Magnetoelectric Properties of Multiferroic *R*MnO_3

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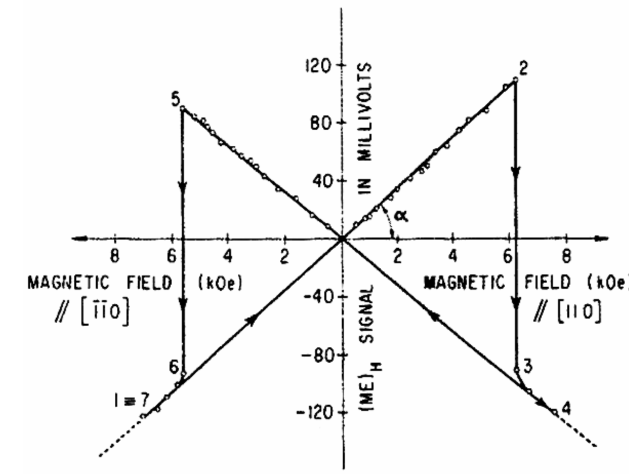
Magnetoelectric Properties of Multiferroic $RMnO_3$

- **Multiferroics and the Magnetoelectric Effect**
- Nonlinear Optics
- Hexagonal Manganites
- Experimental Results
- Summary

Multiferroic Compounds

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

⇒ **Multiferroics**



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

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:

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

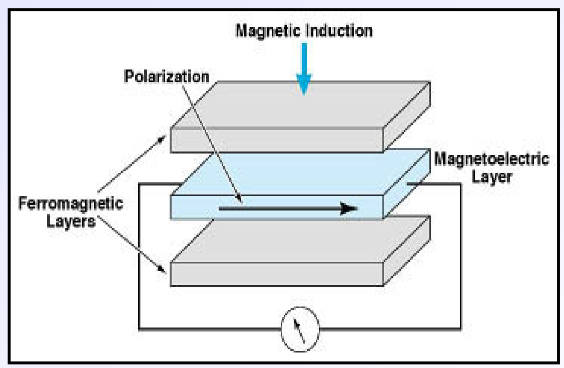
$$F_{\mu\nu} = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -cB_z & cB_y \\ E_y & cB_z & 0 & -cB_x \\ E_z & -cB_y & cB_x & 0 \end{pmatrix}$$

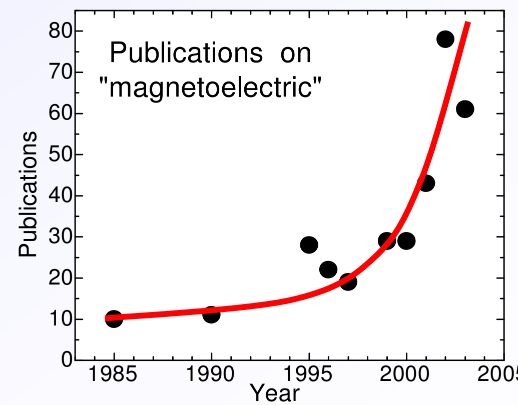
Relativistic equivalence of electric and magnetic fields requires "**magneto-electric**" cross-correlation (~ α) in matter:

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

1960:

- 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

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Optical Second Harmonic Generation

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

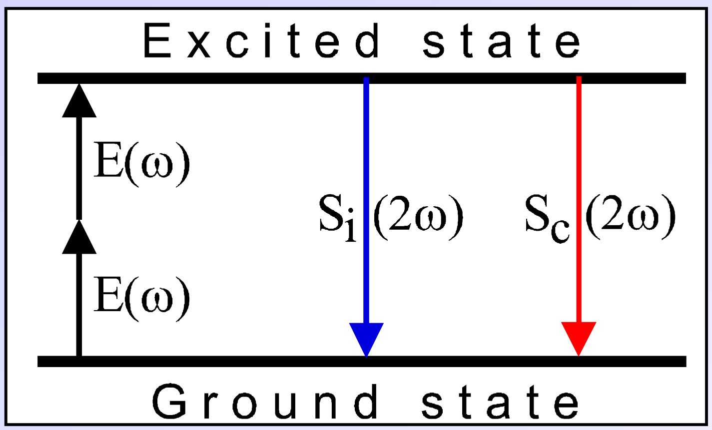
$$\vec{S} = \mu_0 \frac{\partial^2 \vec{P}^{NL}}{\partial t^2} + \mu_0 \left(\vec{\nabla} \times \frac{\partial \vec{M}^{NL}}{\partial t} \right) - \mu_0 \left(\vec{\nabla} \frac{\partial^2 \hat{Q}^{NL}}{\partial t^2} \right)$$

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

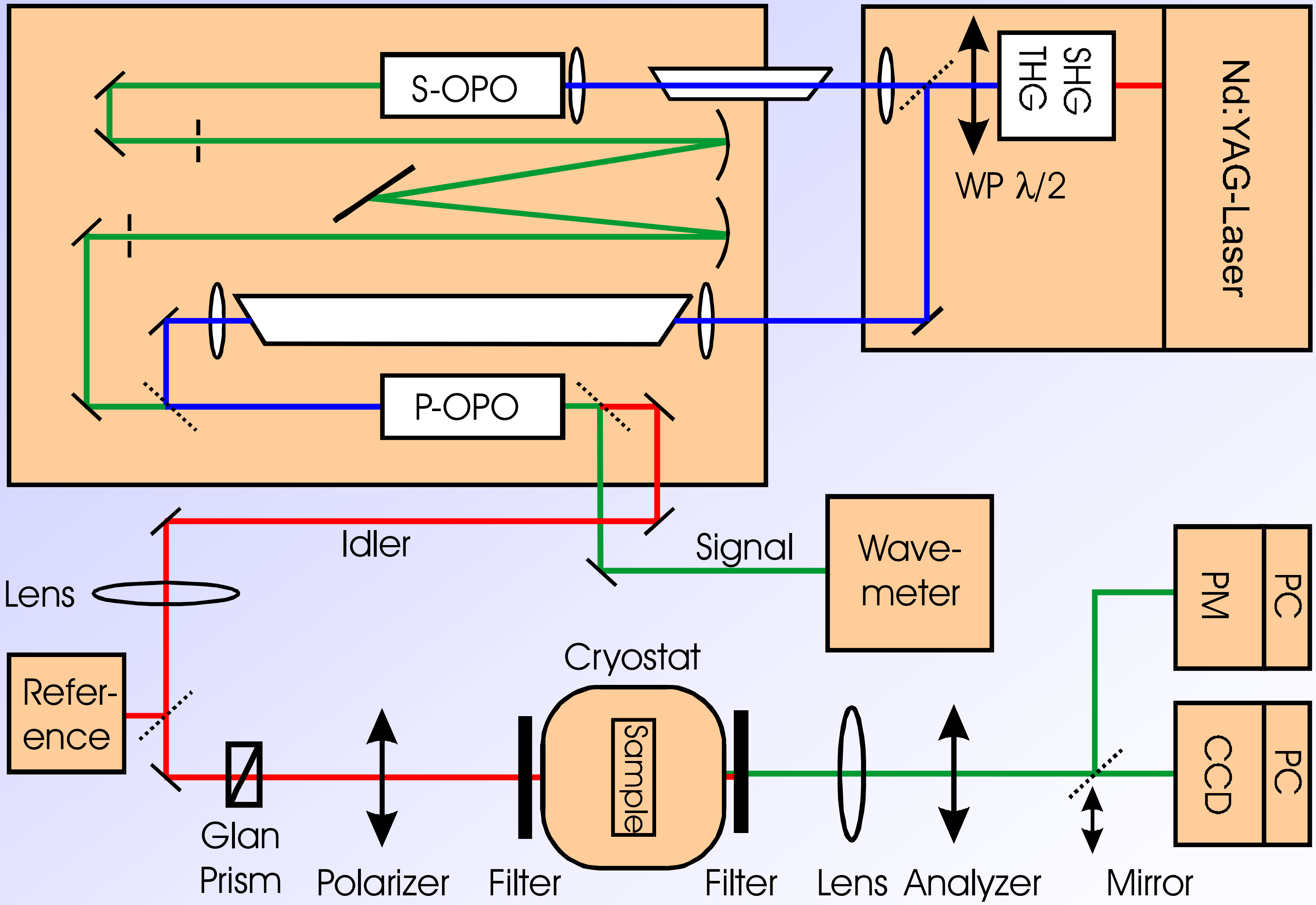
SH intensity: $I_{SH} \propto |S(c) + S(i)|^2$

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

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

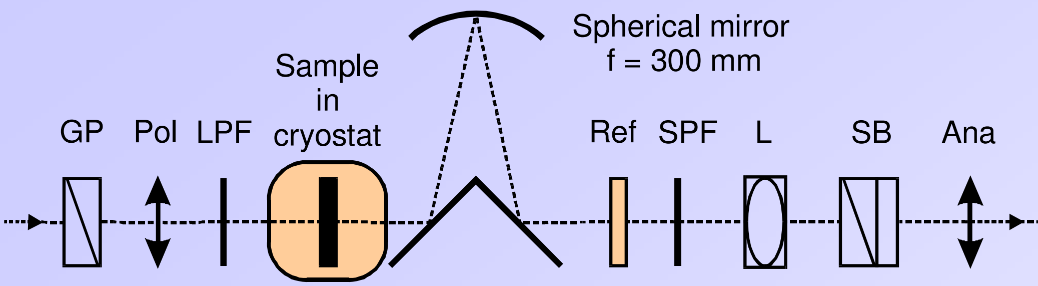
Amplitude A and phase ψ can be controlled in the experiment.

Experimental Setup

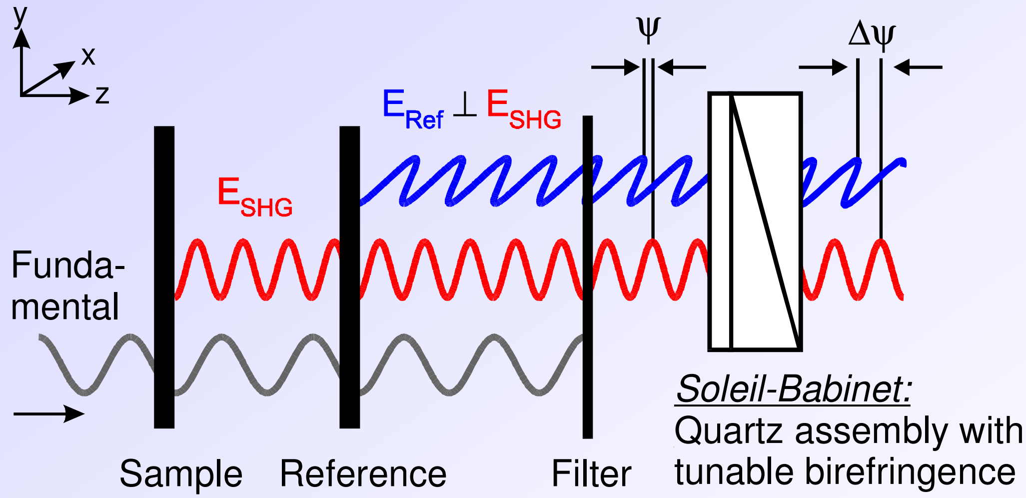


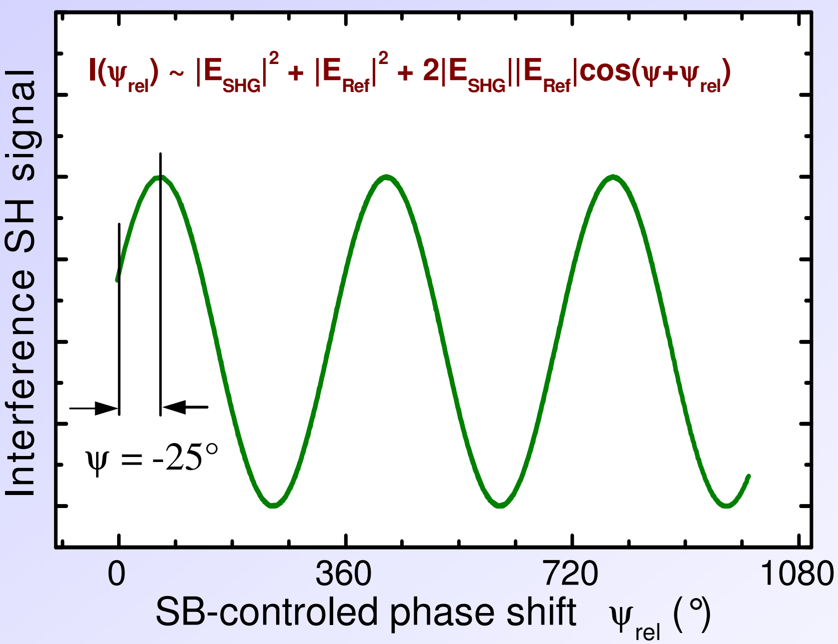
Basic setup with a pulsed Nd:YAG - OPO laser system (3 ns, ≤100 Hz, 0.4 - 3.0 μm)

Phase Resolved SH Imaging

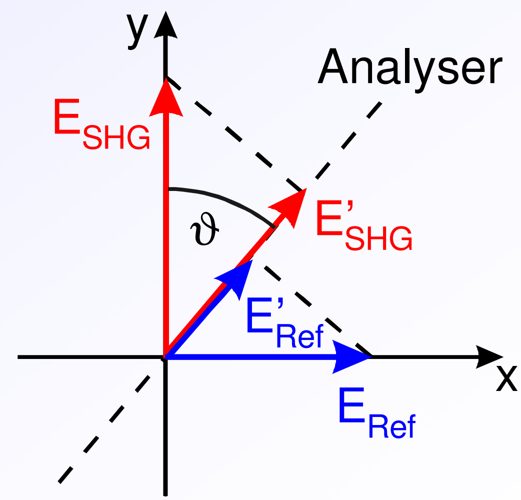


Achromatic beam imaging of sample onto reference crystal in phase measurements



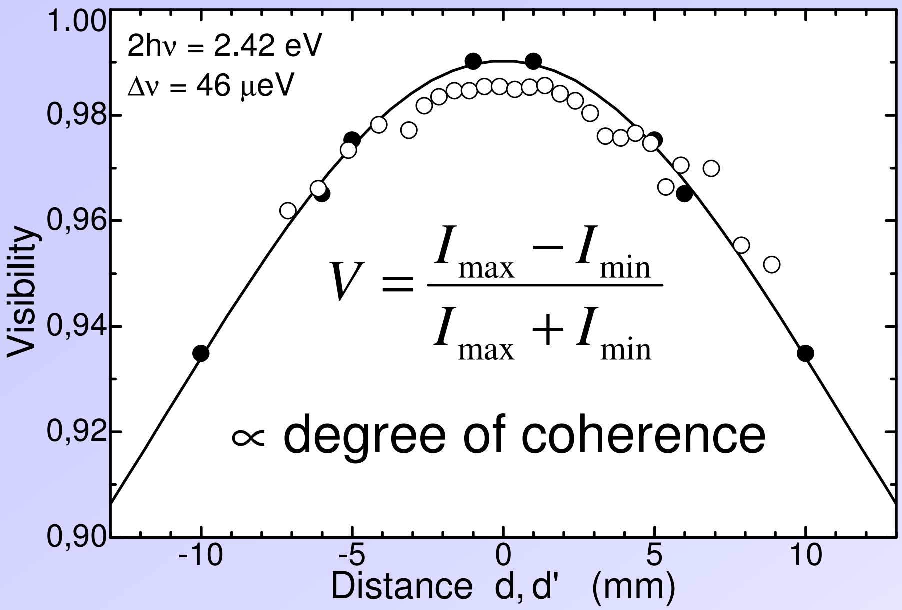


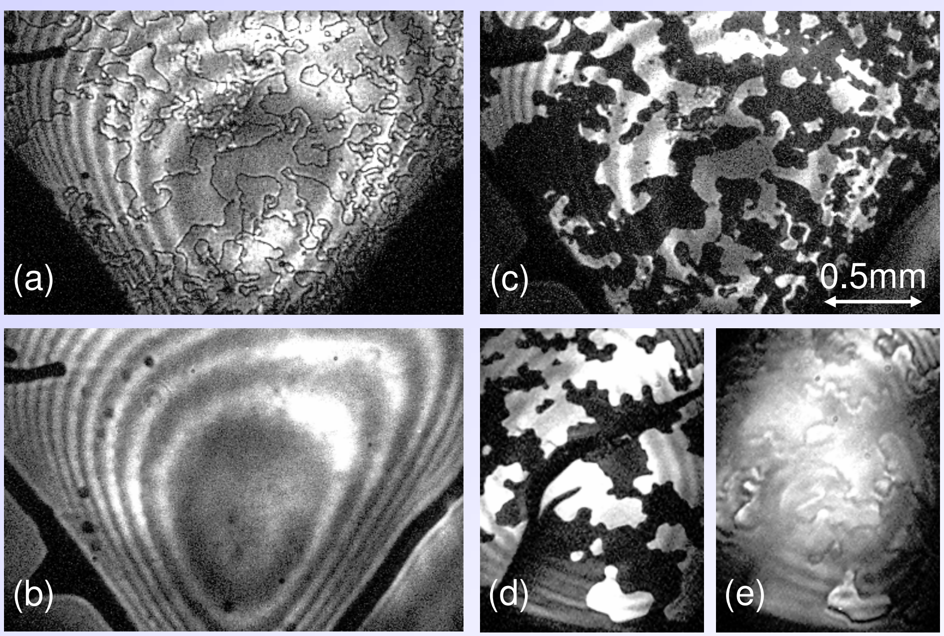
Holographic interference of SH signal from sample and SH reference wave from quartz crystal → amplitude and phase of signal wave



Opt. Lett. **24**, 1520 (1999), Opt. Lett. **29**, 41 (2004)

Phase-Resolved SH Imaging (Results)





Visibility nearly 100%

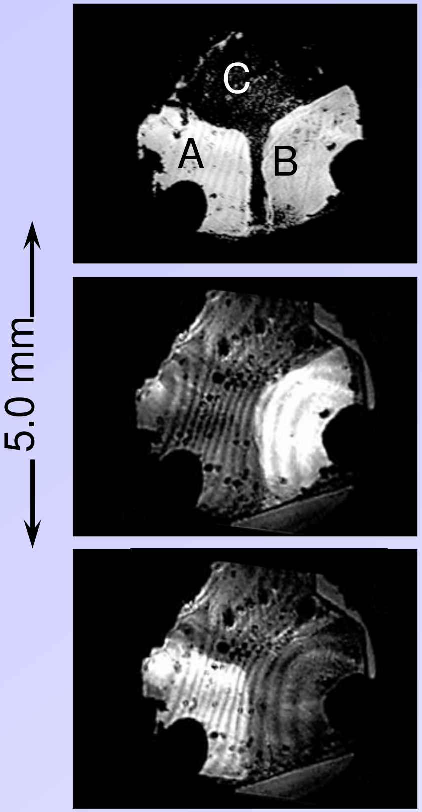
Loss of spatial coherence fully compensated!

Advantages:

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

Opt. Lett. **29**, 41 (2004)

SHG on Ferroelectric $HoMnO_3$ Domains



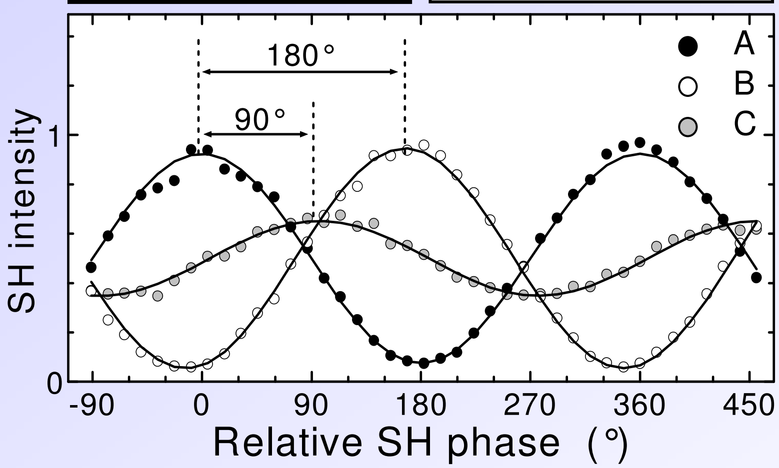
SHG from sample
A: + 90 kV/cm
B: - 90 kV/cm
C: no field

SHG from sample and reference

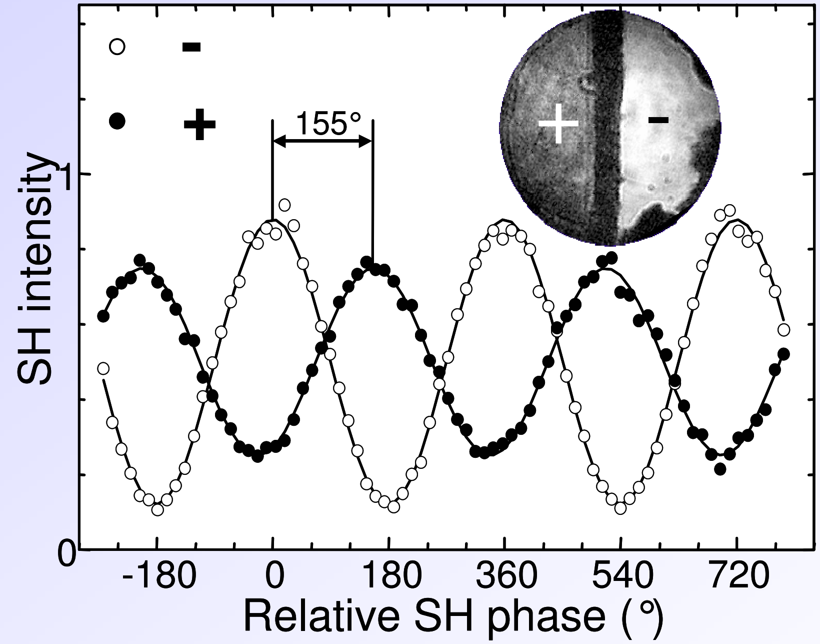
Phase: φ = 180°

SHG from sample and reference

Phase: φ = 0°



But also:



- 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

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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:

- Crytallographic and magnetic structure
- Thin films and ferroelctric properties ($\rightarrow$ application)
- Multiferroic/magnetoelectric properties

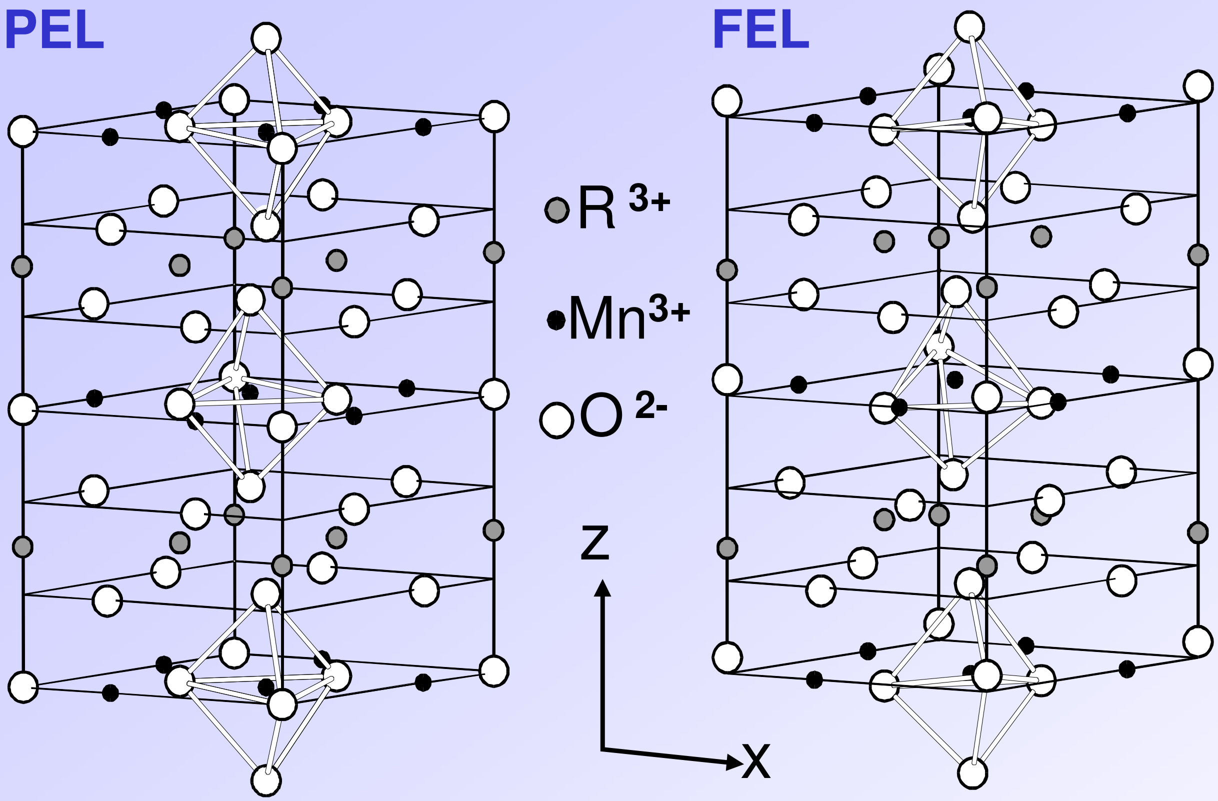
Hexagonal manganites $RMnO_3$ (R = Sc, Y, In, Ho, Er, Tm, Yb, Lu)

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

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

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

Crystallographic and Magnetic Structure

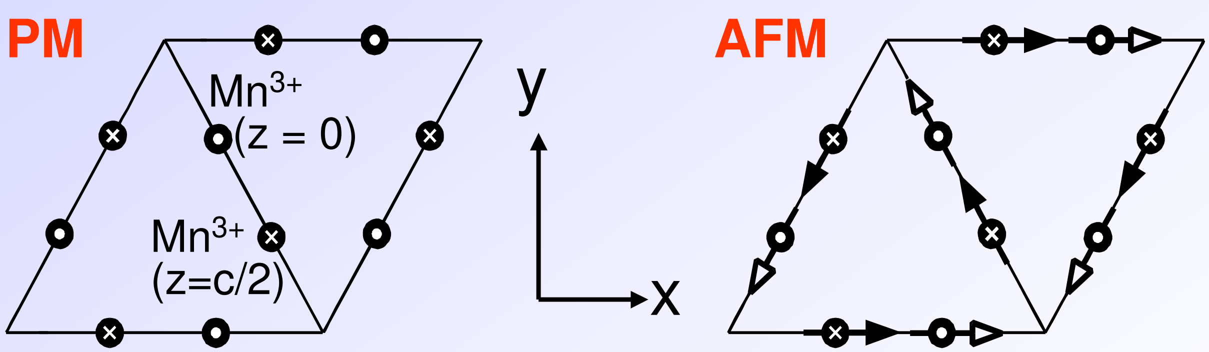


Ferroelectric phase transition:

Breaking of inversion symmetry I!

Order parameter: $\mathcal{P}$

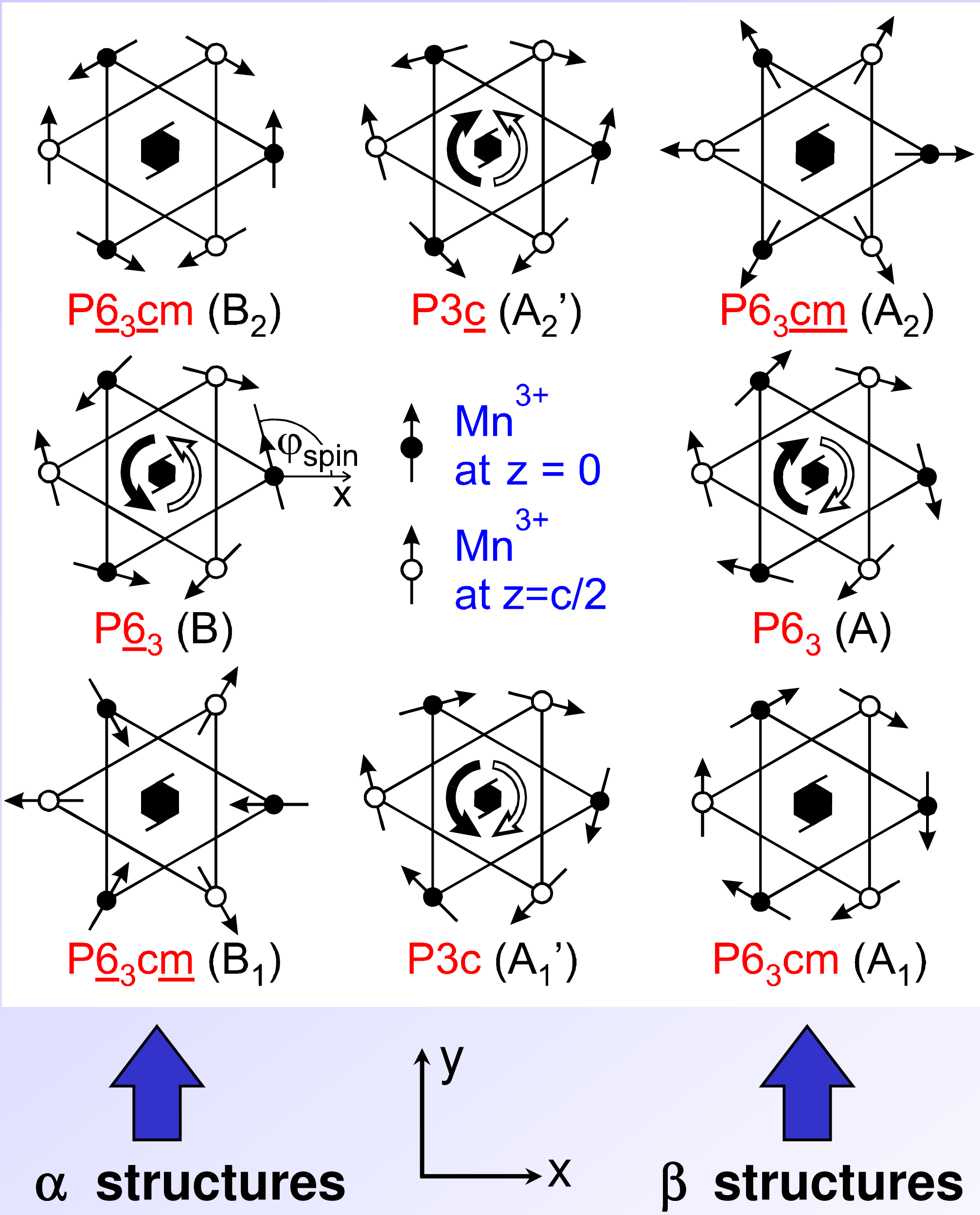
Antiferromagnetic phase transition of the Mn^{3+} sublattice:



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

Order parameter: ℓ

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!

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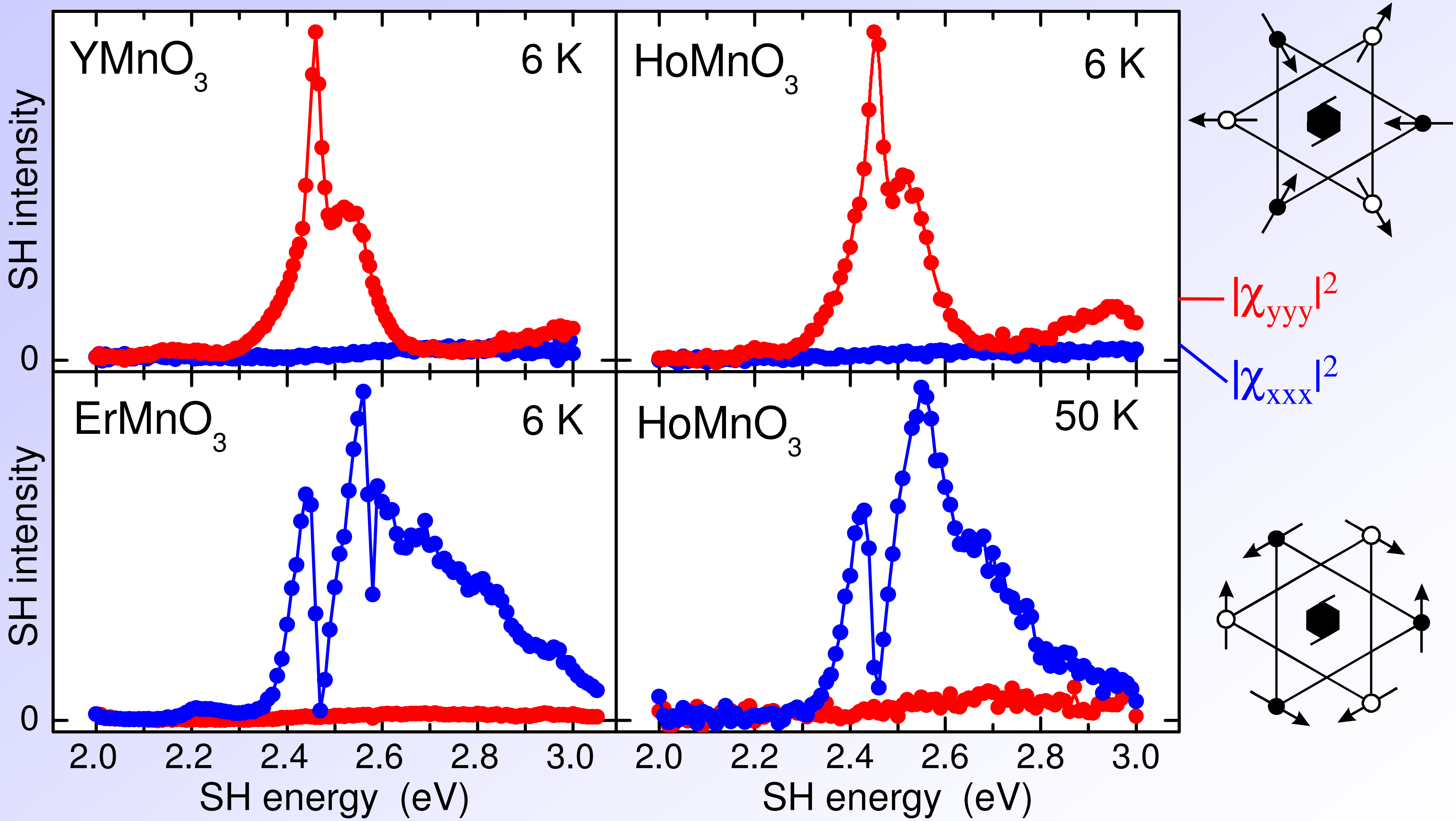
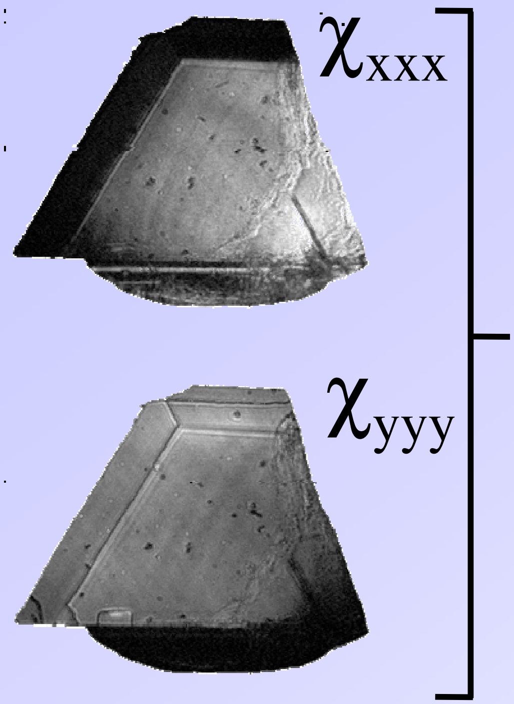
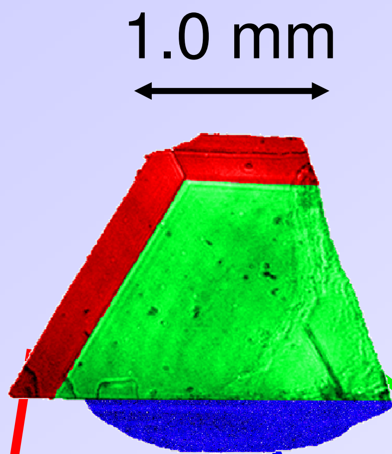
SH spectrum and Magnetic Symmetry

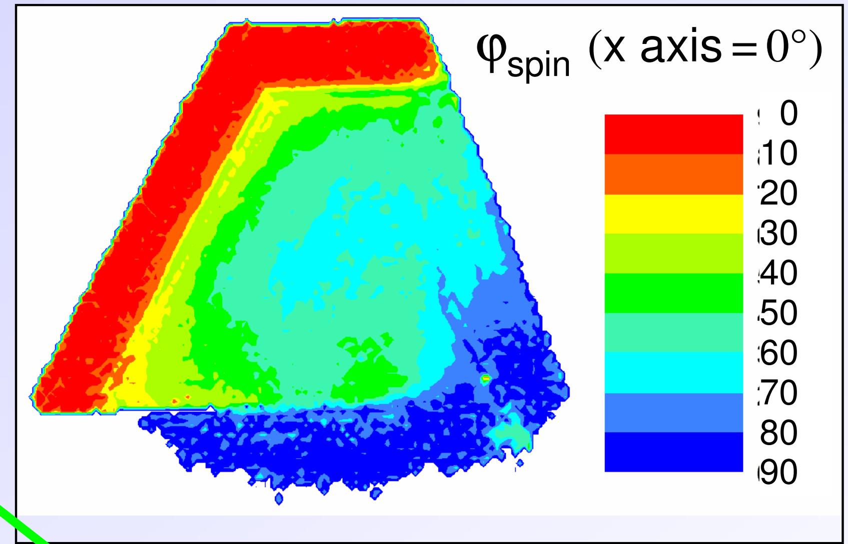


The magnetic symmetry, ***not*** the R ion, determines the SH spectrum of *R*MnO_3

Phase Coexistence and Spin Topography in $ScMnO_3$

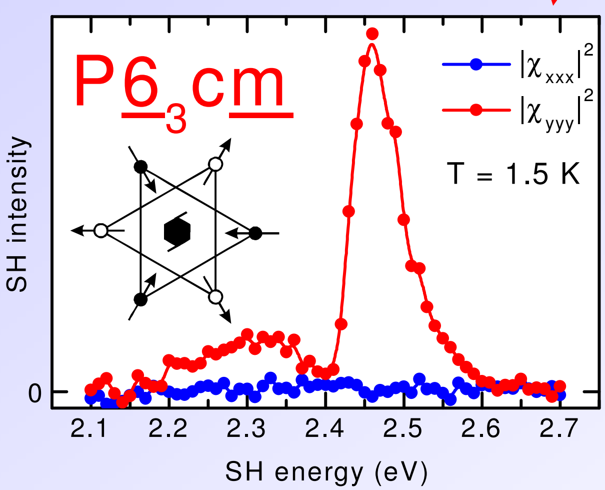


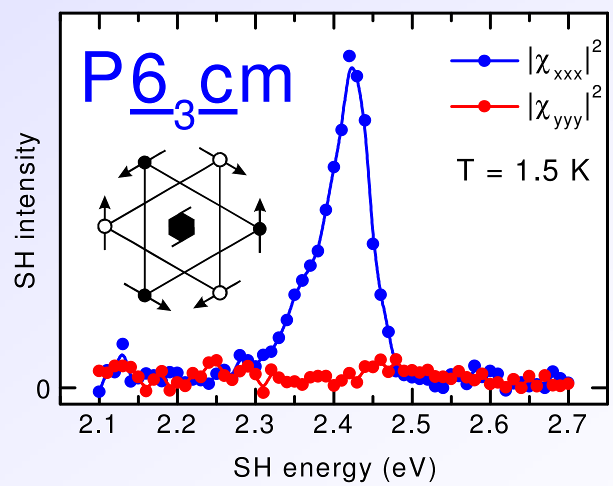


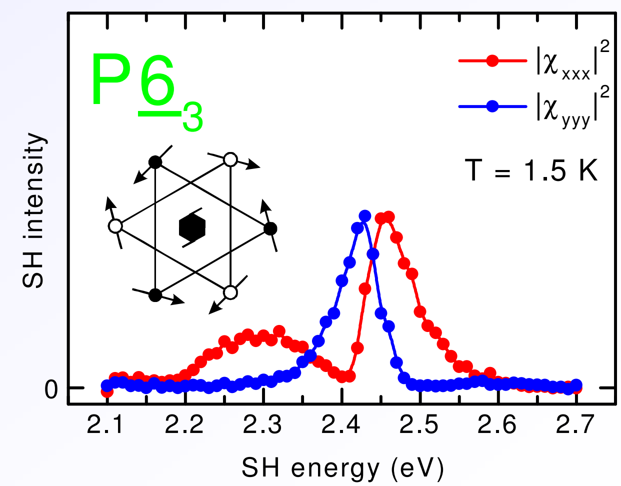


Spin - angle topography

Appl. Phys. Lett. **77**, 4401 (2000)

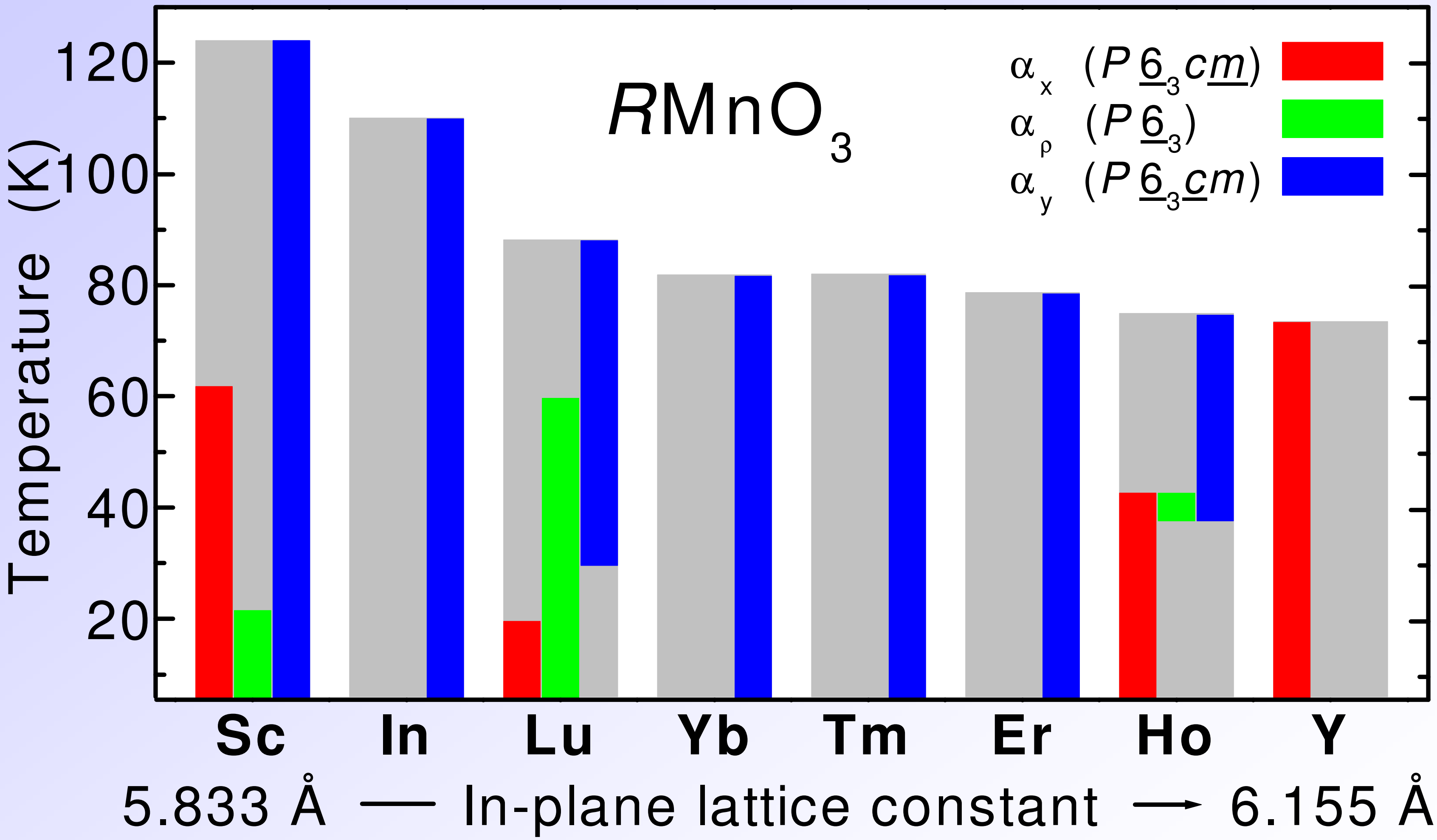






Magnetic Symmetry of Hexagonal $RMnO_3$

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



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

SHG in a Multiferroic Compound

Two-dimensional expansion of the SH susceptibility χ for electric and magnetic 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	
$\chi(\mathcal{P}\ell)$:	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

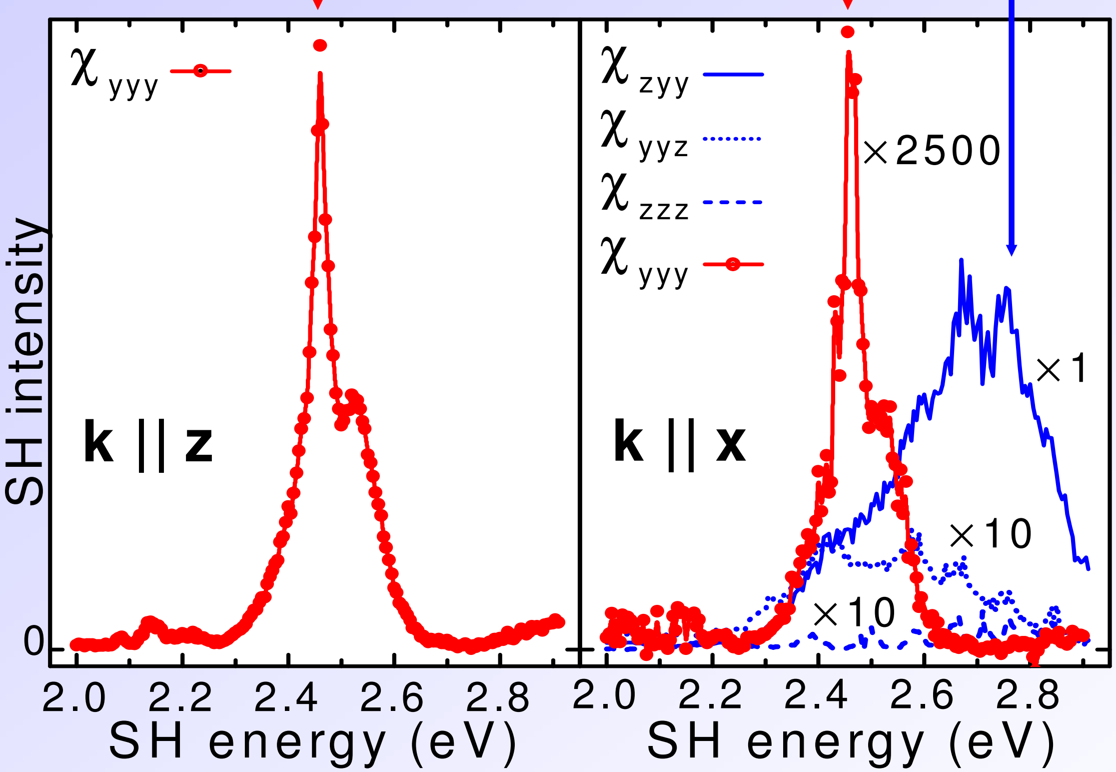
Symmetry analysis

Ordered Sublattice	Space group	Parity - type symmetry operation	Order parameter
(para)	$P6_3/mmc$	I, T, IT	---
FEL	$P6_3cm$	T	$\mathcal{P}$
AFM	$P\underline{6_3}/\underline{m}c\underline{m}$	I	ℓ
FEL + AFM	$P\underline{6_3}c\underline{m}$	---	$\mathcal{P}\cdot\ell$

		$\mathbf{S}^{ED}(\mathcal{P})$	$\mathbf{S}^{MD}(\ell)$	$\mathbf{S}^{EQ}(\ell)$	$\mathbf{S}^{ED}(\mathcal{P}\cdot\ell)$
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	---	$-2m_1E_xE_y$	$-2q_3E_xE_y$	$-2e_1E_xE_y$
	S_y	---	$m_1(E_y^2 - E_x^2)$	$q_3(E_y^2 - E_x^2)$	$e_1(E_y^2 - E_x^2)$

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* || *z*	= 0	= 0	≠ 0	≠ 0
SHG for *k* || *x*	= 0	≠ 0	= 0	

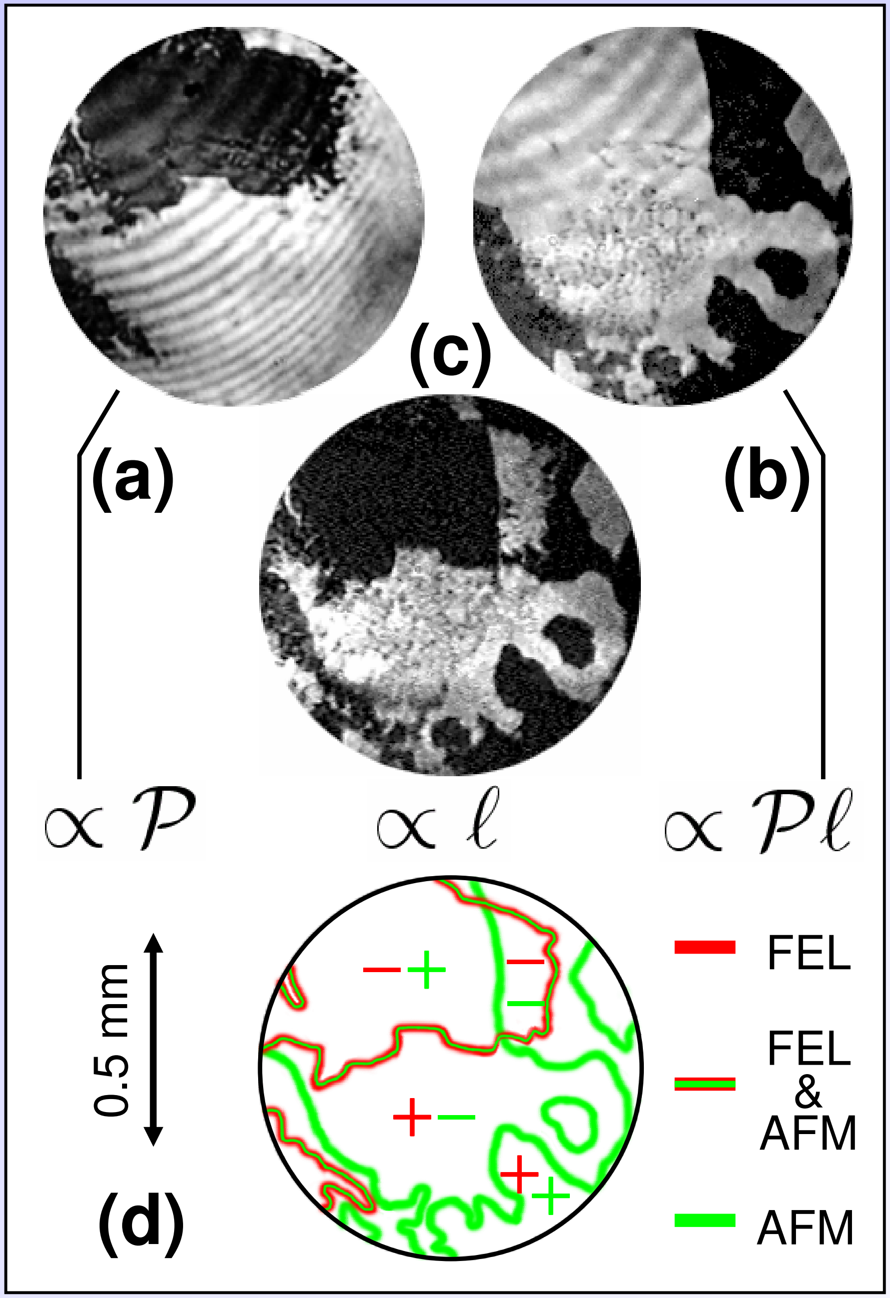


Identical magnetic spectra for k||z and k||x indicate **bilinear coupling to $\mathcal{P}$, ℓ.**

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

Nature **419**, 818 (2002)

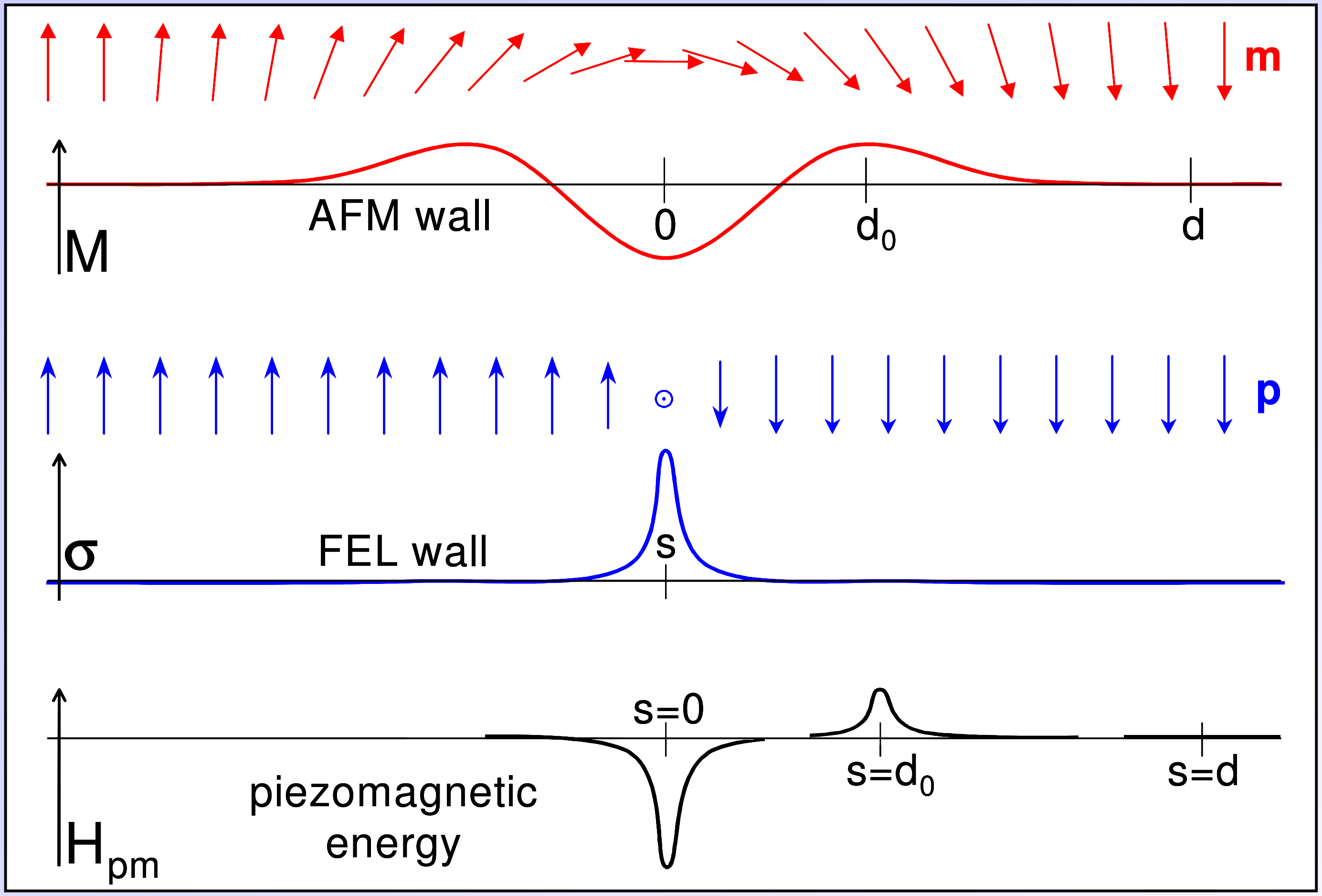
Observation of Ferroelectromagnetic Domains



- Independent ferroelectric ($\propto \mathcal{P}$) and ferroelectromagnetic ($\propto \mathcal{P}\ell$) domain structures; antiferromagnetic domain structure ($\propto \ell$) is not!
- "Ferroelectromagnetic domains":
  $\mathcal{P}\ell$ = +1 for $\mathcal{P} = \pm1$, $\ell = \pm1$
  $\mathcal{P}\ell$ = -1 for $\mathcal{P} = \pm1$, $\ell = \mp1$
- 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

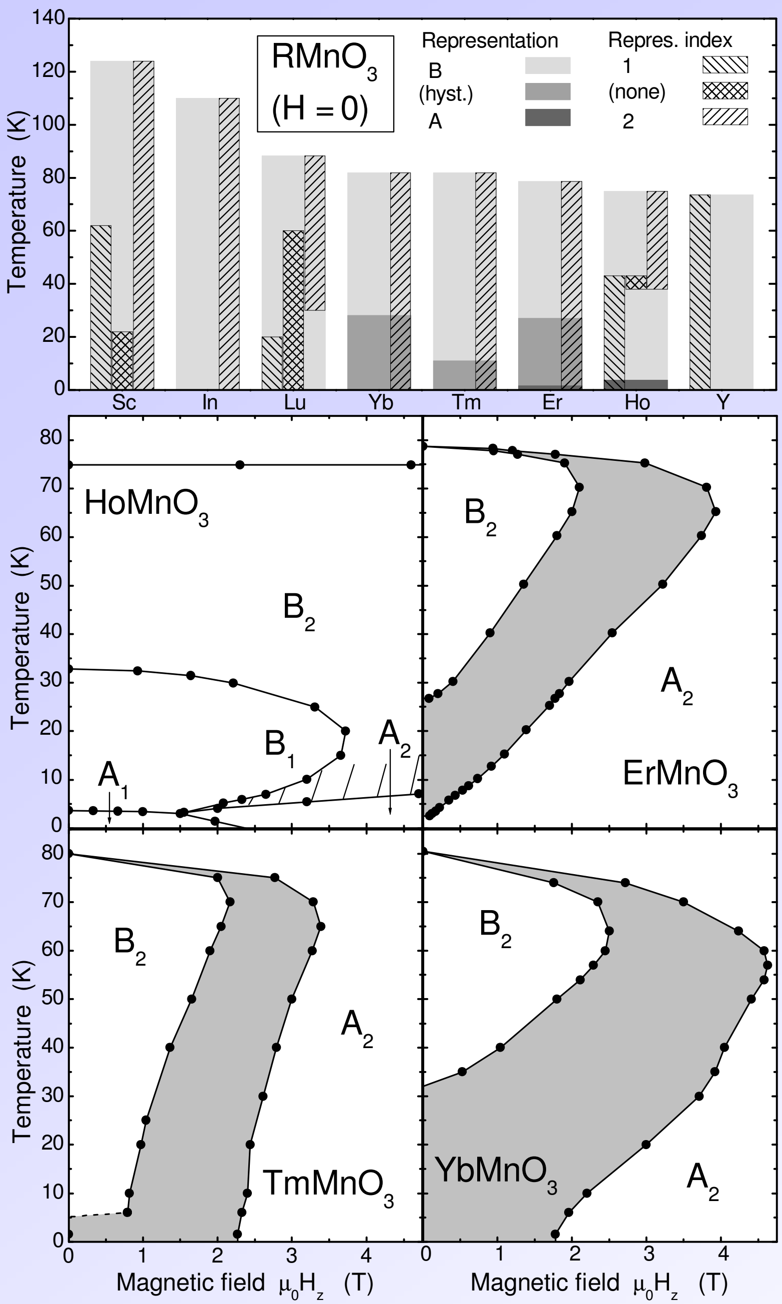
- FEL wall induces strain due to switching of polarization

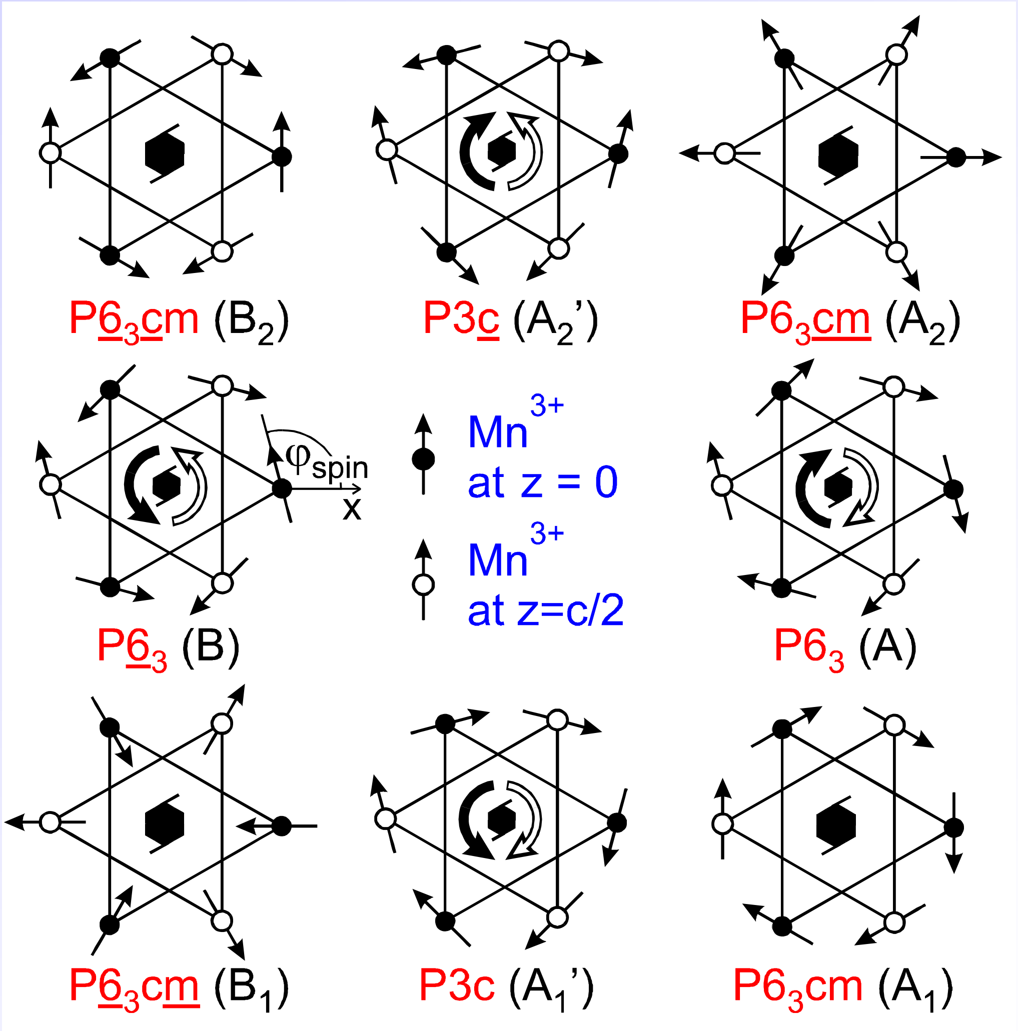
- Width of walls:
  - AFM - $O[10^3]$ unit cells: small in-plane anisotropy
  - iii • FEL – $O[10^0]$ unit cells: large uniaxial anisotropy

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)

H/T Phase Diagram of Hexagonal *R*MnO_3



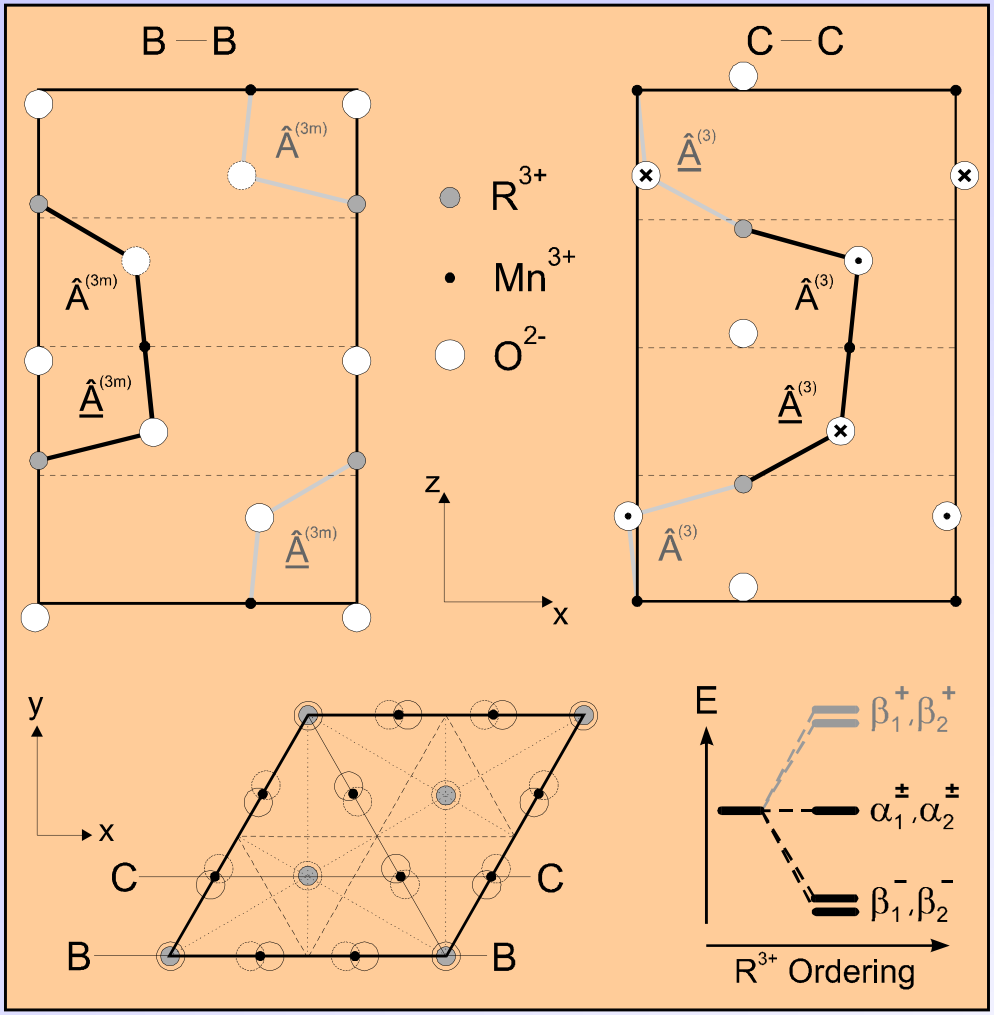


α structures

y x

β structures

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



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

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

- 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:

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

Ferroelectric distortion modifies the superexchange:

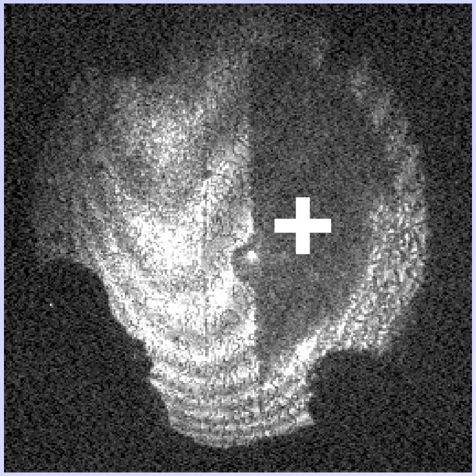
$\delta\hat{A} \equiv \hat{A} - \underline{\hat{A}}\,,\quad \delta\hat{A} = \delta\hat{A}_0 P_z$ Scales with order par.

$\alpha_{zz} \equiv 6\ell S_y^{\mathrm{Mn}}(\delta A_0^{3m} \pm \delta A_0^{3})_{zy}$ Substitution leads to:

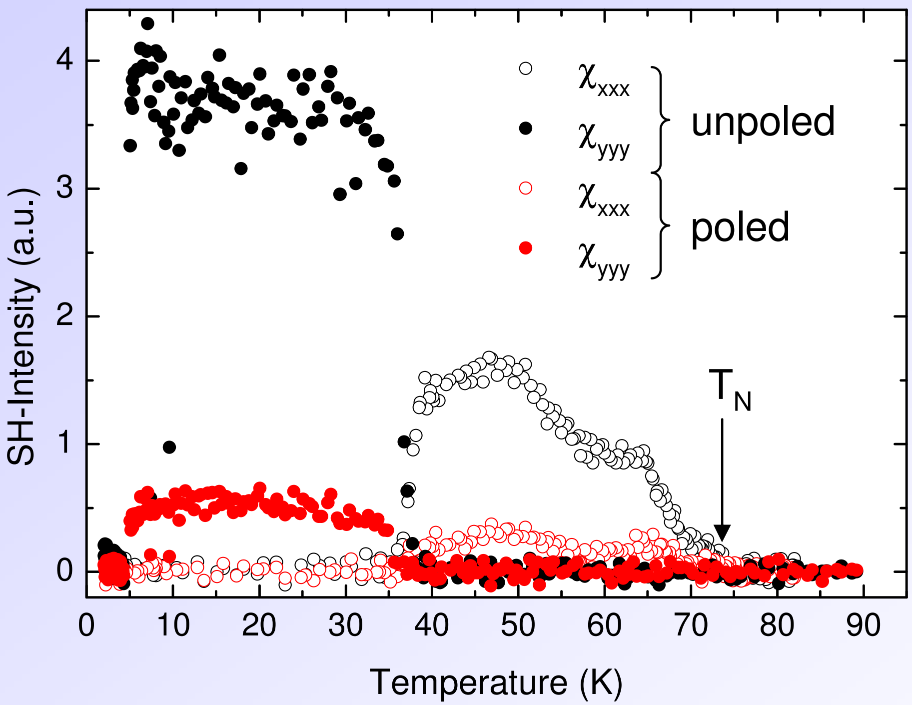
$H_{ex}(\beta_x) = \alpha_{zz} P_z S_z^R$ **ME contribution**

Spontaneous Magnetoelectric Effect in $HoMnO_3$

Antiferromagnetic SH



Ferroelectric poling quenches magnetic signal!



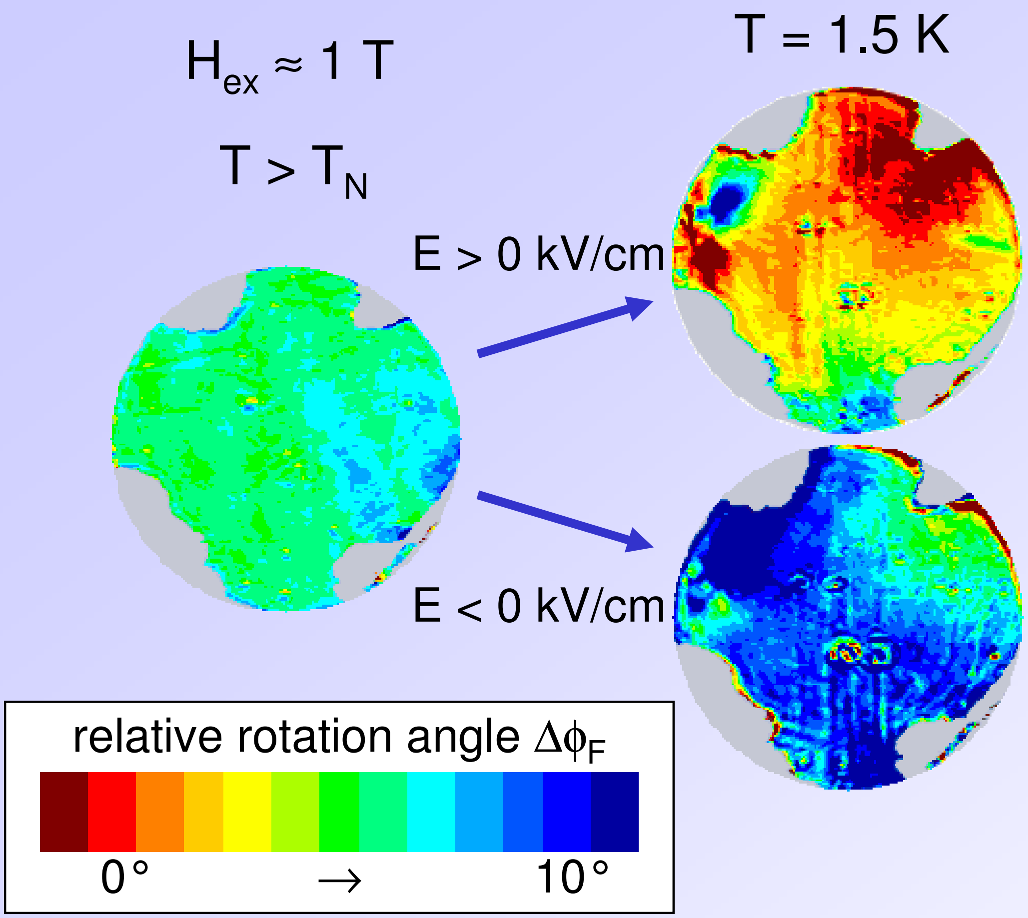
Only Explanation:

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 $HoMnO_3$



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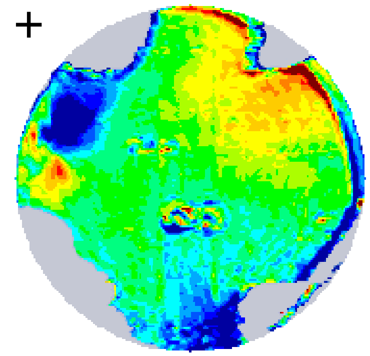

Average Farraday rotation induced bei external magnetic field

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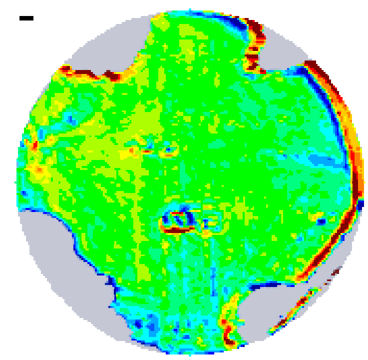

Additional Farraday rotation due to phase transition induced bei external electric field

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!

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- Multiferroics and the Magnetoelectric Effect
- Nonlinear Optics
- Hexagonal Manganites
- Experimental Results
- **Summary**

Summary

Multiferroic hexagonal manganites $R\text{MnO}_3$ are a modell substance to investigate magnetoelectric interactions in a ferroelctromagnetic material:

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

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