Part IV – Multiferroic $RMnO_3$

- Ferroelectric & magnetic ordering
- SHG spectroscopy
- SHG topography
- Identification of multiferroic interactions

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Multiferroic Hexagonal Manganites $RMnO_3$

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

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

$T < T_N \approx$ 65-130 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

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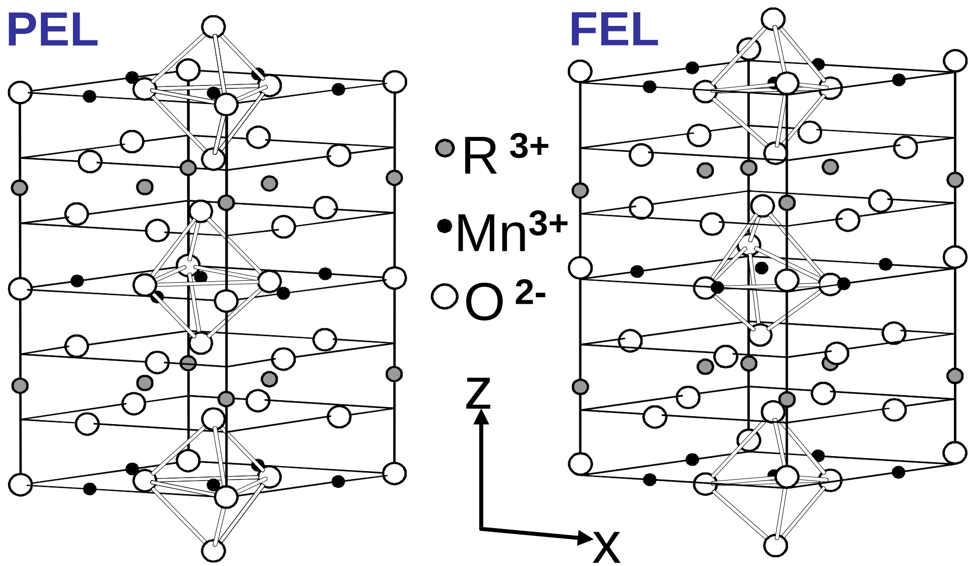
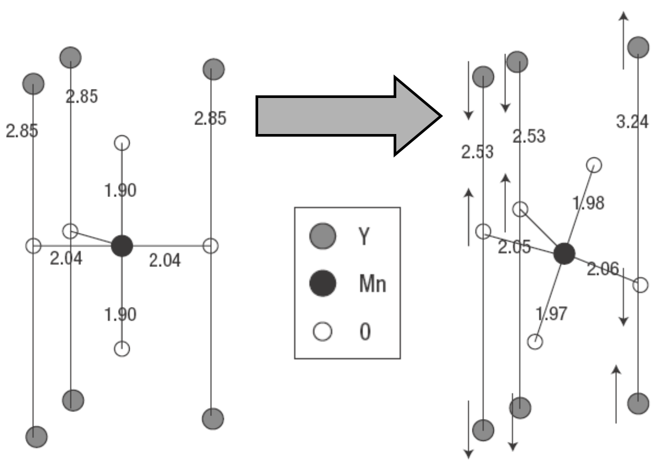
Ferroelectric order of $RMnO_3$





B.B. van Aken, Nature Mater. **3**, 164 (2004)

Ferroelectric phase transition at $T_C \approx 900$ K

Breaking of inversion symmetry I

PG: 6/mmm → 6mm

Order parameter $\mathscr{P}$

↔ ferroelectric polarization

$\mathbf{P} = (0, 0, P_z)$

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Ferroelectric SHG contributions

Point group 6mm → broken inversion symmetry → ED-SHG

$$\Rightarrow \quad \chi_{ijk}^{ED}(T < T_C) = \chi_{ijkz}(T > T_C)\mathscr{P}_z$$

Allowed components of χ^{ED}: χ_{zzz}, $\chi_{xxz}(3) = \chi_{yyz}(3)$

$$\Rightarrow \quad \vec{P}(2\omega) \propto \begin{pmatrix} 2\chi_{xxz}E_x(\omega)E_z(\omega) \\ 2\chi_{xxz}E_y(\omega)E_z(\omega) \\ \chi_{zxx}\left(E_x^2(\omega) + E_y^2(\omega)\right) + \chi_{zzz}E_z^2(\omega) \end{pmatrix}$$

No SHG for k||z!

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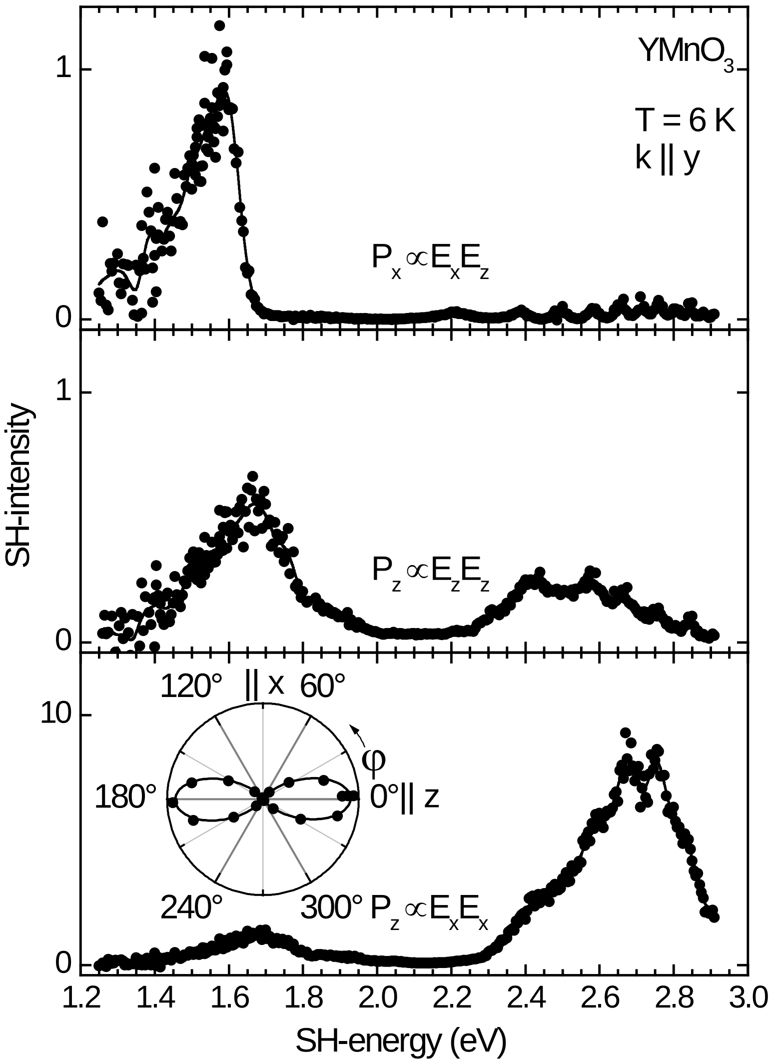
Ferroelectric SHG contributions



$$\vec{P}(2\omega) \propto \begin{pmatrix} 2\chi_{xxz} E_x(\omega) E_z(\omega) \\ 2\chi_{xxz} E_y(\omega) E_z(\omega) \\ \chi_{zxx}\left(E_x^2(\omega) + E_y^2(\omega)\right) + \chi_{zzz} E_z^2(\omega) \end{pmatrix}$$

- All expected SH contributions detectible
- Leading contribution χ_{zxx}
- No dependence on the *R*-ion

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Antiferromagnetic order of $RMnO_3$

In-plane triangular spin structure

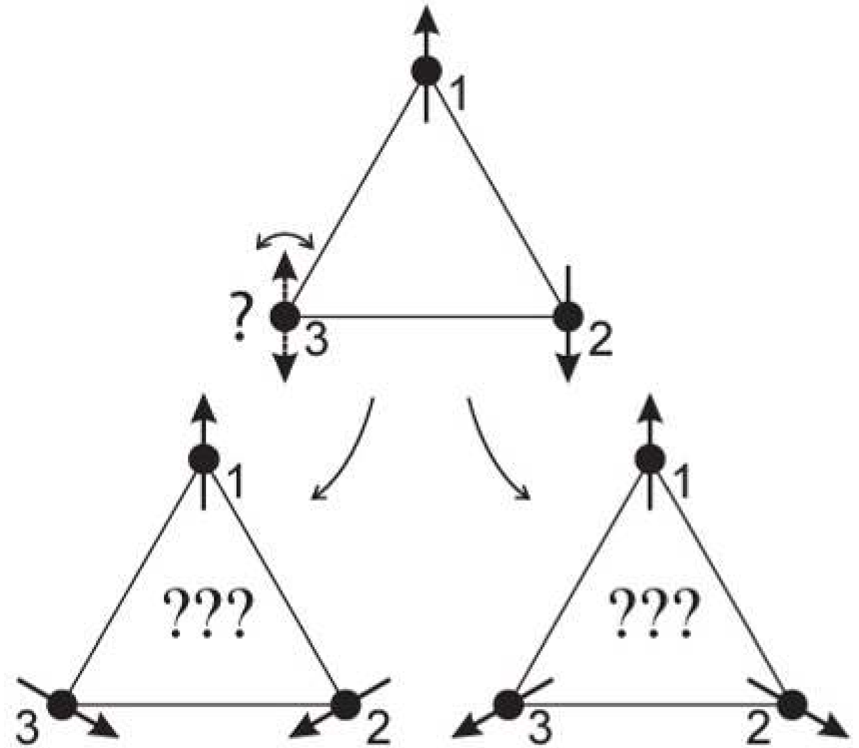
⇒ geometric frustration

⇒ 120°-spin structure

+ inter-plane ordering

+ sublattice interaction Mn ↔ R

⇒ complex magnetic system!



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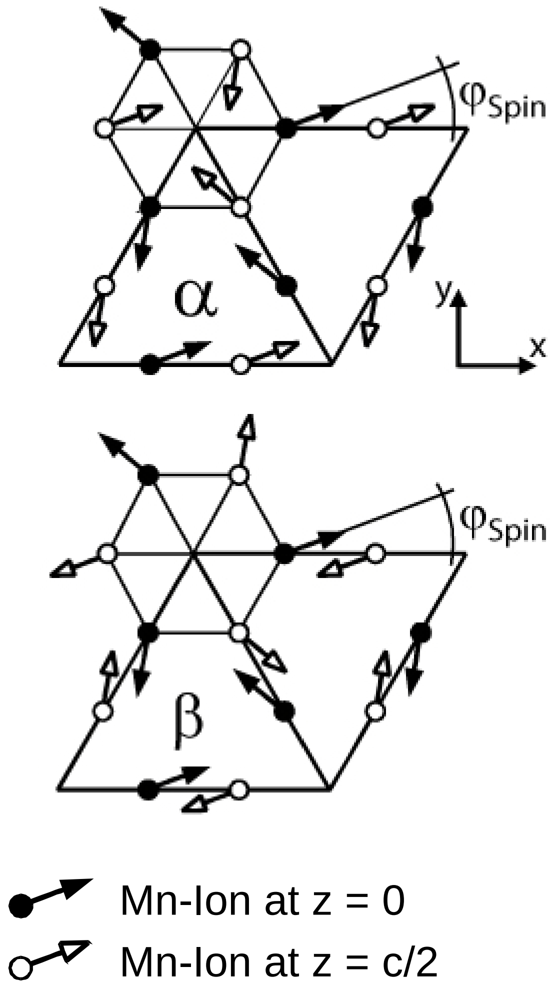
Antiferromagnetic α- and β-order



- Ferromagnetic interplane coupling
- Spin lattice is inversion symmetric

- Antiferromagnetic interplane coupling
- Spin lattice is not inversion symmetric

α and β structures not distinguishable with diffraction techniques!

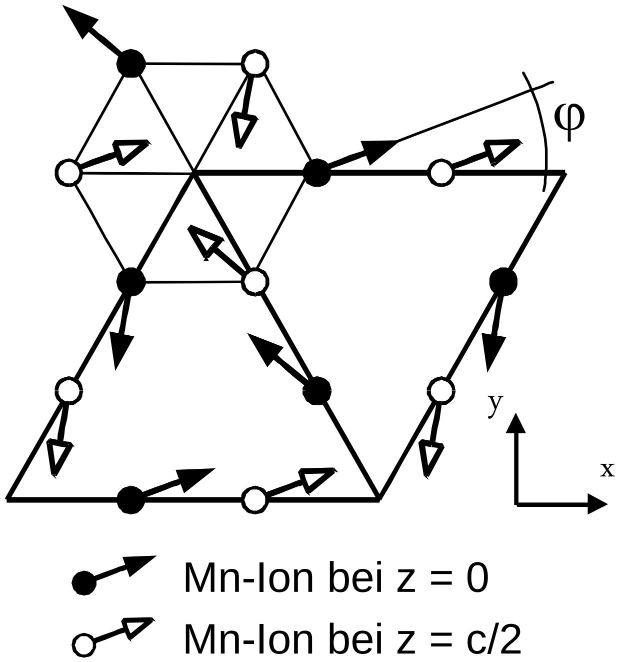
Anitferromagnetic α-order

Three different spin-orders depending on the spin-angle φ distinguishable:

α_x (φ=0°): PG $\underline{6}m\underline{m}$
ED: $-\chi_{yyy}=\chi_{yxx}=\chi_{xxy}=\chi_{xyx}$

α_y (φ=90°): PG $\underline{6m}m$
ED: $-\chi_{xxx}=\chi_{xyy}=\chi_{yxy}=\chi_{yyx}$

α_φ (φ=0°…90°): PG $\underline{6}$
ED: $\alpha_x \oplus \alpha_y$



Spin order distinguishable by SHG polarization!

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Anitferromagnetic β-order

Three different spin-orders depending on the spin-angle φ distinguishable:

β_x (φ=0°):   PG 6<u>mm</u>

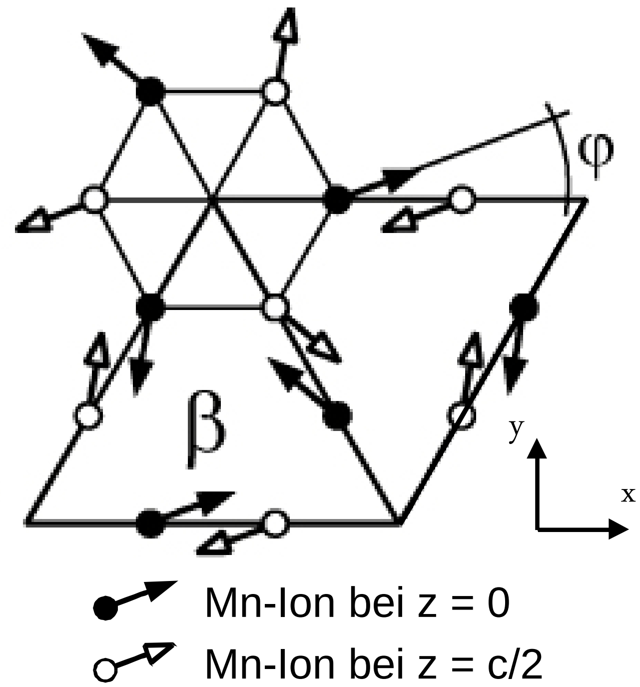
ED: $\chi_{xyz}=\chi_{xzy}=-\chi_{yxz}=-\chi_{yzx}$

β_y (φ=90°): PG 6mm

ED: χ_{zzz}, $\chi_{xxz}(3) = \chi_{yyz}(3)$

β_φ (φ=0°…90°): PG 6

ED: $\beta_x \oplus \beta_y$



No SHG for k||z!

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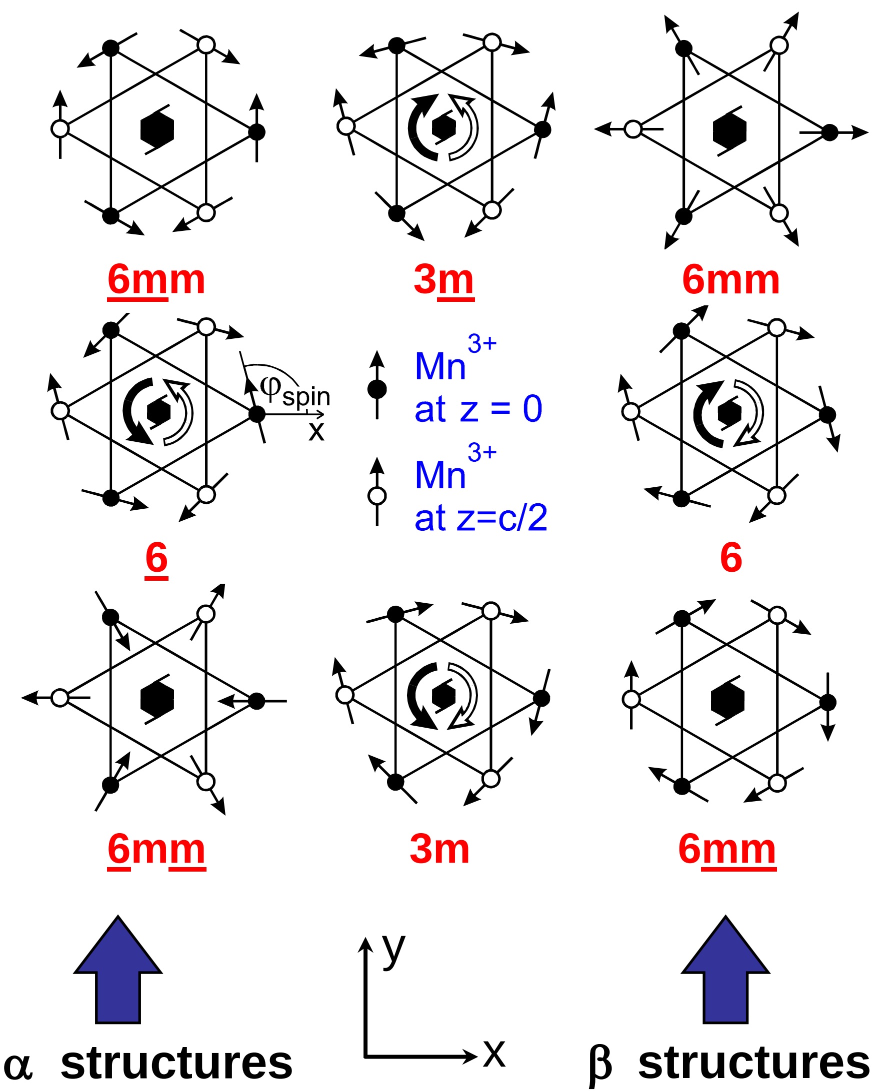
Magnetic Structure and SHG Selection Rules



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

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

6mm : $E_x(\omega) \rightarrow P_x(2\omega)$ $\sim \chi_{xxx}$

6mm : $E_x(\omega) \rightarrow P_y(2\omega)$ $\sim \chi_{yyy}$

6 : $E_x(\omega) \rightarrow P_x(2\omega) \oplus P_y(2\omega)$

6.. : $E_x(\omega) \rightarrow 0$

etc.

Polarization of ingoing and outgoing light reveals the magnetic symmetry

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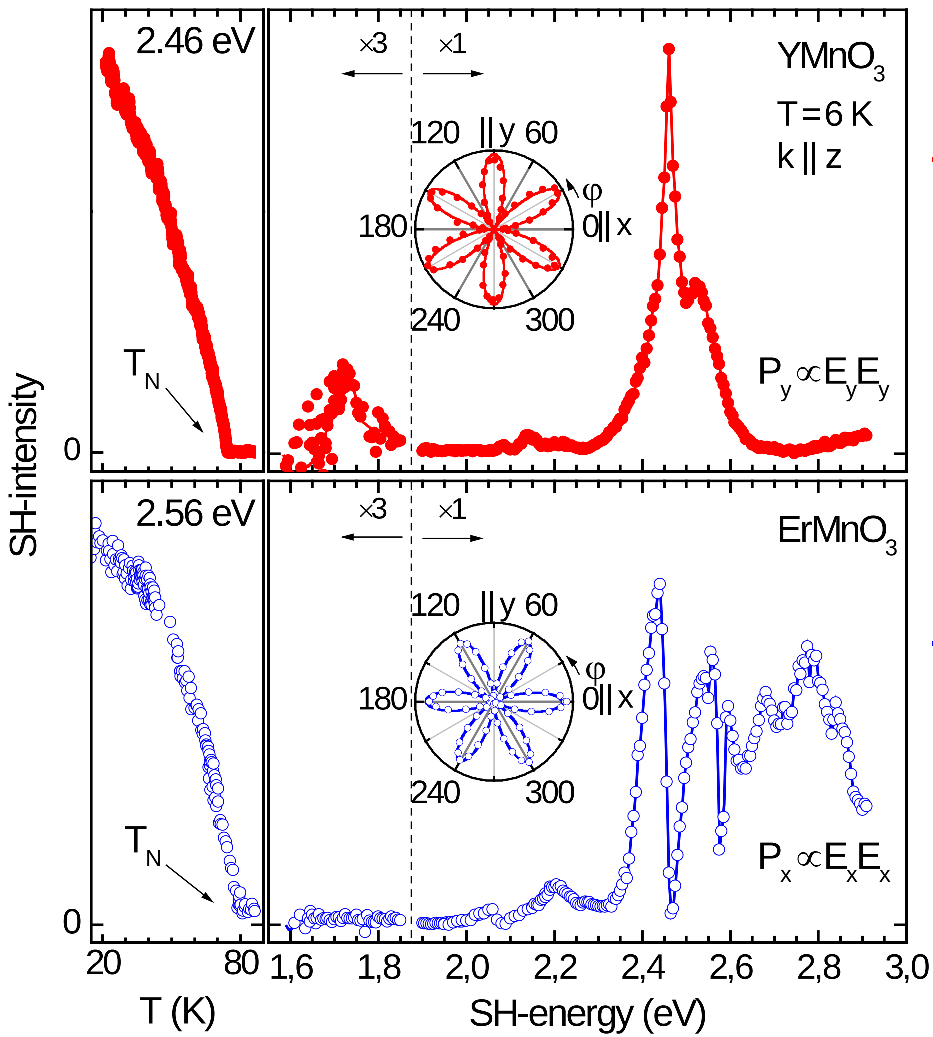
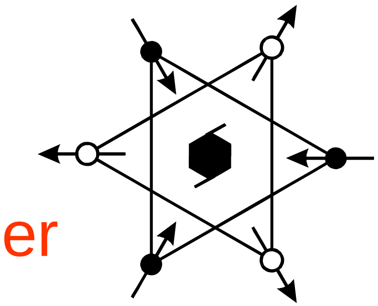
Symmetry determination by SHG spectroscopy



y polarized SHG

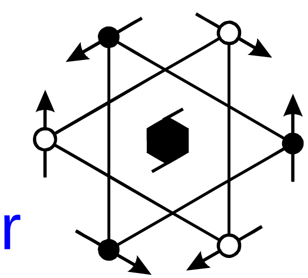
$\underline{6}m\underline{m} \propto |\chi_{yyy}|^2$



α_x order

x polarized SHG

$\underline{6m}m \propto |\chi_{xxx}|^2$



α_y order

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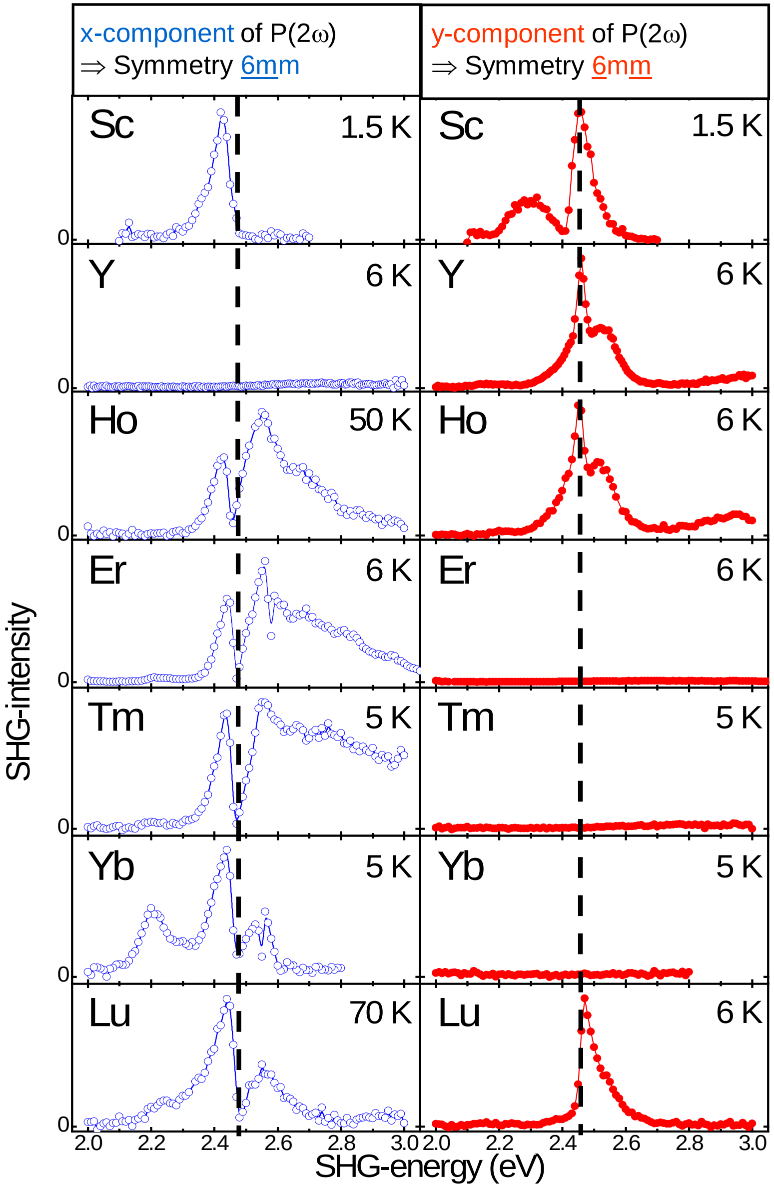
Symmetry determination by SHG spectroscopy



Spin || x-axis (Symmetry 6mm)

⇒ Intensity maximum at 2.46 eV

Spin || y-axis (Symmetry 6mm)

⇒ Intensity minimum at 2.46 eV

Just by using the spectral degree of freedom the magnetic symmetry can be determined!

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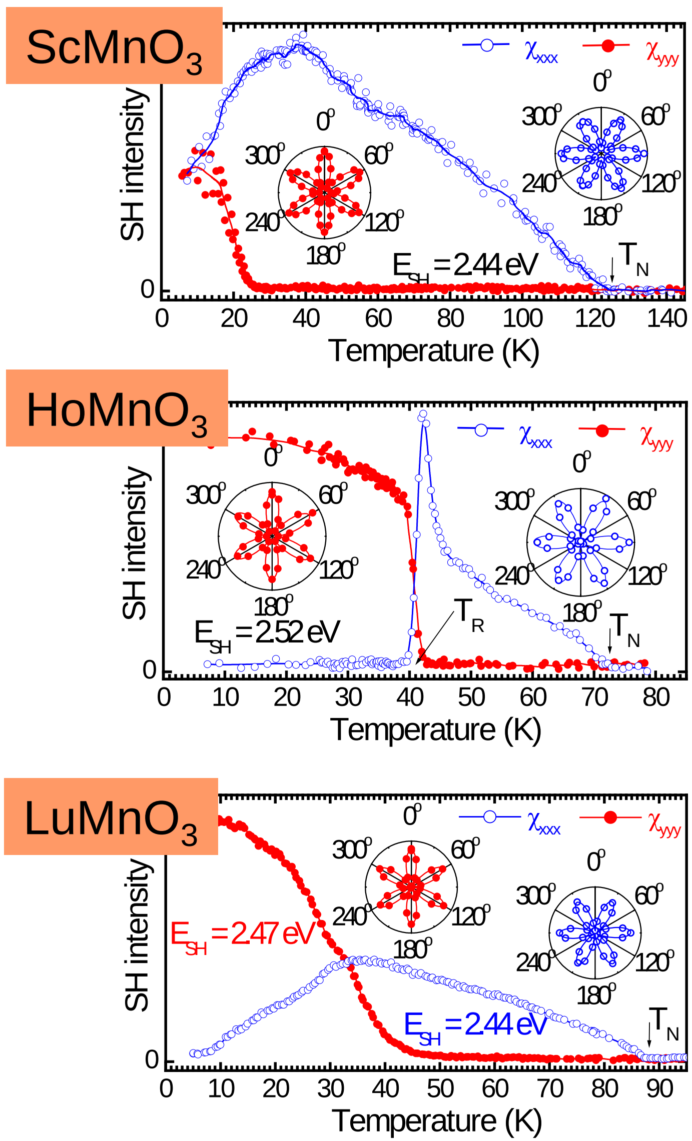
Phase Transitions in *R*MnO$_3$ (*R* = Sc, Ho, Lu)



Temperature depended change of symmetry:

High T: 6mm

Low T: 6mm

In addition temperature ranges with coexisting phases and reduced symmetry!

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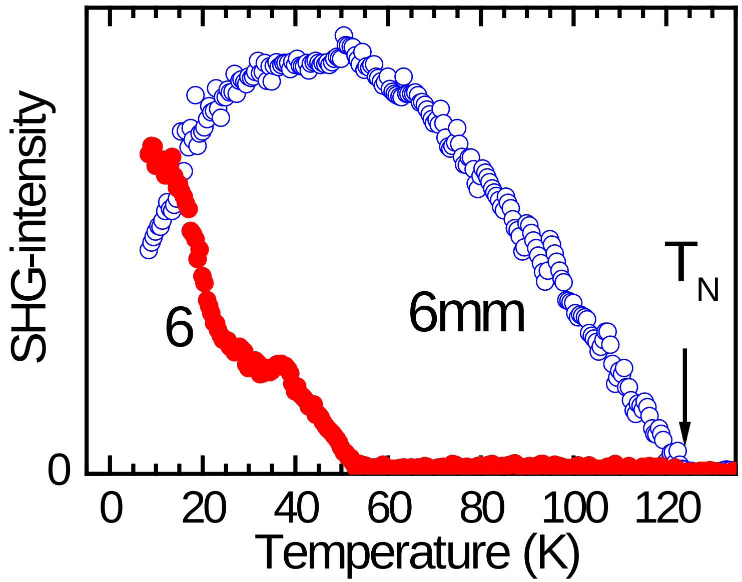
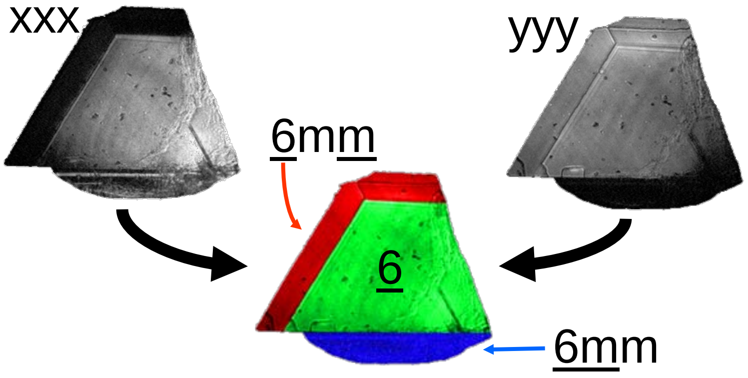
Phase Coexistence in $ScMnO_3$

Temperature depended



Spatial resolved



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Geometric Model for Spin-Angle Calculation

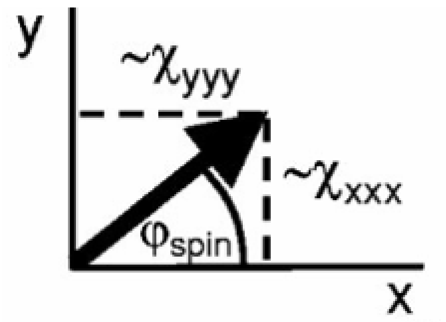
From symmetry:

PG	φ_{spin}	χ_{xxx}	χ_{yyy}
6mm	0°	0	≠0
6mm	90°	≠0	0
6	0°…90°	≠0	≠0

Geometric model: Calculating spin-angle from SHG intensities

$\chi_{xxx}(\varphi_{spin})=\chi^0_{xxx}\sin(\varphi_{spin})$

$\chi_{yyy}(\varphi_{spin})=\chi^0_{yyy}\cos(\varphi_{spin})$



$$\varphi_{\mathrm{spin}}(T)=\arctan\left(\frac{|\chi^0_{yyy}(T)|}{|\chi^0_{xxx}(T)|}\sqrt{\frac{I^x_{\mathrm{SH}}(T)}{I^y_{\mathrm{SH}}(T)}}\right)$$

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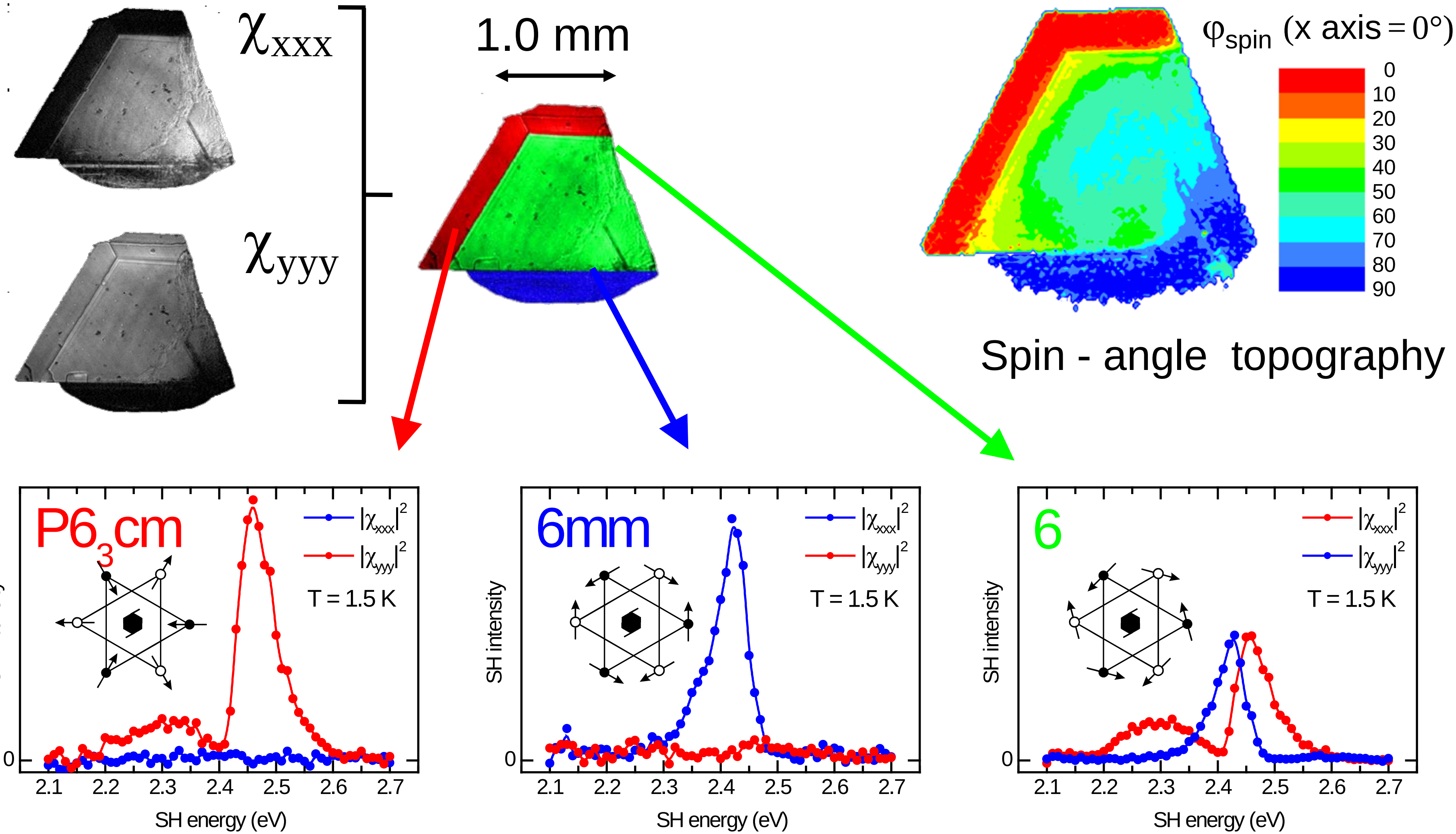
Phase Coexistence & Spin Topography ($ScMnO_3$)



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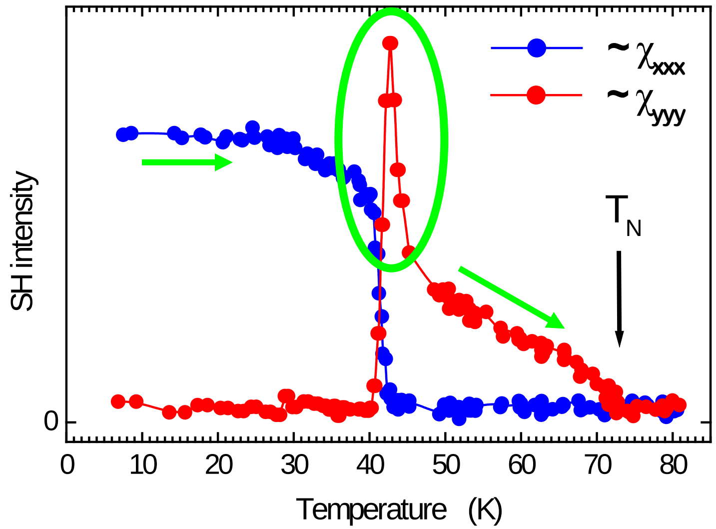
Spin Rotation in $HoMnO_3$

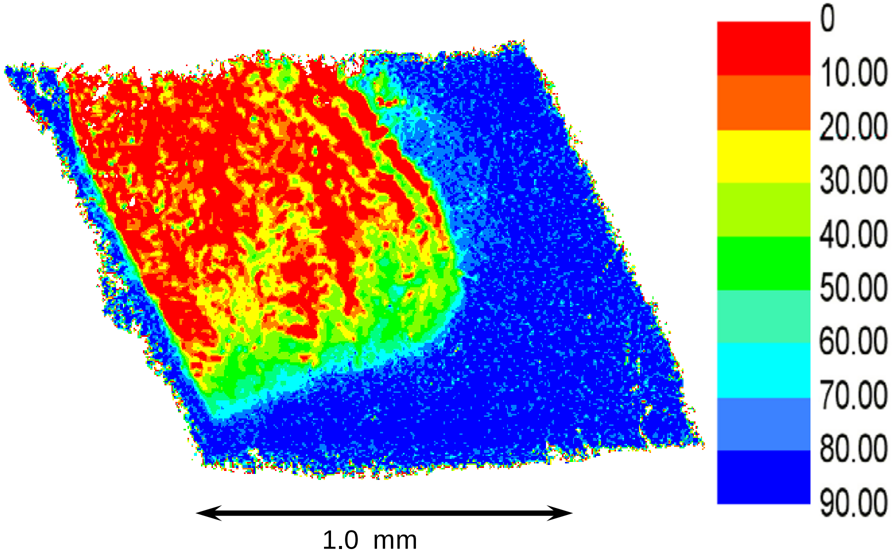


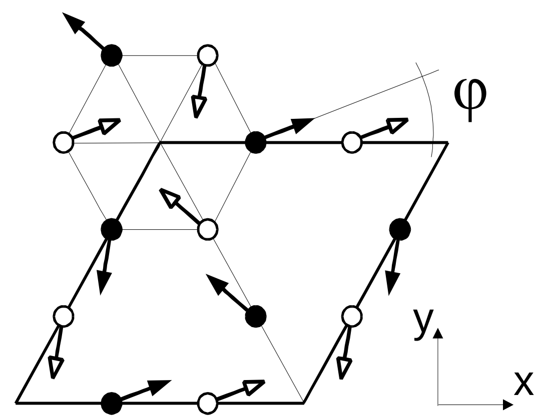
Phase transition at ≈41 K:

$T < T_R$: Symmetry <u>6</u>m<u>m</u>

$T > T_R$: Symmetry <u>6mm</u>

⇒ 90° spin rotation at T_R = 41 K





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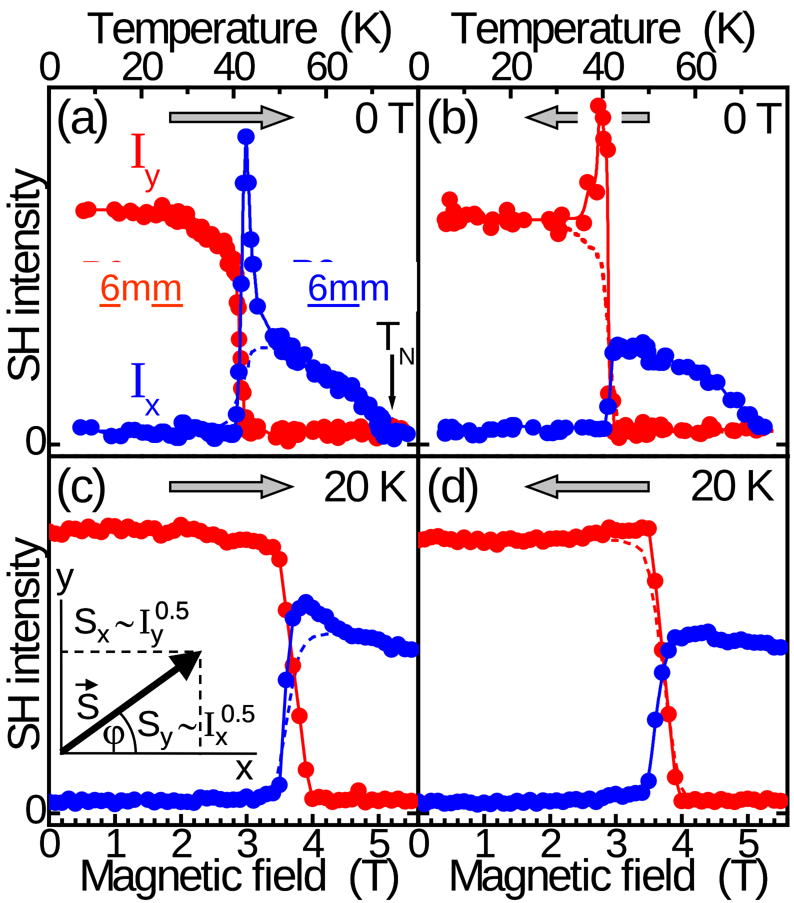
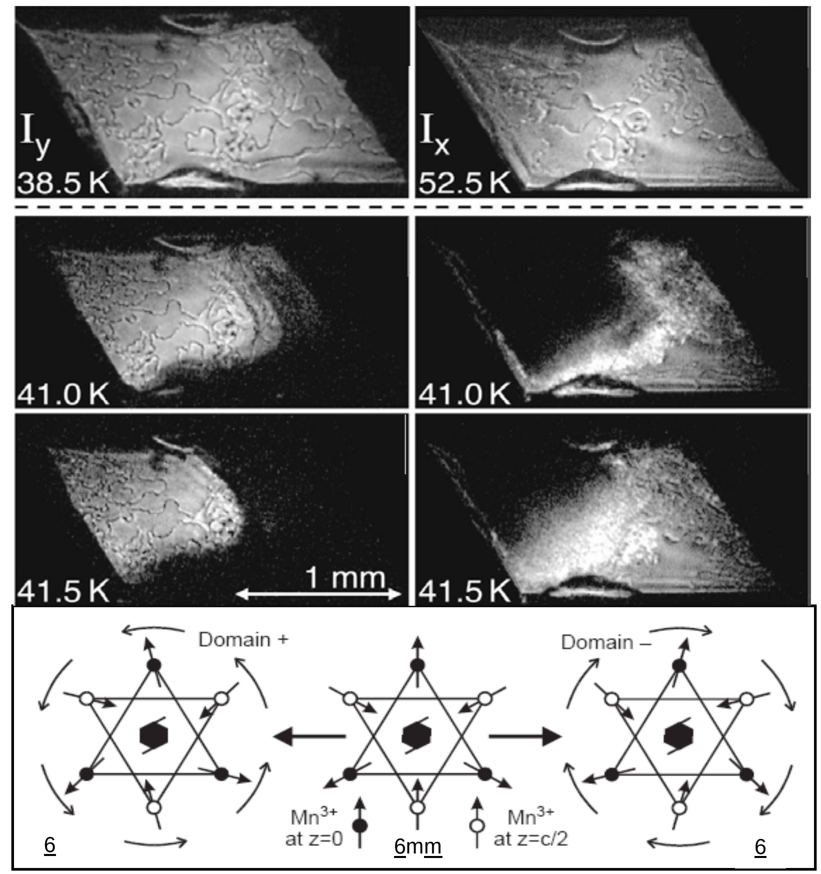
Spin-Rotation Domains in $HoMnO_3$



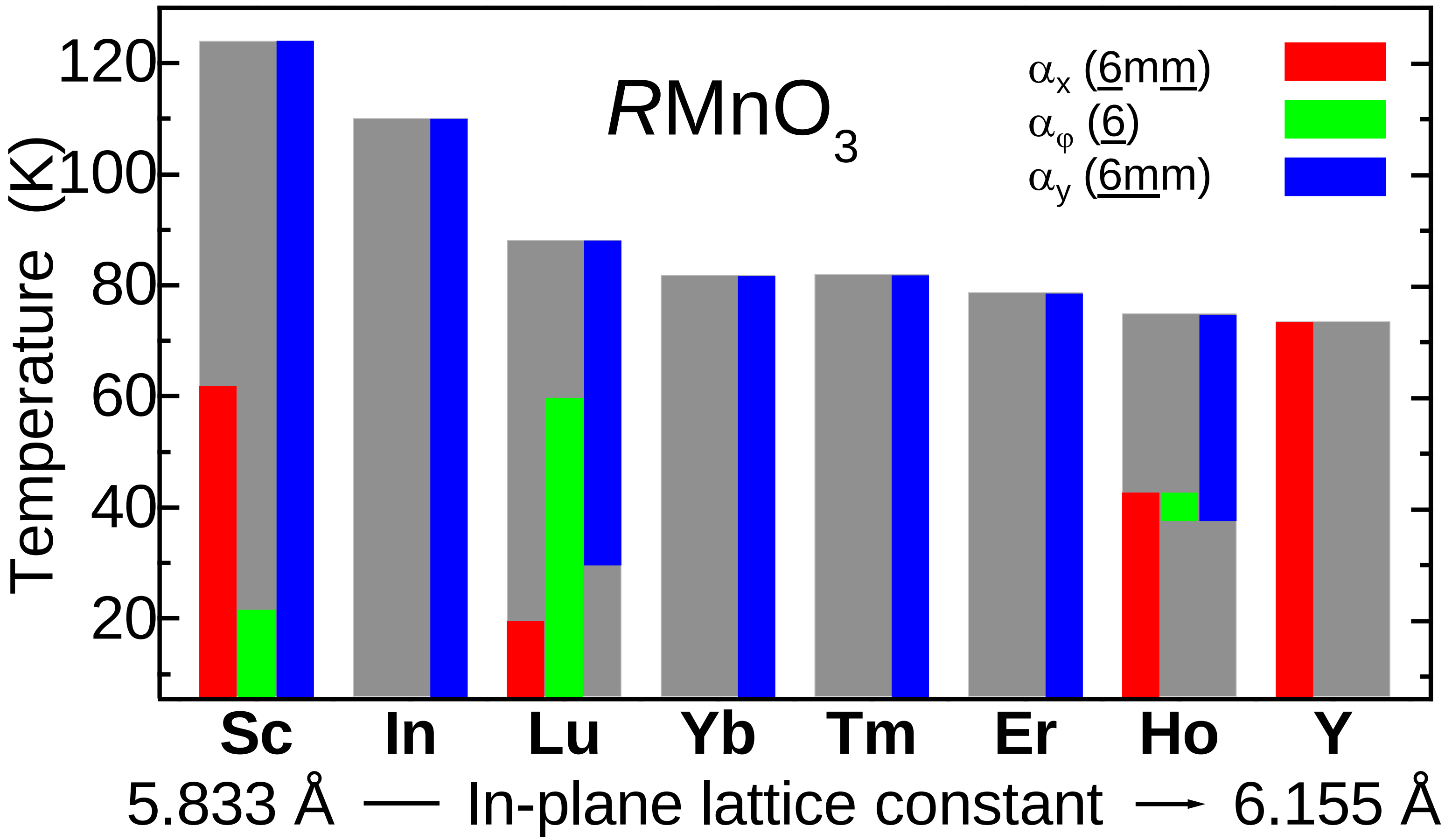


Inside AFM domain walls reduced local symmetry
$\underline{2}$ due to uncompensated magnetic moment.

$\underline{2}$ allows ME contribution $P_z \propto \alpha_{zx,y} M_{x,y}$

⇒ **Local ME effect**

Magnetic Phase Diagram of Hexagonal *R*MnO3



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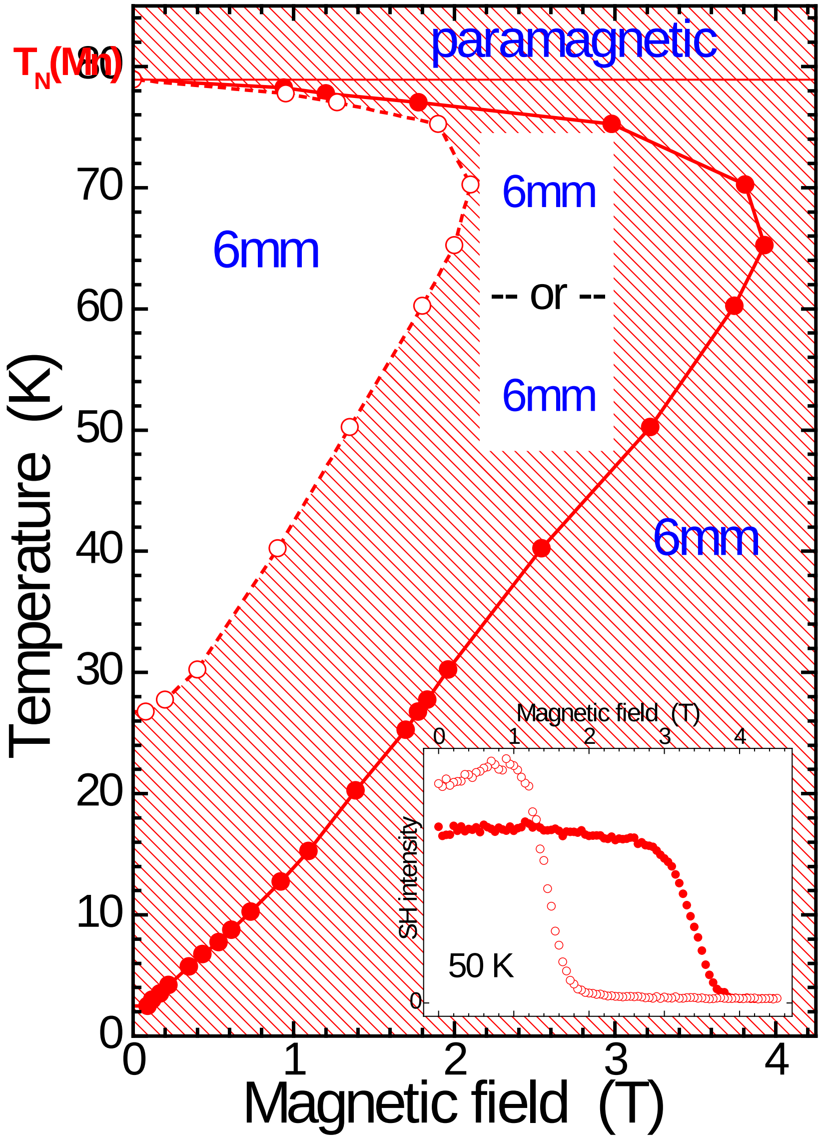
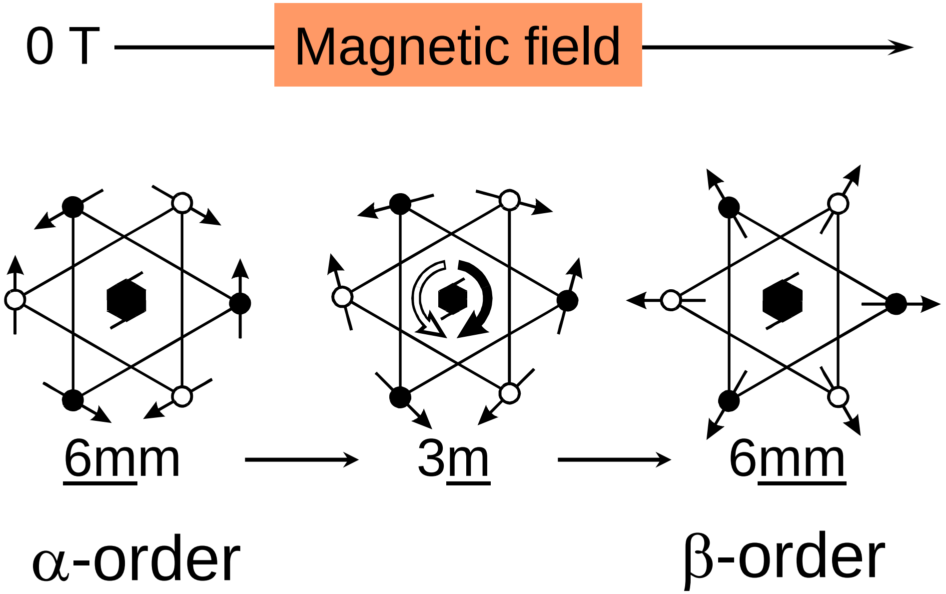
Magnetic Phase Diagram of $ErMnO_3$



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

Reorientation of Mn^{3+} sublattice in magnetic field along hexagonal axis



Magnetoelectric effect:

forbidden → **allowed**

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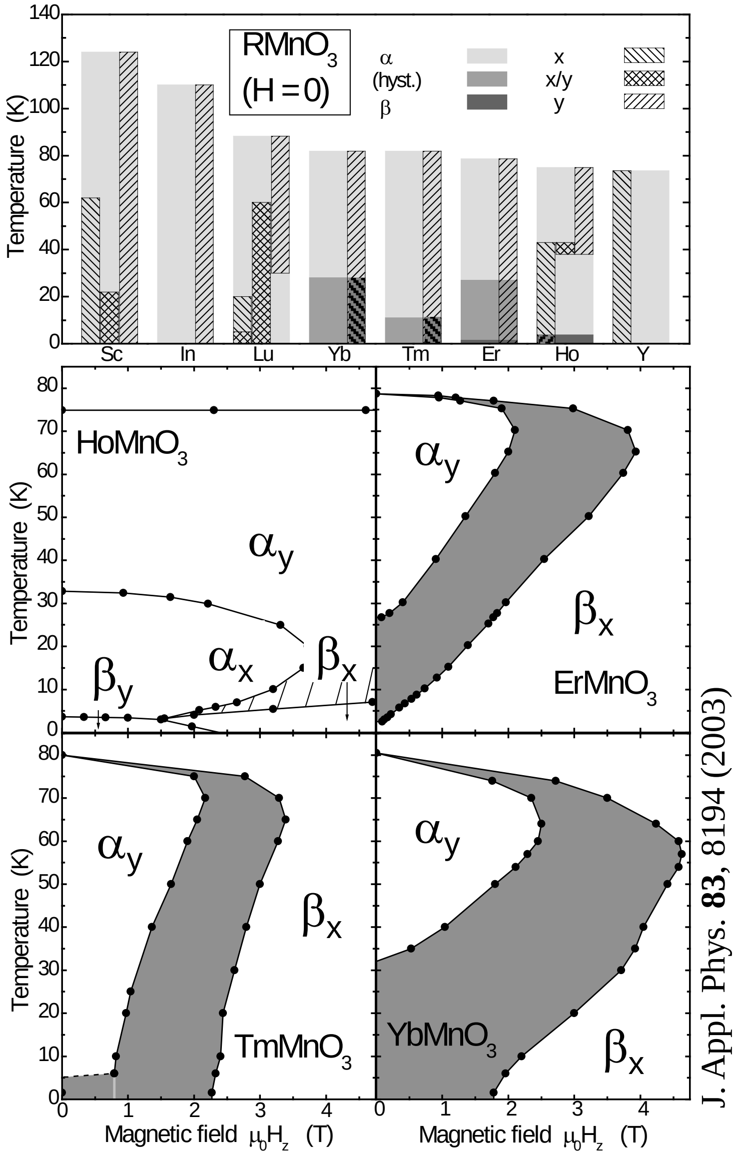
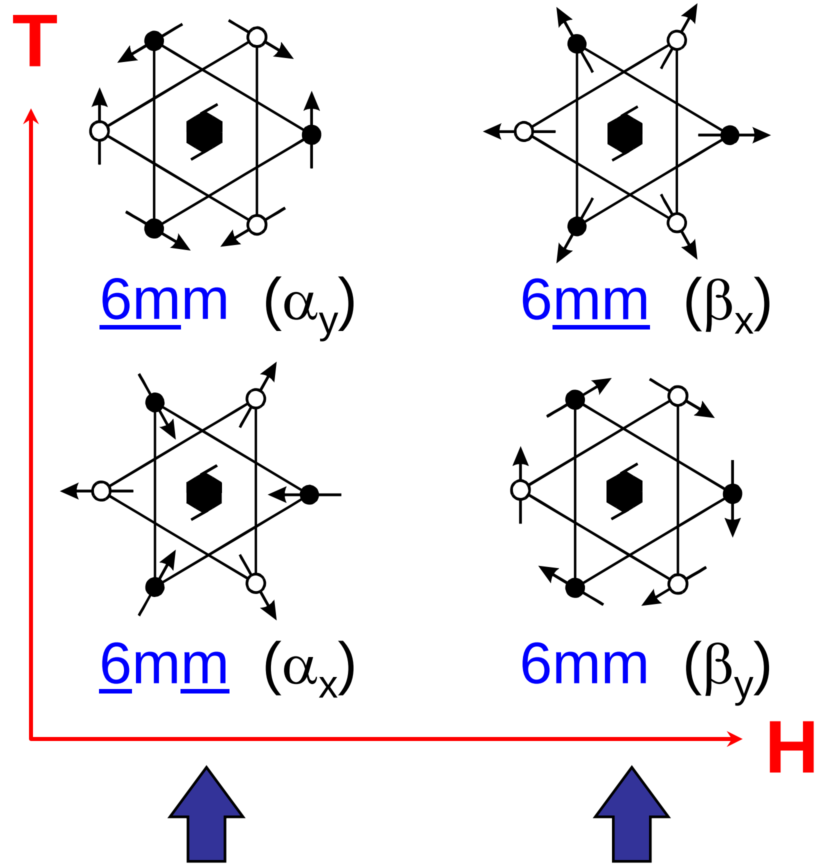
H/T Phase Diagram of Hexagonal $RMnO_3$





ME effect forbidden

ME effect allowed

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So far…

- Detection of obviously FEL/AFM induced SHG
- Analysis of magnetic ordering
- Phase diagrams depending on temperature & magnetic field

But what about the multiferroic nature of $RMnO_3$?

SHG in a Multiferroic Compound

ED contribution for magnetic ferroelectrics:

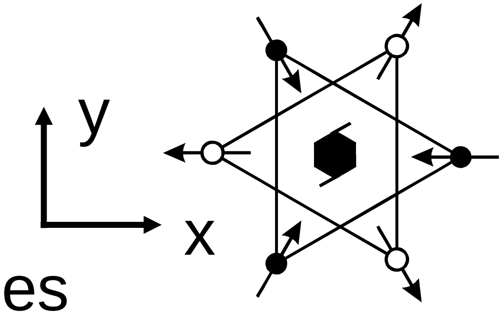
$$\vec{P}^{NL}(2\omega) = \varepsilon_0 \left[\hat{\chi}(0) + \hat{\chi}(\wp) + \hat{\chi}(\ell) + \hat{\chi}(\wp\ell) + \ldots \right] \vec{E}(\omega)\vec{E}(\omega)$$

$\chi(0)$:	Paraelectric paramagnetic contribution	always allowed
$\chi(\mathcal{P})$:	Ferroelectric contribution	allowed below the respective ordering temperature
$\chi(\ell)$:	Antiferromagnetic contribution	
$\chi(\mathcal{P}\ell)$:	Ferroelectromagnetic contribution	

Analog for MD and EQ $\Rightarrow$ in total 12 possible contributions!

But later ones only taken into account if ED not allowed.

Symmetry analysis



- Only α_x order taken into account
- FEL, AFM & FEL+AFM as separated sublattices

Ordered Sublattice	Point group	Parity - type symmetry operation	Order parameter
(para)	6/mmm	I, T, IT	---
FEL	6mm	T	$\mathcal{P}$
AFM	6/mmm	I	ℓ
FEL + AFM	6mm	---	$\mathcal{P}\ell$

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SHG contributions

Lowest order non-zero contributions to SHG:

Zero order: Electric dipole (ED): $\hat{\chi}^{\mathrm{ED}}(\mathscr{P}) = \mathrm{i}_1, \mathrm{i}_2, \mathrm{i}_3$ and $\hat{\chi}^{\mathrm{ED}}(\mathscr{P} \cdot \ell) = \mathrm{e}_1$

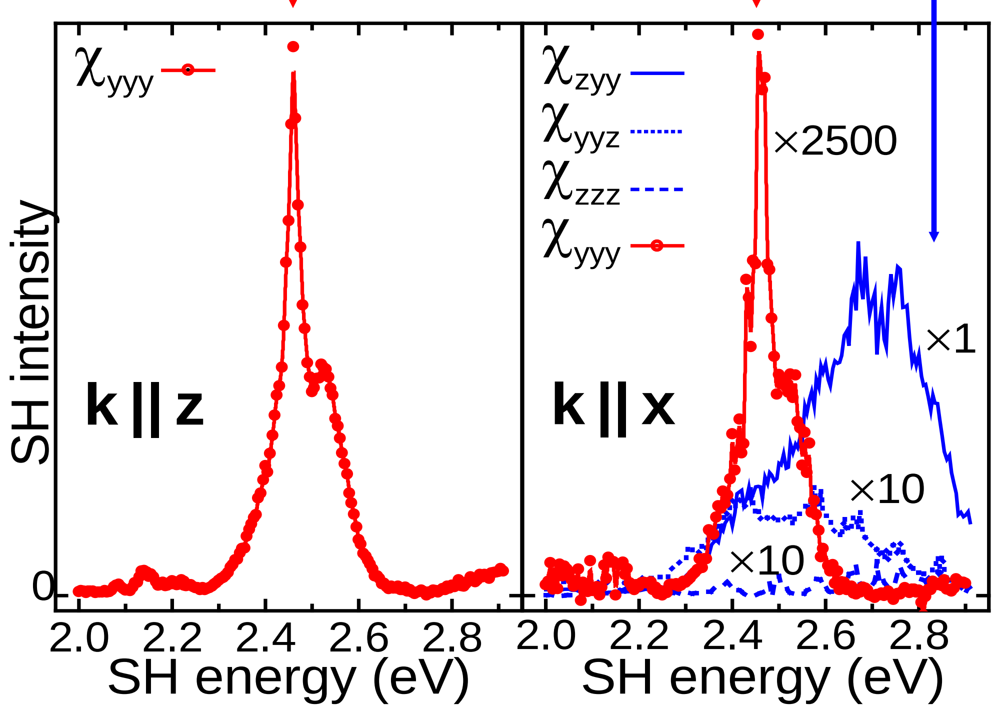
First order: Magnetic dipole (MD): $\hat{\chi}^{\mathrm{MD}}(\ell) = \mathrm{m}_1$

First order: Electric quadrupole (EQ): $\hat{\chi}^{\mathrm{EQ}}(\ell) = \mathrm{q}_1, \mathrm{q}_2, \mathrm{q}_3$

		$\mathbf{S}^{ED}(\mathcal{P})$	$\mathbf{S}^{MD}(\ell)$	$\mathbf{S}^{EQ}(\ell)$	$\mathbf{S}^{ED}(\mathcal{P}\cdot\ell)$
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 SHG

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



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

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

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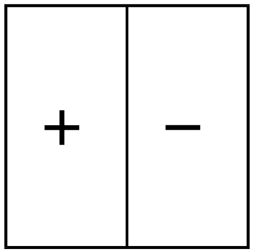
What about domains?

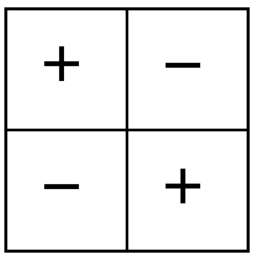
Ferroelectric domains

$\propto \hat{\mathcal{P}}$



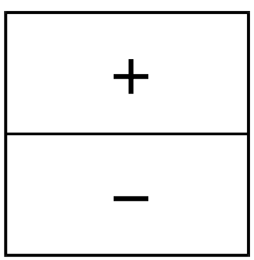
Ferroelectromagnetic domains

$\propto \hat{\mathcal{P}}\hat{\ell}$

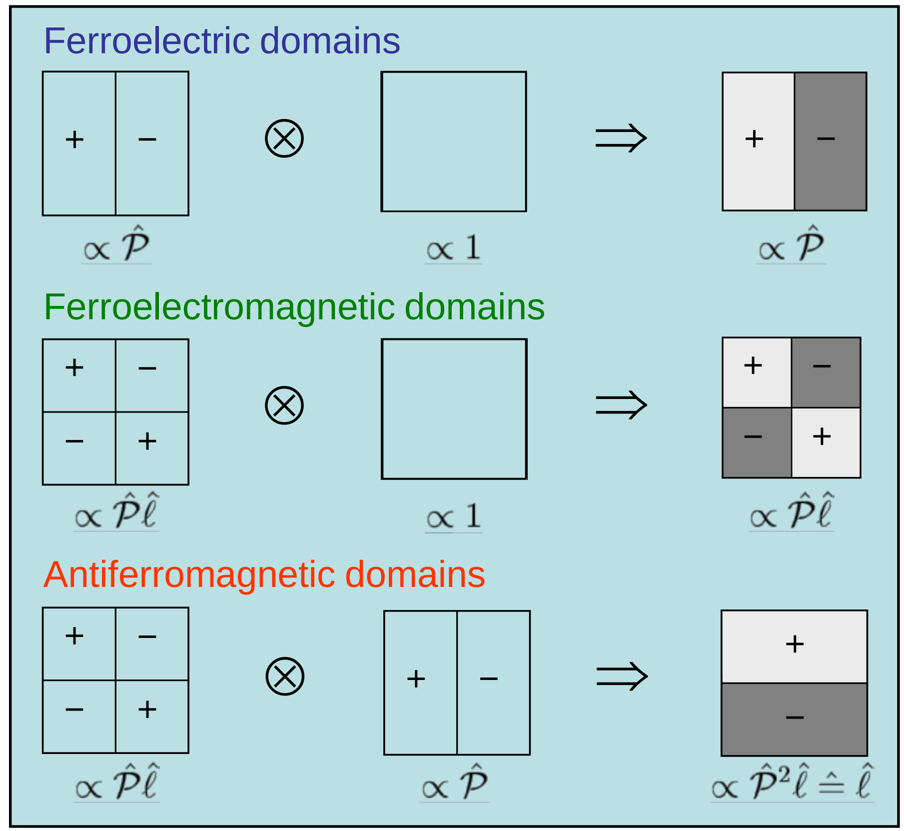


Antiferromagnetic domains

$\propto \hat{\ell}$



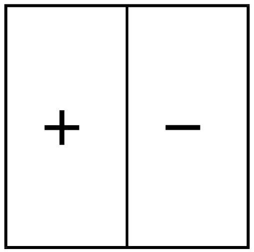
Ferroelectric and ferroelectromagnetic SHG contribution allow three experiments:



Ferroelectromagnetic Domains

Ferroelectric domains

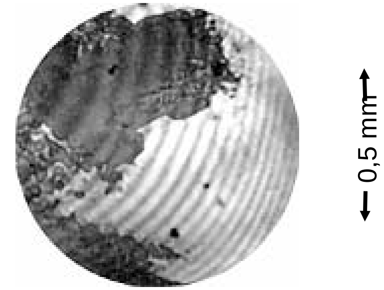
$\propto \hat{\mathcal{P}}$



Model

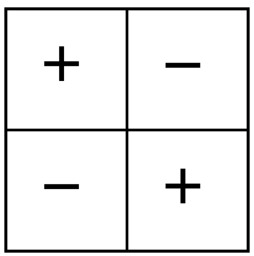
Ferroelectric domains

$\propto \hat{\mathcal{P}}$



Ferroelectromagnetic domains

$\propto \hat{\mathcal{P}}\hat{\ell}$

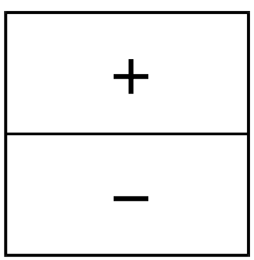


Ferroelectromagnetic domains

$\propto \hat{\mathcal{P}}\hat{\ell}$

Antiferromagnetic domains

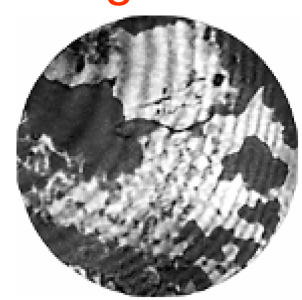
$\propto \hat{\ell}$



Experiment

Antiferromagnetic domains

$\propto \hat{\ell}$



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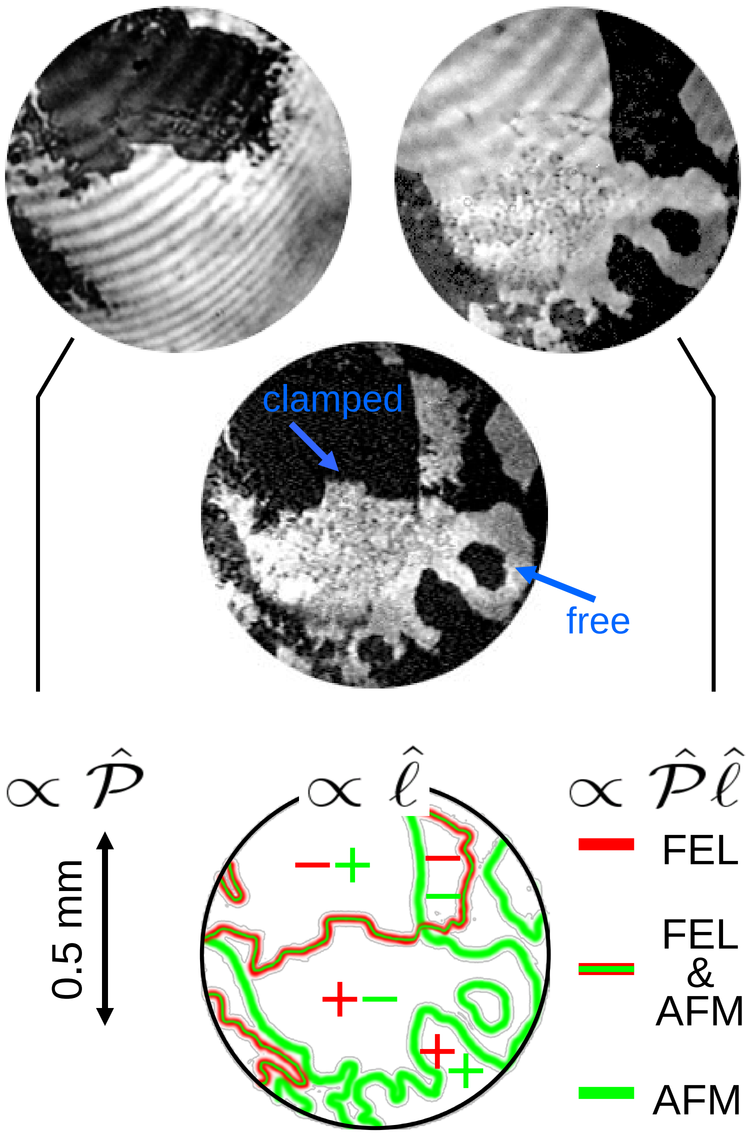
Clamping of Antiferromagnetic Domains



Coexisting domains in $YMnO_3$:

✧ Ferroelectric domains: $\propto \mathcal{P}$

✧ Antiferromagnetic domains: $\propto \ell$

✧ "Magnetoelectric" domains: $\propto \mathcal{P}\ell$

$\mathcal{P}\ell$ **= +1** for $\mathcal{P} = \pm 1$, $\ell = \pm 1$

$\mathcal{P}\ell$ **= -1** for $\mathcal{P} = \pm 1$, $\ell = \mp 1$

- Any reversal of FEL order parameter clamped to reversal of the AFM order parameter $\rightarrow$ *local* ME effect
- Coexistence of "free" and "clamped" AFM walls

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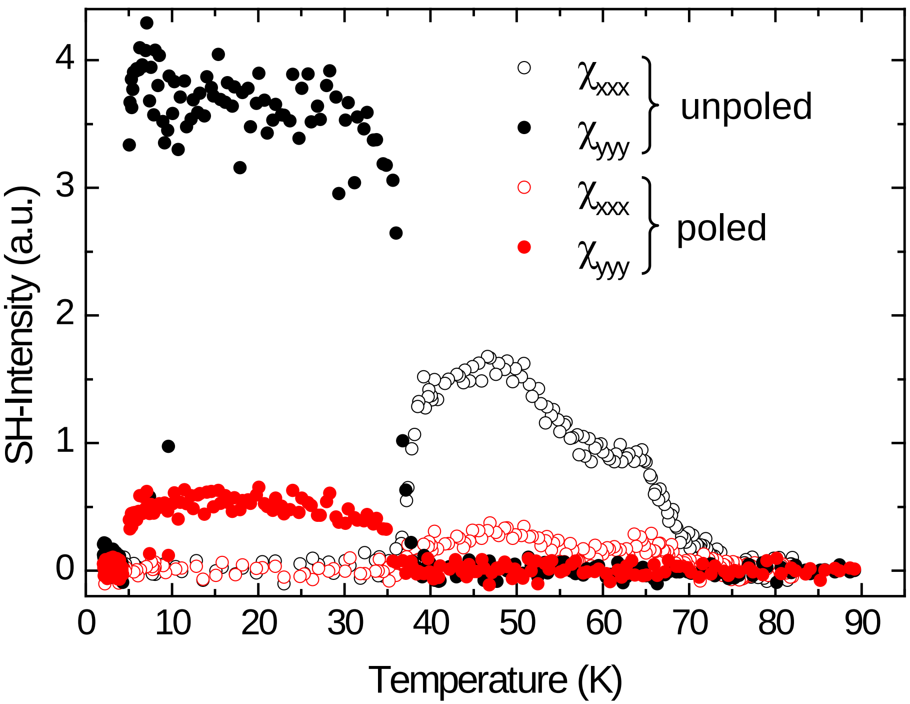
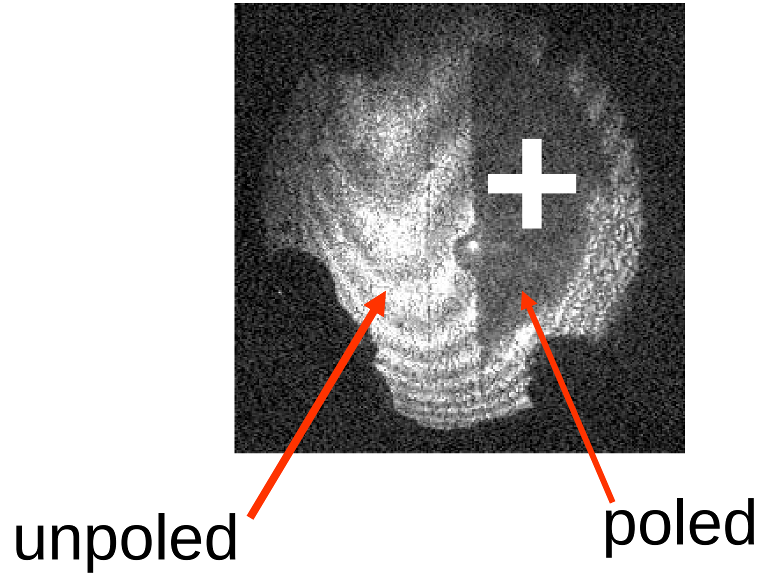
E-Field induced ME effect

Applying an electric field (= *ferroelectric poling*) above the magnetic phase transition temperature leads to quenching of the magnetic SHG signal!



Magnetic SHG image



Transition from α to β order?

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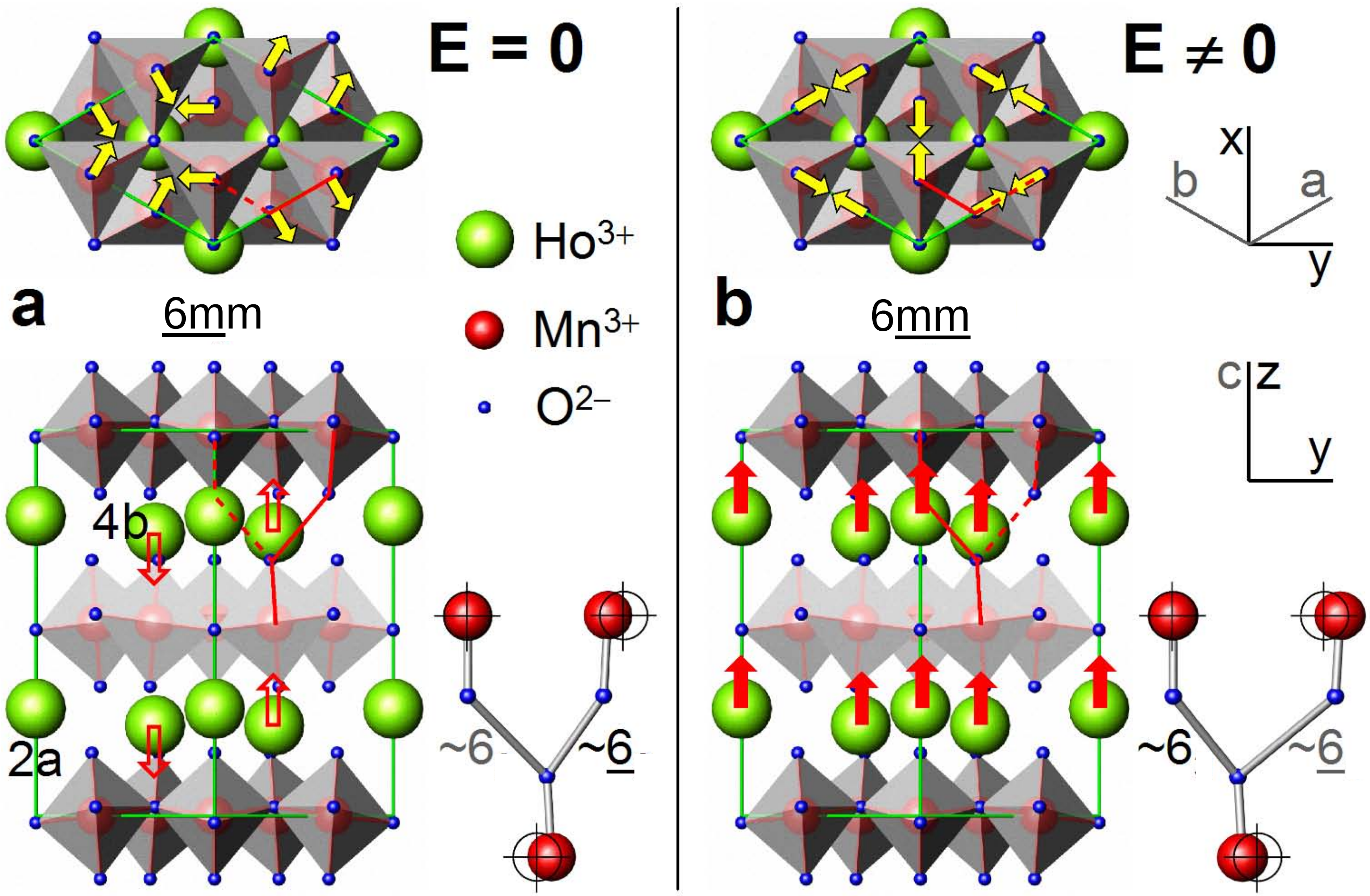
Magnetic Phase Control by Electric Field



Nature **430**, 541 (2004)

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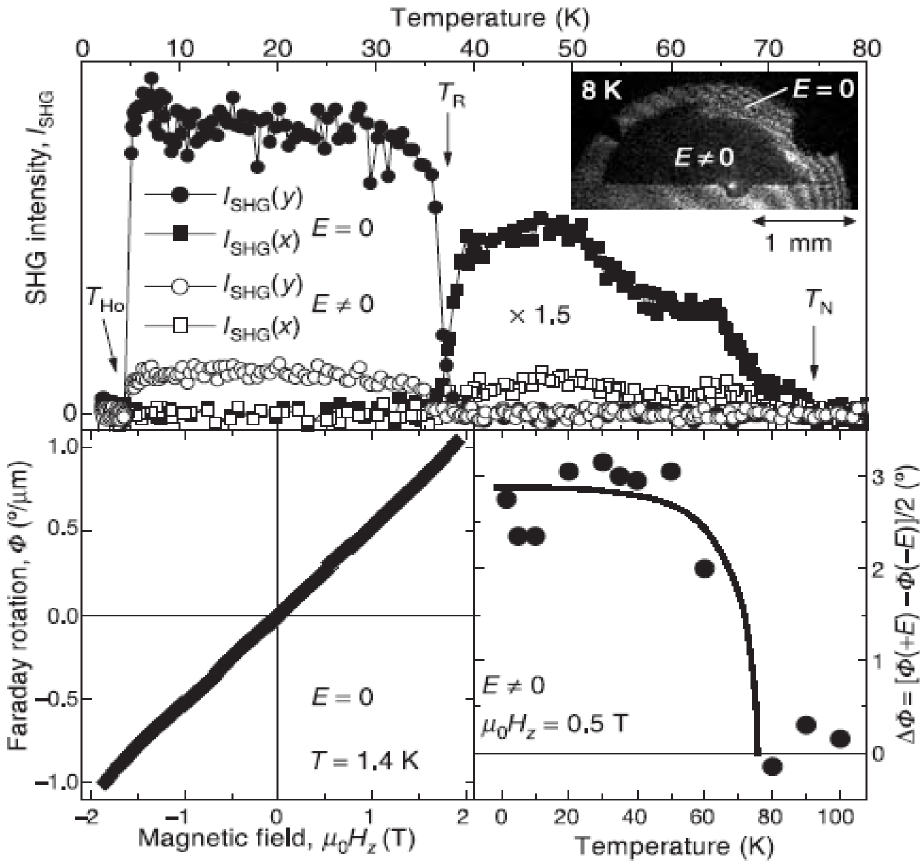
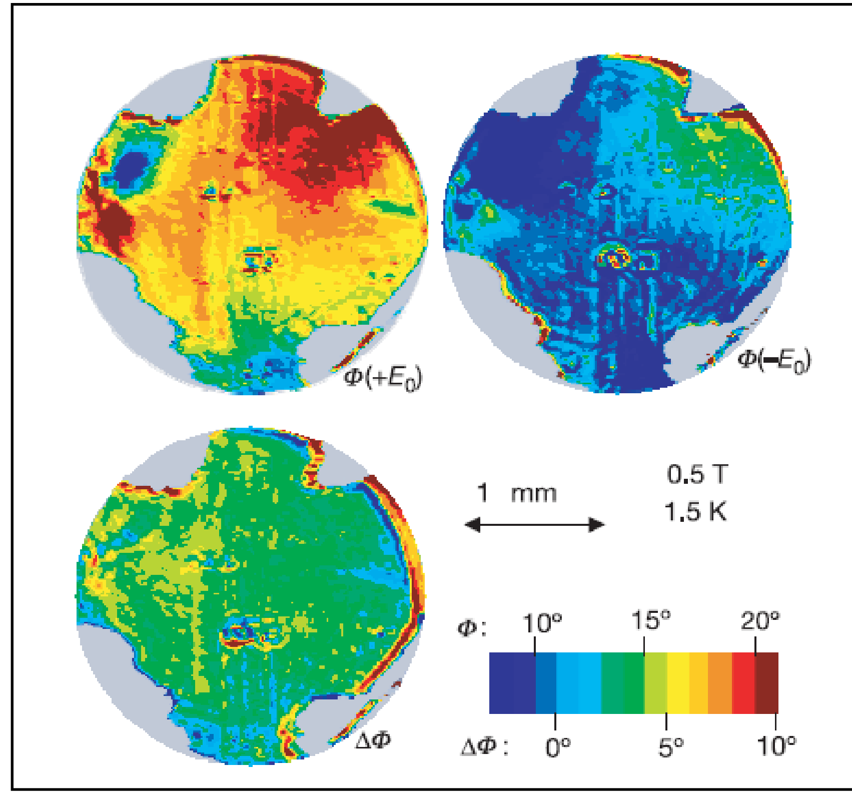
Magnetic Phase Control by Electric Field





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

⇒ **Induction of magnetic phase transition!**

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Summary

Nonlinear optics on multiferroics:

- Nonlinear optics is based on symmetry: $\chi_{ijk} \leftrightarrow$ symmetry $\leftrightarrow$ structure
- Simultaneous study of all ferroic structures with the *same* technique

Access to:

- Electric-magnetic phase diagrams
- Magnetoelectric interactions
- Multiferroic domain topology
- Ultrafast dynamics
- Etc. etc.

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