Control of Magnetic Order by Electric Field in $HoMnO_3$

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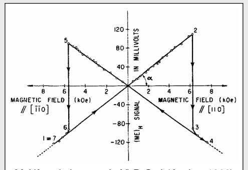
Multiferroics

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

⇒ **Multiferroics** (Aizu 1969)



Multiferroic hysteresis $Ni_3B_7O_{13}I$ (Ascher 1966)

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 multicferroic properties by Wood and Austin

...

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

Linear magnetoelectric effect

Polarization and magnetization of a medium:

$$P_i = \epsilon_0 \chi^e_{ij} E_j \qquad M_i = \chi^m_{ij} H_j$$

Covariant relativistic formulation:

$$\mu_o c M^{\alpha\beta} = \frac{1}{2}\xi^{\alpha\beta}_{\mu\nu} F^{\mu\nu}$$

with:

$$M_{\alpha\beta} = \begin{pmatrix} 0 & cP_x & cP_y & cP_z \\ -cP_x & 0 & -M_z & M_y \\ -cP_y & M_z & 0 & -M_x \\ -cP_z & -M_y & M_x & 0 \end{pmatrix}$$

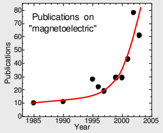
$$F_{\mu\nu} = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -cB_z & cB_y \\ E_y & cB_z & 0 & -cB_x \\ E_z & -cB_y & cB_x & 0 \end{pmatrix}$$

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

$$P_i = \epsilon_0 \chi^e_{ij} E_j \boxed{+ \frac{1}{c}\alpha_{ij} H_j} \qquad M_i = \chi^m_{ij} H_j \boxed{+ \frac{1}{\mu_o c}\alpha_{ji} E_j}$$

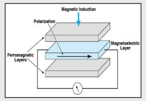
1960:

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



2000:

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



Multiferroic $RMnO_3$

Maganites $RMnO_3$ (R = Sc, Y, In, Ho, Er, Tm, Yb, Lu):

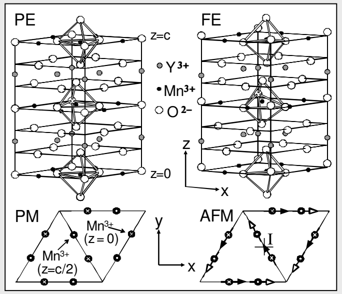
Multiferroic compunds with simultaneous ferroelctric and antiferromagnetic ordering.

Question: Results the multiferroic nature in the existence of any magnetoelectric effects?

Experimental methods:

- Second harmonic generation (SHG)
    - Polarization dependent spectroscopy
    - Nonlinear phase sensitive domain topography
- Neutron diffraction

Electric and magnetic ordering of $RMnO_3$



***R*MnO_3: A highly correlated and ordered system**

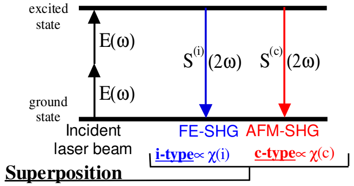
- **Paraelectric → Ferroelectric** (PEL - FEL): T_C = 570 - 990 K
- **Para- → Antiferromagnetic** (PM - AFM): T_N = 70 - 130 K

Ferroelectromagnetism: Coexisting electric and magnetic order

- Ferroelectromagnetism for R = Sc, Y, In, Ho, Er, Tm, Yb, Lu
- Additional rare-earth order at $T_C \approx 5$ K for Ho, Er, Tm, Yb

Second harmonic generation

SHG of electric-dipole type:



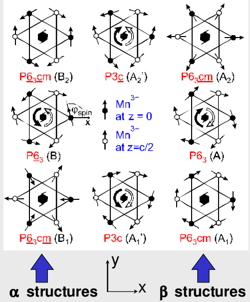
Source term for SHG: $P_i(2\omega) = \varepsilon_0 \chi^{SH}_{ijk} E_j(\omega) E_k(\omega)$

Intensity of SH signal:

$$\begin{aligned} I_{SH} &\propto |P(c) + P(i)|^2 \\ &\propto |\chi(c) + A e^{i\varphi} \chi(i)|^2 I^2(\omega) \\ &= (\underbrace{\chi^2(c) + A^2 \chi^2(i)}_{\text{always} > 0} + \underbrace{2A\chi(c)\chi(i)\cos\varphi}_{\text{interference term}}) I^2(\omega) \end{aligned}$$

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

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||z allowed**

α_x ($\varphi = 0°$): $\chi_{xxx} = 0$, $\chi_{yyy} \neq 0$
α_y ($\varphi = 90°$): $\chi_{xxx} \neq 0$, $\chi_{yyy} = 0$
α_ρ (φ = 0-90°): $\chi_{xxx} \propto \sin\varphi$, $\chi_{yyy} \propto \cos\varphi$

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

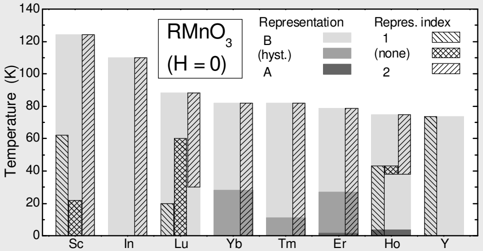
$\beta_x, \beta_y, \beta_\rho$: $\chi_{xxx} = 0$, $\chi_{yyy} = 0$

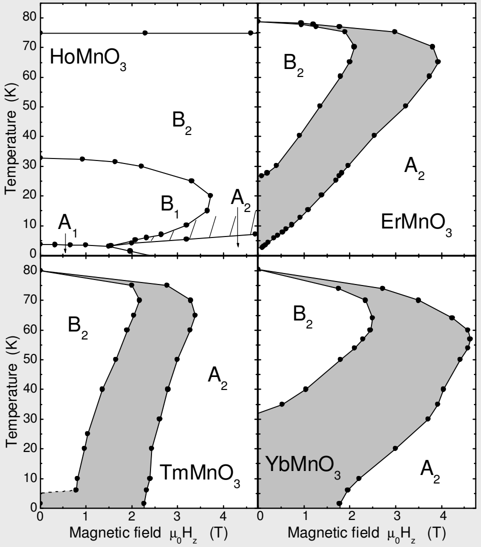
Determine β structure from α-β transition

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

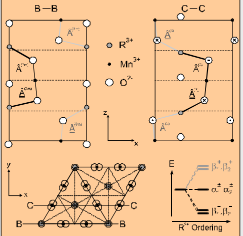
Contrary to diffraction techniques: α and β models clearly distinguishable!

H/T phase diagram





Magnetoelectric 3d-4f superexchange in $RMnO_3$



Gigantic magnetoelectric effect which originates in *3d-4f* superexchange; triggers hidden phase transition!

$$H_{ex} = \sum_{k=3m,3} \sum_{i_k=1}^{4\,(k=3)\,/\,2\,(k=3m)} \sum_{j=1}^{6} \vec{S}^{R^k(i_k)} \hat{A}^{k,i_k,j} \vec{S}^{Mn(j)}$$

k: R sites with 3 and 3m symmetries
i_k: all R ions at k sites (4+2)
j: 6 Mn ions neighboring an R ion
A: Mn-R exchange matrix (4 types)
S: spins of Mn and R ions

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

β model: lowers ground-state energy:

$$\begin{aligned} H^\ell_{ex}(\beta_x) &= 6\ell S^R S^{Mn} \left[(A^{3m}_{zx} - \underline{A}^{3m}_{zx}) - (A^3_{zx} - \underline{A}^3_{zx}) \right] \\ H^\ell_{ex}(\beta_y) &= 6\ell S^R S^{Mn} \left[(A^{3m}_{zy} + \underline{A}^{3m}_{zy}) - (A^3_{zy} + \underline{A}^3_{zy}) \right] \end{aligned}$$

Ferroelectric distortion modifies the superexchange:

$\delta\hat{A} \equiv \hat{A} - \underline{\hat{A}}$, $\delta\hat{A} = \delta\hat{A}_0 P_z$ Scales with order par.

$\alpha_{zz} \equiv 6\ell S^{Mn}_y (\delta A^{3m}_0 \pm \delta A^3_0)_{zy}$ Substitution leads to:

$H_{ex}(\beta_x) = \alpha_{zz} P_z S^R_z$ **ME contribution**

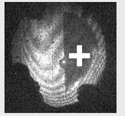
Electric field induced magnetoelectric effect

$$H_{me} = \alpha D B$$

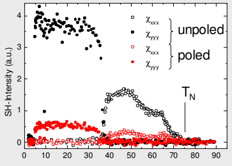
Increase of B leads to phase transition!

Increase of D?

Antiferromagnetic SH



Ferroelectric poling quenches magnetic signal!



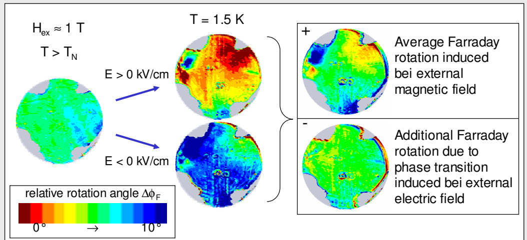
Only Explanation:

Magnetic phase transition triggered by the internal electric field!

⇒ **spontaneous magnetoelectric effect!**

Magnetoelectric effect only allowed for β_x phase with ferromagnetic ordering of Ho^{3+}-spins!

Magnetization control by electric field



Average Farraday rotation induced bei external magnetic field

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

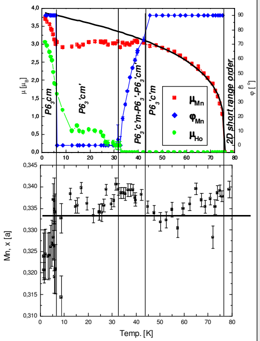
Farraday rotation depends on the direction of the external **electric** field!

Only possible due to magnetoelectric effect!

Magnetoelectric effect only alowed for β_x phase in $HoMnO_3$!

Evidence of magnetic phase transition induced by magneto-electric effect!

Neutron diffraction results



- 2D short range order above T_N due to Mn-O-Mn intra planar superexchange
- 3D long range order via Mn-O-O-Mn interplanar super-superexchange
- Antiferromagnetic in-chain alignment of Ho due to interplanar Ho-O-Ho superexchange, stabilized by DM-exchange leads to diffusive phase transition
- Intra planar Ho-ordering leads to low temperature phase transition

Change of Mn-position at low temperature phase transition:

Connected with ferroelectric distortion ||c

→ **Magnetoelectric phase transition**