Magnetoelectric Effects in Multiferroics

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PROMOX2, APRIL 2005

Magnetoelectric Effects in Multiferroics

- **Introduction: Magnetoelectric Effect & Multiferroics**
- Multiferroic Manganites with Perovskite Structure
  - Electric Polarization Control by Magnetic Field
- Multiferroic Manganites with Hexagonal Structure
  - Magnetization Control by Electric Field
  - Magnetoelectric Second Harmonic Generation (SHG)
  - Domains and Domain Walls
- Superlattices as Artificial Multiferroics

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:

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

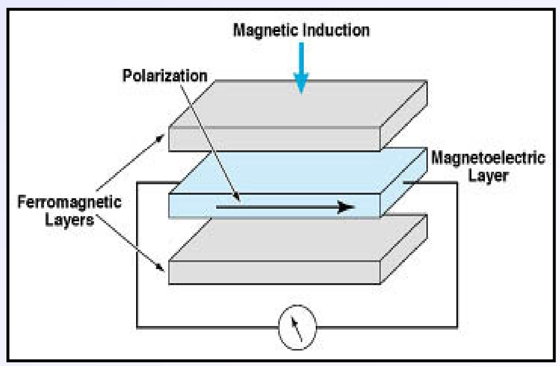
$$F_{\mu\nu} = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -cB_z & cB_y \\ E_y & cB_z & 0 & -cB_x \\ E_z & -cB_y & cB_x & 0 \end{pmatrix}$$

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

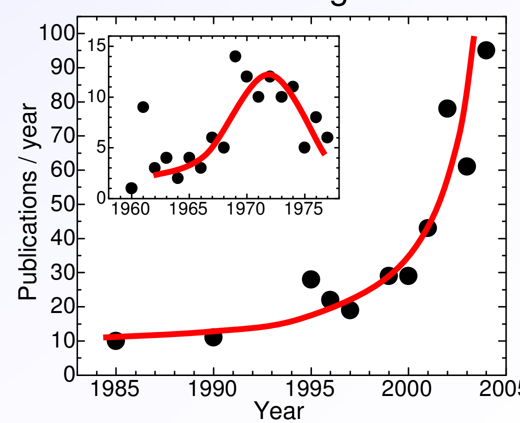
$$P_i = \epsilon_0 \chi^e_{ij} E_j + \frac{1}{c} \alpha_{ij} H_j \qquad M_i = \chi^m_{ij} H_j + \frac{1}{\mu_o c} \alpha_{ji} E_j$$

1960:

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



Publications on magnetoelectric



2000:

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

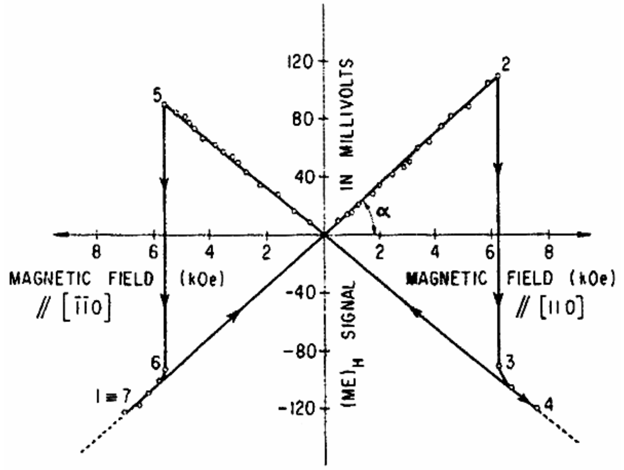
Multiferroic Compounds

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

$\Rightarrow$ **Multiferroics**

Compounds with only simultaneous magnetic and electric ordering

$\Rightarrow$ **Magnetic ferroelectrics** or **ferroelectromagnets**



Multiferroic hysteresis in $Ni_3B_7O_{13}I$ (Ascher et al. 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

Why Multiferroics?

The magnetoelectric coupling constant α_{ij} is small ($\alpha_{ij}^2 < \chi^e_{ii}\chi^m_{jj}$)

$\Rightarrow$ Applying external magnetic/electric fields lead only to small ME effects

Multiferroics with magnetic and electric ordering exhibit strong internal electromagnetic fields!

ME contribution to free energy: $H_{ME} = \alpha\, DB$ with $D = \varepsilon_0(E+P)$, $B = \mu_0(H+M)$

$\Rightarrow$ **Observation of ‘giant‘ ME effects**

- Magnetic or electric phase transitions
- Control of magnetization/polarization by electric/magnetic field

Other effects based on the coexisting orders in multiferroics:

- Interaction of magnetic and electric domains and domain walls
- Appereance of ME contributions to nonlinear optical signals

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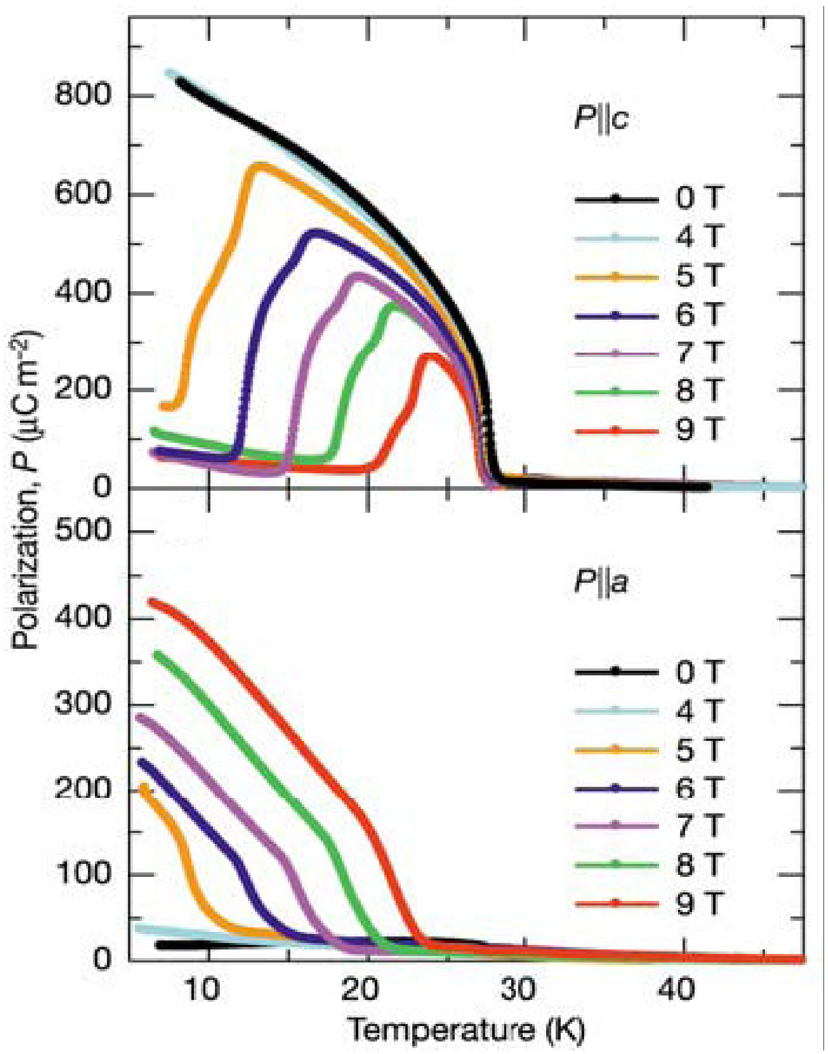
Electric Polarization Control by Magnetic Field



Kimura et. al., Nature **426**, 55 (2003)

Magnetic control of ferroelectric polarization in $TbMnO_3$:

At 42 K incommensurate antiferromagnetic Mn^{3+} ordering

At 27 K incommensurate/commensurate 'lock-in' transition of Mn^{3+} spins

⇒ magnetoeleastic displacements of Mn^{3+} ions

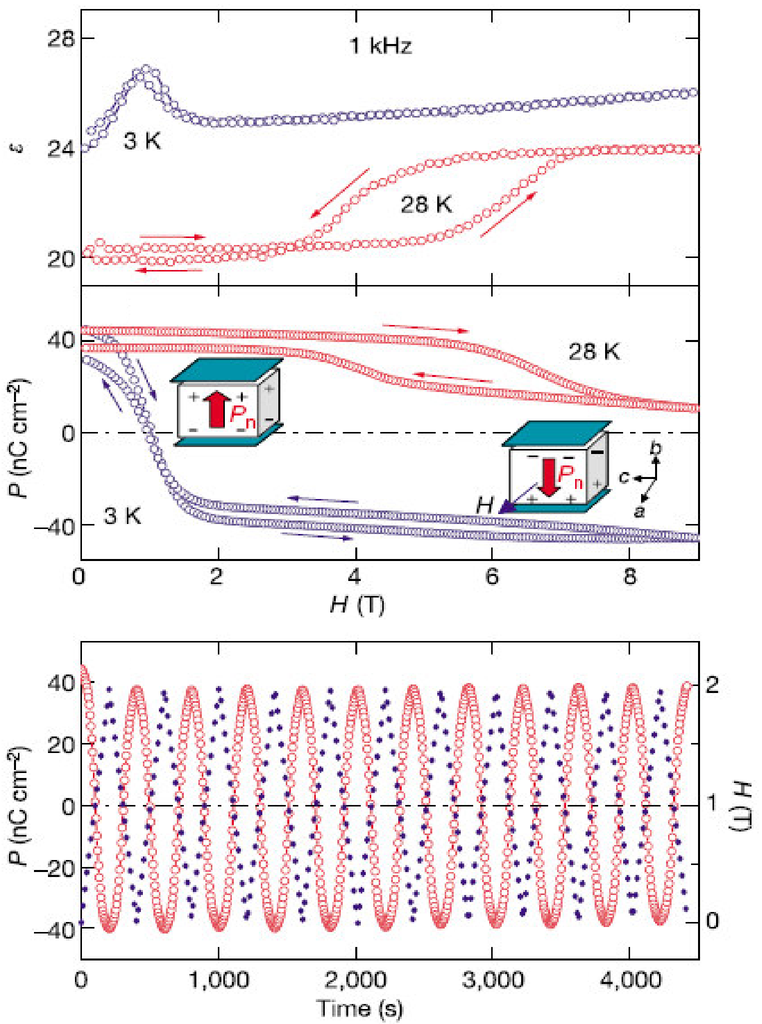
⇒ spatial variation of electric dipolmoments

⇒ ferroelectric ordered phase

Applying of an external magnetic field leads to 90° rotation of polarization

⇒ 'giant' ME effect!

Electric Polarization Control by Magnetic Field



Hur et. al., Nature **429**, 392 (2004)

Electric polarization reversal and memory in in $TbMn_2O_5$ induced by magnetic fields:

Exchange interactions between Mn^{3+}, Mn^{4+}, Tb^{3+} spins and lattice polarization lead to several phase transitions.

Below 10 K:

Magnetic ordring of Mn^{3+}/Mn^{4+} and Tb^{3+} spins

Ferroelectric polarization $P = P_1 + P_2(H)$ with P_1 antiparallel P_2

Modulation of $P_2(H)$ by external magnetic field leads to sign reversal of the overall polarization P

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Optical Second Harmonic Generation

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

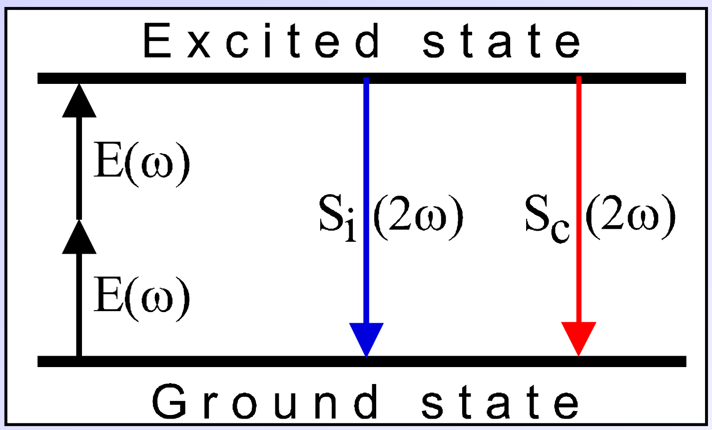
$$\vec{S} = \mu_0 \frac{\partial^2 \vec{P}^{NL}}{\partial t^2} + \mu_0 \left(\vec{\nabla} \times \frac{\partial \vec{M}^{NL}}{\partial t} \right) - \mu_0 \left(\vec{\nabla} \frac{\partial^2 \hat{Q}^{NL}}{\partial t^2} \right)$$

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



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

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

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

Amplitude A and phase ψ can be controlled in the experiment.

SHG in a Ferroelectromagnetic Multiferroic

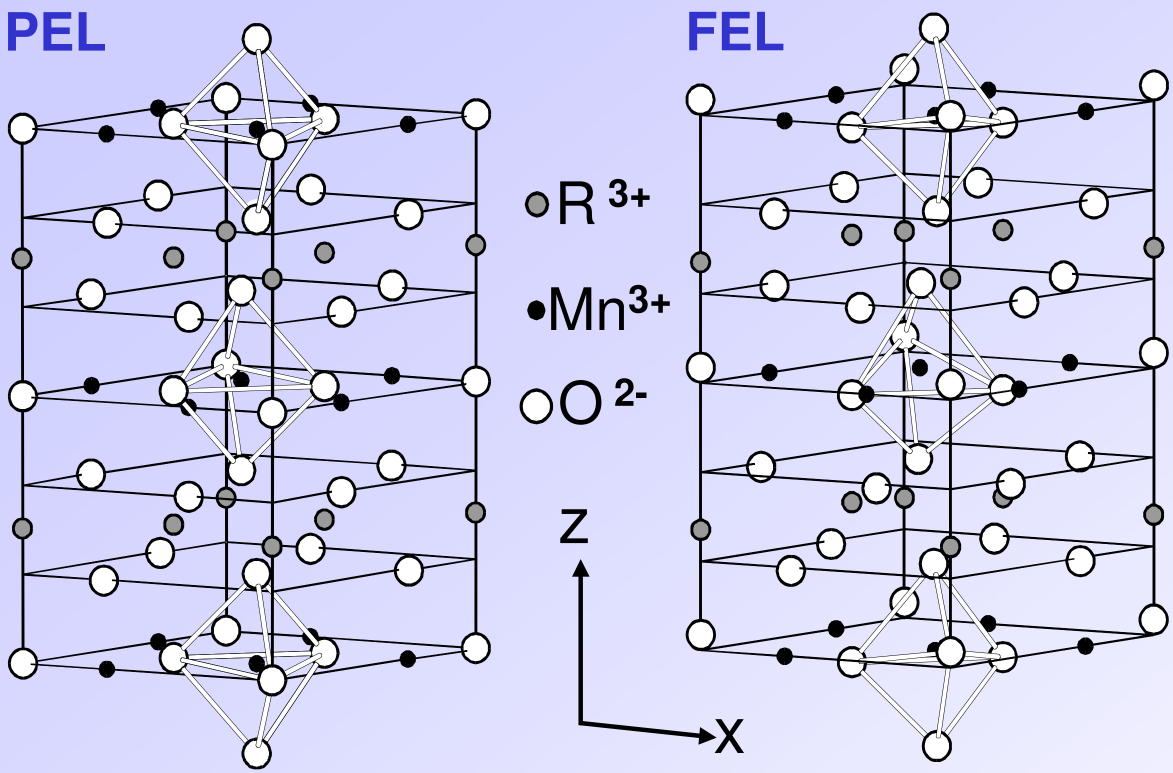
Two-dimensional expansion of the Second Harmonic (SH) susceptibility χ for electric ($\mathcal{P}$) and magnetic (ℓ) order parameters

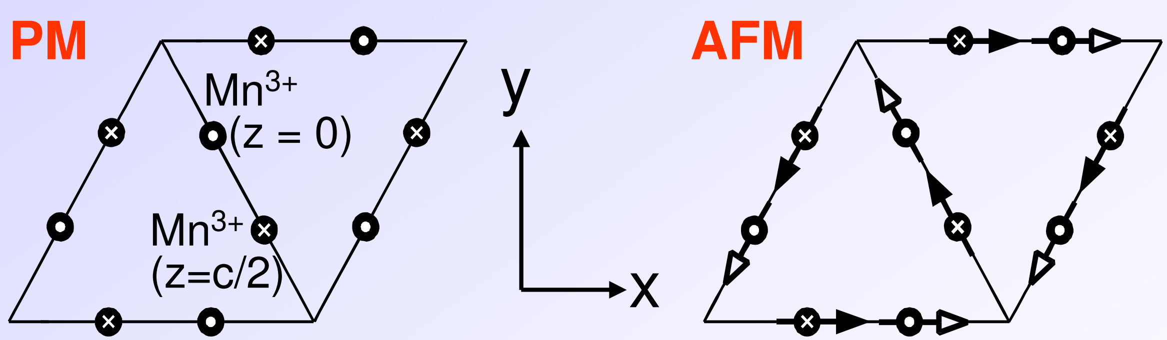
$$\vec{P}^{NL}(2\omega) = \varepsilon_0\left[\hat{\chi}(0) + \hat{\chi}(\wp) + \hat{\chi}(\ell) + \hat{\chi}(\wp\ell) + \ldots\right] \vec{E}(\omega)\vec{E}(\omega)$$

$\chi(0)$:	Paraelectric paramagnetic contribution	always allowed
$\chi(\mathcal{P})$:	(Anti)ferroelectric contribution	allowed below the respective ordering temperature
$\chi(\ell)$:	(Anti)ferromagnetic contribution	
$\chi(\mathcal{P}\ell)$:	Multiferroic contribution	

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

Crystallographic and Magnetic Structure of *R*MnO_3





_R_MnO3 (_R_ = Sc, Y, In, Ho, Er, Tm, Yb, Lu) : A highly correlated and ordered system!

Ferroelectric phase transition:

T_C = 570 - 990 K

Breaking of inversion symmetry I!

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

T_N = 70 - 130 K

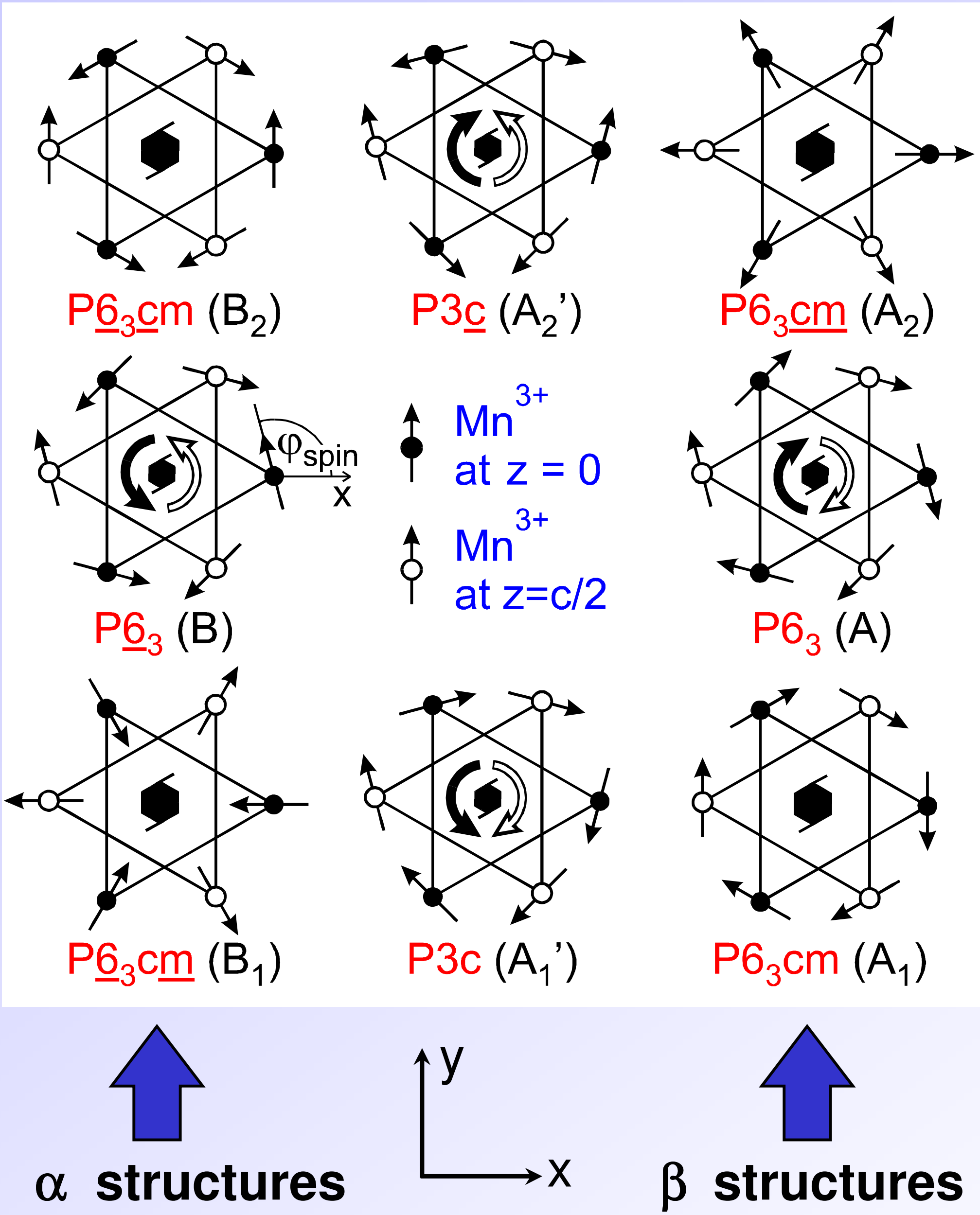
Breaking of time-reversal symmetry T, but *not* of inversion symmetry I!

Additional rare-earth order:

$T_C \approx 5$ K

for Ho, Er, Tm, Yb

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

β structures: SHG for k||z not allowed

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

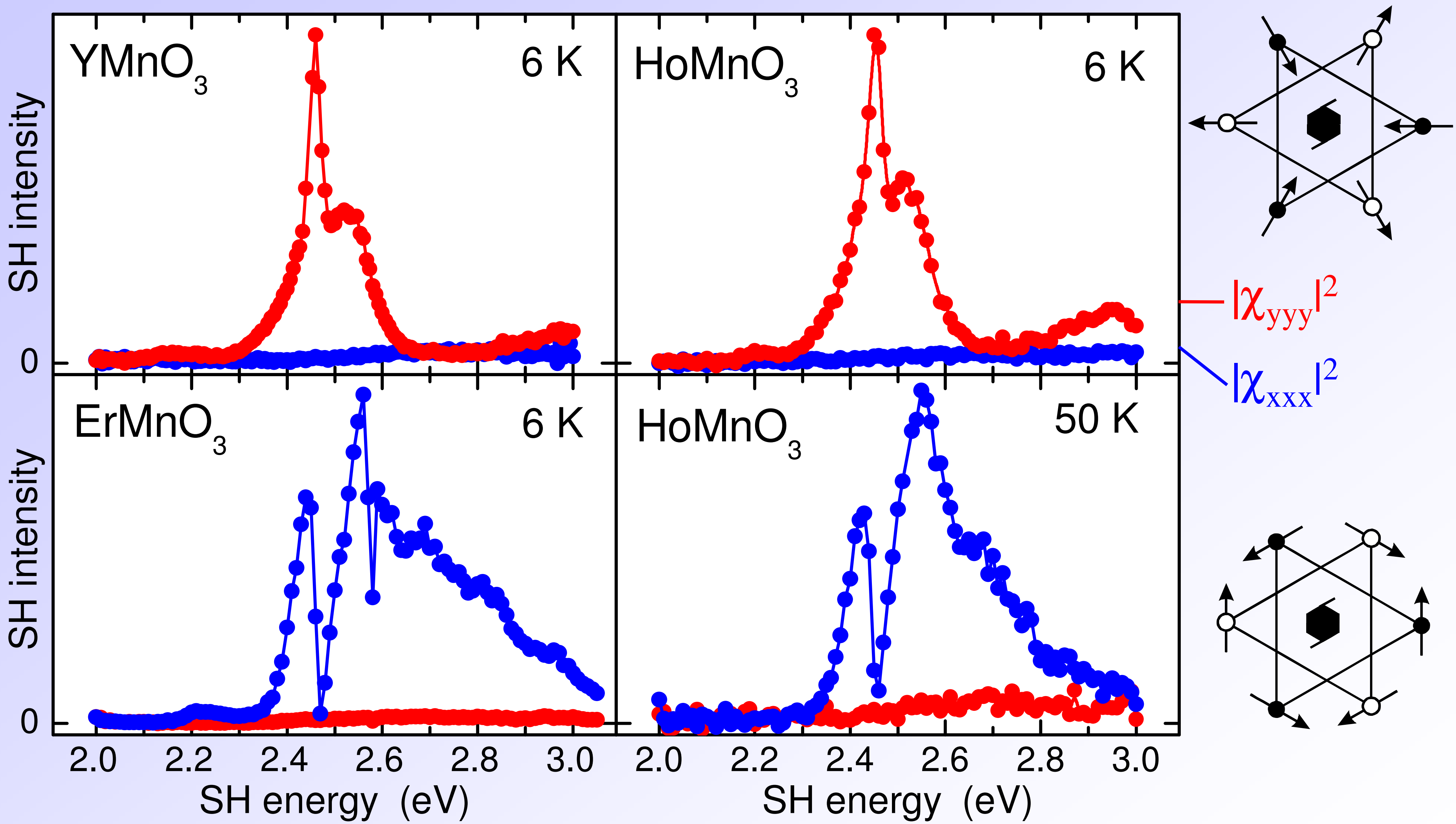
Determine β structure from α-β transition

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

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

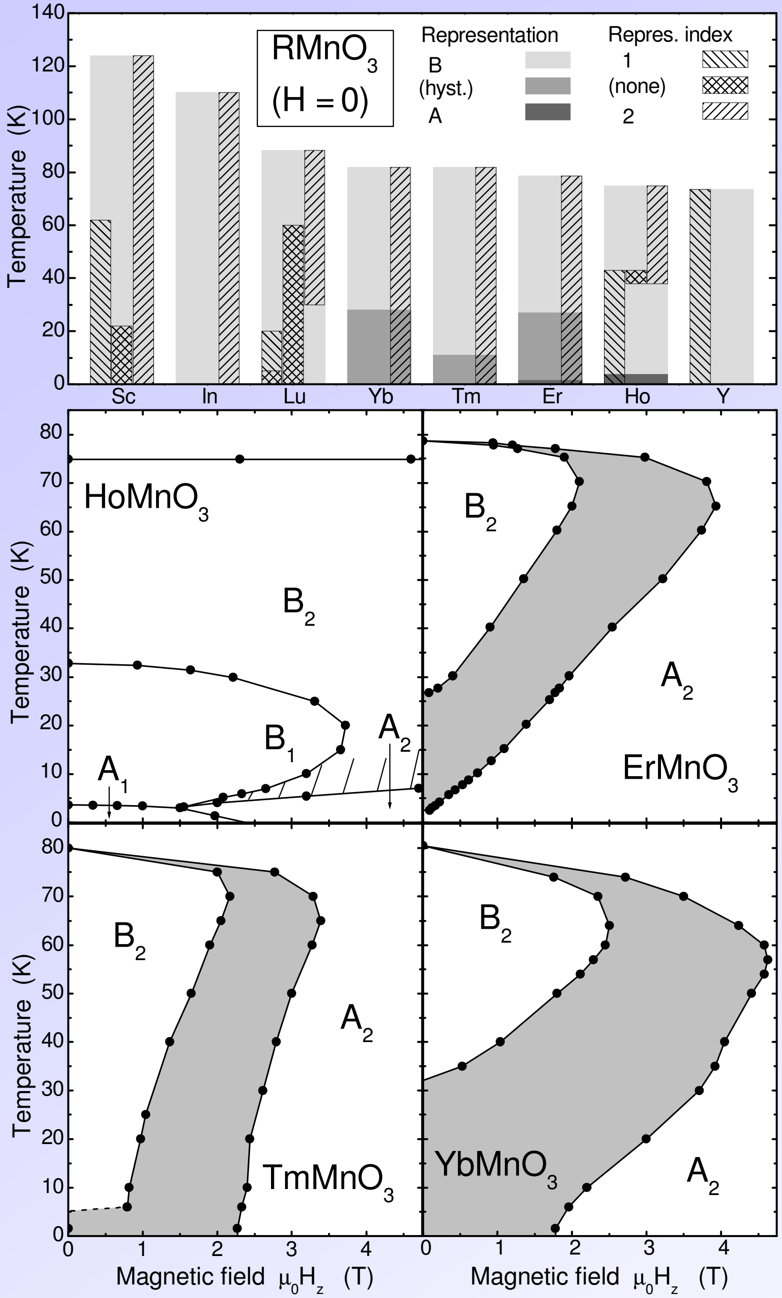
Contrary to diffraction techniques:
α and β models clearly distinguishable!

SH spectrum and Magnetic Symmetry

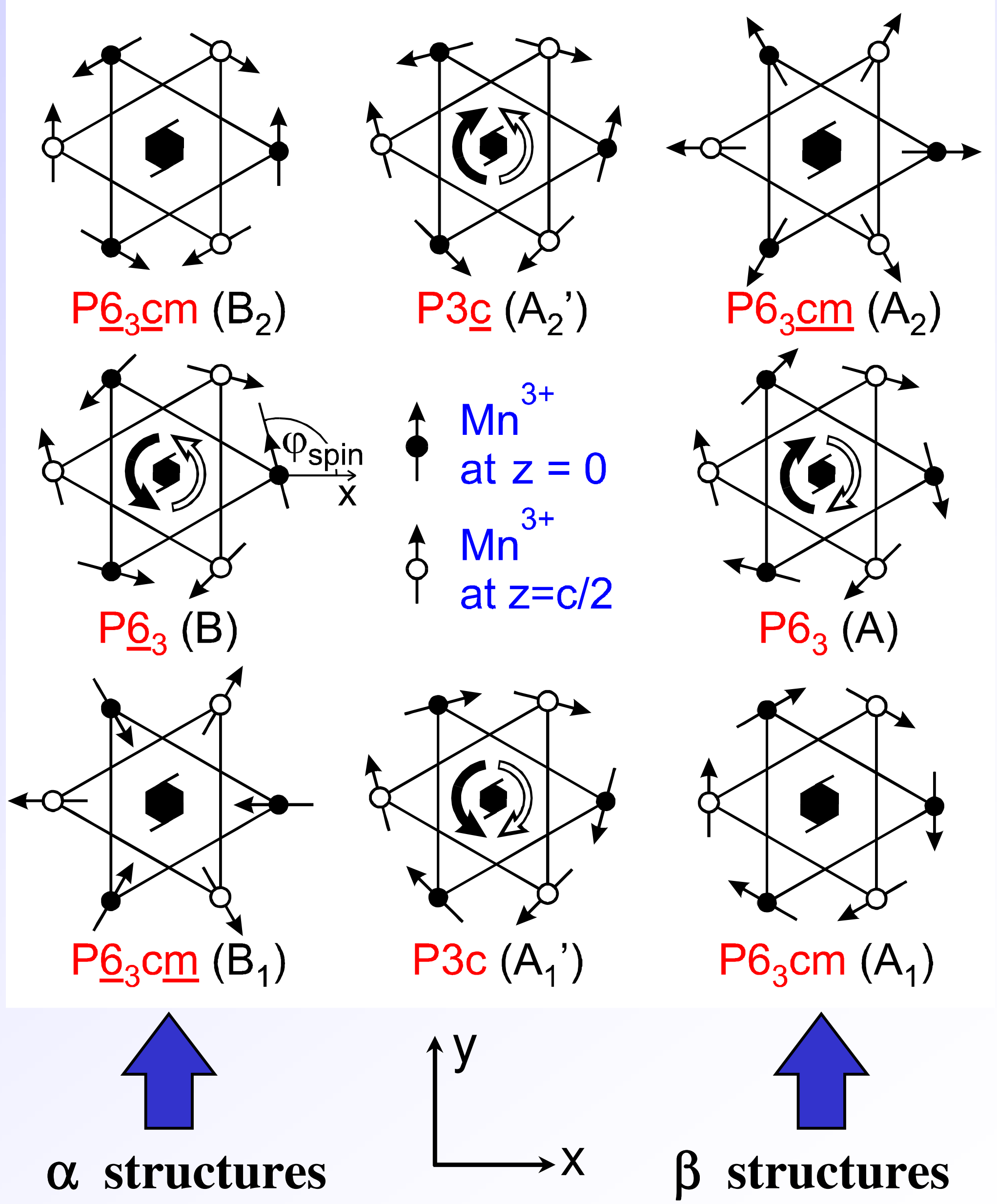


The magnetic symmetry, ***not*** the R ion, determines the SH spectrum of $RMnO_3$

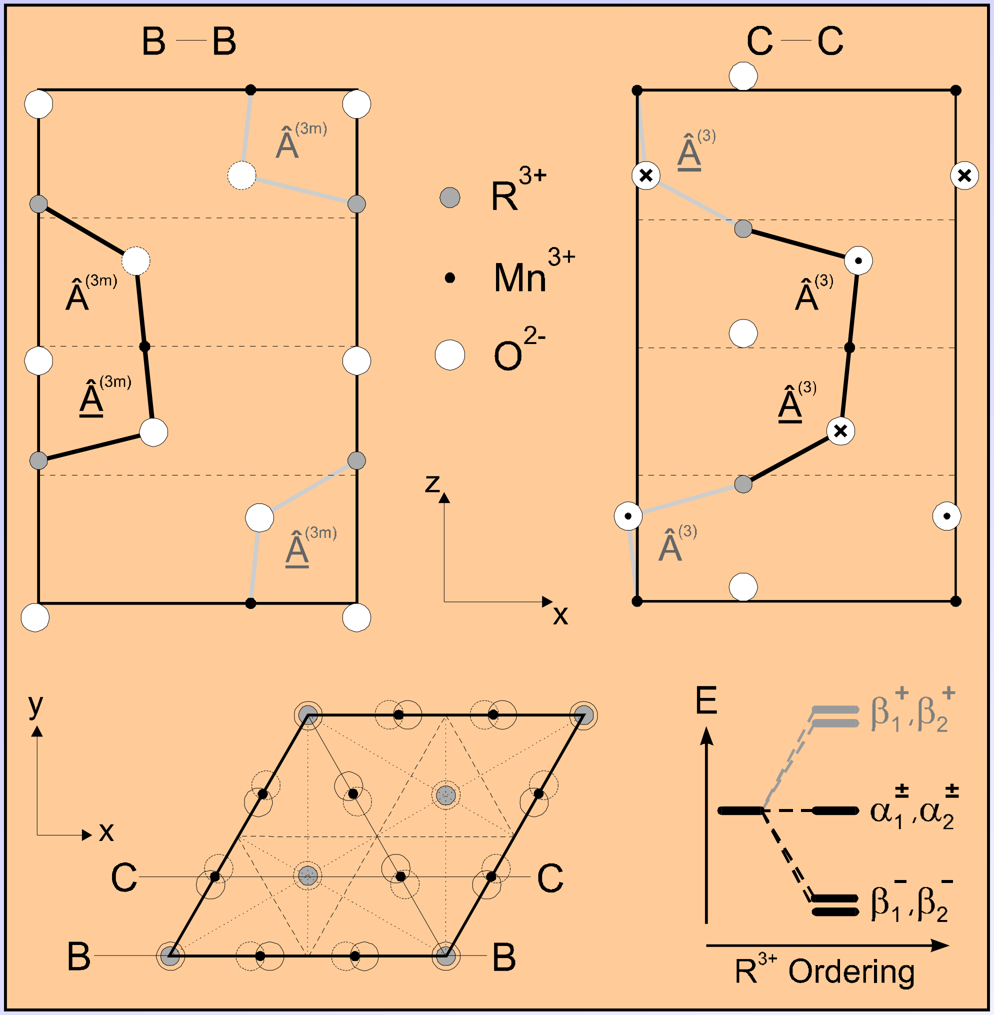
H/T Phase Diagram of Hexagonal $RMnO_3$



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!

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

- 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:

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

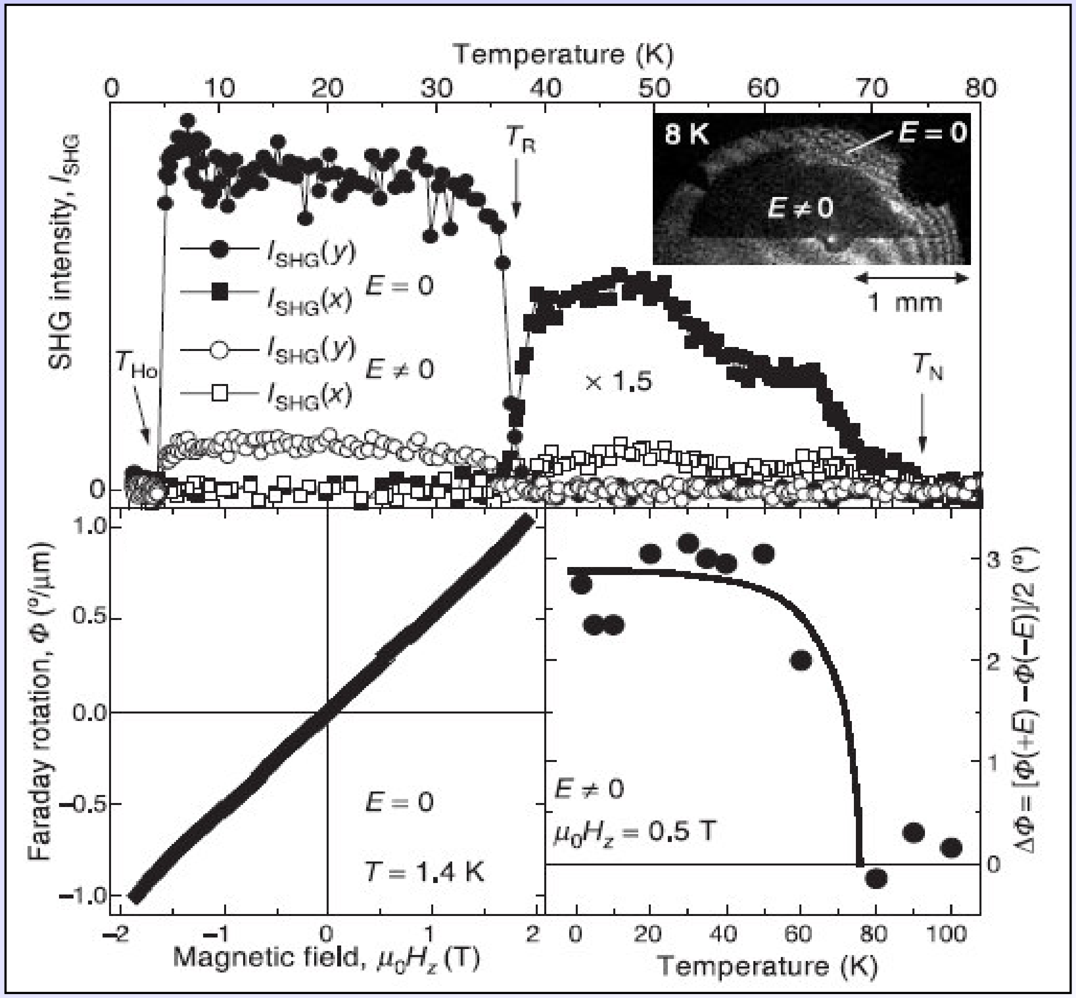
$\alpha_{zz} \equiv 6\ell S^{\rm Mn}_y (\delta A^{\rm 3m}_0 \pm \delta A^3_0)_{zy}$ Substitution leads to:

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

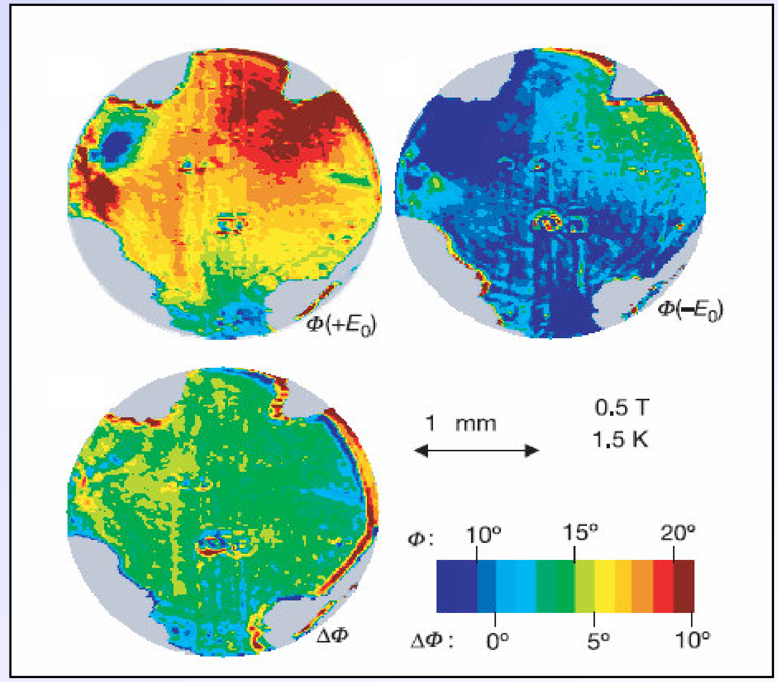
Magnetization Control by Electric Field

Electric field suppresses magnetic SHG and leads to additional field depended contribution to Faraday rotation

⇒ **Induction of magnetic phase transition!**



Nature **430**, 541 (2004)



ME contribution to free energy:

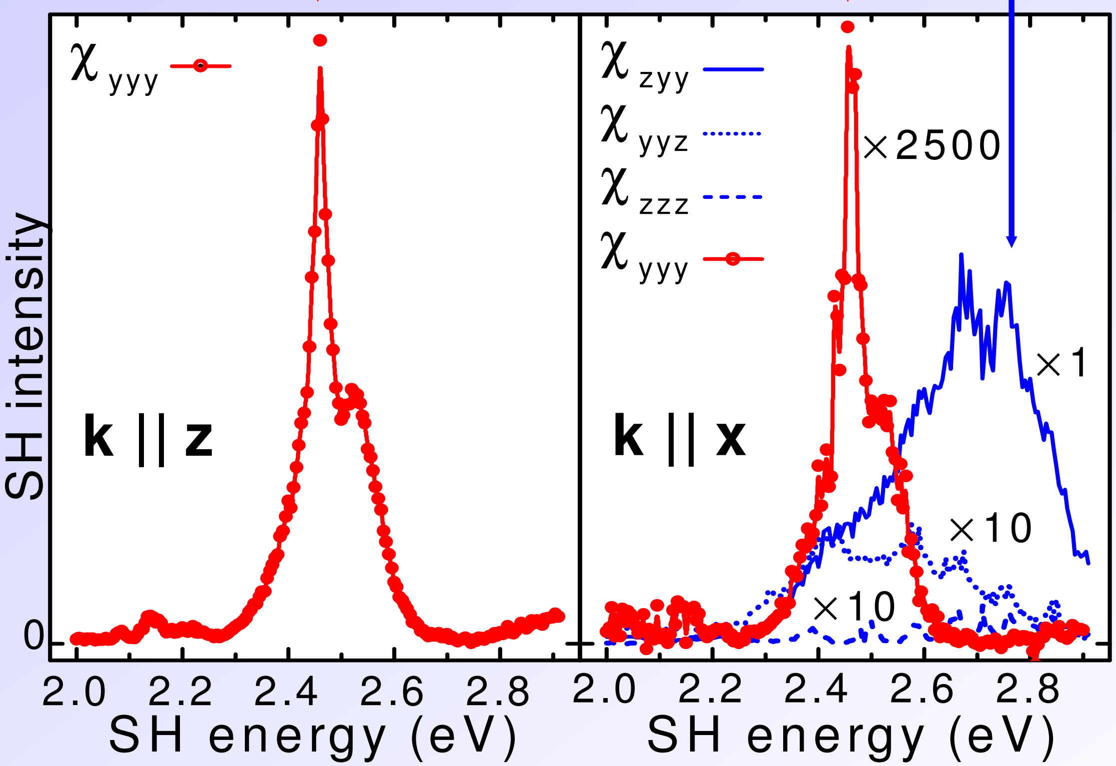
$$H \propto \alpha_{zz} P_z S_z^{Ho}$$

Ferroelectric poling and ferromagnetic ordering of Ho^{3+} spins

⇒ **'giant' ME effect**

Magnetoelectric Second Harmonic Generation

Source term	$S^{ED}(0)$	$S^{ED}(\mathcal{P})$	$S^{MD,EQ}(\ell)$	$S^{ED}(\mathcal{P}\ell)$
Sublattice sym.	$P6_3/mcm$	$P6_3cm$	$P\underline{6_3}/\underline{m}c\underline{m}$	$P\underline{6_3}c\underline{m}$
SHG for $k \parallel z$	$= 0$	$= 0$	$\neq 0$	$\neq 0$
SHG for $k \parallel x$	$= 0$	$\neq 0$	$= 0$	

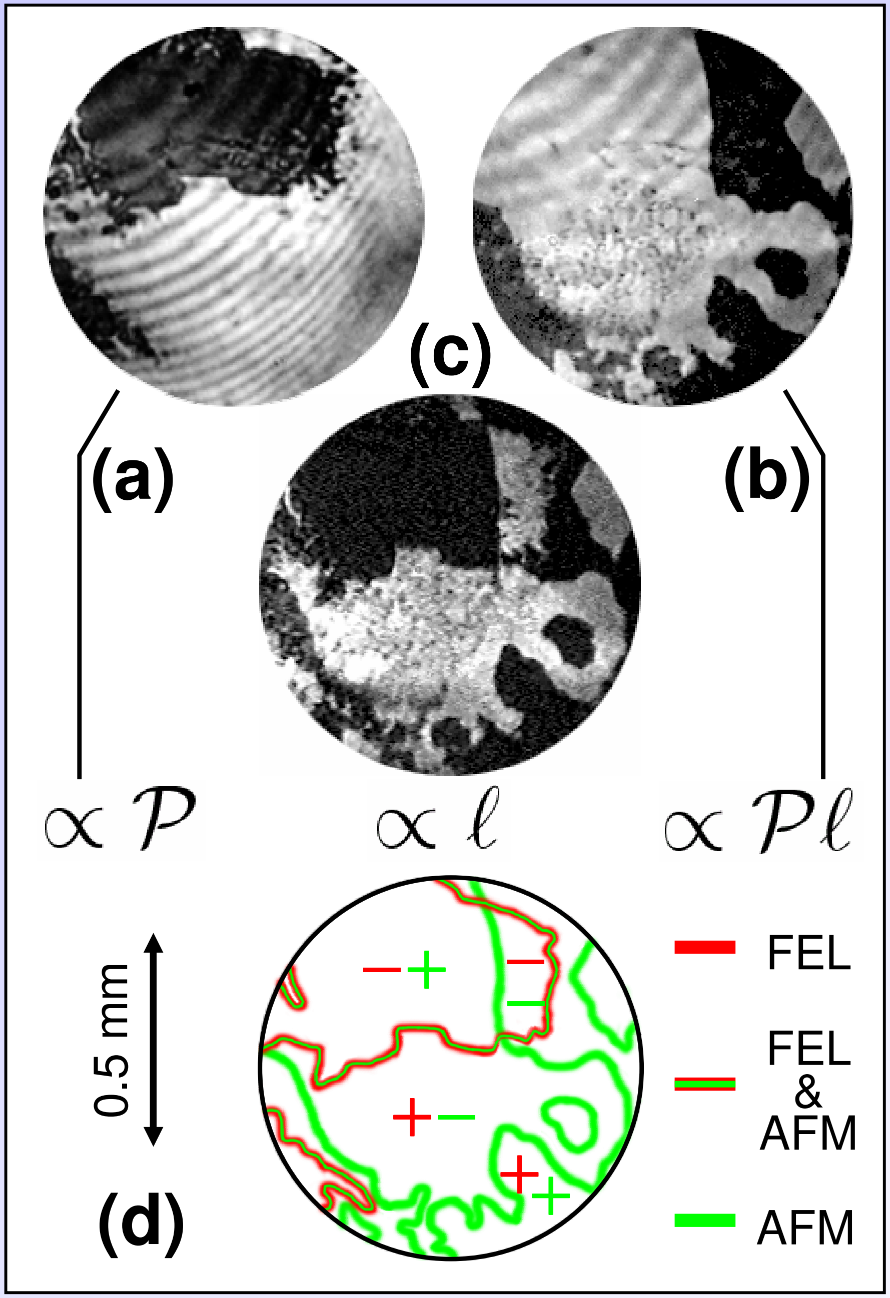


Identical magnetic spectra for k||z and k||x indicate **bilinear coupling to** $\mathcal{P}$, ℓ.

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

Nature **419**, 818 (2002)

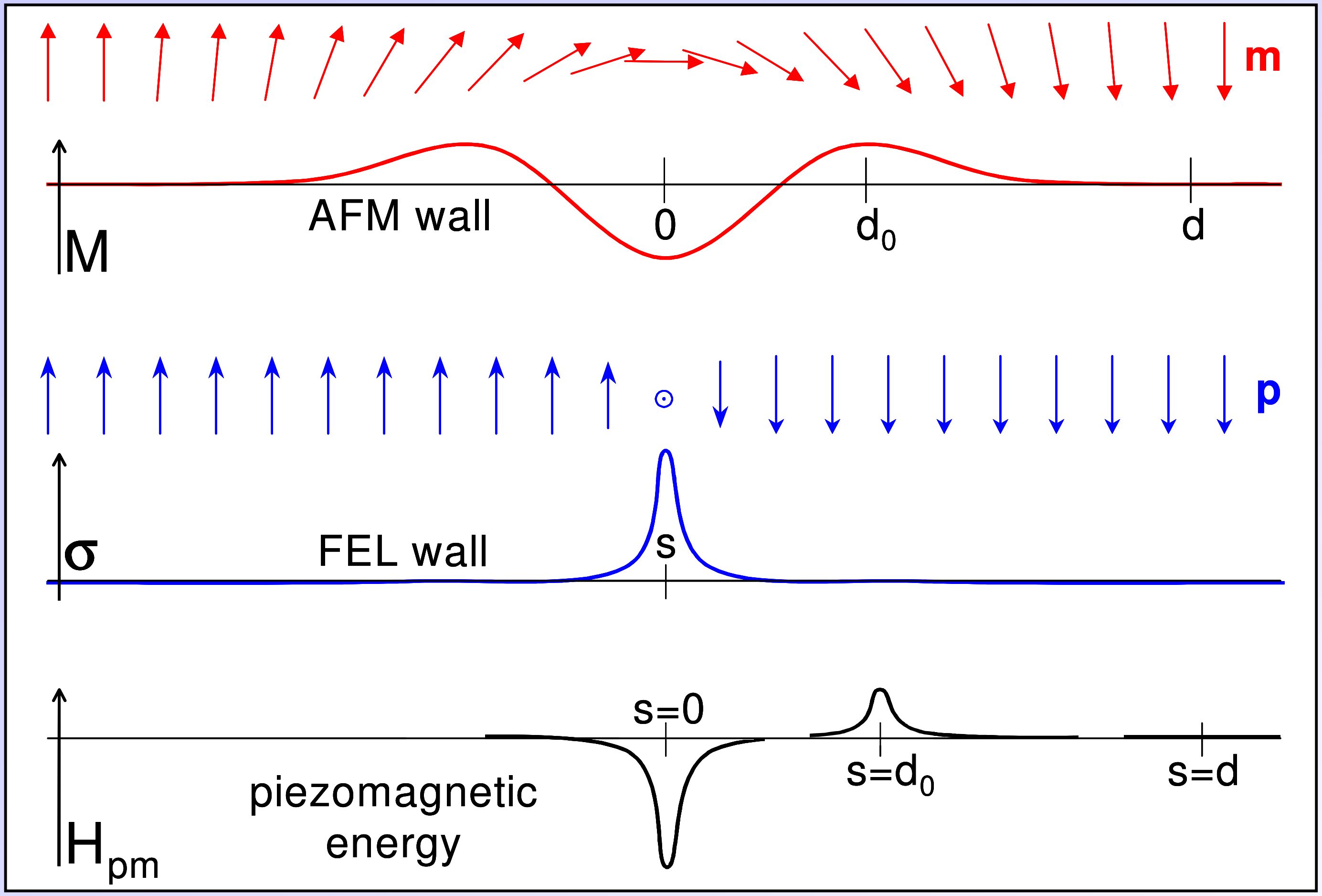
Observation of Multiferroic Domains



- Independent ferroelectric ($\propto \mathcal{P}$) and ferroelectromagnetic ($\propto \mathcal{P}\ \ell$) domain structures; antiferromagnetic domain structure ($\propto \ell$) is not!
- „Multiferroic domains":
  $\mathcal{P}\ell$ **= +1** for $\mathcal{P} = \pm 1$, $\ell = \pm 1$
  $\mathcal{P}\ell$ **= -1** for $\mathcal{P} = \pm 1$, $\ell = \mp 1$
- 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

Nature **419**, 818 (2002)

Interaction of electric and magnetic domain walls



- AFM wall carries an intrinsic macroscopic mag-netization
- FEL wall induces strain due to switching of polarization
- Width of walls:
  - AFM - O[10^3] unit cells: small in-plane anisotropy
  - iii • FEL – O[10^0] unit cells: large uniaxial anisotropy

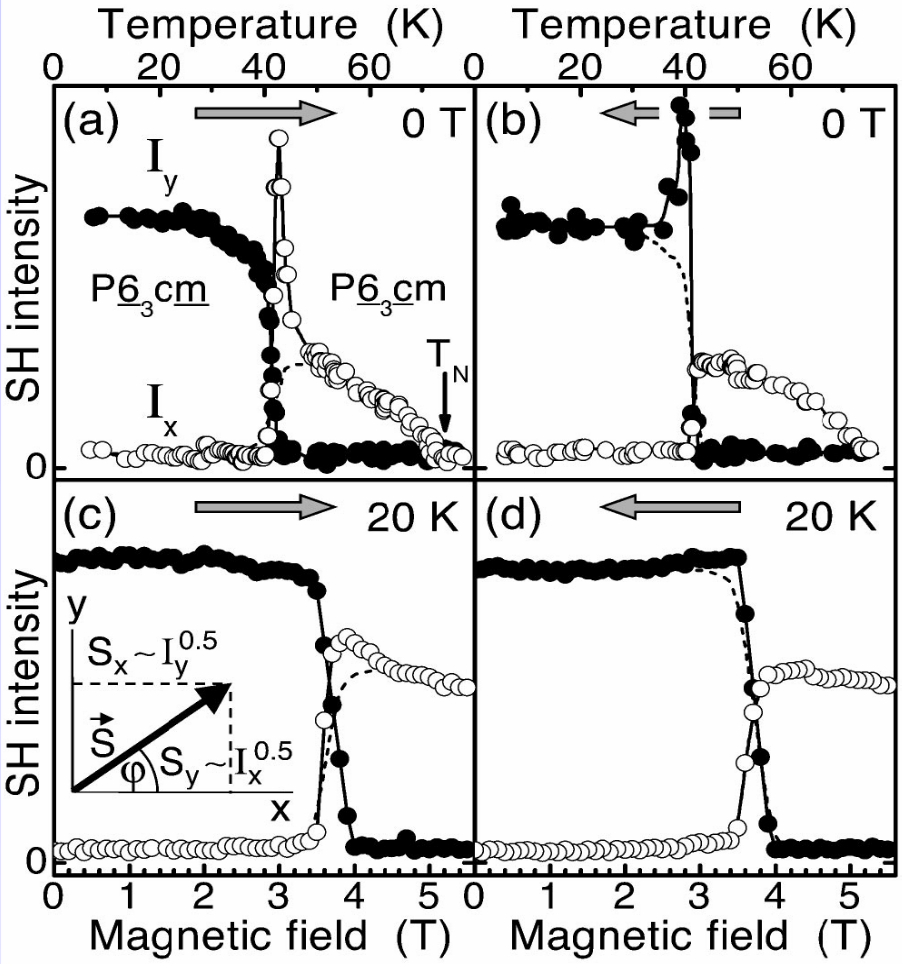
Piezomagnetic contribution $H_{pm} = q_{ijk} M_i \sigma_{jk}$ with $\sigma \propto P_z$ $\rightarrow$ higher-order magnetoelectric effect

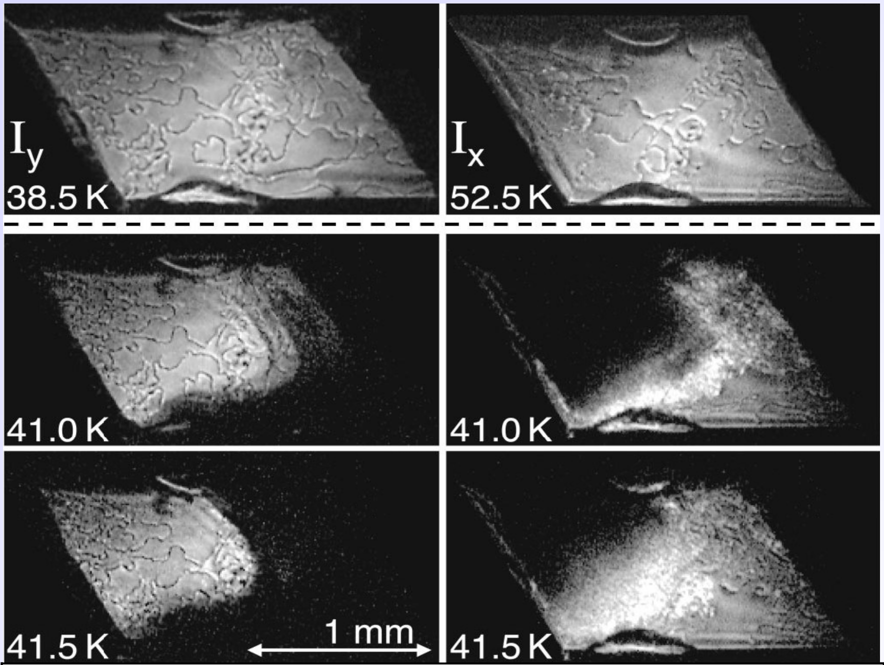
Generation of an antiferromagnetic wall clamped to a ferroelectric wall leads to reduction of free energy. Phys. Rev. Lett. **90**, 177204 (2003)

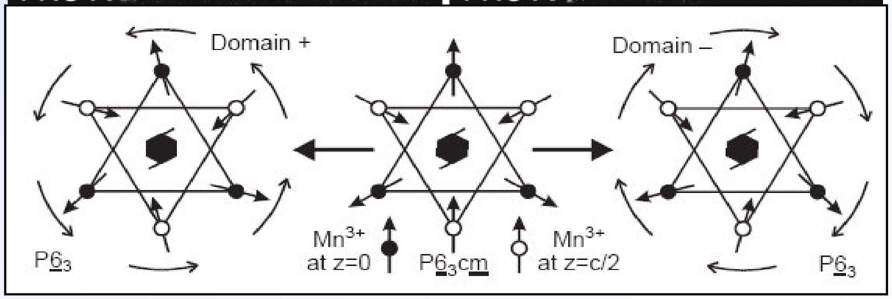
Spin-Rotation Domains in $HoMnO_3$

Observation of drastically increased *dielectric constant* during *magnetic spin-reorientation* phase transition by Lorenz et. al. (PRL 92, 87204 (2004))

But: ME not allowed by symmetry considerations!







Inside AFM domain walls reduced local symmetry P2 due to uncompensated magnetic moment.

P2 allows ME contribution $P_z \propto \alpha_{zx,y} M_{x,y}$

$\Rightarrow$ **Local ME effect**

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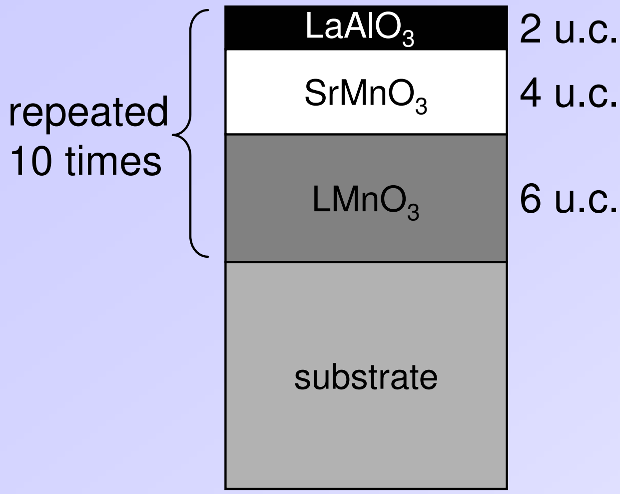
Superlattices as Artificial Multiferroics

'Tricolor' superlattice

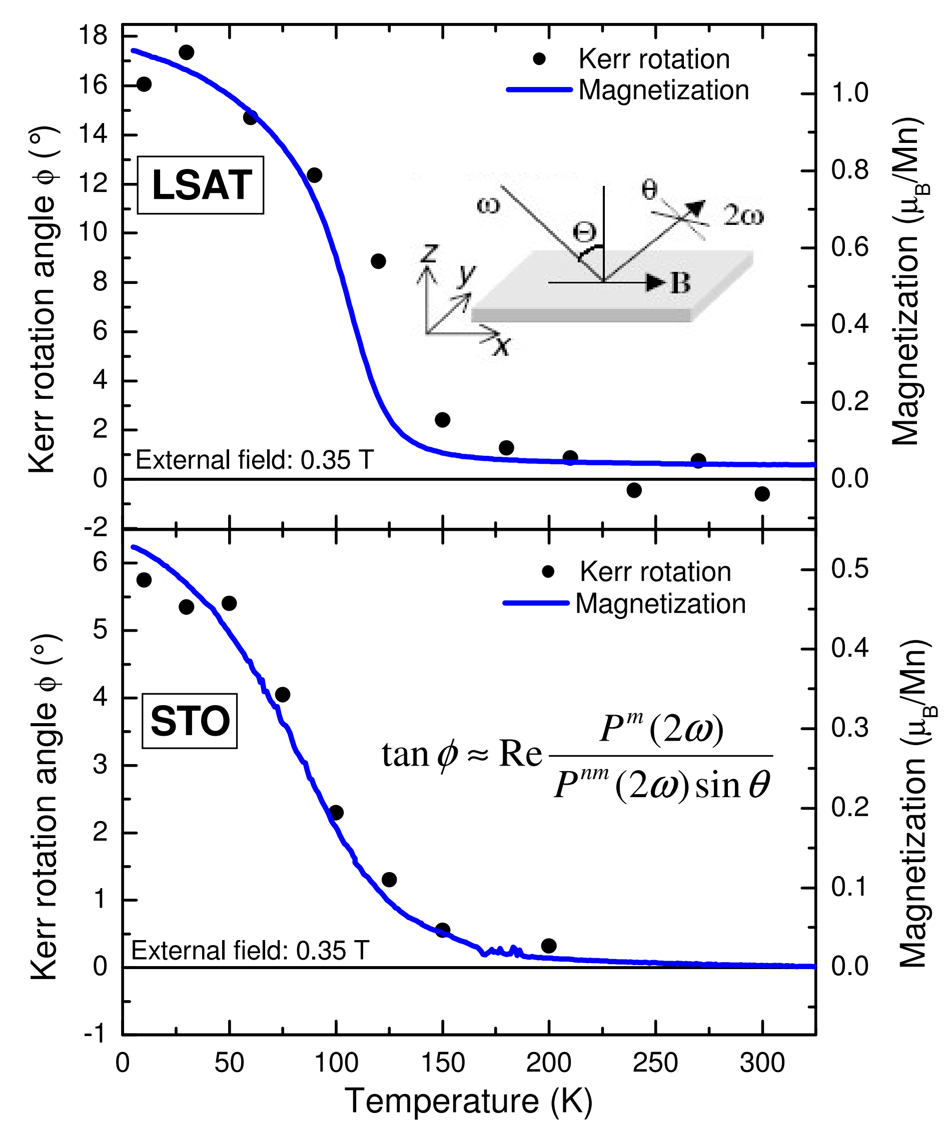


1. Asymmetric sequence of layers breaks inversion symmetry
2. Ferromagnetic ordering at SrMnO3/LaMn03 interface

⬇

Polar ferromagnet

Nonlinear magneto-optical Kerr rotation (NOMOKE)



Summary

- Coexistence of magnetic and electric ordering in multiferroics allow ‘giant�‘ magnetoelectric effects:
  - **Electric/magnetic phase transitions**
  - **Control of polarization/magnetization by external magnetic/electric fields**
- New effects based on the specific nature of multiferroics:
  - **Interaction of magnetic and electric domains and domain walls**
  - **Magnetolectric second harmonic generation**

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