \ell )</td>
</tr>
<tr>
<td>FEL + AFM</td>
<td>P\textsubscript{6_3cm}</td>
<td>---</td>
<td>( \mathcal{P} \cdot \ell )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( k \parallel x )</th>
<th>( S^E_D(\mathcal{P}) )</th>
<th>( S^M_D(\ell) )</th>
<th>( S^E_Q(\ell) )</th>
<th>( S^E_D(\mathcal{P} \cdot \ell) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_y )</td>
<td>( 2i_1E_yE_z )</td>
<td>---</td>
<td>---</td>
<td>( e_1E_y^2 )</td>
</tr>
<tr>
<td>( S_z )</td>
<td>( i_2E_y^2 + i_3E_z^2 )</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( k \parallel y )</td>
<td>( S_x )</td>
<td>( 2i_1E_xE_z )</td>
<td>---</td>
<td>( -2q_1E_xE_z )</td>
</tr>
<tr>
<td></td>
<td>( S_z )</td>
<td>( i_2E_x^2 + i_3E_z^2 )</td>
<td>( m_1E_x^2 )</td>
<td>( -q_2E_x^2 )</td>
</tr>
<tr>
<td>( k \parallel z )</td>
<td>( S_x )</td>
<td>---</td>
<td>( -2m_1E_xE_y )</td>
<td>( -2q_3E_xE_y )</td>
</tr>
<tr>
<td></td>
<td>( S_y )</td>
<td>( -2m_1E_xE_y )</td>
<td>( -2q_3E_xE_y )</td>
<td>( -2e_1E_xE_y )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( m_1(E_y^2 - E_x^2) )</td>
<td>( q_3(E_y^2 - E_x^2) )</td>
<td>( e_1(E_y^2 - E_x^2) )</td>
</tr>
</tbody>
</table>
Magnetoelectric Second Harmonic Generation

<table>
<thead>
<tr>
<th>Source term</th>
<th>$S^{ED}(0)$</th>
<th>$S^{ED}(P)$</th>
<th>$S^{MD,EQ}(\ell)$</th>
<th>$S^{ED}(P \ell)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sublattice sym.</td>
<td>P6$_3$/mcm</td>
<td>P6$_3$cm</td>
<td>P6$_3$/mcm</td>
<td>P6$_3$cm</td>
</tr>
<tr>
<td>SHG for $k \parallel z$</td>
<td>= 0</td>
<td>= 0</td>
<td>≠ 0</td>
<td>≠ 0</td>
</tr>
<tr>
<td>SHG for $k \parallel x$</td>
<td>= 0</td>
<td>≠ 0</td>
<td>= 0</td>
<td></td>
</tr>
</tbody>
</table>

Identical magnetic spectra for $k \parallel z$ and $k \parallel x$ indicate bilinear coupling to $P, \ell$.

Unarbitrary evidence for the first observation of "magnetoelectric SHG".

Observation of Ferroelectromagnetic Domains

- Independent ferroelectric ($\propto P$) and ferroelectromagnetic ($\propto P\ell$) domain structures; antiferromagnetic domain structure ($\propto \ell$) is not!

- "Ferroelectromagnetic domains":
  \[ P\ell = +1 \text{ for } P = \pm 1, \ell = \pm 1 \]
  \[ P\ell = -1 \text{ for } P = \pm 1, \ell = \mp 1 \]

- Any reversal of the FEL order parameter is clamped to a reversal of the AFM order parameter

- Origin: Piezomagnetic interaction between lattice distortions at the FEL domain wall and magnetization induced by the AFM domain wall decreases the free energy

Piezomagnetic contribution $H_{pm} = q_{ijk} M_i \sigma_{jk}$ with $\sigma \propto P_z \rightarrow$ higher-order magnetoelectric effect

Generation of an antiferromagnetic wall clamped to a ferroelectric wall leads to reduction of free energy.

H/T Phase Diagram of Hexagonal $RMnO_3$

Magnetoelectric Properties of Multiferroic $RMnO_3$
Gigantic magnetoelectric effect which originates in 3d-4f superexchange; triggers hidden phase transition!

**α model:** \( H_{\text{ex}}(\alpha) = 0 \) no change!

**β model:** lowers ground-state energy:

\[
H_{\text{ex}}(\beta_x) = 6\ell S^R S^Mn \left[ (A^{3m}_{zz} - A^{3m}_{zx}) - (A^3_{zx} - A^3_{zz}) \right]
\]

\[
H_{\text{ex}}(\beta_y) = 6\ell S^R S^Mn \left[ (A^{3m}_{zy} + A^{3m}_{zy}) - (A^3_{zy} + A^3_{zy}) \right]
\]

Ferroelectric distortion modifies the superexchange:

\[
\delta \hat{A} = \hat{A} - \hat{A}, \quad \delta \hat{A} = \delta \hat{A}_0 P_z
\]

Scales with order par.

Substitution leads to:

\[
H_{\text{ex}}(\beta_x) = \alpha_{zz} P_z S^R_z
\]

ME contribution
Spontaneous Magnetolectric Effect in HoMnO₃

Antiferromagnetic SH

Ferroelectric poling quenches magnetic signal!

Only Explanation:

Magnetic phase transition triggered by the internal electric field!

⇒ spontaneous magnetolectric effect!

Magnetoelectric effect only allowed for $\beta_x$ phase with ferromagnetic ordering of Ho³⁺-spins!
Magnetization Control by Electric Field in HoMnO$_3$

$H_{\text{ex}} \approx 1 \text{ T}$

$T > T_N$

$E > 0 \text{ kV/cm}$

$E < 0 \text{ kV/cm}$

$T = 1.5 \text{ K}$

Average Faraday rotation induced bei external magnetic field

Additional Faraday rotation due to phase transition induced bei external electric field

Relative rotation angle $\Delta \phi_F$

0° $\rightarrow$ 10°

Faraday rotation depends on the direction of the external electric field!

Only possible due to magnetoelectric effect!

Magnetoelectric effect only allowed for $\beta_x$ phase in HoMnO$_3$!
Magnetoelectric Properties of Multiferroic \( RMnO_3 \)

- Multiferroics and the Magnetoelectric Effect
- Nonlinear Optics
- Hexagonal Manganites
- Experimental Results
- Summary
Multiferroic hexagonal manganites $RMnO_3$ are a model substance to investigate magnetoelectric interactions in a ferroelectromagnetic material:

- Coupling of ferroelectric and antiferromagnetic order parameters leads to “magnetoelectric” SHG
- “Ferroelectromagnetic” domains due to interaction of ferroelectric and antiferromagnetic domain walls
- Magnetoelectric effect leads to spontaneous phase transition in compounds with $R = Ho – Yb$
- Control of the magnetic phase by the electric field due to magnetoelectric effect
Acknowledgment

Germany:

D. Fröhlich, M. Fiebig, St. Leute, C. Degenhard, M. Maat, S. Kallenbach, Th. Lonkai

Russia:

R.V. Pisarev, V.V. Pavlov, A.V. Goltsev

Japan:

K. Kohn, Y. Tanabe, E. Hanamura