Magnetoelectric Correlations in Multiferroics

- The magnetoelectric effect & multiferroics: early history
- Composite "pseudo" multiferroics
- Intrinsic, single-phase multiferroics
- Magnetoelectric effect in the IR to visible range
- New concepts
- Conclusion & outlook

Manfred Fiebig, HISKP, University of Bonn
European School on Multiferroics
Grenoble, 2-6 July 2007

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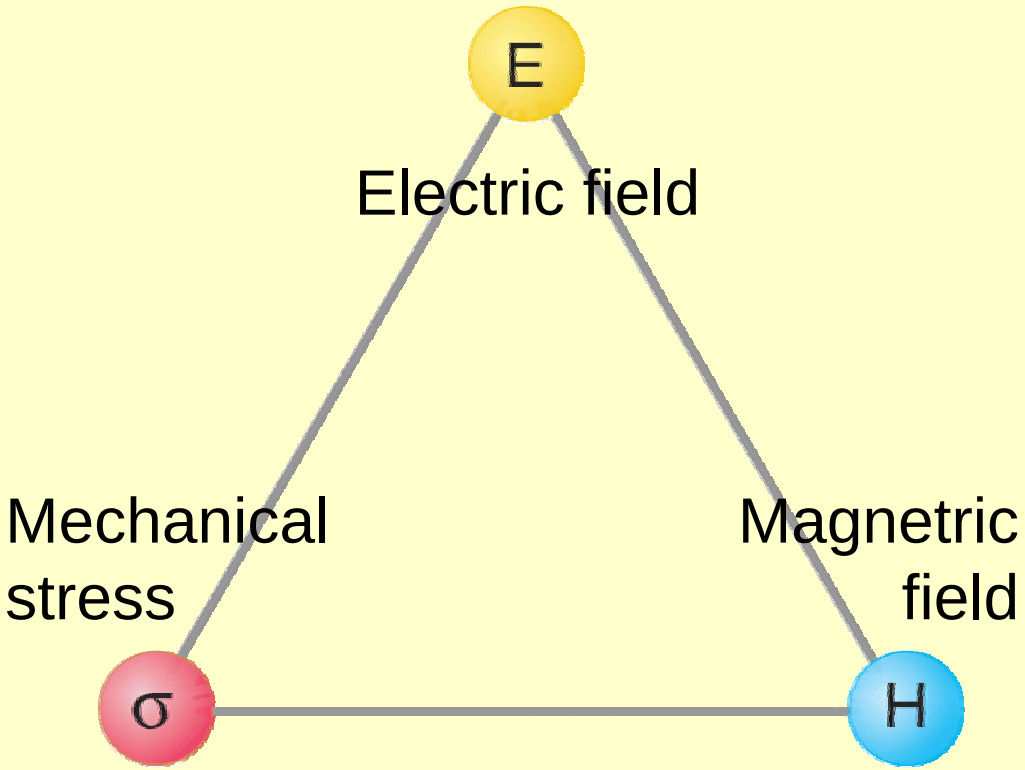
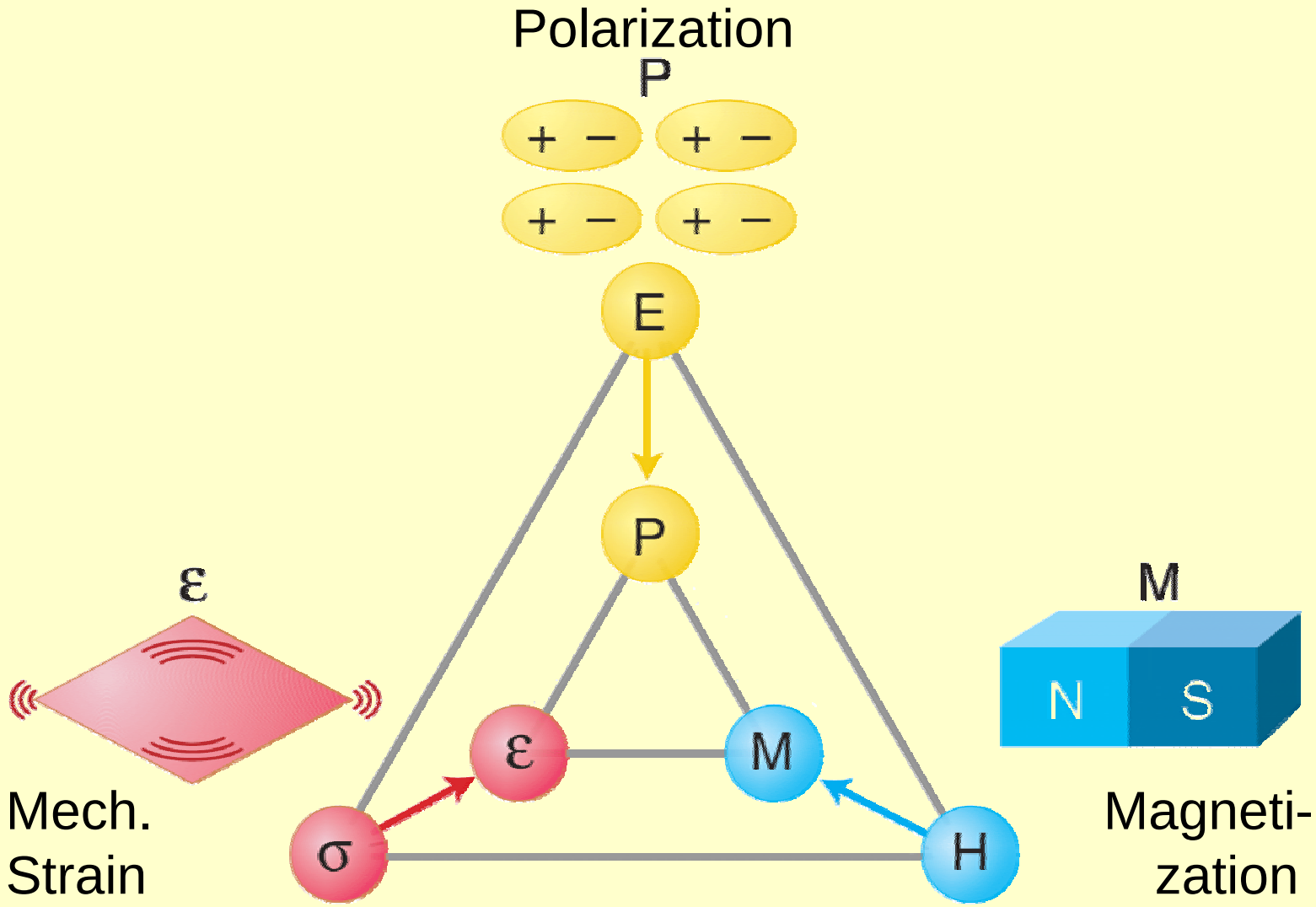
- **New concepts**
- **Conclusion & outlook**

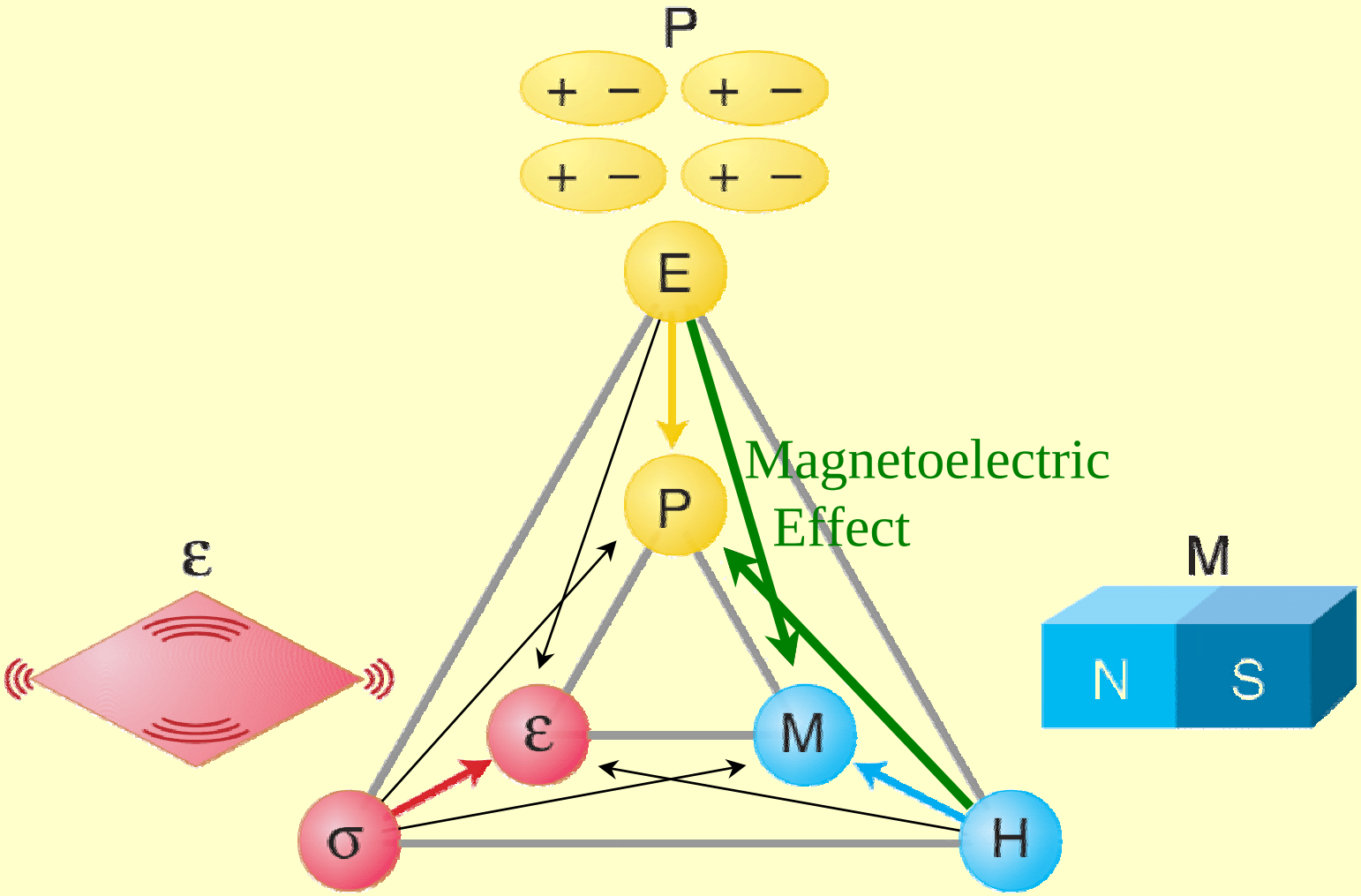
Idea of the Magnetoelectric Effect



Idea of the Magnetoelectric Effect



Idea of the Magnetoelectric Effect



Quantification of the Linear Magnetoelectric Effect

Free energy $F(\vec{E},\vec{H})$ with polarization $P_i = -\partial F/\partial E_i$ and magnetization $M_i = -\partial F/\partial H_i$

$$F(\vec{E},\vec{H}) = F_0 - P_i^S E_i - M_i^S H_i$$

Spontaneous polarization and magnetization

$$-\tfrac{1}{2}\epsilon_0\epsilon_{ij}E_iE_j - \tfrac{1}{2}\mu_0\mu_{ij}H_iH_j - \alpha_{ij}E_iH_j$$

Permittivity & permeability effects:

$P_i = \varepsilon_0\varepsilon_{ij}E_j$, $M_i = \mu_0\mu_{ij}H_j$

Linear magnetoelectric effect:

$P_i = \alpha_{ij}H_j$, $M_j = \alpha_{ij}E_i$

$$-\tfrac{1}{2}\beta_{ijk}E_iH_jH_k - \tfrac{1}{2}\gamma_{ijk}H_iE_jE_k - \cdots$$

Higher-order magnetoelectric effects

"The" magneto-electric effect

Magnetoelectric Effect: Historical Survey

1894 — First discussion of an intrinsic correlation between magnetic and electric properties

P. Curie, J. de Physique (3rd Series) **3,** 393 (1894)

"Les conditions de symétrie nos permettons d'imaginer qu'un corps à molécule dissymétrique se polarise peut-être magnétiquement lorsqu'on le place dans un champ électrique.

1926 — Introduction of the term "magnetoelectric" for these correlations

P. Debye, Z. Phys. **36,** 300 (1926)

Title: *Bemerkung zu einigen neuen Versuchen über einen magneto-elektrischen Richteffekt*

1957 — Magnetoelectric effect only in time-asymmetric (i.e. magnetically ordered) media!

L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960)

"The magnetoelectric effect is odd with respect to time reversal and vanishes in materials without magnetic structure"

1959 — Magnetoelectric effect predicted for antiferromagnetic Cr_2O_3

I. E. Dzyaloshinskii, J. Exptl. Teor. Fiz. **37,** 881 (1959); Sov. Phys.—JETP **10,** 628 (1959)

"We should like to show here that among the well known antiferromagnetic substances there is one, namely Cr_2O_3, where the magnetoelectric effect should occur from symmetry considerations."

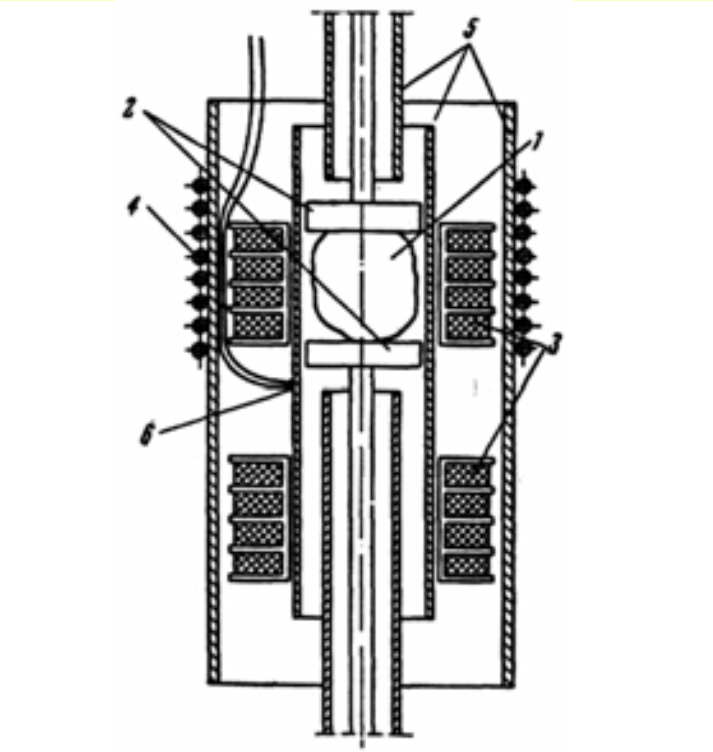
1960/61 — First observation in Cr_2O_3

<u>E → M:</u> D. N. Astrov, J. Exptl. Teor. Fiz. 38, 984 (1960); Sov. Phys.—JETP **11,** 708 (1960)

<u>H → P:</u> V. J. Folen, G. T. Rado, and E. W. Stalder, Phys. Rev. Lett. **6,** 607 (1961)

Astrov's Discovery of the Magnetoelectric Effect

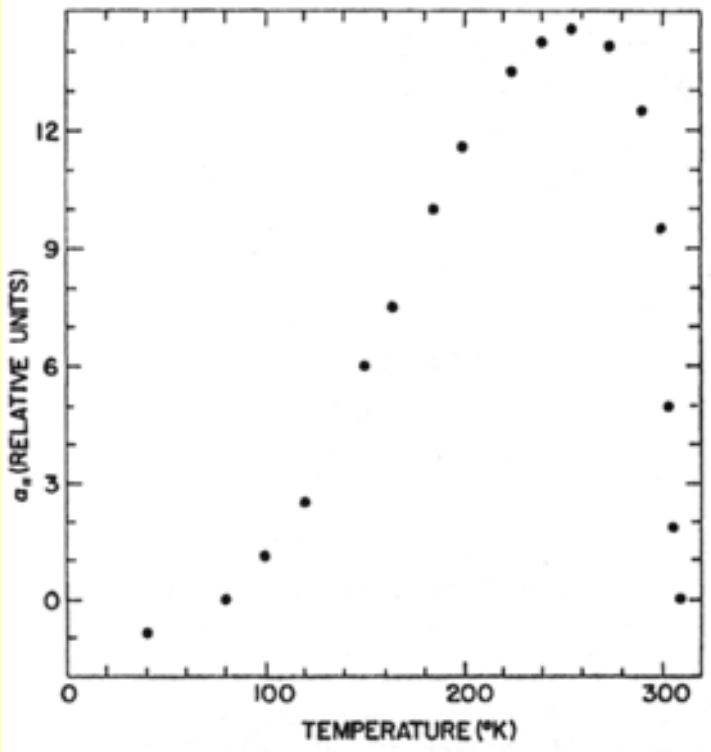
The apparatus



1: sample
2: electrodes
3: cooling
4: coil
5: shielding
6: wires

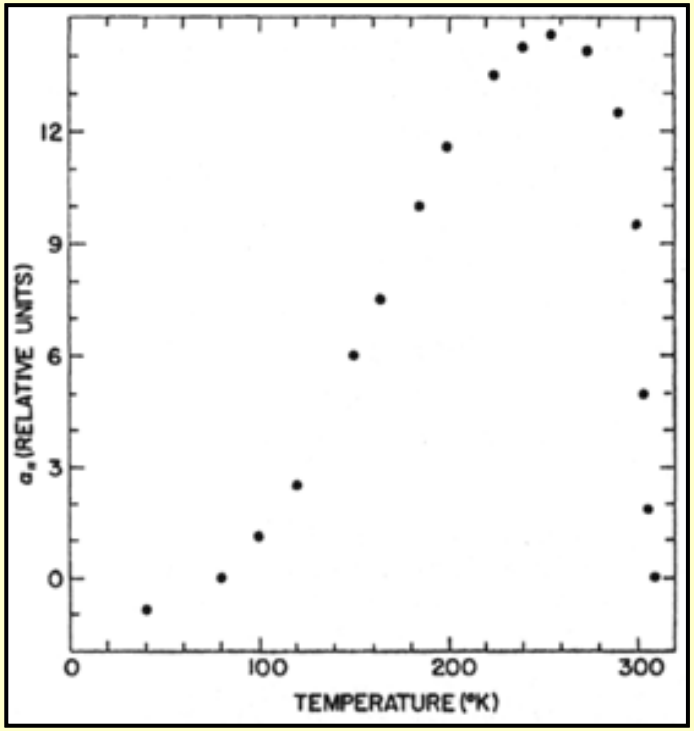
D.N. Astrov,
JETP **11,** 708 (1960)

The data



$$\mathbf{M} \propto \alpha\, \mathbf{E}$$

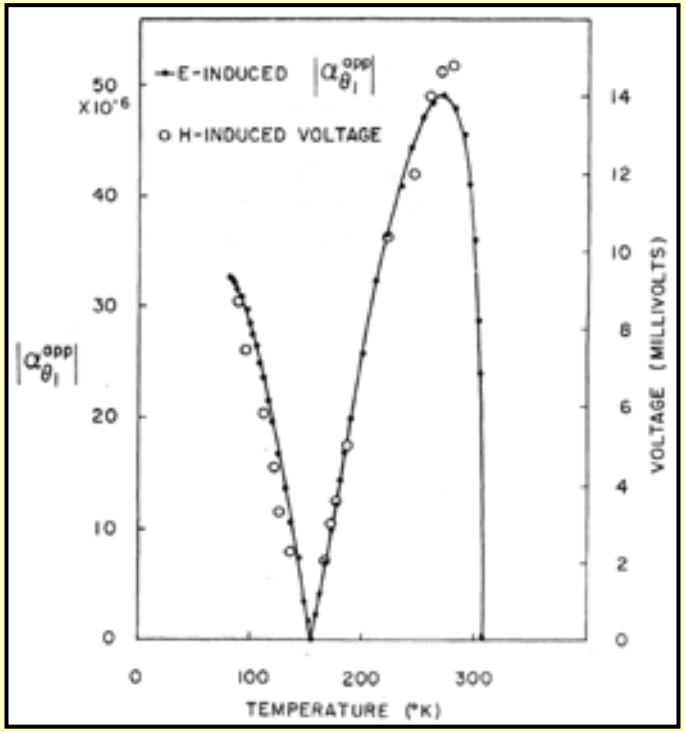
Reciprocity



1960:
$M \propto \alpha E$

Cr_2O_3

1961:
$P \propto \alpha^* H$

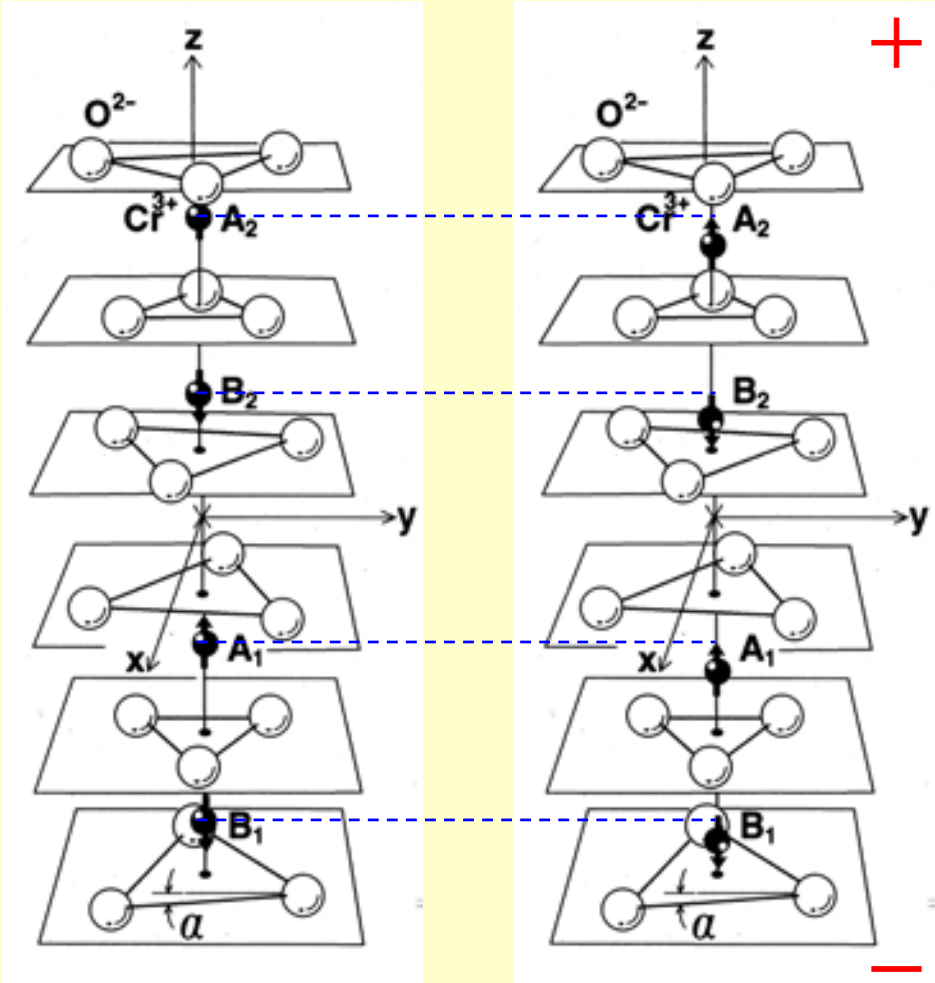


D.N. Astrov,
JETP **11,** 708 (1960)

V.J. Folen,
PRL **6,** 607 (1961)

Sources of the Magnetoelectric Effect

E = 0 **Cr_2O_3** **E ≠ 0**



Source in Cr_2O_3:

- Electric field E || z moves ions with respect to ligands
- $A_{1,2}$ and $B_{1,2}$ sites are no longer equivalent → M || z

Other mechanisms:

- Single-ion anisotropy
- Symmetric superexchange
- Antisym. superexchange
- Dipole interaction
- Zeeman energy

See:
R.M. Hornreich et al., Phys. Rev. **161**, 506 (1967)
G.A. Gehring, Ferroelectrics **161**, 275 (1994)

Limitations …

Limitation of the magnetoelectric effect:

Cannot be larger than the geometric mean of electric and magnetic permeability [W. F. Brown, R. M. Hornreich, S. Shtrikman, Phys. Rev. **168,** 574 (1968)]

$$\alpha_{ij}^{2} < \chi_{ii}^{e}\, \chi_{jj}^{m}$$

The magnetoelectric effect is small!

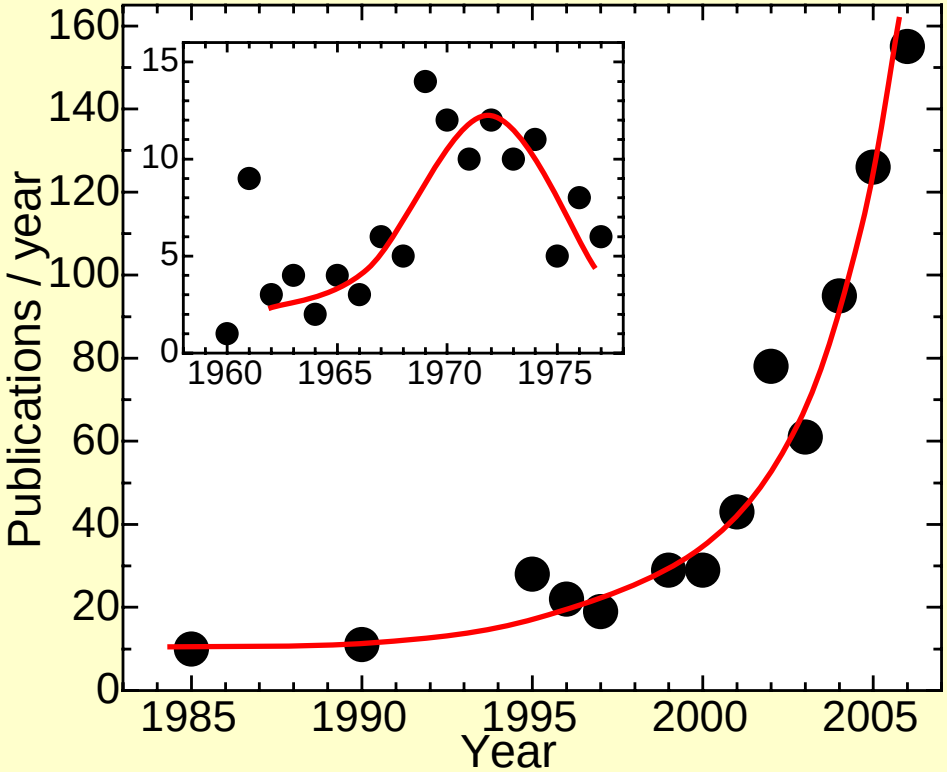
- Maximum value in Cr_2O_3: 4.13 pT/Vm^{-1}
  (corresponds to reversal of one in a million spins at 10^6 V/cm)
- Record value found in $TbPO_4$: 36.7 pT/Vm^{-1}

Other problems:

- Limited choice of compounds
- No general theoretical concept

→ **Decline of research activities after 1973**

The Revival



Publications under the keyword "magnetoelectric"

Web of Science

Since about the year 2000:

- New theoretical concepts
- "Giant" effects: induction of phase transitions
- New materials: "magnetoelectricity on design"

Generating Large Magnetoelectric Effects

Limitation of the magnetoelectric effect:

Cannot be larger than the geometric mean of electric and magnetic permeability [W. F. Brown, R. M. Hornreich, S. Shtrikman, Phys. Rev. **168,** 574 (1968)]

$$\alpha_{ij}^{2} < \chi_{ii}^{e}\, \chi_{jj}^{m}$$

Large magnetoelectric effects:

- In ferroelectric samples
- In ferromagnetic samples

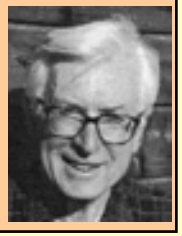
Largest: in ferroelectric ferromagnetics

Do ferroelectric ferromagnetics exist?

Yes!! They are called *multiferroics*!

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.”

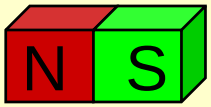


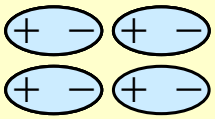
Hans Schmid (University of Geneva, Switzerland)
in: M. Fiebig et al. (ed.), *Magnetoelectric Interaction Phenomena in Crystals*, (Kluwer, Dordrecht, 2004)

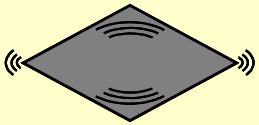
Primary ferroic ↔ formation of switchable domains:

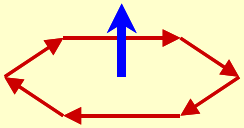
Excludes anti-ferroic forms of ordering

Ferromagnetism	Ferroelectricity	Ferroelasticity	Ferrotoroidicity
spontaneous magnetization	spontaneous polarization	spontaneous strain	spontaneous magnetic vortex









Extension to anti-ferroic forms of ordering:

Compounds consisting of multiferroic sublattices (one or more of) whose primary ferroic properties cancel in the macroscopic crystal

Relation: Magnetoelectric ↔ Multiferroic

Not all magnetoelectrics are multiferroics!

Example: Cr_2O_3 is a magnetoelectric antiferromagnet without electric ordering

Not all multiferroics are magnetoelectrics!

Example: Hexagonal $YMnO_3$ is a ferroelectric antiferromagnet in which the magnetoelectric effect is forbidden by symmetry

All ferroelectric ferromagnets can be magnetoelectric!

Example: $Ni_3B_7O_{13}I$

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What is a Composite Multiferroic?

Constituent 1:
Piezoelectric

$BaTiO_3$
$PbZr_{1-x}Ti_xO_3$ (PZT)
$Ba_{0.8}Pb_{0.2}TiO_3$
$Bi_4Ti_3O_{12}$
PVDF
$PbMg_{1/3}V_{2/3}O_3$ ...

$\otimes$

Constituent 2:
Magnetostrictive

$CoFe_2O_4$
$Tb_{1-x}Dy_xFe_2$
(= Terfenol-D)
$LiFe_5O_8$
YIG
Permendur ...

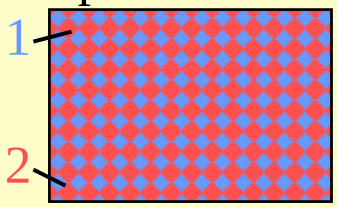
$\rightarrow$

Composite
Pseudo-magnetoelectric

- End compounds are not magnetoelectric!
- Magnetoelectric effect is a product effect!

layered

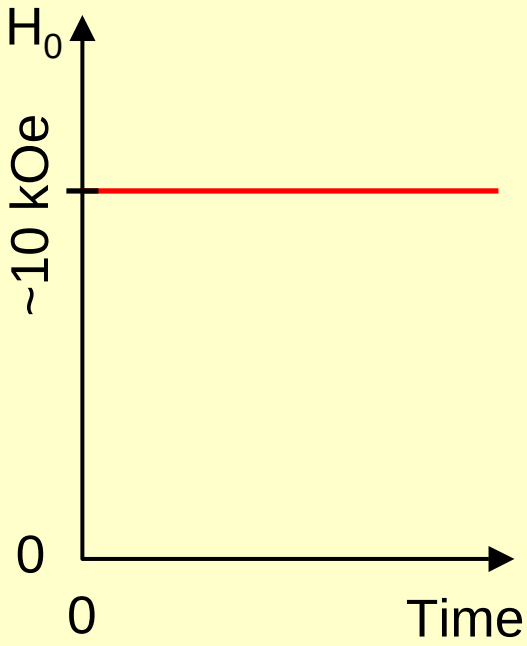
particulate

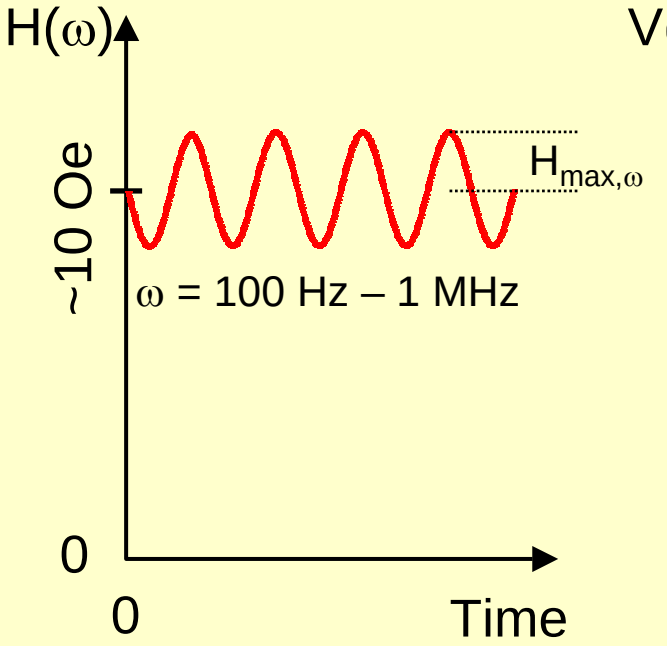


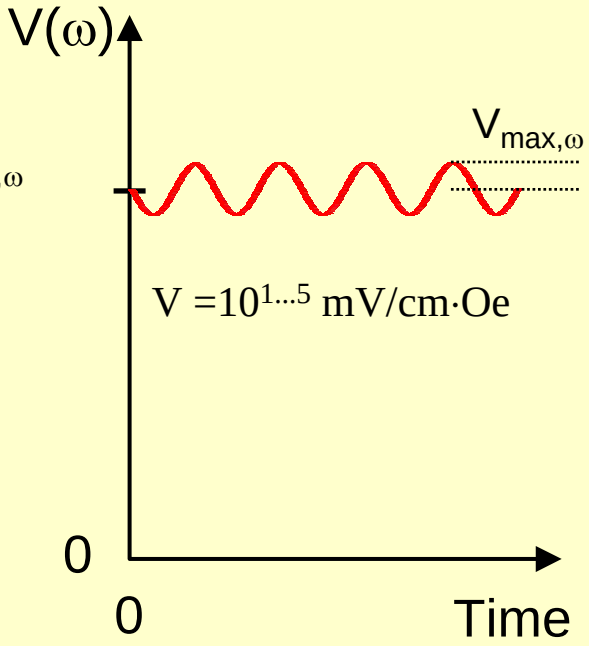
$$\text{ME effect} = \frac{\text{electrical}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}$$

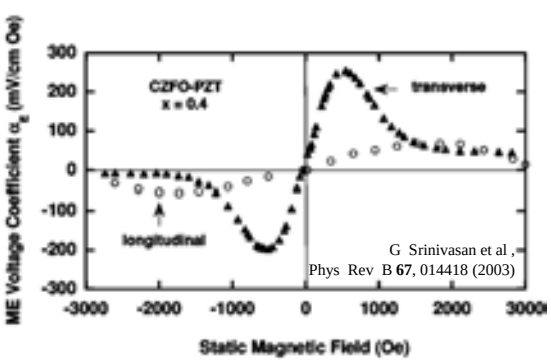
- Magnetic field $\rightarrow$ magnetostrictive deformation
- Transfer of deformation constituent 2 $\rightarrow$ constituent 1
- Deformation via piezoelectric effect $\rightarrow$ voltage

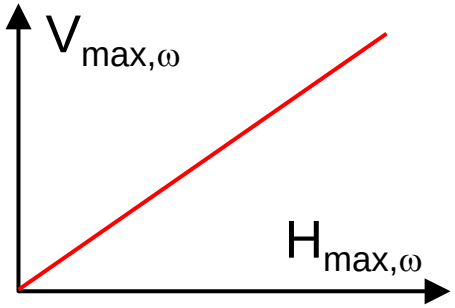
Measuring Magnetoelectric Response in Composites











- The composite ME effect is an AC effect
- Linear response for small intervals only

First Composite Magnetoelectric Effect

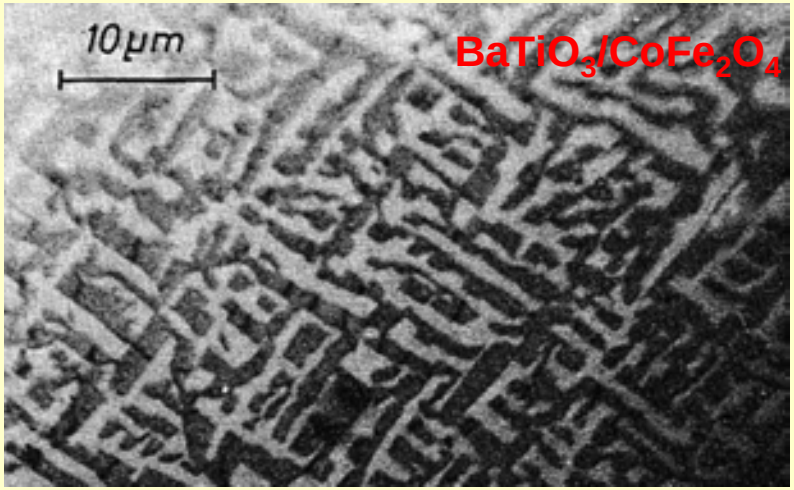
R 784 Philips Res. Repts 27, 28-37, 1972

PRODUCT PROPERTIES: A NEW APPLICATION OF COMPOSITE MATERIALS

by J. van SUCHTELEN

Abstract

A new class of physical properties of composite materials is that of "product properties" in which the phases or submaterials of the composite are selected in such a way that an effect in one of the phases or submaterials leads to a second effect in the other phase. A typical example is the magneto-electric effect in a composite material with one magnetostrictive and one piezoelectric phase: a magnetic field induces a distortion of the magnetostrictive phase, which in turn distorts the piezoelectric phase in which an electric field is generated. The composite as a whole can be considered macroscopically as a new, homogeneous material with a magneto-electric effect not exhibited by any of the composing phases on their own. The coupling, in this case, is of the mechanical kind. The entire class of product properties can be searched systematically for interesting properties by a kind of matrix scanning procedure. Typical examples will be given in the present paper.



Result:

Value of the magnetoelectric pseudo effect in $BaTiO_3/CoFe_2O_4$:

$dE/dH = 130$ mV/cm·Oe

$\alpha = 720$ pT/Vm^{-1}

Compare to best single-phase magnetoelectrics:

Cr_2O_3: $\alpha = 4.13$ pT/Vm^{-1}

$TbPO_4$: $\alpha = 36.7$ pT/Vm^{-1}

No significant advances on this initial result until the year 2000!

Ways of Fabricating Composite Multiferroics

Particulate composites

- Grinding, mixing, pressing, sintering the constituents

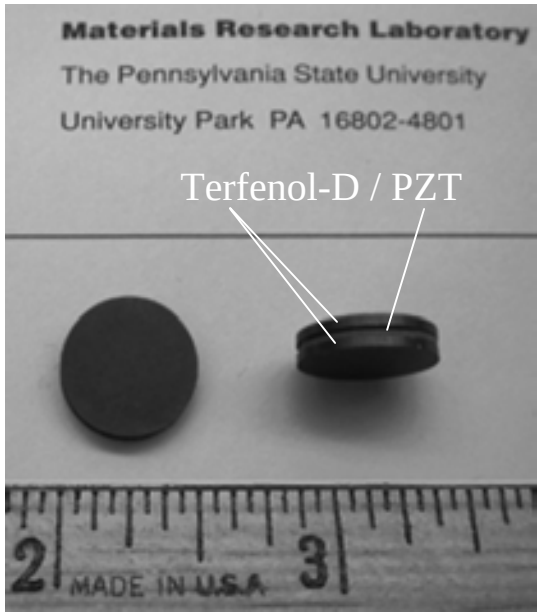
Disadvantages

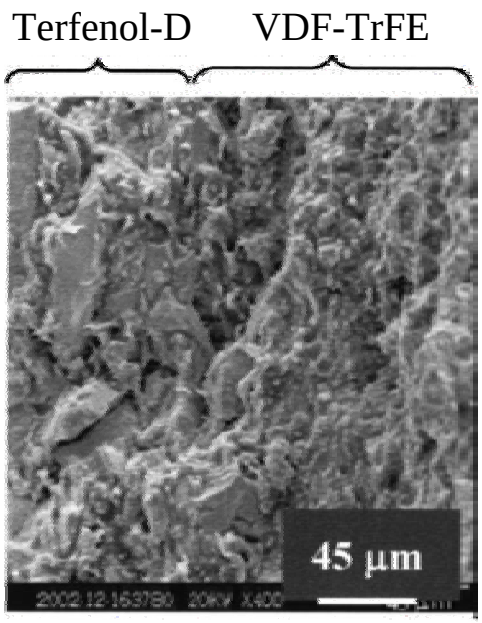
- Chemical reaction between constituents
- Poor mechanical contact
- Low-resistivity constituent phases → percolation
- Poor mechanical contact (defects, connectivity)
- Random orientation of particles

Limitations

- Magnetoelectric effect does not exceed ~100 mV/cm·Oe
- New approaches since 2001

Laminar Composites





J. Ryu et al., Jpn. J. Appl. Phys. **40**, 4948 (2001)

Separate fabrication of piezoelectric and magnetostrictive constituents

- Pressing: $d \approx 1$ mm
- Tape casting: $d \leq 10$ µm

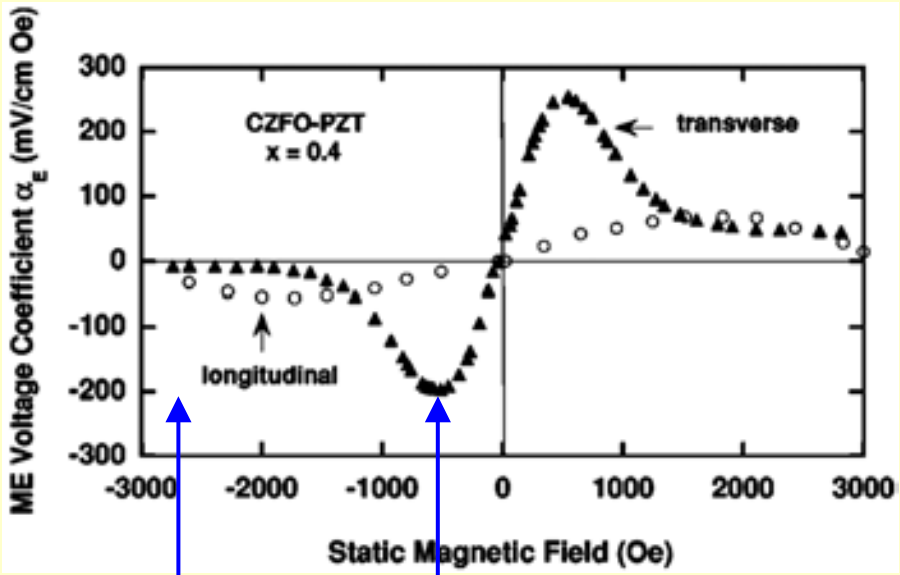
Connection by

- Silver epoxy
- Glue
- Hot pressing

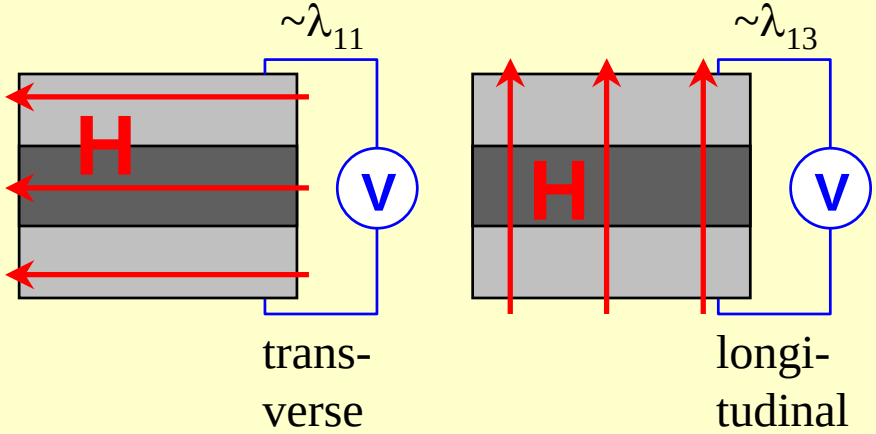
First attempt:

- PZT/Terfenol-D trilayer stack
- dE/dH = 4.68 V/cm·Oe
- Exceeds maximum particulate composit value by factor 36!

Origin of the ME Effect in Laminate Composites



Saturation, $E>E_C$ Domain motion, $E\approx E_C$

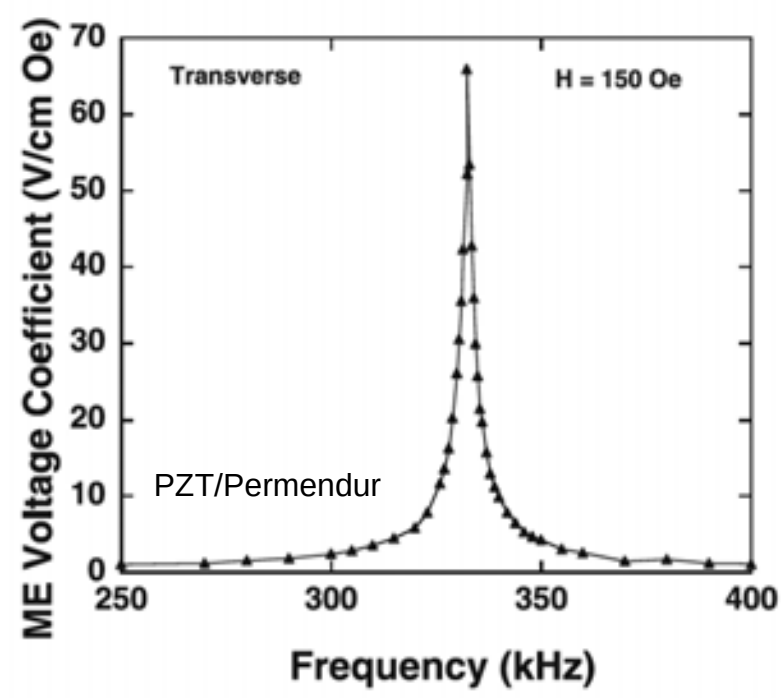


G. Srinivasan et al.,
Phys. Rev. B **67**, 014418 (2003)

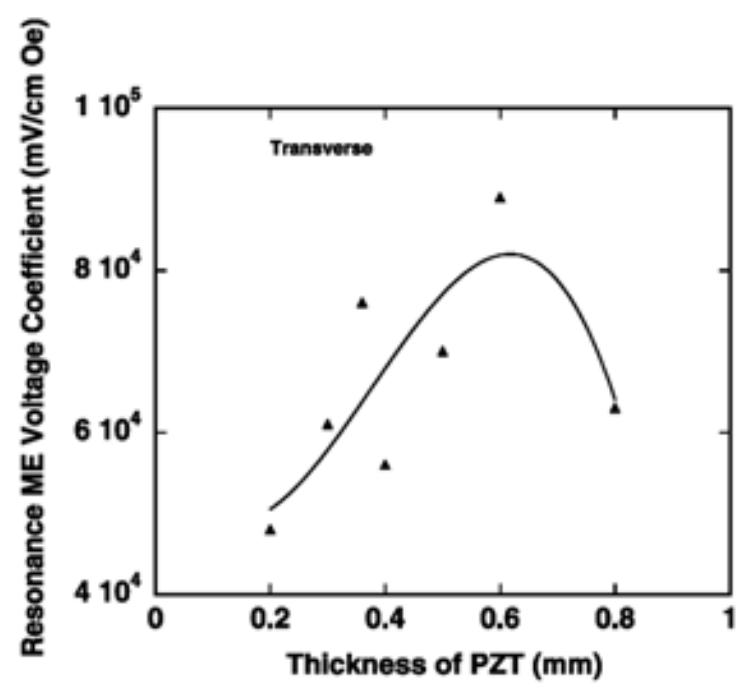
- Major source of magnetoelectric response: domain wall motion
- Magnetostriction: $\lambda_{13} << \lambda_{11}$ $\Rightarrow$ transverse effect dominates
- Large magnetoelectric response for
  - Large magnetostrictive and piezoelectric coefficients
  - Efficient mechanical contact between constituents

Resonance Magnetoelectric Effect

- Frequency of the magnetic AC field may coincide with electric, magnetic, or mechanical eigenmodes of the system
- Can lead to resonance enhancement of magnetoelectric response

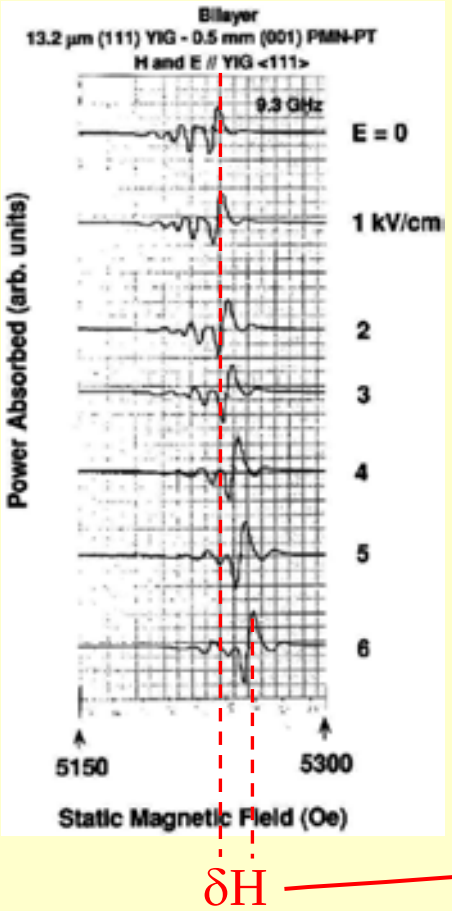


U. Laletsin et al., Appl.Phys. A **78**, 33 (2004)



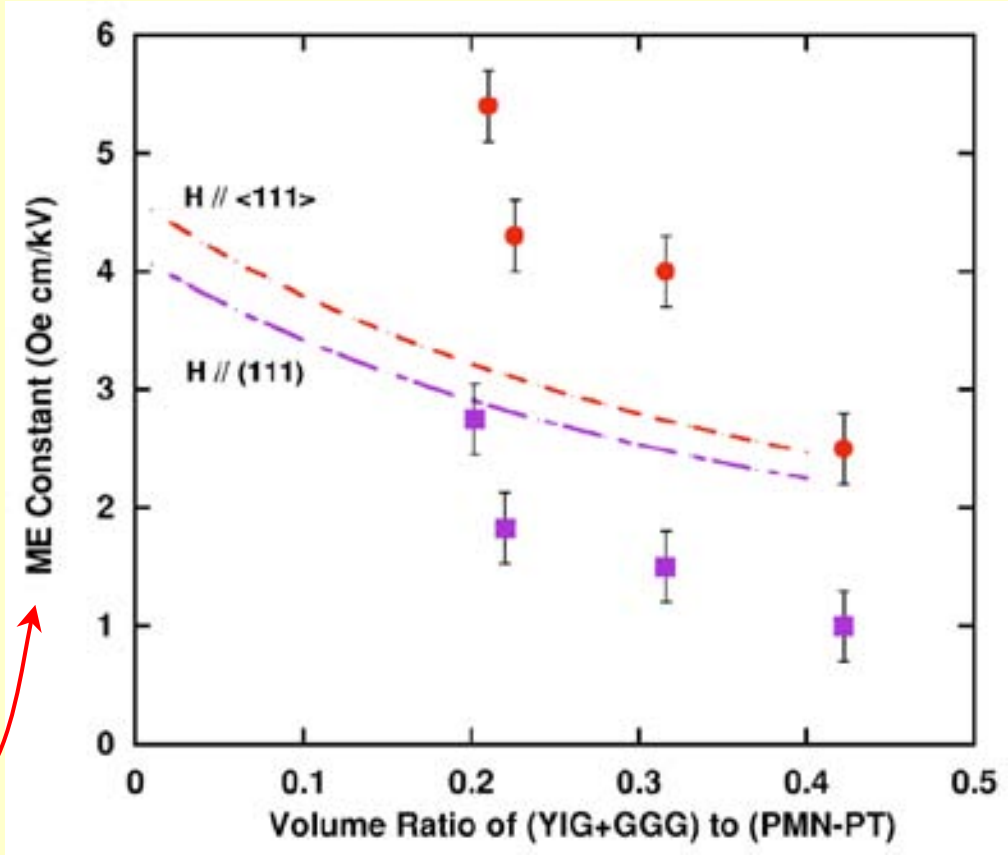
Values dE/dH up to 90 V/cm·Oe (~10^4 times Cr_2O_3) were achieved

"Inverse" Magnetoelectric Effect in Composites



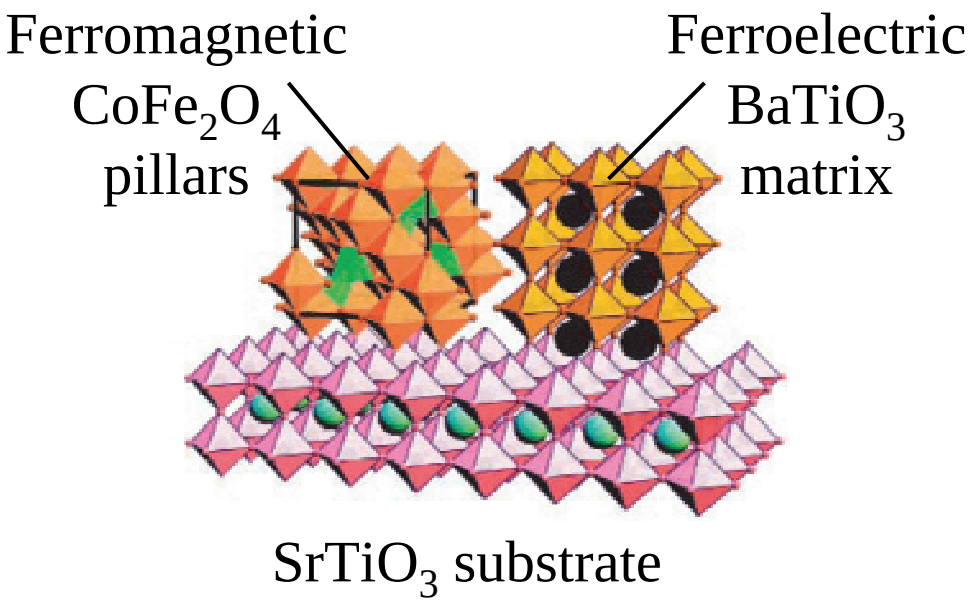
δH

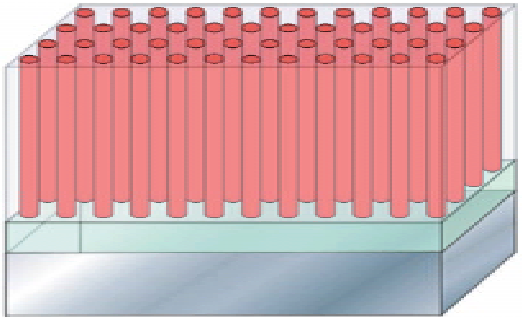
S. Shastry et al., Phys. Rev. B 70, 064416 (2004)

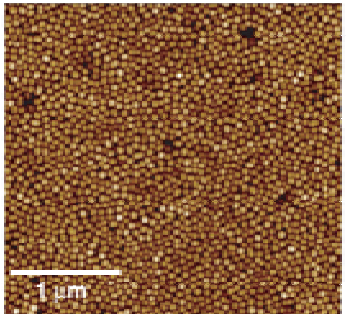


- Static electric field shifts the ferromagnetic resonance by δH
- Gives inverse magnetoelectric effect up to $\delta H/\Delta E = 1$ cm·Oe/kV

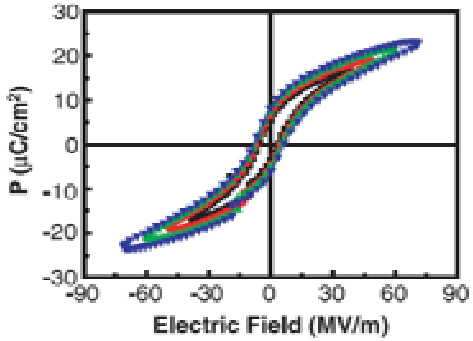
Self-Assembled Nanocomposites



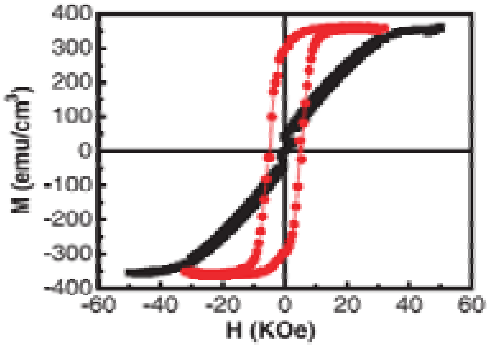




Ferroelectric properties



Ferromagnetic properties

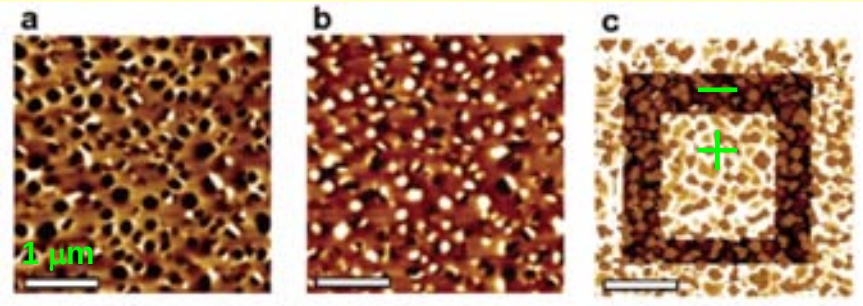


ME coupling and phase control also observed ?

H. Zheng et al., Science **303**, 661 (2004)

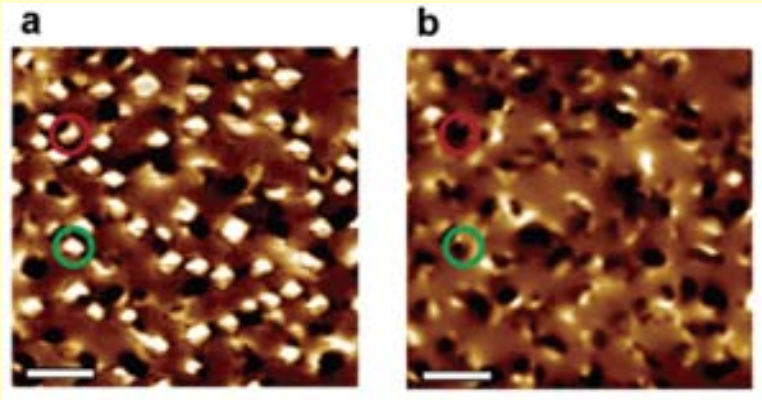
Magnetoelectric Phase Control in Nanocomposites

Force microscopy on $BiFeO_3/CoFe_2O_4$

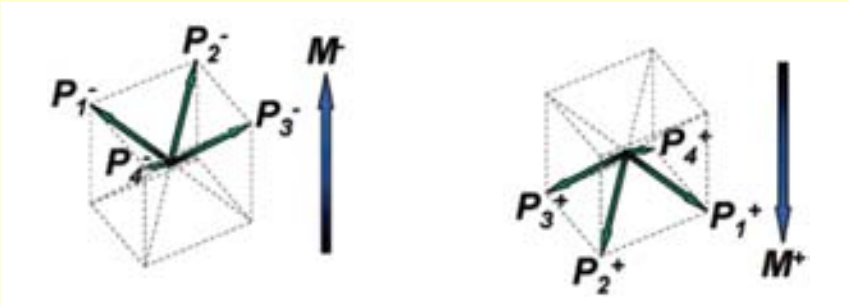


Magnetic +20 kOe | Magnetic –20 kOe | Electric ±8 V

Magnetic control by electric field

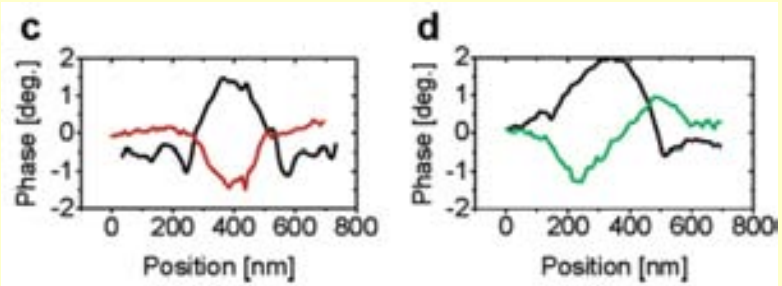


MFM **before** application of +12 V | MFM **after**



ME coupling mediated by strain

Estimated: $(10\ V/cm{\cdot}Oe)^{-1}$



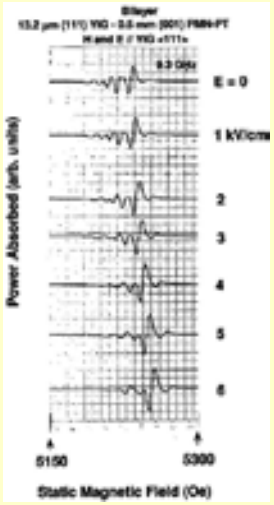
Line scans of marked regions

F. Zavaliche et al., Nano Lett. **5**, 1793 (2005)

Applications of Composites

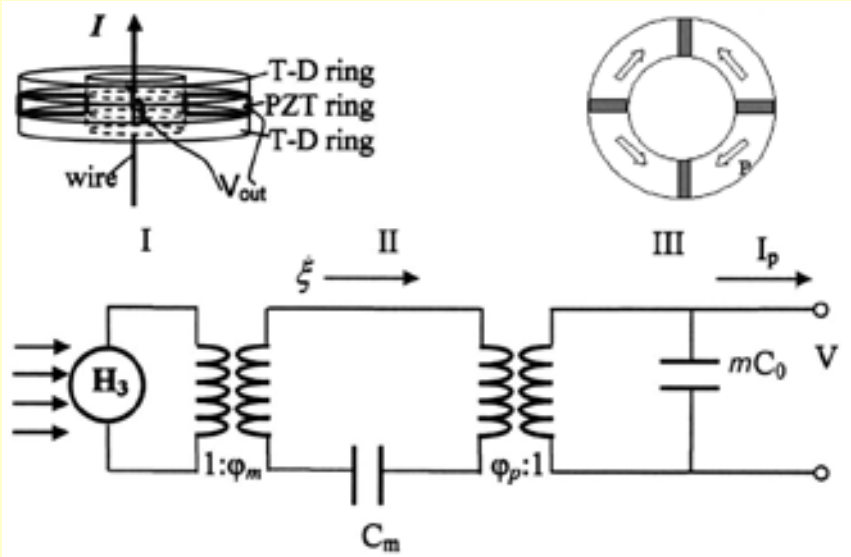
Predominantly microvave applications

- Transducer: $H(\omega) \rightarrow E(\omega)$ at resonance frequency ω_{res}
  - electromechanical: 100 kHz
  - ferromagnetic: 10 GHz
  - antiferromagnetic: 100 GHz
- Tunable filter/attenuator: $\omega_{res} \equiv \omega_{res}(E_0,H_0)$ FM. res.



Further applications

- Magnetic field probe with $H \rightarrow V$ conversion
- Memory application with fast, current-less electric writing of a magnetic bit



S.X. Dong et al., Appl. Phys. Lett. **85**, 2307 (2004)

Magnetoelectric Correlations in Multiferroics

- The magnetoelectric effect & multiferroics: early history
- Composite "pseudo" multiferroics
- **Intrinsic, single-phase multiferroics**
- Magnetoelectric effect in the IR to visible range
- New concepts
- Conclusion & outlook

Types of Single-Phase Multiferroics (I)

Three natural crystals

Congolite
$Fe_3B_7O_{13}Cl$

Hubnerite
$MnWO_4$

Chambersite
$Mn_3B_7O_{13}Cl$

Types of Single-Phase Multiferroics (II)

Compounds with perovskite structure

ABO_3, $A_2B'B''O_6$ compounds like $PbFe_{1/2}Nb_{1/2}O_3$, $BiFeO_3$

Compounds with hexagonal structure

$RMnO_3$ with R = Sc, Y, In, Ho, Er, Tm, Yb, Lu

Boracites compounds

$M_3B_7O_{13}X$ with M = Cr, Mn, Fe, Co, Cu, Ni; X = Cl, Br, I

Compounds with spin spirals

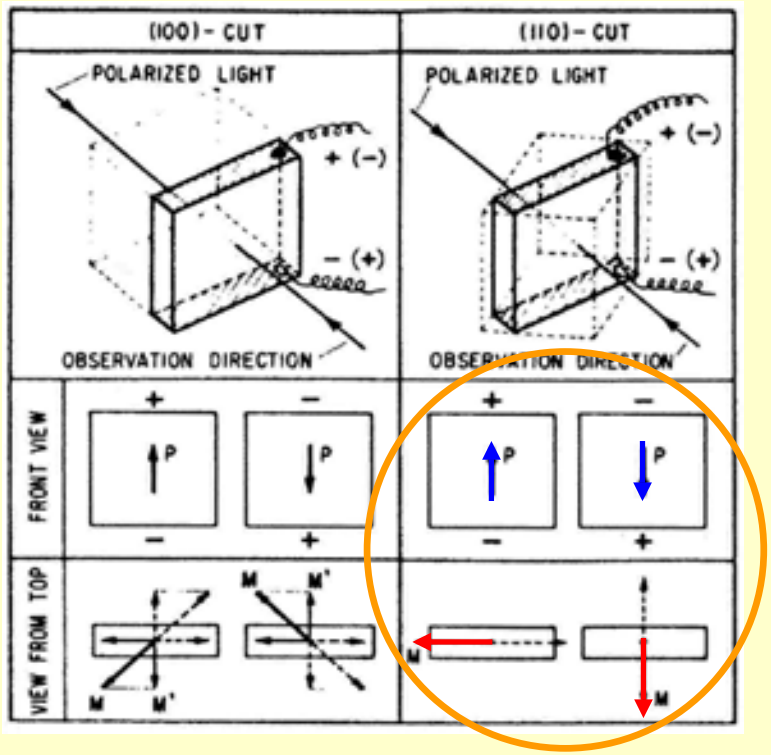
$TbMnO_3$, $TbMn_2O_5$, $MnWO_4$, $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$, etc.

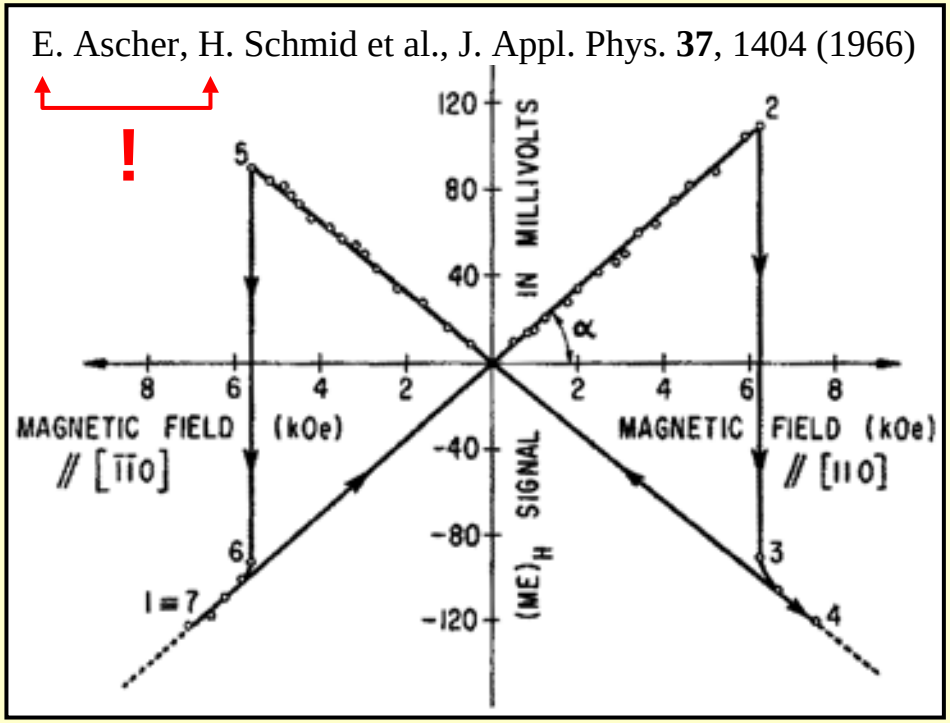
Orthorhombic $BaMF_4$ compounds

with M = Mg, Mn, Fe, Co, Ni, Zn

... and others (about 100 in total)

$Ni_3B_7O_{13}I$ – A Milestone of Multiferroics Research

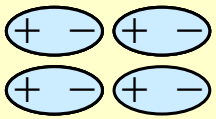


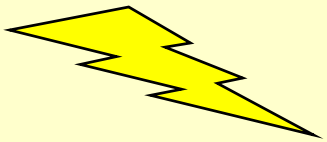


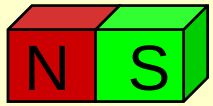
- Rotation of magnetization by 90° [$\underline{11}$0] → [$\underline{1}$10]
- Triggers reversal of ferroelectric polarization [001] → [00$\underline{1}$]
- First example of magnetoelectric cross-control

Ferroelectric Ferromagnets

Most promising for applications, but not many compounds exist because...





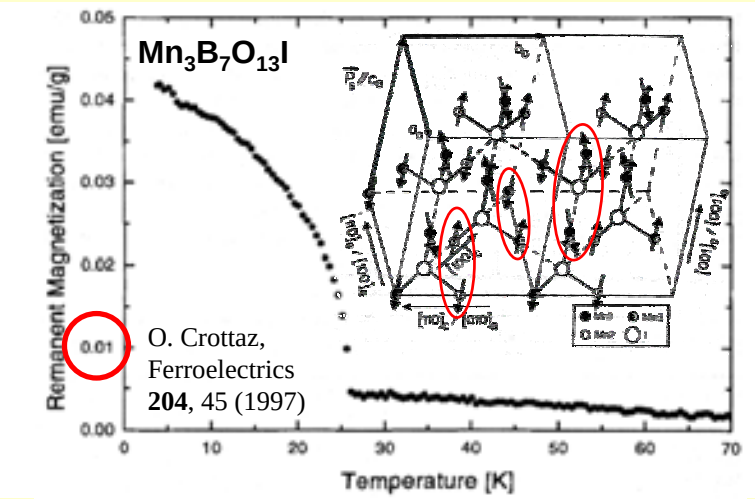


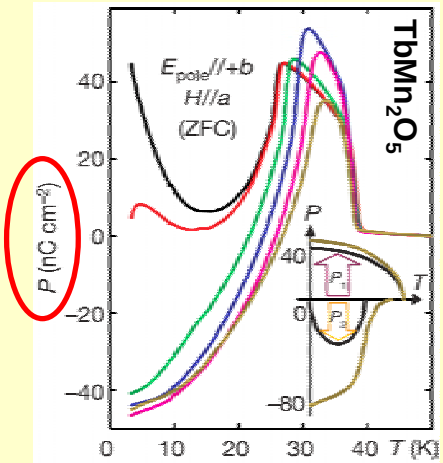
Likes $3d^n$ with **n=0**

N.A. Hill, J. Phys. Chem. B **104**, 6694 (2000)

Likes $3d^n$ with **n≠0**

The existing ferromagnetic ferroelectrics are usually *anti*-ferroic with only a weak ferromagnetic or ferroelectric component:



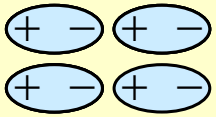


N. Hur, Nature **429**, 392 (2004)

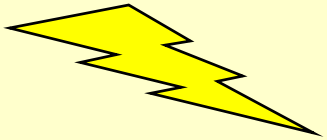
Any ME multiferroic is "unusual" because it circumvents the $3d^0/3d^n$ problem

Ferroelectric Ferromagnets

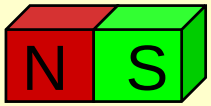
Most promising for applications, but not many compounds exist because...



Likes $3d^n$ with **n=0**



N.A. Hill, J. Phys. Chem. B **104**, 6694 (2000)



Likes $3d^n$ with **n≠0**

Need alternative ways for uniting electric and magnetic order

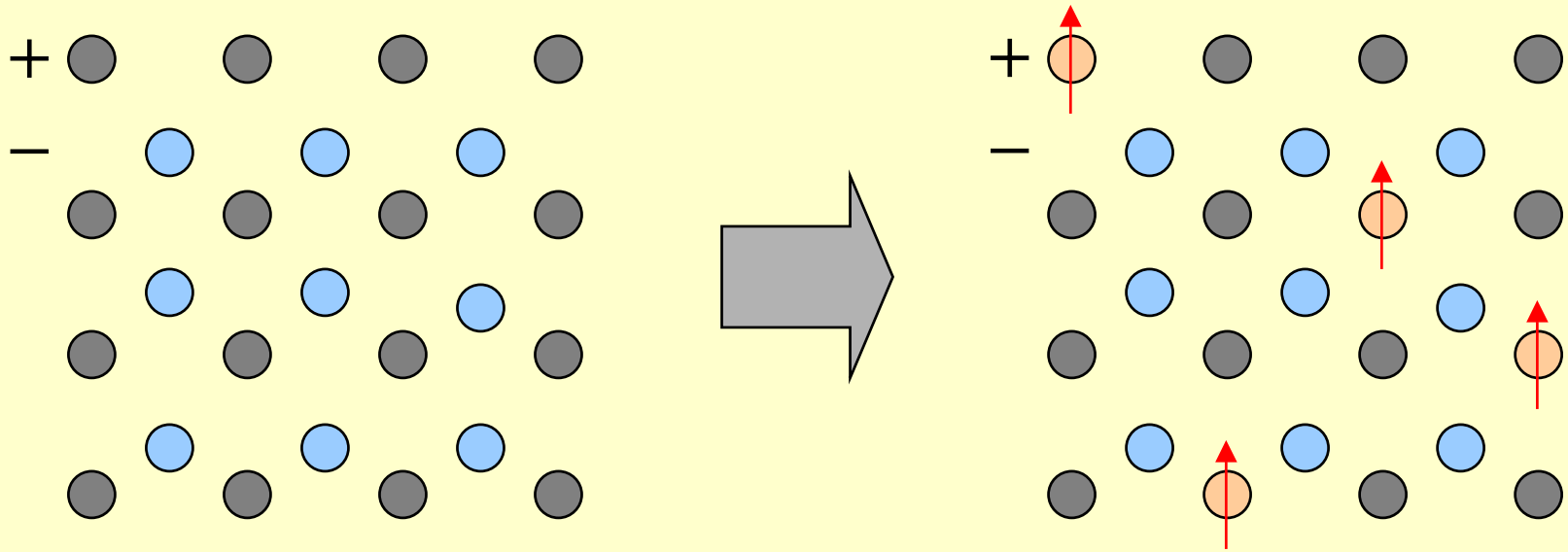
Most promising:

Look for alternative ways of generating ferroelectricity !

Modified types of Ferroelectricity (1)

Dope paramagnetic ions into a diamagnetic ferroelectric

... and hope for the best

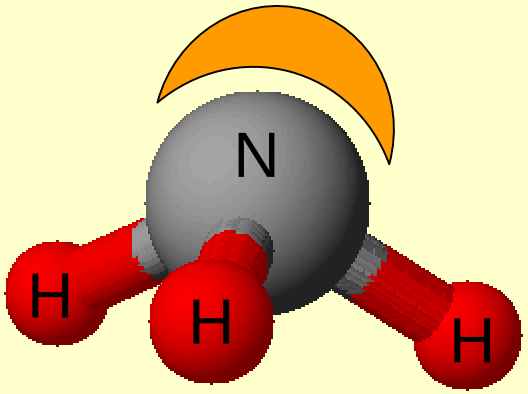


Historic examples like $PbFe_{1/2}Nb_{1/2}O_3$ (before 1960)

Modified types of Ferroelectricity (2)

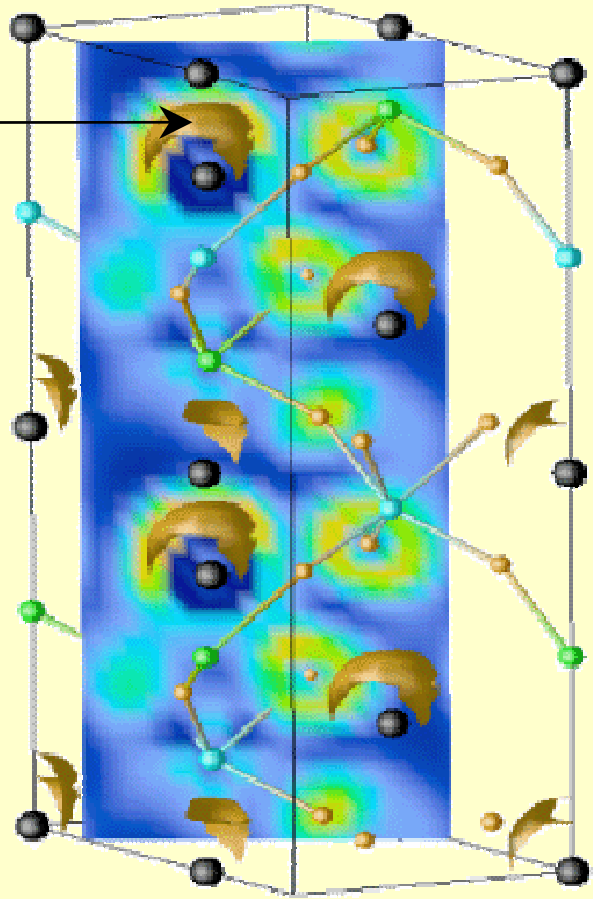
Electronic lone pair creates charge asymmetry

The NH_3 lone pair:



Courtesy N. Spaldin

Bi lone pair in Bi*M*O_3



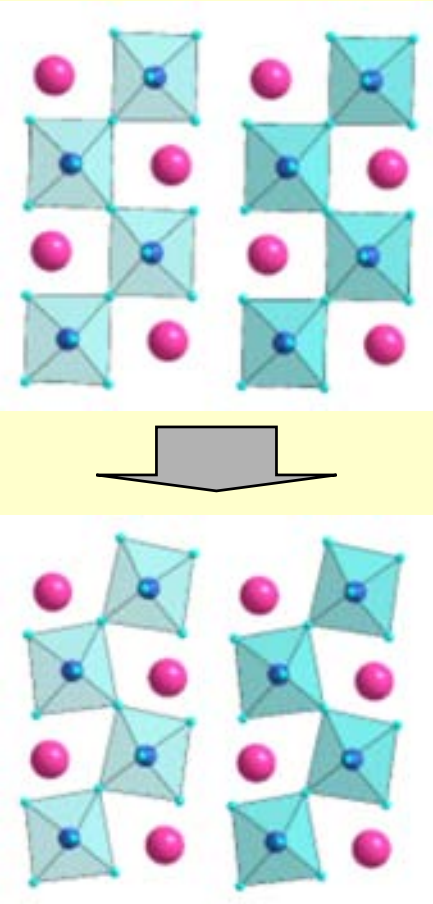
p^0 criterion instead of d^0 criterion

Explains multiferroicity of $BiMnO_3$, $BiFeO_3$

R. Seshadri, Chem. Mater. **13**, 2892 (2001)

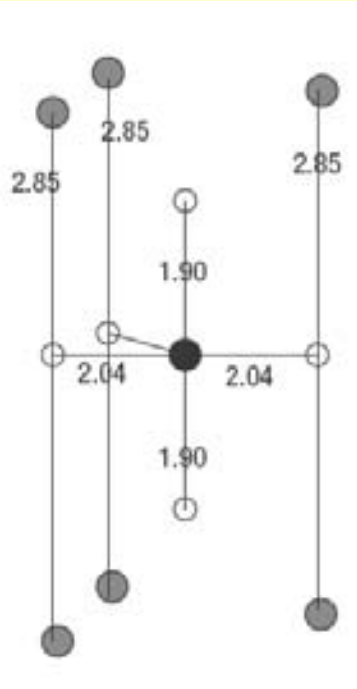
Modified types of Ferroelectricity (3)

Geometric rearrangement of ions without charge hybridization (electrostatic ferroelectricity)

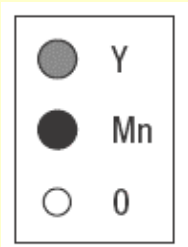


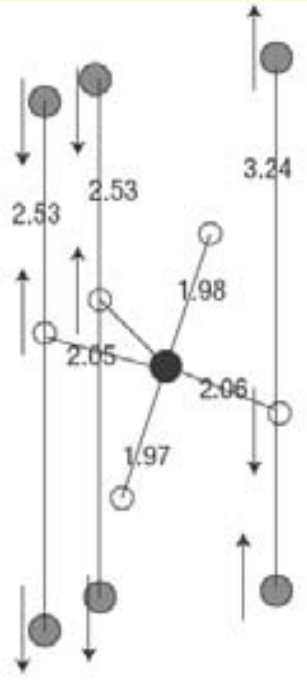
$BaNiF_4$

C. Ederer, Phys. Rev. B **74**, 1024102 (2006)



$YMnO_3$

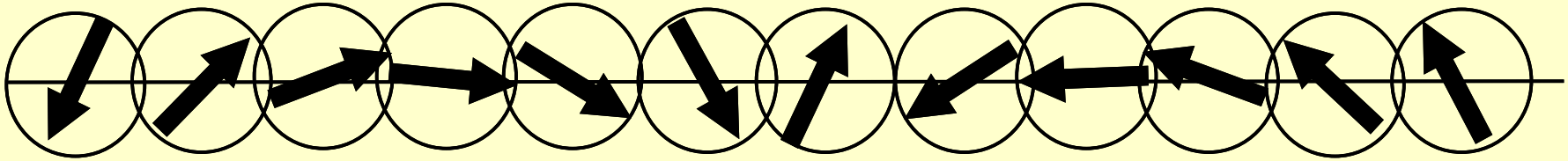




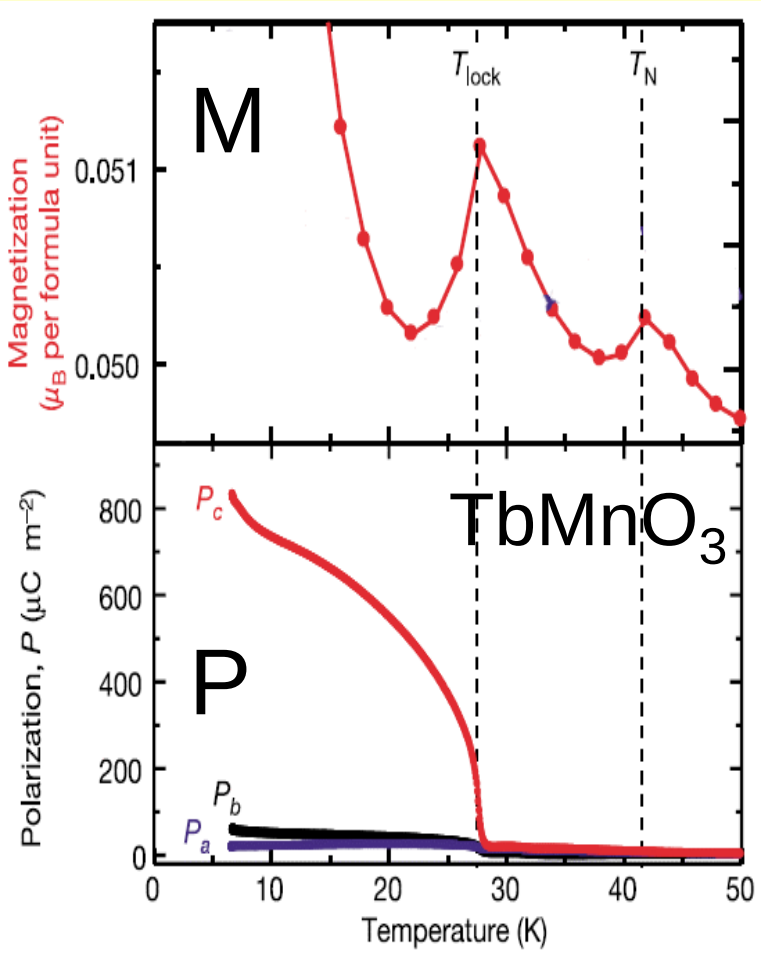
B.B. van Aken, Nature Mater. **3**, 164 (2004)

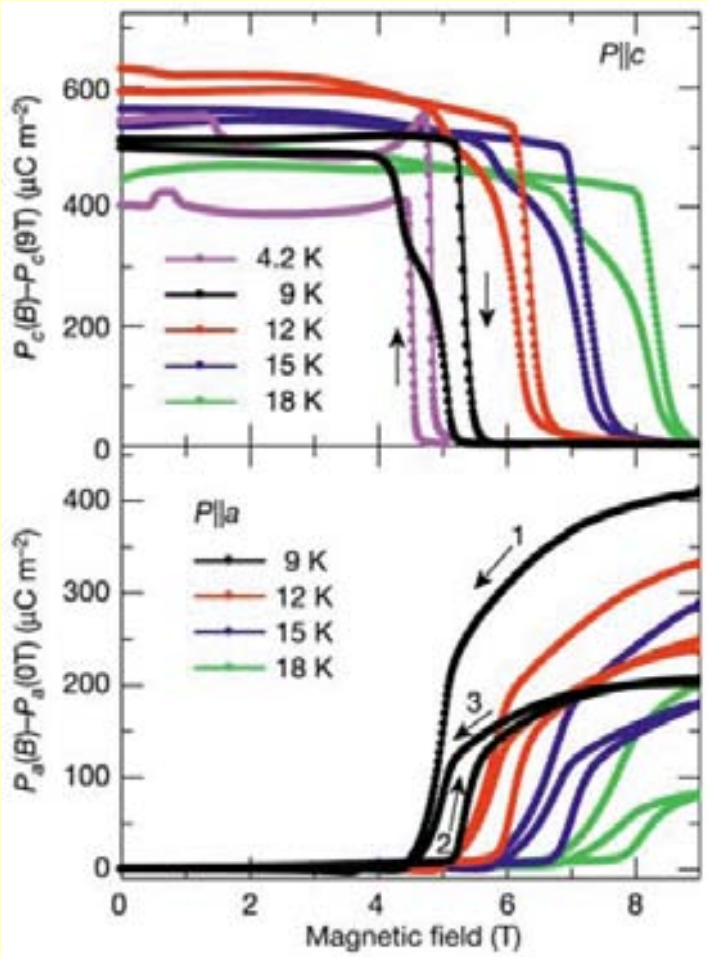
Modified types of Ferroelectricity (4)

Magnetically induced ferroelectricity
e.g. through spin spirals



Magnetic Control of Ferroelectricity in $TbMnO_3$

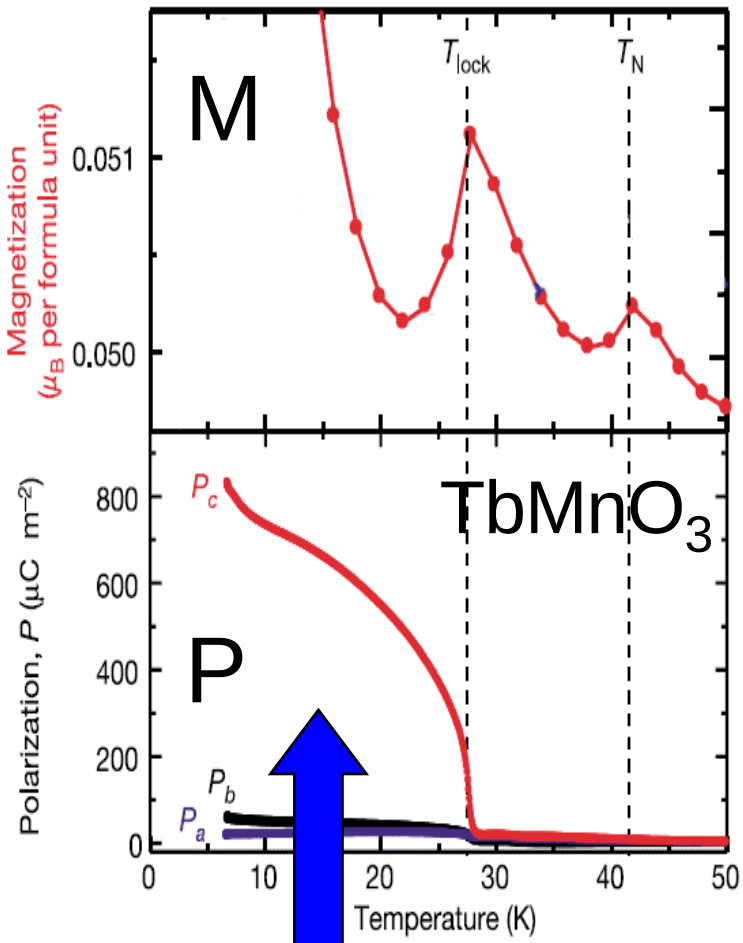




Magnetic field triggers a ferroelectric phase transition with polarization rotation by 90°

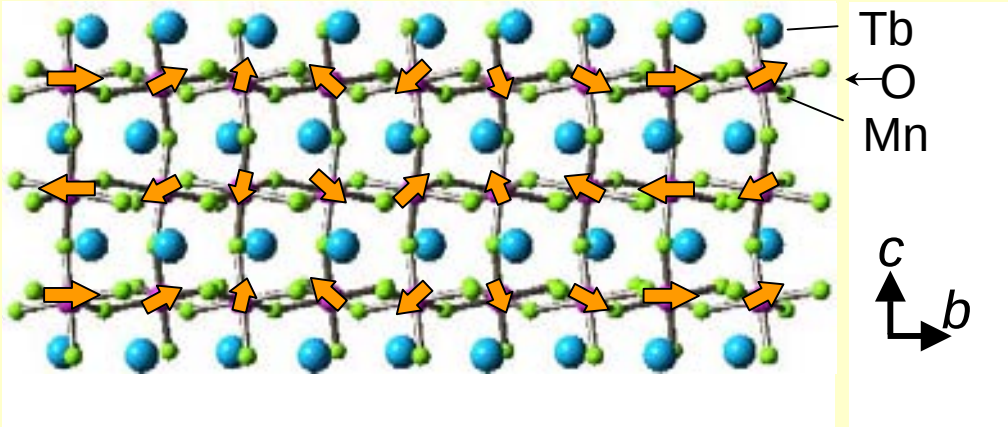
T. Kimura et al., Nature **426**, 55 (2003)

Spiral Magnetism in $TbMnO_3$

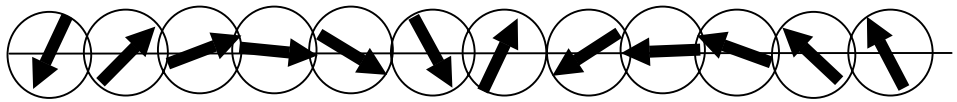


Incommensurate spiral-like spin structure

In ferroelectric phase



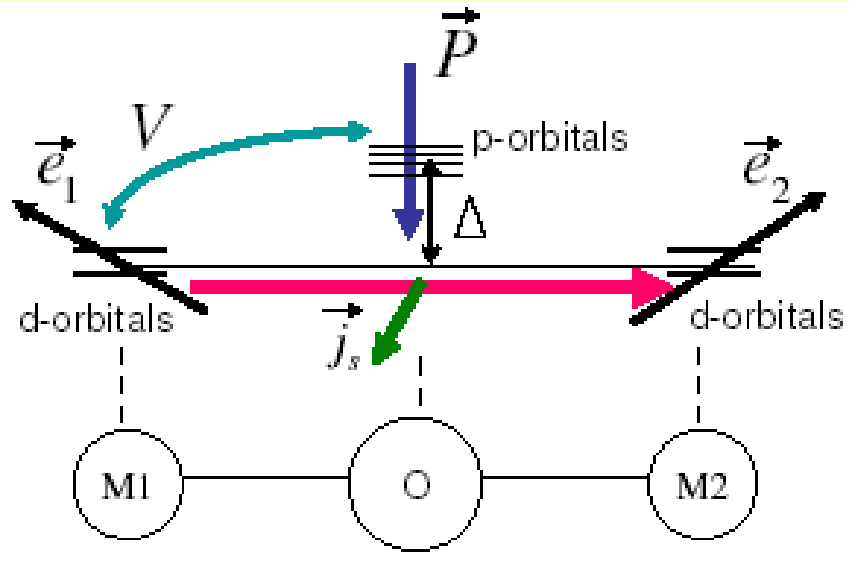
Spiral spin structure

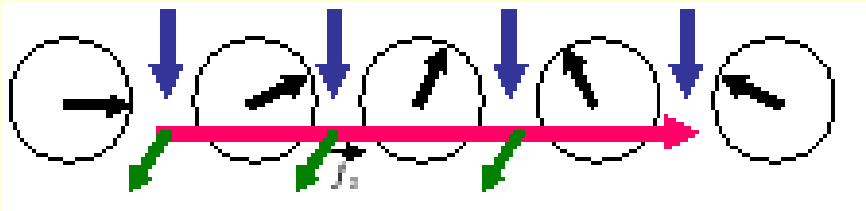


Apparent relation between polarization and magnetic spiral structure

M. Kenzelmann et al., Phys. Rev. Lett. **95**, 087206 (2005)
T. Arima et al., Phys. Rev. Lett. **96**, 097202 (2006)
(Courtesy T. Kimura)

Spin Spirals as Source of Polarization





e_1, e_2:	magnetic moment
P:	polarization
j_s:	"spin current"
→	$\vec{P} \sim \vec{r}_{M1\text{-}M2} \times (\vec{S}_i \times \vec{S}_j)$

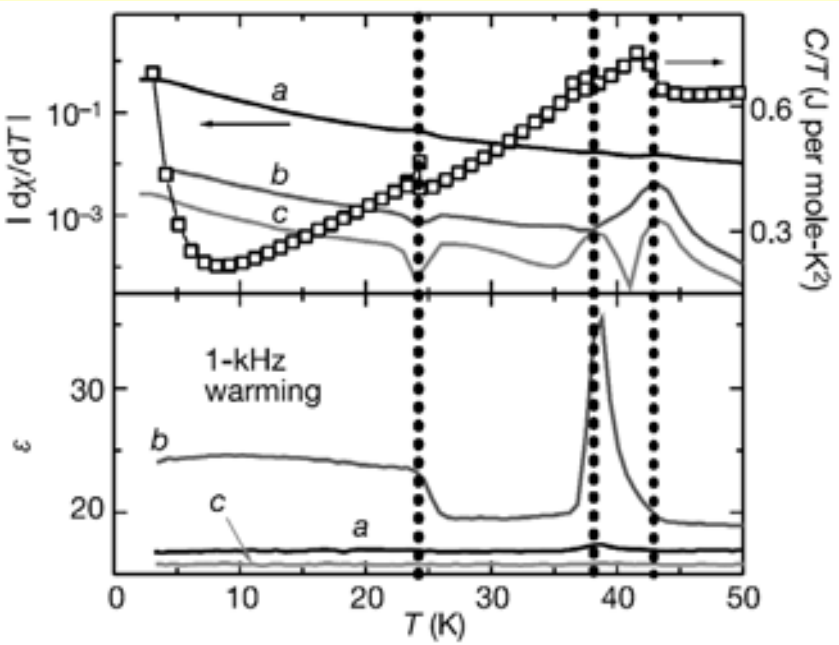
Katsura et al., Phys. Rev. Lett. **95**, 057205 (2005)

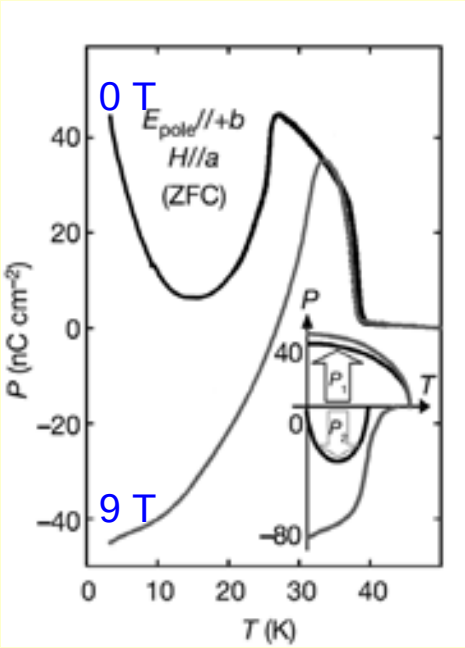
(Courtesy T. Kimura)

Spiral magnetism

- Breaks time and space inversion symmetry
- Allows a term $P \propto r_{M1\text{-}M2} \times (S_1 \times S_2)$ with the properties of an electric polarization
- Magnetic asymmetry induces ferroelectricity
- Magnetic field modifies the spiral structure and therefore the polarization

Magnetic Control of Ferroelectricity in $TbMn_2O_5$

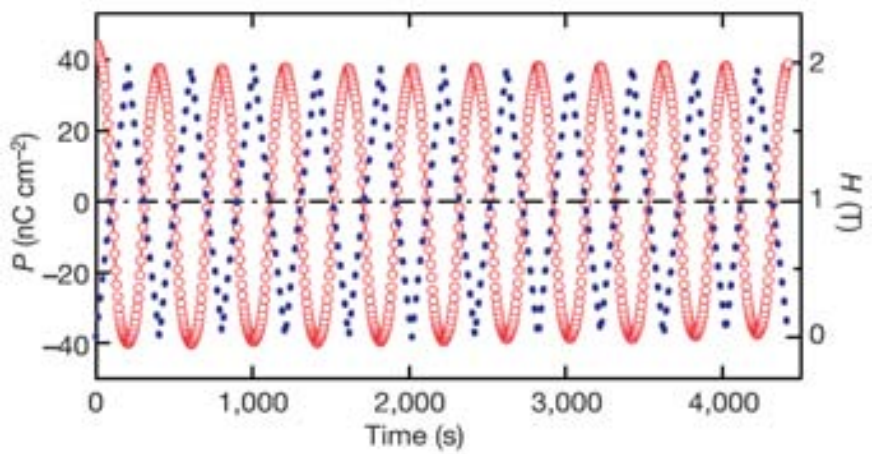




$P = P_1 + P_2(H)$
Allows to reverse plarization in magnetic field *without* changing the directions of P_1 and P_2 → full reversibility

- Simultaneous response of magnetic and electric properties
- Points to spin-spiral ferro-electricity as in Tb_2MnO_5

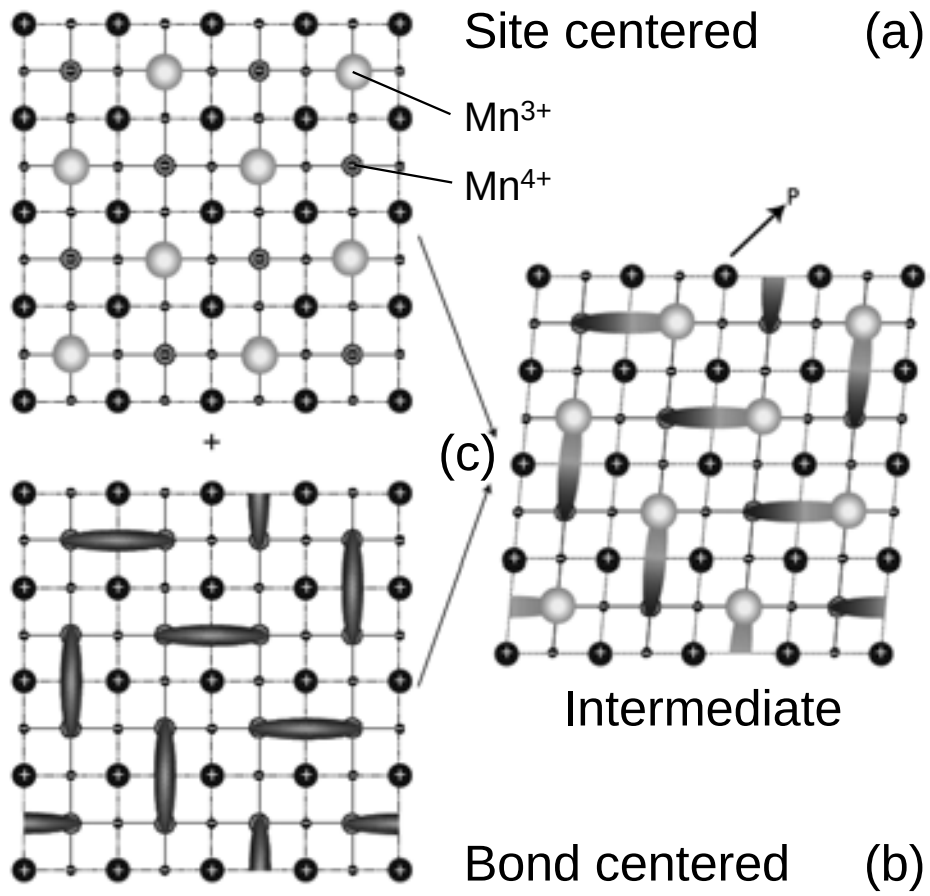
N. Hur et al., Nature **429**, 392 (2004)



Modified types of Ferroelectricity (5)

Electronic ferroelectricity: electron shift replaces ion shift

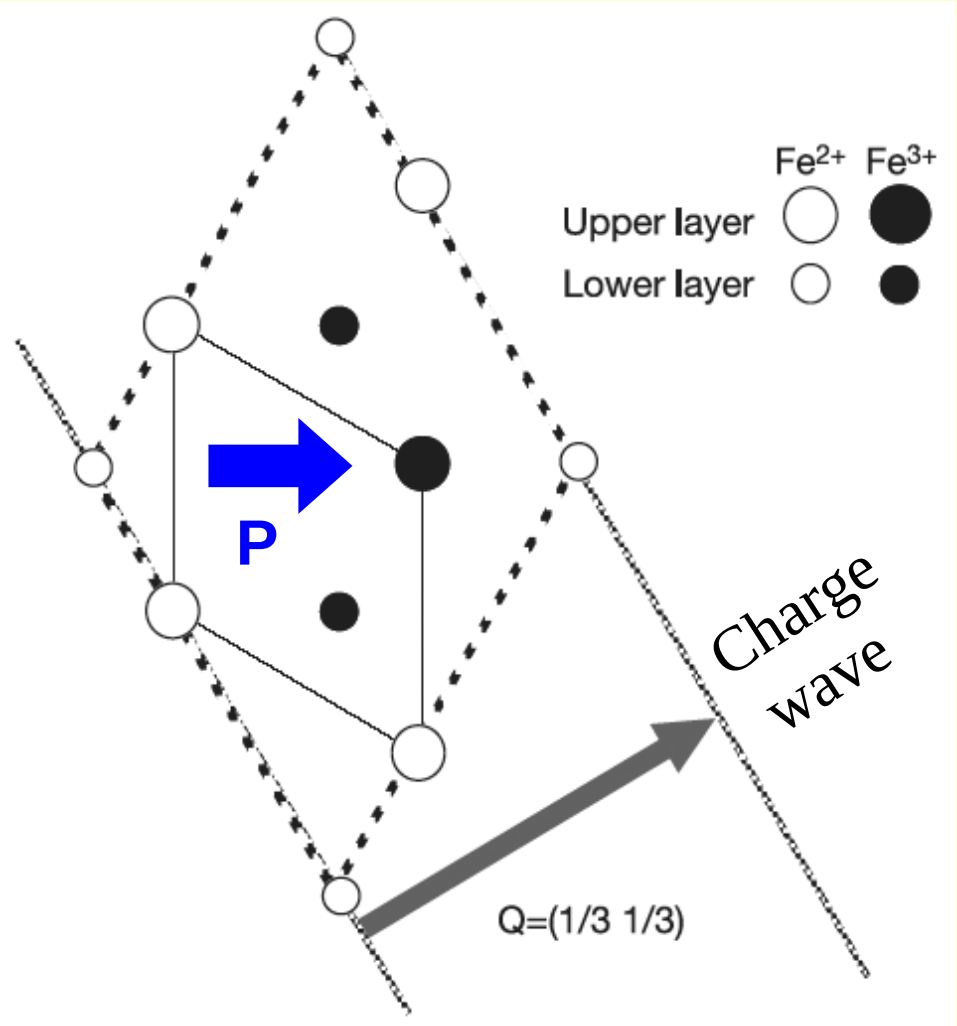
Mn^{3+} electron localization in colossal magnetoresistive $Pr_{1-x}Ca_xMnO_3$



- In the intermediate case symmetry is reduced and allows the formation of a magnetization - induced ferroelectric polarization
- Observed very recently: C. Jooss et al., Proc. Nat. Acad. Sci. USA (2007)

D.V. Efremov et al., N. Mater **3**, 853 (2004)
C. Ederer et al., N. Mater **3**, 849 (2004)

Electronic Ferroelectricity in $LuFe_2O_4$



Charge order

⇓

Asymmetry

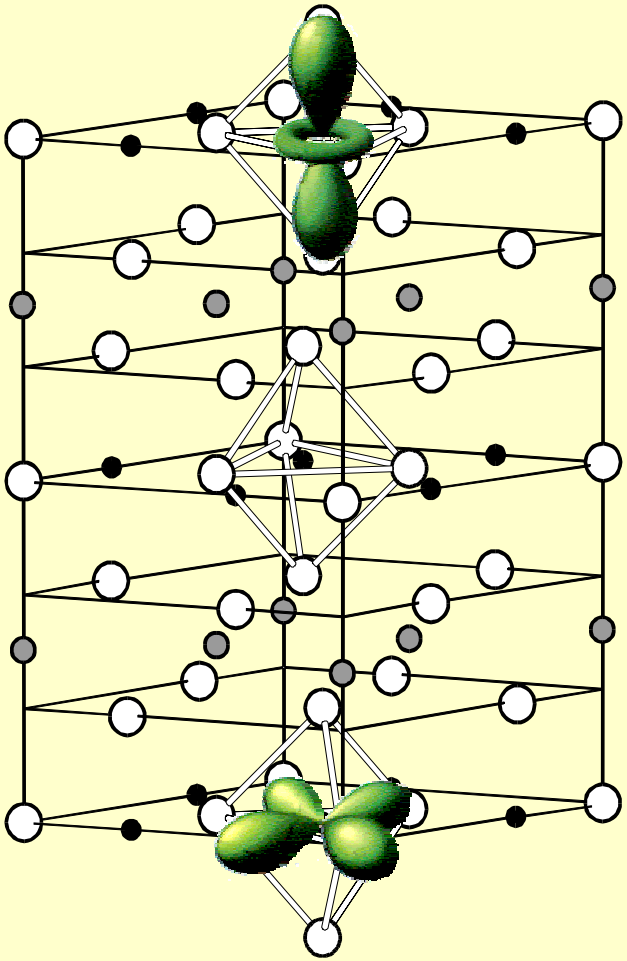
⇓

Spontaneous polarization

N. Ikeda et al., Nature **436**, 1136 (2005)

Modified types of Ferroelectricity (6)

Anisotropic coexistence of ferroelectricity and magnetism



d_{z^2}

Empty:
hybridization
⇓
ferroelectricity

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

d_{xy}

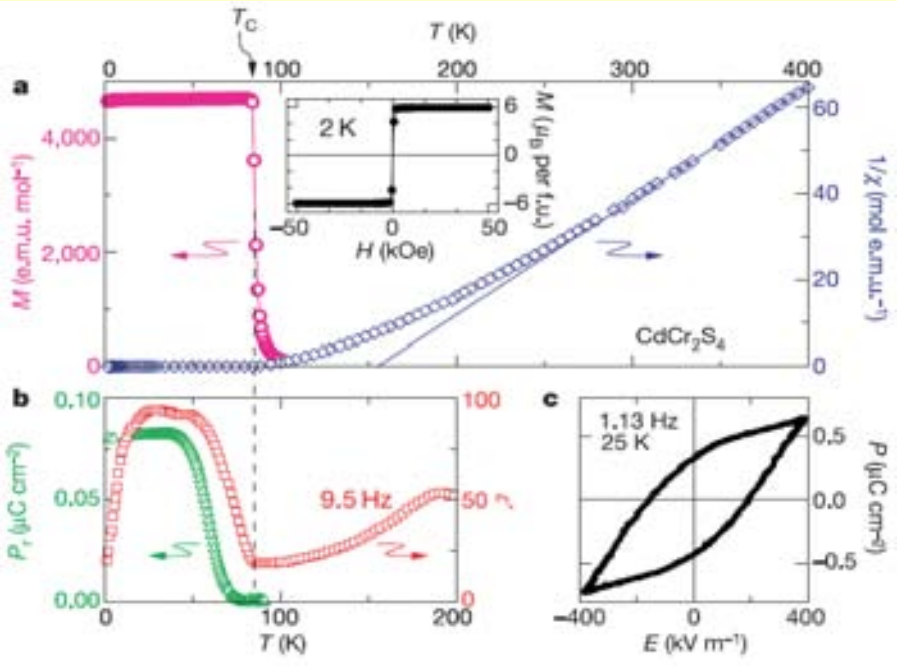
Filled:
exchange
⇓
magnetic order

R^{3+} O^{2-} Mn^{3+}

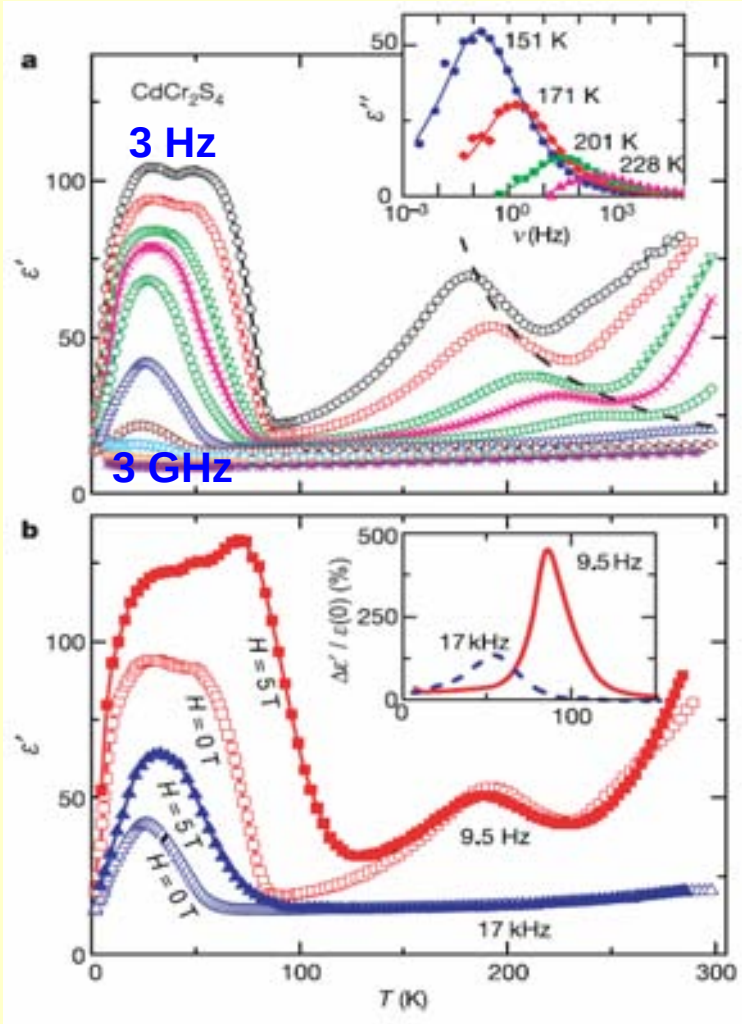
Assumed for $YMnO_3$ but discarded later

Modified types of Ferroelectricity (7)

Relaxor ferroelectricity



J. Hemberger et al., Nature **434**, 364 (2005)



$CdCr_2S_4$:

- Relaxor (smeared out) ferroelectricity
- Weak ferromagnetism

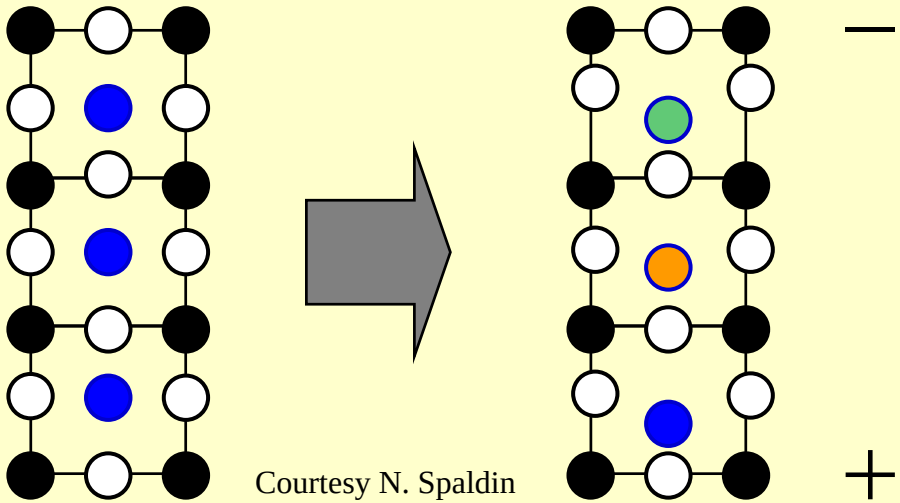
Exhibits colossal magnetocapacitance

Modified types of Ferroelectricity (8)

Compositional inversion symmetry breaking

Creating asymmetry by

- Tricolor superlattices (ABCABC...)
- Ordered substitution ($RAO_3 \rightarrow R_2AA'O_6$)



Courtesy N. Spaldin

Composition (e.g.)

$CaTiO_3$, $SrTiO_3$, $BaTiO_3$

Asymmetry leads to

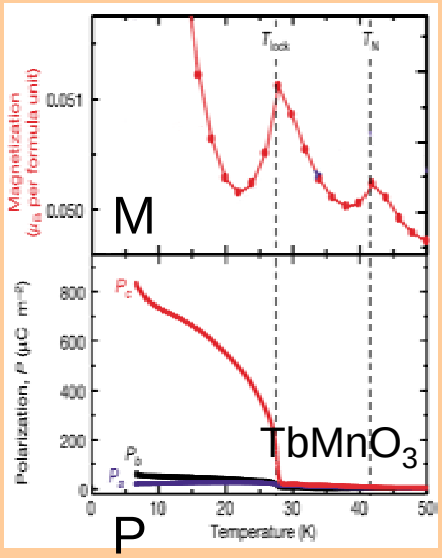
- P, M at interface
- P, M in the bulk

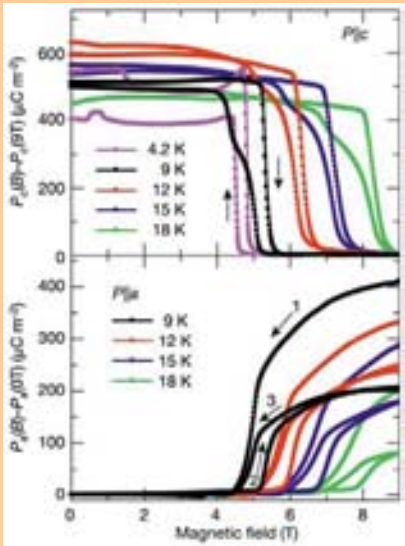
Prediction: N. Sai, et al., Phys. Rev. Lett. **84**, 5636 (2000)

Experiment: M. P. Warusawithna et al., Phys. Rev. Lett. **90**, 036802 (2003)

Magnetoelectric Phase Control in Multiferroics

Electric phase control by a magnetic field



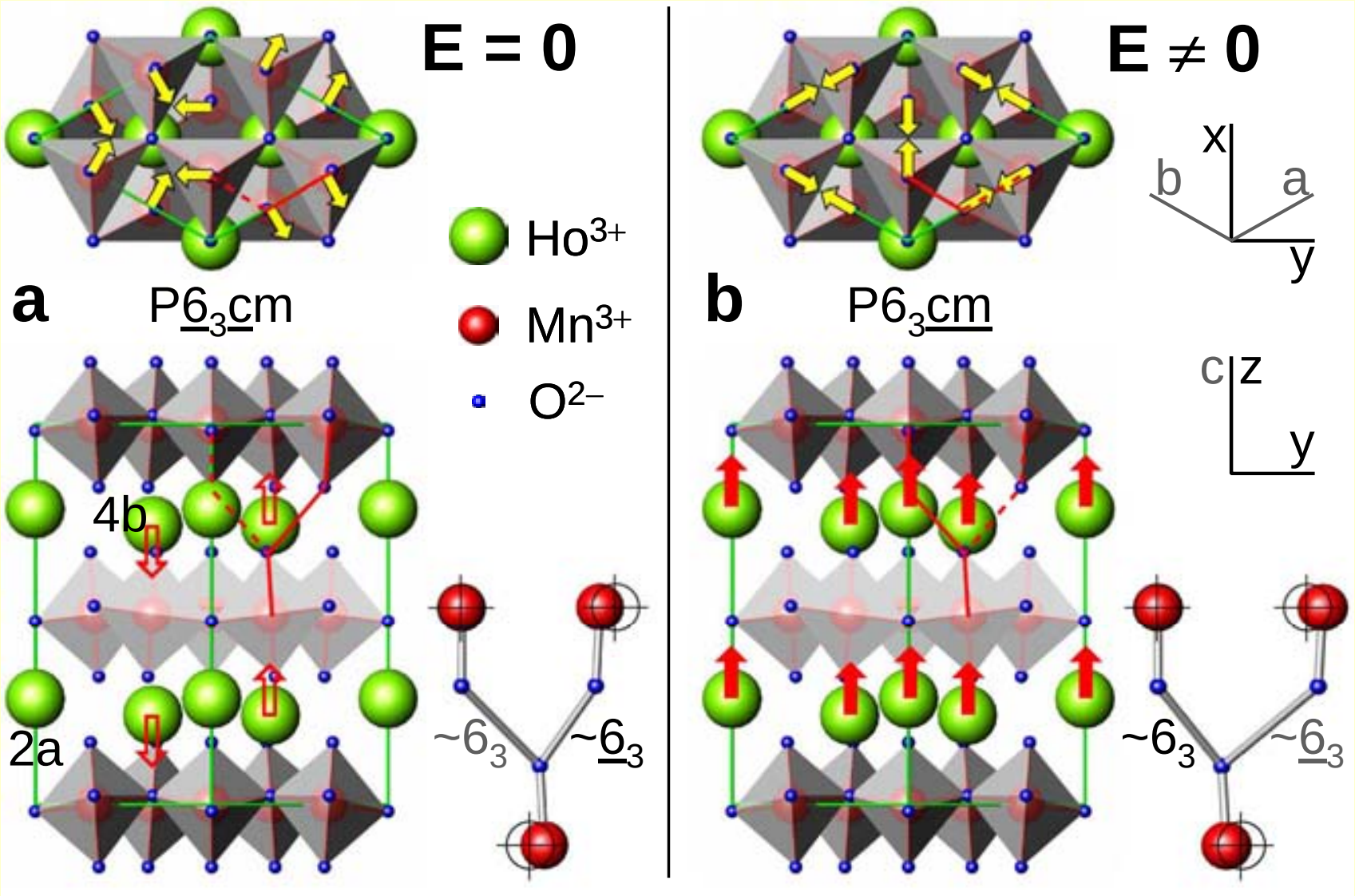


T. Kimura et al., Nature **426**, 55 (2003)

Magnetic phase control by an electric field

?

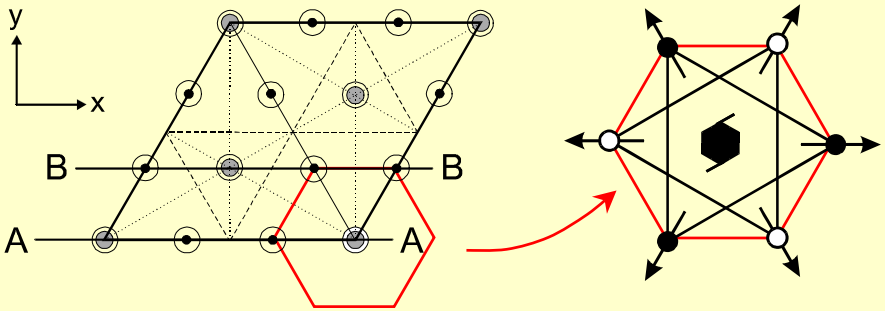
Magnetic Phase Control by Electric Field in $HoMnO_3$

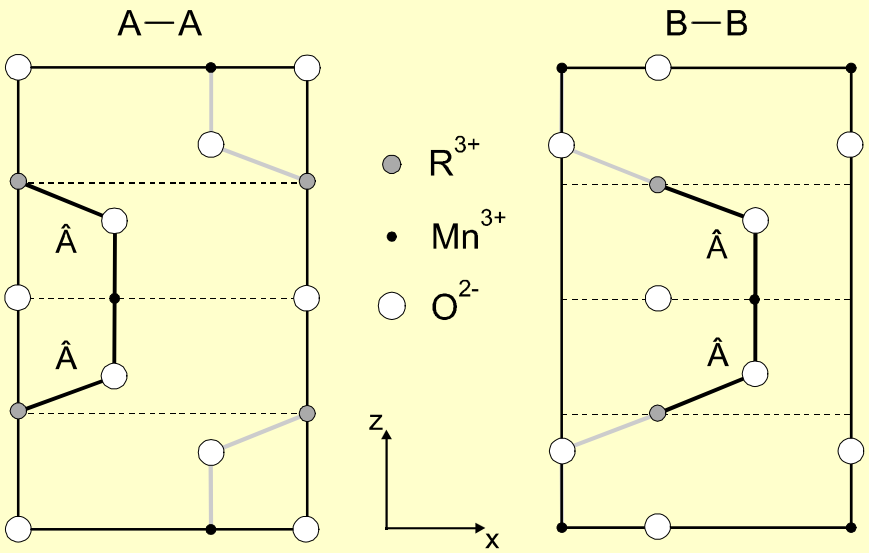


T. Lottermoser et al., Nature **430**, 541 (2004)

3*d* - 4*f* Superexchange in Dielectric $RoMnO_3$

Ferroelectric distortion neglected:





M. Fiebig et al., Phys. Rev. Lett. **88**, 027203 (2002)

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

- k: R sites with 3 and 3m symmetries
- i_k: all R ions at k sites (4+2)
- j: 6 Mn ions neighboring an R ion
- A: Mn-R exchange matrix (4 types)
- S: spins of Mn and R ions

Only one 3*d*–4*f* superexchange path: Â

Superexchange energy:

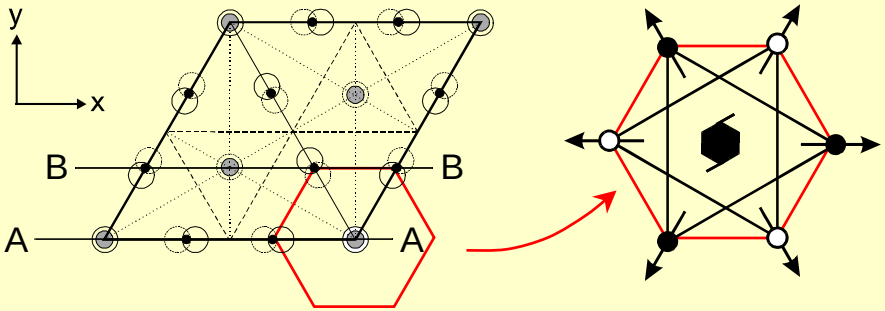
$$H_{\rm ex} = 6\ell\, S^{\rm Er} S^{\rm Mn} \left[(A_{zx} - A_{zx}) - (A_{zx} - A_{zx})\right]$$

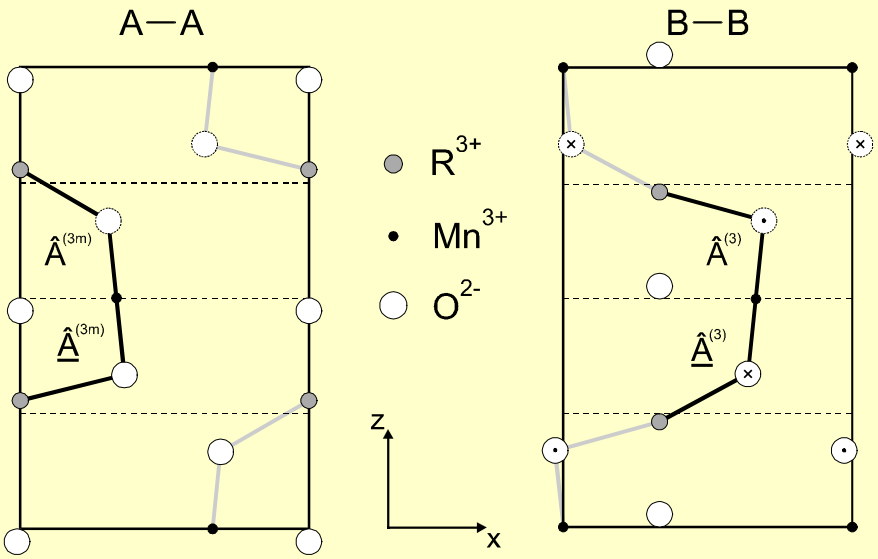
➢➢➢ $H_{\rm ex} = 0$ ⮜⮜⮜

- ➢ Cancellation of the contributions to the superexchange energy
- ➢ Because of the equality of all the superexchange paths

$3d$ - $4f$ Superexchange in Ferroelectric $RMnO_3$

Ferroelectric distortion included:





M. Fiebig et al., Phys. Rev. Lett. **88**, 027203 (2002)

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

- 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

Four exchange paths: $\hat{A}^{3m}$, $\underline{\hat{A}}^{3m}$, $\hat{A}^{3}$, $\underline{\hat{A}}^{3}$

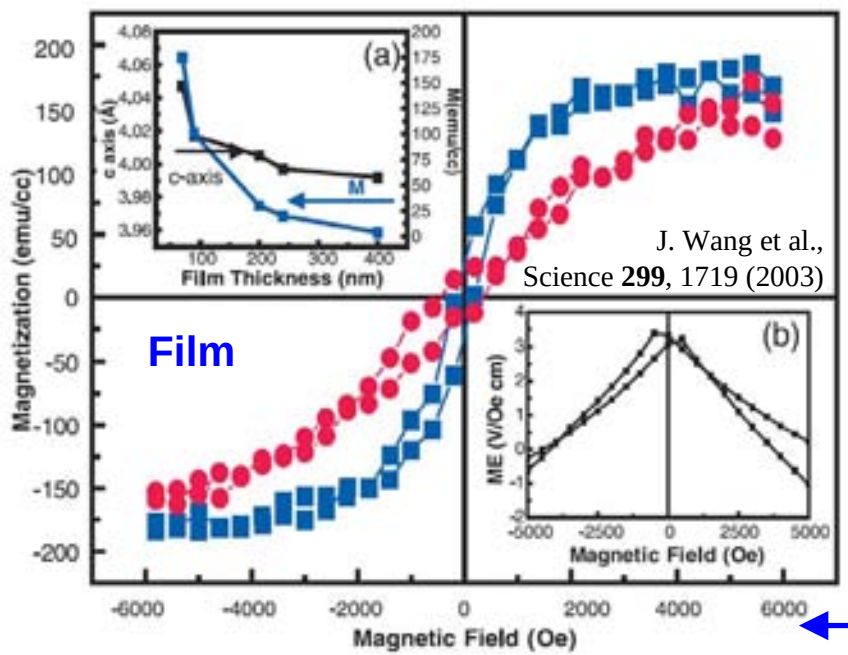
Superexchange energy:

$$H_{\text{ex}} = 6\ell\, S^{\text{Er}} S^{\text{Mn}} \left[(A^{3m}_{zx} - \underline{A}^{3m}_{zx}) - (A^{3}_{zx} - \underline{A}^{3}_{zx}) \right]$$

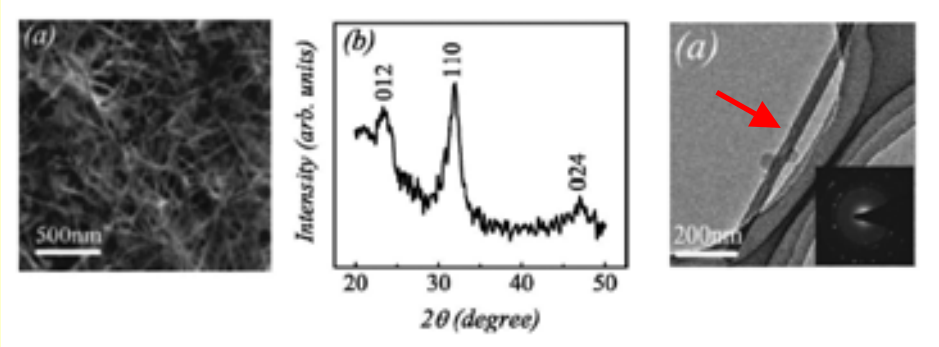
➢➢➢ $H_{\text{ex}} \neq 0$ ⮜⮜⮜

- ➢ Ferroelectric distortion breaks symmetry of Er^{3+}–Mn^{3+} superexchange
- ➢ Represents magnetoelectric interaction on the microscopic scale

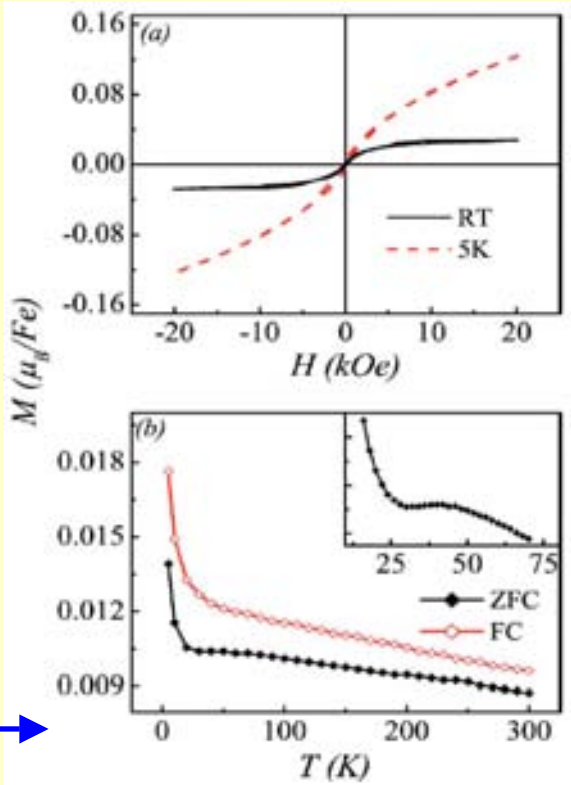
Multiferroic Films and Wires: $BiFeO_3$



J. Wang et al., Science **299**, 1719 (2003)



J. Wang et al., Science **299**, 1719 (2003)



F. Gao et al., Appl. Phys. Lett. **89**, 102506 (2003)

$BiFeO_3$: multiferroic with the highest ordering temperatures:

Electric: $T_C = 1103$ K
Magnetic: $T_N = 643$ K

Bulk: $P \neq 0$, $M = 0$ (spin spiral)
Film: P enhanced, $M \neq 0$
Wire: $M \neq 0$ at RT, $M = 0$ at LT

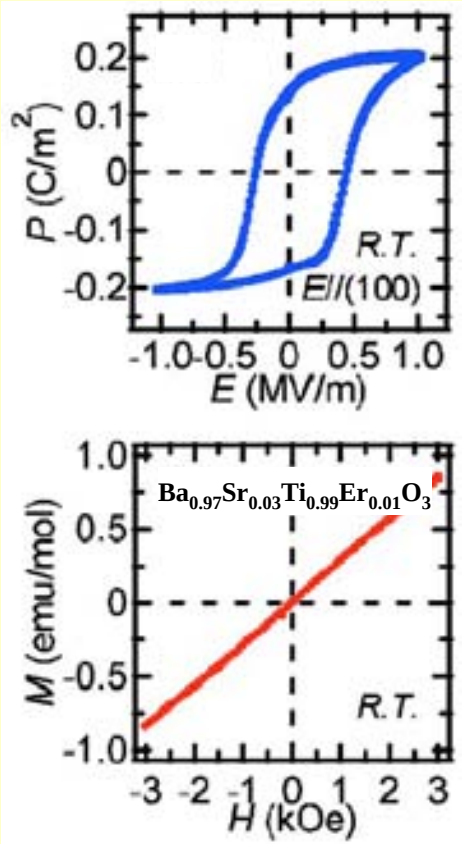
Magnetoelectric Correlations in Multiferroics

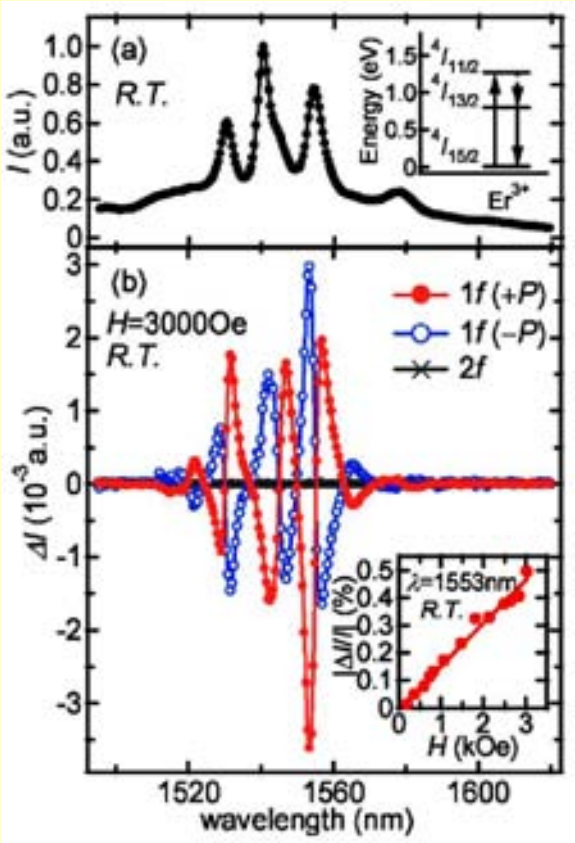
- The magnetoelectric effect & multiferroics: early history
- Composite "pseudo" multiferroics
- Intrinsic, single-phase multiferroics
- **Magnetoelectric effect in the IR to visible range**
- New concepts
- Conclusion & outlook

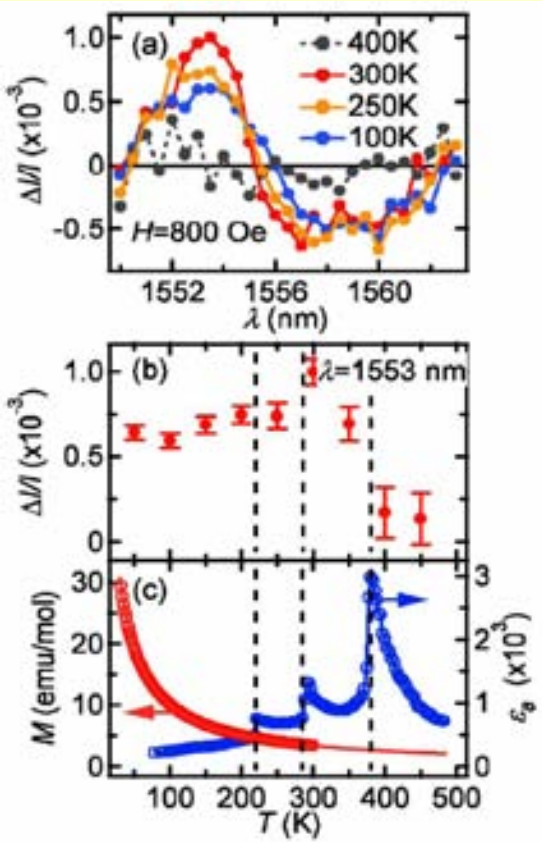
Optical Magnetoelectric Effect in $(Ba,Sr)TiO_3$:Er

$$\delta P(\omega) = \underbrace{(\beta(\omega)H_0/\omega\mu)}_{\text{Magnetic-field induced ME effect}}\ \underbrace{k\times E(\omega)}_{H(\omega)}$$

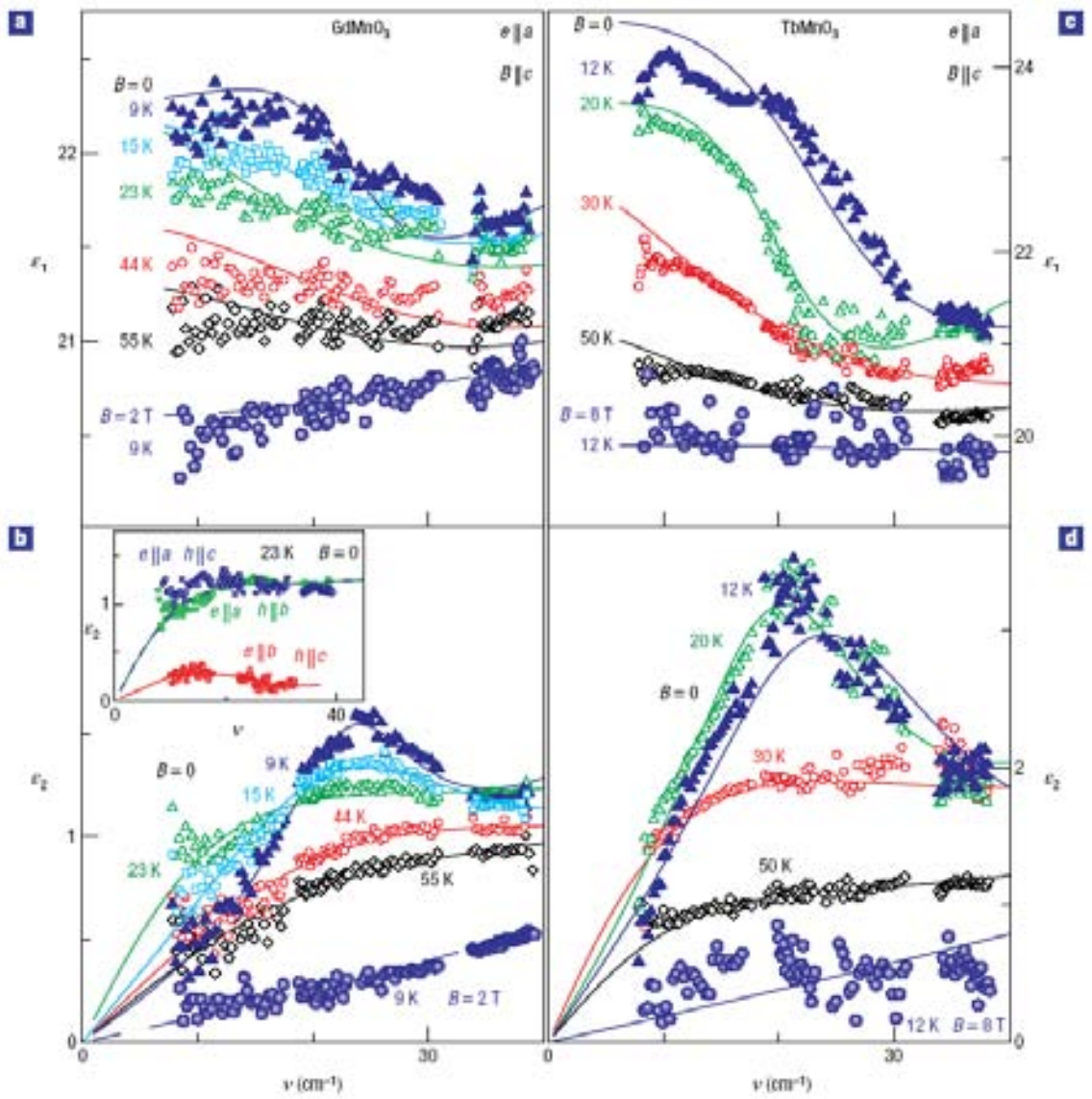
- ✓ Observed δP scales linearly with H_0
- ✓ Reversal of β upon reversal of P
- ✓ $\delta P \rightarrow 0$ at ferroelectric T_C







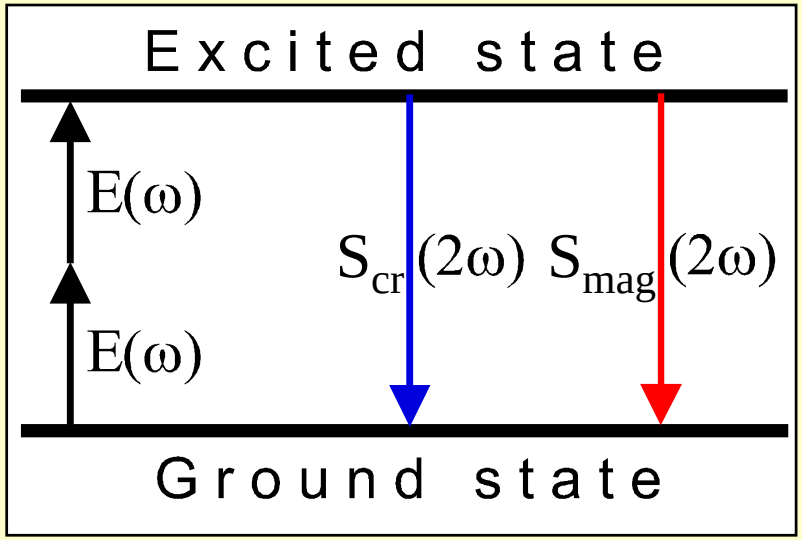
"Electromagnons" in $GdMnO_3$ and $TbMnO_3$



- A far-infrared resonance in the dielectric function
- Quenched by magnetic phase transition through:
  - Temperature increase
  - Magnetic field
- Mixed magnon-dielectric state
- "electromagnon"

A. Pimenov et al., N. Physics **2**, 97 (2006)

Second Harmonic Generation for Probing Multiferroics



Incident laser beam

Nonlinear signal:

electrical magnetic

Interference !

SHG: $\mathbf{S_i(2\omega) \propto \chi_{ijk}\, E_j(\omega)\, E_k(\omega)}$

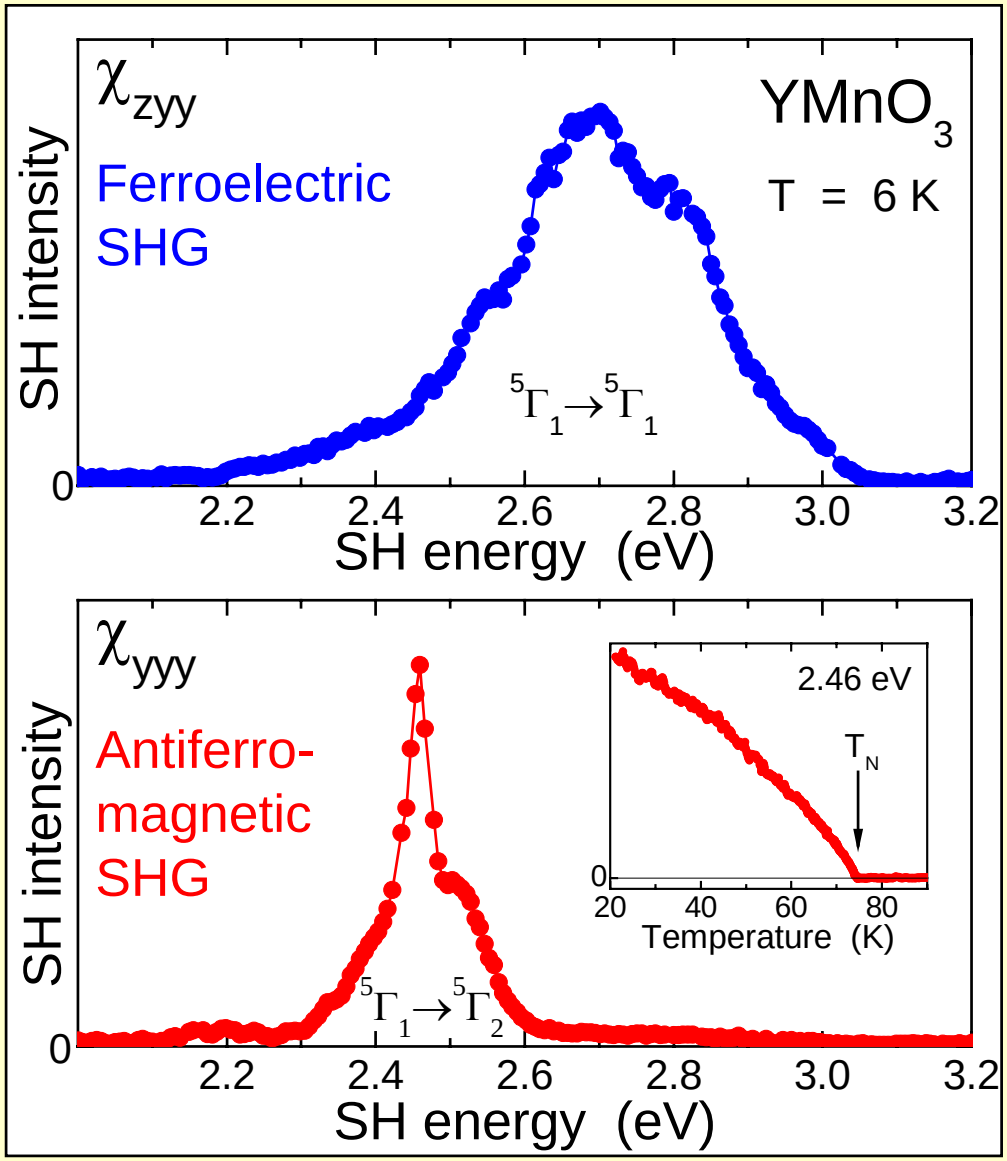
- Access to magnetic *and* electrical structure with the *same* technique
- Only based on symmetry arguments: $\chi_{ijk} \leftrightarrow$ symmetry $\leftrightarrow$ structure

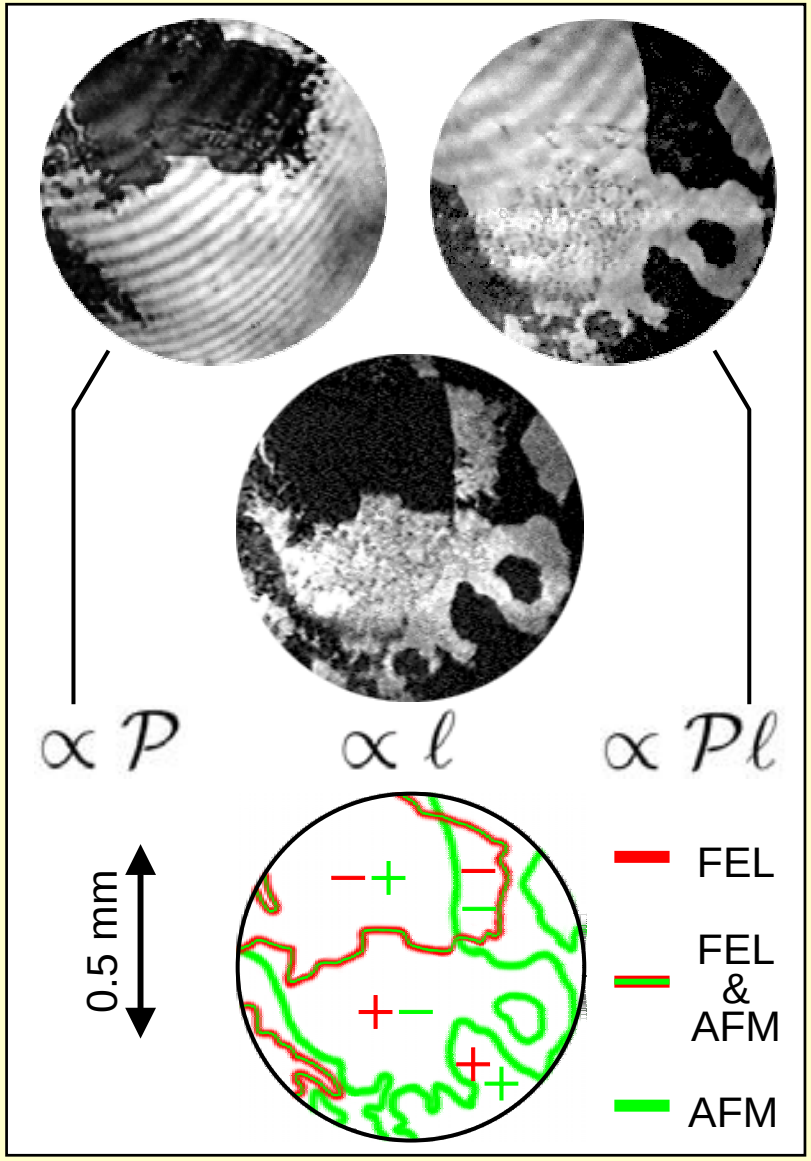
Optical degrees of freedom:

- Spectroscopy: Excitation and emitted signal are sublattice selective
- Spatial resolution: imaging of domain structures, inhomogeneities
- Temporal resolution: dynamics down to sub-picosecond range

Nonlinear optics: particularly suitable for probing multiferroic phase coexistence

Second-Harmonic Spectroscopy of $YMnO_3$





Magnetoelectric Correlations in Multiferroics

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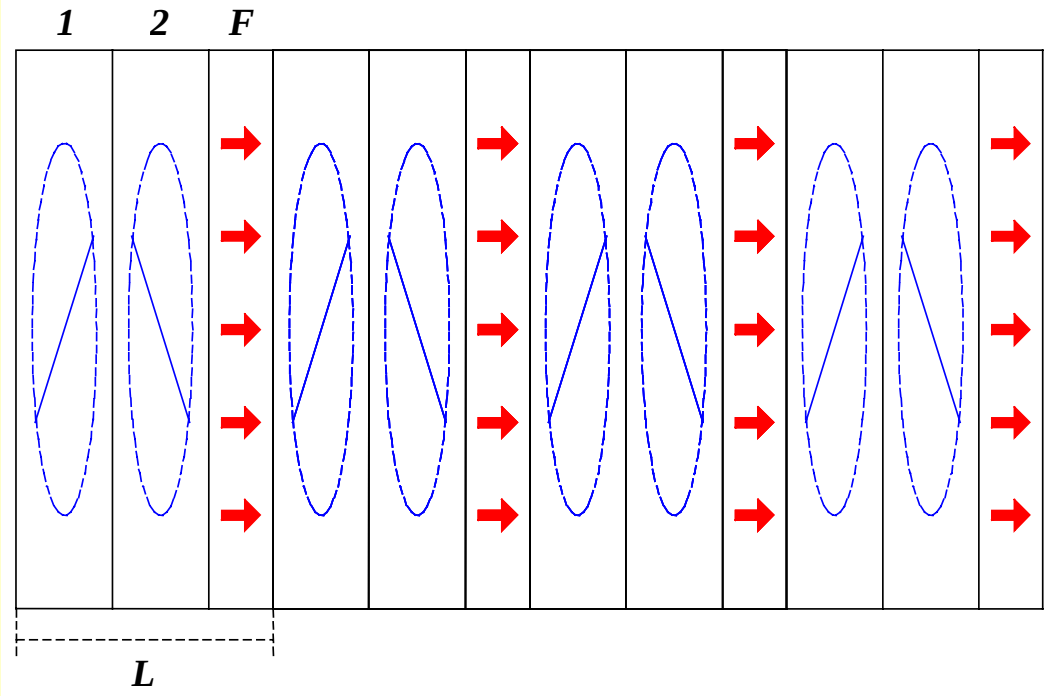
- Intrinsic, single-phase multiferroics
- Magnetoelectric effect in the IR to visible range
- New concepts
- Conclusion & outlook

Magnetoelectric Photonic Crystals



Three-layer superlattice with:

1: Dielectric, orientation 1

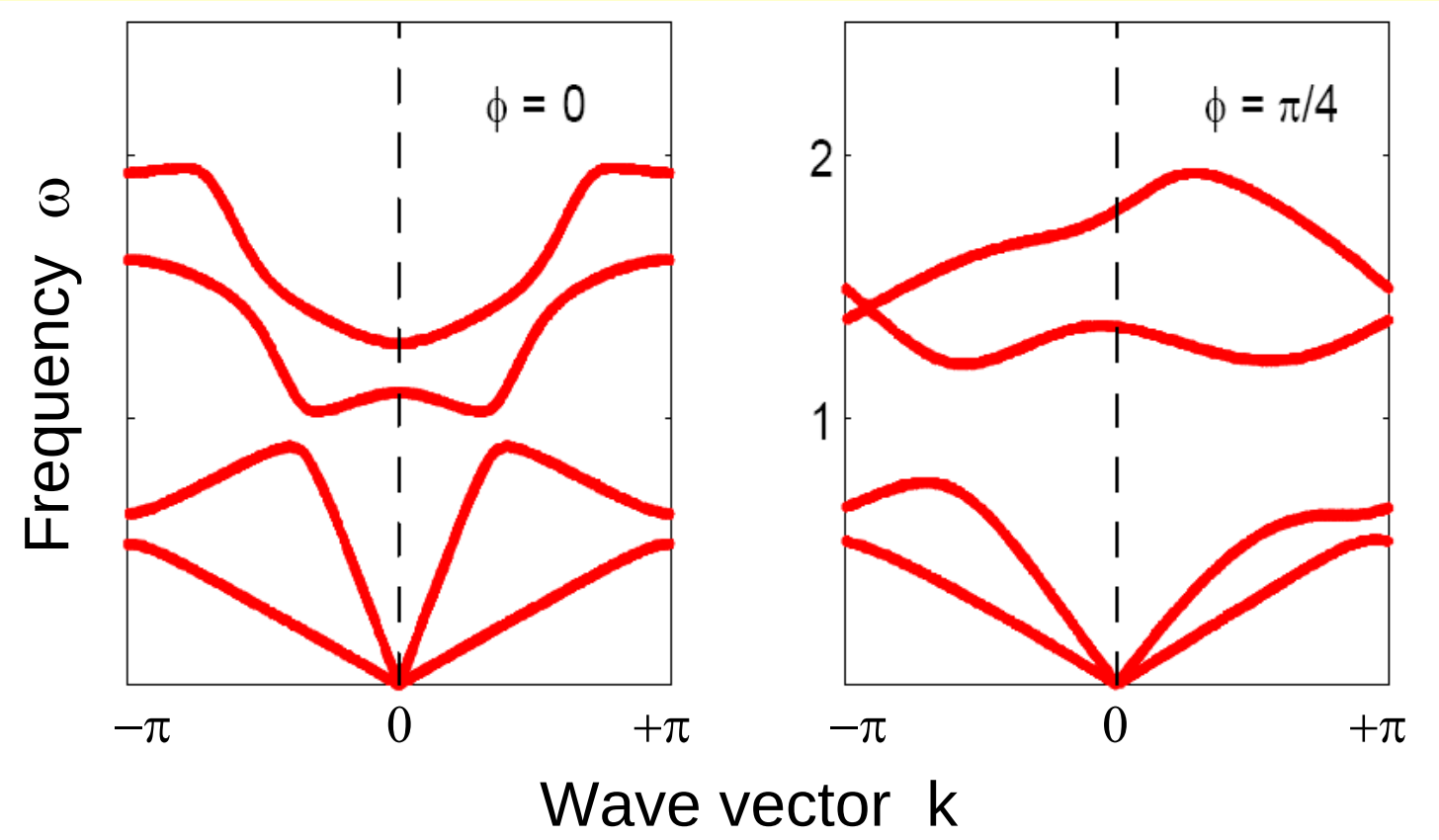
2: Dielectric, orientation 2

F: Ferromagnetic layer

Superlattice properties:

- Breaks space- and time-inversion symmetry
- Asymmetric dispersion: $\varepsilon(\omega) \neq \varepsilon(-\omega)$, $\omega(k) \neq \omega(-k)$
- Novel properties expected (optical and others)

Optical Superlattice Properties

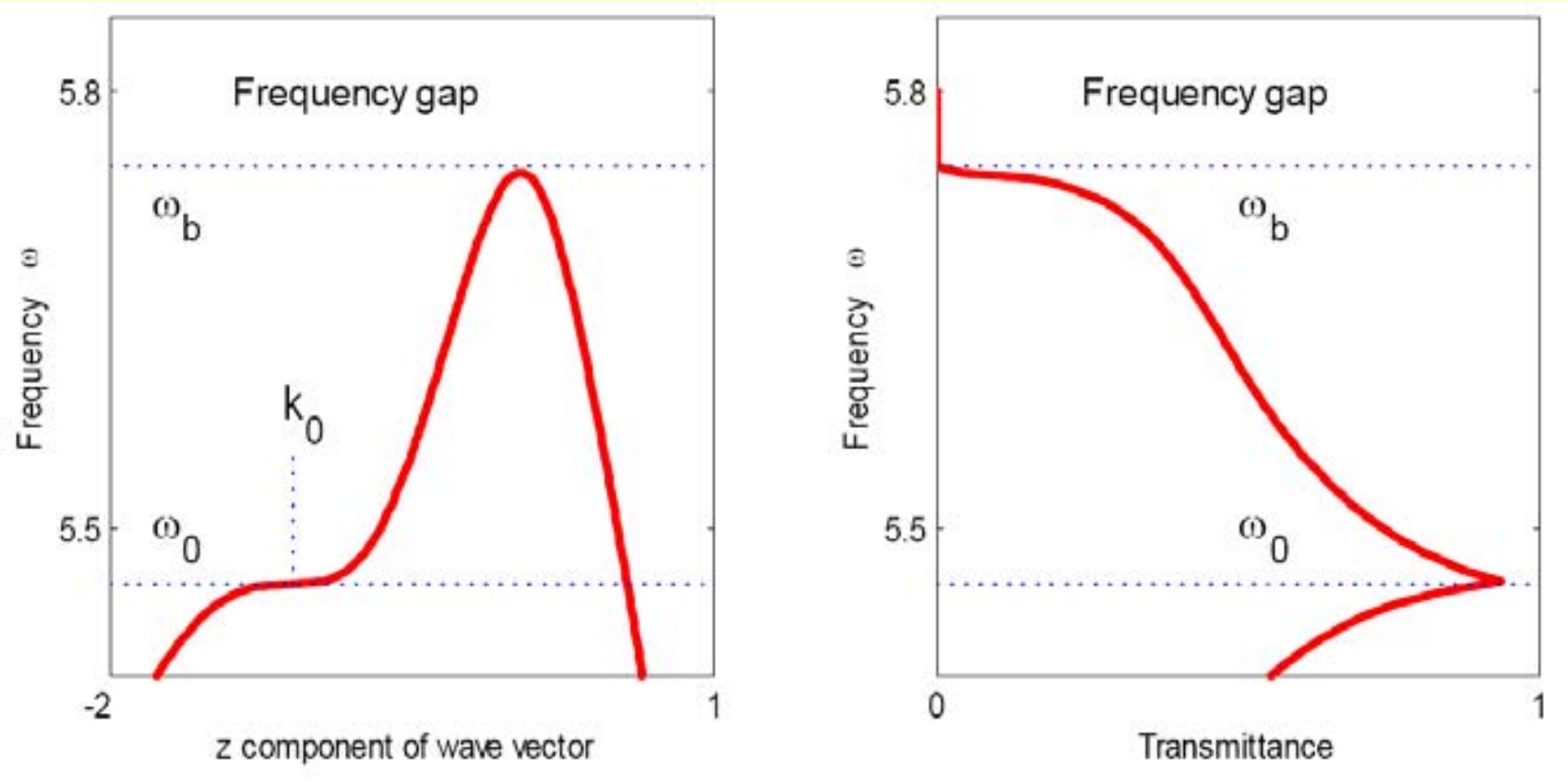


ϕ : Angle of rotation between the dielectric layers

$\rightarrow$ Leads to asymmetric dispersion

Depends on dispersion, dichroism, layer thickness, ϕ

Unidirectional Propagation



- No propagation of light at (ω_0, k_0)
- But at (ω_0, $-k_0$) propagation is possible
- Novel form of optical diode !

For details see:
A. Figotin, I. Vitebskiy,
Phys. Rev. B **67**, 165210 (2003)

What is a "Multiferroic"?

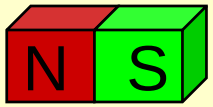
"Crystals can be defined as multiferroic when two or more of the primary ferroic properties [...] are united in the same phase."

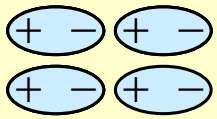
Hans Schmid (University of Geneva, Switzerland) in: M. Fiebig et al. (ed.), *Magnetoelectric Interaction Phenomena in Crystals*, (Kluwer, Dordrecht, 2004)

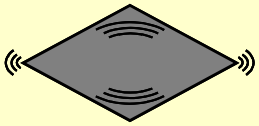
Primary ferroic ↔ formation of switchable domains:

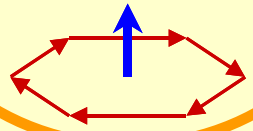
Excludes anti-ferroic forms of ordering

Ferromagnetism	Ferroelectricity	Ferroelasticity	Ferrotoroidicity
spontaneous magnetization	spontaneous polarization	spontaneous strain	spontaneous magnetic vortex





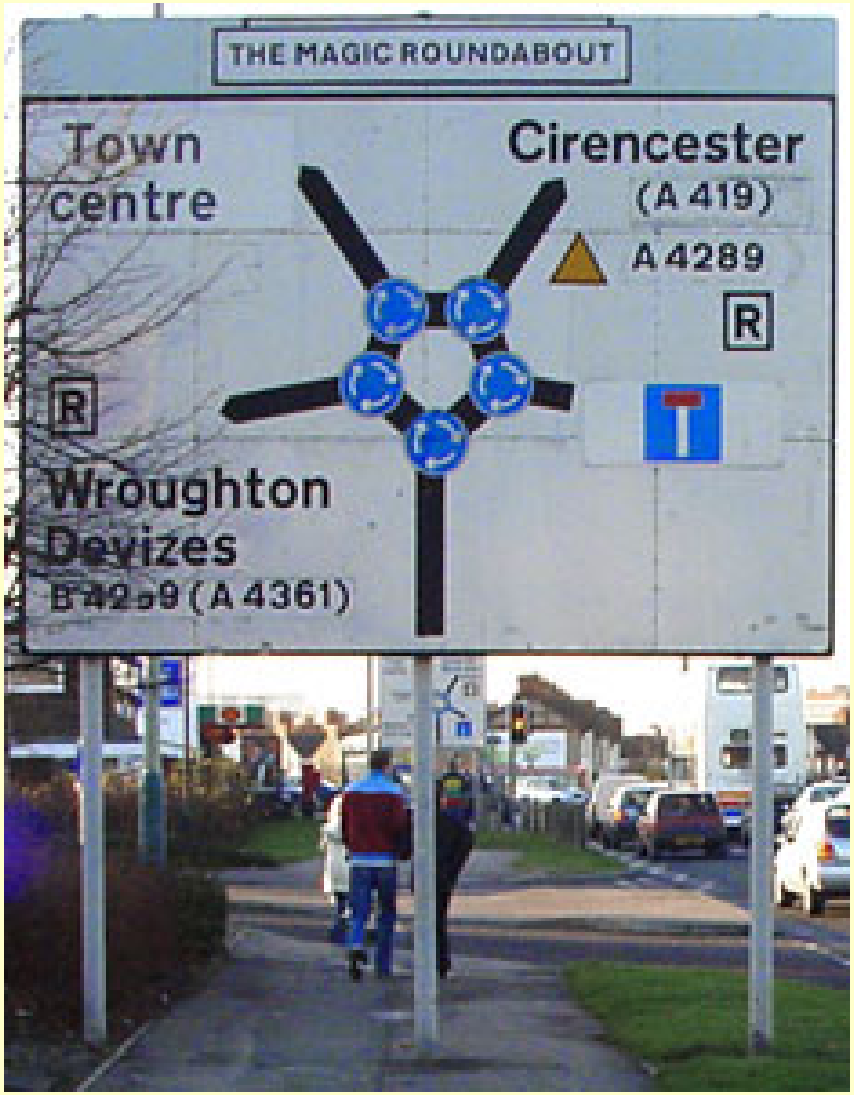




Extension to anti-ferroic forms of ordering:

Compounds consisting of multiferroic sublattices (one or more of) whose primary ferroic properties cancel in the macroscopic crystal

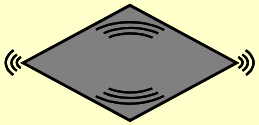
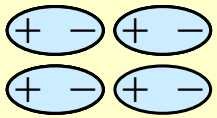
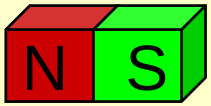
What is a Toroidal Moment?



Not this!

A classification of ferroic properties

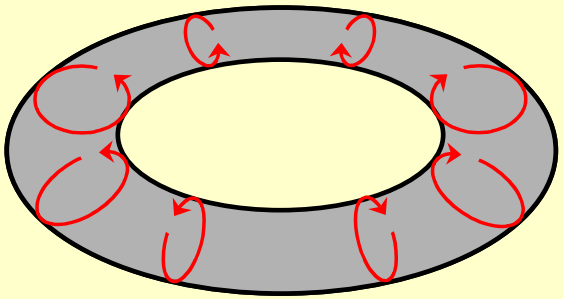
Time \ Space	invariant	change
invariant	ferroelastic	ferroelectric
change	ferromagnetic	???

Time \ Space	invariant	change
invariant		
change		???

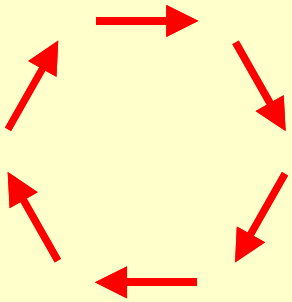
A fourth, time/space asymmetric, ferroic order seems to be missing

Toroidal Moments

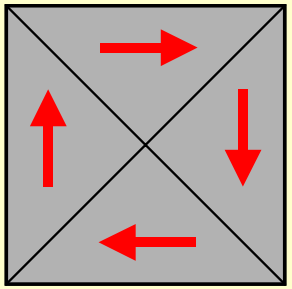
Structures with a toroidal moment ("toroidization"):



Selenoid with even number of windings

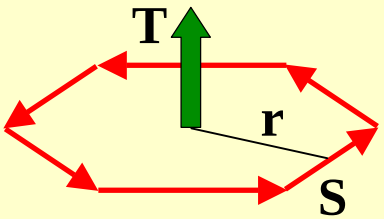


Frustrated antiferromagnets



Ferromagnetic domain structures

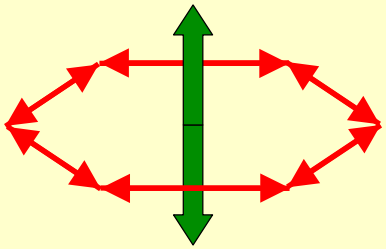
Definition:



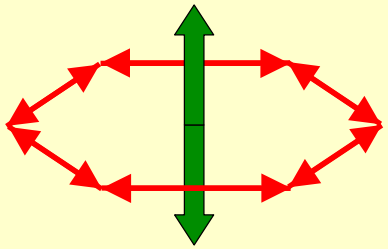
Spin part:

$$\mathbf{T} \propto \sum \mathbf{r} \times \mathbf{S}$$

Time reversal



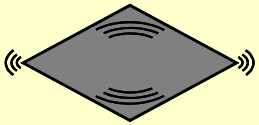
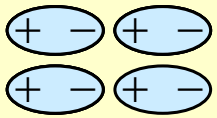
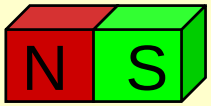
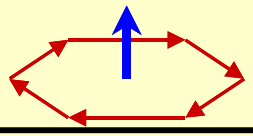
Inversion



T violates time ***and*** space reversal !

A classification of ferroic properties

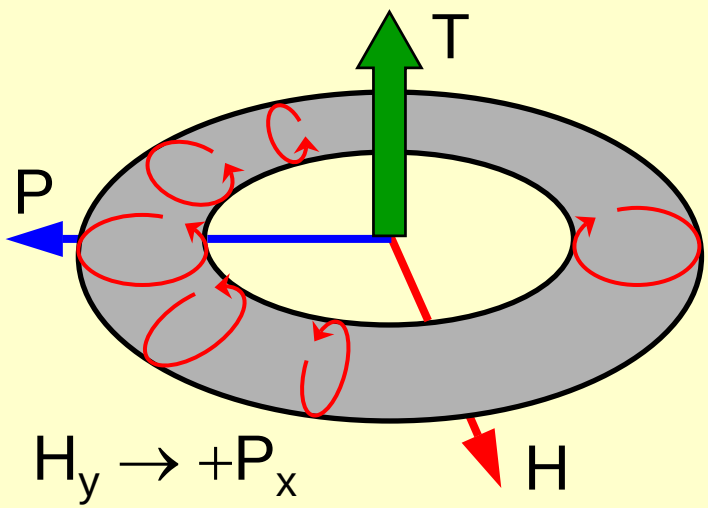
Time \ Space	invariant	change
invariant	ferroelastic	ferroelectric
change	ferromagnetic	ferrotoroidic

Time \ Space	invariant	change
invariant		
change		

Ferrotoroidic order completes the picture !

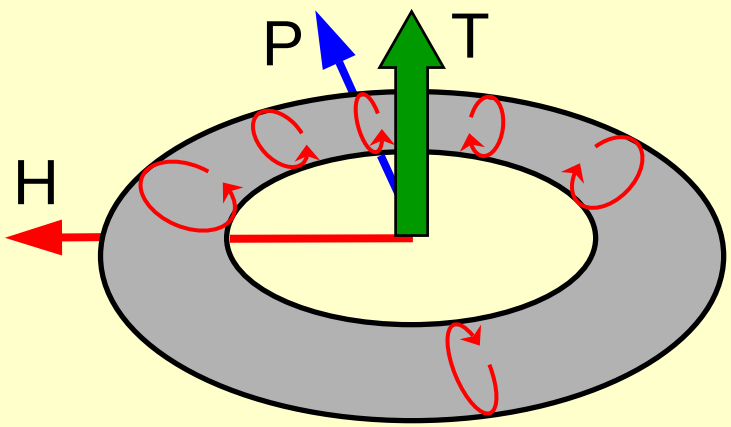
Toroidal Moment and Magnetoelectric Effect

Toroidal moment manifests as off-diagonal component of the magnetoelectric effect $\mathbf{P} = \alpha\mathbf{H}$: $\alpha_{ij} = -\alpha_{ji}$



$H_y \rightarrow +P_x$

$\sim \alpha_{xy}$

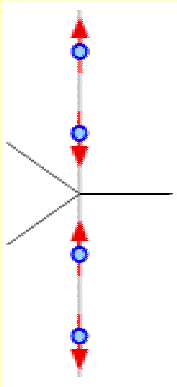


$H_x \rightarrow -P_y$

$\sim \alpha_{yx} = -\alpha_{xy}$

Manifestation of the Toroidal Moment

Asymmetric magnetoelectric coefficient:

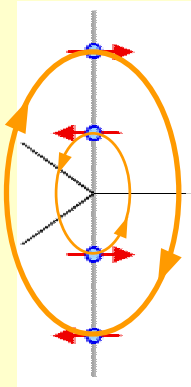


Cr_2O_3 at H = 0:

Symmetry $\bar{3}m$

$\alpha_{xx} = \alpha_{yy}, \alpha_{zz}$

T = 0

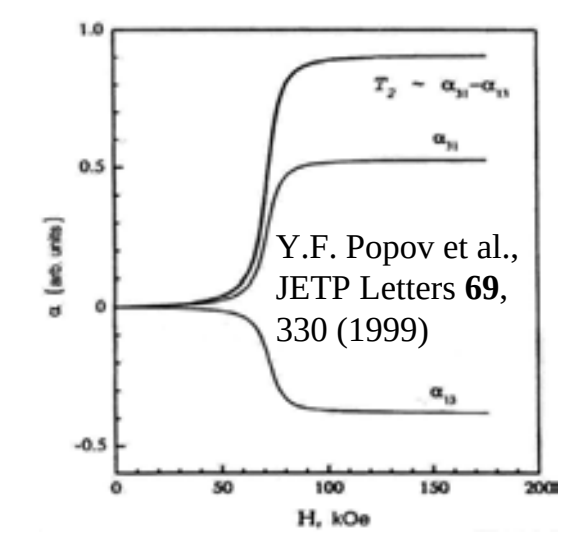


Cr_2O_3 >5.8 T:

Symmetry $2/m$

$\alpha_{xz}, \alpha_{zx}, \alpha_{yz}, \alpha_{zy}$

$T \neq 0$



Divergence of magnetoelectric coefficient:

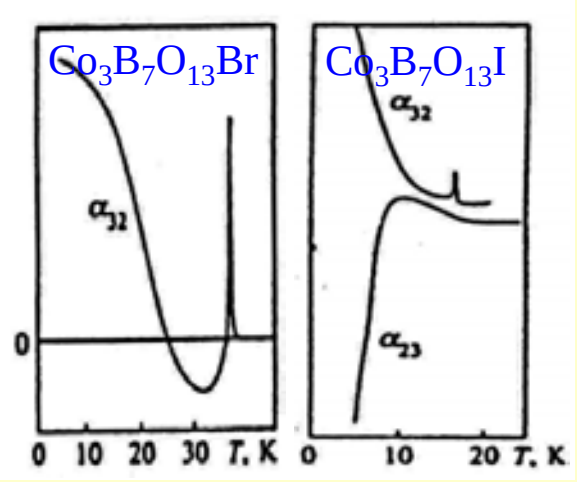
Follows from free energy of toroidal structures

$$\alpha_{32} = \frac{DaP_0}{xBC}\frac{1}{T_1} + \frac{1}{xB}\left(a + \frac{3D^2}{xC}a + \frac{3D}{C}b\right)T_1$$

$$\alpha_{23} = -\frac{a}{\tilde{x}B}T_1$$

Divergence at the ordering temperature

D.E. Sannikov, Ferroelectrics **219**, 177 (1989)



Toroidal domains ???

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Conclusion & Outlook

Types of multiferroics

- Composites for application
- Single-phase compounds for basic research

Synergy effects: interaction between disjunct areas

- Magnetism community & ferro-/dielectrics community
- Application & basic research
- Theory & experiment

Outlook

- Almost no work on thin films
- No work at all on the dynamic properties

The quest for compounds uniting strong ferroelectricity and strong ferromagnetism at 300 K is still far from being solved!

Literature on the Magnetoelectric Effect

An excellent source with many good articles:

Procedings of the MEIPIC series of conferences

***M**agneto**E**lectric **I**nteraction **P**henomena **I**n **C**rystals*

Freeman A J and Schmid H (ed) 1975 *Magnetoelectric Interaction Phenomena in Crystals Proc. MEIPIC-1 (Seattle, USA, 21–24 May 1973)* (London: Gordon and Breach)

Schmid H, Janner A, Grimmer H, Rivera J P and Ye Z G (ed) 1994 *Proc. MEIPIC-2 (Ascona, Switzerland, 13–18 September 1993) Ferroelectrics* **161–162** conference volume

Bichurin M (ed) 1997 *Proc. MEIPIC-3 (Novgorod, Russia, 16–20 September 1996) Ferroelectrics* **204** conference volume

Bichurin M (ed) 2002 *Proc. MEIPIC-4 (Novgorod, Russia, 16–19 October 2001) Ferroelectrics* **279–280** conference volume

Fiebig M, Eremenko V V and Chupis I E (ed) 2004 *Magnetoelectric Interaction Phenomena in Crystals* (Dordrecht: Kluwer) *Proc. MEIPIC-5 (Sudak, Ukraine, 21–24 September 2003)*

For symmetry issues add:

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