Multiferroic Ordering of Hexagonal Manganites

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Multiferroic $RMnO_3$

Multiferroics or Ferroelectromagnets:
Materials with simultaneous long-range (anti-) ferromagnetic, ferroelectric and/or ferroeleastic order.

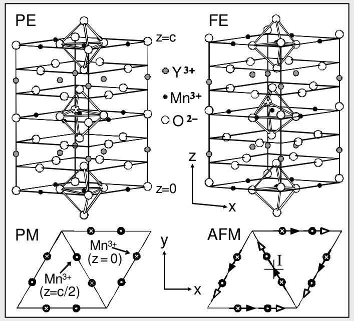
Hexagonal maganites $RMnO_3$ (R = Sc, Y, Ho, Er, Tm, Yb, Lu)

$T < T_C \approx$ 600-1000 K ⇒ ferroelectric (FEL) + paramagnetic (PM)

$T < T_N \approx$ 70-130 K ⇒ ferroelectric (FEL) + antiferromagnetic (AFM)

$T < T_{RE} \approx$ 5 K ⇒ FM or AFM order of R^{3+}-spins for R = Ho - Yb

Electric/magnetic order



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: ℓ

Optical second harmonic generation (SHG)

In general: Multipole expansion of source term $\vec{S}$ for SHG:

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

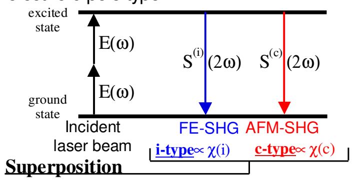
⇨ Three nonlinear contributions:

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

SHG of electric-dipole type:



Superposition

Source term for SHG: $P_i(2\omega) = \varepsilon_0 \chi^{SH}_{ijk} E_j(\omega) E_k(\omega)$

Intensity of SH signal: $I_{SH} \propto |P(c) + P(i)|^2$

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

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

always > 0 interference term

A : amplitude ratio of i-type and c-type terms

φ : phase shift between complex contributions

A and φ can be fully controlled in experiment

Susceptibility χ couples linearly to order-parameter!

Observation of ferro-electromagnetic SHG

Order	Space group	Symmetry operation	Order parameter
PE + PM	$P6_3/mmc$	I, T, IT	---
FE + PM	$P6_3cm$	T	P
PE + AFM	$P\underline{6_3}/\underline{m}c\underline{m}$	I	ℓ
FE + AFM	$P\underline{6_3}c\underline{m}$	---	$P \cdot \ell$

Expansion of coupling of SHG to the order parameters:

$$\vec{P}^{NL}(2\omega) = \epsilon_0(\hat{\chi}^{ED}(0) + \hat{\chi}^{ED}(\mathcal{P}) + \hat{\chi}^{ED}(\ell) + \hat{\chi}^{ED}(\mathcal{P}\ell))\vec{E}(\omega)\vec{E}(\omega)$$

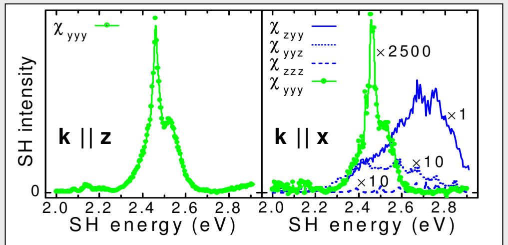
Lowest order non-zero contributions to SHG:

Zero order: Electric dipole (ED): $\hat{\chi}^{ED}(P) = i_1, i_2, i_3$ and $\hat{\chi}^{ED}(P \cdot \ell) = e_1$

First order: Magnetic dipole (MD): $\hat{\chi}^{MD}(\ell) = m_1$

First order: Electric quadrupole (EQ): $\hat{\chi}^{EQ}(\ell) = q_1, q_2, q_3$

		$\mathbf{S}^{ED}(\mathcal{P})$	$\mathbf{S}^{ED}(\mathcal{P}\cdot\ell)$	$\mathbf{S}^{MD}(\ell)$	$\mathbf{S}^{EQ}(\ell)$
k ∥ x	S_y	$2i_1E_yE_z$	$e_1E_y^2$	---	---
	S_z	$i_2E_y^2 + i_3E_z^2$	---	---	---
k ∥ y	S_x	$2i_1E_xE_z$	---	---	$-2q_1E_xE_z$
	S_z	$i_2E_x^2 + i_3E_z^2$	---	$m_1E_x^2$	$-q_2E_x^2$
k ∥ z	S_x	---	$-2e_1E_xE_y$	$-2m_1E_xE_y$	$-2q_3E_xE_y$
	S_y	---	$e_1(E_y^2 - E_x^2)$	$m_1(E_y^2 - E_x^2)$	$q_3(E_y^2 - E_x^2)$



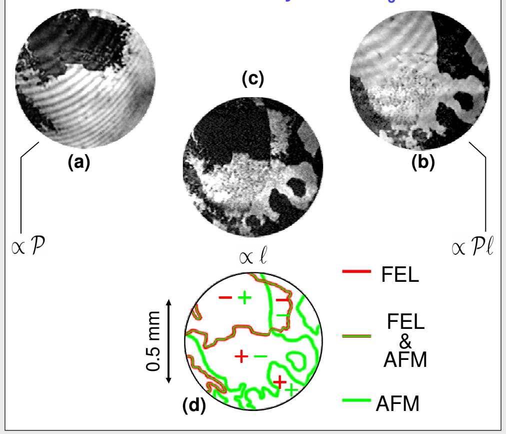
Identical magnetic spectra for k || z and k || x

⇨ **bilinear coupling to P · ℓ.**

First observation of ferroelectromagnetic (FEM) SHG!

Coexisting domains

Observed simultaneously in $YMnO_3$ at 6 K



Coexisting types of domains:

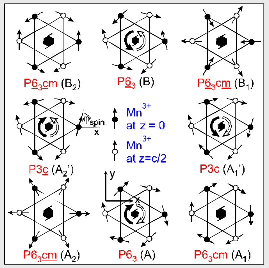
FEL: ∝ P AFM: ∝ ℓ "Magneto-electric": ∝ $P\ell$

$P\ell = +1$ for $P = \pm1$, $\ell = \pm1$ $P\ell = -1$ for $P = \pm1$, $\ell = \mp1$

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

➢ "Free" and "confined" AFM walls

Magnetic structure



α structures

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

Coupled by in-phase or anti-phase spin rotation at 0 and c/2

β structures

α structures: SHG for k||z **allowed**

B_1 (φ_{spin}= 0°): $\chi_{xxx} = 0$, $\chi_{yyy} \neq 0$

B_2 (φ_{spin}= 90°): $\chi_{xxx} \neq 0$, $\chi_{yyy} = 0$

B (φ_{spin}= 0°... 90°): $\chi_{xxx} \propto \sin\varphi_{spin}$, $\chi_{yyy} \propto \cos\varphi_{spin}$

β structures: SHG for k||z **not allowed**

A_1, A_2, A: $\chi_{xxx} = 0$, $\chi_{yyy} = 0$

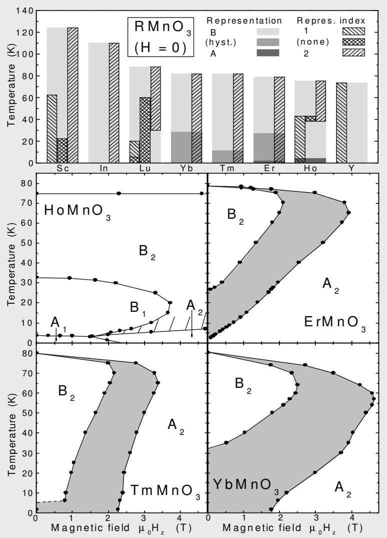
Distinction between β structures via α→β transition:

$B_1 \rightarrow A_1$ through A_1': $\chi_{xxx} = 0$, $\chi_{yyy} \propto \cos\varphi_{spin}$

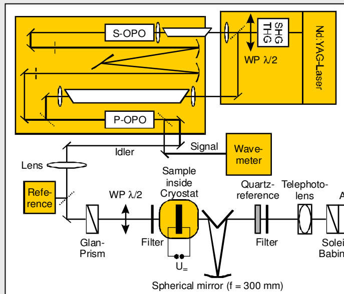
$B_2 \rightarrow A_2$ through A_2': $\chi_{xxx} \propto \sin\varphi_{spin}$, $\chi_{yyy} = 0$

Contrary to diffraction techniques: α and β clearly distinguishable!

Magnetic phase diagram



Experimental setup



Laser system:

Frequency tripeled Nd:YAG-Laser (3 ns, max. 100 Hz)

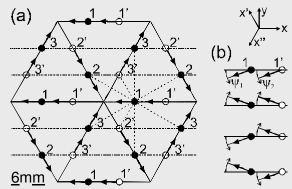
+

Optical-parametric-oscillator (OPO)

Spectral range: 400-2800 nm

SHG/THG: Second/third harmonic generation, **OPO:** Optical-parametric oscillator, **S/P-OPO:** Seed/power OPO, **WP:** Waveplate, **U=:** DC source-meter **MC:** Monochromator, **PM:** Photomultiplier, **CCD:** Camera, **PC:** Computer

Interaction of domain walls



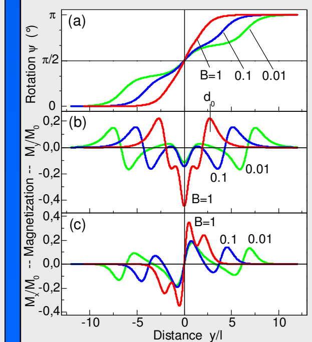
a) Exchange paths of ion 1

b) Wall types:

1. in-phase, soliton
2. in-phase, anti-soliton
3. anti-phase, soliton
4. anti-phase, anti-soliton

1,2 ~ confined AFM walls

3,4 ~ free AFM walls



Walls as topological solitons:

$$6l_\pm^2 \frac{d^2\psi}{dy^2} = \sin 6\psi + B \sin 2\psi$$

l: characteristic length

ψ: spin angle in wall

sin 6ψ: paraelectric term

sin 2ψ: ferroelectric term

B: anisotropy parameter

Piezomagnetic effect:

$H = q_{ijk} M_i \sigma_{jk}$

H: piezomagnetic energy

q_{ijk}: piezomagnetic tensor

M_i: magnetization in AFM wall

σ_{jk}: strain in FEL wall