Nonlinear Optics Applied to Multiferroics

- **What is a multiferroic?**
- **Introduction to nonlinear optics**
- **Experimental setups for nonlinear (multi-) ferro-optics**
- **Nonlinear optics on multiferroics:**
  - **Split-order-parameter multiferroics**
  - **Joint-order-parameter multiferroics**
  - **Sublattice selectivity**

Manfred Fiebig (ETH Zurich)

5th European School on Multiferroics
Ascona, January 29 - February 3, 2012

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Eidgenössische Technische Hochschule Zürich
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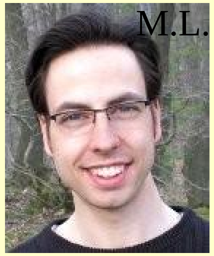

HISKP universitätbonn

MAMA nano materials — SEVENTH FRAMEWORK PROGRAMME

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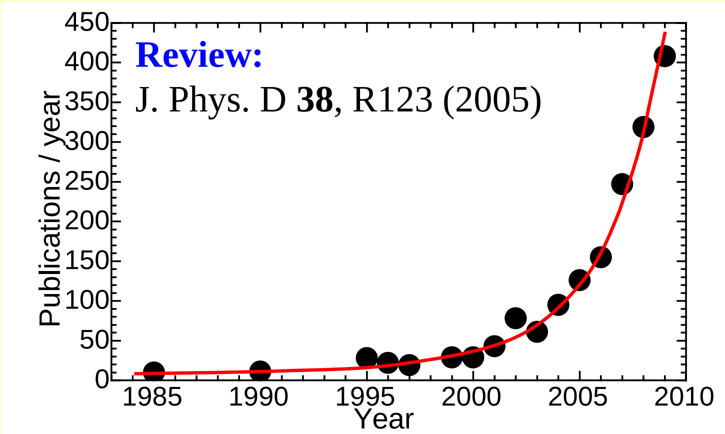
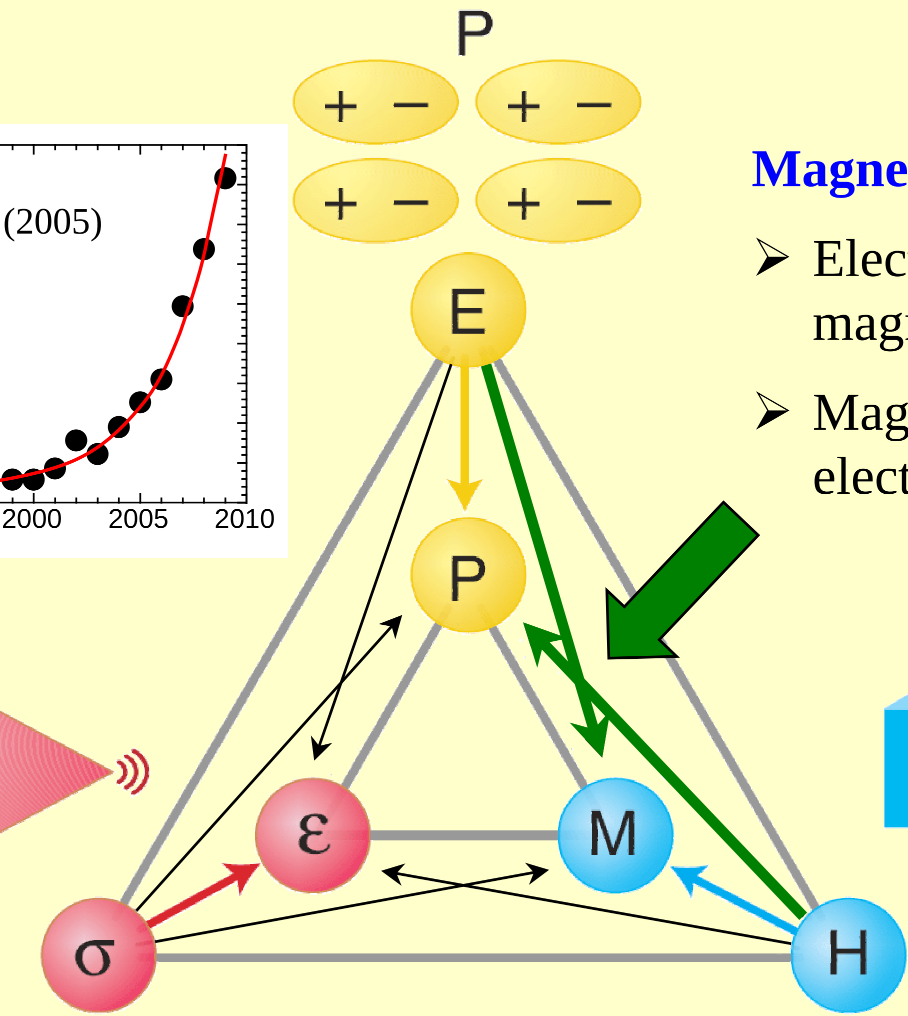
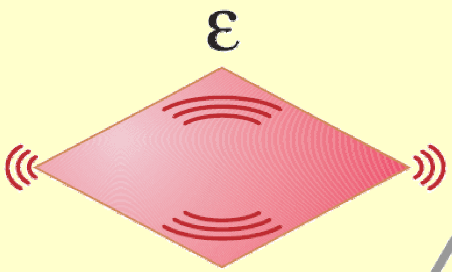
  - **Joint-order-parameter multiferroics: $MnWO_4$**
  - **Sublattice selectivity: $TbMn_2O_5$**

Magnetoelectric Effect and Multiferroics

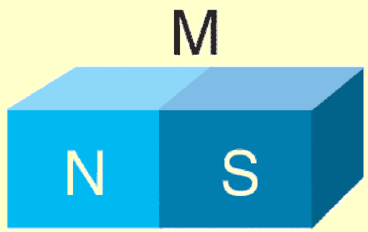






Magnetoelectric effect

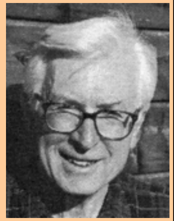
- ➢ Electric control of magnetic order
- ➢ Magnetic control of electric order



Science **309**, 391 (2005)

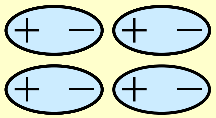
What is a “Multiferroic”?

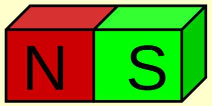
“Crystals can be defined as multiferroic when two or more of the primary ferroic properties are united in the same phase.”

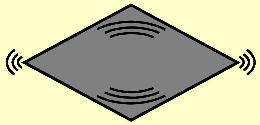


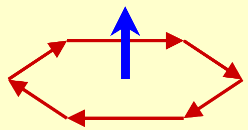
Hans Schmid (University of Geneva, Switzerland)
in: M. Fiebig et al. (ed.), *Magnetoelectric Interaction Phenomena in Crystals*, (Kluwer, Dordrecht, 2004)

<u>Ferroelectricity</u>	<u>Ferromagnetism</u>	<u>Ferroelasticity</u>	<u>Ferrotoroidicity</u>
spontaneous polarization	spontaneous magnetization	spontaneous strain	spontaneous magnetic vortex





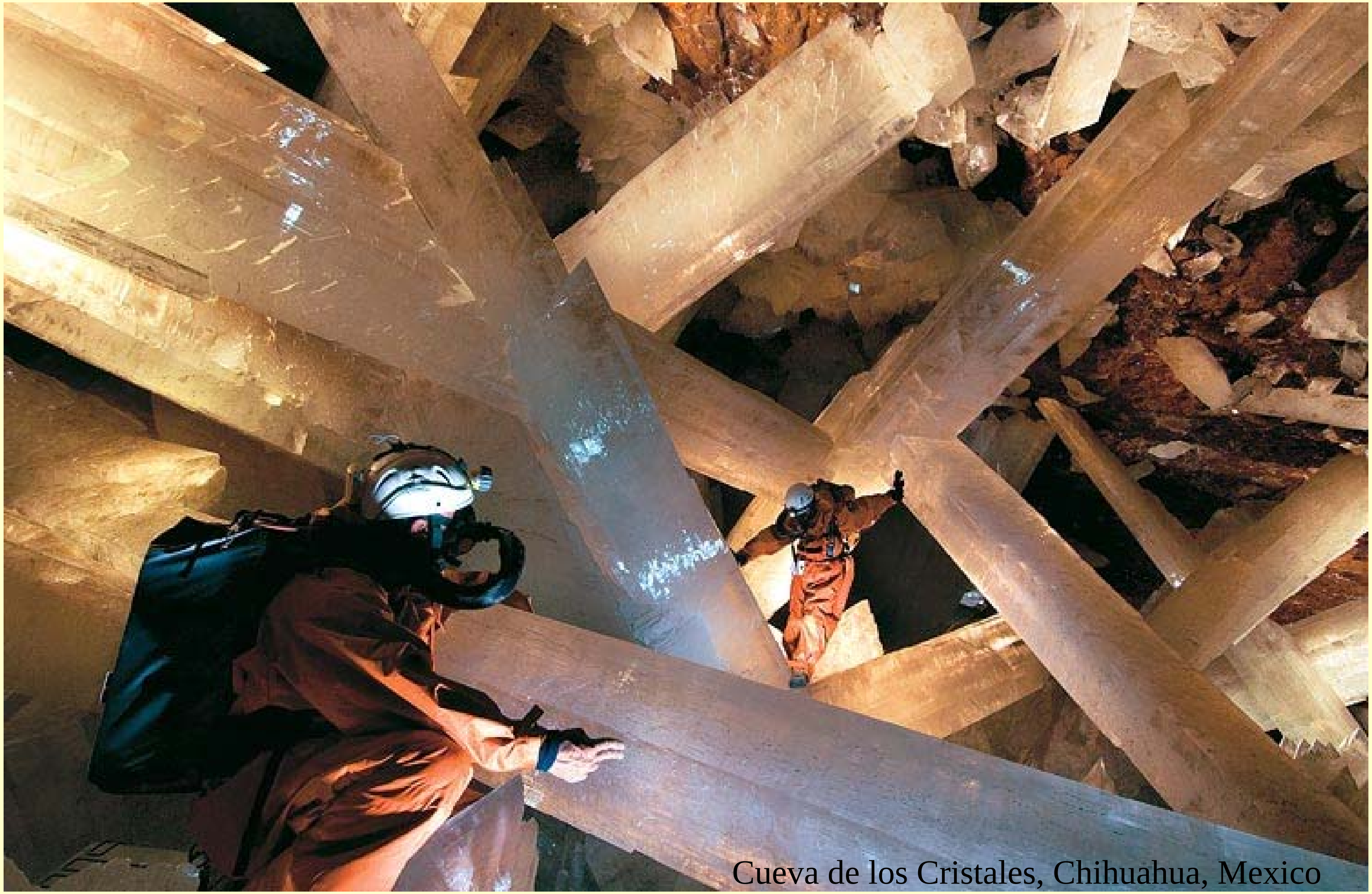




... and their anti-ferroic counterparts

- Multifunctionalities expected from magneto-electric interactions

Nature's Treasure Trove is Impressive…

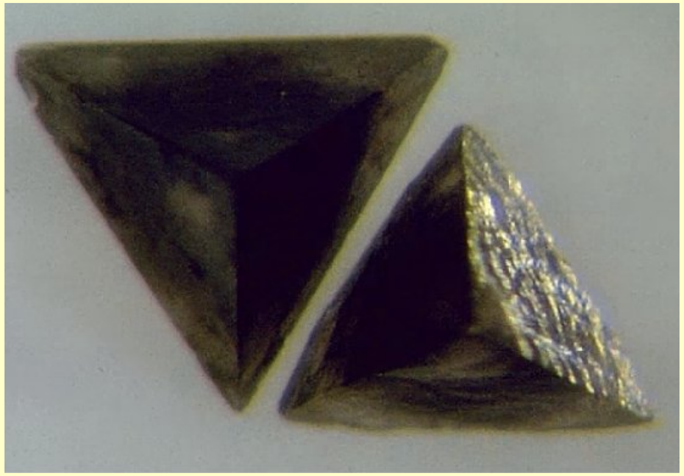


Cueva de los Cristales, Chihuahua, Mexico

…But with Little Room for Multiferroics

Three natural crystals uniting magnetic and electric order

Congolite	Hubnerite	Chambersite
$Fe_3B_7O_{13}Cl$	$MnWO_4$	$Mn_3B_7O_{13}Cl$



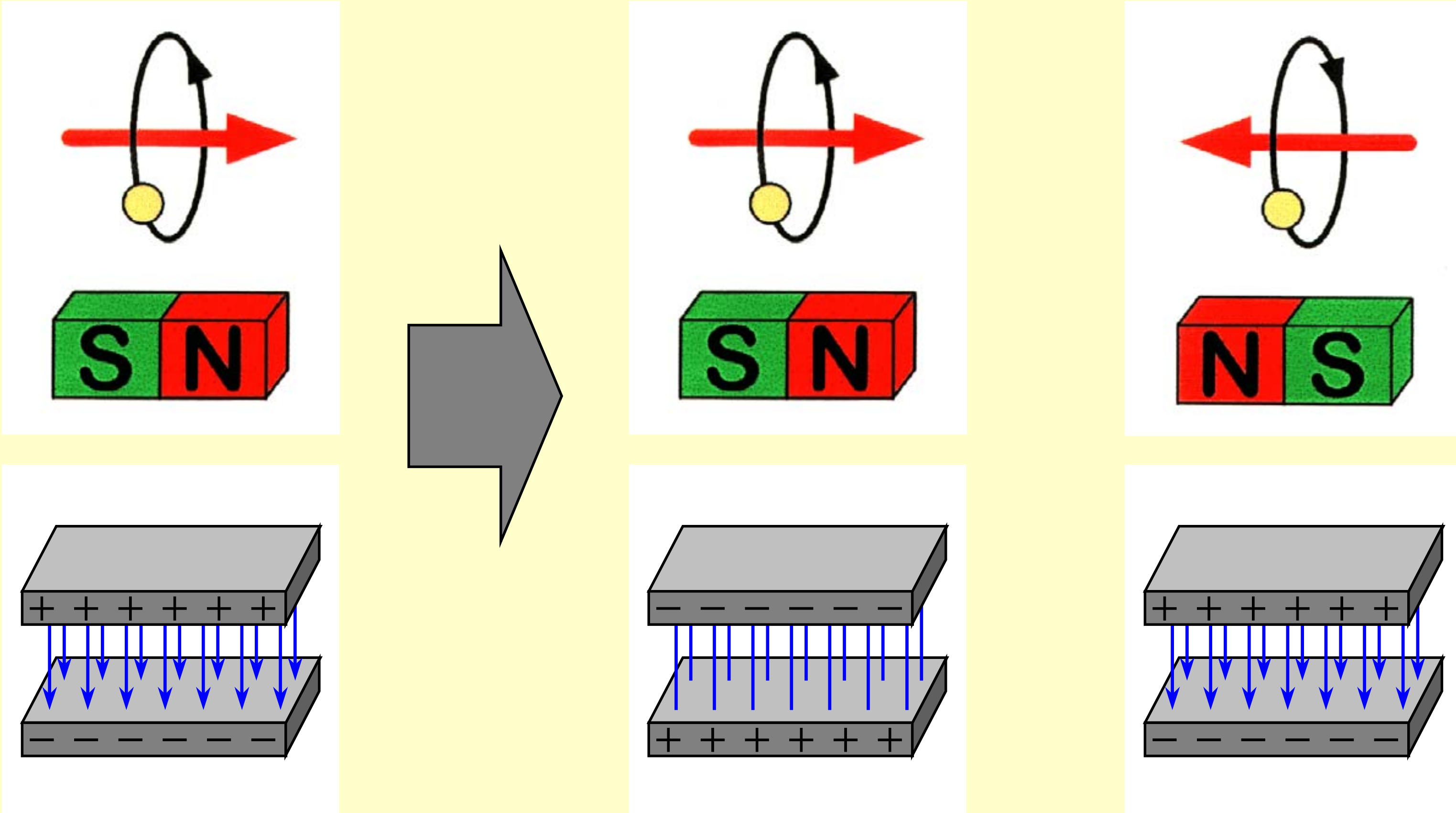
...and about 200 more compounds grown in the lab!

Magnetoelectric Multiferroics and Symmetry

Long - range ordering | Space inversion | Time reversal

Magnetic

Electric



Magnetoelectric effect requires simultaneous breaking of the temporal and the spatial inversion symmetry!

Manifestations of the Magnetoelectric Effect

Systems with broken space- and time-inversion symmetry?

Two order parameters ⚠ **ME coupling might be weak**

- ➢ Ferroelectric order violates spatial inversion symmetry
- ➢ (Ferro)magnetic order violates time-reversal symmetry

→ Split-order-parameter multiferroics hexagonal $RMnO_3$

One order parameter ⚠ **ME coupling intrinsically strong**

- ➢ Single order violates space- *and* time-inversion symmetry

→ Joint-order-parameter multiferroics $MnWO_4$, $TbMn_2O_5$

Observation of space- and time-inversion symmetry violation?

A technique strongly based on symmetries → **nonlinear optics!**

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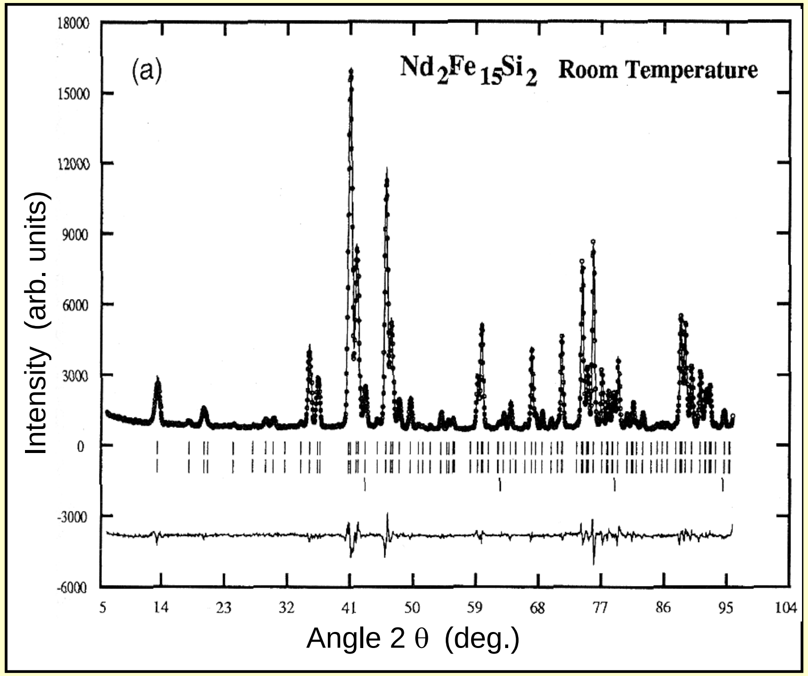
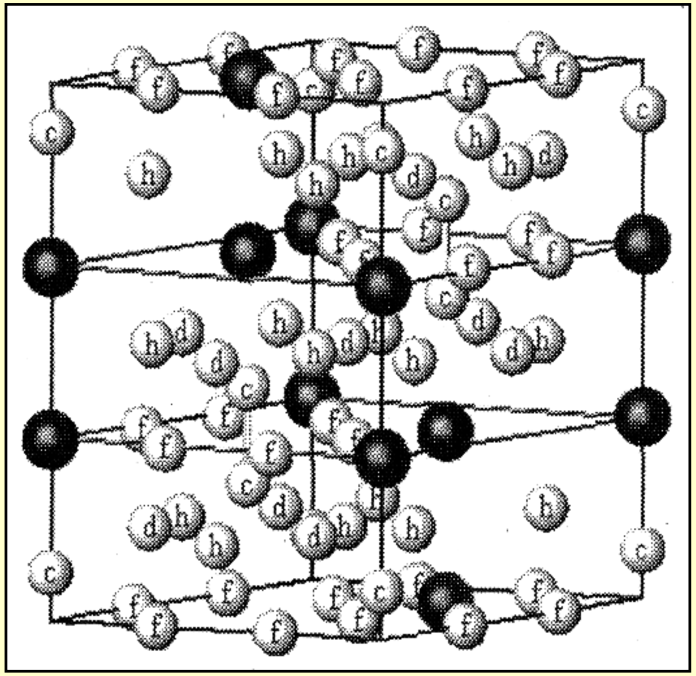
Determination of Magneto-Crystalline Structures

Often by diffraction with x rays, electrons, or neutrons

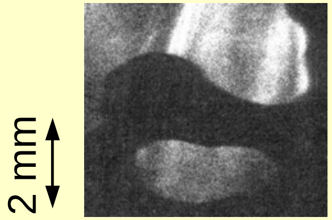




- Very powerful access to the microscopic struture
- What could be the benefit of an investigation by nonlinear optics, a technique basically of macroscopic nature?

Why Using Additional Techniques?

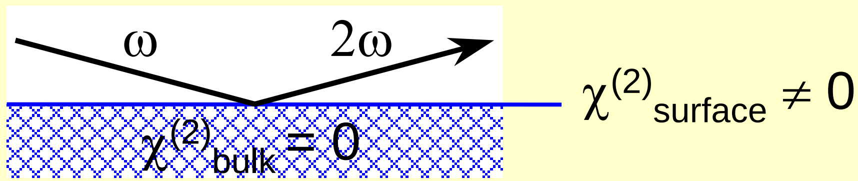
- Spatial resolution: domains



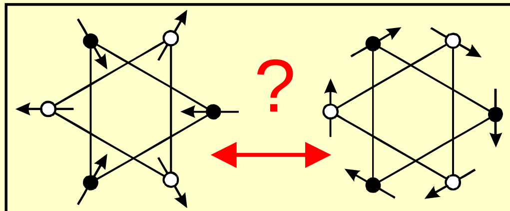
Antiferromagnetic MnF_2 domains

~24 h, 100 μm

- Interface sensitivity (suppress bulk signals)

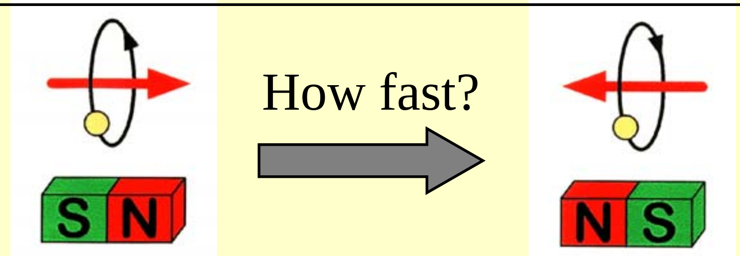


- Accidental structural ambiguities



$ErMnO_3$:
Spin structure?

- Dynamical processes down to the fs time scale



- Financial issues

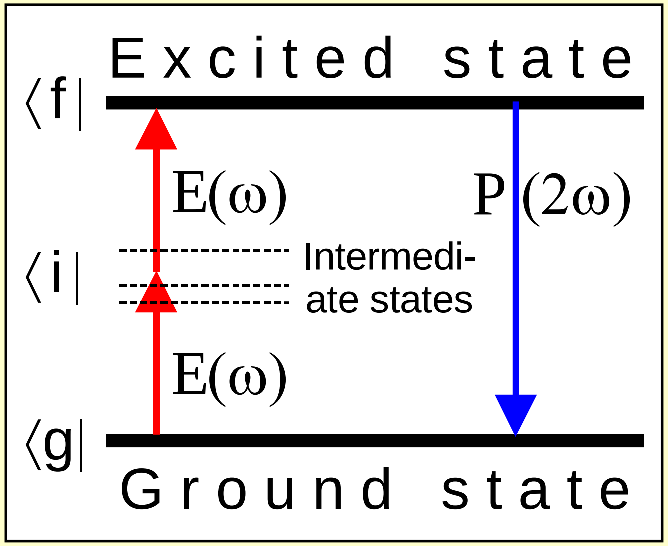
Some large-scale equipment ...

Nonlinear Optics

Electric field in matter:

$P(\omega) = \varepsilon_0 \, \chi \, E(\omega)$

$P(\omega) \sim e^{i\omega t}$, $E(\omega) \sim e^{i\omega t}$



Yet for strong electromagnetic fields (e.g. laser):

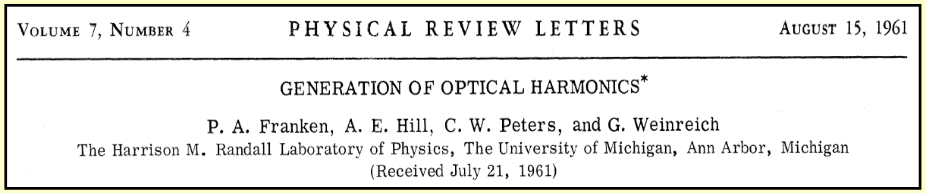
$P = \varepsilon_0 \, (\chi^{(1)} E + \chi^{(2)} E \, E + \chi^{(3)} E \, E \, E + \ldots)$

With leading-order nonlinear term:

$P(2\omega) = \varepsilon_0 \, \chi^{(2)} \, E(\omega) \, E(\omega)$

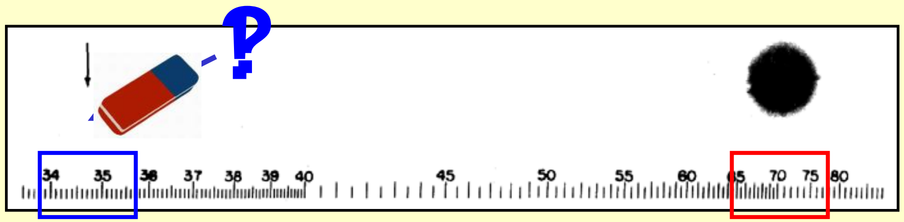
$P(2\omega) \sim e^{i2\omega t}$, $E(\omega) \sim e^{i\omega t}$, $E(\omega) \sim e^{i\omega t}$

→ **Frequency doubling** ("second harmonic generation", SHG)


VOLUME 7, NUMBER 4 PHYSICAL REVIEW LETTERS AUGUST 15, 1961

GENERATION OF OPTICAL HARMONICS*

P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich
The Harrison M. Randall Laboratory of Physics, The University of Michigan, Ann Arbor, Michigan
(Received July 21, 1961)



Nonlinear Optics – The Very First Work

CHRISTIE'S

GOEPPERT-MAYER, MARIA (1906-72). ÜBER ELEMENTARAKTE MIT ZWEI QUANTENSPRÜNGEN. OFFPRINT FROM: ANNALEN DER PHYSIK 5, FOLGE BAND 9. LEIPZIG: JOHANN AMBROSIUS BARTH, 1931.

Lot 117 / Sale 1174

Price Realized
$1,912
Price includes buyer's premium

Estimate
$2,000 - $3,000

Sale Information
Sale 1174
The History of Quantum Mechanics and the Theory of Relativity: The Harvey Plotnick Library
4 October 2002
New York, Rockefeller Plaza

Lot Description
GOEPPERT-MAYER, Maria (1906-72). *Über Elementarakte mit zwei Quantensprüngen*. Offprint from: *Annalen der Physik* 5, Folge Band 9. Leipzig: Johann Ambrosius Barth, 1931.

8o. Unbound. *Provenance*: Theodore von Kármán (1881-1963) (with signature in pencil and library markings on first leaf).

Über Elementarakte mit zwei Quantensprüngen
Von Maria Göppert-Mayer
(Göttinger Dissertation)
(Mit 5 Figuren)

Einleitung

Der erste Teil dieser Arbeit beschäftigt sich mit dem Zusammenwirken zweier Lichtquanten in einem Elementarakt. Mit Hilfe der Diracschen Dispersionstheorie [1]) wird die Wahrscheinlichkeit eines dem Ramaneffekt analogen Prozesses, nämlich der Simultanemission zweier Lichtquanten, berechnet. Es zeigt sich, daß eine Wahrscheinlichkeit dafür besteht, daß ein angeregtes Atom seine Anregungsenergie in zwei Lichtquanten aufteilt, deren Energien in Summe die Anregungsenergie ergeben, aber sonst beliebig sind. Fällt auf das Atom Licht, dessen Frequenz kleiner ist, als die entsprechende Eigenfrequenz des Atoms, so tritt außerdem noch eine erzwungene Doppelemission hinzu, bei der das Atom seine Energie in ein Lichtquant der eingesandten und eins der Differenzfrequenz aufteilt. Kramers und Heisenberg [2]) haben die Wahrscheinlichkeit dieses letzteren Prozesses korrespondenzmäßig berechnet.

Außerdem wird die Umkehrung dieses Prozesses betrachtet, nämlich der Fall, daß zwei Lichtquanten, deren Frequenzsumme gleich der Anregungsfrequenz des Atoms ist, zusammenwirken, um das Atom anzuregen.

Ferner wird untersucht, wie sich ein Atom gegenüber stoßenden Teilchen verhalten kann, wenn es gleichzeitig die Möglichkeit hat, spontan Licht zu emittieren. Oldenberg [3]) findet experimentell eine Verbreiterung der Resonanzlinie des Quecksilbers, wenn er die angeregten Atome vielfach mit lang-

1) P. A. M. Dirac, Proc. of R. S. vol. 114. S. 143 u. 710. 1927.
2) H. A. Kramers u. W. Heisenberg, Ztschr. f. Phys. 31. S. 681. 1925.
3) O. Oldenberg, Ztschr. f. Phys. 51. S. 605. 1928.

FIRST EDITION, offprint issue. The doctoral thesis of Maria Goeppert-Mayer, the mathematical physicist who shared the 1963 Nobel Prize for physics with Hans Jensen for their discoveries regarding the shell structure of nuclear particles.

How does SHG Probe a Material?

$$P_i(2\omega) = \varepsilon_0 \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega)$$

i-polarized emitted photon at 2ω

k-polarized incident photon No. 1 at ω

j-polarized incident photon No. 2 at ω

This susceptibility represents the material with all its symmetry and internal order

Symmetry Sensitivity of SHG

- Consider system with inversion symmetry
- Von-Neumann principle:

  Physical properties ↔ symmetry ↔ structure
- Thus inversion symmetry requires $I(\chi_{ijk}) = \chi_{ijk}$
- Consequence for SHG:

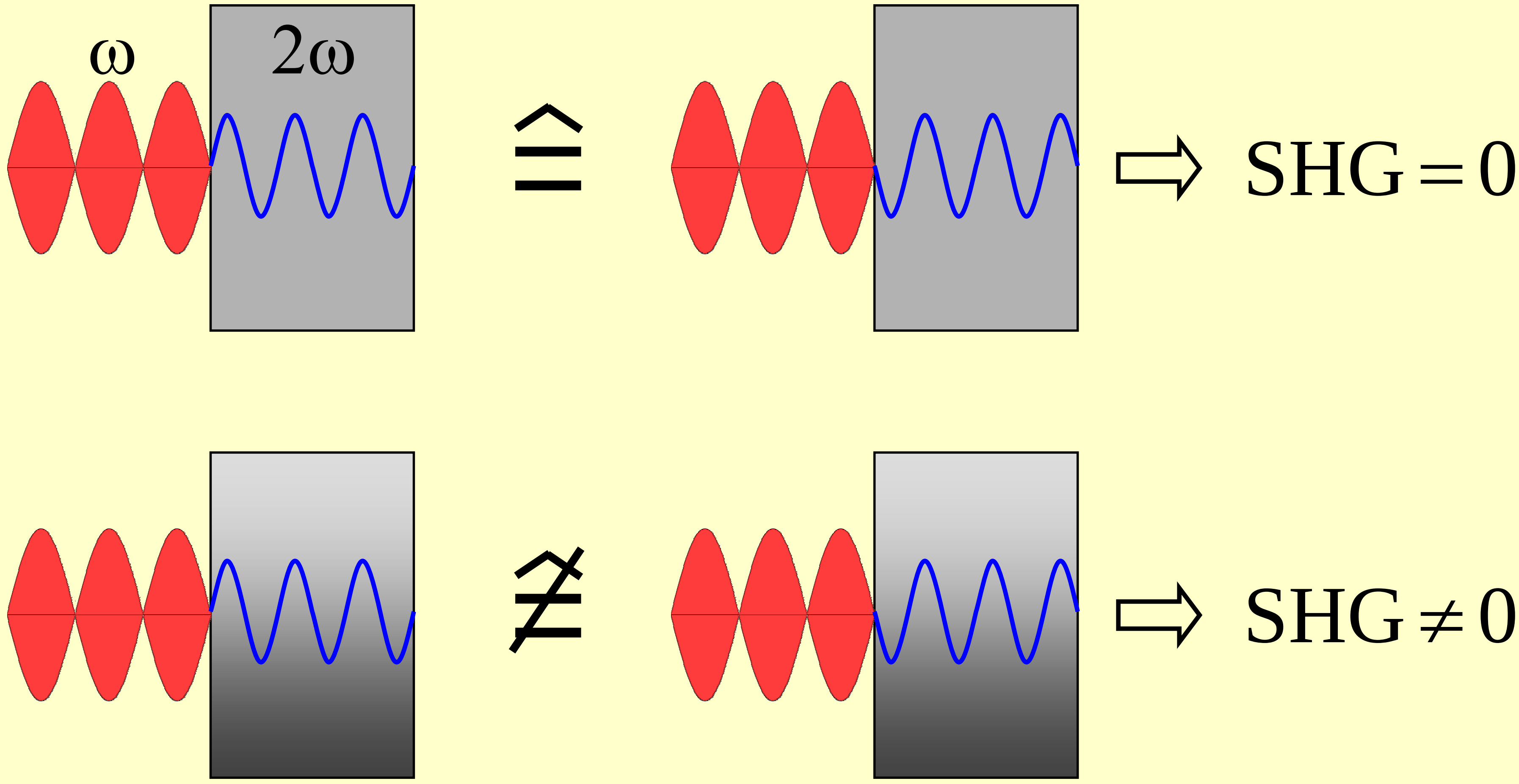
$$P_i(2\omega) \propto \boxed{\chi_{ijk}} E_j(\omega)\, E_k(\omega) \qquad | \text{ Apply inversion}$$

$$[-P_i(2\omega)] \propto I(\chi_{ijk})\, [-E_j(\omega)]\, [-E_k(\omega)] \qquad | \times(-1)$$

$$P_i(2\omega) \propto \boxed{[-\, I(\chi_{ijk})]} E_j(\omega)\, E_k(\omega) \qquad | \text{ thus } -I(\chi_{ijk}) \equiv -\chi_{ijk} \overset{!}{=} \chi_{ijk} \equiv 0$$

There is no (leading-order) SHG in systems with inversion symmetry!

Why Inversion Symmetry Suppresses SHG



Magnetic Ordering and Symmetry

Nonlinear optical susceptibility of magnetically ordered crystals

N. N. Akhmediev, S. B. Borisov, A. K. Zvezdin, I. L. Lyubchanskiĭ, and Yu. V. Melikhov

Physicotechnical Institute, Academy of Sciences of the Ukrainian SSR, Donetsk

(Submitted September 24, 1984)

Fiz. Tverd. Tela (Leningrad) **27**, 1075–1078 (April 1985) Sov. Phys. Solid State **27**(4), 650, April 1985

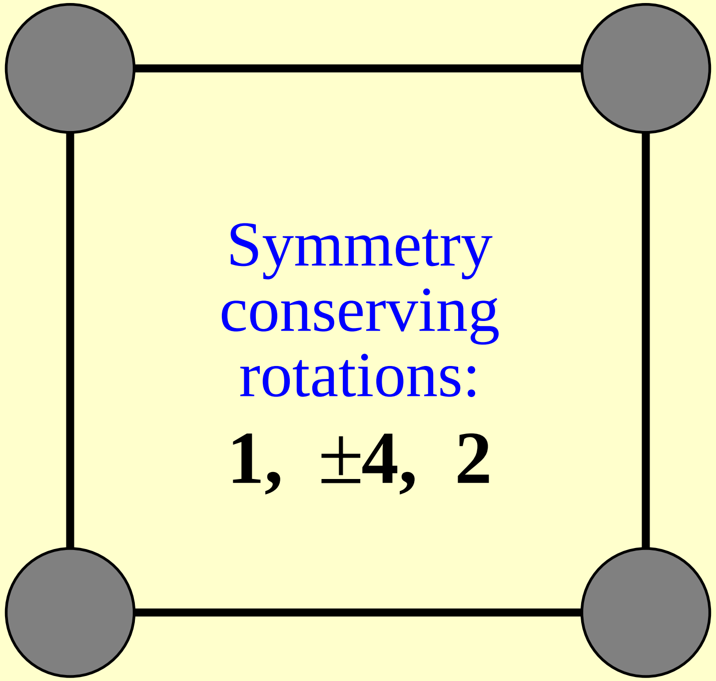
Group-theoretic analysis is given of the nonlinear optical susceptibility of magnetic materials due to their magnetic ordering and due to an applied magnetic field. Rare-earth orthoferrites are considered as an example.

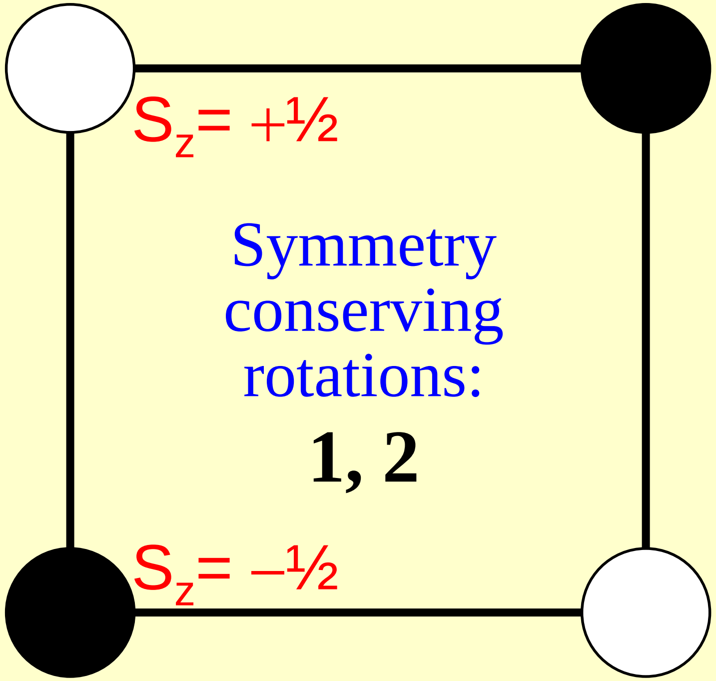
"When the effects related to magnetic ordering and the presence of an applied magnetic field are studied, it is necessary to take account of the fact that the **symmetry of the magnetic subsystem can be lower than the symmetry of the crystal lattice**."

Further Symmetry Reduction by Magnetic Order

Without magnetic order

With antiferromagnetism

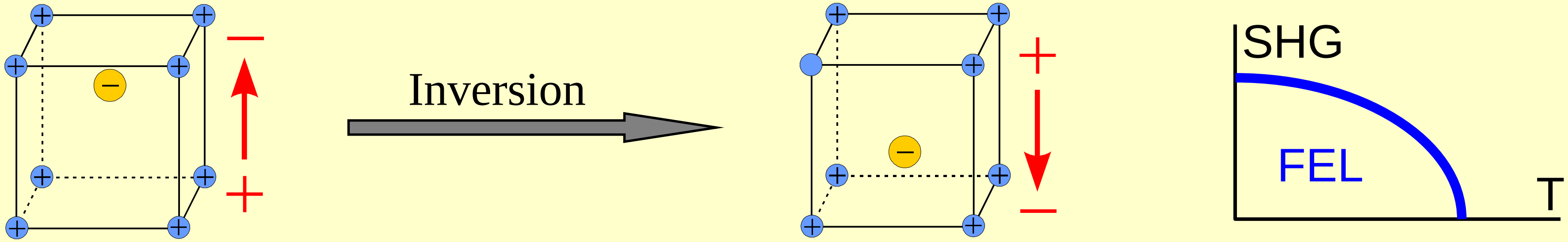




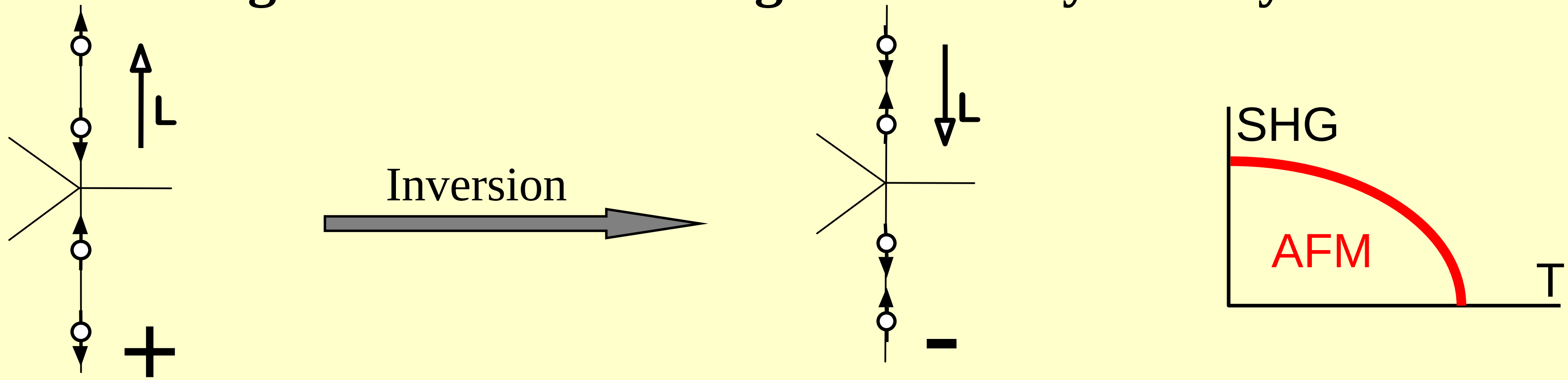
Symmetry operations other than inversion and time reversal may be broken by magnetic order

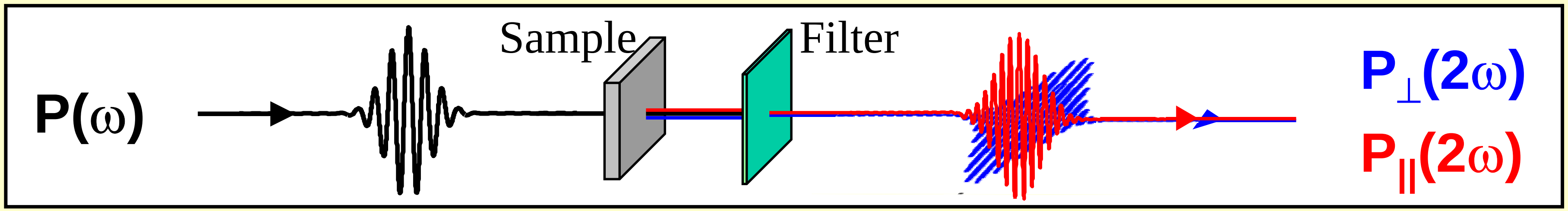
SHG and (Multi-) Ferroic Order

Ferroelectric order breaking inversion symmetry



Antferromagnetic order breaking inversion symmetry





First Magnetic SHG Experiment

VOLUME 67, NUMBER 20 PHYSICAL REVIEW LETTERS 11 NOVEMBER 1991

Effects of Surface Magnetism on Optical Second Harmonic Generation

J. Reif, J. C. Zink, C.-M. Schneider, and J. Kirschner
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, W-1000 Berlin 33, Germany
(Received 21 May 1991)

We report on the first experiments showing the influence of surface magnetization on optical second harmonic generation in reflection at a Fe(110) surface. The magneto-optical Kerr effect modifies the hyperpolarizability of the surface in the optical field, leading to a dependence of the second harmonic yield on the direction of magnetization relative to the light fields. For the clean surface an effect of 25% was determined, which decays exponentially with surface contamination by the residual gas, thus demonstrating the high surface sensitivity of this technique.

PACS numbers: 75.30.Pd, 78.20.Ls, 78.65.Ez

2878

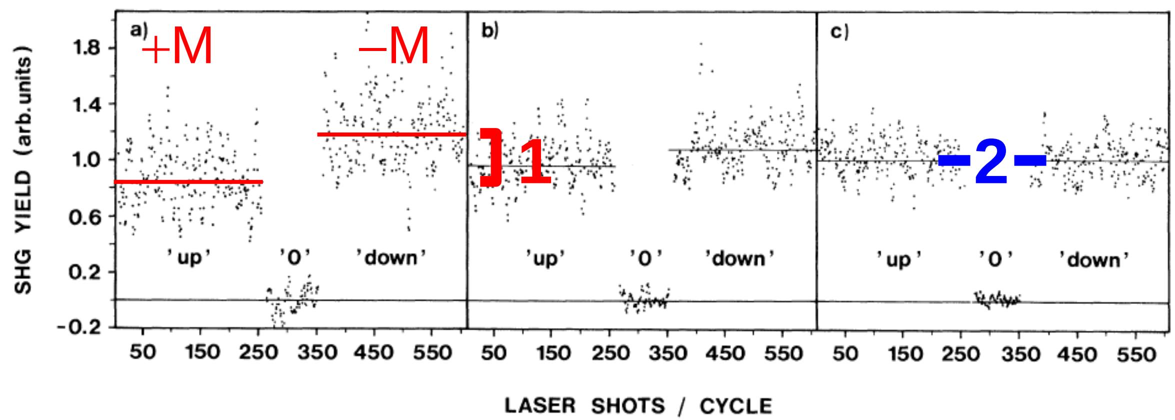


FIG. 2. Relative magnetization dependence of second harmonic signal for three different times elapsed since sample preparation [(a) ≈45 min, (b) ≈60 min, (c) ≥180 min]. Shown is, in each panel, an averaged [superposition of (a) 220, (b) 550, and (c) 750 cycles] experimental cycle, consisting of 250 pulses with magnetization "up," 100 pulses with no SHG signal (obtained by means of a UV blocking glass filter), and 250 pulses with magnetization "down." All signals are normalized to the expected value without influence of magnetization [cf. Eq. (1)]. The solid lines represent the average of the respective regions of interest.

1: Magnetic contribution: (broken time-reversal symmetry)

2: Nonmagnetic surface contribution: (broken space-inversion symmetry)

Magnetization of Thin Films Derived from SHG

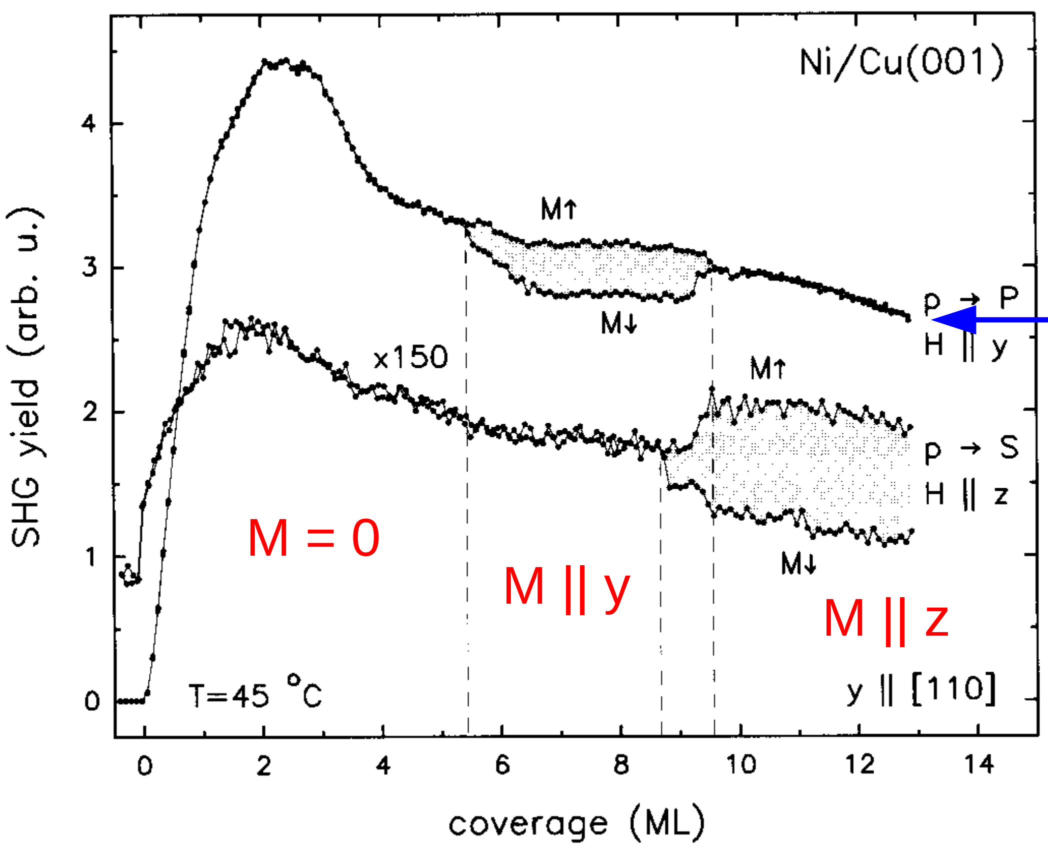
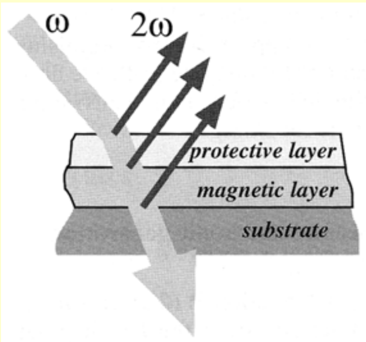


Fig. 4. SHG yield evolution during growth of Ni/Cu(001) for p_{in}-P_{out} and p_{in}-S_{out} polarization combinations. The external magnetic field was switched alternately between $+y$ and $-y$, or $+z$ and $-z$, respectively. The onset of in-plane magnetic order at 5.4 ML is reflected by the splitting of the two SH components for $H \| y$. The converging in-plane and diverging out-of-plane SH yield indicates the gradual reorientation of $\boldsymbol{M}$ from the y into the z direction between 8.7 to 9.6 ML

Even ~ crystallographic

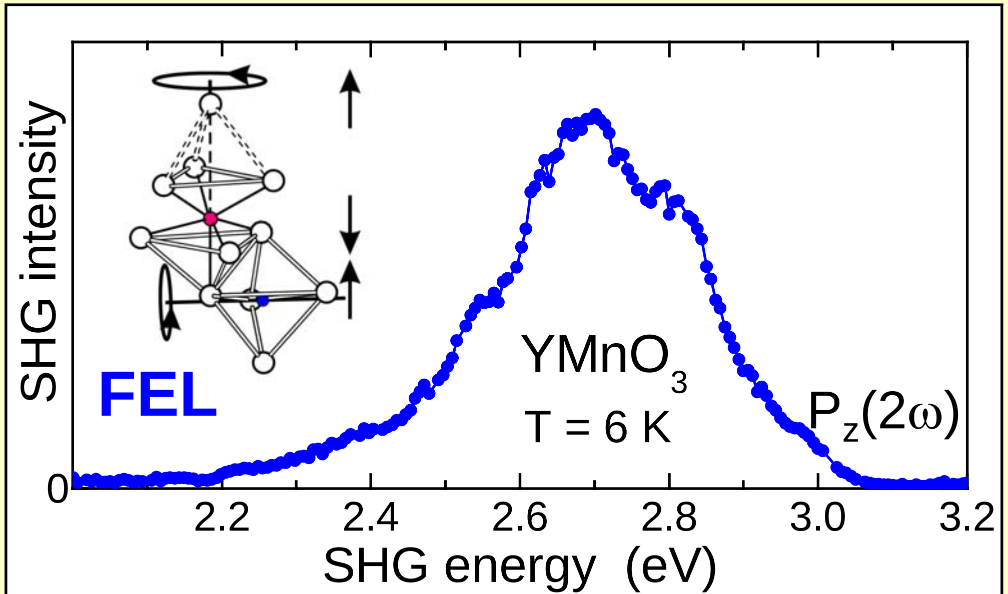
Odd ~ magnetic

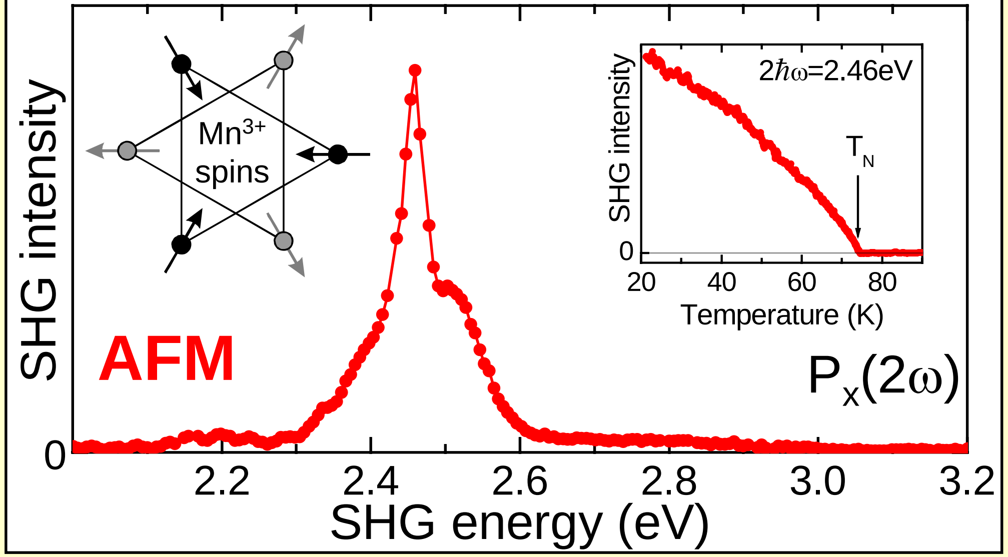
Ex-peri-ment

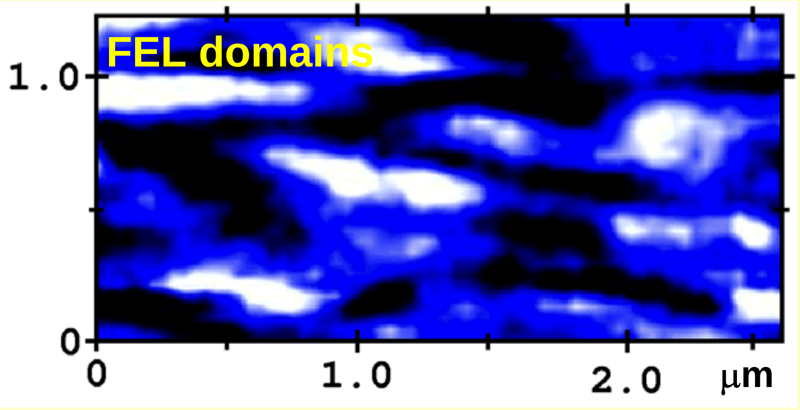


V. Jähnke et al. Appl. Phys. B **68**, 485 (1999)

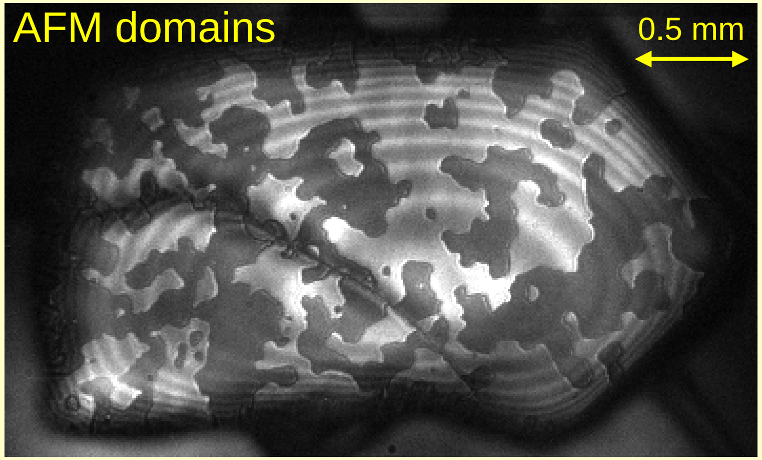
SHG on Multiferroic $YMnO_3$







SHG with M. Raschke: Phys. Rev. B **79**, 100107(R) (2009)
PFM with E. Soergel: Appl. Phys. Lett. **97**, 012904 (2010)



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

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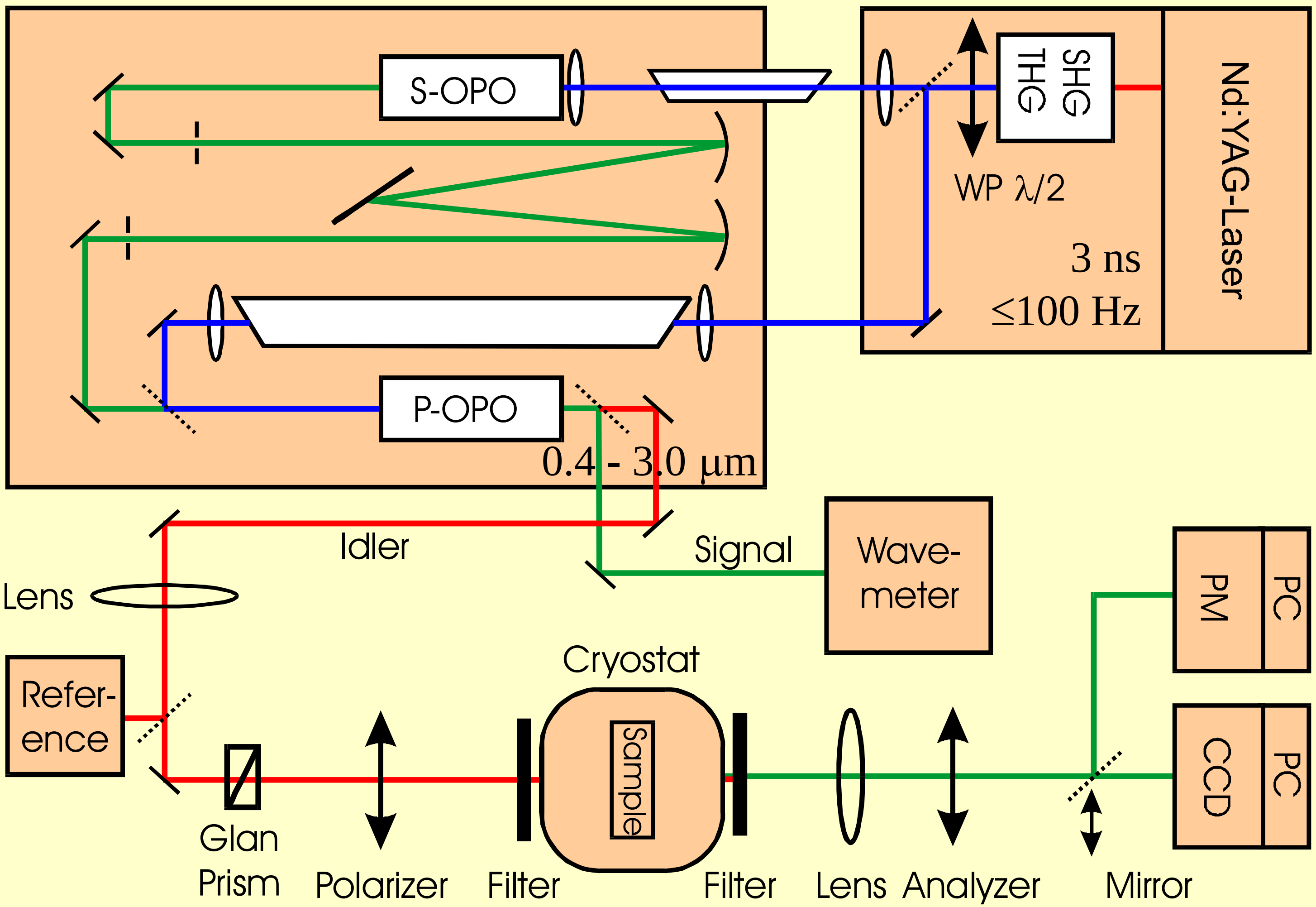
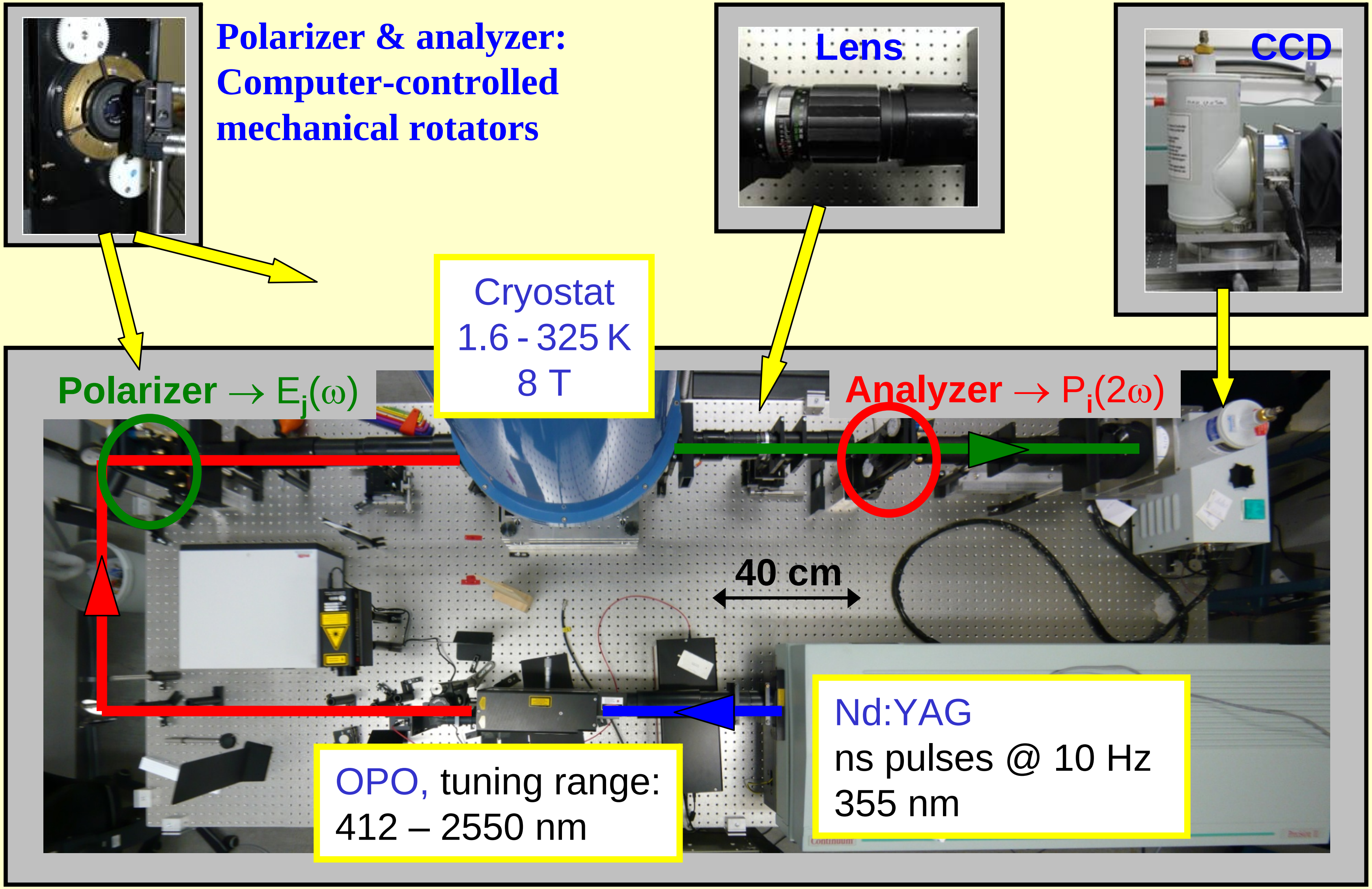
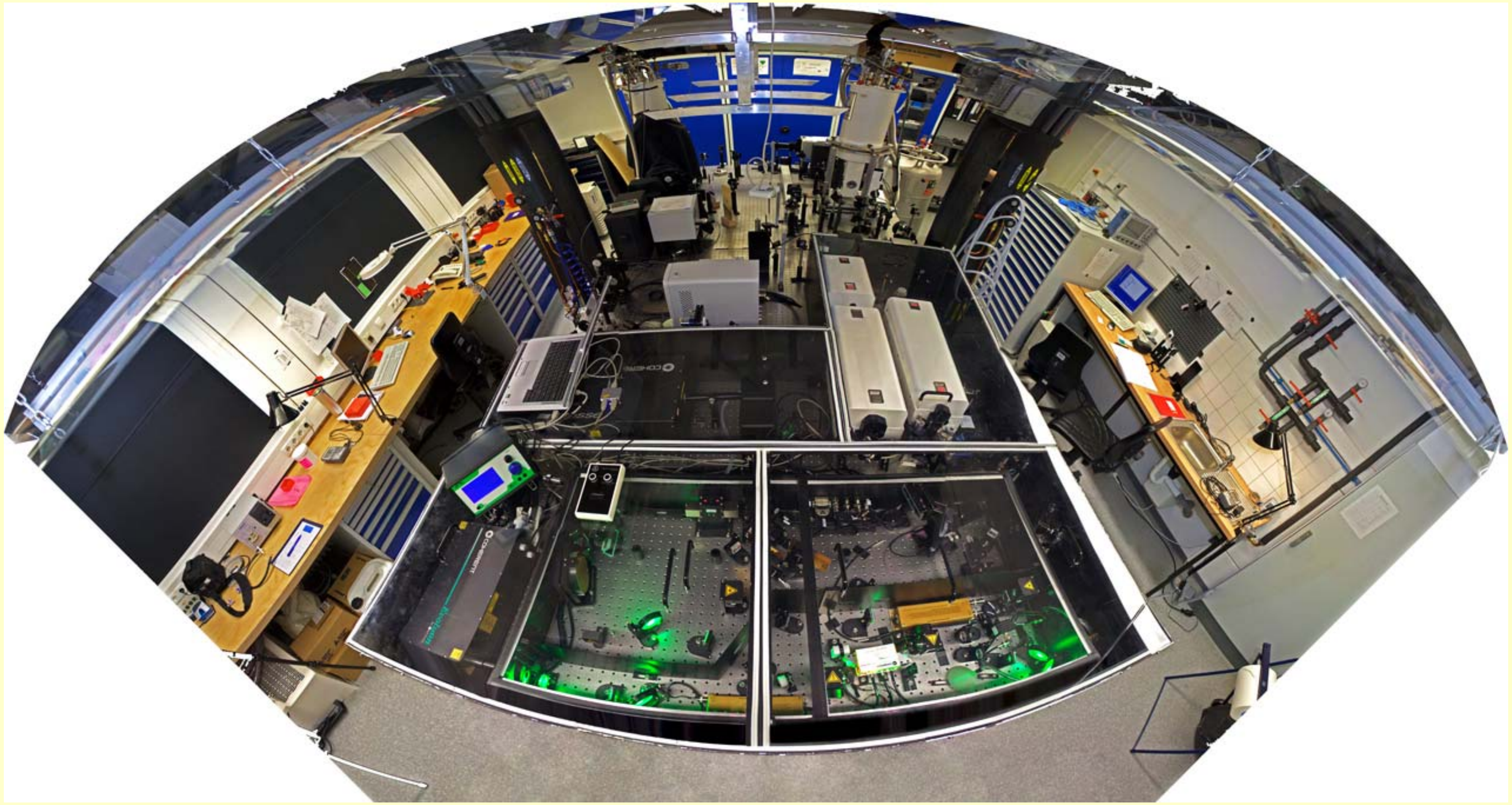
Experimental Setup for SHG

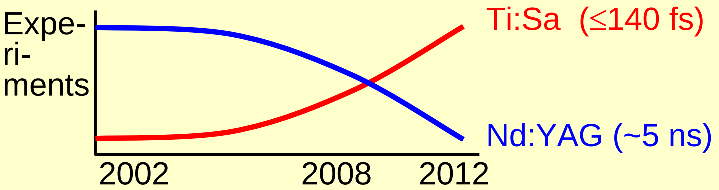


Laboratory for Nanosecond Spectroscopy



Laboratory for Femtosecond Spectroscopy



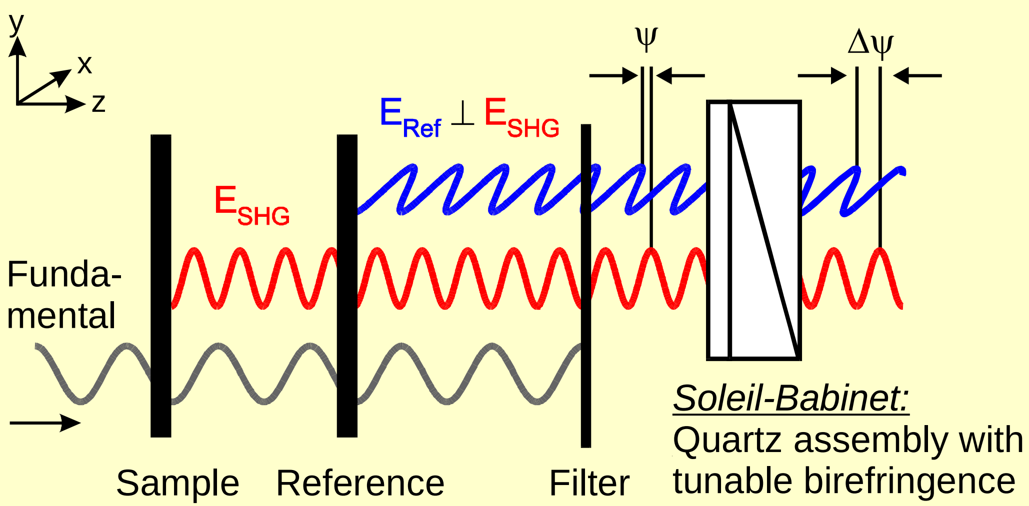


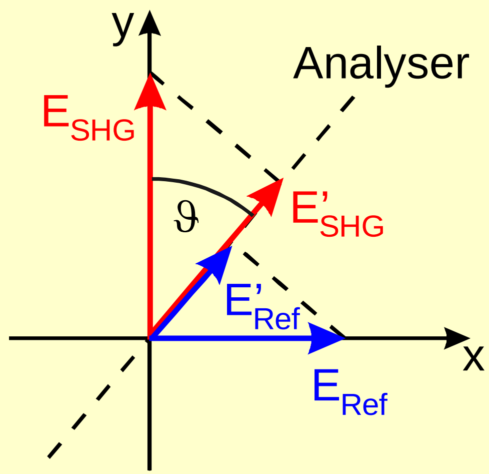
Amplified fs laser systems for ...

- Spectroscopy (Peak intensity!)
- Ultrafast dynamics

Setup for Phase-Sensitive SHG

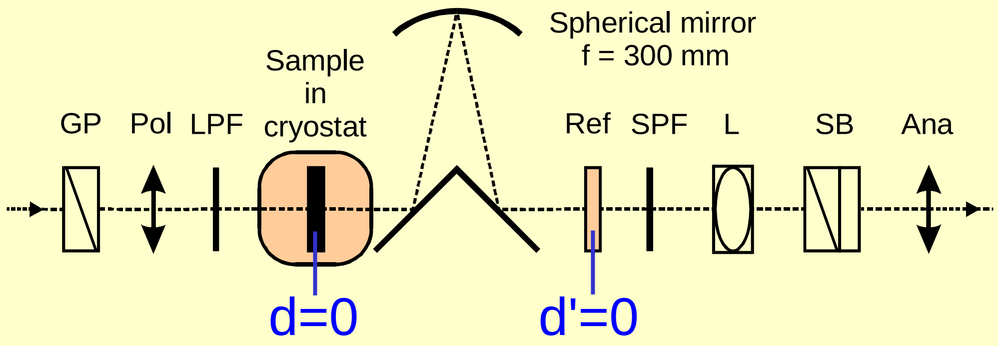
- Phase of SHG wave may carry important information
- E.g. distinguish any pair of order-parameter-reversal domains
- So how to measure the SHG phase?

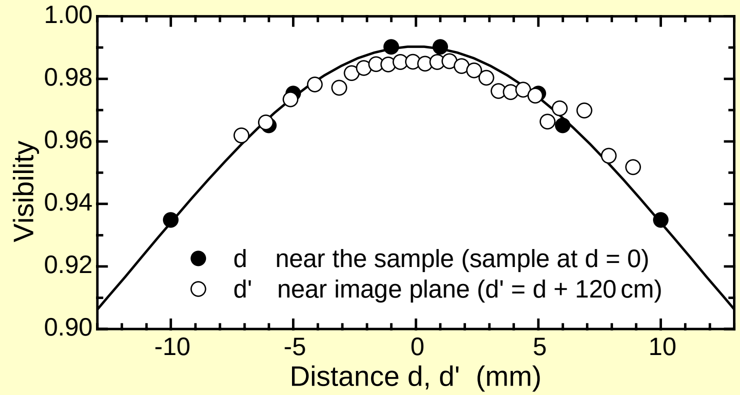




Interference of SHG signal from sample and SHG reference wave from quartz crystal → amplitude and phase of signal wave

Phase- and Amplitude-Sensitive SHG





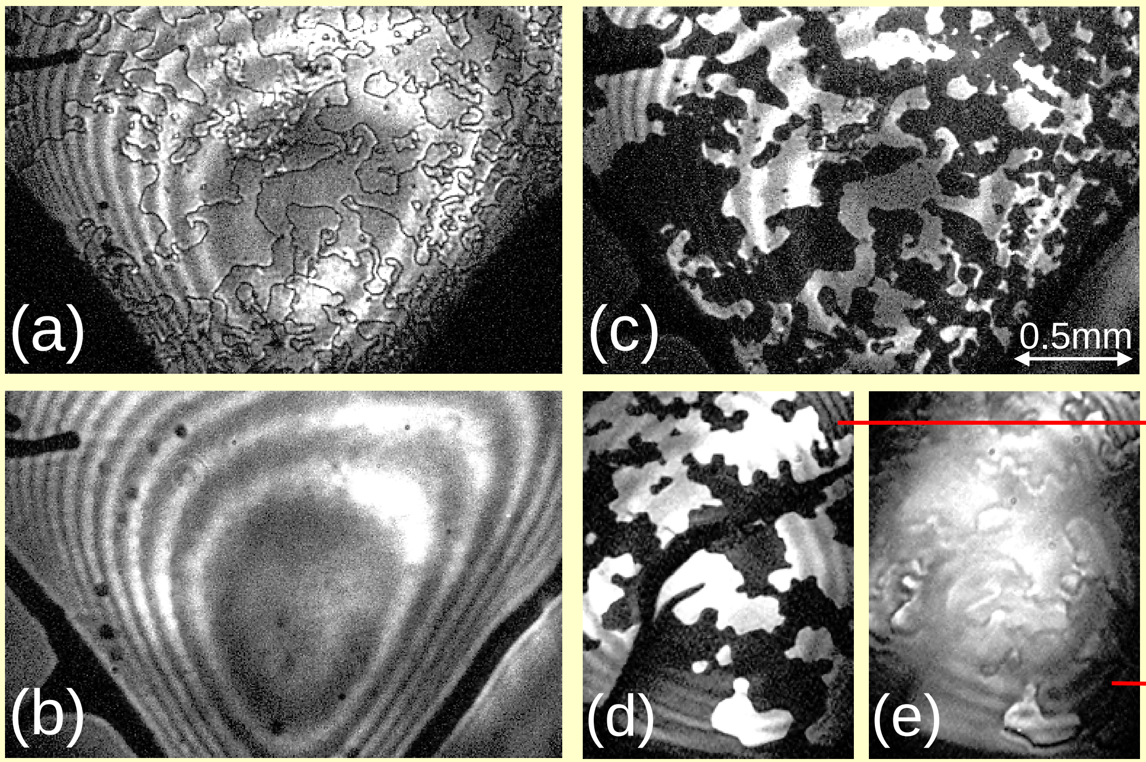
Magnetic SHG from sample

Signal + reference

Crystallographic SHG from reference quartz

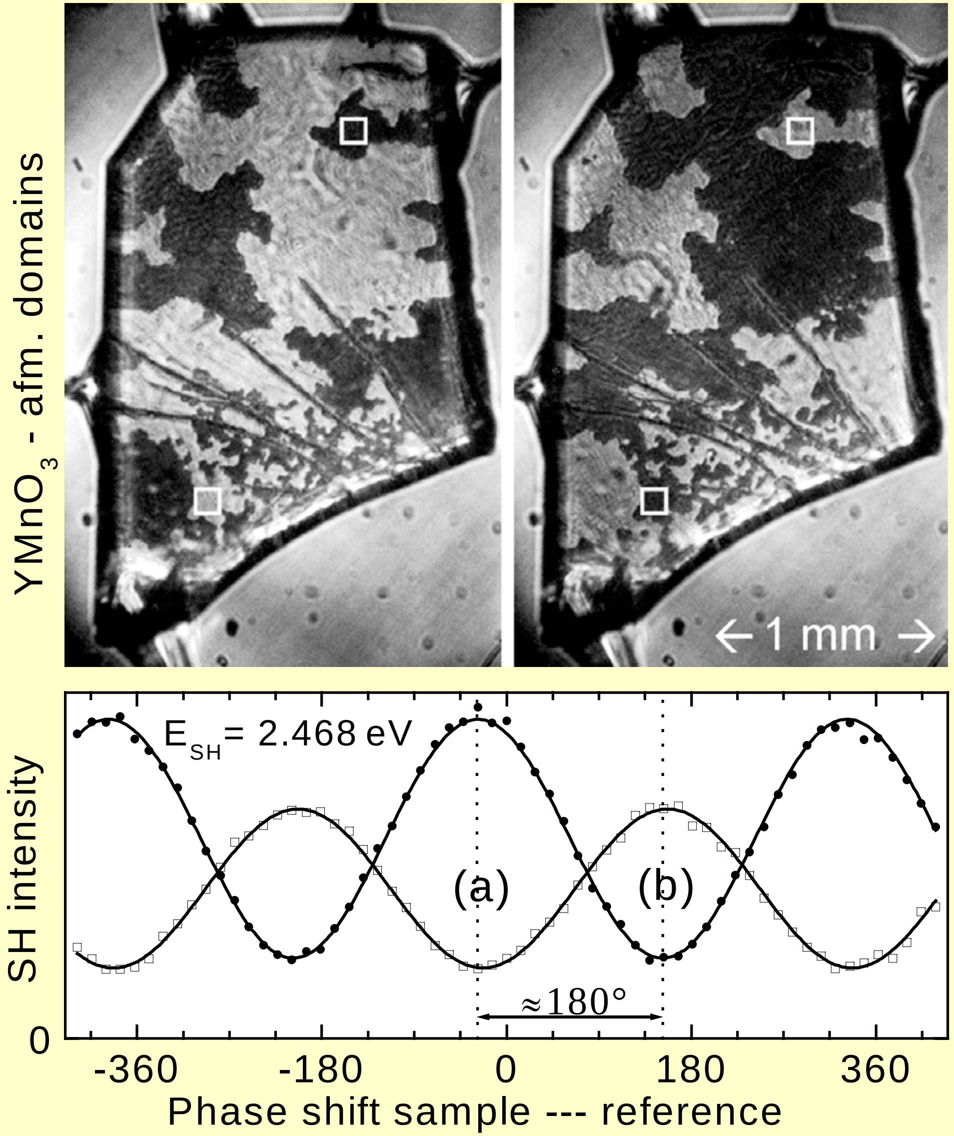
With imaging

Without imaging



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

Antiferromagnetic 180° Domains in $YMnO_3$



Second harmonic generation from opposite 180° domains:

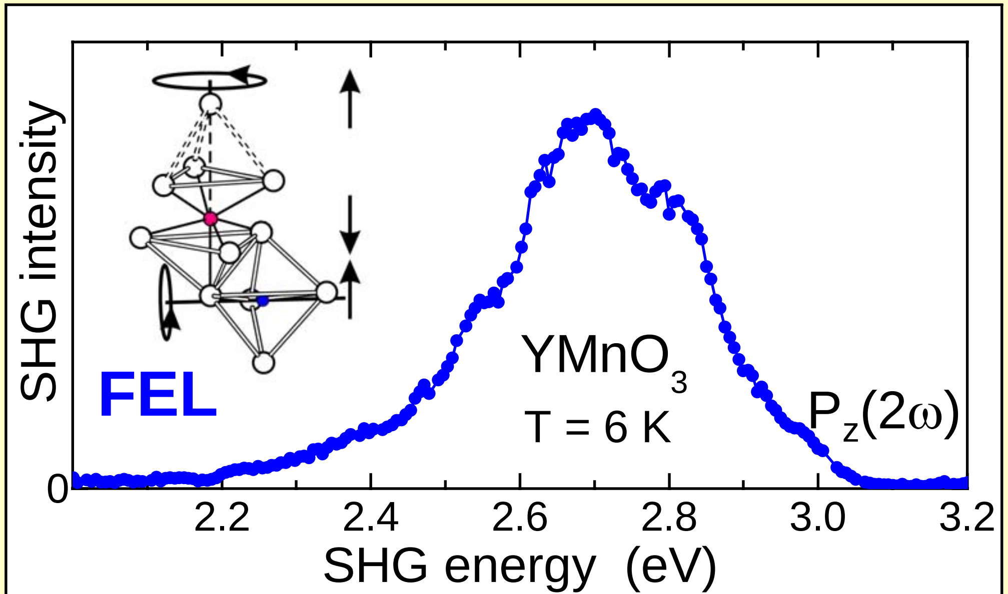
$$+\chi^{(2)}(c) \leftrightarrow -\chi^{(2)}(c)$$

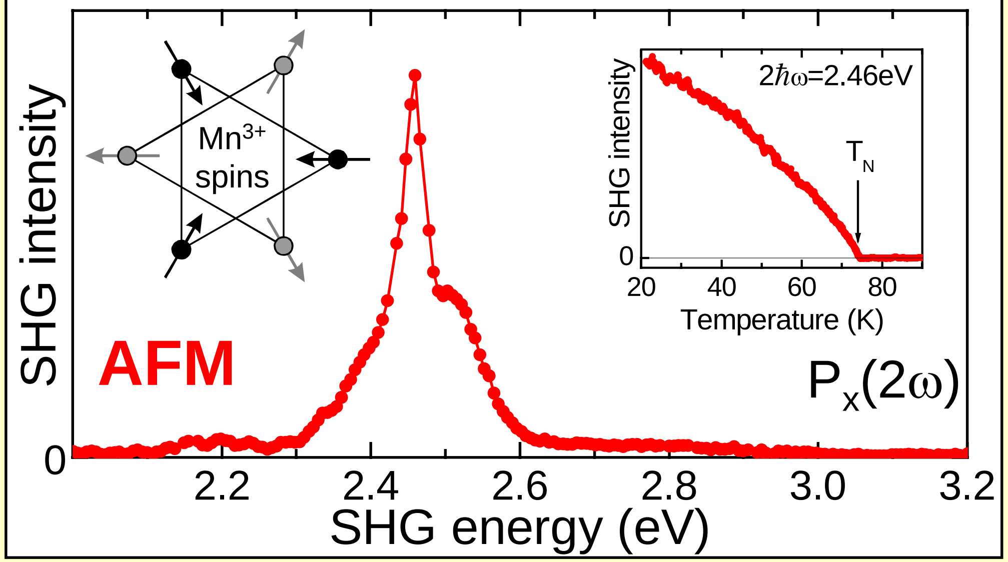
Leads to 180° phase shift in the corresponding magnetic SHG light fields

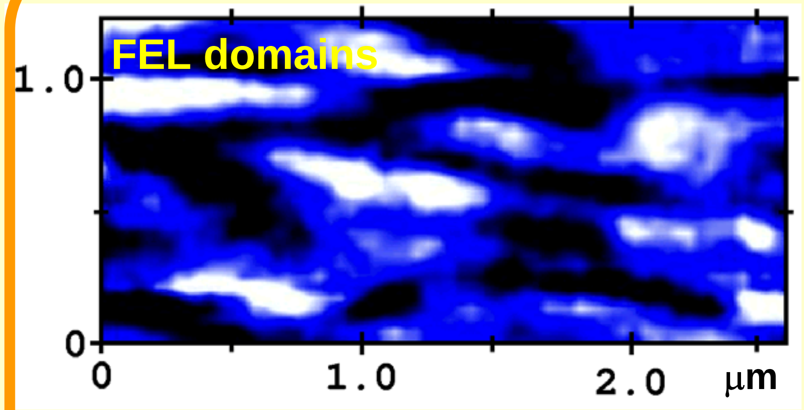
SHG is the only convenient technique for imaging of antiferromagnetic 180° domains

Opt. Lett. **24**, 1520 (1999)

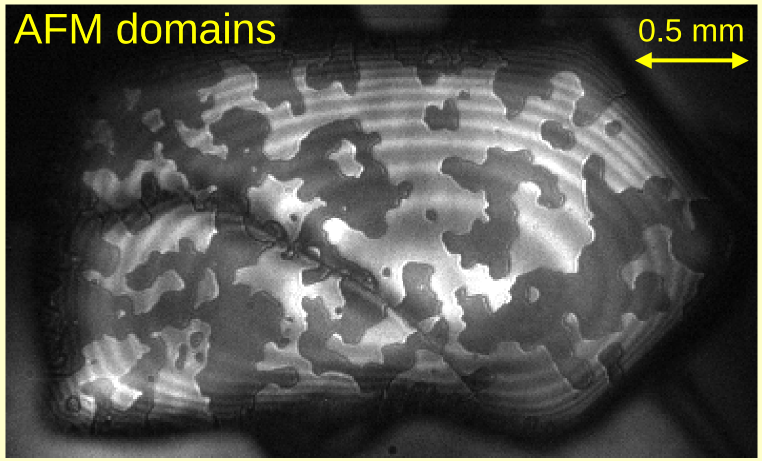
SHG on Multiferroic $YMnO_3$







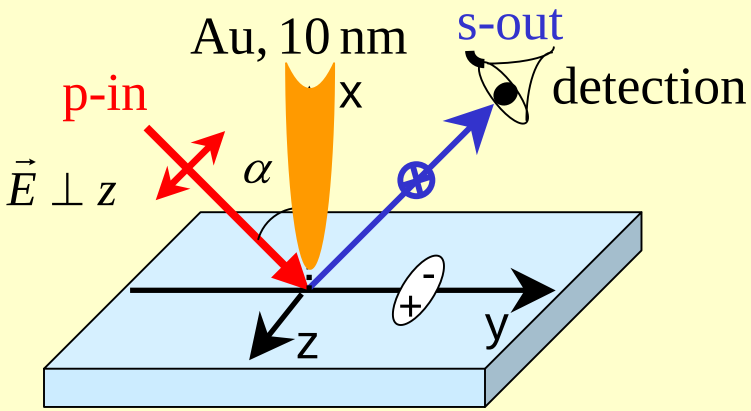
SHG with M. Raschke: Phys. Rev. B **79**, 100107(R) (2009)
PFM with E. Soergel: Appl. Phys. Lett. **97**, 012904 (2010)



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

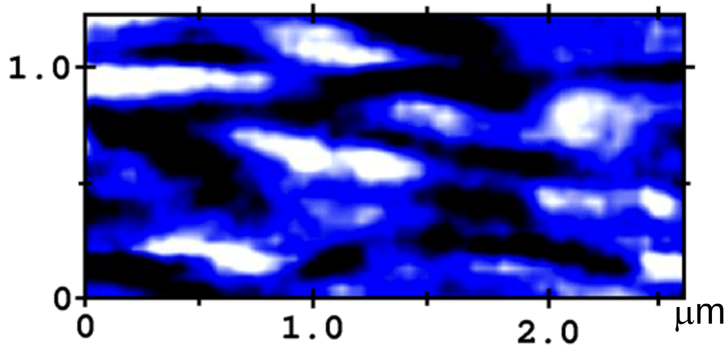
Near-Field Images of Intrinsic Ferroelectric Domains

Apertureless near-field SHG microscopy:

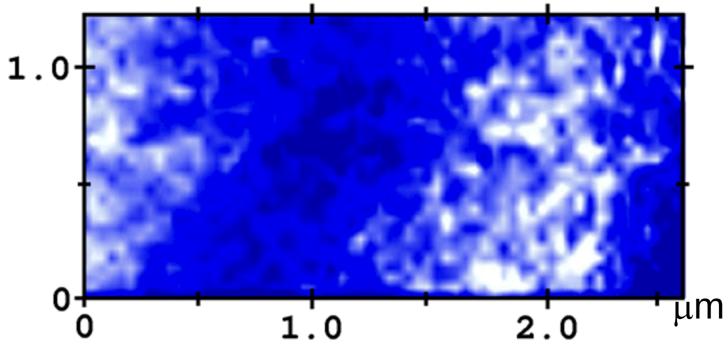


$$P_z^{(2)}(2\omega) \approx \chi_{zxx}^{(2)}[E_x]^2 + \chi_{zyy}^{(2)}[E_y]^2$$

S out: ferroelectric SHG



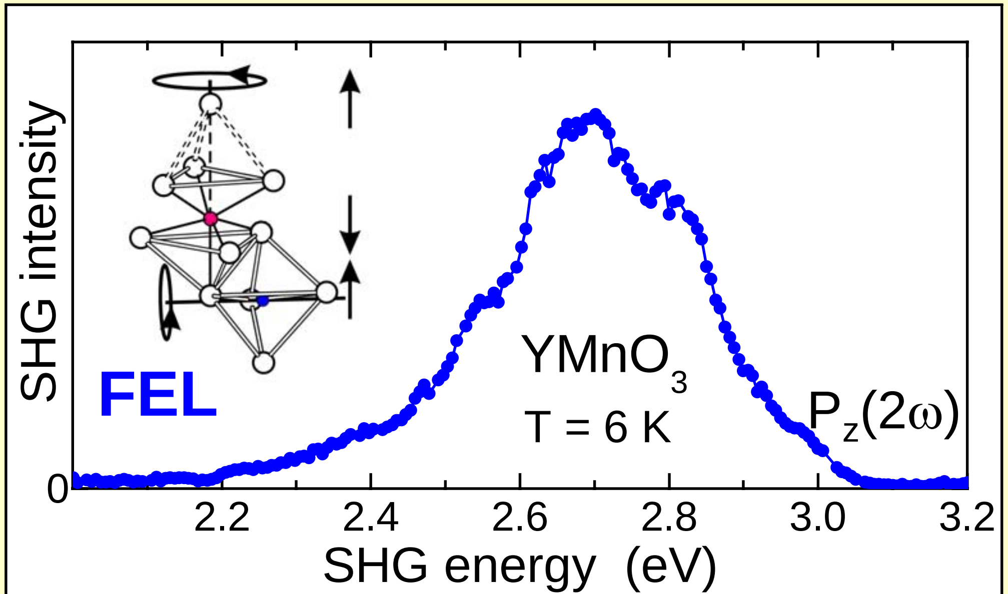
P out: background

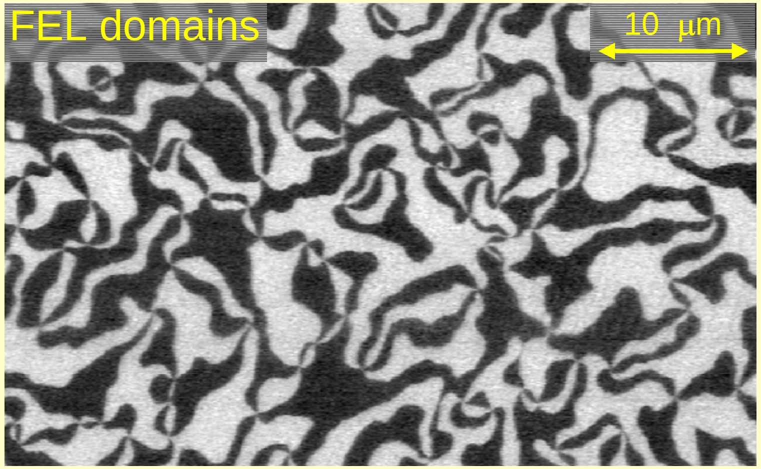


- Resolution limit: 30 – 300 nm
- Size of unpoled domains: 0.1–1 µm

C. Neacsu et al.
Phys. Rev. B **79**, 100107(R) (2009)

SHG on Multiferroic $YMnO_3$





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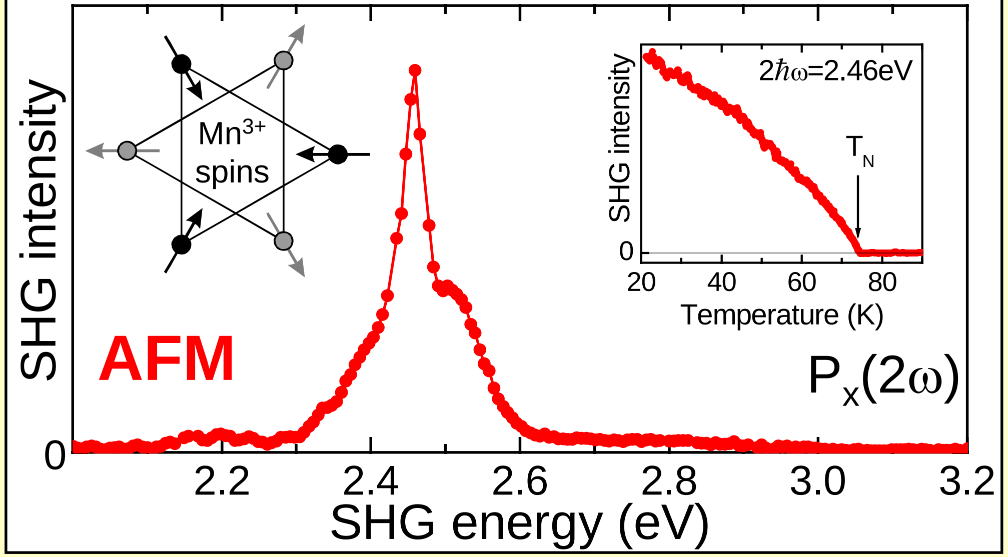

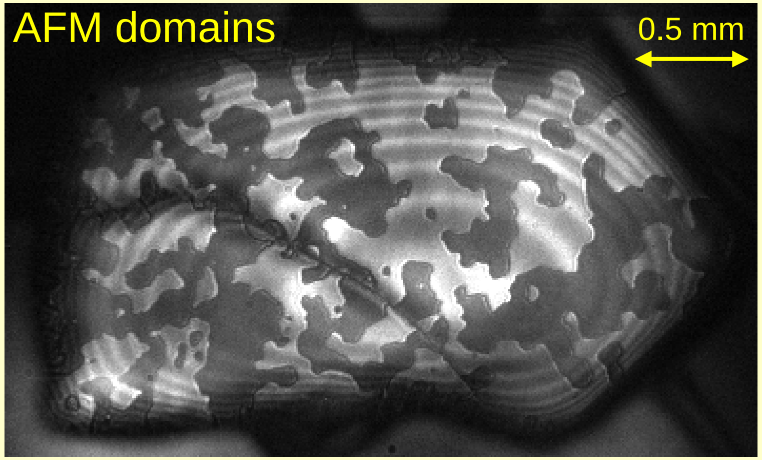

SHG: Phys. Rev. Lett. **84**, 5620 (2000)

Nonlinear Optics Applied to Multiferroics

- What is a multiferroic?
- Introduction to nonlinear optics
- Experimental setups for nonlinear (multi-) ferro-optics
- **Nonlinear optics on multiferroics**
  - Split-order-parameter multiferroics: hex. $RMnO_3$
  - Joint-order-parameter multiferroics: $MnWO_4$
  - Sublattice selectivity: $TbMn_2O_5$

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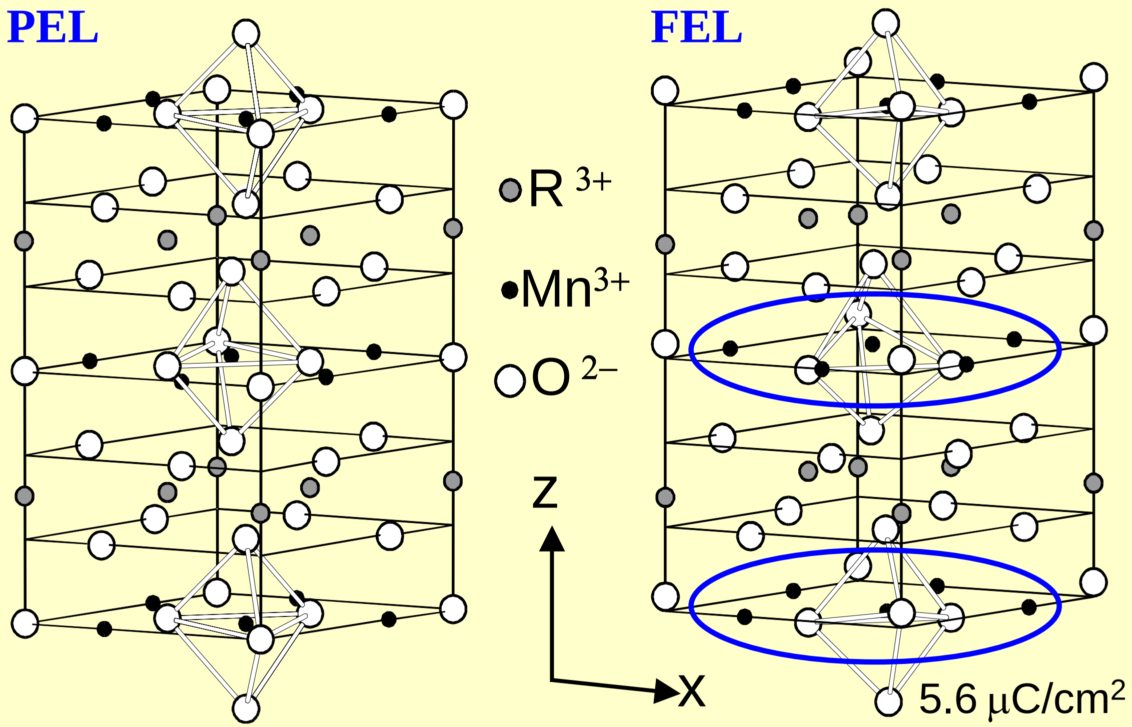
  - Sublattice selectivity: $TbMn_2O_5$

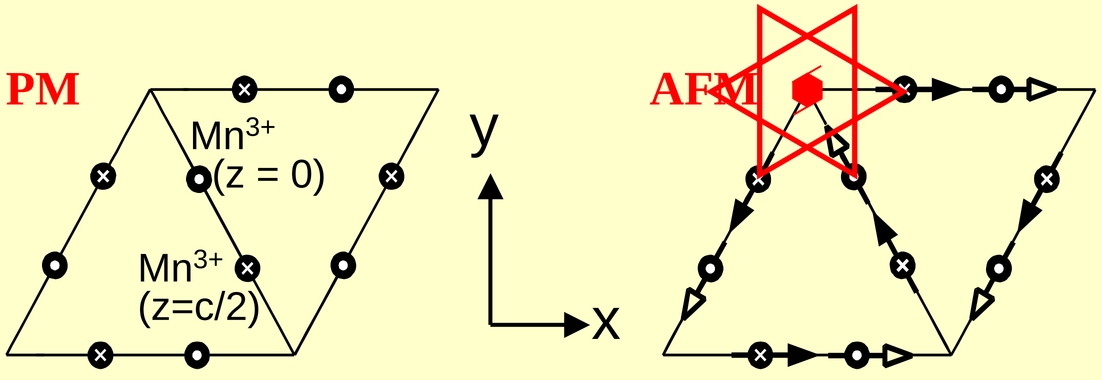
Magnetic Symmetry of Hexagonal $RMnO_3$



***R*MnO$_3$: A highly correlated and ordered system**

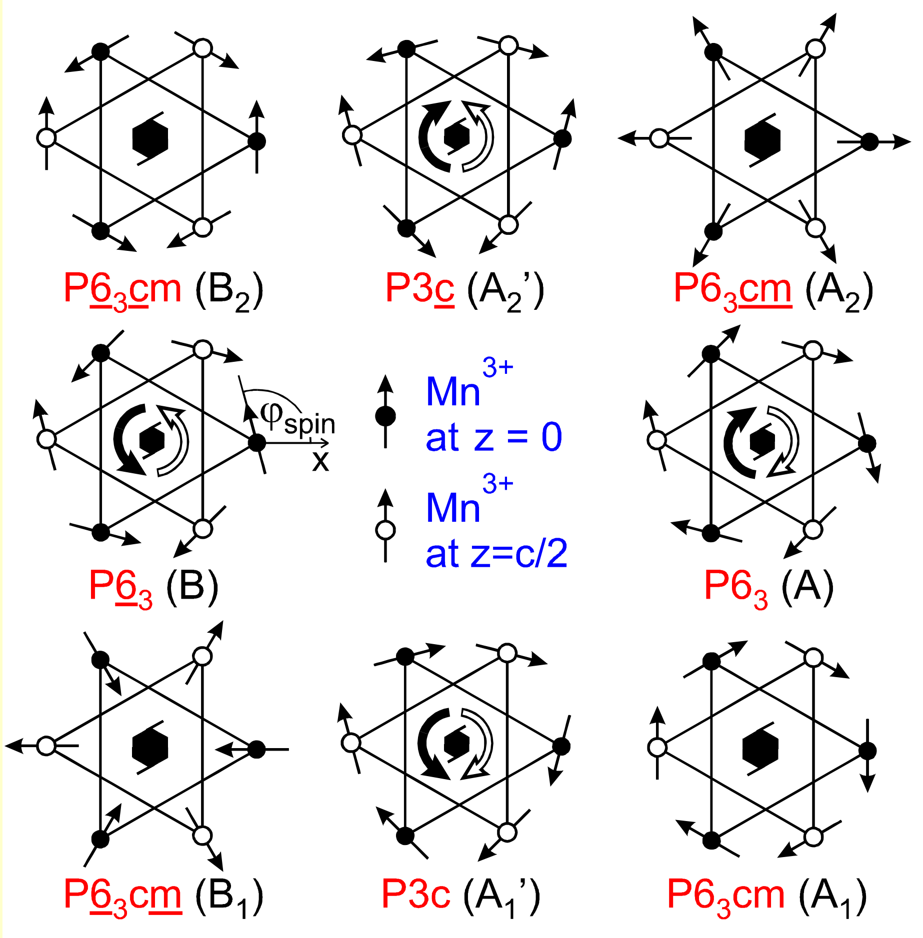
- **Paraelectric → Ferroelectric**
  (PEL - FEL): T_C = 570 - 990 K
  Two 180° domains with $\pm P_z$

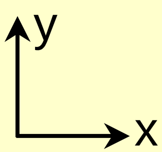
- **Para- → Antiferromagnetic**
  (PM - AFM): T_N = 70 - 130 K
  8 frustrated triangle structures



- Multiferroic/hexagonal for
  R = Sc,Y,Dy,Ho,Er,Tm,Yb,Lu
- Additional rare-earth order at
  ≈ 5 K for Dy, Ho, Er, Tm, Yb

Magnetic Structure and Selection Rules for SHG





At least 8 different structures with different symmetries

Different symmetry leads to different SHG contributions for all 8 structures

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

P6₃cm : $E_x(\omega) \rightarrow P_x(2\omega) \quad \sim \chi_{xxx}$

P6₃cm : $E_x(\omega) \rightarrow P_y(2\omega) \quad \sim \chi_{yyy}$

P6₃ : $E_x(\omega) \rightarrow P_x(2\omega) \oplus P_y(2\omega)$

P6₃.. : $E_x(\omega) \rightarrow 0$

usw.

Polarization of ingoing and outgoing light reveals the magnetic symmetry

First magnetoelectric material: Cr_2O_3

Courtesy T. Kimura

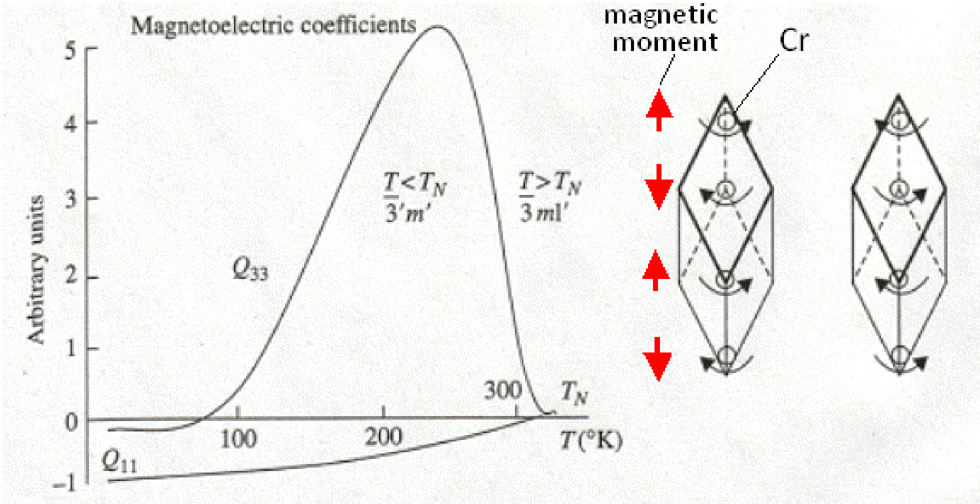
Crystal structure: corundum (=Al_2O_3)

Antiferromagnet with T_N *=307 K*

Magnetic point group: $\bar{3}'m'$

Generating elements

$m' \perp Z_1$, $\bar{3}' // Z_3$



$m' \perp Z_1$

Time reversal

Handedness change by mirror

$$\begin{pmatrix} Q'_{11} & Q'_{12} & Q'_{13} \\ Q'_{21} & Q'_{22} & Q'_{23} \\ Q'_{31} & Q'_{32} & Q'_{33} \end{pmatrix} = (-1)(-1) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} Q_{11} & -Q_{12} & -Q_{13} \\ -Q_{21} & Q_{22} & Q_{23} \\ -Q_{31} & Q_{32} & Q_{33} \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \end{pmatrix}$$

This equality can be satisfied if $Q_{12} = Q_{13} = Q_{21} = Q_{31} = 0$ $\longrightarrow$

$$\begin{pmatrix} Q_{11} & 0 & 0 \\ 0 & Q_{22} & Q_{23} \\ 0 & Q_{32} & Q_{33} \end{pmatrix}$$

Courtesy T. Kimura

$\bar{3}' \,//\, Z_3$

Time reversal

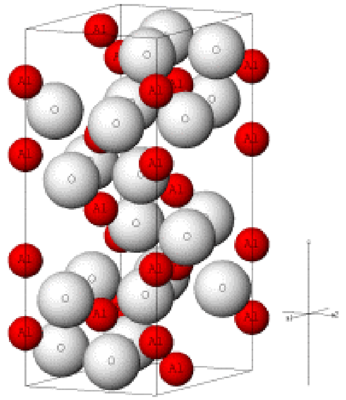
Handedness change by inversion

$$\begin{pmatrix} Q'_{11} & Q'_{12} & Q'_{13} \\ Q'_{21} & Q'_{22} & Q'_{23} \\ Q'_{31} & Q'_{32} & Q'_{33} \end{pmatrix} = (-1)(-1) \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} Q_{11} & 0 & 0 \\ 0 & Q_{22} & Q_{23} \\ 0 & Q_{32} & Q_{33} \end{pmatrix} \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} (1/4Q_{11}+3/4Q_{22}) & (-\sqrt{3}/4Q_{11}+\sqrt{3}/4Q_{22}) & (\sqrt{3}/2Q_{23}) \\ (\sqrt{3}/4Q_{11}-\sqrt{3}/4Q_{22}) & (3/4Q_{11}+1/4Q_{22}) & (-1/2Q_{23}) \\ (\sqrt{3}/2Q_{32}) & (-1/2Q_{32}) & (Q_{33}) \end{pmatrix}$$

$$= \begin{pmatrix} Q_{11} & 0 & 0 \\ 0 & Q_{22} & Q_{23} \\ 0 & Q_{32} & Q_{33} \end{pmatrix}$$

This equality can be satisfied if $Q_{11} = Q_{22}$ & $Q_{23} = Q_{32} = 0$



Therefore the magnetoelectric matrix for point group $\bar{3}'m'$ is

$$\begin{pmatrix} Q_{11} & 0 & 0 \\ 0 & Q_{11} & 0 \\ 0 & 0 & Q_{33} \end{pmatrix}$$

Symmetry and Tensor Components

$P_i \sim \alpha_{ij} H_j$, α as 2^{nd}-rank axial tensor violating time-reversal symmetry

"even" "axial" "c-type"

L_2

"The Bible": R.R. Birss, *Symmetry and Magnetism*, North-Holland, Amsterdam, 1966

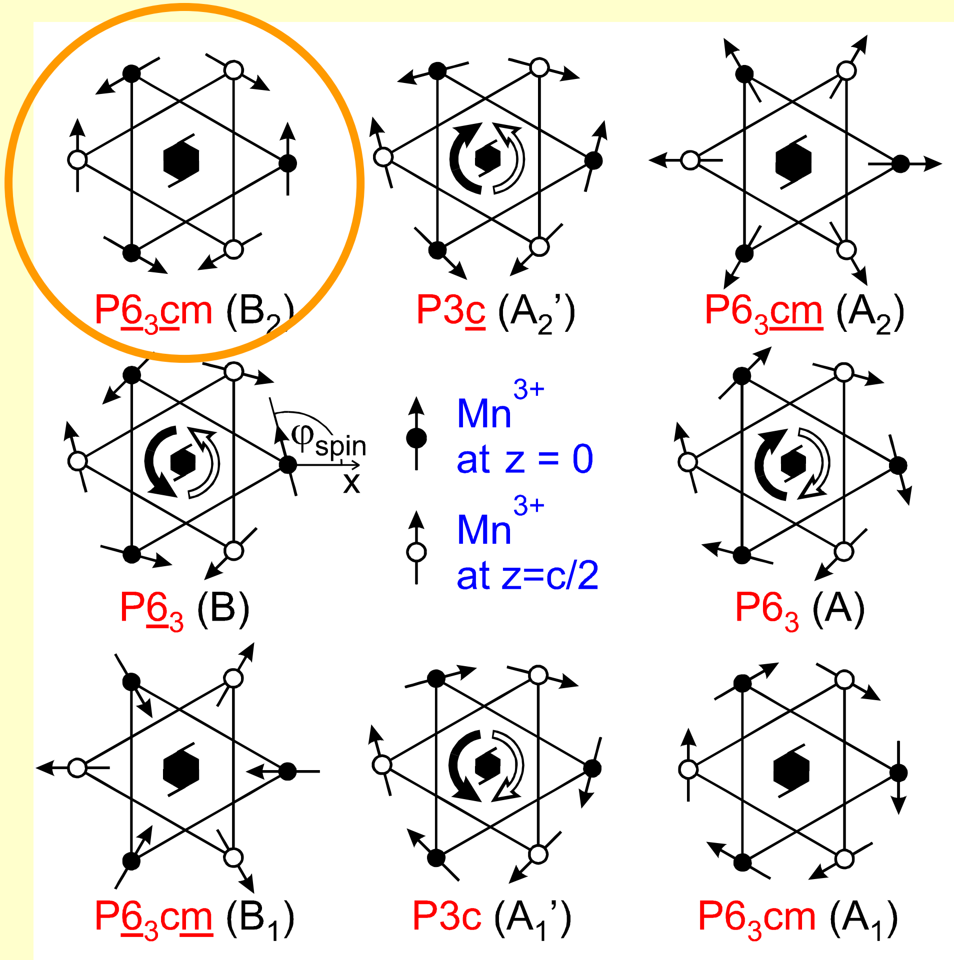
1	2	3	4	5	6	7	8	9	10	11	12
				i-tensors				c-tensors			
System	Magnetic point group $\mathcal{M}'$	Associated classical groups $\mathcal{A}$	$\mathcal{B}$	Polar tensor of even rank m	Axial tensor of even rank m	Polar tensor of odd rank n	Axial tensor of odd rank n	Polar tensor of even rank m	Axial tensor of even rank m	Polar tensor of odd rank n	Axial tensor of odd rank n
trigonal	$\bar{3}m$	32	$\bar{3}m$	L_m	—	—	L_n	—	L_m	L_n	—

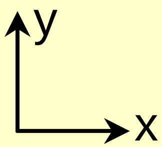
$m = 2$	xx	yy	zz	xy	yx	$xz(2)$	$yz(2)$
L_2	xx	xx	zz	0	0	0	0

$\alpha_{xx} = \alpha_{yy} = Q_{11}$

$\alpha_{zz} = Q_{33}$

Magnetic Structure and Selection Rules for SHG





At least 8 different structures with different symmetries

Different symmetry leads to different SHG contributions for all 8 structures

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

$P6_3cm$: $E_x(\omega) \rightarrow P_x(2\omega)$ $\sim \chi_{xxx}$

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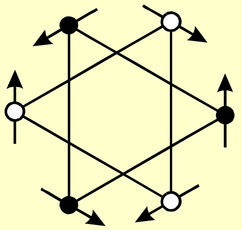
$P6_3$: $E_x(\omega) \rightarrow P_x(2\omega) \oplus P_y(2\omega)$

$P6_3..$: $E_x(\omega) \rightarrow 0$

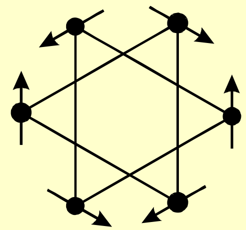
usw.

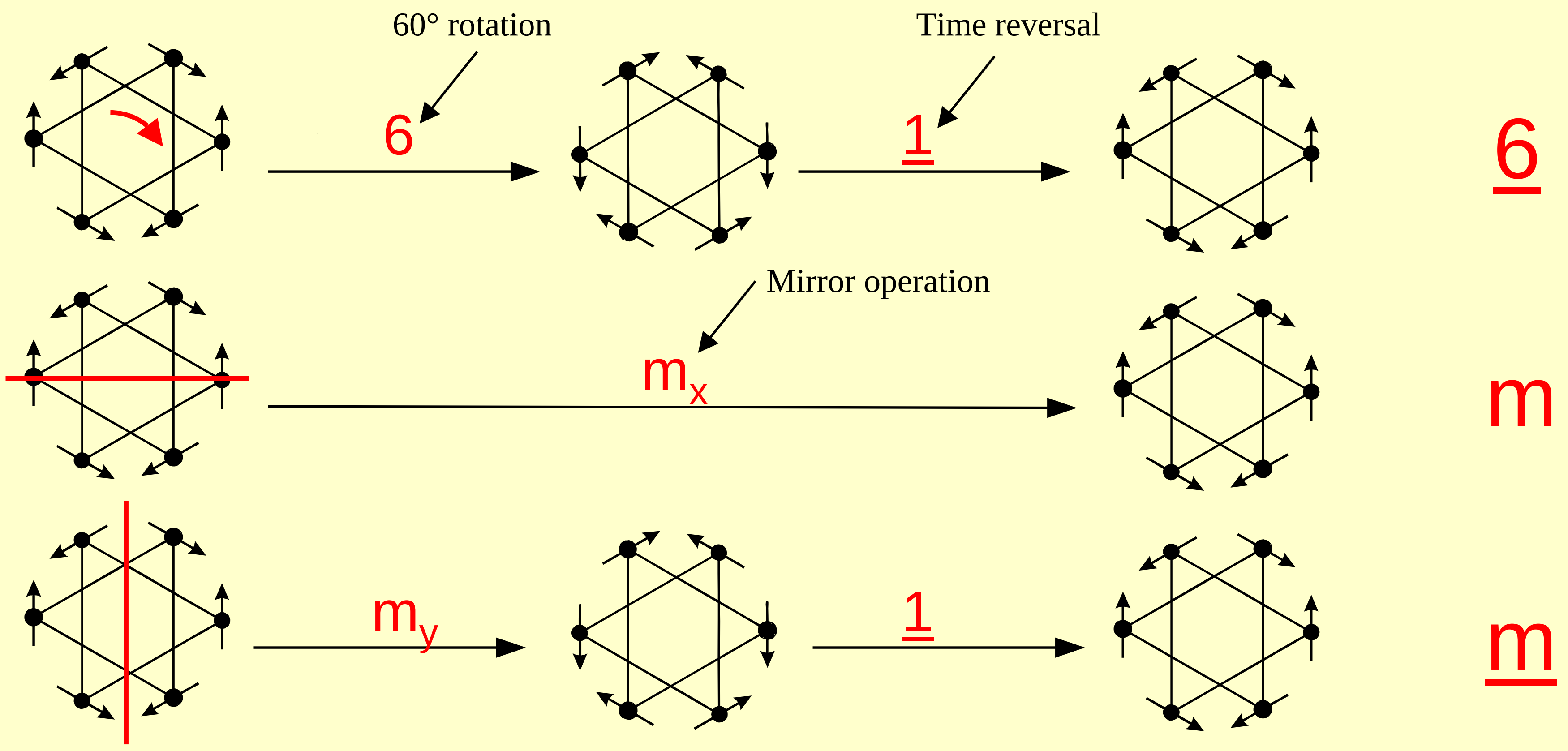
Polarization of ingoing and outgoing light reveals the magnetic symmetry

Symmetry Operations



Space symmetry $P\underline{6}_3c\underline{m}$ → point symmetry $\underline{6}m\underline{m}$
(neglect translations since << light wavelength)





Looking up SHG Components for 6mm

Birss, table 6

Hexa-gonal	6mm	6·m	3m	3·m	1, $3(\bar{2}_\perp)$, $\pm 3_z$, 2_z, $3(\bar{2}_\perp)$, $\pm 6_z$	$\sigma^{(4)}$, $\sigma^{(6)}$	$\sigma^{(3)}$

Birss, table 7

$$P_i(2\omega) = \chi^{(2)}_{ijk}\, E_j(\omega)\, E_k(\omega)$$

System	Magnetic point group $\mathcal{M}'$	Associated classical groups $\mathcal{A}$	Associated classical groups $\mathcal{B}$	i-tensors: Polar tensor of even rank m	i-tensors: Axial tensor of even rank m	i-tensors: Polar tensor of odd rank n	i-tensors: Axial tensor of odd rank n	c-tensors: Polar tensor of even rank m	c-tensors: Axial tensor of even rank m	c-tensors: Polar tensor of odd rank n	c-tensors: Axial tensor of odd rank n
Hexa-gonal	6mm	$\bar{6}$m2	($\bar{6}$2m)	P_m	Q_m	Q_n	P_n	(R_m)	R_m	R_n	(R_n)

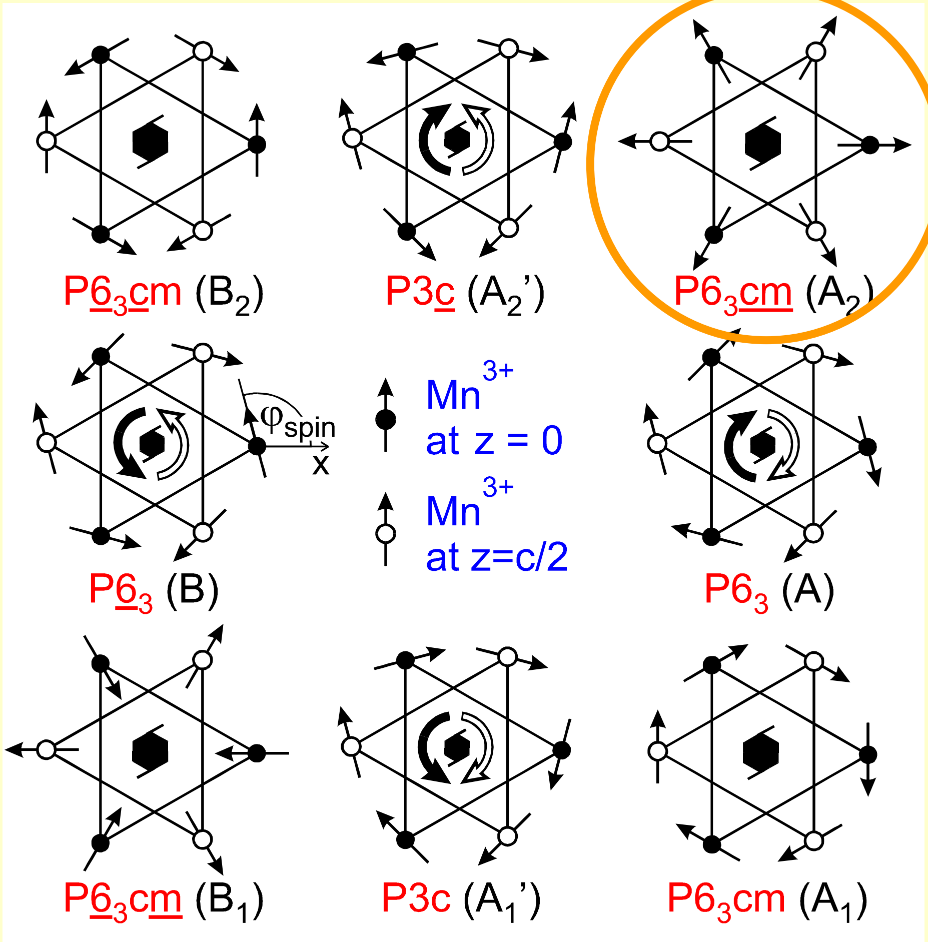
Birss, table 4

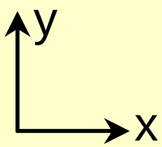
yyx(3) → yyx, yxy, xyy

$n = 3$	xxx	yyy	zzz	$xxy(3)$	$yyx(3)$	$xxz(3)$	$yyz(3)$	$zzx(3)$	$zzy(3)$	xyz	xzy	zxy	yxz	yzx	zyx
R_3	xxx	0	0	0	$-xxx$	0	0	0	0	0	0	0	0	0	0

Reveals: $\chi_{xxx} = -\chi_{xxy} = -\chi_{xyx} = -\chi_{yxx}$

Magnetic Structure and Selection Rules for SHG





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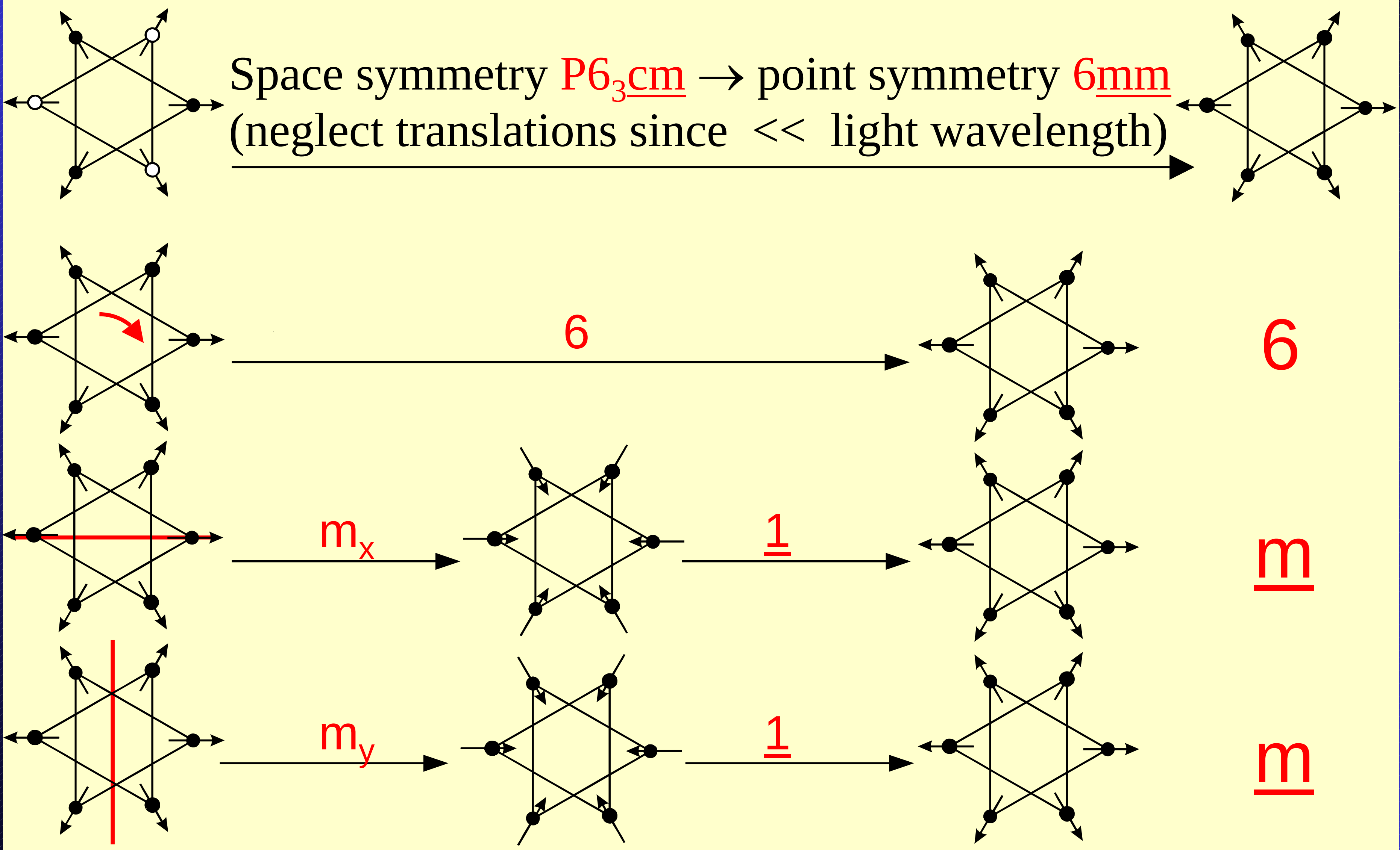


Looking up SHG Components for 6$\underline{mm}$

Birss, table 6

Hexa-gonal	6$\underline{mm}$	$6 \cdot \underline{m}$	6	6	$1, 2_z, \pm 3_z, \pm 6_z, 6(\underline{2}_\perp)$	$\sigma^{(3)}, \sigma^{(6)}$	$\underline{\sigma}^{(4)}$

Birss, table 7

$$P_i(2\omega) = \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega)$$

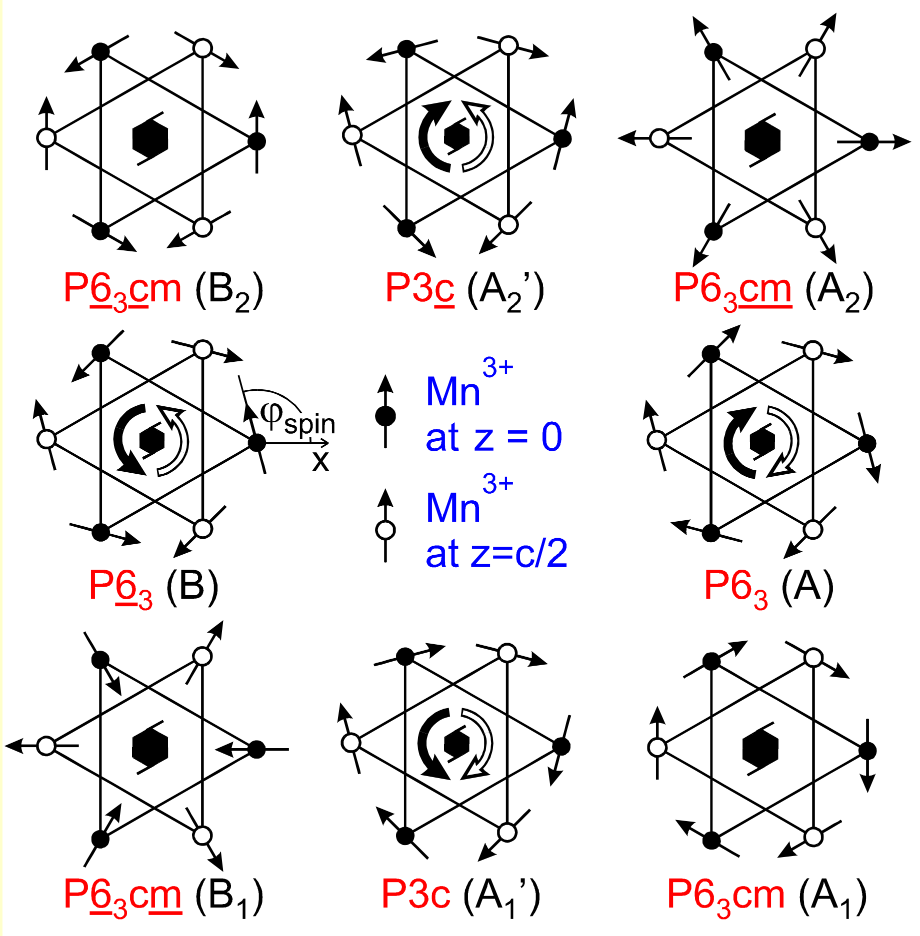
System	Magnetic point group $\mathscr{M}'$	Associated classical groups $\mathscr{A}$	$\mathscr{B}$	i-tensors: Polar tensor of even rank m	Axial tensor of even rank m	Polar tensor of odd rank n	Axial tensor of odd rank n	c-tensors: Polar tensor of even rank m	Axial tensor of even rank m	Polar tensor of odd rank n	Axial tensor of odd rank n
Hexa-gonal	6$\underline{mm}$	622	6mm	P_m	Q_m	Q_n	P_n	Q_m	P_m	P_n	Q_n

Birss, table 4

$n = 3$	xxx	yyy	zzz	$xxy(3)$	$yyx(3)$	$xxz(3)$	$yyz(3)$	$zzx(3)$	$zzy(3)$	xyz	xzy	zxy	yxz	yzx	zyx
P_3	0	0	0	0	0	0	0	0	0	xyz	xzy	zxy	$-xyz$	$-xzy$	$-zxy$

Reveals: χ_{xyz} etc.: inaccessible for light with k || z $\rightarrow$ no SHG!

Magnetic Structure and Selection Rules for SHG



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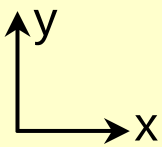
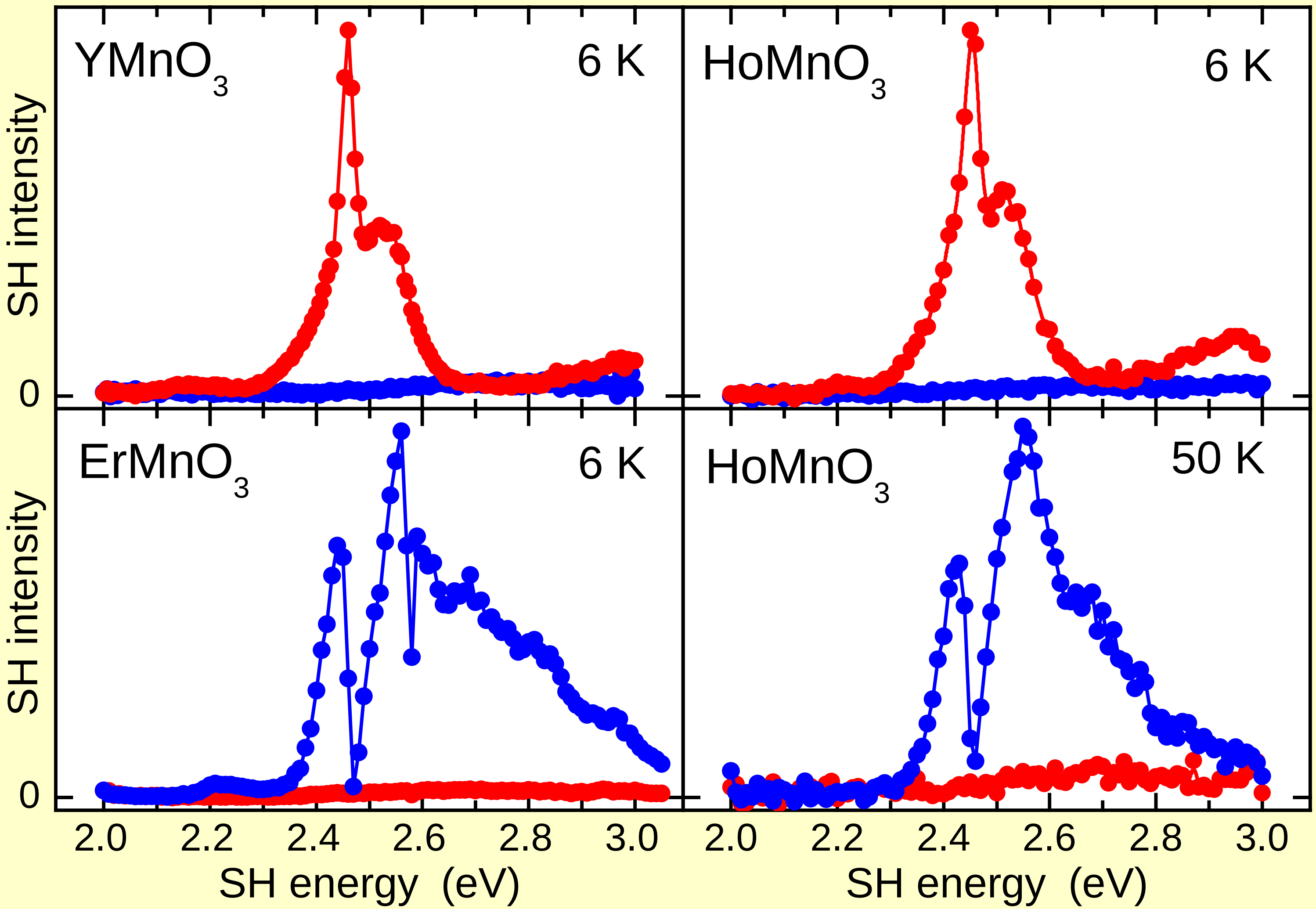
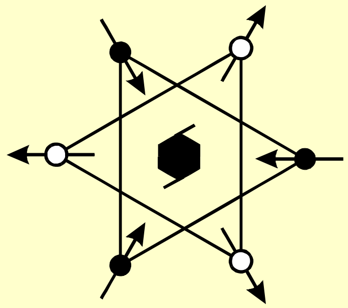


At least 8 different structures with different symmetries

Polarization of ingoing and outgoing light reveals the magnetic symmetry

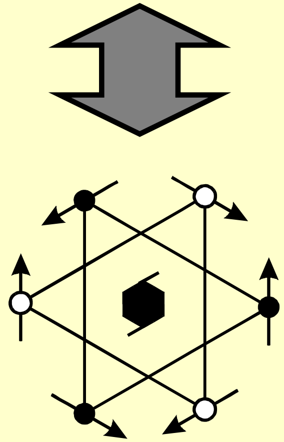
SHG Spectrum and Magnetic Symmetry





y polarized SHG

$P\underline{6}_3c\underline{m} \propto |\chi_{yyy}|^2$



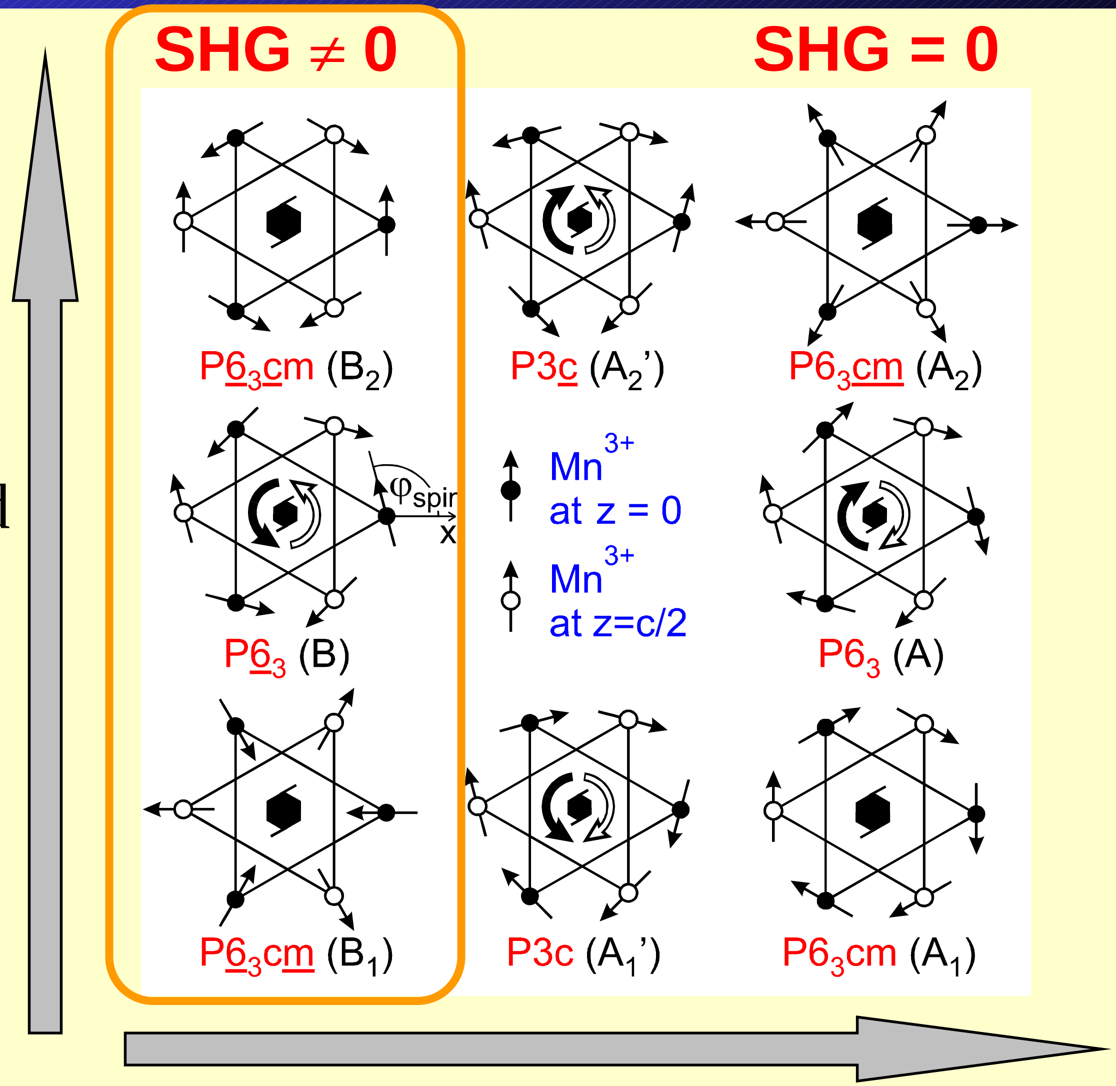
x polarized SHG

$P\underline{6}_3\underline{c}m \propto |\chi_{xxx}|^2$

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

Why is this Result Important?

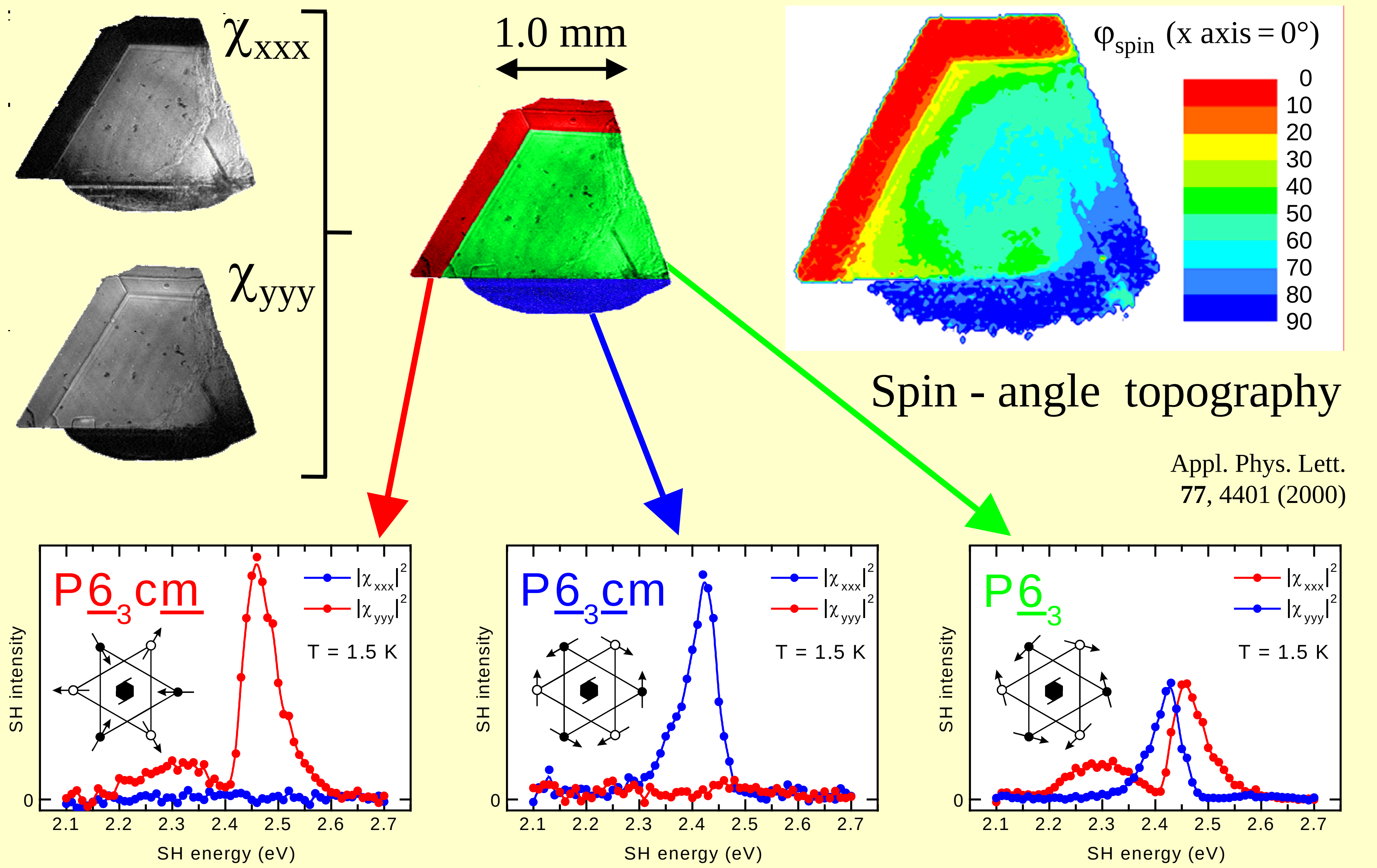
Distinguished
By
diffraction



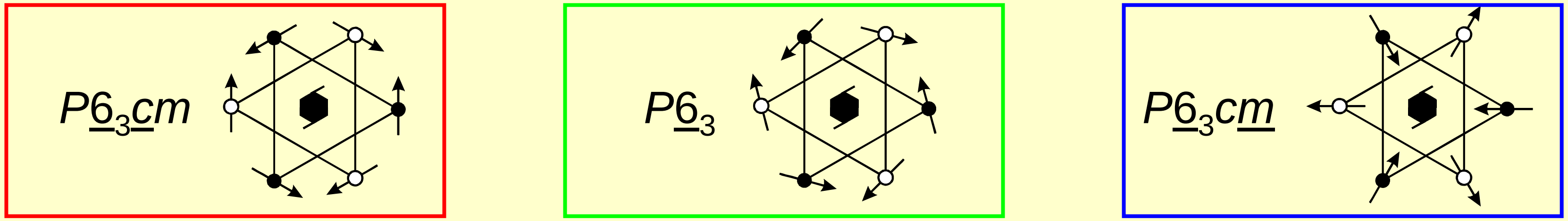
40 years of controversy about the correct structure !

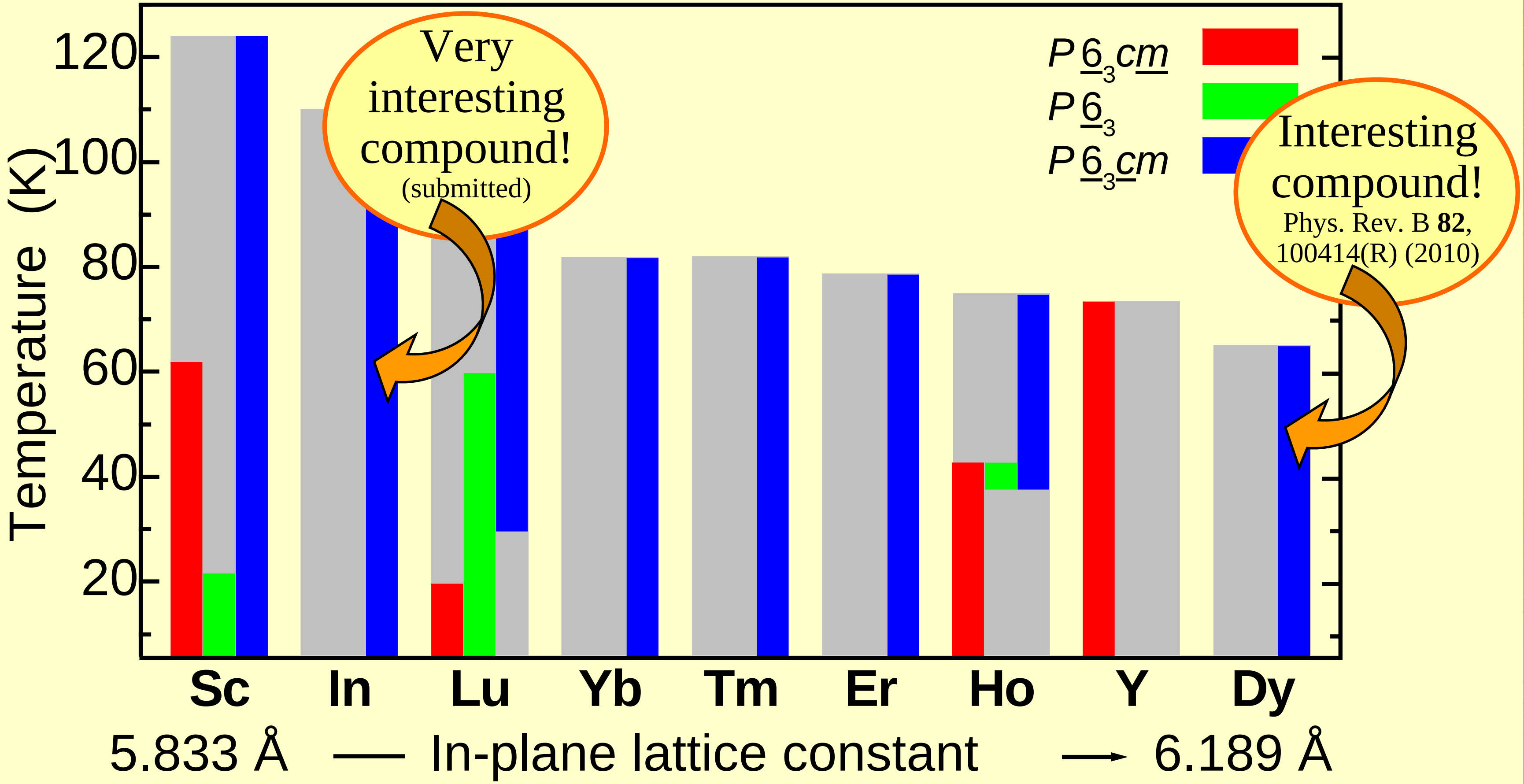
Not distinguished by diffraction

Phase Coexistence and Spin Topography in $ScMnO_3$



Magnetic Symmetry of Hexagonal $RMnO_3$





Microscopic Origin of Two-Order-Parameter SHG

1. Trigonal bipyramidal field from O^{2-} ligands splits $3d^4$ state of free Mn^{3+} ion
2. Ferroelectric distortion of ligand field breaks local centrosymmetry and induces *p-d* mixing
3. Spin-orbit interaction mediates the coupling between the Mn^{3+} spins and the light waves at ω and 2ω
4. Leads to SHG coupling bilinearly to the antiferromagnetic and ferroelectric order parameters
5. Spectra dominated by excitonic Mn^{3+}– Mn^{3+} exchange
6. Constructive or destructive interference of excitonic subbands

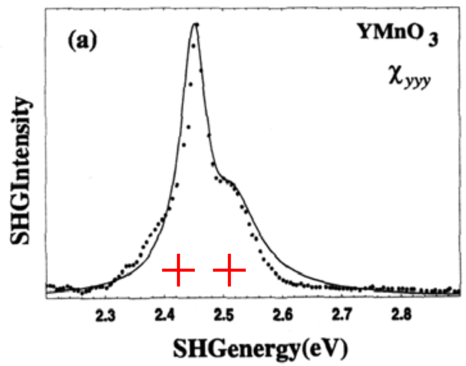
INSTITUTE OF PHYSICS PUBLISHING — JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **13** (2001) 3031–3055 www.iop.org/Journals/cm PII: S0953-8984(01)19896-6

Second-harmonic-generation spectra of the hexagonal manganites $RMnO_3$

Takako Iizuka-Sakano[1], Eiichi Hanamura[2] and Yukito Tanabe[3]

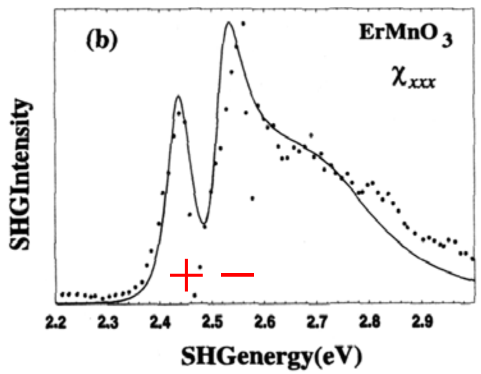
[1] Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan
[2] Chitose Institute of Science and Technology and CREST, JST (Japan Science and Technology Corporation), 785-65 Bibi, Chitose-City, Hokkaido 066-8655, Japan
[3] Department of Applied Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received 8 December 2000 3031



$$\epsilon_0 \chi^{(1)}_{yyy} = -\mathrm{i}\frac{3}{2}c^3 c' pq \langle S_x \rangle \times \left[\sum_\nu \frac{(\nu_1\lambda/\Delta E(1,4) - \nu_2\lambda/\Delta E(2,3))}{(E(\nu \mathrm{E}_2) - 2\hbar\omega)\,\Delta E} \times (\nu_1 v_{zx}/\Delta E(1,3) - \nu_2 v_{zx}/\Delta E(2,4)) + \sum_\mu \frac{(\mu_1 v_{zx}/\Delta E(1,3) - \mu_2 v_{zx}/\Delta E(2,4))}{(E(\mu \mathrm{E}_1) - 2\hbar\omega)\,\Delta E} \times (\mu_1\lambda/\Delta E(1,4) - \mu_2\lambda/\Delta E(2,3)) \right].$$

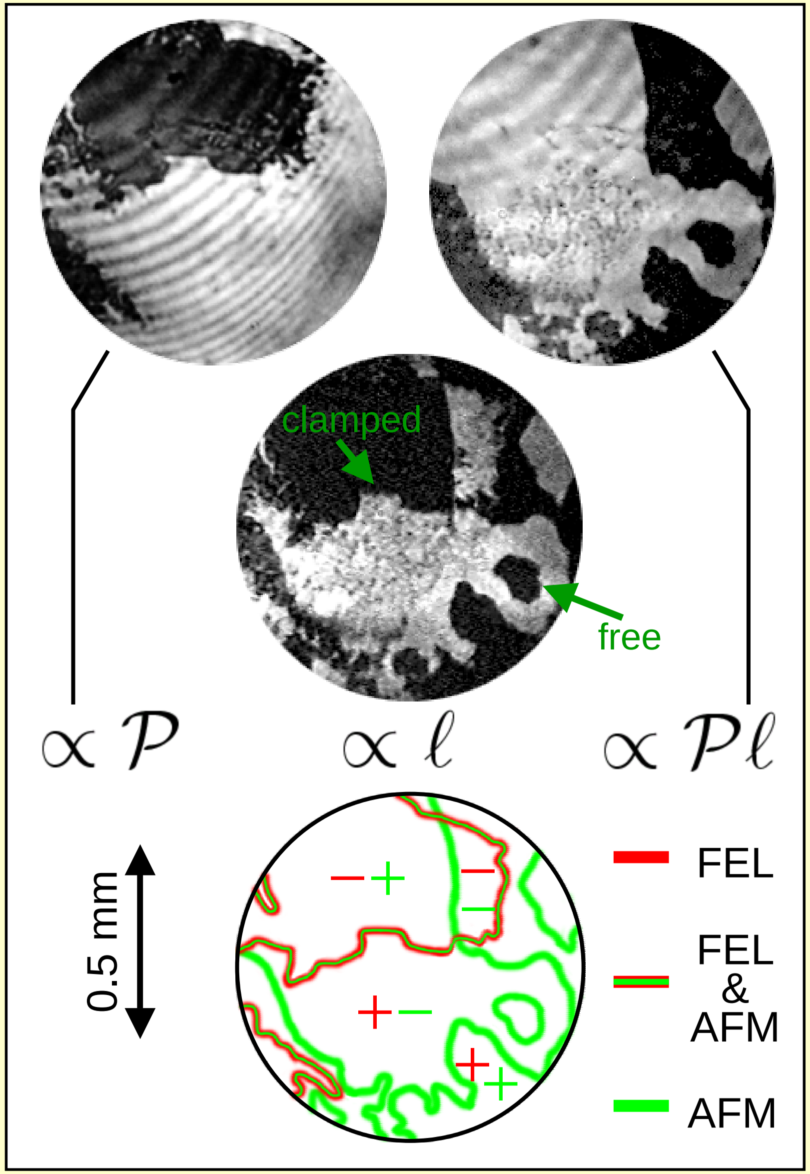
Spins along x



$$\epsilon_0 \chi^{(1)}_{xxx} = \mathrm{i}\frac{3}{2}c^3 c' pq \langle S_y \rangle \times \left[\sum_\nu \frac{(\nu_1\lambda/\Delta E(1,3) - \nu_2\lambda/\Delta E(2,4))}{(E(\nu \mathrm{E}_2) - 2\hbar\omega)\,\Delta E} \times (\nu_1 v_{zx}/\Delta E(1,3) - \nu_2 v_{zx}/\Delta E(2,4)) - \sum_\mu \frac{(\mu_1 v_{zx}/\Delta E(1,3) - \mu_2 v_{zx}/\Delta E(2,4))}{(E(\mu \mathrm{E}_1) - 2\hbar\omega)\,\Delta E} \times (\mu_1\lambda/\Delta E(1,3) - \mu_2\lambda/\Delta E(2,4)) \right].$$

Spins along y

Magnetoelectric Effect (1): Coupled Domain Walls

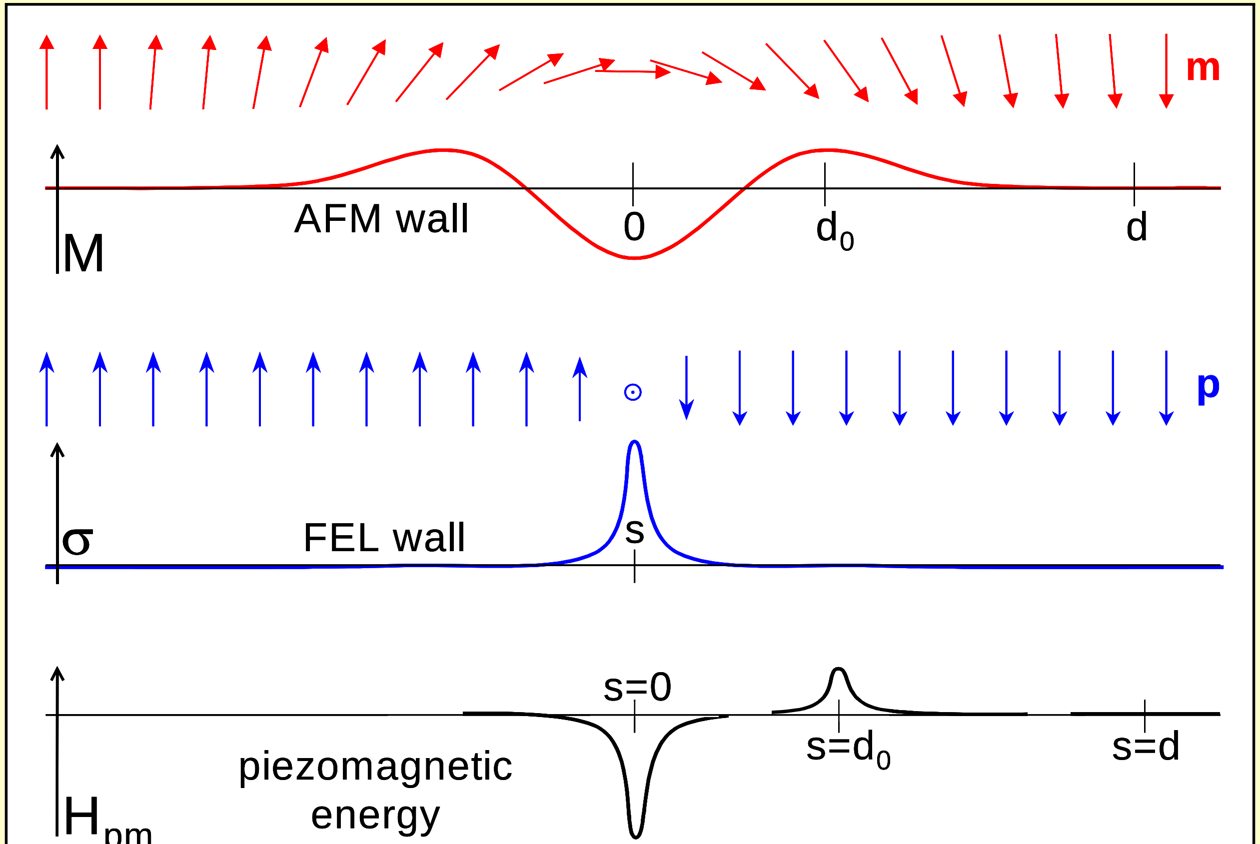


Domains in $YMnO_3$ by SHG:

- Reversal of the ferroelectric (FEL) order couples to the reversal of the antiferromagnetic (AFM) order
- Coexistence of "free" and "clamped" antiferromagnetic walls
- Strong magnetoelectric coupling at the *walls*, but no coupling in the *bulk*
- Multiferroics not a mandatory source of strong magnetoelectric effects!

Nature **419**, 818 (2002)

Magnetoelectric Effect (1): Coupled Domain Walls



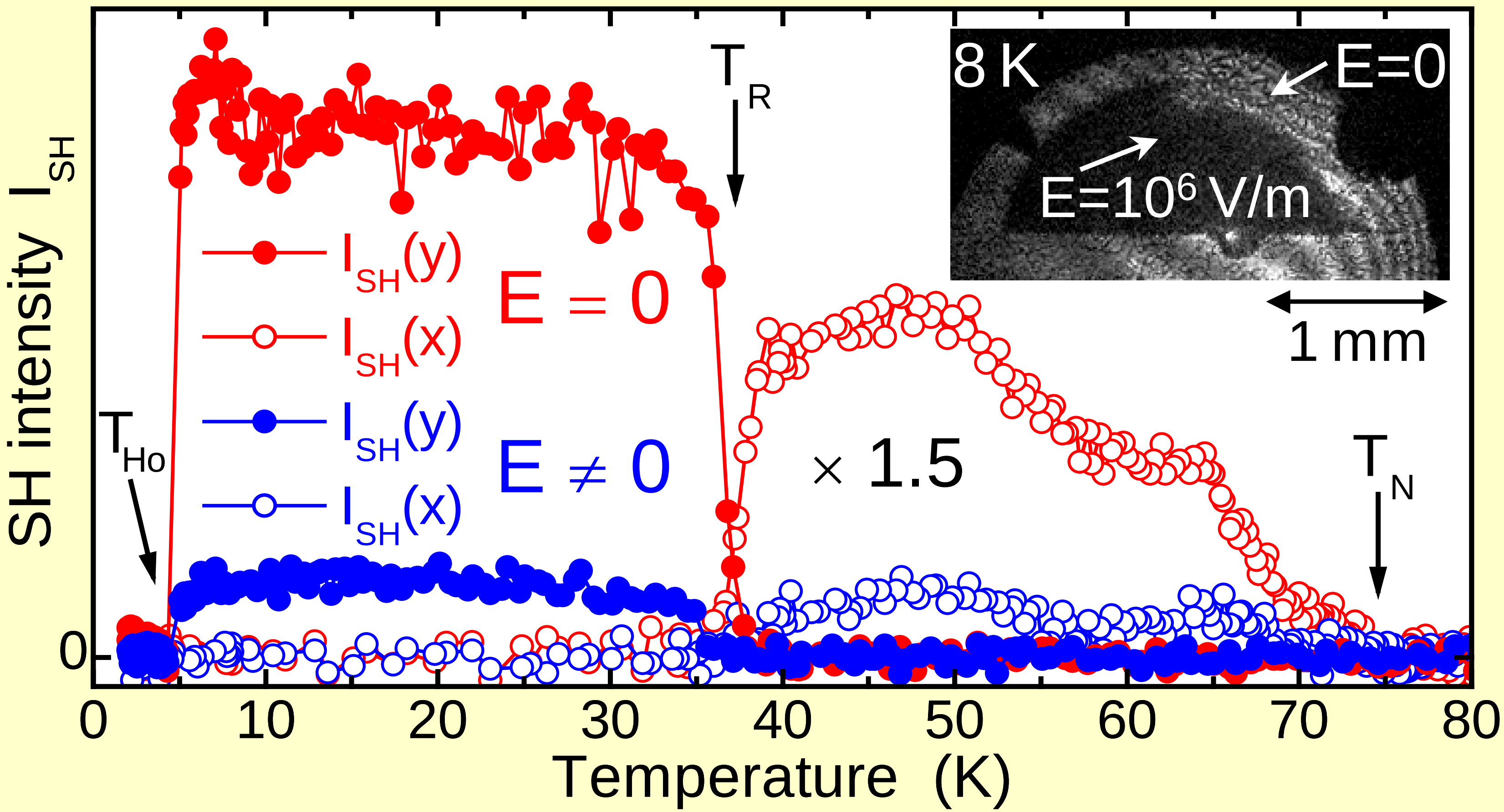
Phys. Rev. Lett. **90**, 177204 (2003)

- AFM wall carries magnetization **M**
- FEL wall induces strain σ
- Width of walls:
  - AFM – O[10^3] unit cells: small in-plane anisotropy
  - FEL – O[10^0] unit cells: large uniaxial anisotropy

Piezomagnetic effect $\mathbf{H_{pm} = q_{ijk} M_i \sigma_{jk}}$ as higher-order magnetoelectric effect

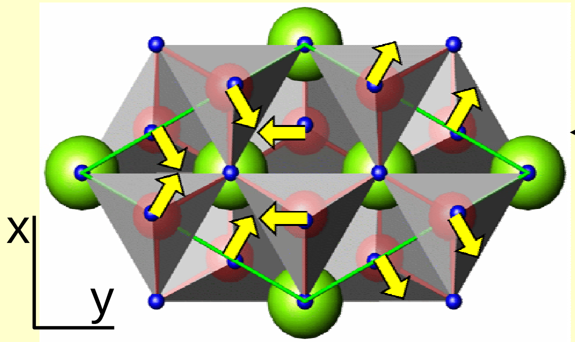
Coupling of antiferromagnetic to ferroelectric wall reduces free energy!

Magnetic Phase Control by Electric Field in $HoMnO_3$



Electric field E changes magnetic structure right below $T_N = 75$ K

Magnetoelectric Effect (2): E-Field → Magnetism



$P6_3cm$

E = 0 ←

$P_{multidomain} = 0$

$H_{ME} \propto PM = 0$

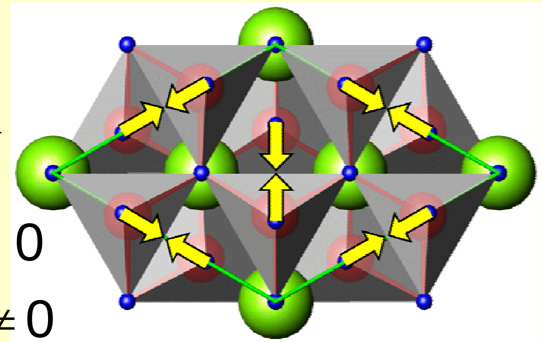
In any case

E ≠ 0 →

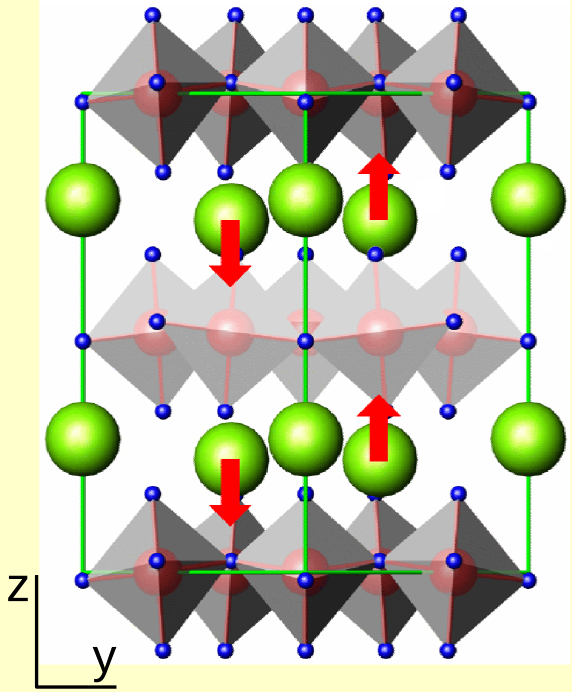
$P_{single\,dom.} \neq 0$

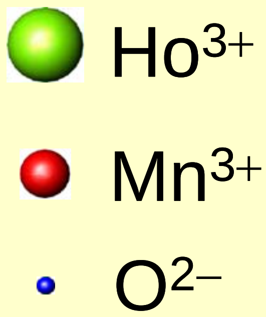
$H_{ME} \propto PM \neq 0$

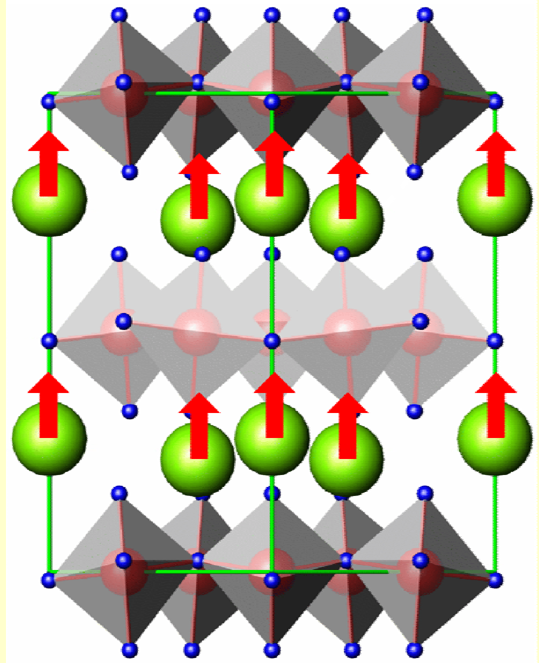
If $M \rightarrow \neq 0$



$P6_3cm$





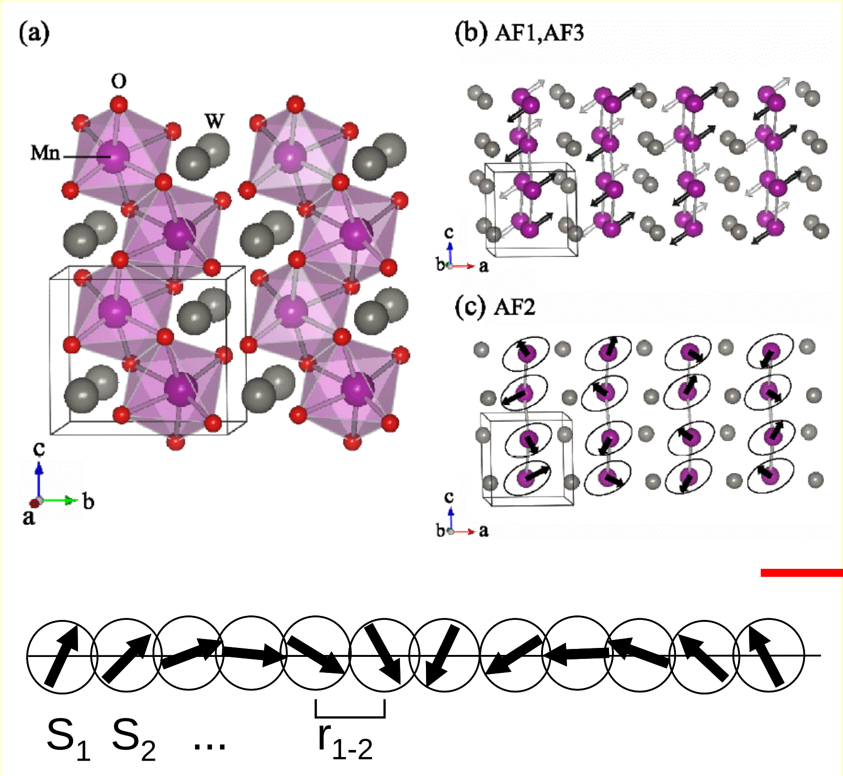


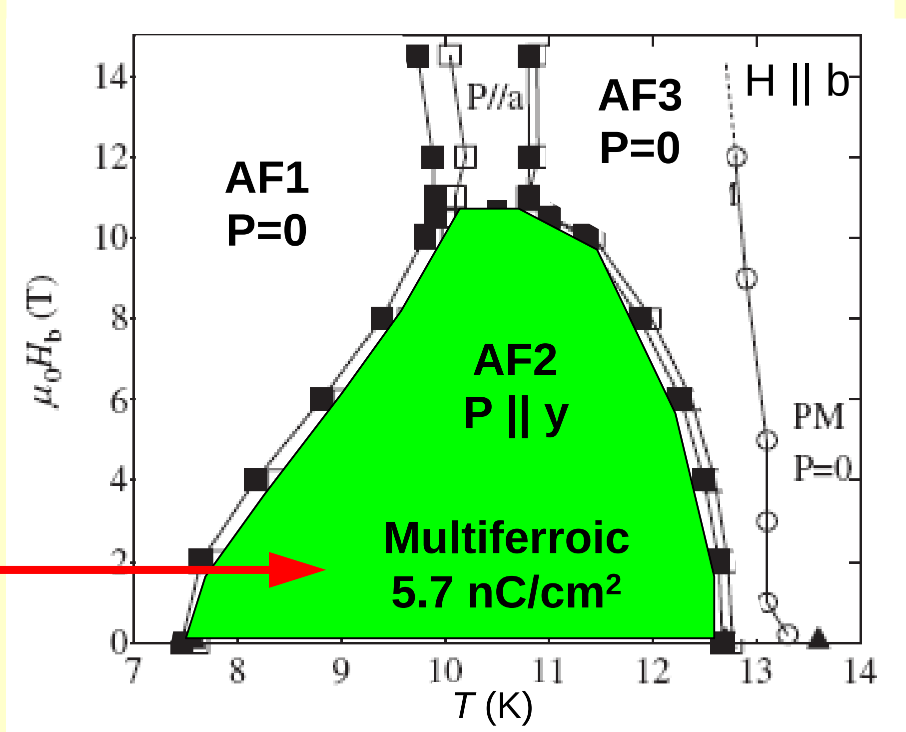
Nature **430**, 541 (2004)

Nonlinear Optics Applied to Multiferroics

- What is a multiferroic?
- Introduction to nonlinear optics
- Experimental setups for nonlinear (multi-) ferro-optics
- Nonlinear optics on multiferroics
  - Split-order-parameter multiferroics: hex. $RMnO_3$
  - **Joint-order-parameter multiferroics: $MnWO_4$**
  - Sublattice selectivity: $TbMn_2O_5$

Magnetically Induced Ferroelectricity in $MnWO_4$

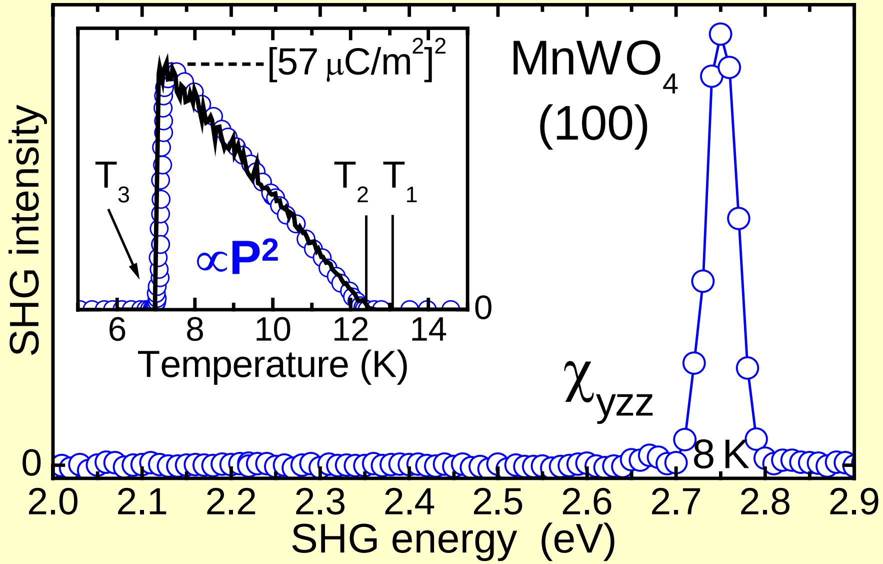




Taniguchi et al., Phys. Rev. Lett. **97**, 097203 (2006)

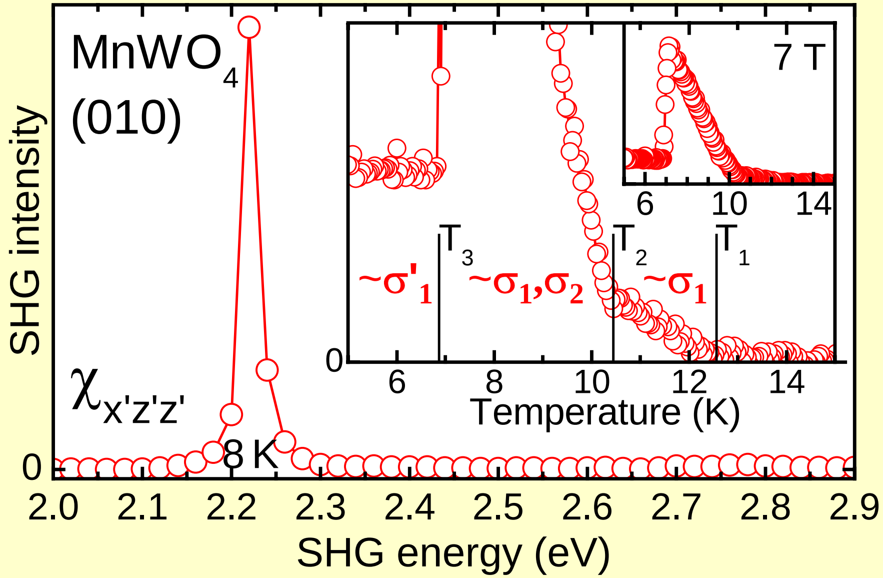
- **Spiral magnetism** breaks time and space inversion symmetry
- **Electric polarization** allowed according to $P \propto r_{1\text{-}2} \times (S_1 \times S_2)$
- **Domains**: Are they present? Are they "magnetic" or "electric"?

SHG in the Multiferroic Phase



SHG coupling to polarization

- In multiferroic AF2 phase only
- Scaling with polarization P
- $I_{SHG} \sim P^2$ (pseudoproper)

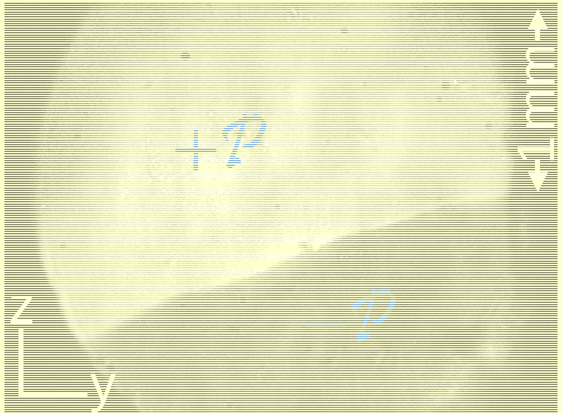


SHG coupling to magnetization

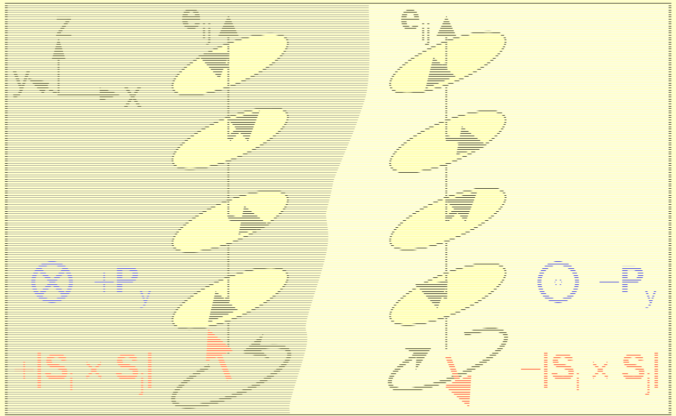
- In all phases AF1, AF2, AF3
- Scaling with magnetic order parameters: σ_1, σ_2, σ_1'

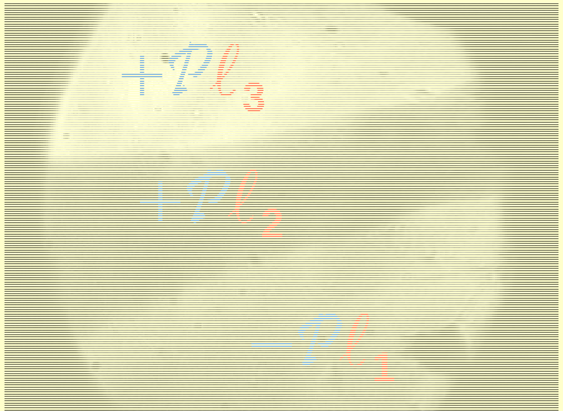
Phys. Rev. Lett. **102**, 107202 (2009)
Phys. Rev. B **80**, 224420 (2009)
Phys. Rev. B **82**, 155112 (2010)
Phys. Rev. Lett. **106**, 257601 (2011)

Magnetically Induced Ferroelectric Domains

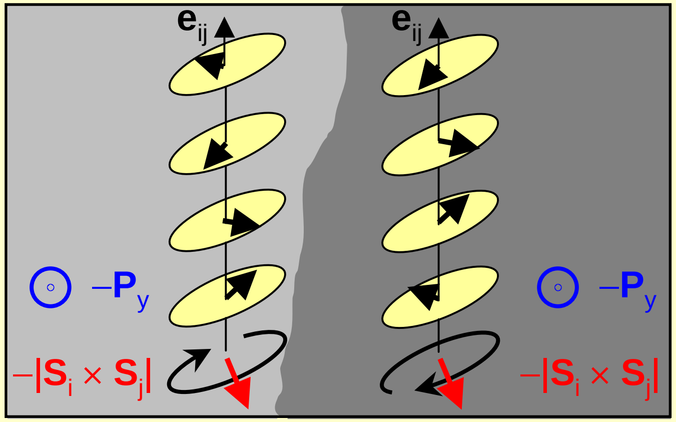


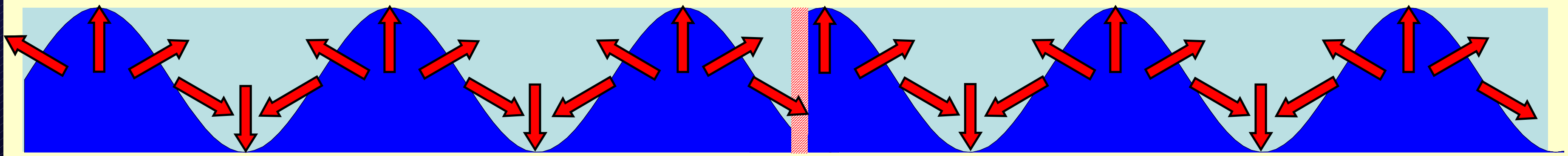
Polarization domains



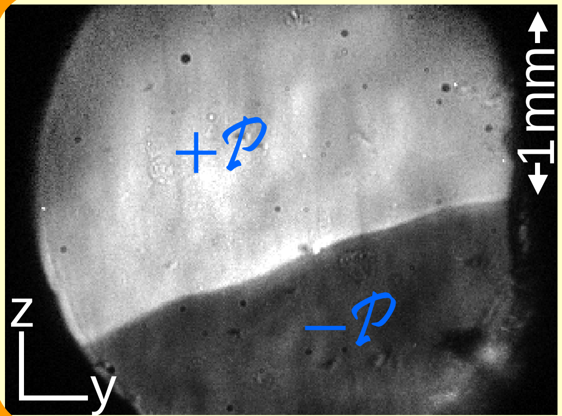


Magnetization domains

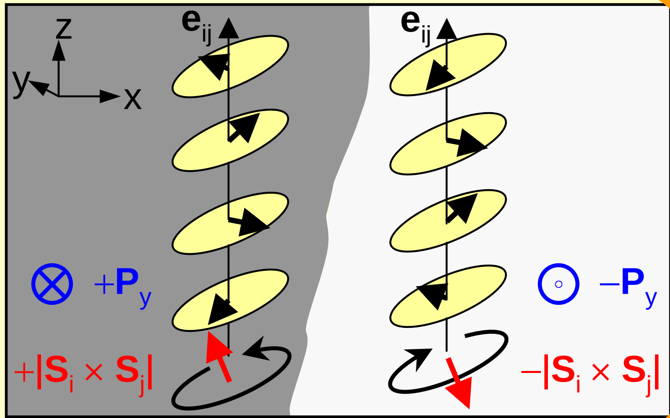


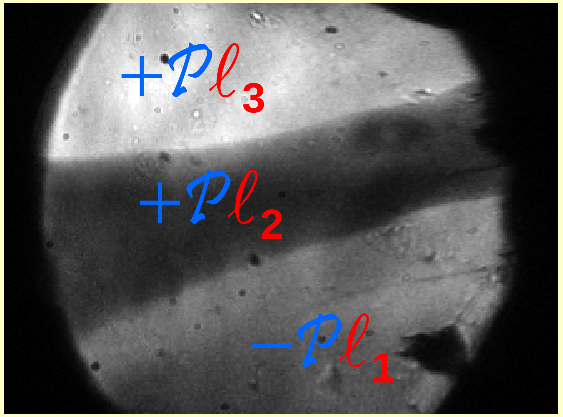


Magnetically Induced Ferroelectric Domains

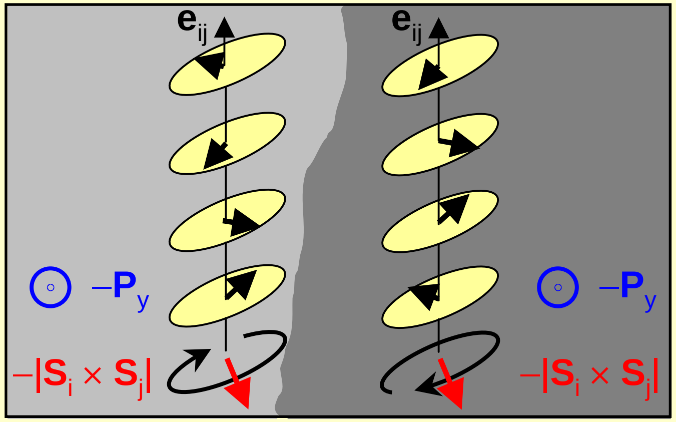


Polarization domains





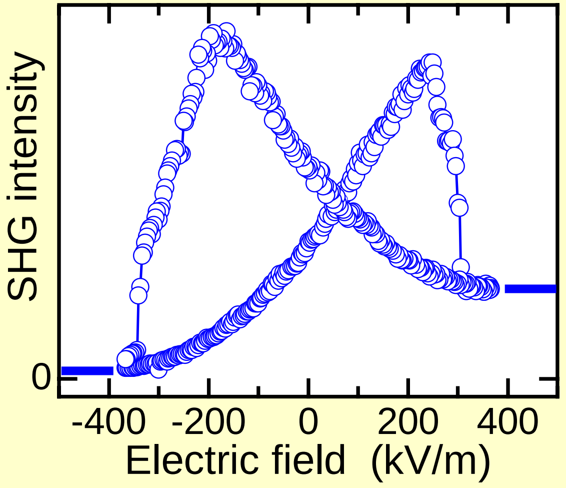
Magnetization domains



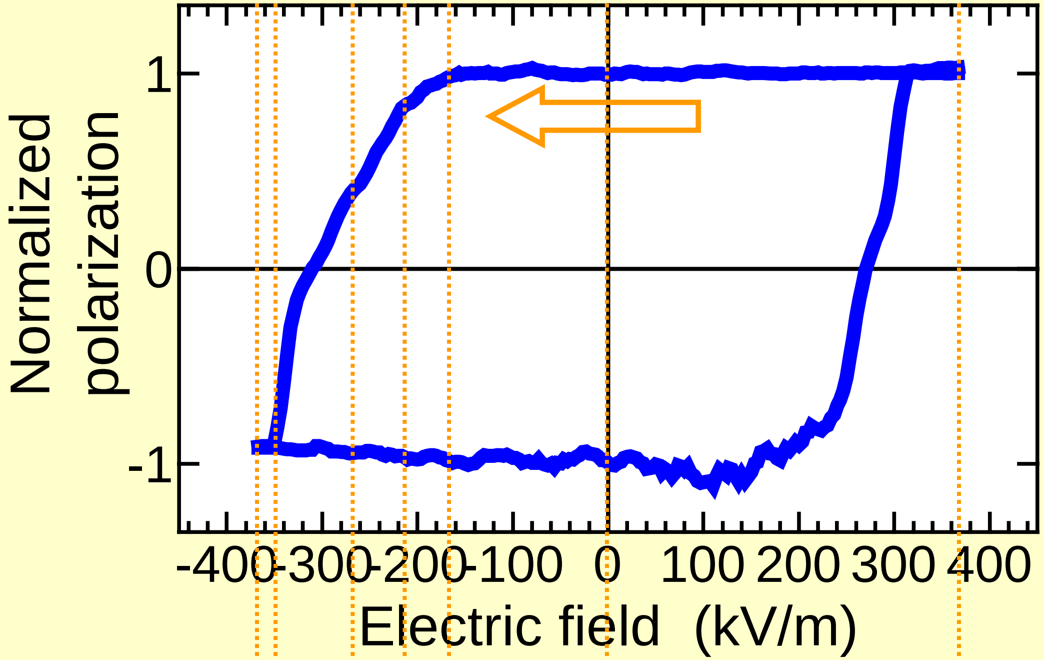
Polarization domains: different orientation of order parameters

Magnetic sub-domains: same orientation of order parameters

$MnWO_4$ Domains: Ferroelectric Field Response



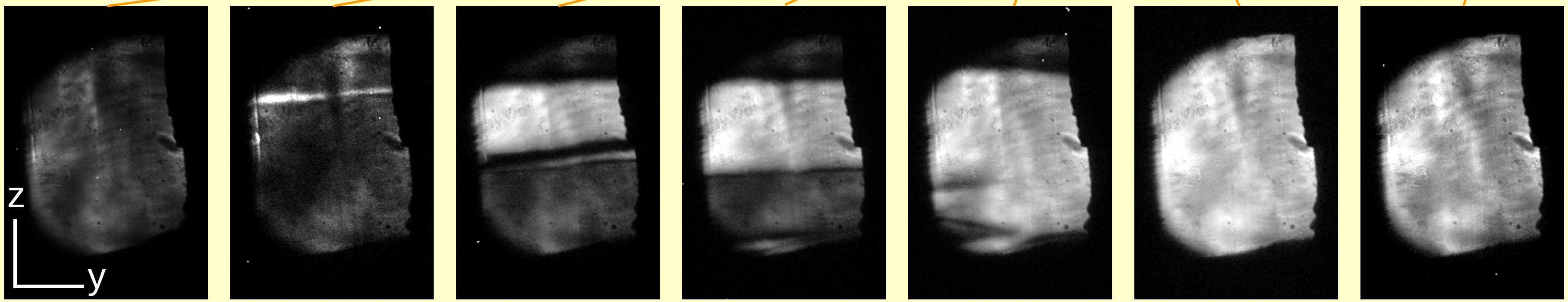
$$I(2\omega) \propto |p(\mathcal{E})\chi_{\rm FEL} + \chi_{\rm para}e^{i\varphi} + \mathcal{E}\chi_{\rm EFISH}e^{i\varphi'}|^2|\vec{E}(\omega)|^4$$



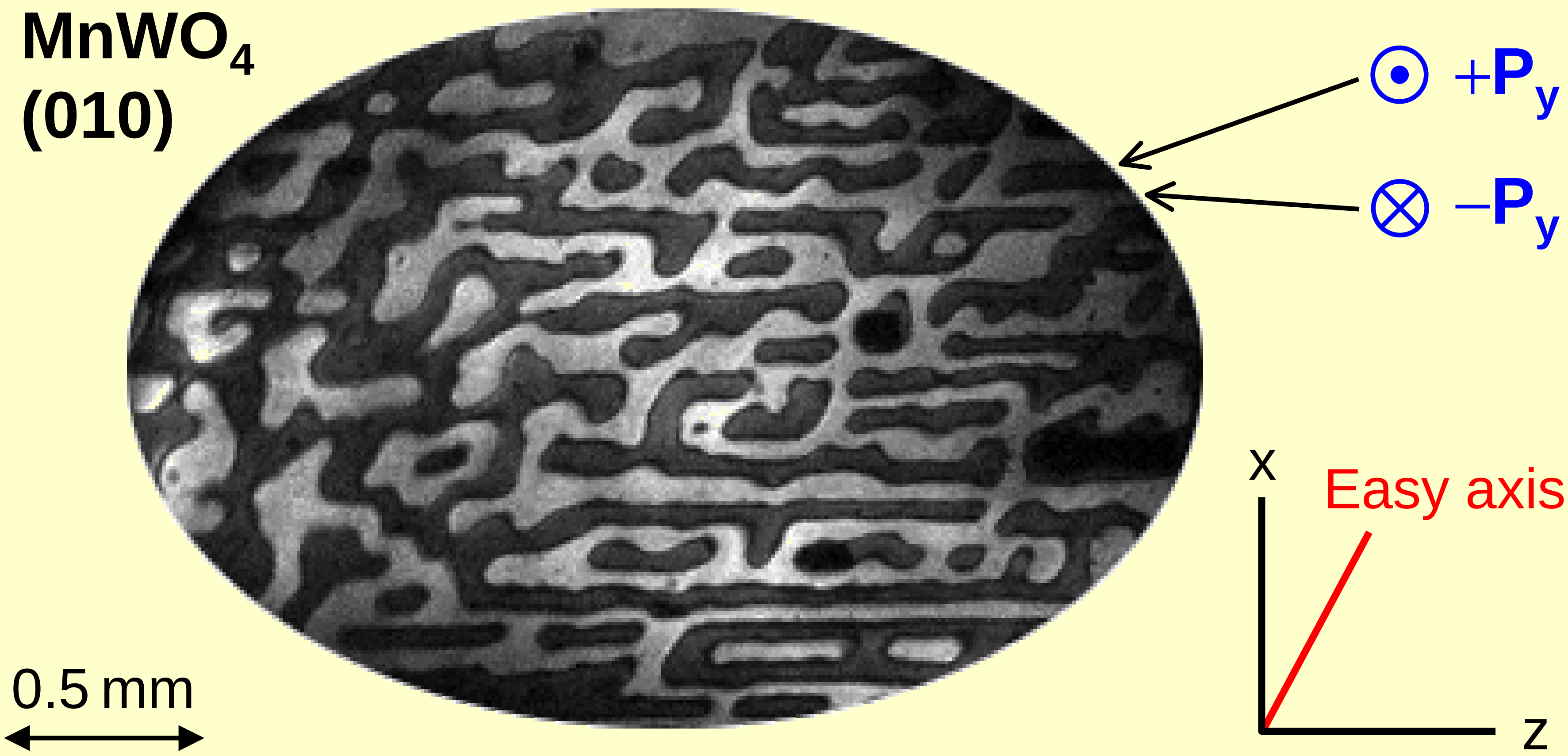
$MnWO_4$(100)

↔ P

Behave as ferroelectric domains



$MnWO_4$ Domains: Magnetic Topology

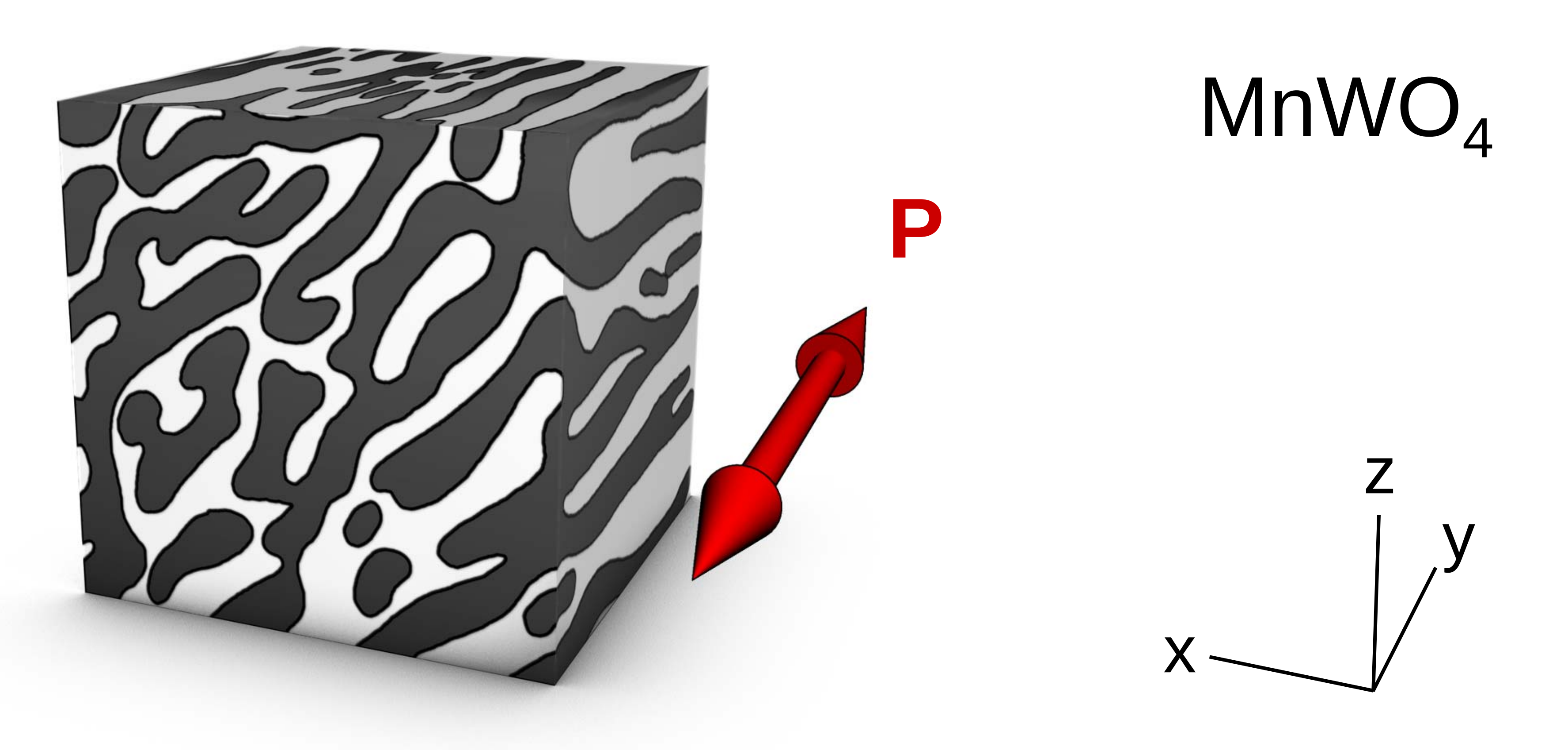


Domain topology reveals:

- Magnetic bubble topology
- Magnetic easy axis

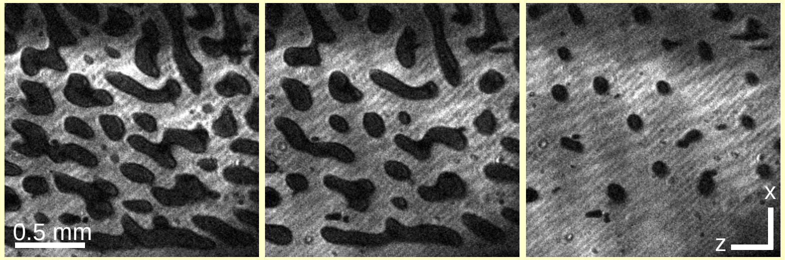
Behave as magnetic domains

Multiferroic Hybrid Domains

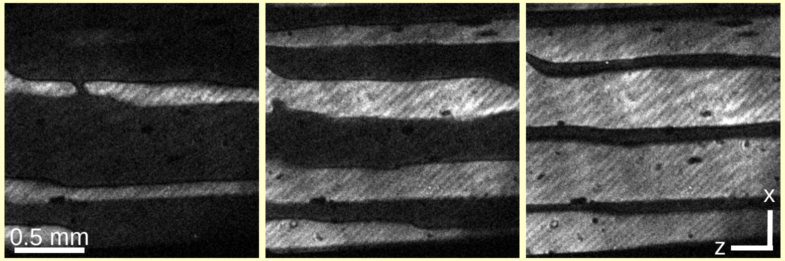


- "Multiferroic domains" ~ inseparable magnetic-electric properties
- Domains form platelets in the plane defined by:
  ➔ **Magnetic easy axis** ➔ **Spontaneous electric polarization**

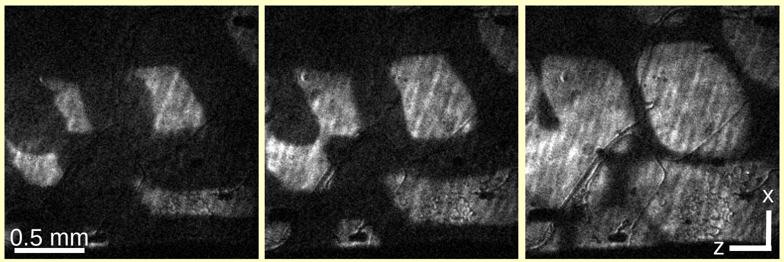
Dynamic Switching of Multiferroic Domains



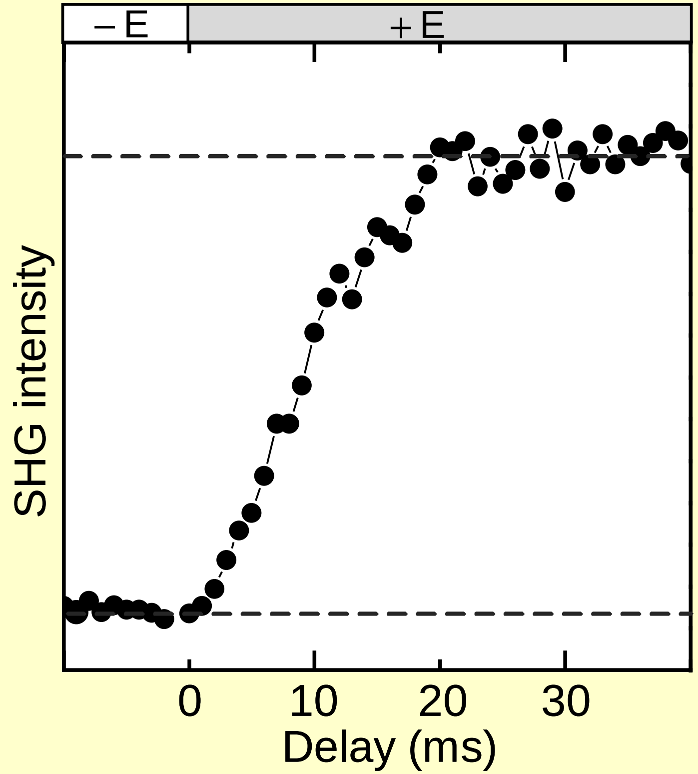
0-field cooling → −E ~ 1 s →



Field cooling → −E ~ 1 s →

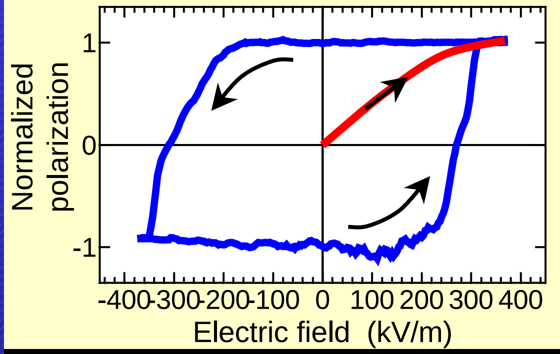


Field cooling → −E~20 ns →



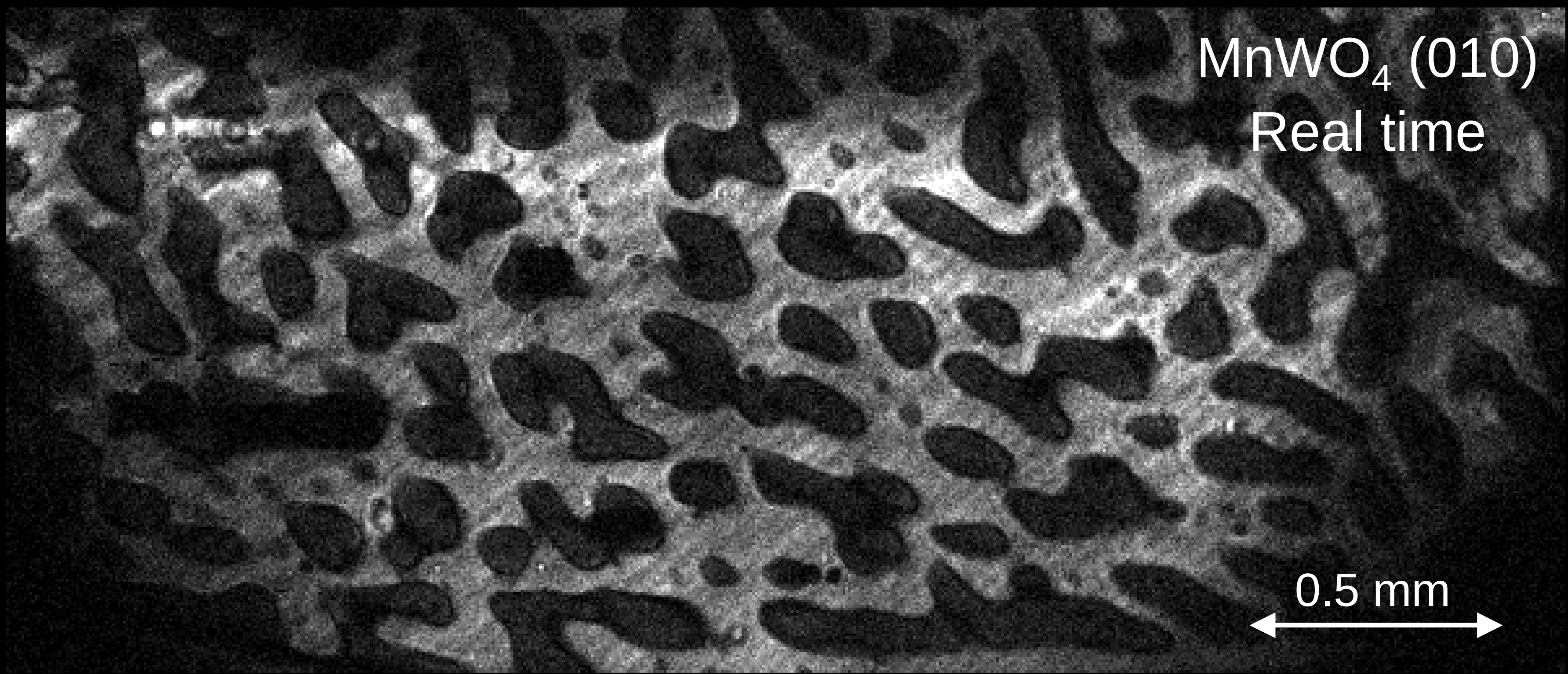
- Electric-field-induced magnetic reversal is surprisingly slow: ~20 ms
- Easy-axis-dominated

Switching Multiferroic Domains

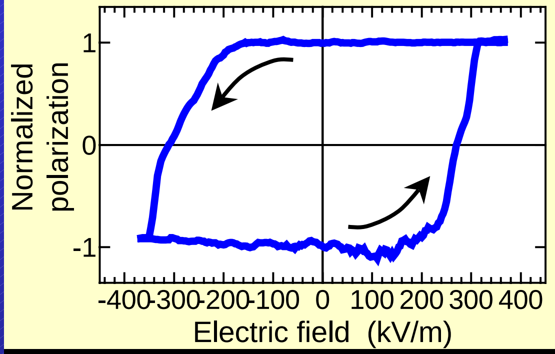


- SHG movie of magnetoelectric $MnWO_4$ domain reversal: **quasistatic (~1 s)**

Phys. Rev. B **84**, 184404 (2011), Editor's Choice

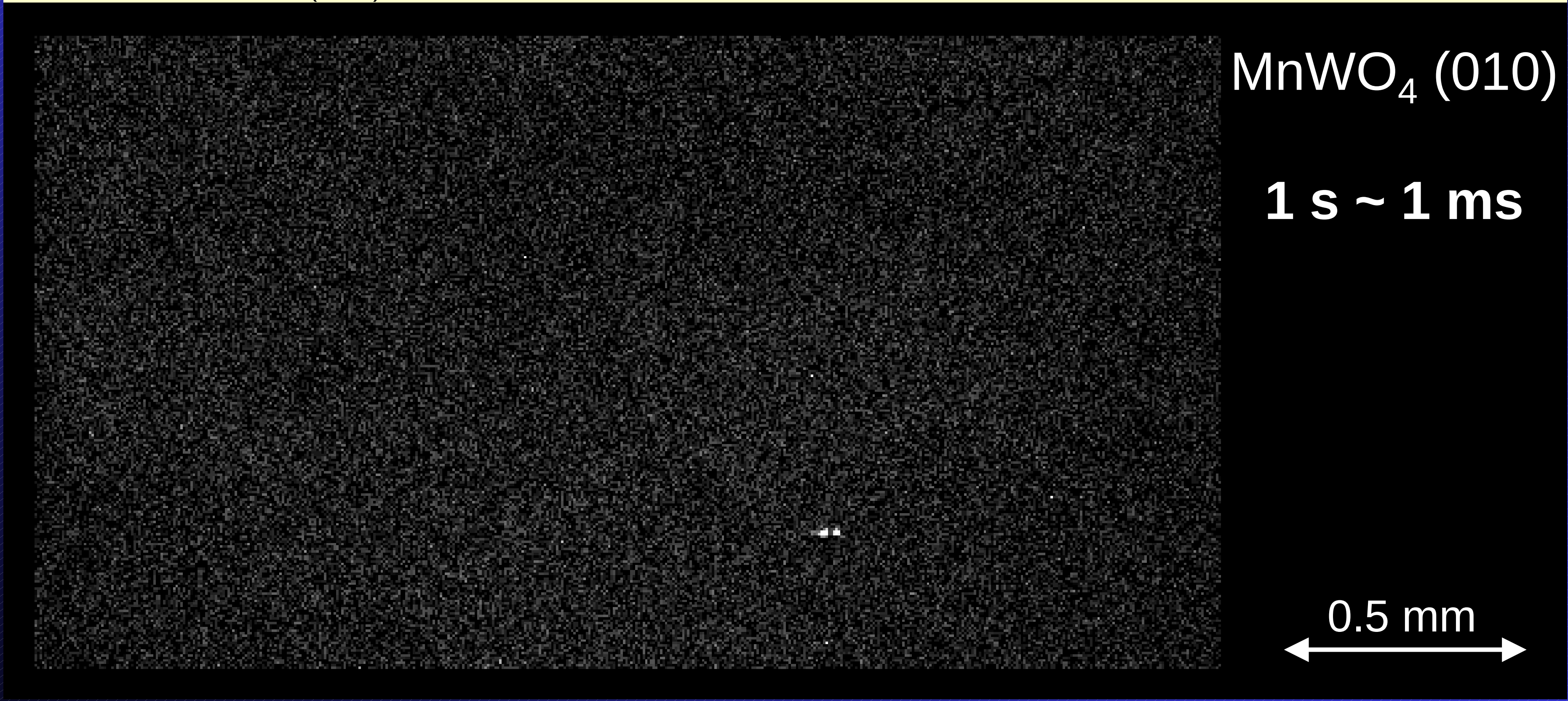


Switching Multiferroic Domains

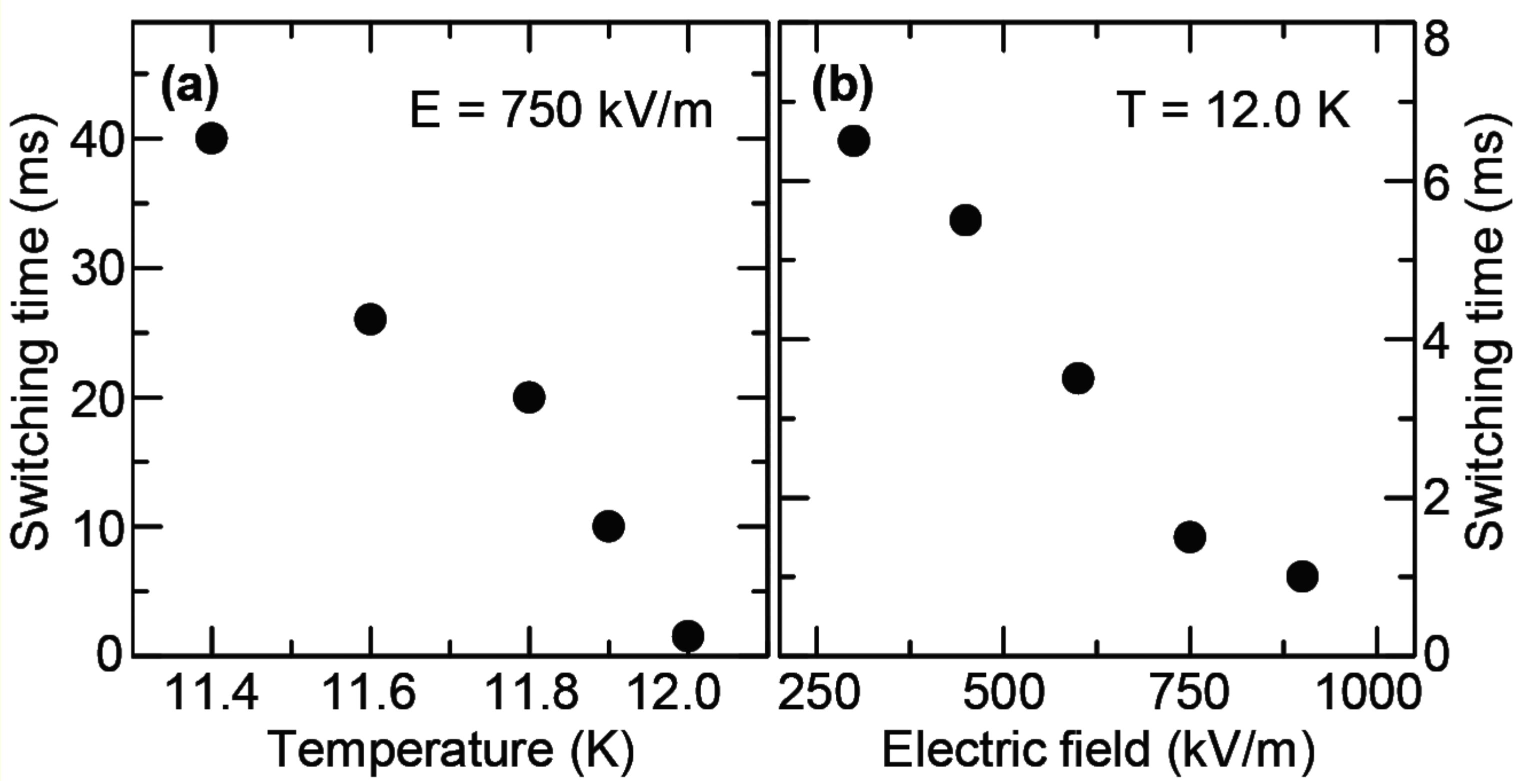


- SHG movie of magnetoelectric $MnWO_4$ domain reversal: **dynamic (~1 ms)**

Phys. Rev. B **84**, 184404 (2011), Editor's Choice



Magnetoelectric Domain Reversal Time

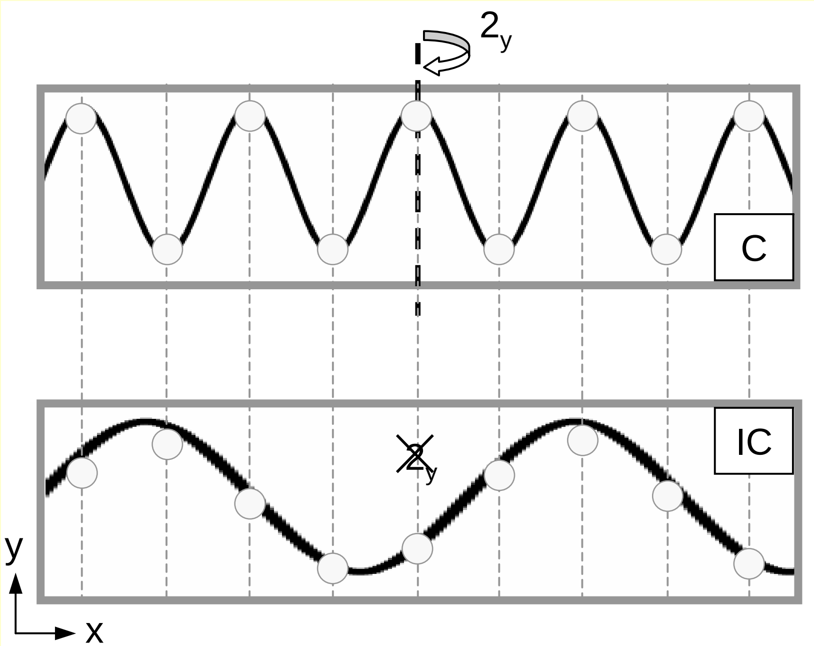


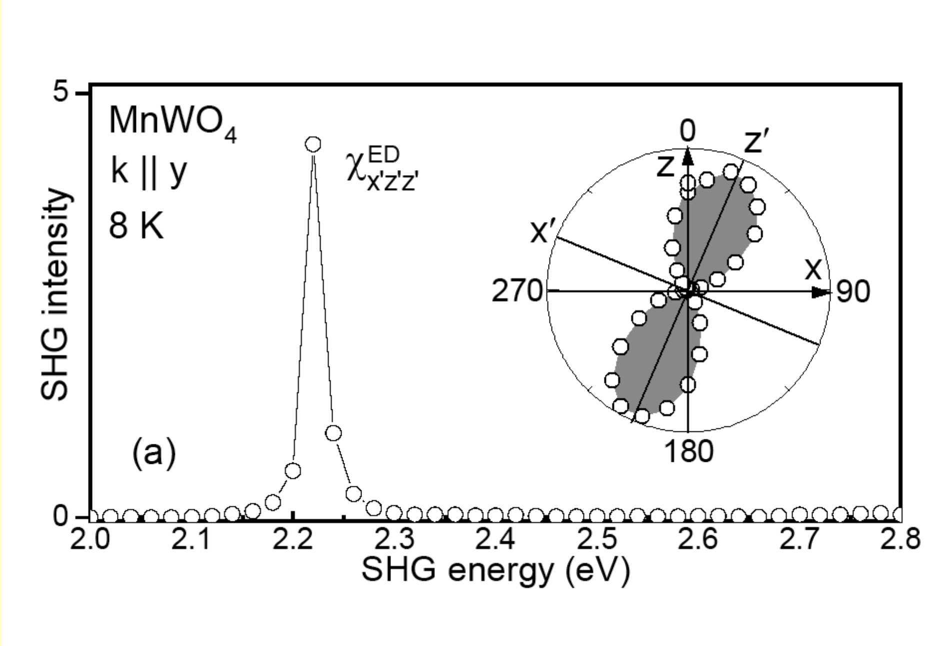
Phys. Rev. B **84**, 184404 (2011), Editor's Choice

Why is the switching so slow?

- Guided by ferroelectric field energy vs. magnetic anisotropy ~ 1:100
- Thus due to domain wall movement ↔ pinning

Incommensurate Order, Symmetry, and SHG





- Incommensurate order reduces the symmetry
- New SHG contributions forbidden by lattice periodicity
- Background-free probe of incommensurate state

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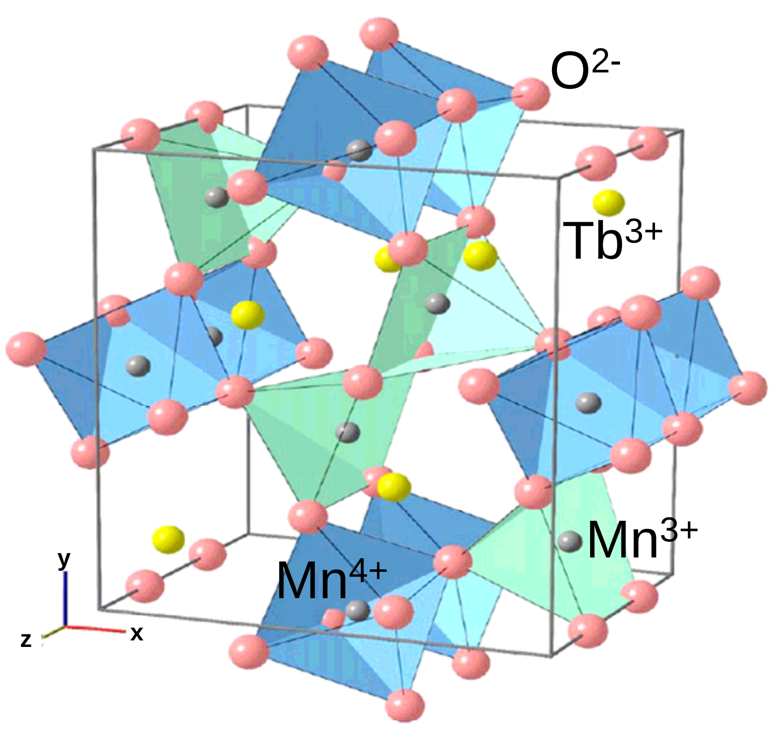
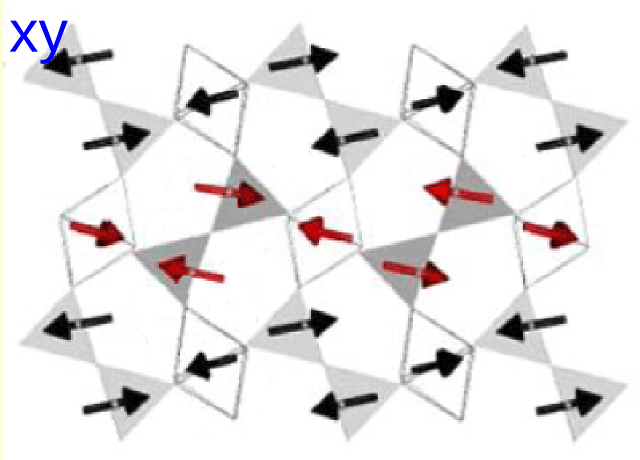
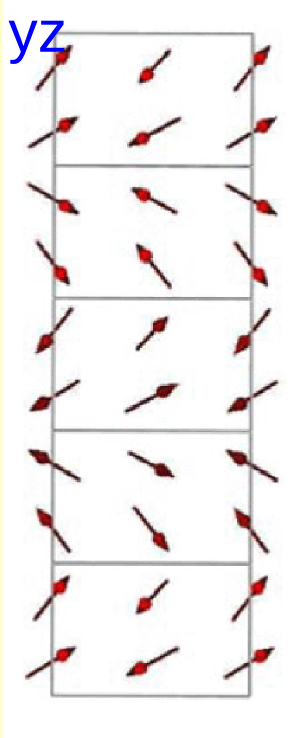
  - Split-order-parameter multiferroics: hex. $RMnO_3$
  - Joint-order-parameter multiferroics: $MnWO_4$
  - Sublattice selectivity: $TbMn_2O_5$

Magnetically Induced Ferroelectricity in $TbMn_2O_5$





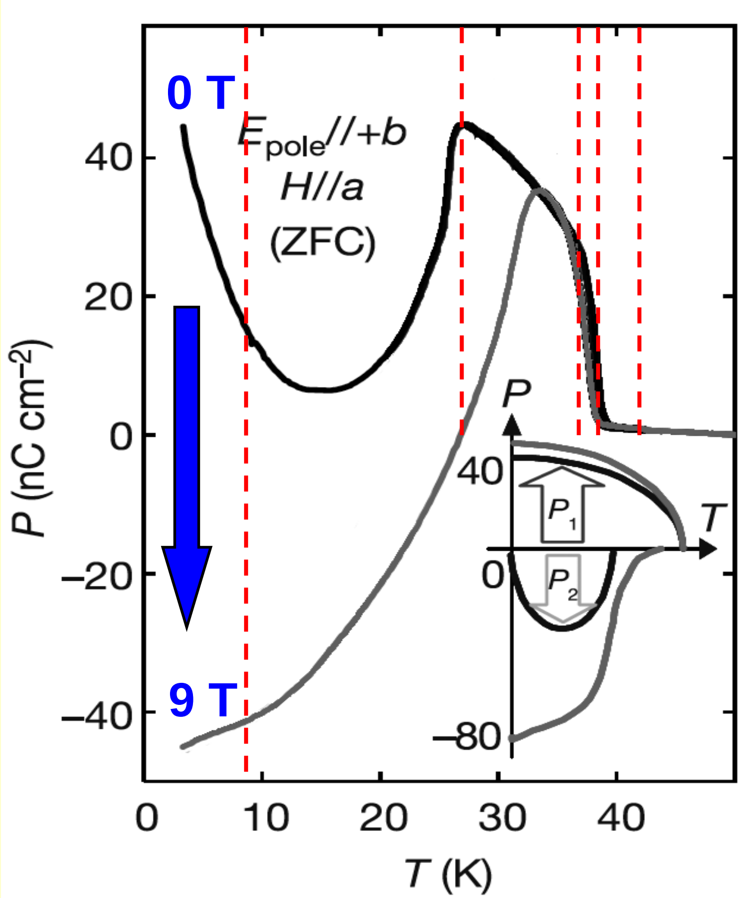


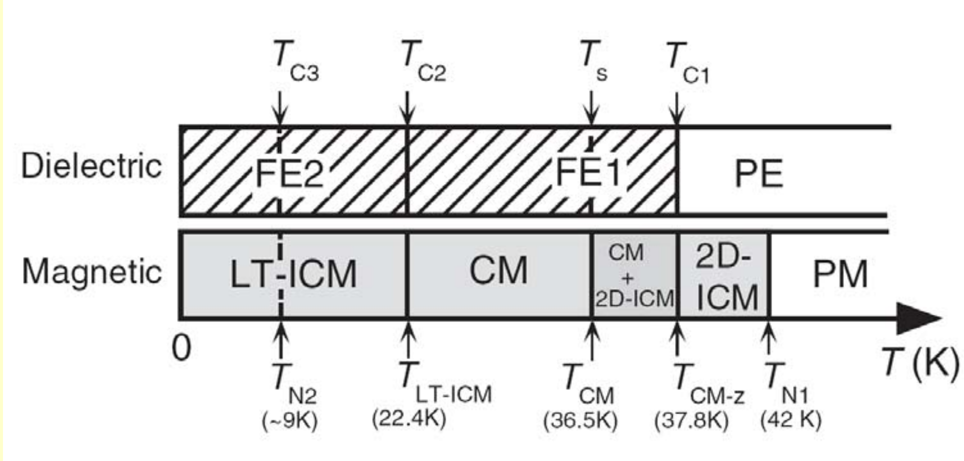
Radaelli et al., Phys. Rev. Lett. **101**, 067205 (2008)
Wang et al., Phys. Rev. B **77**, 134113 (2008)
Moskvin et al., Phys. Rev. B **78**, 024102 (2008)

xy: Antisymmetric exchange (Dzyal.-Moriya): $\mathbf{P}_a = \sum_{mn} [\mathbf{\Pi}^a_{mn} \times [\mathbf{S}_m \times \mathbf{S}_n]]$

yz: Symmetric exchange (magnetostrictive): $\mathbf{P}_s = \sum_{mn} \mathbf{\Pi}^s_{mn} (\mathbf{S}_m \cdot \mathbf{S}_n)$

Composite Nature of Multiferroic Polarization





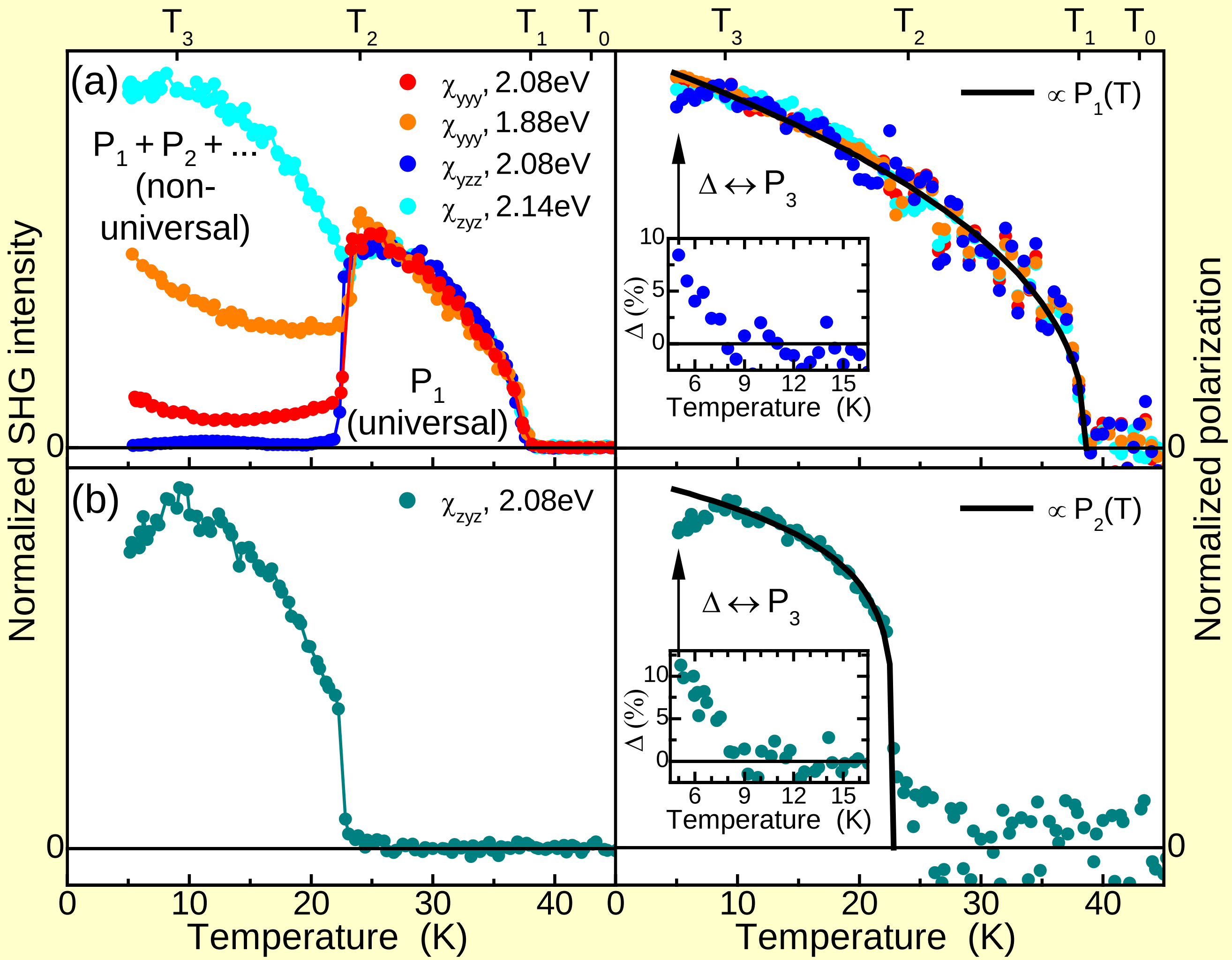
Polarization reversal in a magnetic field

Hur et al., Nature **429**, 392 (2004)
Kobayashi et al., J. Phys. Soc. Jpn. **73**, 3439 (2004)

- Model: composit… $= P_1 – P_2(H)$
- $P_{1,2}$ correspondin… processes in P

Unconfirmed! Check by SHG!

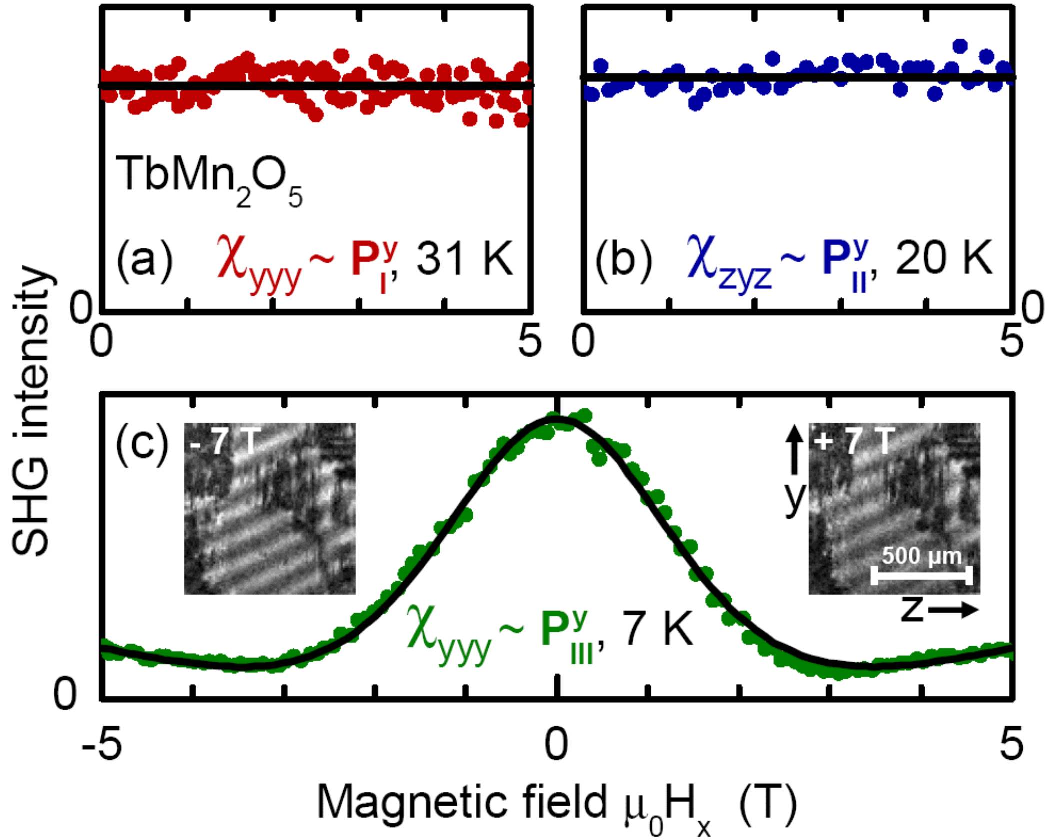
Separation of Multiferroic Polarizations by SHG



SHG couples separately to P_1 and P_2 and reveals additional contribution P_3 from Tb

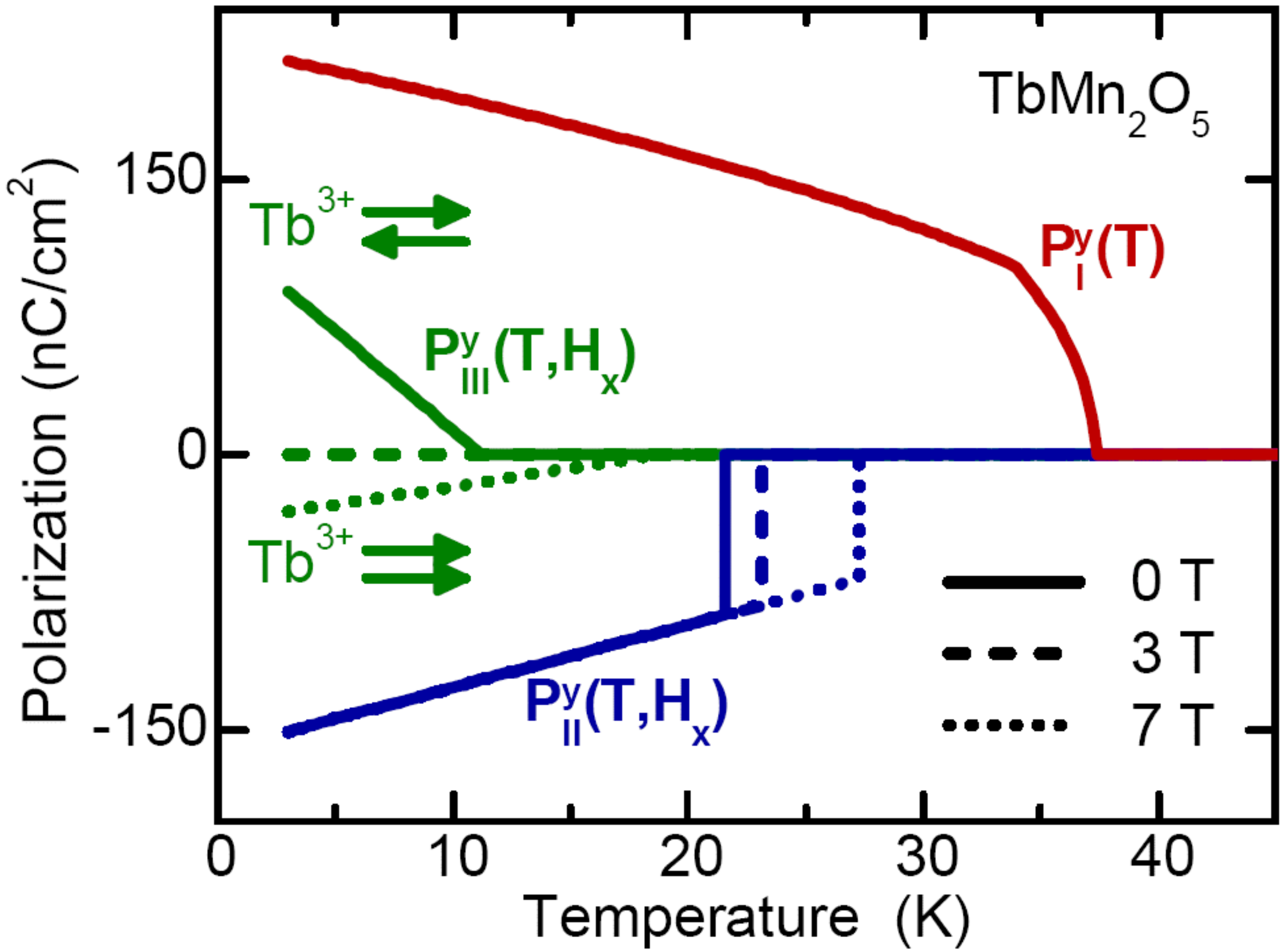
Phys. Rev. B **80**, 100101(R) (2009)

Magnetic-Field Dependence



- ➢ P_I, P_{II} are not magnetic-field dependent
- ➢ Field dependence entirely by $P_{III} \leftrightarrow$ rare-earth order
- ➢ P_{III} changes with H but domain structure does not

Origin of Magnetic-Field-Induced Polarization



P_{III}: Reversal of direction of polarization reversal without switching

Summary

Nonlinear optics

- Nonlinear optics as powerful probe for magnetic *and* electric structures as well as their magnetoelectric interaction
- Symmetry as the major principle
- Access to additional degrees of freedom of optical experiments
  - Spectroscopy: sublattice sensitivity
  - Spatial resolution: domains
  - Time resolution: sub-picosecond dynamics
- Review: M. Fiebig et al., J. Opt. Soc. Amer. B **22**, 96 (2005)