Magnetoelectric Multiferroics

History and fundamentals

Single-phase multiferroics

Composite multiferroics

Experimental techniques

Summary, Literature

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ESM 2007, Cluj-Napoca, 14 September 2007

Thanks to M. Fiebig

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."

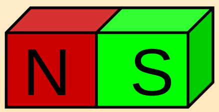
Hans Schmid (University of Geneva, Switzerland)
in: M. Fiebig et al. (ed.), *Magnetoelectric Interaction Phenomena in Crystals*, (Kluwer, Dordrecht, 2004)

Excludes anti-ferroic forms of ordering

Primary ferroic ↔ formation of switchable domains:

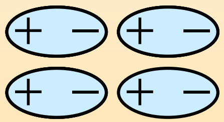
Ferromagnetism

spontaneous magnetization



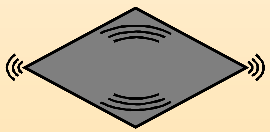
Ferroelectricity

spontaneous polarization



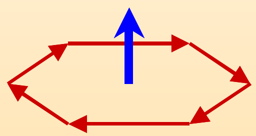
Ferroelasticity

spontaneous strain



Ferrotoroidicity

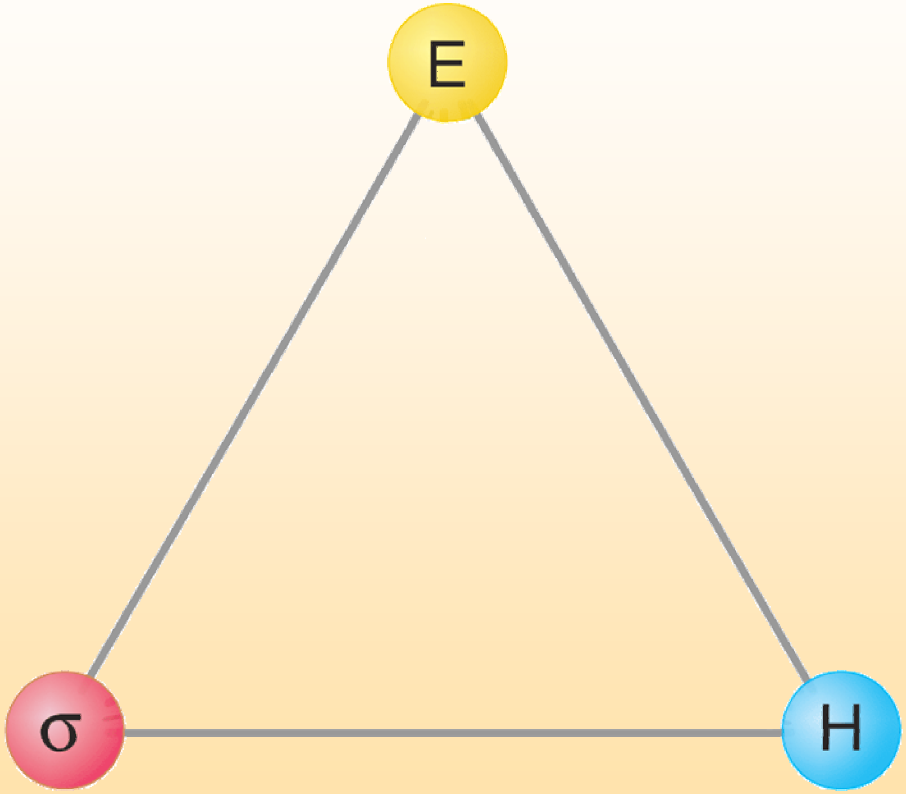
spontaneous magnetic vortex



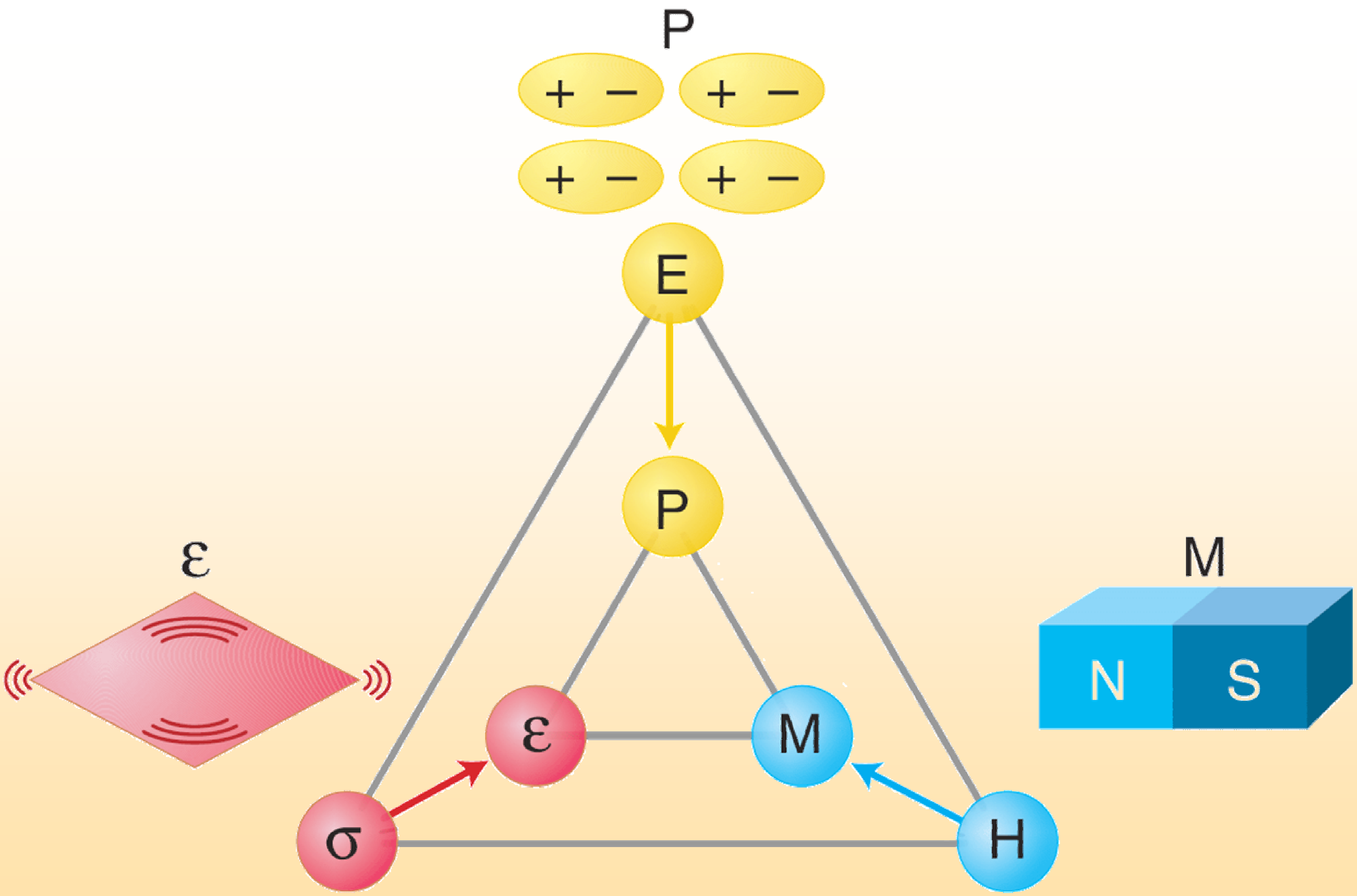
Extension to anti-ferroic forms of ordering:

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

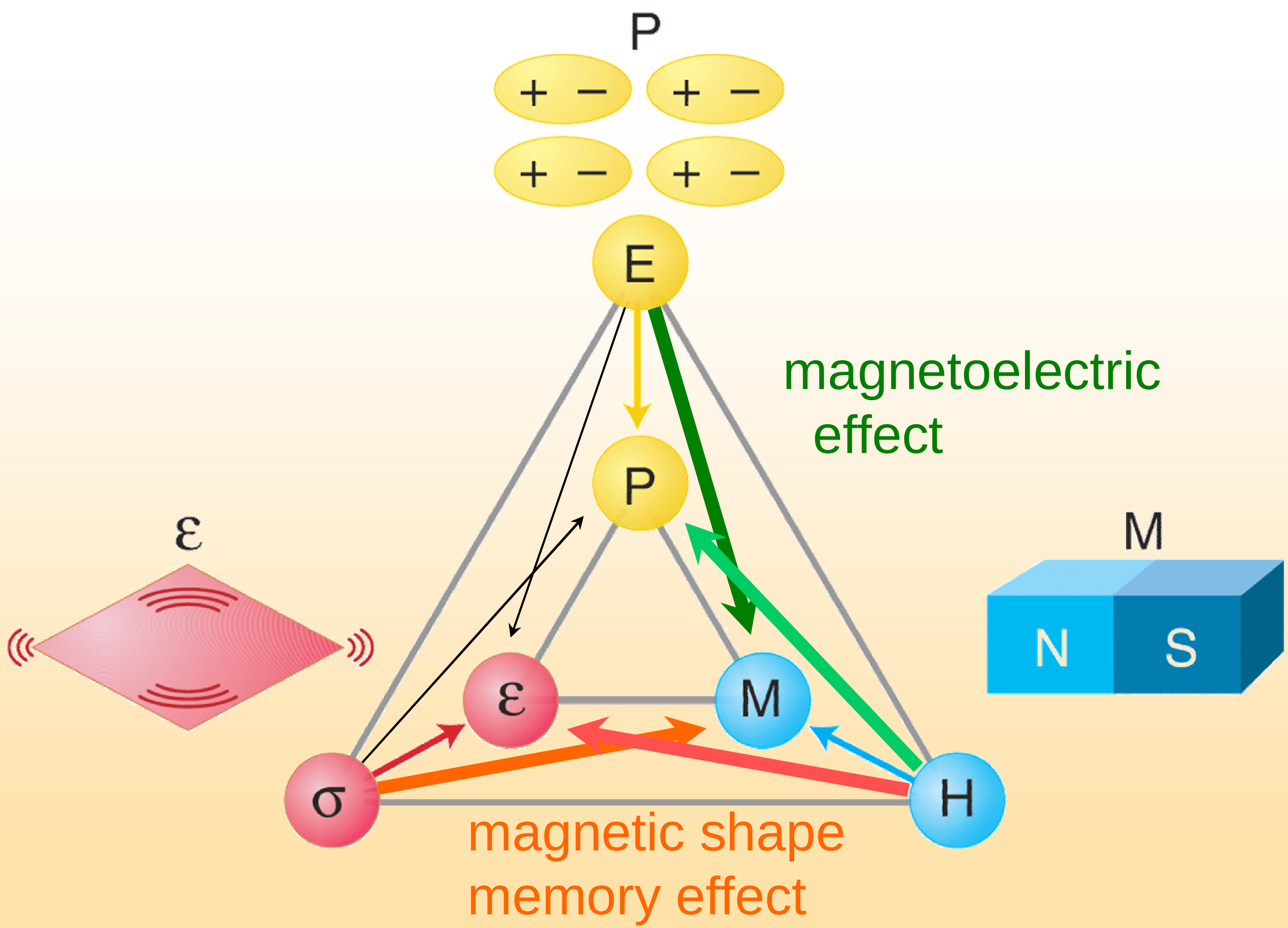
Idea of the magnetoelectric effect



Idea of the magnetoelectric effect



Idea of the magnetoelectric effect



Quantification of the ME effect

Free energy of magnetoelectric materials with „mixed terms" in *E*, *H*:

$$F(E_i, H_j) = -\alpha_{ij} E_i H_j - \tfrac{1}{2}\beta_{ijk} E_i H_j H_k - \tfrac{1}{2}\gamma_{ijk} E_i E_j H_k$$

magnetization: $M(E) = -dF/dH$

electric polarization: $P(H) = -dF/dE$

⇒ requires breaking of time-reversal and space-inversion symmetries

- ***Linear magnetoelectric effect:*** $P_i = \alpha_{ij} H_j$; $M_j = \alpha_{ij} E_i$

  "the" magnetoelectric effect

- ***Higher order terms for*** $\beta \neq 0$, $\gamma \neq 0$

IFW

History

1894 P. Curie: discussed correlation of magnetic and electric properties in low-symmetry crystals

1926 P. Debye: "magneto-elektrischer Richteffekt"

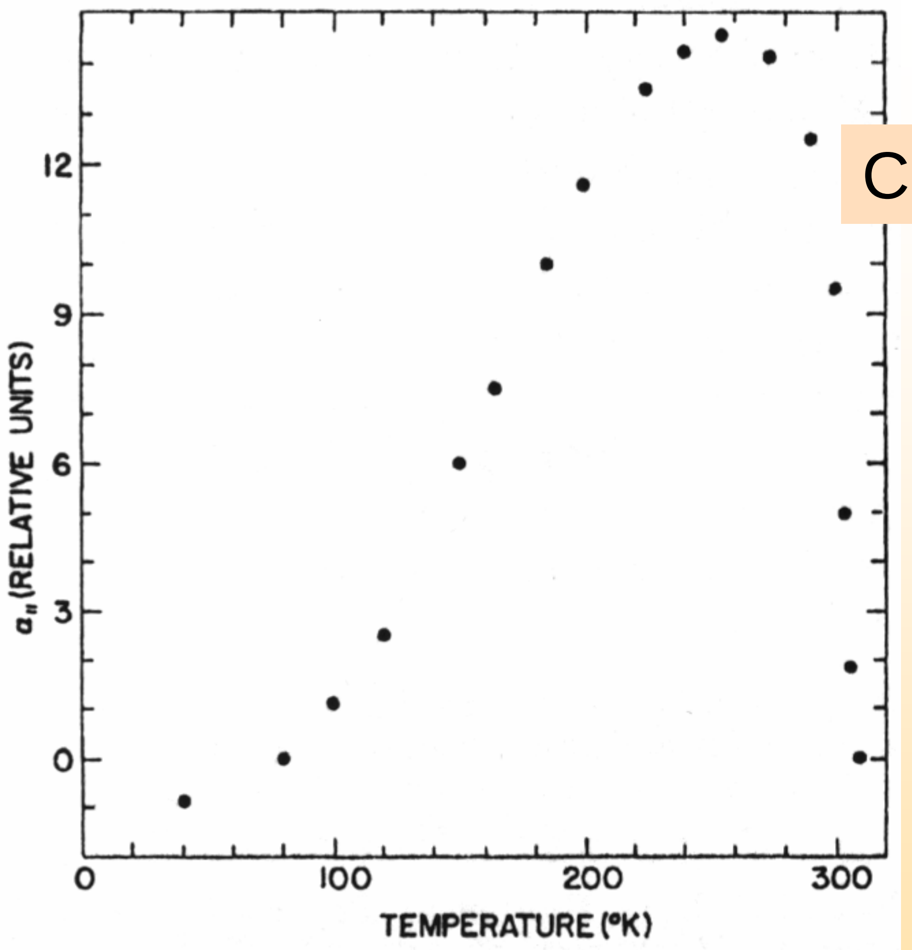
1957 L. D. Landau, E. M. Lifshitz: "The magnetoelectric effect is odd with respect to time reversal and vanishes in materials without magnetic structure."

1959 I. E. Dzyaloshinskii: predicted the magnetoelectric effect in Cr_2O_3

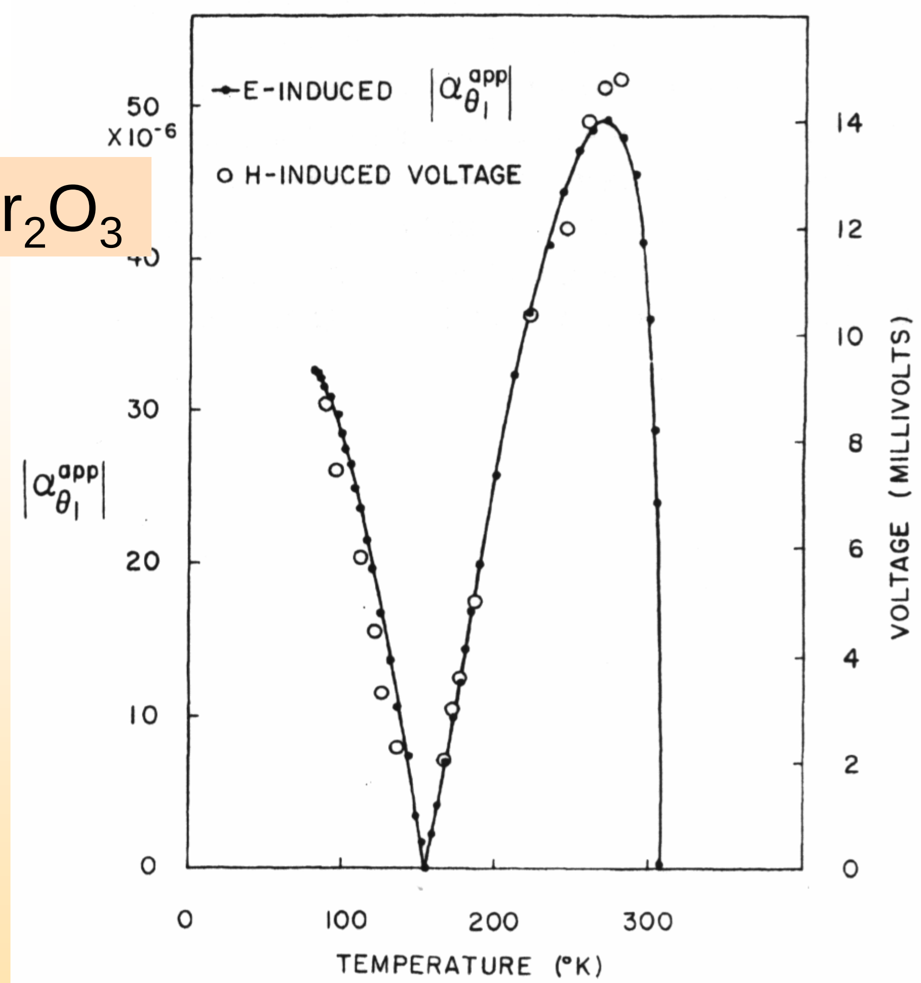
1960 D. N. Astrov: first observation in Cr_2O_3

"C'est la dissymmétrie qui crée le phénomène"
(P. Curie, 1894)

History



Cr_2O_3



$M \propto \alpha E$

$P \propto \alpha^* H$

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

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

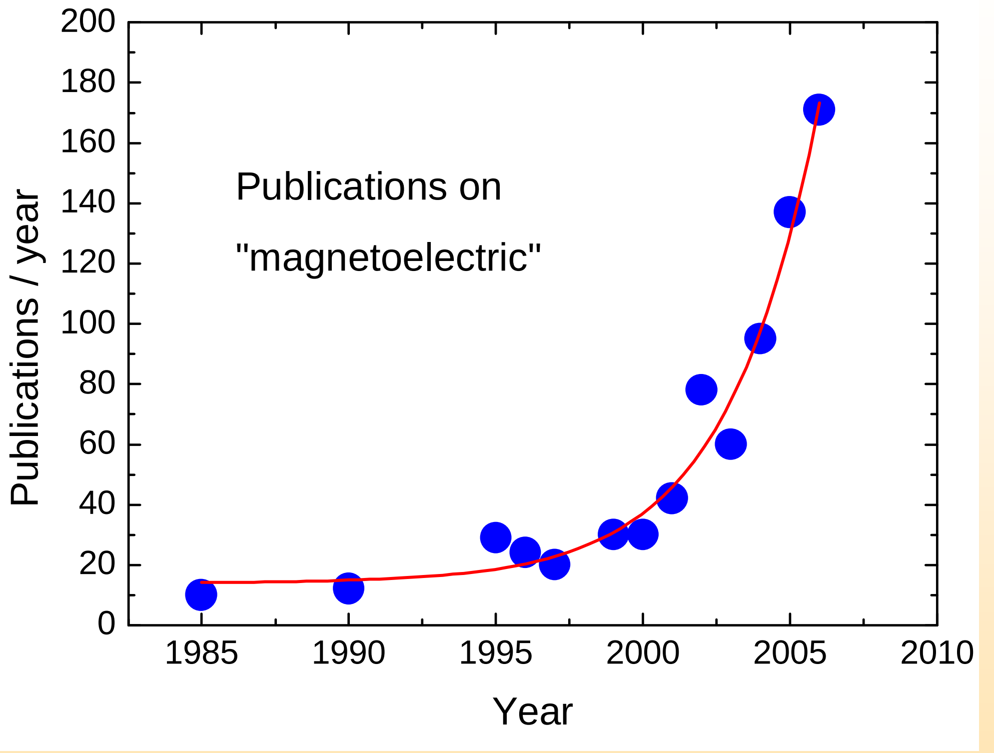
The revival

Since about the year 2000:

♦ New materials ("designed" composites) with much larger ME effect

♦ New theoretical approaches / concepts

♦ New experimental techniques (neutron scattering, non-linear optics)



Sources of the magnetoelectric effect

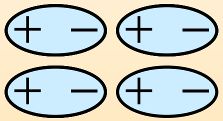
- Limitation of the magnetoelectric effect: $\alpha_{ij}^2 < \chi_{ii}^e \chi_{jj}^m$

  χ_{ii}^e: electric susceptibility χ_{jj}^m: magnetic susceptibility

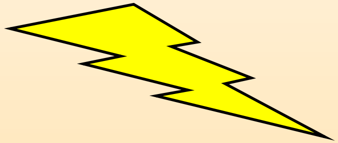
  W. F. Brown et al., Phys. Rev. 168, 574 (1968)

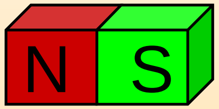
- Large in ferroelectric and ferromagnetic samples → **multiferroics**

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



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





"Likes" $3d^n$ with **n≠0**

There are very few magnetic ferroelectrics. **(N. Hill alias Nicola Spaldin)**

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Single-phase multiferroics: overview

- ***Perovskite type:***
  ABO_3, $A_2B`B``O_6$ (e. g., $BiFeO_3$, $TbMnO_3$)
- ***Hexagonal structure:***
  $RMnO_3$ with R = Sc, Y, Ho-Lu
- ***Boracites:***
  $M_3B_7O_{13}X$ with M = Cr, Mn, Fe ...; X = Cl, Br, I
- ***Orthorhombic $BaMF_4$ compounds***
  M = Mg, Mn, Fe, Co, Ni, Zn

and further ones (about 100)

- ***Non-multiferroic magnetoelectrics:***

$GdFeO_3$, $LuFe_2O_4$

Multiferroics "unusual" because they circumvent the d^0 / d^n problem [1]

Most are anti-ferroic in one of the orders (magnetic / electric)

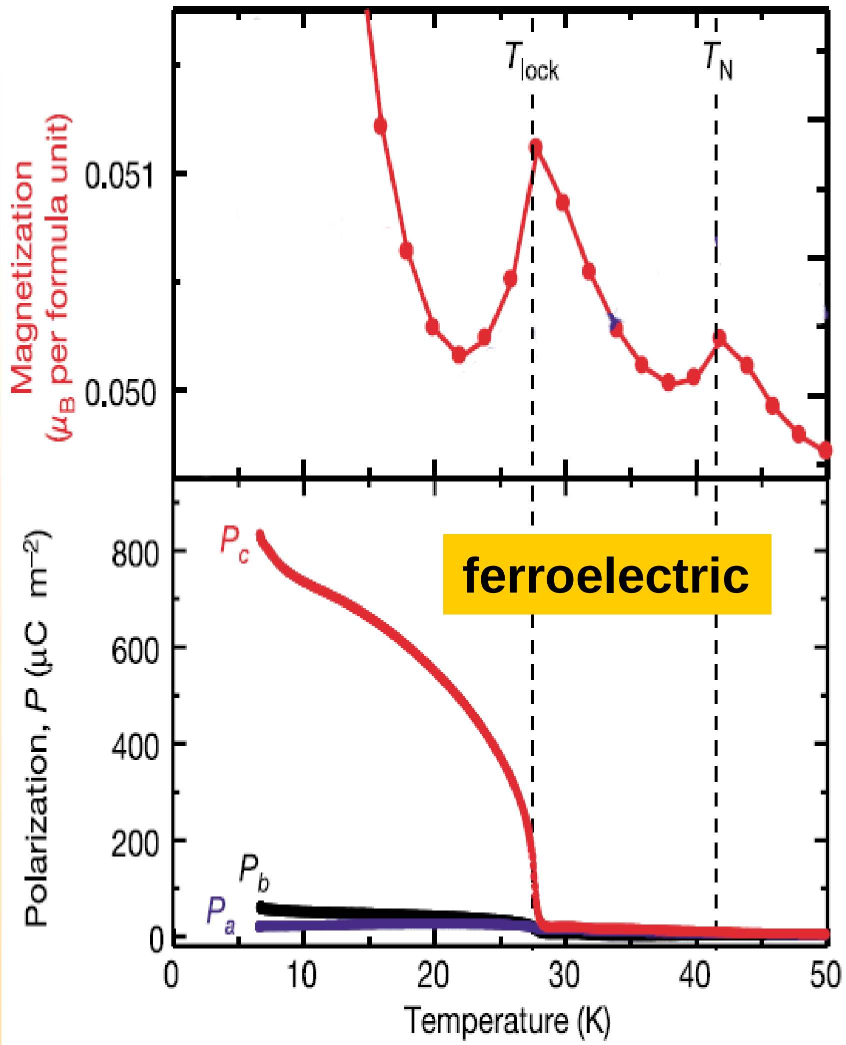
$\rightarrow$ small magnitude of M or P

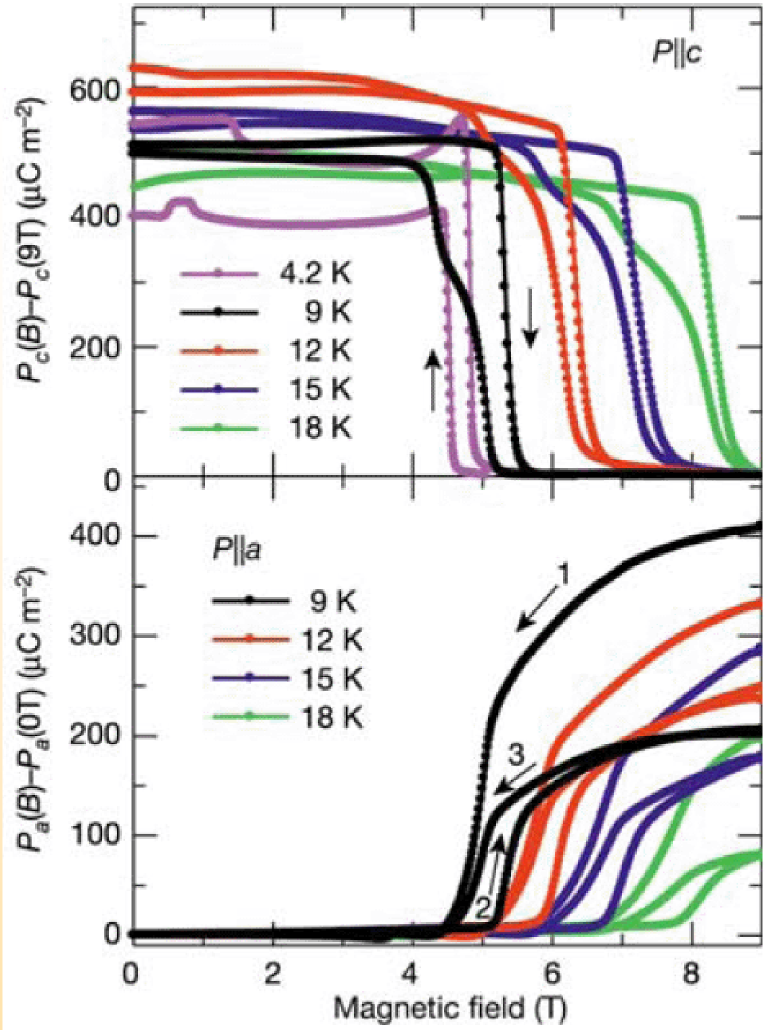
Very rare: RT multiferroics

(BiFeO3: ferroelectric + antif.mag)

[1] C. Ederer and N. A. Spaldin, Curr. Opin. Sol. Stat. Mat. Sci. 9, 128 (05)

Magnetic control of ferroelectricity: $TbMnO_3$





P changes direction in large magnetic field

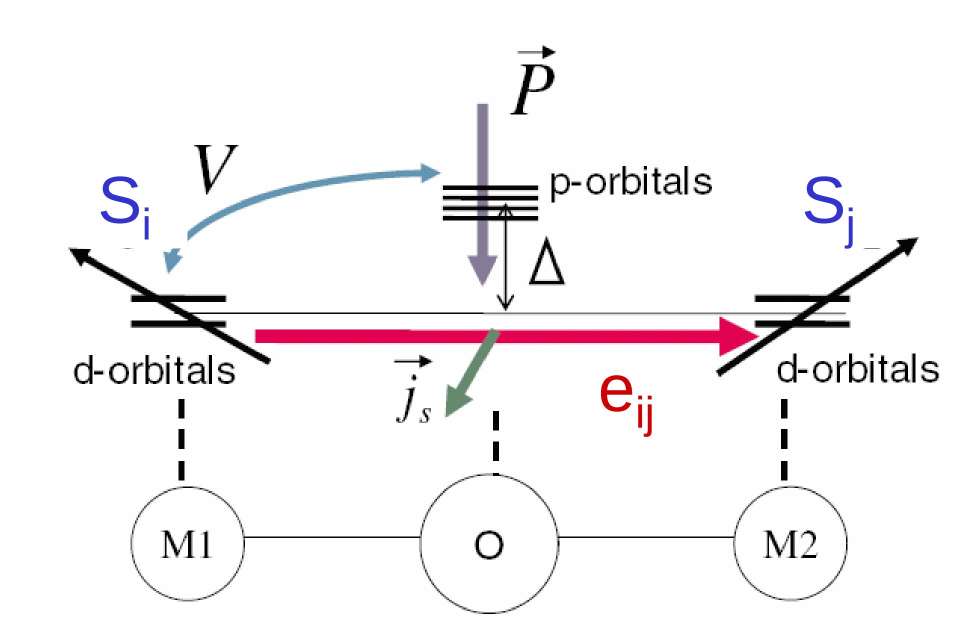
T. Kimura et al., Nature 426, 55 (2003)

Spin spirals as source of polarization

In $TbMnO_3$, a spiral spin structure and ferroelectricity appear at $T \leq T_{lock}$.

♌ Spin spirals break time and space inversion symmetry (promising for ME effect)

Polarization $\boldsymbol{P} \propto \boldsymbol{e}_{ij}\, x\, (\boldsymbol{S}_i\, x\, \boldsymbol{S}_j)$ proposed **(H. Katsura)**



$\boldsymbol{S}_i$, $\boldsymbol{S}_j$: magnetic moments

$\boldsymbol{e}_{ij}$: unit vector connecting sites i, j

P: polarization

$\boldsymbol{j}_s$: “spin current“

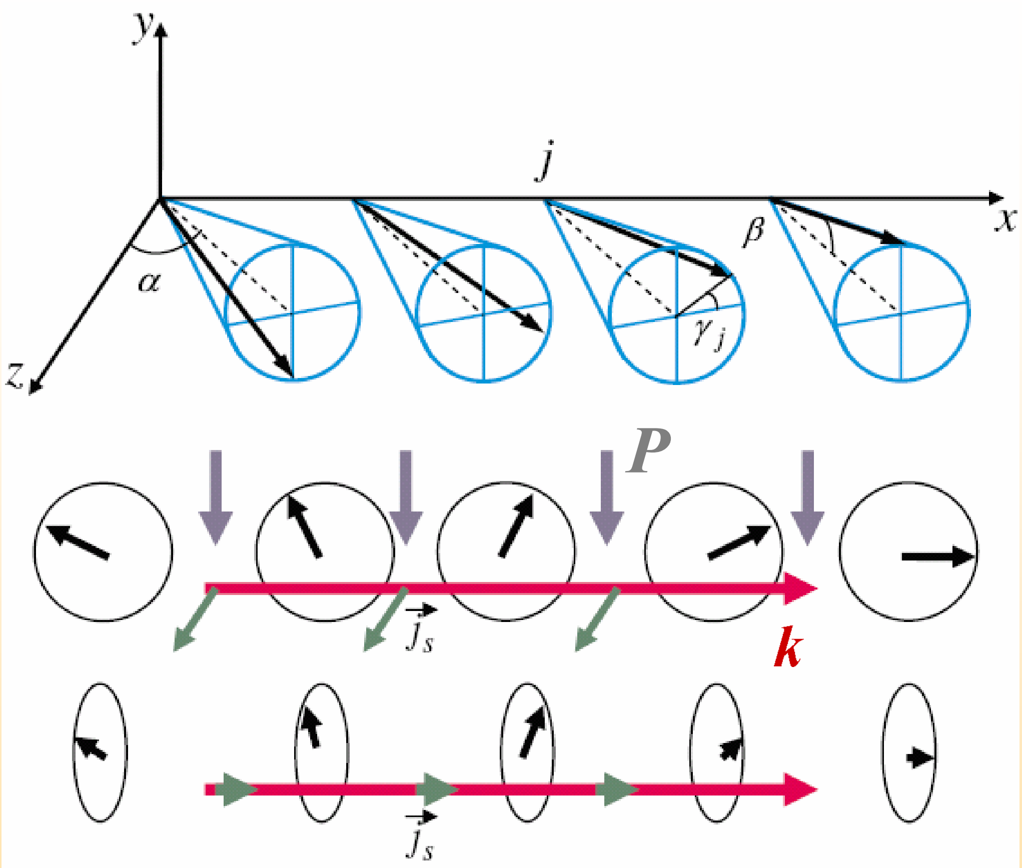
H. Katsura et al., PRL 95, 057205 (2005)

Spin spirals as source of polarization

A spin spiral can be characte-rized by the propagation vector k, the rotation plane (j_S) and the cone angle β.

Note: not all spirals cause polarization !

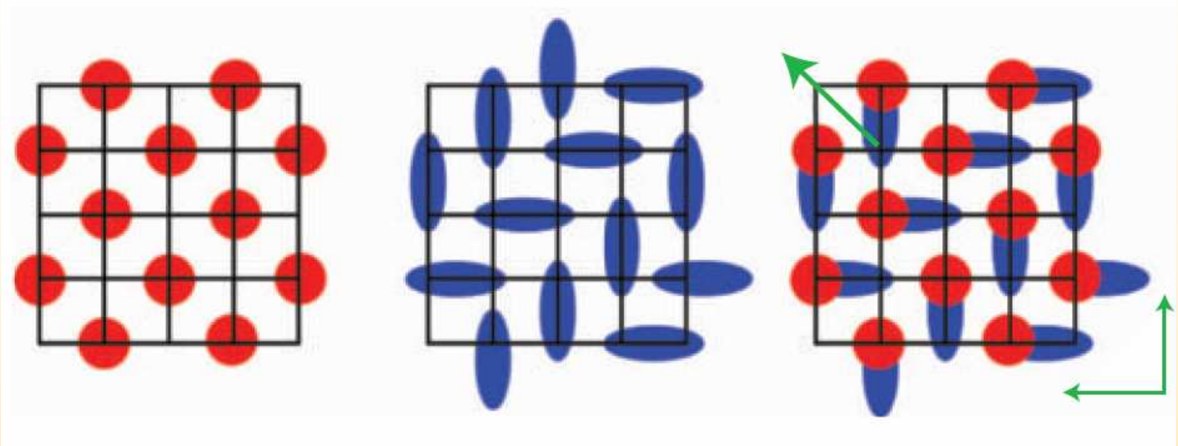
Neutron diffraction: determine spin spiral structure



Charge-ordered compounds

Transition metal oxides (e. g. $Pr_{1-x}Ca_xMnO_3$):

e_g electrons order in insulating phases



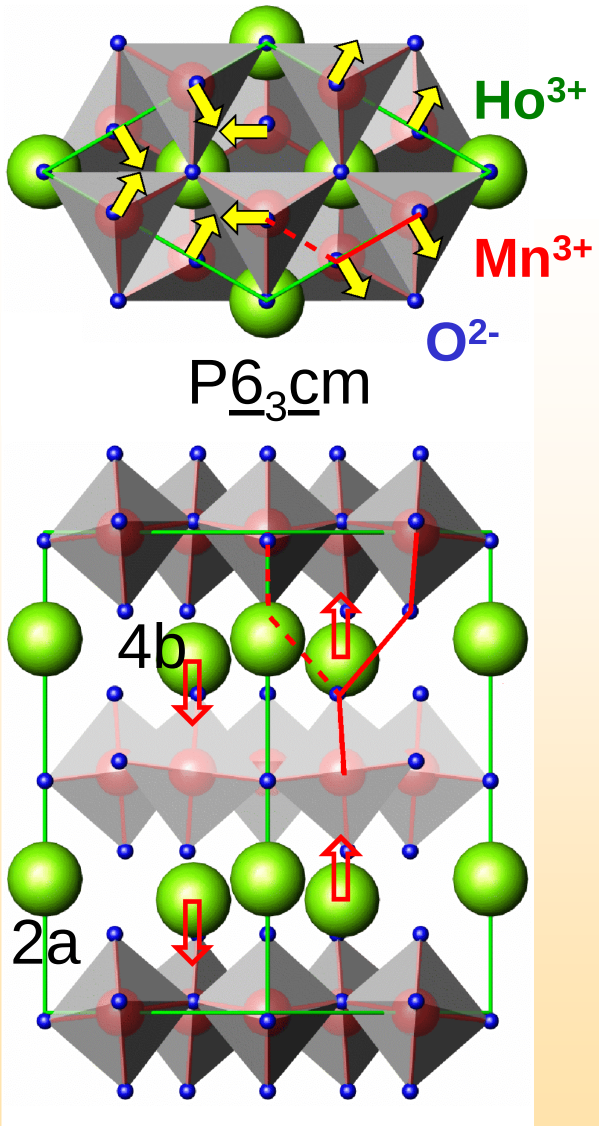
a) “site-centered“ b) “bond-centered“ c) intermediate

(a) Mn4+ order or (b) electron hole at the O ?

♌ Intermediate case (c) with broken space inversion symmetry

D. V. Efremov et al., Nature Mat. 3, 853 (04)

$HoMnO_3$

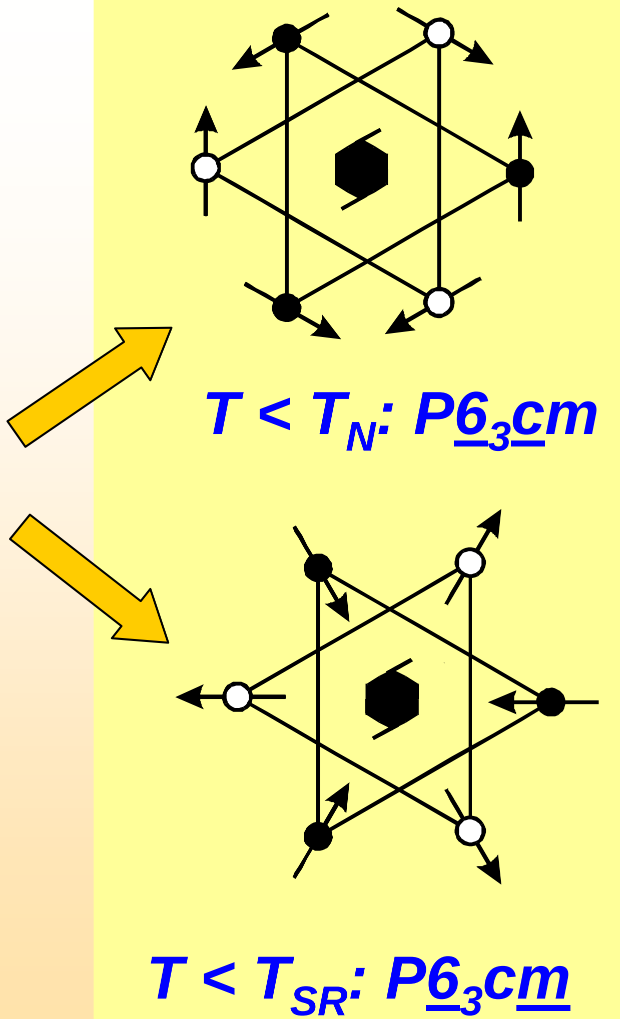


hexagonal structure

ferroelectric at ~870 K

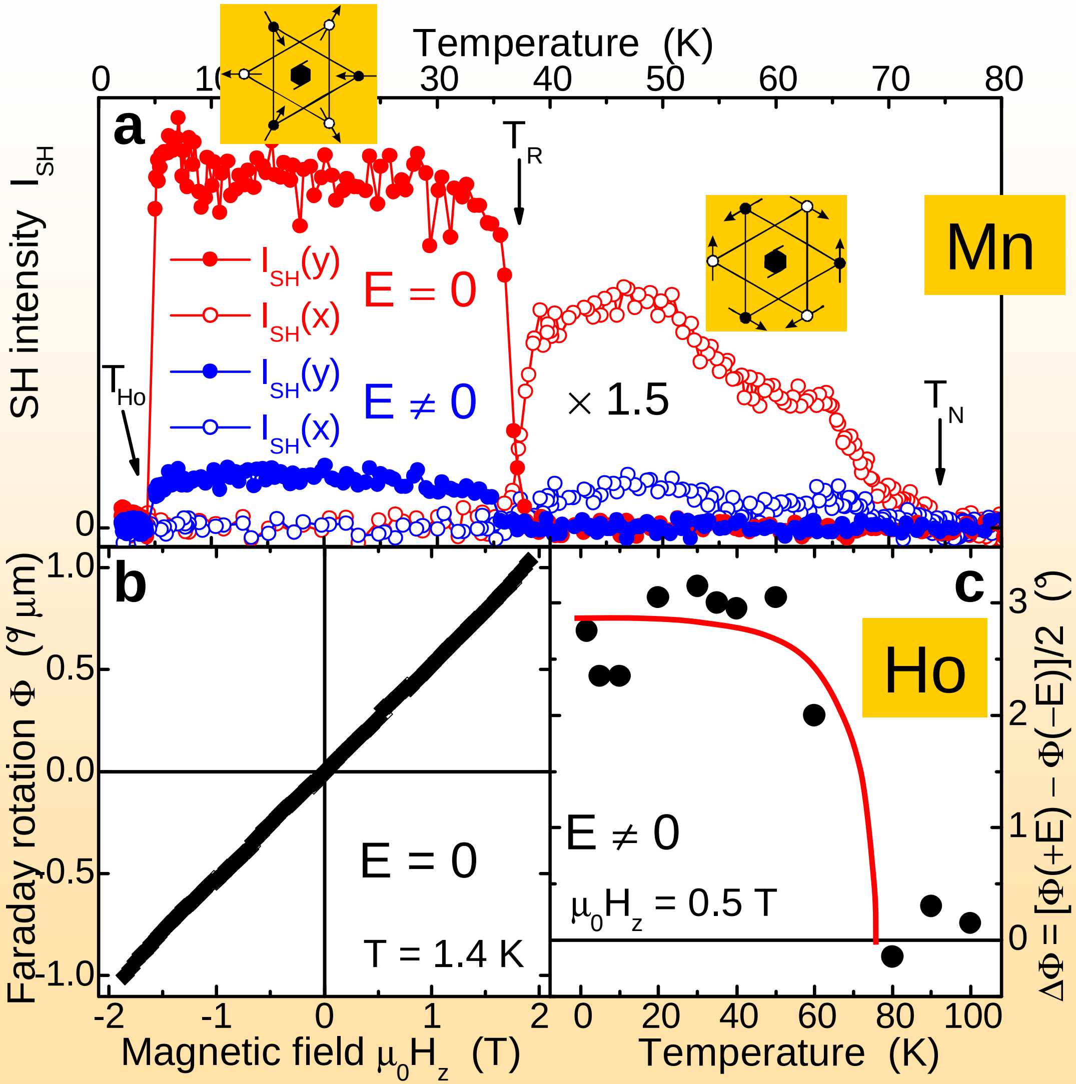
Mn( ): antiferromagnetic,
T_N = 76 K, T_{SR} = 34 – 40 K

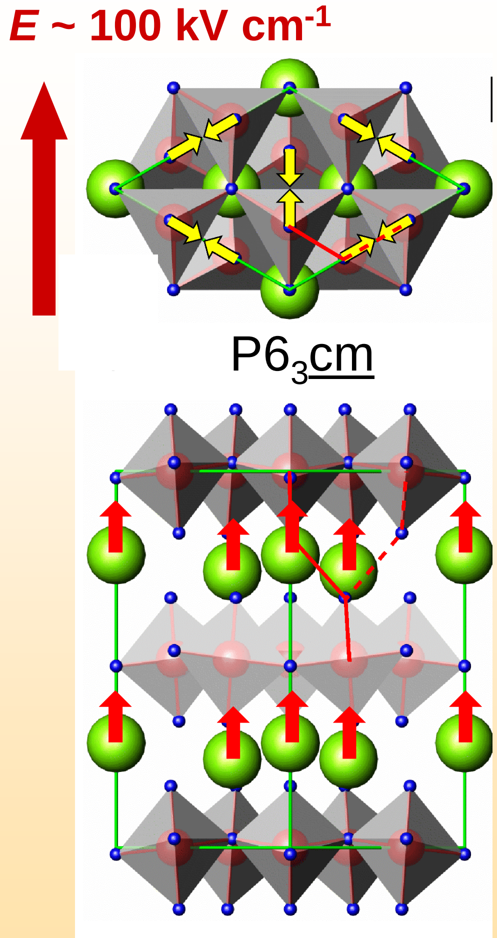
Ho ( ): antiferromagnetic,
order sets in at T_{SR},
full order at T_{Ho} = 6 K



$HoMnO_3$: magnetic phase control by electric field

- Mn and Ho magnetic structures are coupled.
- In electric field, Mn reorients and Ho becomes ferromagnetic.





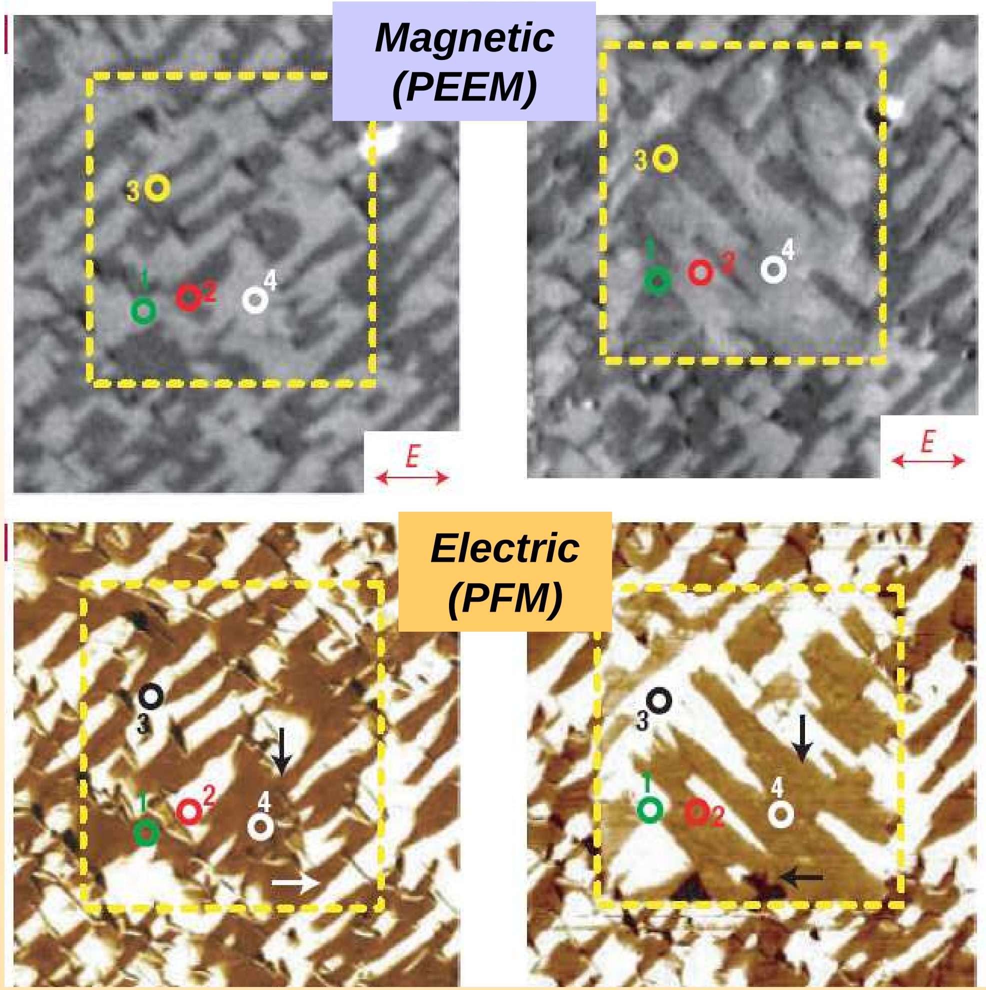
T. Lottermoser, M. Fiebig et al., Nature 430, 541 (2004)

$BiFeO_3$

- perovskite type structure
- multiferroic with the **highest ordering temperatures**:

ferroelectric: T_C = 1103 K

antiferromagnetic: T_N = 643 K (spin spiral)



Switching of FE domains (PFM tip) ⇒ switching of AFM domains in $BiFeO_3$ films *at 300 K*

Application: control the exchange bias by electric field

T. Zhao et al., Nature Mat. 5 (06)

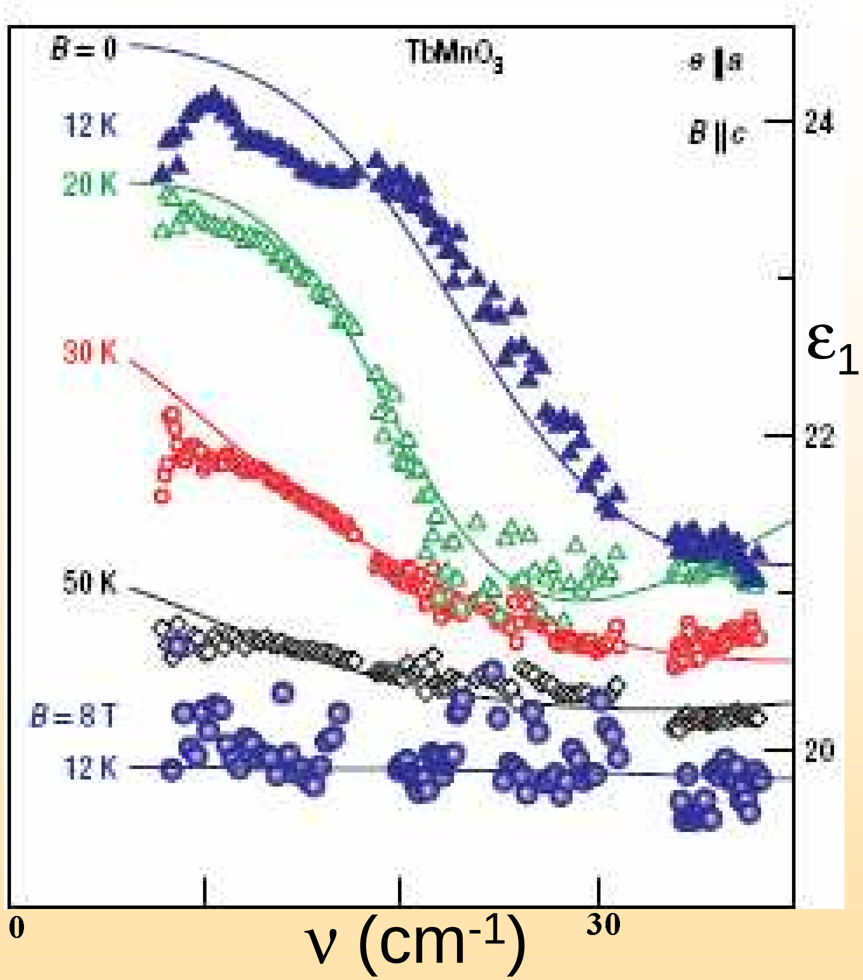
“Electromagnons“

In magnetoelectrics, **new excitations / quasiparticles** are possible:

Magnons (spin waves) associated with dielectric polarization excited by GHz electric field

⇒ **“electromagnons“**

Resonances in the dielectric function, suppressed by magnetic field



A. Pimenov et al., Nature Physics 2, 97 (06)

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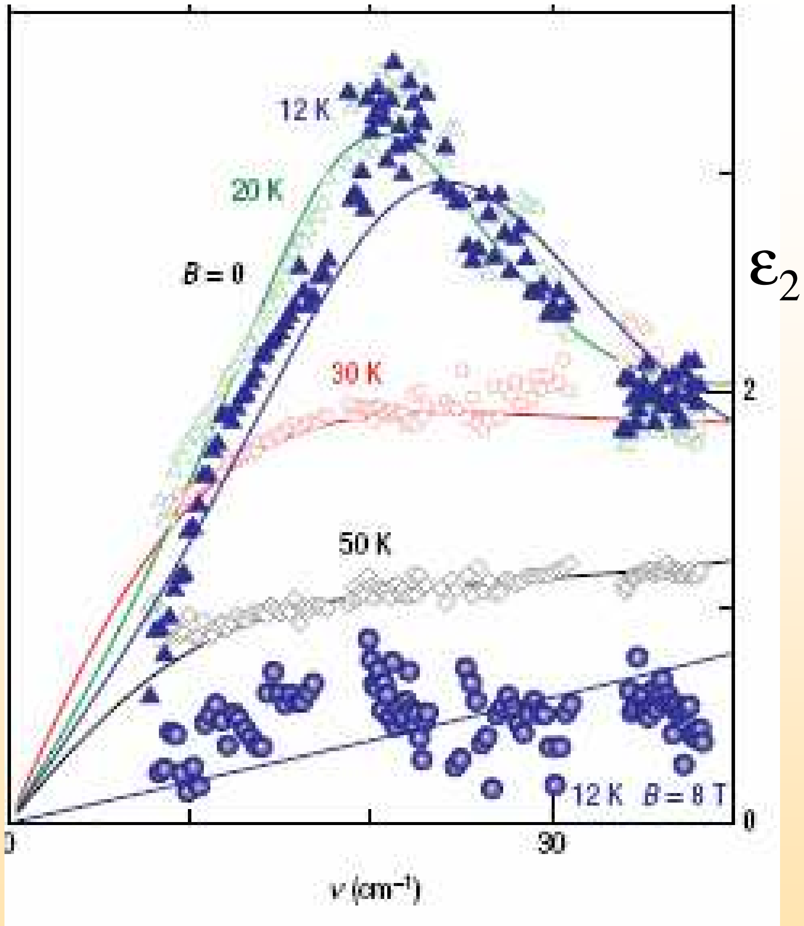

A. Pimenov et al., Nature Physics 2, 97 (06)

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Composite multiferroics

♌ create large response M(E) or P(H) at ambient temperatures

ferroelectric: $E \rightarrow P$

+

ferromagnet: $H \rightarrow M$

Couple them and expect:

$H \rightarrow P$, $E \rightarrow M$

Magnets

- $Tb_{1-x}Dy_xFe_2$
- $La_{0.7}Sr_{0.3}MnO_3$
- $CoFe_2O_4$
- YIG (garnets)
- Fe, Py, ..

→ ***multiferroic composites*** ←

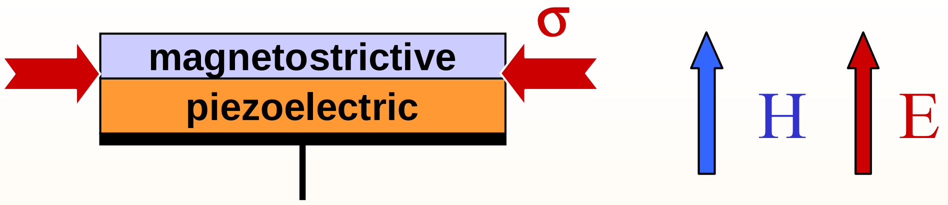
Ferroelectrics

- $BaTiO_3$
- $Pb(Zr,Ti)O_3$
- $SrBi_2Ta_2O_9$
- PMN-PT
- PVDF, …

IFW

Magnetoelectric coupling

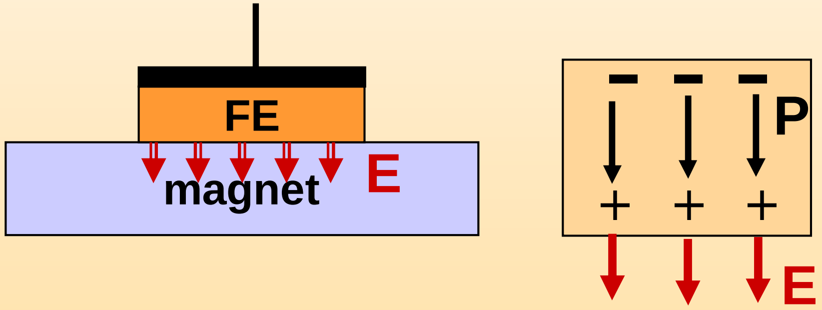
1. Mechanical strain



S. X. Dong, D. Viehland et al., APL 85 (04)

2. Interface charge / bonding effects

a) Field effect



b) Bond effect: change in bonding upon P reversal alters interface magnetization ***C. G. Duan, E. Y. Tsymbal, PRL 95 (06)***

Types of strain-coupled composites

- Mixed, sintered powders
- Free-standing laminar composites
- Layered thin film structures
- Nanostructured composite films

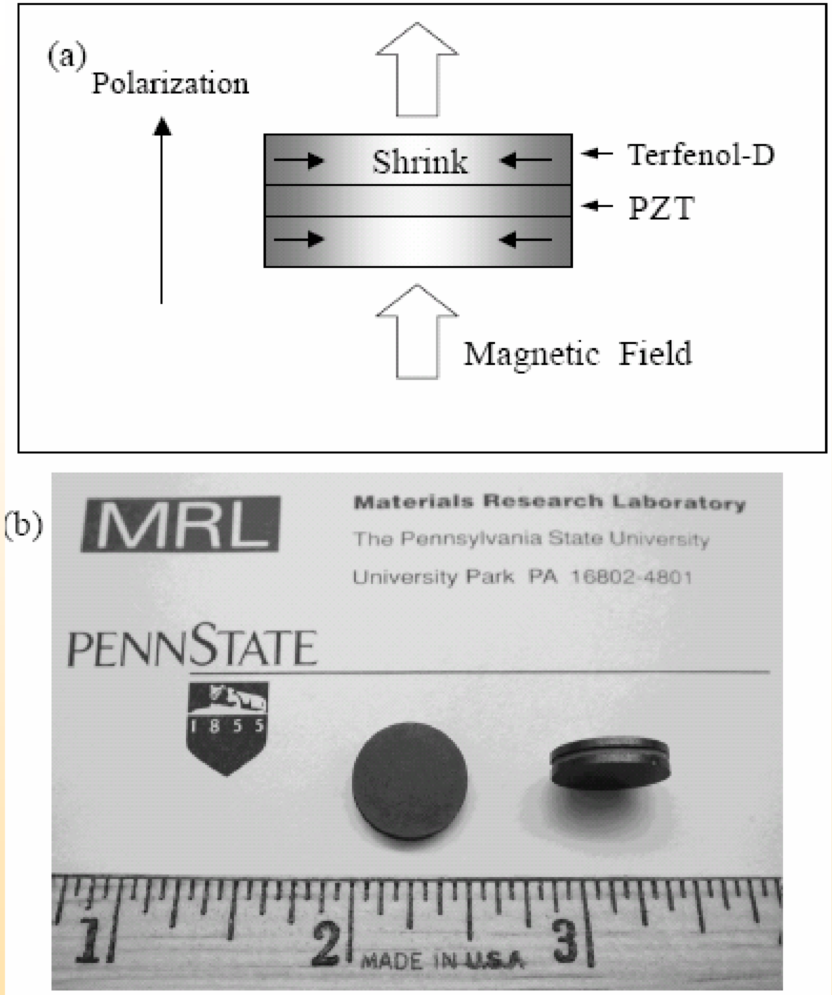
Free-standing laminar composites

Piezoelectric and magnetostrictive components glued or hot-pressed together

Example: PZT/Terfenol-D trilayer

magnetoelectric voltage coefficient:

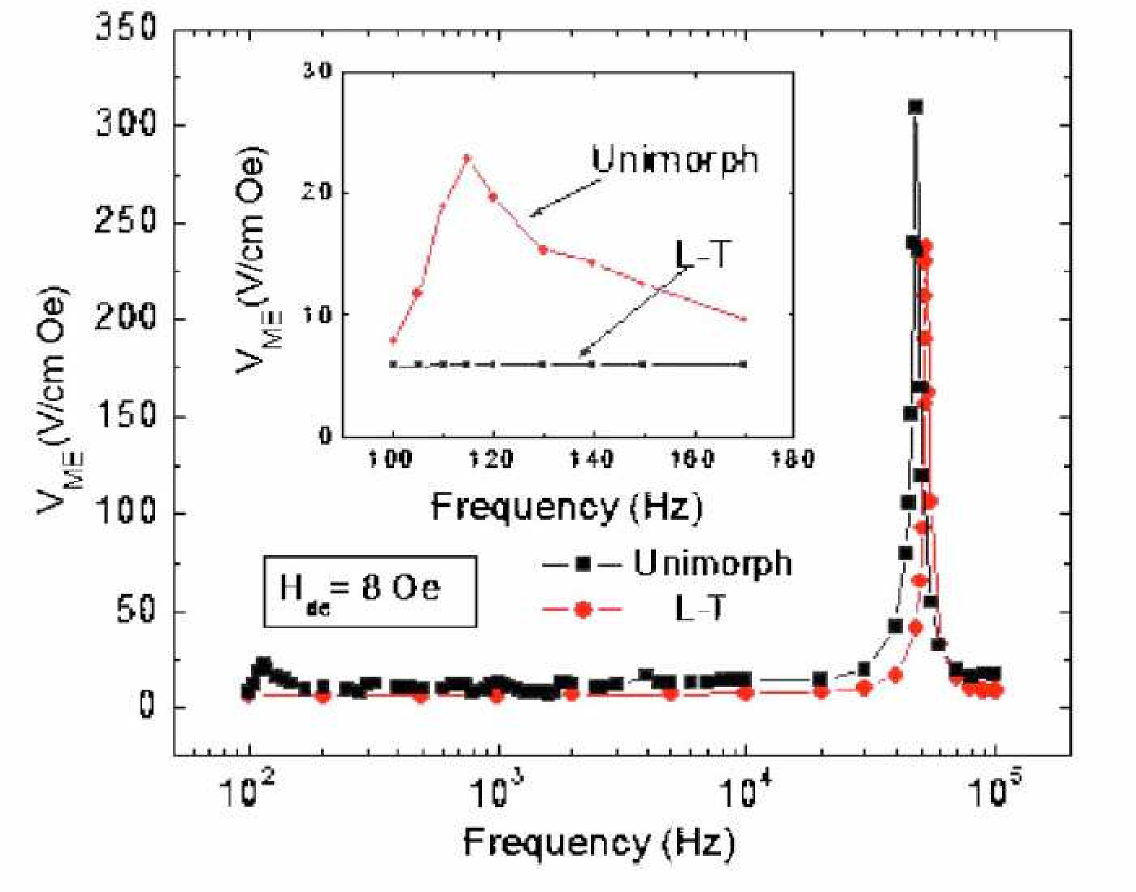
dE/dH = 4.7 V / (cm Oe)



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

Free-standing laminar composites

Piezoelectric and magnetostrictive components glued or hot-pressed together



J. Zhai, D. Viehland et al., APL 89, 83507 (06)

Huge values at **resonances** in the AC magnetic field

Sensitive (low noise) **magnetic field sensors** (D. Viehland et al.)

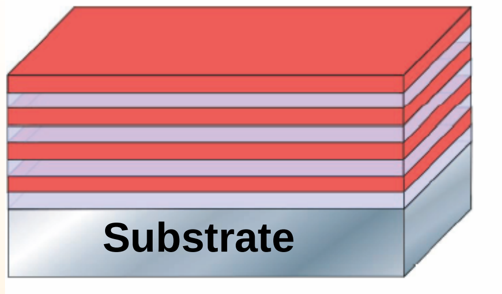
Layered thin film structures

Heteroepitaxial growth of multilayers on monocrystalline substrates

$\Rightarrow$ good elastic coupling at the FE/FM interface

$\Rightarrow$ field effect at interfaces

$\Rightarrow$ further mechanisms: multiferroic tunnel barriers depending on electric and magnetic field (see below)

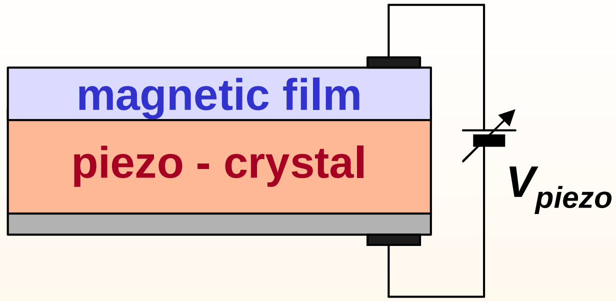


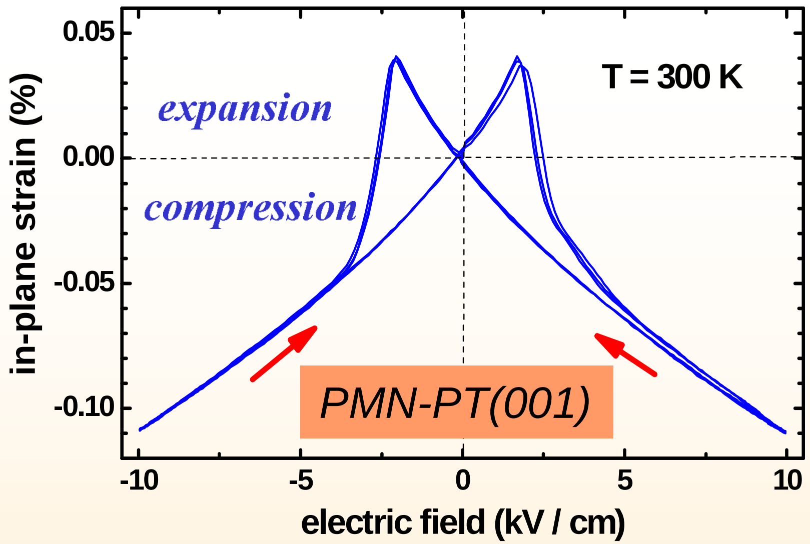
Disadvantage:

Clamping to the substrate, weak strain

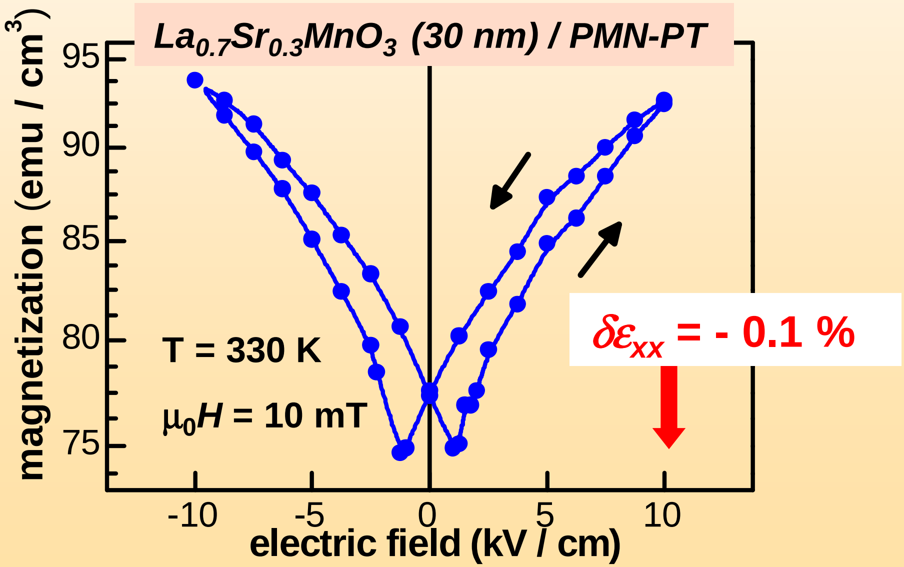
Layered thin film structures

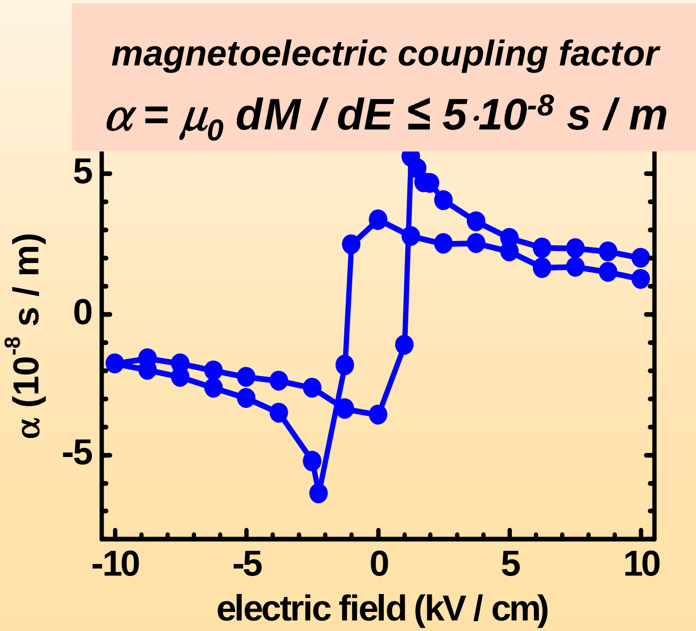
- Films on piezoelectric substrate





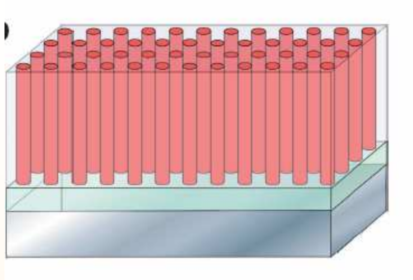
C. Thiele, K. D., Phys. Rev. B 75, 054408 (07)





IFW

Nanocolumnar composites

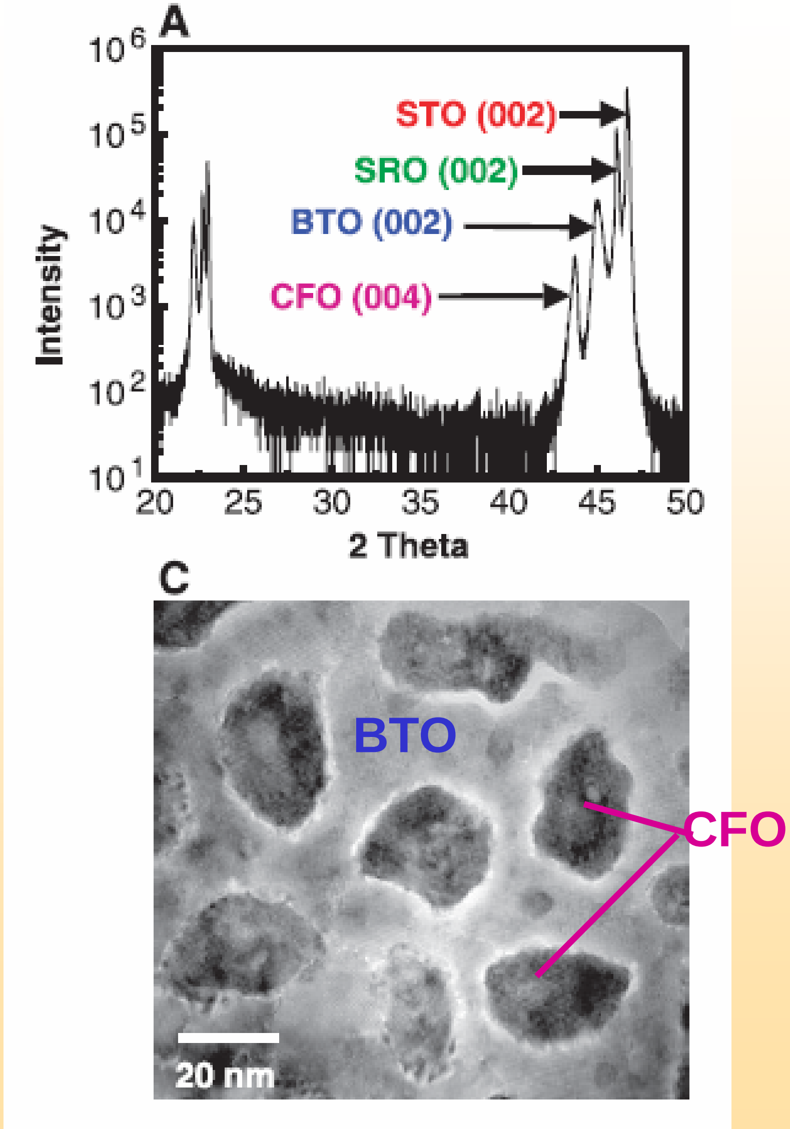


Two-dimensional structures (like columns) may show larger strain on a rigid substrate.

⇒ self-organized growth

⇒ nanofabrication (templates)

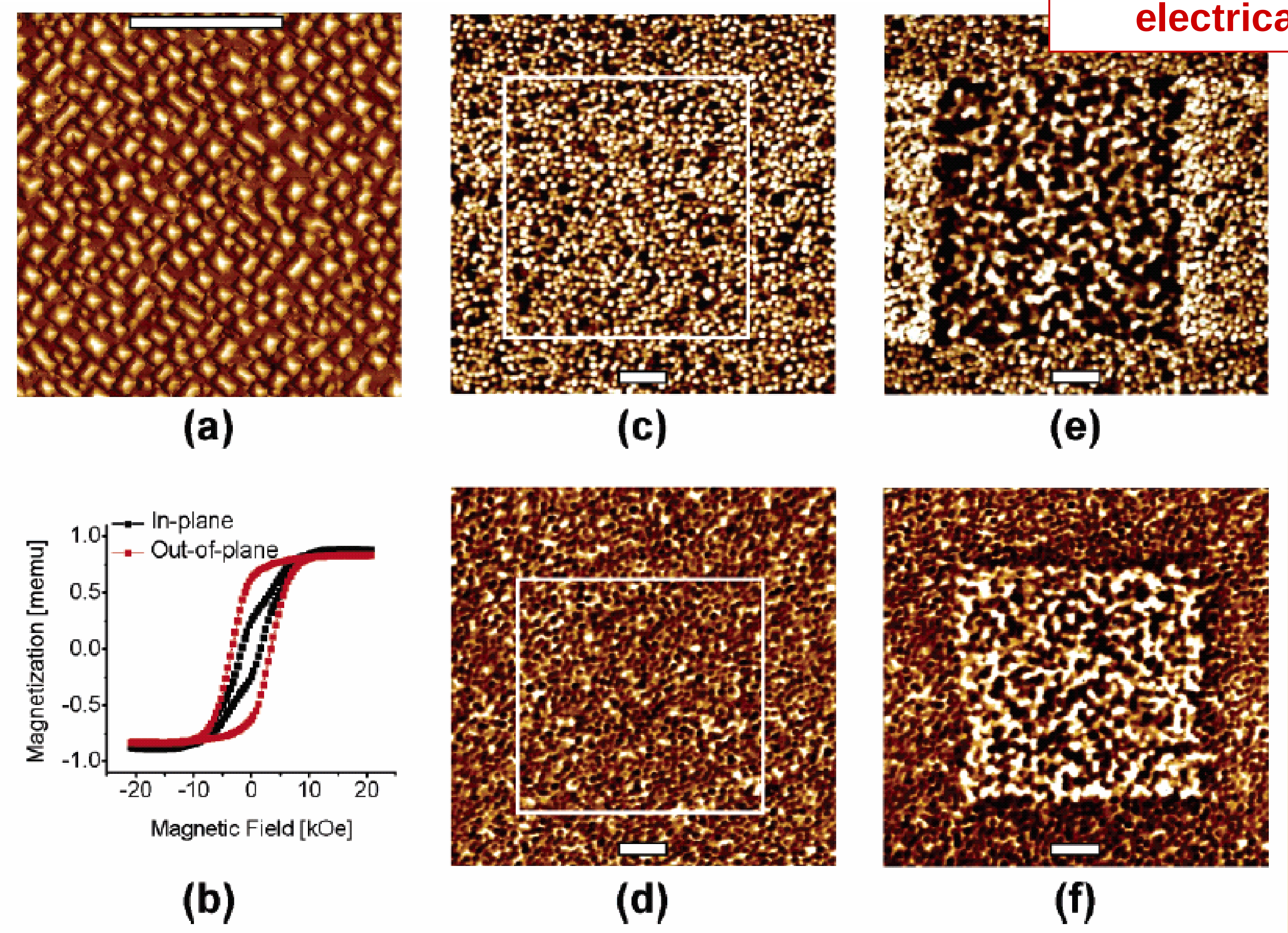
$CoFe_2O_4$ - $BaTiO_3$ nanocolumnar film



H. Zheng et al., Science 303, 661 (04)

Nanocolumnar composites

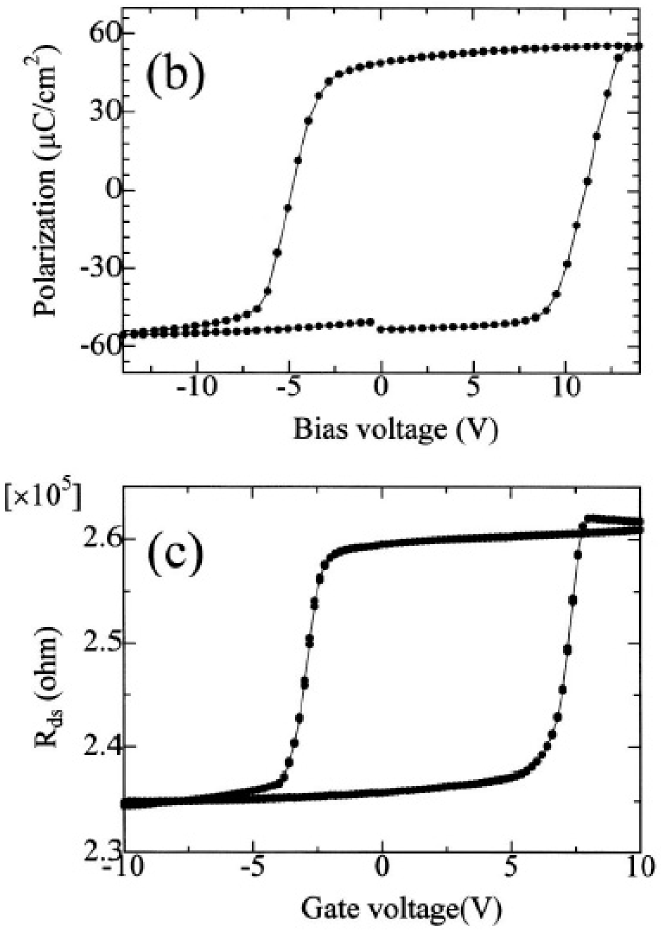
Local magnetization electrically written



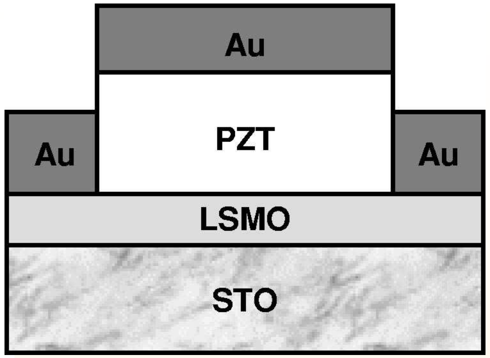
MFM images, quadratic area electrically written @ -16 V

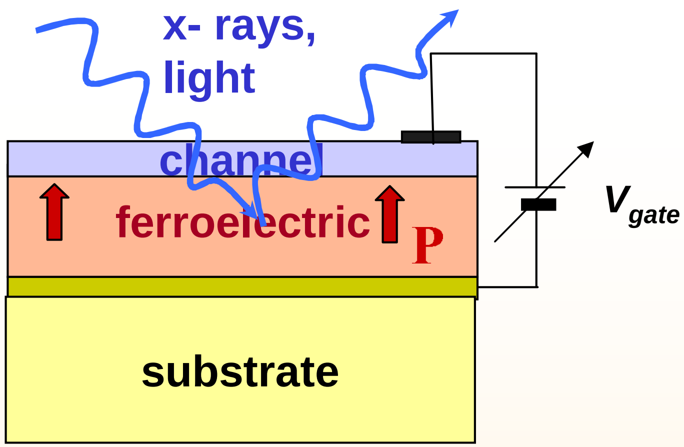
F. Zavaliche, R. Ramesh et al., Nano Lett. 7, 1586 (07)

Field effect experiments

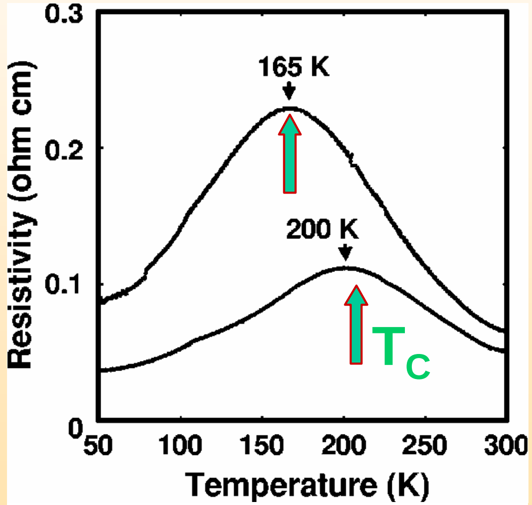


PZT - $La_{0.9}Ba_{0.1}MnO_3$ (6 nm)





- Hysteretic modulation of the charge density in a magnetic channel
- Low screening length ⇒ study and control interface magnetism



PZT – $La_{0.8}Sr_{0.2}MnO_3$ (4 nm)

T. Kanki et al., APL 83, 4860 (03)

X. Hong et al., PRB 68, 134415 (03)

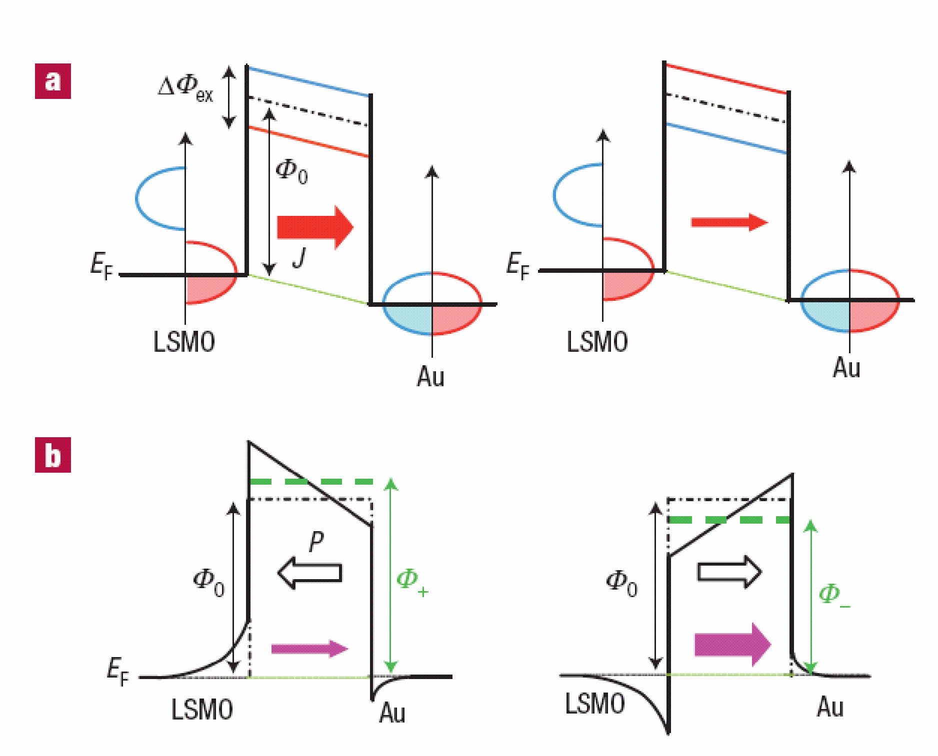
Multiferroic tunnel barrier

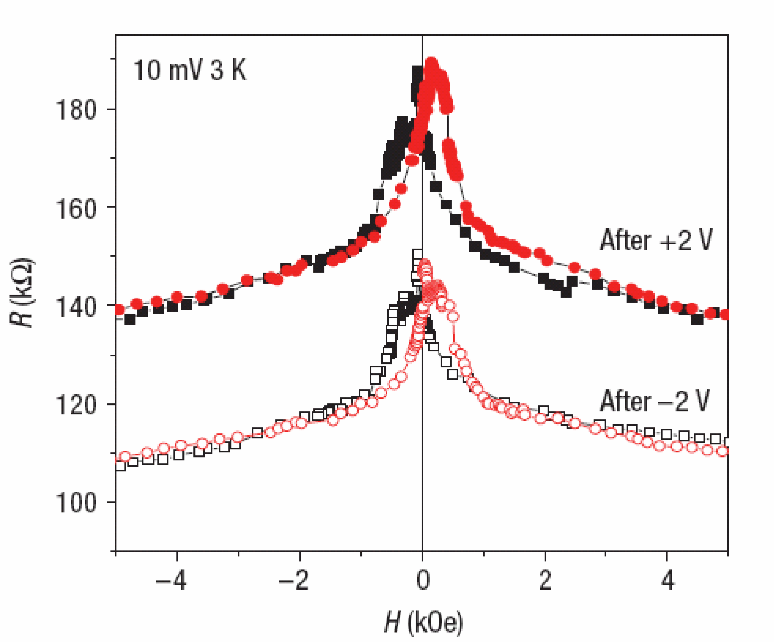
$La_{0.1}Bi_{0.9}MnO_3$ tunnel barriers

a) Ferromagnetic insulator: spin filtering

b) ferroelectric: barrier profile depends on P direction

⇒ Magnetic and electric control of a tunnel current





M. Gajek et al., Nature Mat. 6, 296 (07)

Applications

- Microwave applications:

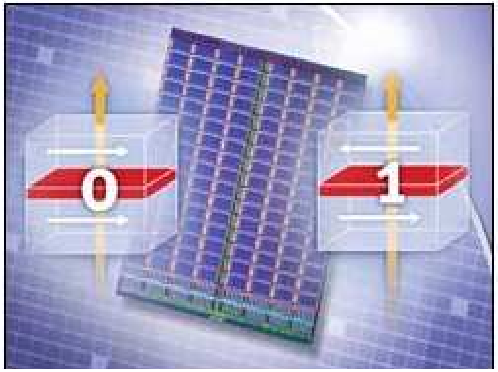
  transducer H(ω) → E(ω)

  electromechanical: 100 kHz, magnetic resonances: 10 – 100 GHz

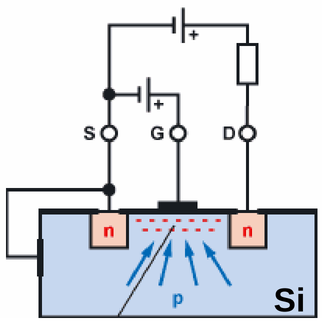
- Magnetic field sensors (free-standing laminar composites)

- Suggested: magnetoelectric electronics

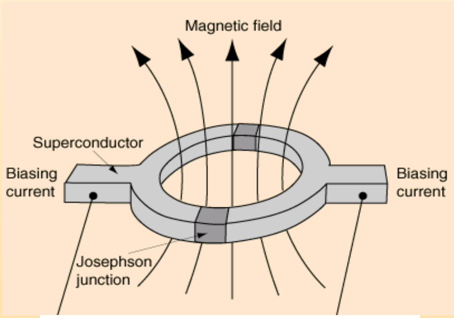
(Electric control of magnetization in memories, logical circuits, ..)



16 Mbit MRAM (IBM, Infineon)



MOS-FET



SQUID

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- History and fundamentals
- Single-phase multiferroics
- Composite multiferroics
- Experimental techniques
- Summary, Literature

Second harmonic generation (SHG)

Electric field in matter: $E(w) = E_0 e^{i\omega t}$

(Incident light wave: frequency, direction, amplitude, polarization)

$P(\omega) = \varepsilon_0 \chi E(\omega) \sim e^{i\omega t}$

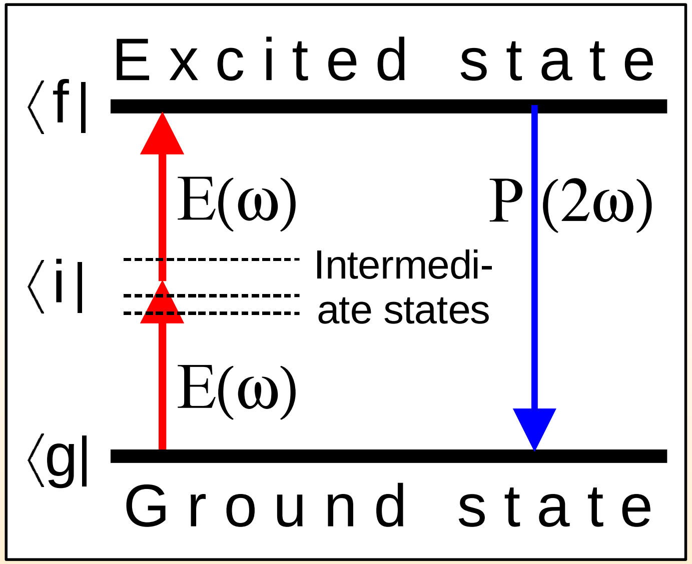
Linear approximation only for weak (light) fields

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:

$P(2\omega) = \varepsilon_0 \chi^{(2)} E(\omega) E(\omega) \sim e^{i2\omega t}$



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

$$\chi^{(2)} \propto \sum_i \frac{\langle g | e\vec{r} | f \rangle \langle f | e\vec{r} | i \rangle \langle i | e\vec{r} | g \rangle}{(E_f - E_g - 2\hbar\omega)(E_i - E_g - \hbar\omega)}$$

Microscopically:
second-order perturbation

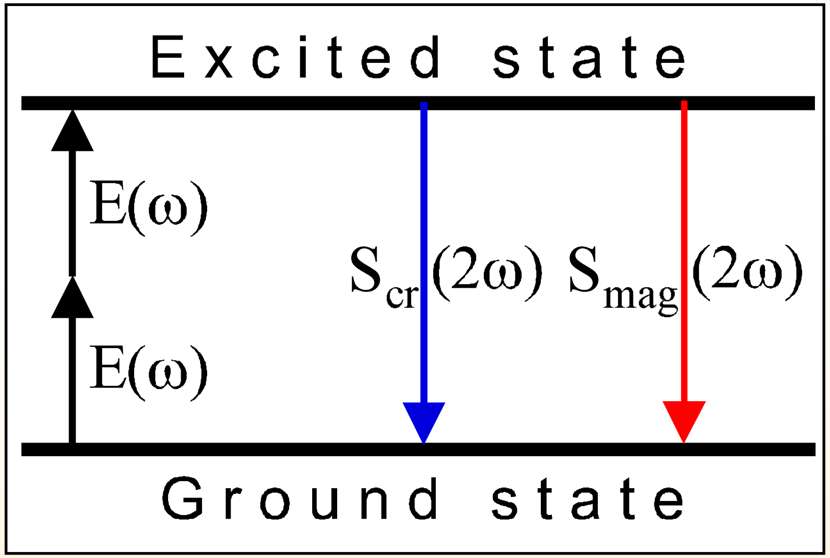
M. Fiebig, thesis (Universität Dortmund, 1996)

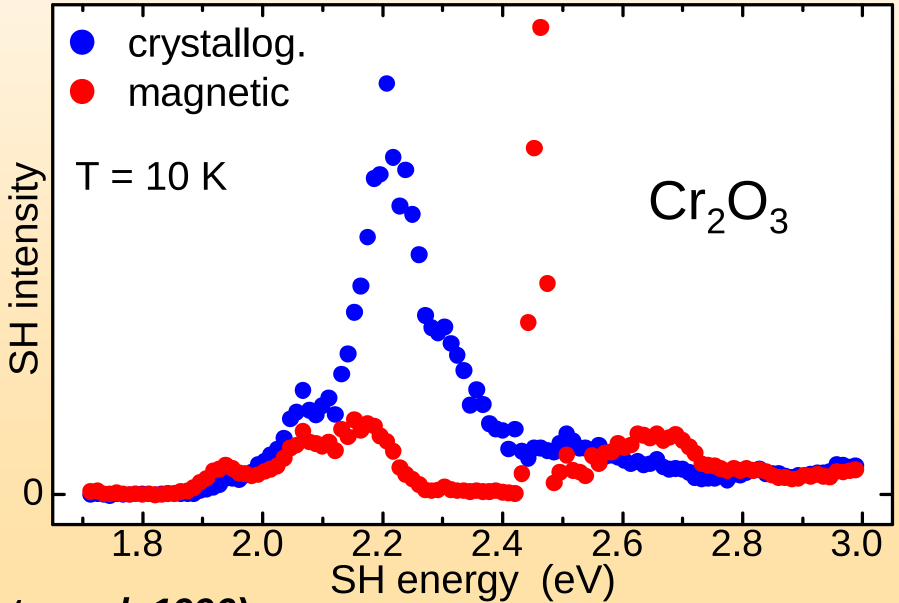
Second harmonic generation (SHG)

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

- χ_{ijk} ↔ **symmetry** ↔ crystallographic and magnetic structure (Note: the higher the symmetry the more χ_{ijk} = 0)
- **Spectroscopy**: sublattice selective excitation
- **Spatial resolution:** imaging of domain structures

Simultaneous access to magnetic and ferroelectric order / domains!

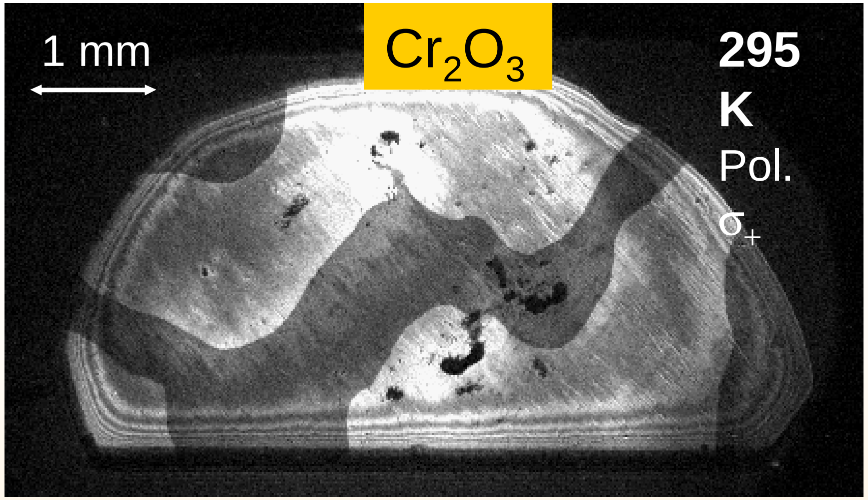




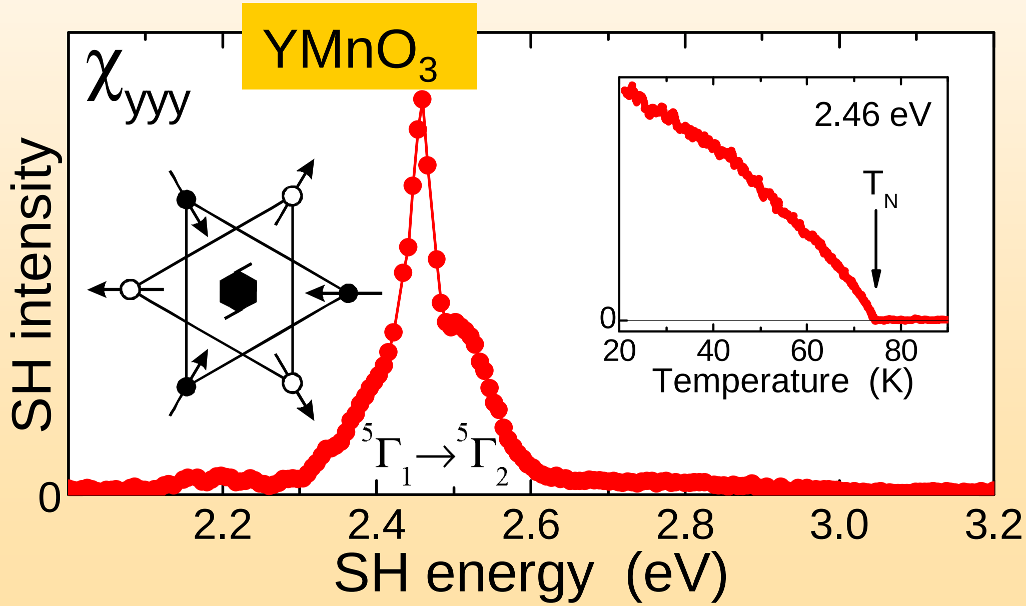
M. Fiebig, thesis (Universität Dortmund, 1996)

Second harmonic generation

Antiferromagnetic domains, contrast depends on (circular) light polarization



Antiferromagnetic 180° domains



Non-vanishing χ_{yyy}:

Mn excitation for this particular triangular structure

M. Fiebig, PRL 1996, and further references years 2000-05

Direct strain on piezoelectric substrates

Find strain-sensitive materials

Doubling the critical temperature of $La_{1.9}Sr_{0.1}CuO_4$ using epitaxial strain

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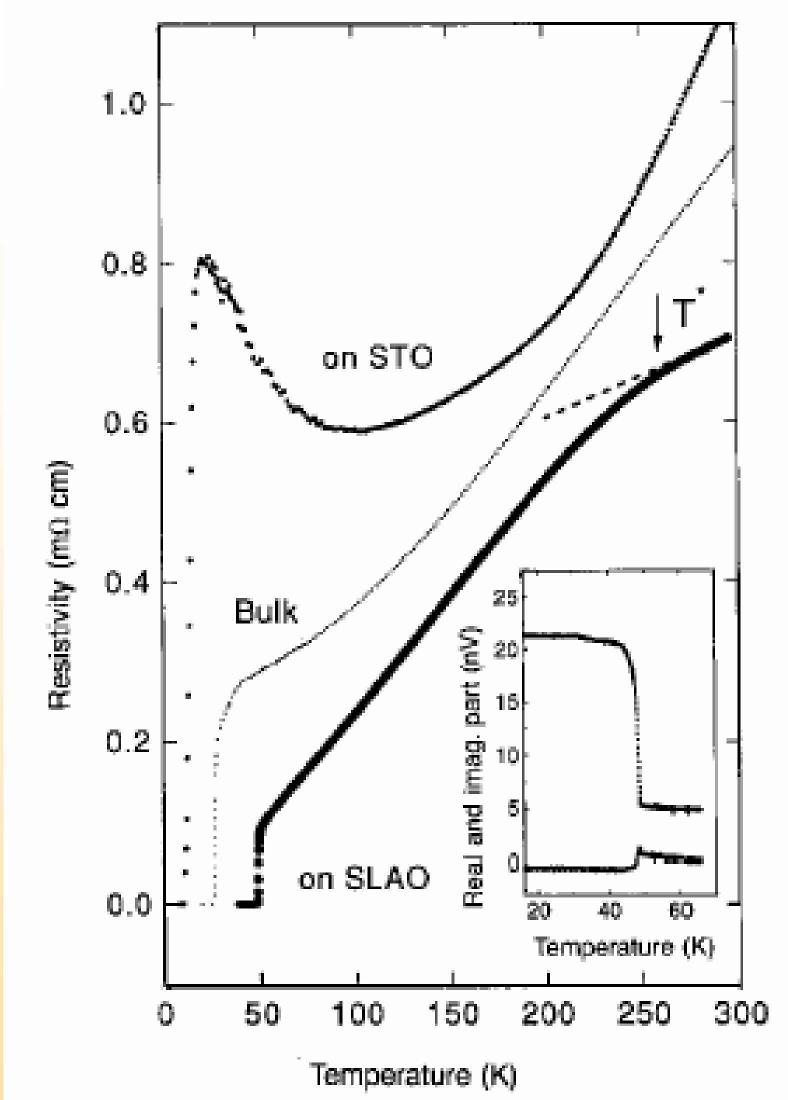
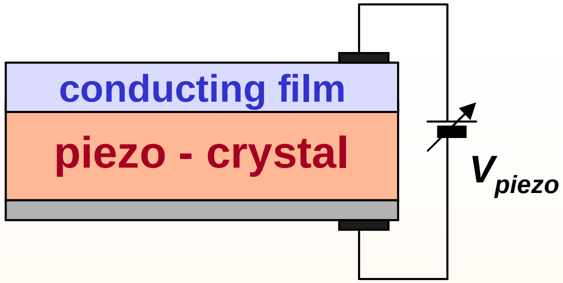
The discovery[1] of high-temperature superconductivity in copper oxides raised the possibility that superconductivity could be achieved at room temperature. But since 1993, when a critical temperature (T_c) of 133 K was observed in the $HgBa_2Ca_2Cu_3O_{8+\delta}$ (ref. 2), no further progress has been made in raising the critical temperature through material design. It has been shown, however, that the application of hydrostatic pressure can raise T_c—up to ~164 K in the case of $HgBa_2Ca_2Cu_3O_{8+\delta}$ (ref. 3). Here we show, by analysing the uniaxial strain and pressure derivatives of T_c, that compressive epitaxial strain in thin films of copper oxide superconductors could in principle generate much larger increases in the critical temperature than obtained by comparable hydrostatic pressures. We demonstrate the experimental feasibility of this

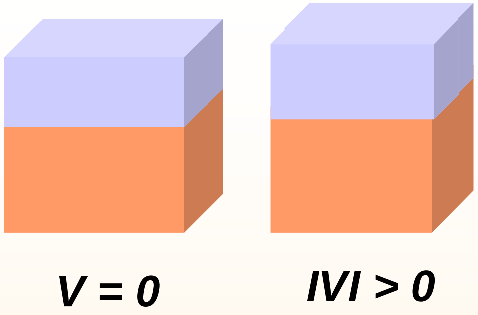


Direct strain on piezoelectric substrates



In-situ strain:

- **biaxial, uniform**
- **reversible**



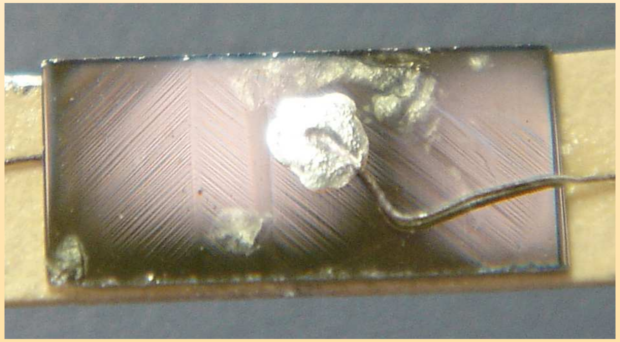
PMN-PT(001)

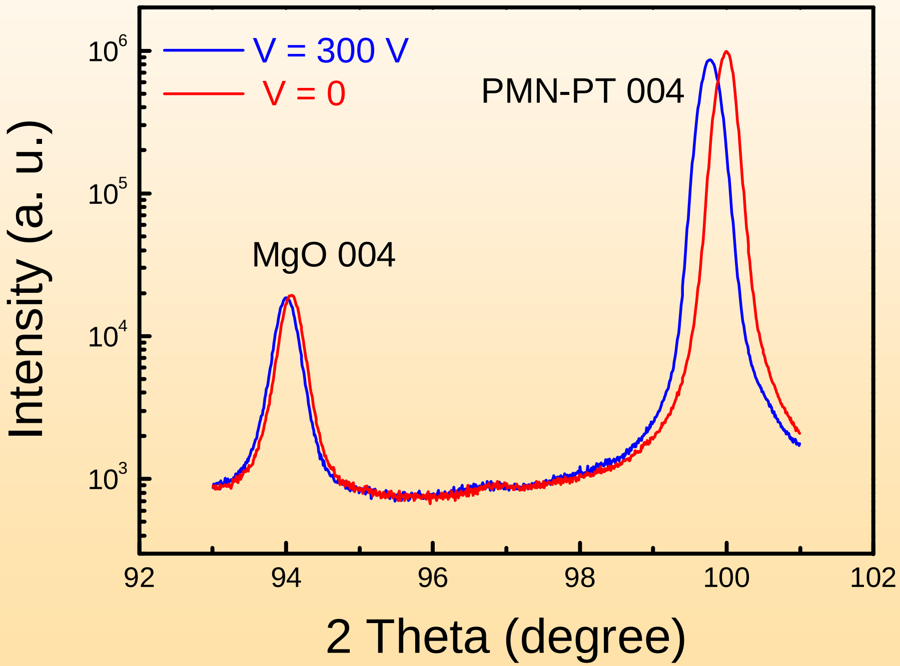
$72Pb(Mg_{1/3}Nb_{2/3})O_3 - 28PbTiO_3$

rhombohedral, a = 4.02 Å

$\alpha = 89.90^o$

cf. $LaAlO_3$: $\alpha = 89.93^o$

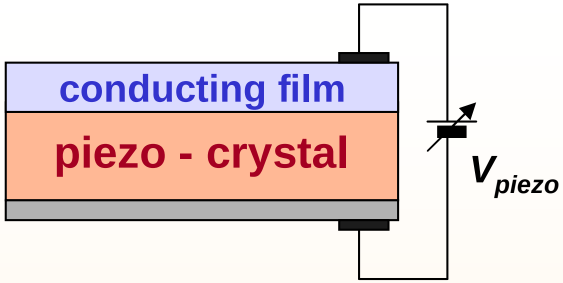




C. Thiele, K. D. at el., APL 87, 262502 (05)

M. Biegalsky, H. M. Christen, K. D. (2007)

Direct strain on piezoelectric substrates



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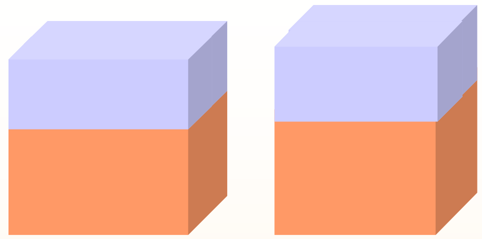

V = 0 ***IVI > 0***

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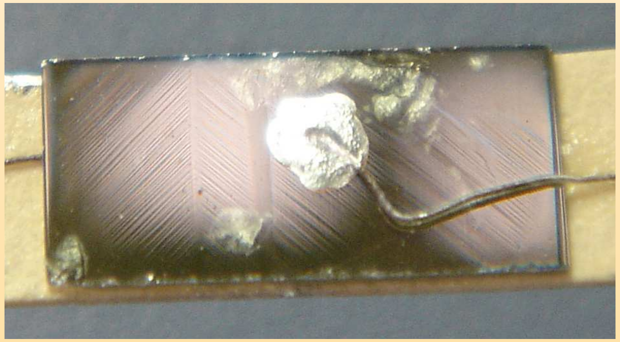

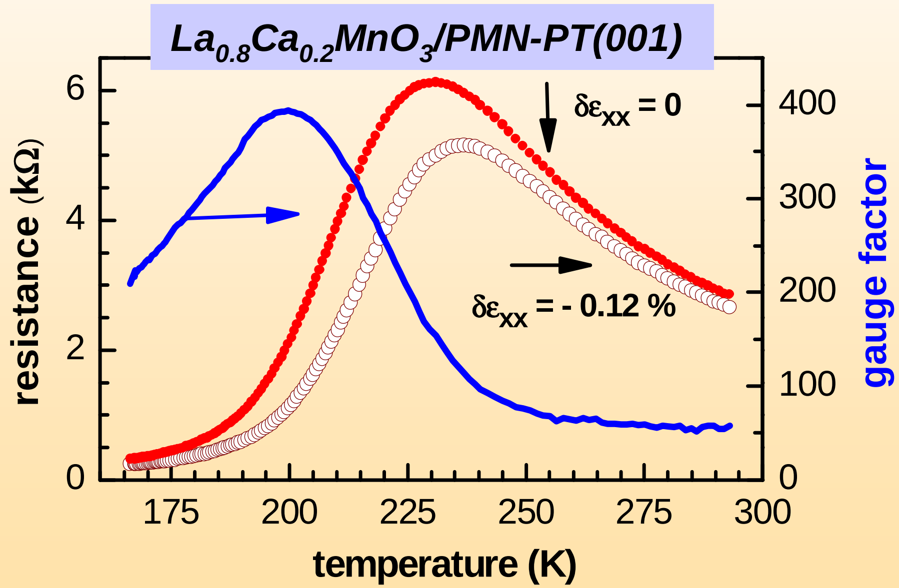

C. Thiele, K. D. at el., APL 87, 262502 (05)

Summary

Magnetoelectric multiferroics:

♦ joined magnetic and electric polarizibility in *one* material

♦ Most single-phase compounds for basic research (low T - apart from $BiFeO_3$, low magnitude of ME effect)

♦ Composites for application (large ME effect at RT, mostly strain-coupled)

Outlook:

♦ Understanding spiral magnetoelectricity

♦ Toroidal domains

♦ Little work on dynamic properties

♦ Stable magnetoelectric switching at 300 K

♦ Superlattices for “unconventional optics“

♦ Charge effects (e. g., field effect) at interfaces

IFW

Literature

Recent reviews :

M. Fiebig: Revival of the magnetoelectric effect, J. Phys. D 38, R123 (2005)

W. Prellier, M. P. Singh, P. Murugavel: The single-phase multiferroic oxides – from bulk to thin film, J. Phys.: Cond. Matter 17, R803 (2005)

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W. Eerenstein, N. D. Mathur, J. Scott: Multiferroic and magnetoelectric materials, Nature 442, 759 (2006)

D. I. Khomskii: Multiferroics – different ways to combine magnetism and ferroelectricity, J. Magn. Magn. Mater. 306, 1 (2006)

*Proceedings of the MEIPIC conferences