Giant magnetoelectric effect in the ferroelectric antiferromagnet $HoMnO_3$

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Linear Magnetoelectric Effect

Polarization and magnetization of a medium:

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

Covariant relativistic formulation:

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

with:

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

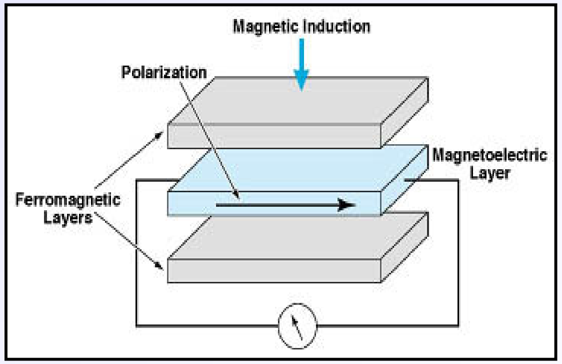
$$F_{\mu\nu} = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -cB_z & cB_y \\ E_y & cB_z & 0 & -cB_x \\ E_z & -cB_y & cB_x & 0 \end{pmatrix}$$

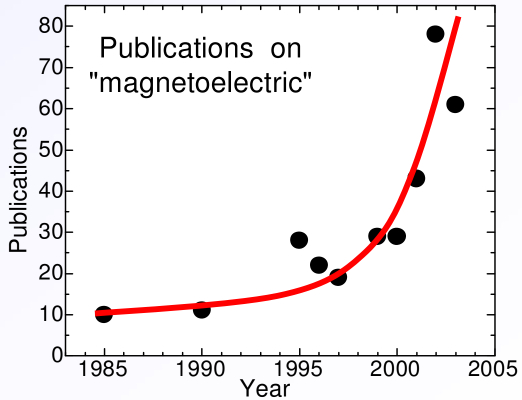
Relativistic equivalence of electric and magnetic fields requires "**magneto-electric**" cross-correlation (~ α) in matter:

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

1960:

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

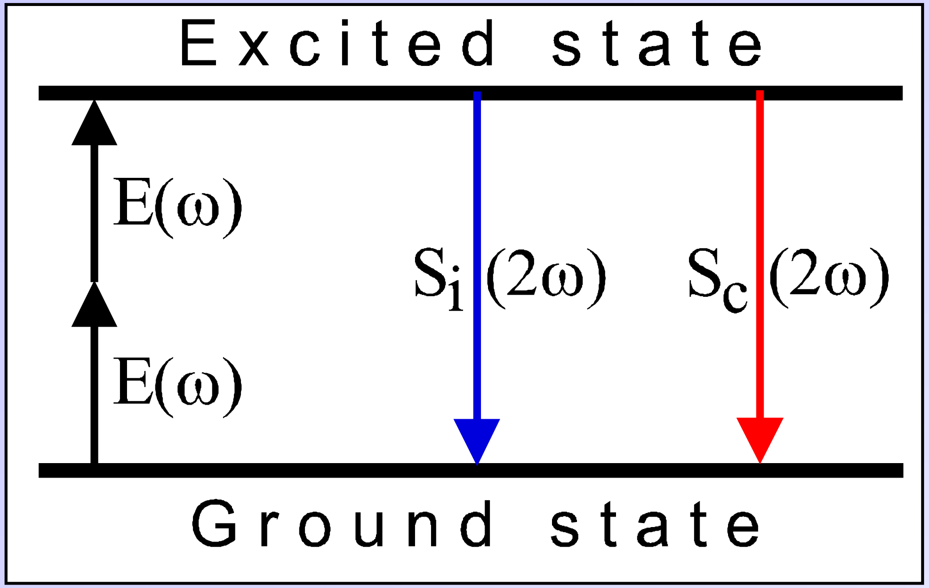




2000:

- New theoretical concepts
- "Gigantic" effects: induction of phase transitions
- New materials: multiferroics, composites, "magnetoelectricity on design"

Optical Second Harmonic Generation



Incident laser beam

Nonlinear signal:

electric, i-type $\propto \chi(i)$ magnetic, c-type $\propto \chi(c)$

Interference !

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

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

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

$$= (\underbrace{\chi^2(c) + A^2 \chi^2(i)}_{\text{always} > 0} + \underbrace{2A\, \chi(c)\, \chi(i) \cos\psi}_{\text{interference term}})\, I^2(\omega)$$

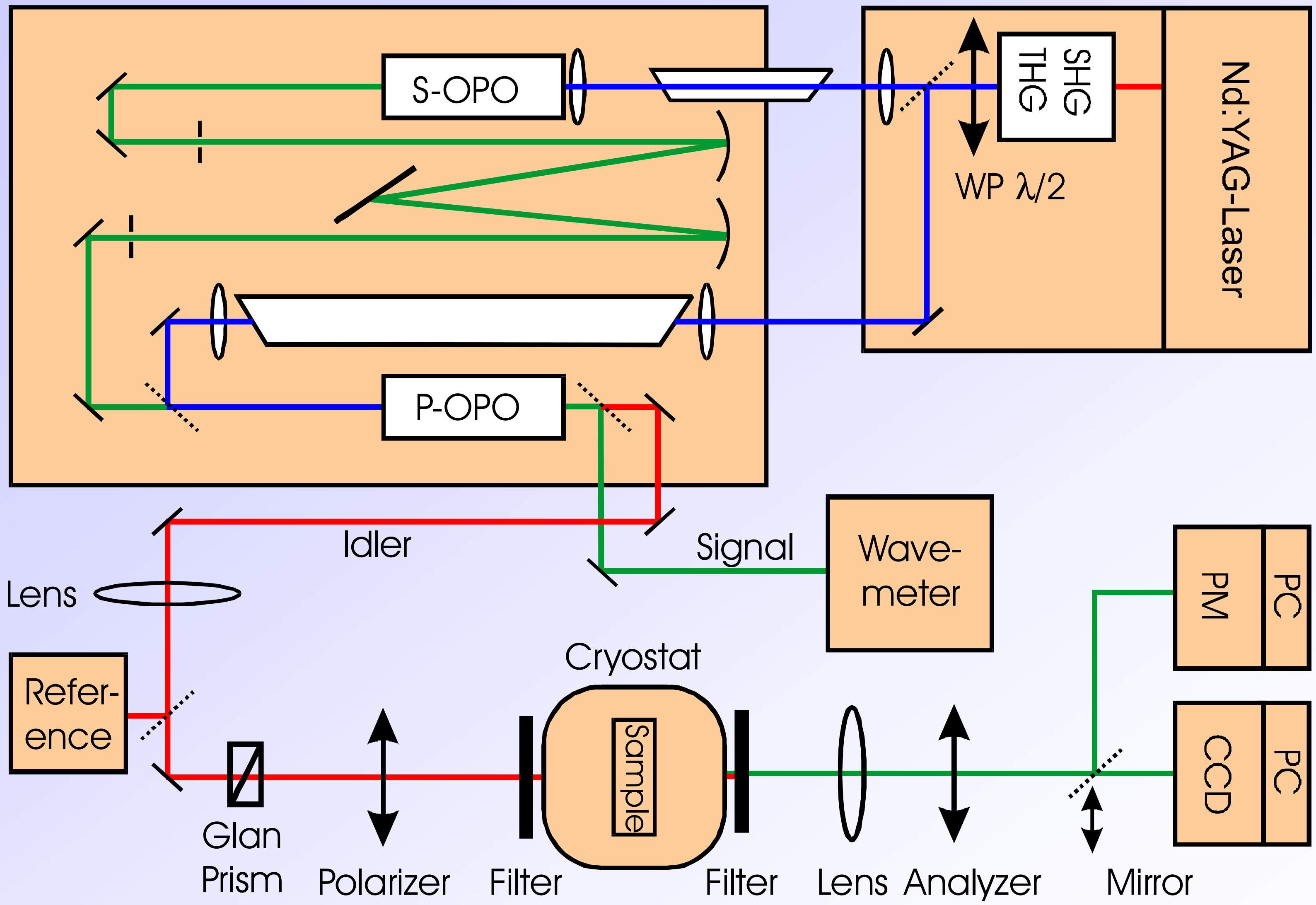
A: amplitude ratio of i- and c-type source terms

φ: phase between the complex contributions

A and φ can be controlled in the experiment.

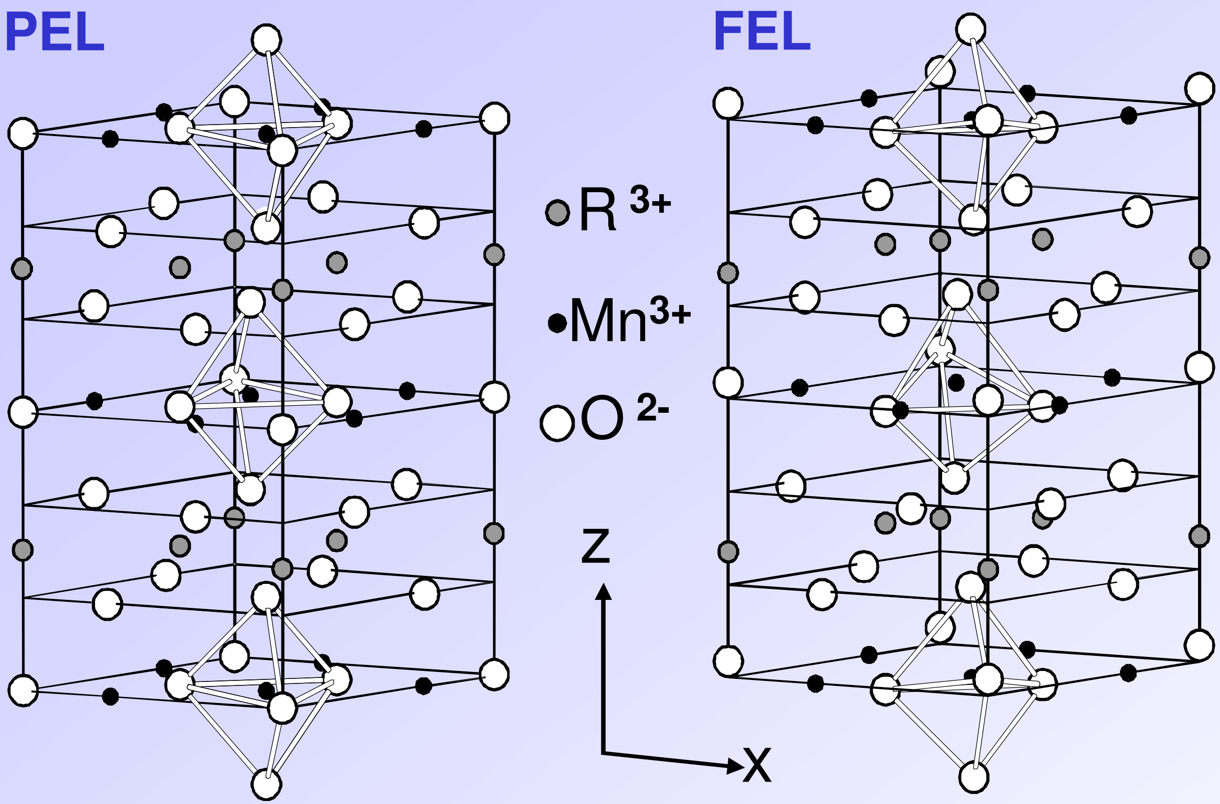
- Linear coupling of SHG to electric order parameter
- Linear coupling of SHG to magnetic order parameter
- SH tensor components χ_{ijk} reveal the electric **and** magnetic structure

Experimental Setup



Basic setup with a pulsed Nd:YAG - OPO laser system (3 ns, ≤100 Hz, 0.4 - 3.0 mm)

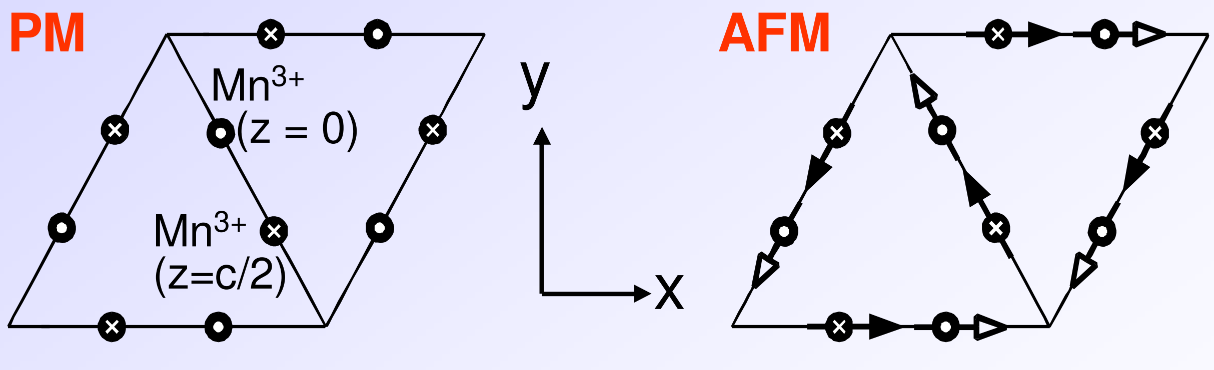
Hexagonal Manganites *R*MnO_3



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

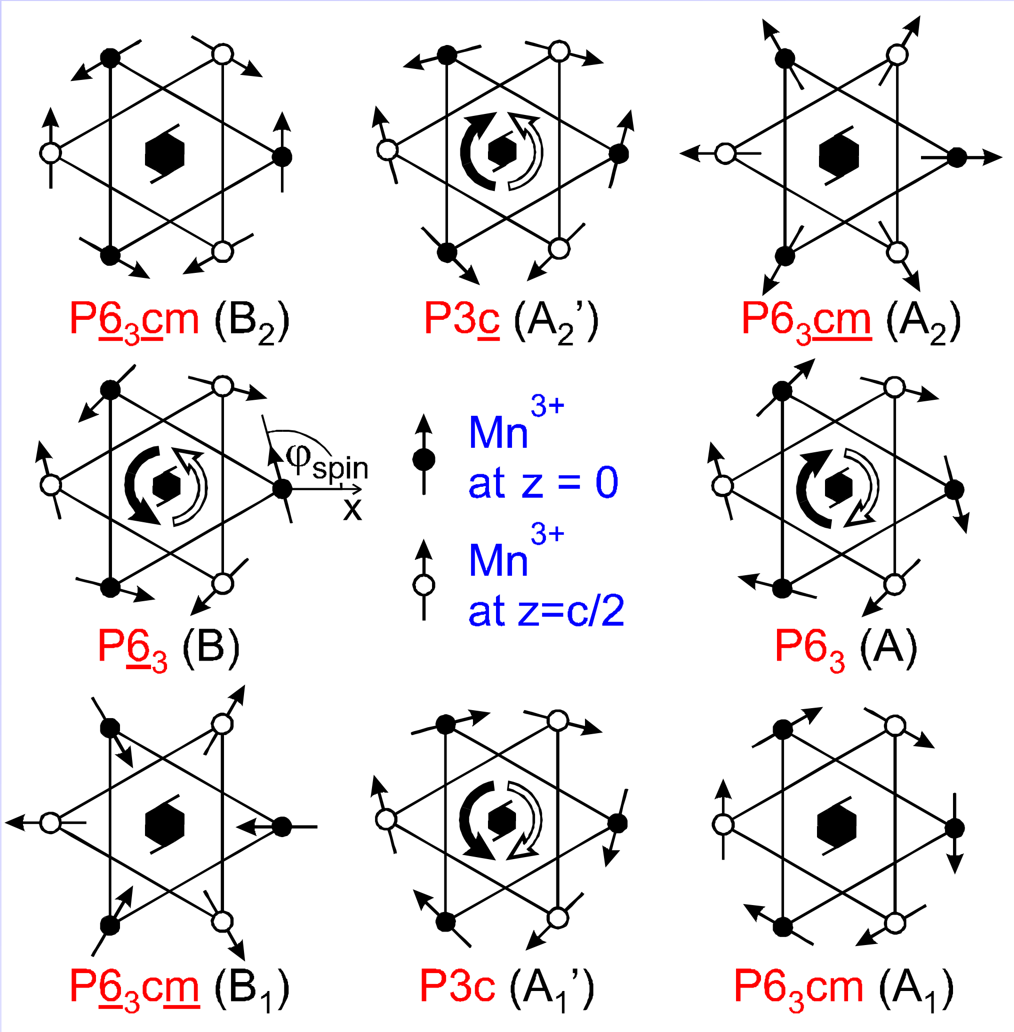
- **Paraelectric → Ferroelectric**
  (PEL - FEL): T_C = 570 - 990 K
- **Para- → Antiferromagnetic**
  (PM - AFM): T_N = 70 - 130 K

Ferroelectromagnetism:
Coexisting electric and magnetic order

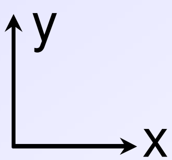


- Ferroelectromagnetism for *R* = Sc, Y, In, Ho, Er, Tm, Yb, Lu
- Additional rare-earth order at $T_C \approx 5$ K for Ho, Er, Tm, Yb

Magnetic Structure and SHG Selection Rules



α structures



β structures

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 ($\varphi = 0\text{-}90°$): $\chi_{xxx} \propto \sin\varphi$, $\chi_{yyy} \propto \cos\varphi$

β structures: SHG for k||z not allowed

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

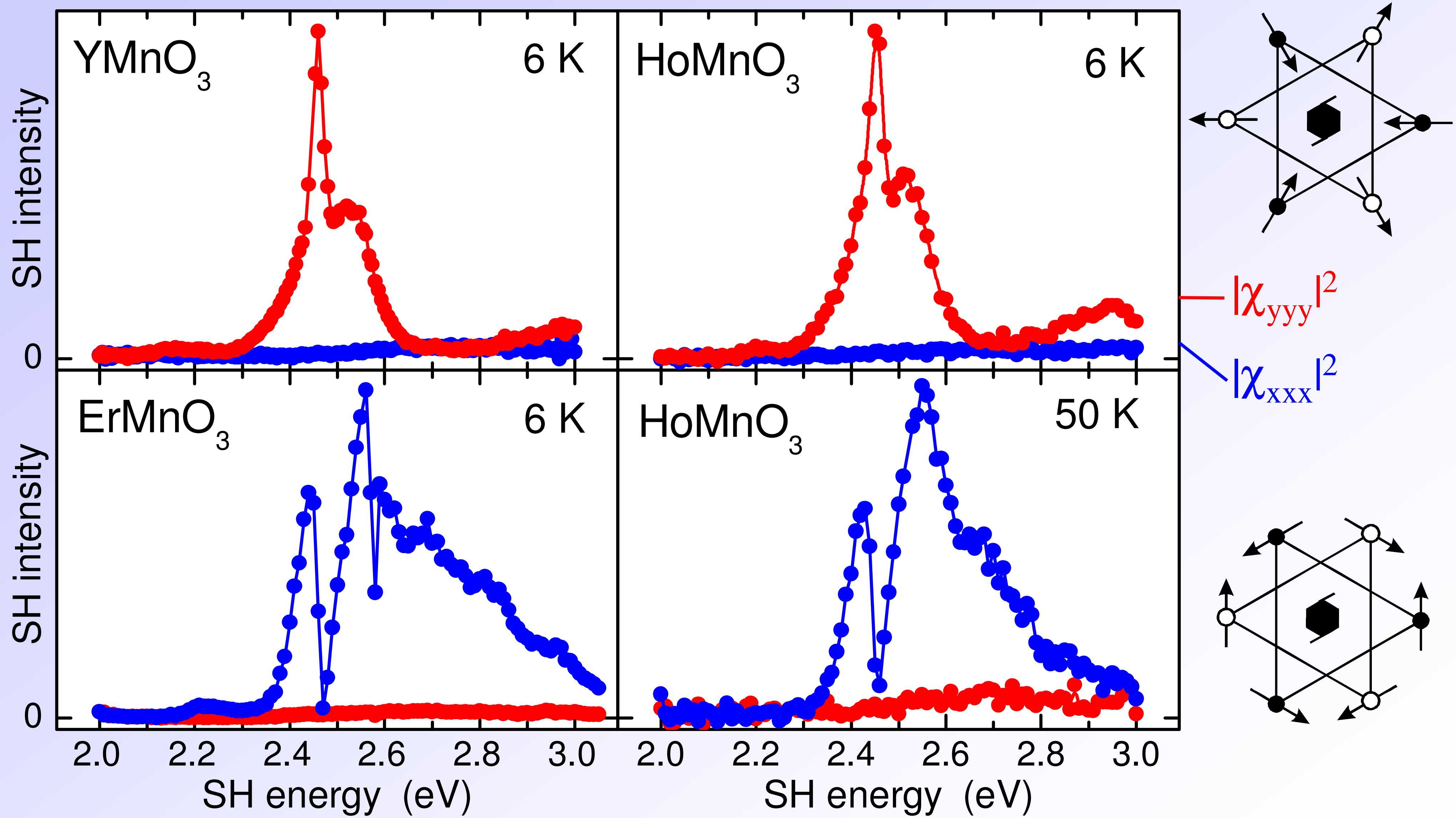
Determine β structure from α-β transition

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

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

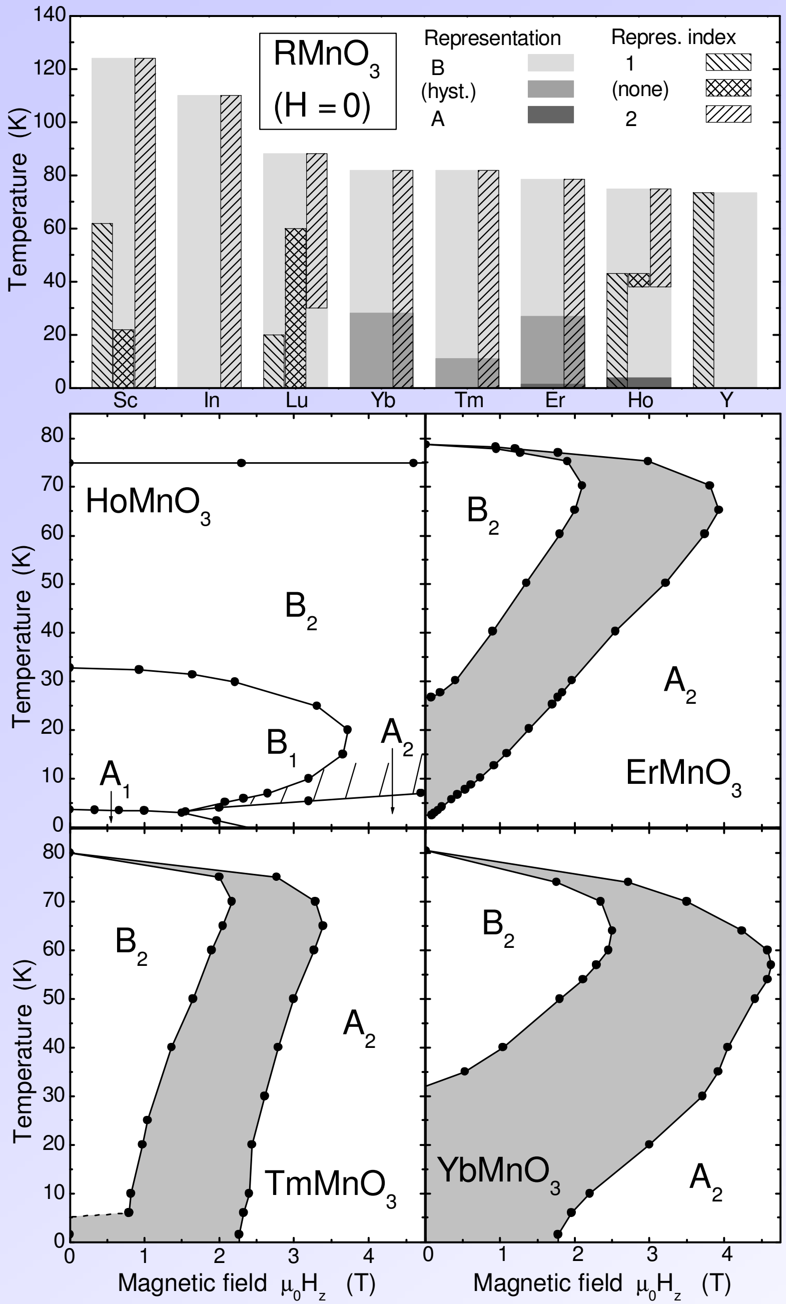
Contrary to diffraction techniques:
α and β models clearly distinguishable!

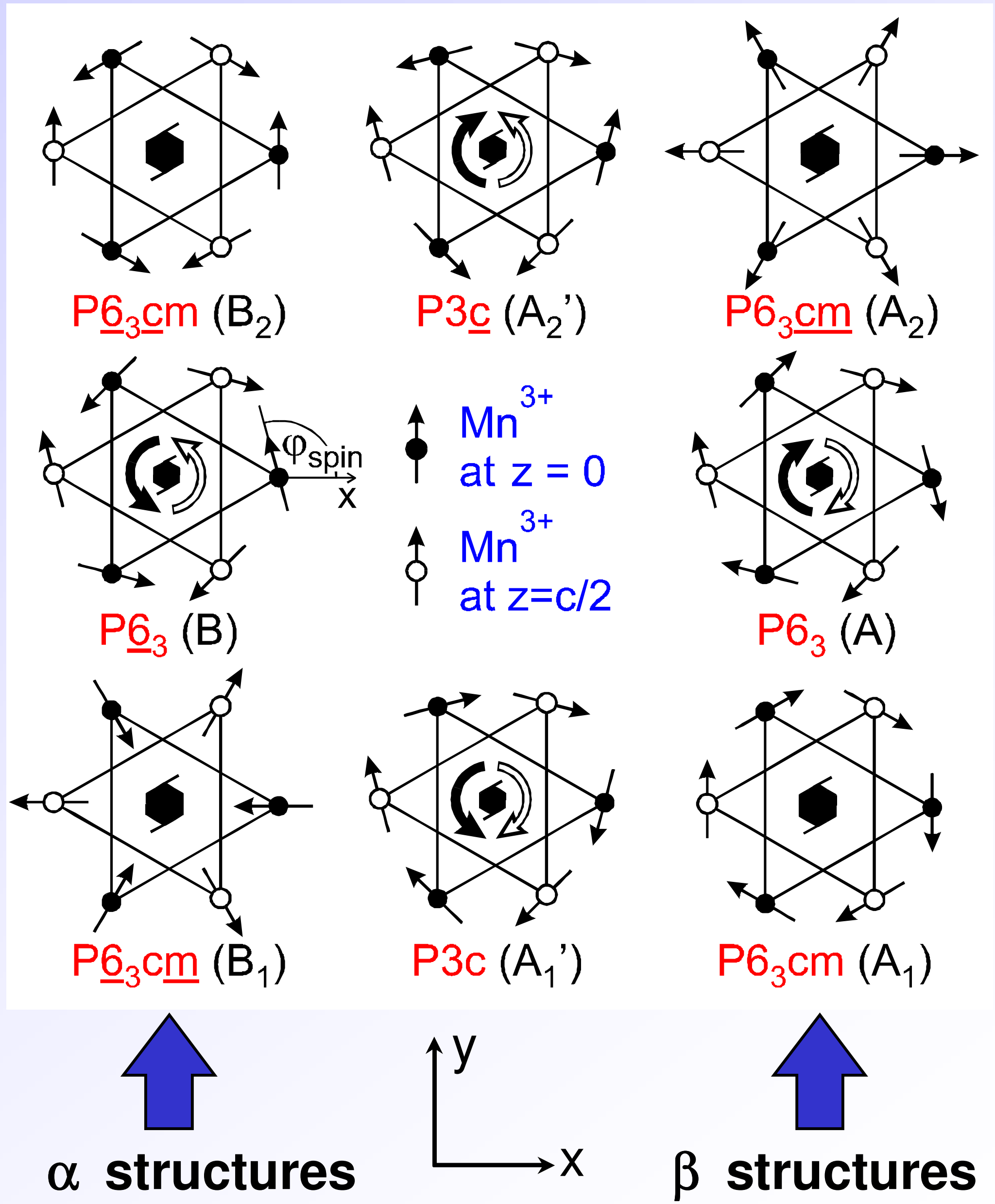
SH spectrum and Magnetic Symmetry



Phys. Rev. Lett. **84**, 5620 (2000)

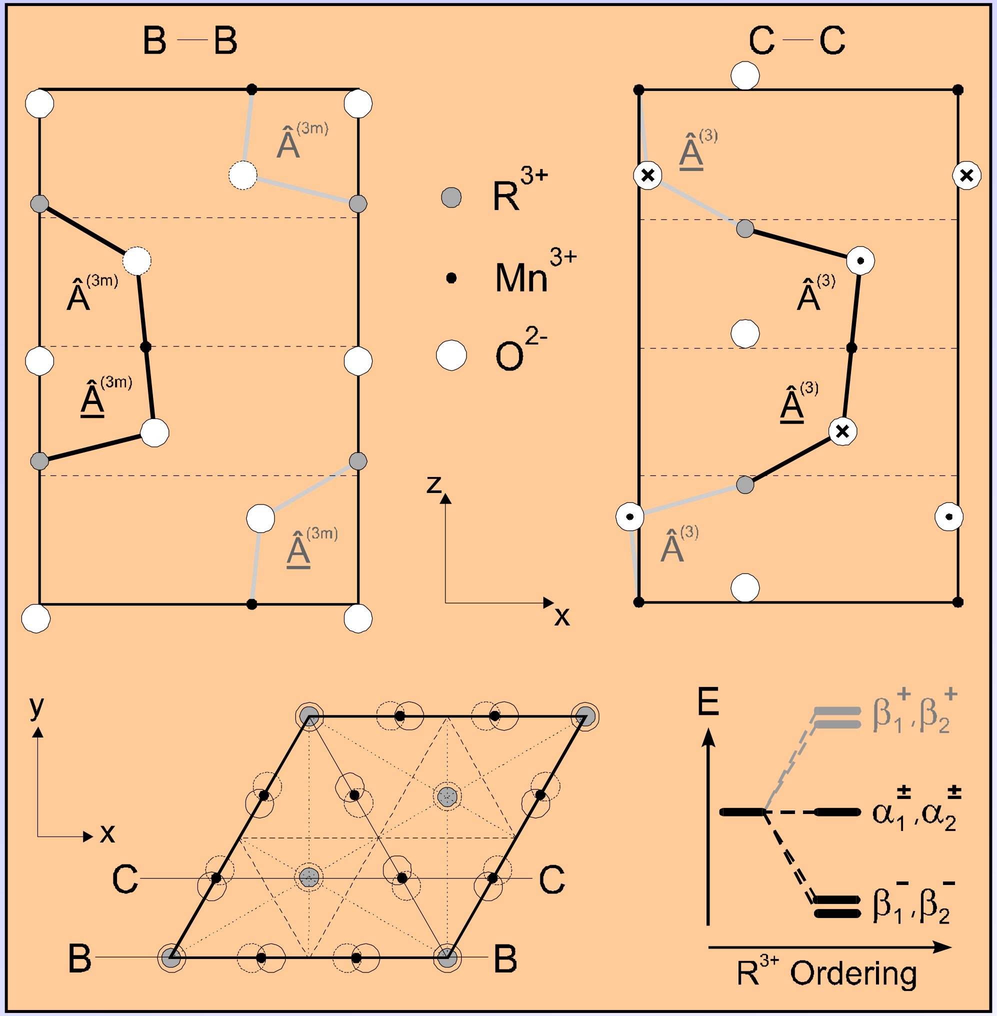
H/T Phase Diagram of Hexagonal $RMnO_3$





J. Appl. Phys. **83**, 8194 (2003)

Magnetoelectric 3*d* - 4*f* Superexchange in $RMnO_3$



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

Phys. Rev. Lett. **88**, 027203 (2002)

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

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

β model: lowers ground-state energy:

$$H^{\ell}_{\rm ex}(\beta_x) = 6\ell\, S^R S^{\rm Mn} \left[(A^{3m}_{zx} - \underline{A}^{3m}_{zx}) - (A^{3}_{zx} - \underline{A}^{3}_{zx}) \right]$$

$$H^{\ell}_{\rm ex}(\beta_y) = 6\ell\, S^R S^{\rm Mn} \left[(A^{3m}_{zy} + \underline{A}^{3m}_{zy}) - (A^{3}_{zy} + \underline{A}^{3}_{zy}) \right]$$

Ferroelectric distortion modifies the superexchange:

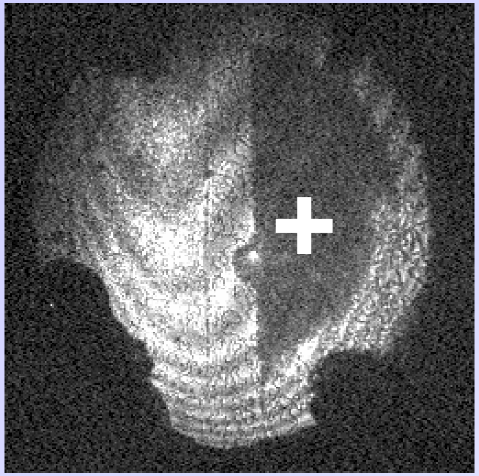
$\delta\hat{A} \equiv \hat{A} - \underline{\hat{A}}\,, \qquad \delta\hat{A} = \delta\hat{A}_0 P_z$ Scales with order par.

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

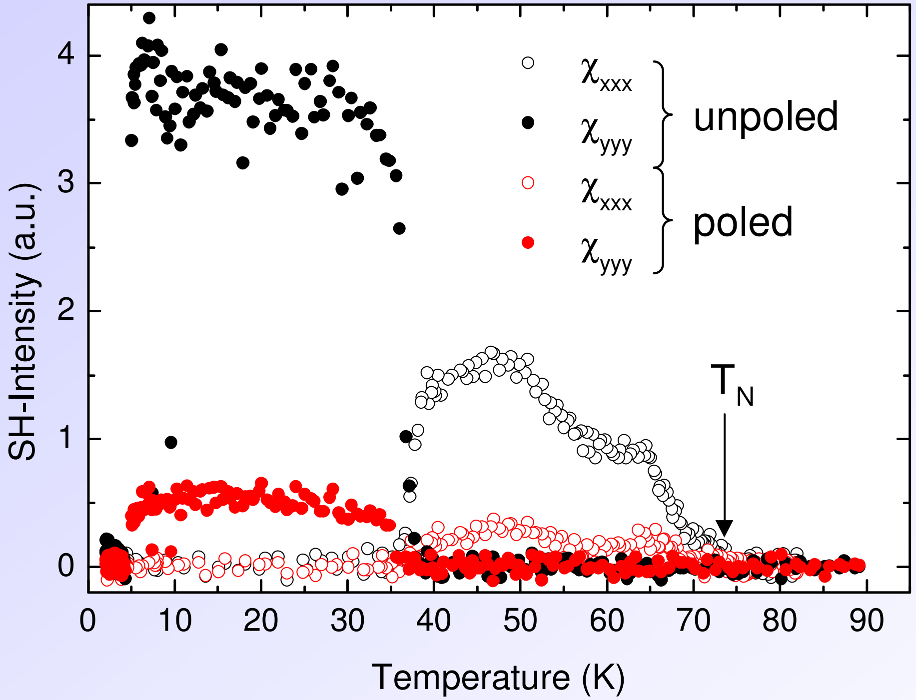
$H_{\rm ex}(\beta_x) = \alpha_{zz} P_z S^{R}_z$ **ME contribution**

Spontaneous Magnetoelectric Effect in $HoMnO_3$

Antiferromagnetic SH



Ferroelectric poling quenches magnetic signal!



Only Explanation:

Magnetic phase transition triggered by the internal electric field!

$\Rightarrow$ **spontaneous magnetoelectric effect!**

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

Magnetization Control by Electric Field in $HoMnO_3$

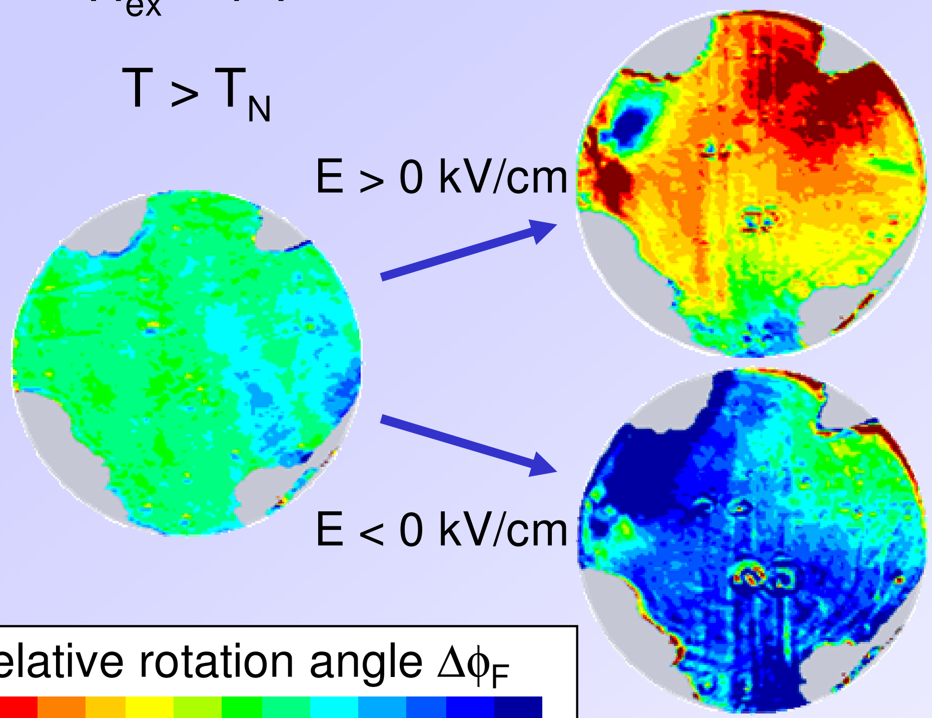
$H_{ex} \approx 1$ T

$T > T_N$

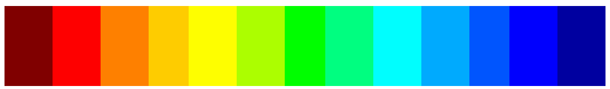
T = 1.5 K

E > 0 kV/cm

E < 0 kV/cm

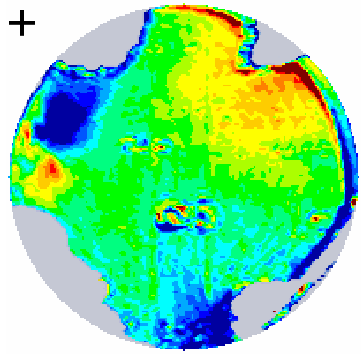


relative rotation angle $\Delta\phi_F$



0° → 10°

\+



Average Farraday rotation induced bei external magnetic field

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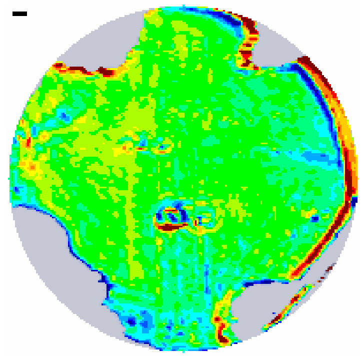


Additional Farraday rotation due to phase transition induced bei external electric field

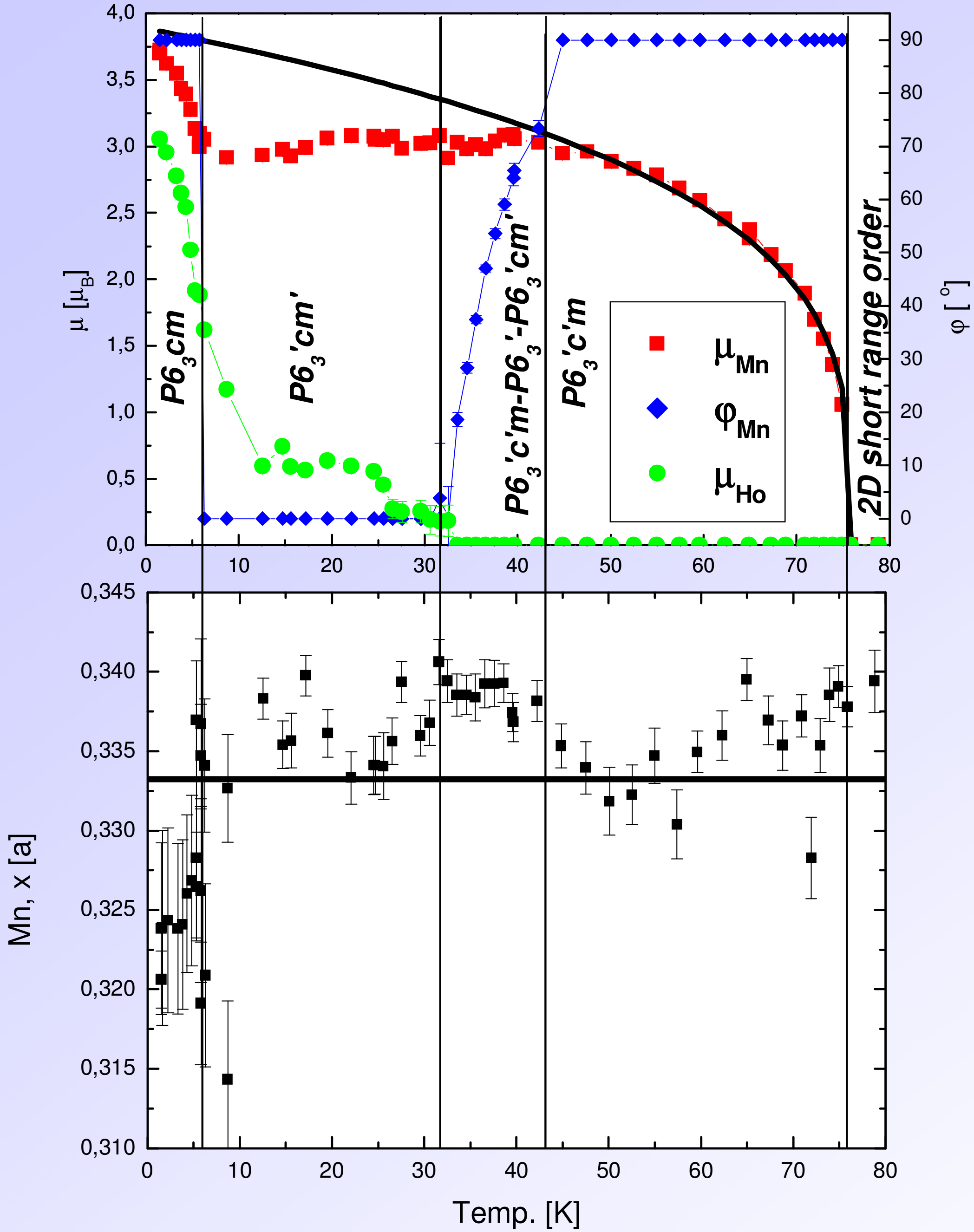
Farraday rotation depends on the direction of the external **electric** field!

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 for $HoMnO_3$



- 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 super-exchange, stabilized by DM-exchange leads to diffusive phase transition
- Intraplanar Ho-Ho-exchange leads to low temperature phase transition

Change of Mn-position at low temperature phase transition:

Connected with ferroelectric distortion ||c

→ **Magnetoelectric phase transition**

Summary

- Magnetoelectric effect in hexagonal manganites $RMnO_3$ with R = Ho – Yb
- Observation with magneto-optical methods
- Microscopic origin by neutron diffraction
- Magnetic phase controlled by electric field: Activation/deactivation of ferromagnetic state
- Origin: "giant" magnetoelectric effect $H_{me} = \alpha DB$