

# Coupled electricity and magnetism: multiferroics and beyond

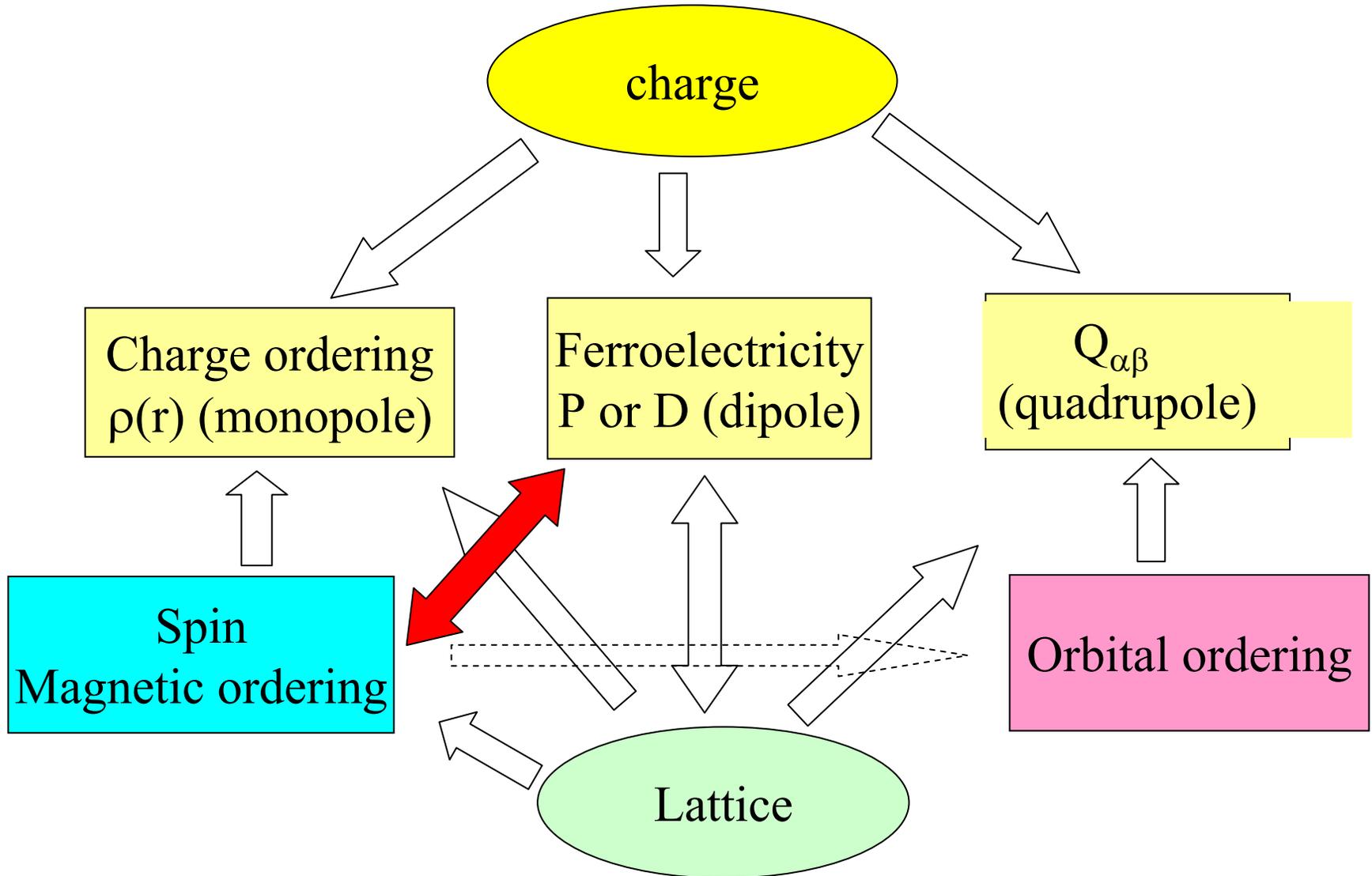
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# Degrees of freedom



## ● Maxwell's equations

$$\nabla \cdot \mathbf{E} = 4\pi\rho_e$$

$$\nabla \cdot \mathbf{B} = 0$$

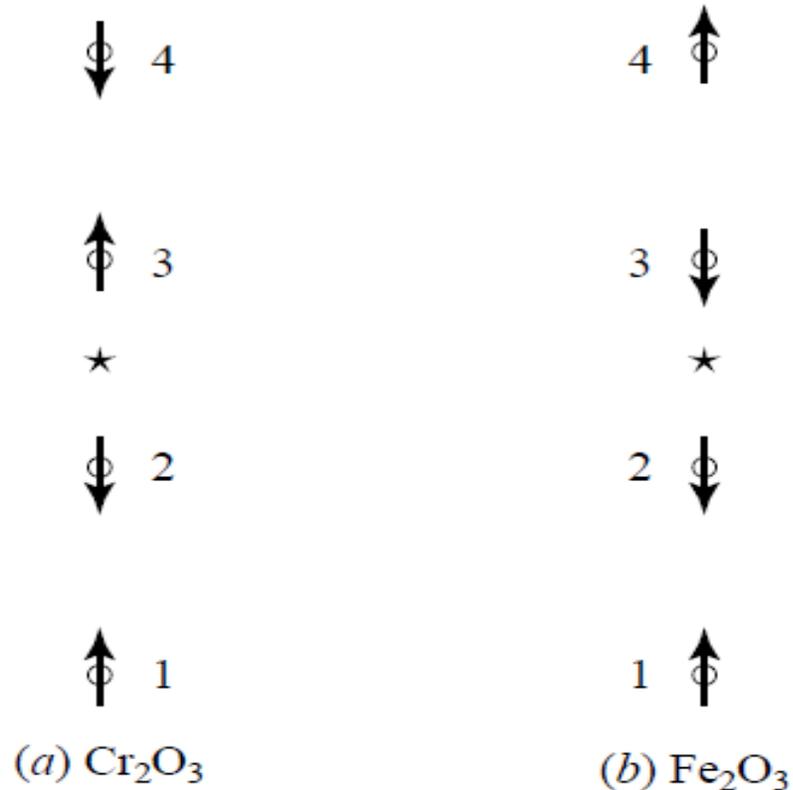
$$-\nabla \times \mathbf{E} = \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \mathbf{j}_e$$

## ● Magnetolectric effect

$$M_i = \sum \alpha_{ij} E_j + \sum \beta_{ijk} E_j E_k + \dots$$

$$P_i = \sum \alpha_{ij} H_j + \sum \beta_{ijk} H_j H_k + \dots$$



In Cr<sub>2</sub>O<sub>3</sub> inversion is broken --- it is linear magnetoelectric

In Fe<sub>2</sub>O<sub>3</sub> – inversion is not broken, it is not ME (but it has weak ferromagnetism)

Magnetoelectric coefficient  $\alpha_{ij}$  can have both symmetric and antisymmetric parts

$$\mathbf{P}_i = \alpha_{ij} \mathbf{H}_i ; \quad \alpha_{ij} = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$$

Symmetric: Then along main axes  $\mathbf{P} \parallel \mathbf{H}$ ,  $\mathbf{M} \parallel \mathbf{E}$

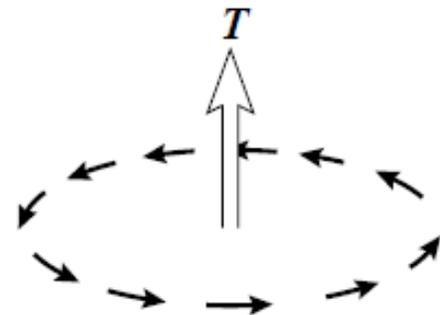
For antisymmetric tensor  $\alpha_{ij}$  one can introduce a dual vector  $T_i = \epsilon_{ijk} \alpha_{jk}$

$\mathbf{T}$  is the **toroidal moment** (both P and T-odd). Then  $\mathbf{P} \perp \mathbf{H}$ ,  $\mathbf{M} \perp \mathbf{E}$ ,

$$\mathbf{P} = [\mathbf{T} \times \mathbf{H}], \quad \mathbf{M} = -[\mathbf{T} \times \mathbf{E}]$$

For localized spins 
$$\mathbf{T} = \sum_i \mathbf{r}_i \times \mathbf{S}_i$$

For example, toroidal moment exists in magnetic vortex



# Coupling of electric polarization to magnetism

## Time reversal symmetry

$$\mathbf{P} \rightarrow +\mathbf{P}$$

$$t \rightarrow -t$$

$$\mathbf{M} \rightarrow -\mathbf{M}$$

## Inversion symmetry

$$\mathbf{P} \rightarrow -\mathbf{P}$$

$$\mathbf{r} \rightarrow -\mathbf{r}$$

$$\mathbf{M} \rightarrow +\mathbf{M}$$

$$E \propto \alpha H E$$

# MULTIFERROICS

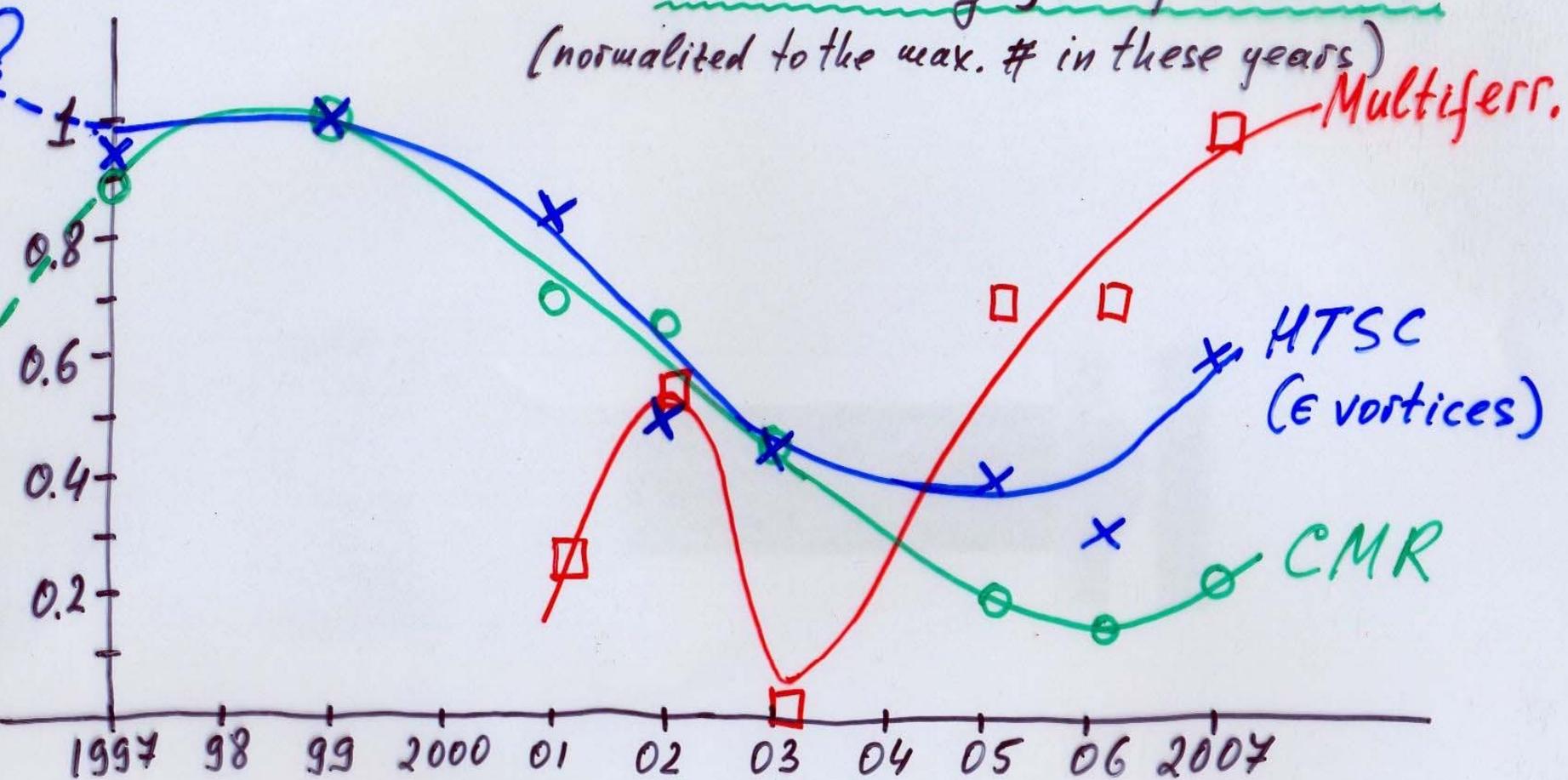
Materials combining ferroelectricity, (ferro)magnetism and (ferro)elasticity

If successful – a lot of possible applications (e.g. electrically controlling magnetic memory, etc)

Field active in 60-th – 70-th, mostly in the Soviet Union

Revival of the interest starting from ~2000

March meetings, # of sessions  
(normalized to the max. # in these years)



- Perovskites: either – or; **why?**
- The ways out:
- **Type-I multiferroics**: Independent FE and magnetic subsystems
  - 1) “Mixed” systems
  - 2) Lone pairs
  - 3) “Geometric” FE
  - 4) FE due to charge ordering
- **Type-II multiferroics**: FE due to magnetic ordering
  - 1) Magnetic spirals (spin-orbit interaction)
  - 2) Exchange striction mechanism
  - 3) Electronic mechanism

## Two general sets of problems:

**Phenomenological treatment** of coupling of M and P;  
symmetry requirements, etc.

**Microscopic conditions** of coexistence of magnetism and ferroelectricity;  
types of multiferroic systems;  
mechanisms of coupling

## Two different groups:

**Type-I:** Magnetism and FE exist **independently**, with certain coupling; different sources; different groups of electrons

**Type-II:** FE **due to** certain type of magnetic ordering; only in magnetic state

material	$T_{\text{FE}}$ (K)	$T_{\text{M}}$ (K)	$P(\mu\text{C cm}^{-2})$
$\text{BiFeO}_3$	1103	643	60 - 90
$\text{YMnO}_3$	914	76	5.5
$\text{HoMnO}_3$	875	72	5.6
$\text{TbMnO}_3$	28	41	0.06
$\text{TbMn}_2\text{O}_5$	38	43	0.04
$\text{Ni}_3\text{V}_2\text{O}_8$	6.3	9.1	0.01

**Magnetism:** In principle clear: spins; exchange interaction; partially filled d-shells

**Ferroelectricity:** Microscopic origin much less clear. Many different types, mechanisms  several different mechanism, types of multiferroics

### **Type-I multiferroics**

- 1) Perovskites:  $d^0$  vs  $d^n$
- 2) “Geometric” multiferroics ( $\text{YMnO}_3$ )
- 3) Lone pairs ( $\text{Bi}$ ;  $\text{Pb}$ , ....)
- 4) FE due to charge ordering

### **Type-II multiferroics**

- 5) FE due to magnetic ordering
  - 5a) Spiral MF
  - 5b) MF due to exchange striction
  - 5c) Electronic mechanism

# Perovskites: $d^0$ vs $d^n$

Empirical rule: FE for perovskites with empty d-shell  
(BaTiO<sub>3</sub>, PbZrO<sub>3</sub>; KNbO<sub>3</sub>)

contain Ti<sup>4+</sup>, Zr<sup>4+</sup>; Nb<sup>5+</sup>, Ta<sup>5+</sup>; Mo<sup>6+</sup>, W<sup>6+</sup>, etc.

Magnetism – partially filled d-shells,  $d^n$ ,  $n > 0$

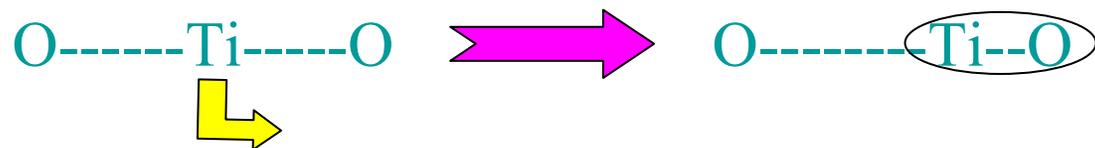
## Why such mutual exclusion?

Not quite clear. Important what is the mechanism of FE in perovskites like BaTiO<sub>3</sub>

Classically: polarization catastrophe; Clausius-Mossotti relations, etc.

Real microscopic reason: **chemical bonds**

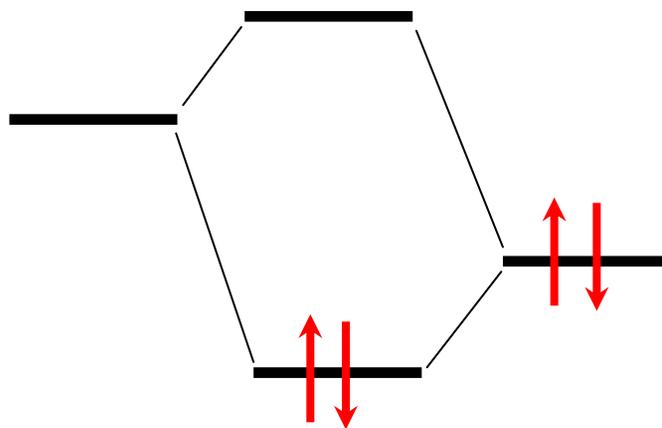
$\text{Ti}^{4+}$ : establishes *covalent bond* with oxygens (which “donate” back the electrons), using empty d-levels



Better to have one strong bond with one oxygen than two weak ones with oxygens on the left and on the right

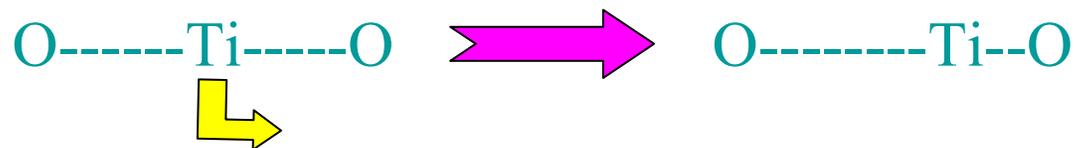
Two possible reasons:

$d^0$  configurations: only bonding orbitals are occupied



Other localized d-electrons break *singlet* chemical bond by Hund's rule pair-breaking (a la pair-breaking of Cooper pairs by magnetic impurities)

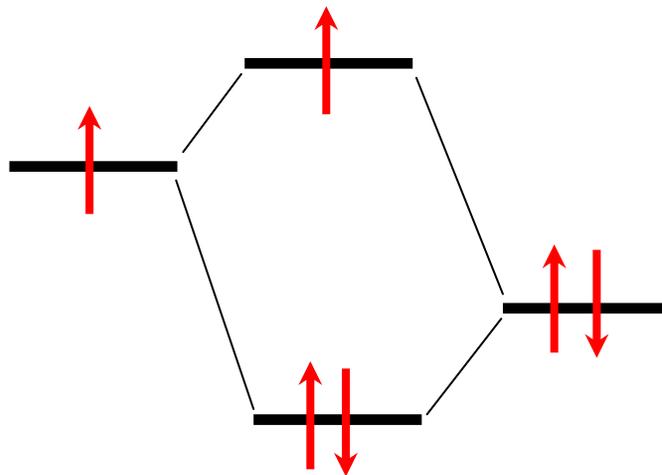
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Suppose there exist yet another localised d-electron,  $\tilde{d} \uparrow$  (e.g. on  $t_{2g}$ -level)

Always strong Hund's rule coupling

$$-J_H d \uparrow \tilde{d} \uparrow = -J_H \vec{S}_d \vec{S}_{\tilde{d}}$$

Spin  $\tilde{d} \uparrow$  - "does not like" the component  $d \uparrow \uparrow$  of the valence bond wavefunction  $|\Psi\rangle$

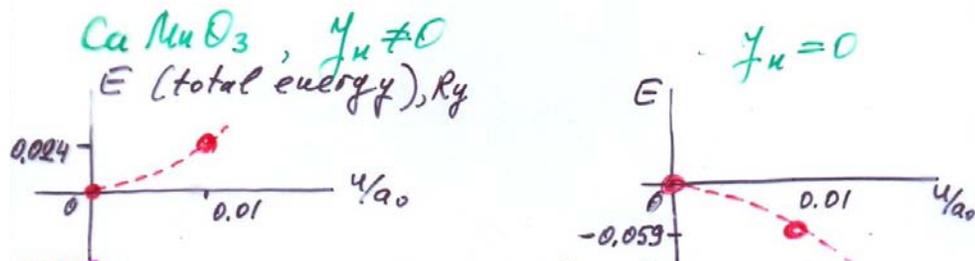
$\Rightarrow$  we lose half of the energy gain  $\delta E$

Thus the Hund's rule decoupling may be destructive for FE

● To check this:

LDA+U - calculations (I. Elfimov) with and without  $J_H$ ; to check the stability vs shift of TM ion

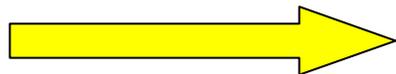
Displacement  $u = 0.01 a_0 = 1\% a_0$



$\Rightarrow$  If we switch off Hund's rule coupling - CaMnO<sub>3</sub> (Mn<sup>4+</sup>(d<sup>3</sup>)) would become unstable wrt ferroelectric displacement

## The ways out:

- (x) “Mixed” systems, with both  $d^0$  and  $d^n$  ion  
( $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ;  $\text{PbCo}_{1/2}\text{W}_{1/2}\text{O}_3$ , ....)
- (x) Independent magnetic and FE subsystems, different subgroups responsible for FE and magnetism.  
E.g. Ni-J boracite  $\text{Ni}_3\text{B}_7\text{O}_{13}\text{J}$
- (x) “Geometric” FE:  $\text{YMnO}_3$ , etc
- (x) Lone pairs:  $\text{Bi}^{3+}$  ( $\text{BiFeO}_3$ ;  $\text{BiMnO}_3$ );  $\text{Pb}^{2+}$  ( $\text{PbVO}_3$ ) ;  
Aurivillius phases with magnetic ions?
- (x) Charge ordering (organics;  $\text{LuFe}_2\text{O}_4$ ;  $\text{Fe}_3\text{O}_4$ ;  $(\text{PrCa})\text{MnO}_3$ ?  
 $\text{RNiO}_3$ ?)



coupling usually weak!

## (x) FE due to magnetic ordering

- 1) Magnetics with spiral magnetic structure ( $\text{TbMnO}_3$ ,  $\text{Ni}_3\text{V}_2\text{O}_8$ ;  $\text{MnWO}_4$ ,  $\text{CuFeO}_2$ ;  $\text{LiCuV}_2\text{O}_4$ )
- 2) Magnetics with FE due to magnetostriction ( $\text{TbMn}_2\text{O}_5$  ? ;  $\text{RbFe}(\text{MoO}_4)_2$ )
- 3) Purely electronic mechanism (in frustrated magnets)

Usually  $T_c$  are low; polarization small; but **coupling strong**

(x) **Composite systems:** multilayers of magnetic and FE materials; “mixtures”, etc.

 *possibly the most realistic route for practical applications*

# “Geometric” multiferroics: hexagonal manganites $\text{RMnO}_3$

$\text{YMnO}_3$ :  $T_{\text{FE}} \sim 900 \text{ K}$ ;  $T_{\text{N}} \sim 70 \text{ K}$

The origin (T.Palstra, N. Spaldin): **tilting** of  $\text{MnO}_5$  trigonal bipyramids – a la tilting of  $\text{MO}_6$  octahedra in the usual perovskites leading to orthorhombic distortion.

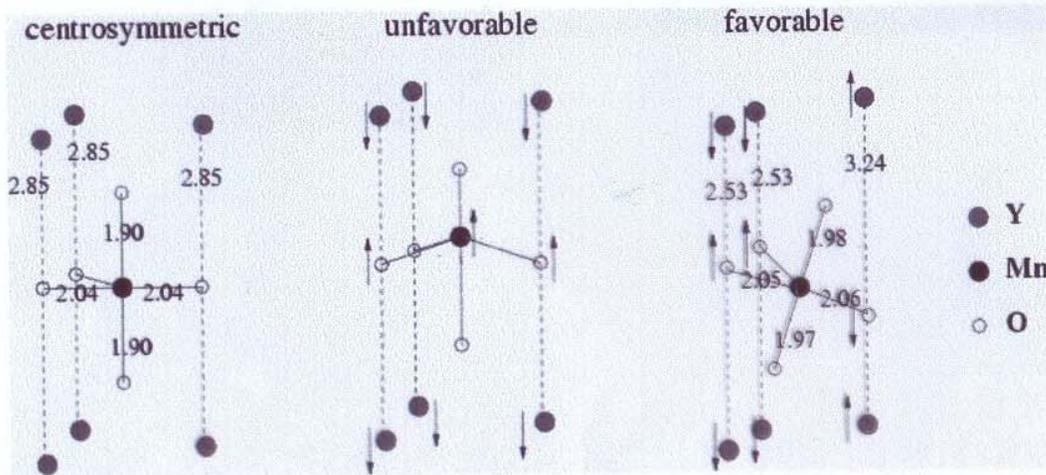
In perovskites one  $\text{AMO}_3$  one  $\text{A-O}$  distance becomes short, but no total dipole moment – dipole moments of neighbouring cells compensate.

In  $\text{YMnO}_3$  – total dipole moment, between  $\text{Y}$  and  $\text{O}$ ; **Mn plays no role!**

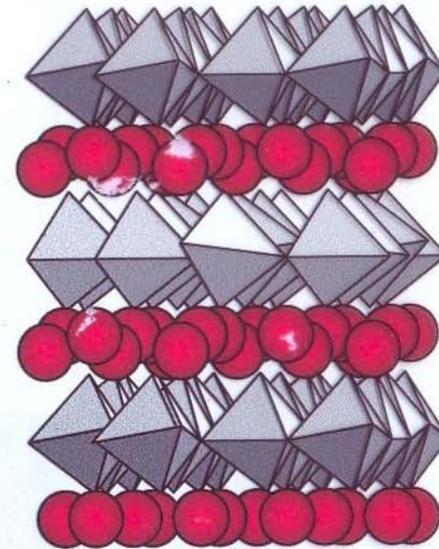
# Crystal structure of $\text{YMnO}_3$

Ferroelectric distortion

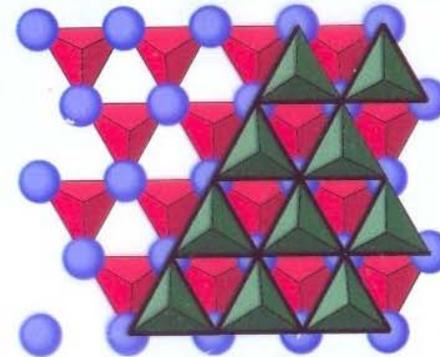
Displacements from:  
centrosymmetric high temp  
to ferroelectric room temp



Van Aken, Palstra, Filipetti, Spaldin, *Nature Materials* 2004



Perpendicular hexagonal axis



Parallel hexagonal axis

B. Van Aken, A. Meetsma, T. Palstra  
*Acta Cryst. C and several E* (2001)

# Lone pairs and ferroelectricity

$\text{Bi}^{3+}$ ;  $\text{Pb}^{2+}$ . Classically – large polarizability. Microscopically – easy orientation of the lone pairs

Many nonmagnetic ferroelectrics with  $\text{Bi}^{3+}$ ;  $\text{Pb}^{2+}$  . – e.g. PZT  
[ $\text{Pb}(\text{ZrTi})\text{O}_3$ ]

Some magnetic:

Aurivillius phases: good ferroelectrics, layered systems with perovskite slabs/ $\text{Bi}_2\text{O}_2$  layers ( $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ;  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ , etc). Exist with **magnetic ions**, but not really studied.

$\text{PbVO}_3$  – a novel compound. Distortion so strong that probably impossible to reverse polarization – i.e. it is probably not ferroelectric, but rather **pyroelectric**

# Synthesis, Structure, and Properties of New Perovskite PbVO<sub>3</sub>

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The new perovskite PbVO<sub>3</sub> was synthesized under high-temperature and high-pressure conditions. Its crystal structure ( $a = 3.80005(6)$  Å,  $c = 4.6703(1)$  Å,  $Z = 1$ , S.G.  $P4mm$ ) contains isolated layers of corner-shared VO<sub>5</sub> pyramids, which are formed instead of octahedra due to a strong tetragonal distortion ( $c/a = 1.23$ ). The lead atom is shifted out of the center of the unit cell toward one of two [VO<sub>2</sub>]-layers due to the influence of the lone pair. This new perovskite exhibits a semiconductor-like  $\rho(T)$  dependence down to 2 K. This behavior can be qualitatively explained by taking into account strong electron correlations in electronic structure calculations.

## Introduction

The rising interest in highly correlated electron systems called for an intensive investigation of reduced vanadium oxides. The perovskite-like compounds AVO<sub>3</sub>, where A is a three or divalent cation, are widely studied due to their simple structures, which allow a deep understanding of the relationship between structure and properties in these systems.

AVO<sub>3</sub> oxides were reported for most of the divalent elements as A-cation. For alkali-earth elements (except Mg) their structures are three-dimensional frameworks consisting of corner-shared VO<sub>6</sub> octahedra. Octahedra in these structures are regular or slightly distorted and no formation of a short vanadyl bond is observed. Thus, SrVO<sub>3</sub> is an ideal cubic perovskite<sup>1,2</sup> and CaVO<sub>3</sub> is an orthorhombically distorted perovskite (GdFeO<sub>3</sub>-type).<sup>1,3</sup>

while BaVO<sub>3</sub> forms trigonal 5H close-packing in a wide range of oxygen nonstoichiometry.<sup>4</sup> Stoichiometric CaVO<sub>3</sub> and SrVO<sub>3</sub> compounds exhibit metallic-like conductivity down to 2–4 K and Pauli paramagnetic behavior. These properties can be changed by variation of oxygen content.<sup>2,5–7</sup>

Until now no information is available on the existence of PbVO<sub>3</sub> despite Pb<sup>2+</sup> cation crystal radius (1.63 Å) being very close to that for Sr<sup>2+</sup> (1.58 Å). The synthesis of this compound looks very attractive, taking into account the influence of the lone pair of the Pb<sup>2+</sup> cation, which can lead to a strong distortion of the perovskite lattice and thus to a decrease of the dimensionality of the structure. Below, we present the results of the

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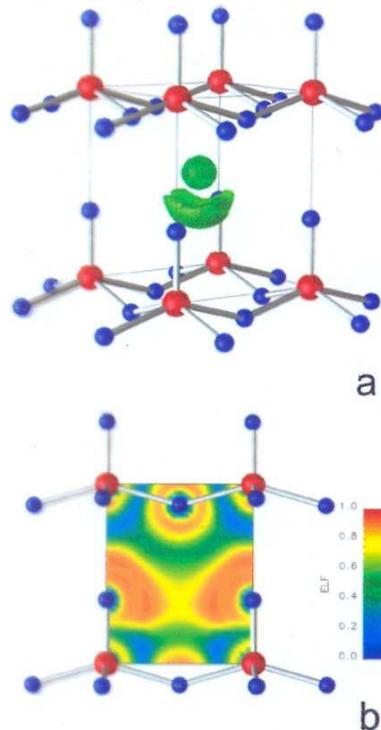
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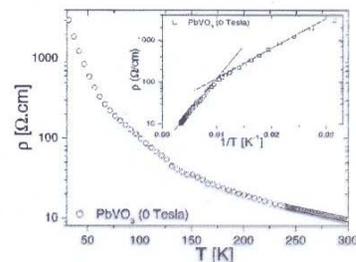


**Figure 3.** (a) Valence electrons ELF isosurface ( $\eta = 0.85$ ) around Pb. (b) ELF distribution in the (100) plane.

consequently of the physical properties of the material. In the case of PbVO<sub>3</sub> we observed neither the presence of superstructure peaks in XPD patterns nor a change of the lattice parameters, which would have indicated an oxygen nonstoichiometry, even in samples prepared with starting compositions PbVO<sub>3</sub> ±  $\delta$  ( $\delta = 0.1, 0.2, 0.3$ ).

**Resistivity Properties and NPD Measurements.** Resistivity measurements performed on a polycrystalline sample evidence semiconducting behavior, with  $\rho(T)$  increasing by 3 orders of magnitude between 300 and 30 K (Figure 4). Below 30 K, the resistance becomes too high for a reliable measurement with our equipment. The increase of  $\rho(T)$  is rather smooth, without clear evidence for a transition. A plot  $\log(\rho)$  versus  $1/T$  suggests a linear dependence and thus activated behavior in two temperature regions, one above 100 K and one between 100 and 50 K. The slopes correspond to activation energies of 340 and 180 K for  $T > 100$  K and  $T < 100$  K, respectively.

Unfortunately, the magnetic properties could not be determined from the susceptibility results because the susceptibility was dominated by a ferromagnetic contribution, which we attributed to be due to the PbV<sub>6</sub>O<sub>11</sub>



**Figure 4.** Temperature dependence of the resistivity of a polycrystalline PbVO<sub>3</sub> sample. Inset:  $\log \rho$  versus  $1/T$  plot, showing the two regions with activated behavior (lines are guide to the eyes).

foreign phase.<sup>19</sup> However, the neutron experiment allows some estimations to be made for magnetic properties of PbVO<sub>3</sub>. Within the accuracy of our NPD data neither extra antiferromagnetic peaks nor an increase in the nuclear Bragg peaks were observed at the temperature  $T = 1.5$  K. The estimation of the low limit of the long-range ordered ferromagnetic moment amounts to  $\leq 0.05 \mu_B$ , assuming a ferromagnetic alignment of the V<sup>4+</sup> spins. The estimation of the low limit of the antiferromagnetic moment is not unambiguous since the magnetic structure factors depend on a particular magnetic structure, which is not known. Assuming a simple antiferromagnetic structure in the (*ab*) plane, the low limit of the antiferromagnetic moment is  $\leq 0.4 \mu_B$ .

**Electronic Structure from the First-Principle Study.** Vanadium oxides are supposed to be systems with strongly correlated electrons;<sup>20</sup> for example, the true insulating and magnetically ordered states were obtained for V<sup>4+</sup> oxide compounds, only taking into account the on-site Coulomb interactions.<sup>21</sup>

First, we performed calculations using local spin density approximation (LSDA) considering both ferromagnetic (FM) and antiferromagnetic (AFM) ordering models for PbVO<sub>3</sub>. The electronic band structure was calculated using the linearized muffin-tin (MT) orbitals method within the atomic-spheres approximation.<sup>22</sup> We considered the unit cell with one V atom and the supercell with four V atoms to model the FM and AFM (C-type) states, respectively.

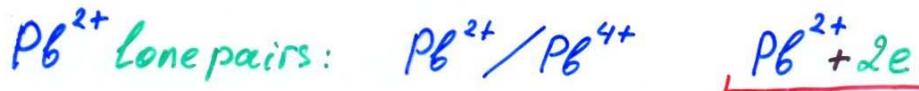
For the FM ordering, the electronic structure is found to be metallic (Figure 5a) with the near the Fermi level DOS determined by the vanadium 3d and antibonding 2p states of O(2) atom ( $\mu = 0.38 \mu_B$  inside the vanadium MT sphere). The character of the states near  $E_F$  evidences significant Vd–O2p hopping and suggests

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## Problems with Bi perovskites:

**BiMnO<sub>3</sub>**: ferromagnetic insulator; Jahn-Teller distorted perovskite; ferroelectric?

**BiFeO<sub>3</sub>**: rhombohedral; good ferroelectric; spiral magnetic structure

**BiCoO<sub>3</sub>**: very strong tetragonal distortion! a la **PbVO<sub>3</sub>** (pyroelectric)

**BiNiO<sub>3</sub>**: Ni<sup>2+</sup>, Bi<sup>4+</sup>  charge segregates into Bi<sup>3+</sup> + Bi<sup>5+</sup>

Under pressure: **BiNiO<sub>3</sub>** goes back to Ni<sup>3+</sup>, Bi<sup>3+</sup>  charge segregates into Ni<sup>2+</sup> + Ni<sup>4+</sup> !

# Bond- versus site-centred ordering and possible ferroelectricity in manganites

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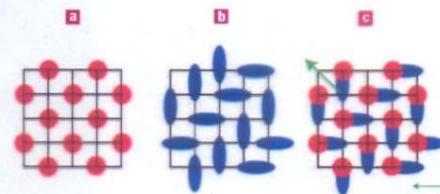
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Transition metal oxides with a perovskite-type structure constitute a large group of compounds with interesting properties. Among them are materials such as the prototypical ferroelectric system BaTiO<sub>3</sub>, colossal magnetoresistance manganites and the high-*T<sub>c</sub>* superconductors. Hundreds of these compounds are magnetic<sup>1</sup>, and hundreds of others are ferroelectric<sup>2</sup>, but these properties very seldom coexist. Compounds with an interdependence of magnetism and ferroelectricity could be very useful: they would open up a plethora of new applications, such as switching of magnetic memory elements by electric fields. Here, we report on a possible way to avoid this incompatibility, and show that in charge-ordered and orbitally ordered perovskites it is possible to make use of the coupling between magnetic and charge ordering to obtain ferroelectric magnets. In particular, in manganites that are less than half doped there is a type of charge ordering that is intermediate between site-centred and bond-centred. Such a state breaks inversion symmetry and is predicted to be magnetic and ferroelectric.

Perovskites consist of corner-sharing O<sub>6</sub> octahedra with a transition metal ion in the centre. Almost all the ferroelectric perovskites contain non-magnetic transition metal ions with an empty *d*-shell (*d<sup>0</sup>* configuration), for example Ti<sup>4+</sup>, Nb<sup>5+</sup> and W<sup>6+</sup>. Apparently the presence of the *d<sup>0</sup>* plays an important role in formation of a ferroelectric state<sup>3,4</sup>. In all of these systems ferroelectricity originates from a shift of the transition metal ion from the centre of the O<sub>6</sub> octahedron. In this way a stronger covalent bond with one (or three) instead of six weaker bonds with neighbouring oxygen atoms is formed<sup>5</sup>.

The problem of why magnetism and ferroelectricity seem to be mutually exclusive has received some attention<sup>3,4</sup>. The most plausible explanation has to do with the Hund's rule coupling that tends to keep the spins of the open transition metal 3*d* shell in parallel orientation. This mechanism breaks the strong covalent bonds that are necessary for ferroelectricity. Thus this makes the usual stabilizing mechanism for ferroelectricity, related to the shift of transition metal ions, ineffective<sup>6</sup>.

There are apparently three exceptions to the empirical assertion of the incompatibility of magnetism and ferroelectricity in perovskites:



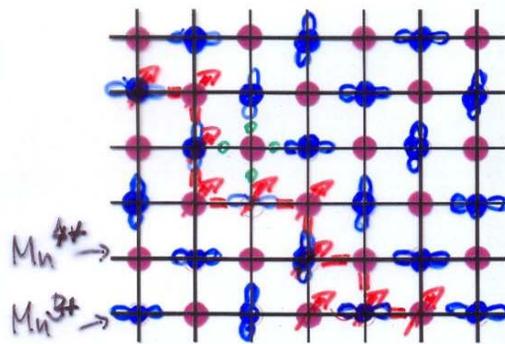
**Figure 1** Three types of charge ordering. **a**, Site-centred charge order; **b**, bond-centred charge order (the Zener polaron state); and **c**, a ferroelectric intermediate state. The charge-ordered structure in **c** lacks inversion symmetry. Thin green arrows indicate the dipole moments of horizontal and vertical dimers, and the diagonal arrow is the total ferroelectric moment.

BiFeO<sub>3</sub>, BiMnO<sub>3</sub> and RMnO<sub>3</sub> (R = Y or another small rare-earth ion). But actually even these compounds are not exceptions to the general rule, as the mechanism of ferroelectricity here is different from the conventional one. In BiFeO<sub>3</sub> and in BiMnO<sub>3</sub>, ferroelectricity is due to the lone pairs of non-magnetic<sup>6</sup> Bi, and in YMnO<sub>3</sub> it is due to tilting of almost rigid MnO<sub>3</sub> trigonal bipyramids<sup>7</sup>. This last example shows that the shift of the transition metal ion from the centre of the O<sub>6</sub> octahedron is not the only feasible mechanism of ferroelectricity. Recently ferroelectricity was observed in TbMnO<sub>3</sub>, and was attributed to magnetic frustration in this system<sup>8</sup>; a similar mechanism seems to operate<sup>9</sup> in TbMn<sub>2</sub>O<sub>5</sub>. Here we present a mechanism for the creation of ferroelectricity that is based on the interplay of magnetic, charge and orbital ordering in doped transition metal oxides, and in particular in manganites.

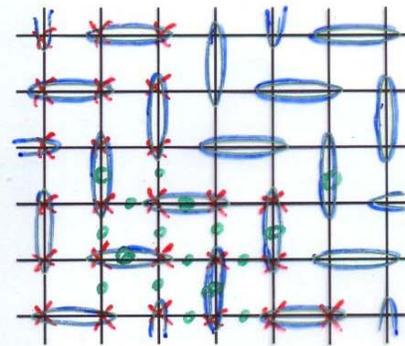
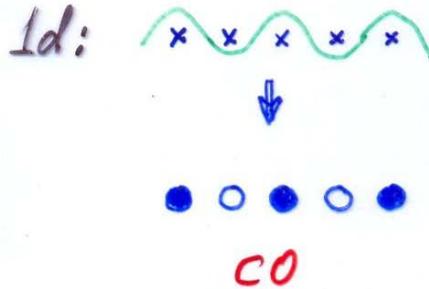
We consider doped manganites of the type R<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub>, with R = La, Pr. Different types of magnetic, charge and orbital orderings are observed in this class of compounds. It becomes more and more clear (see for example, ref. 10) that the charge and orbital

- Charge density waves :
  - manganites
  - magnetite  $\text{Fe}_3\text{O}_4$  (Verwey transition at 119K)

- Bond-centered charge density waves vs site centered charge density waves,

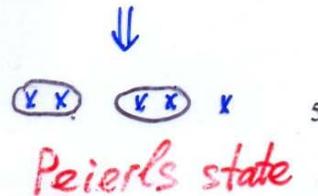


SCDW

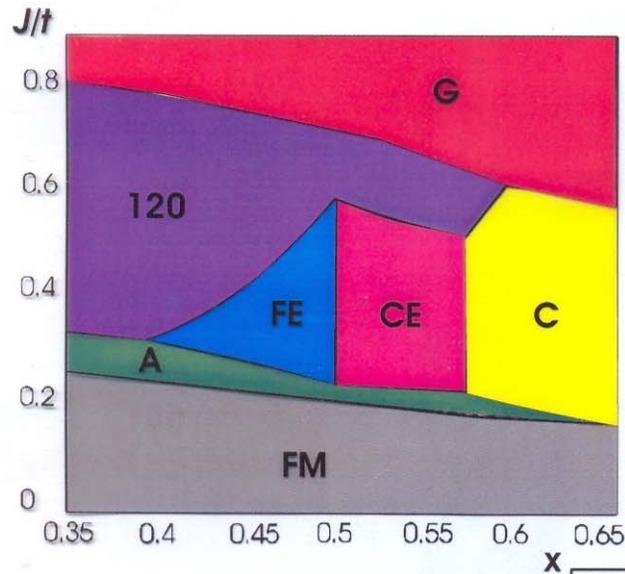


BCDW (Zener polarons)

(Daoud-Aladine et al., PRL 2002)

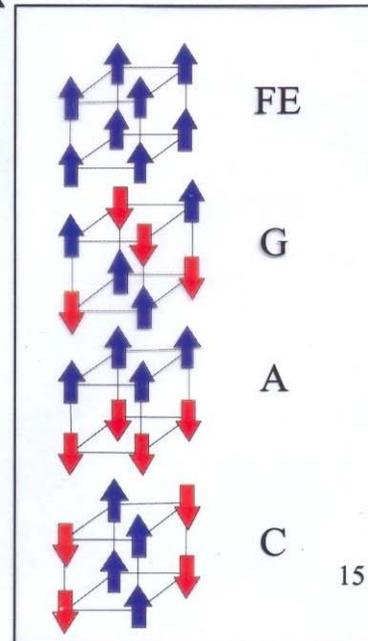


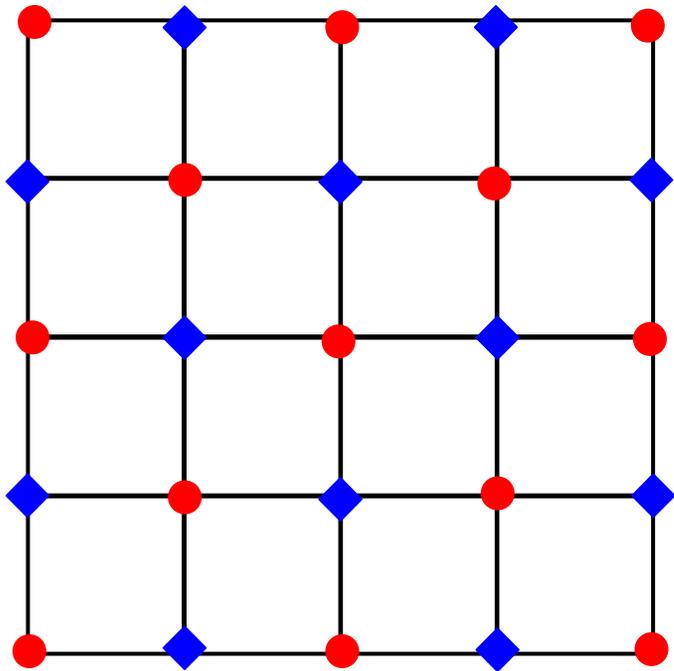
# Phase diagram of manganites near $x=0.5$

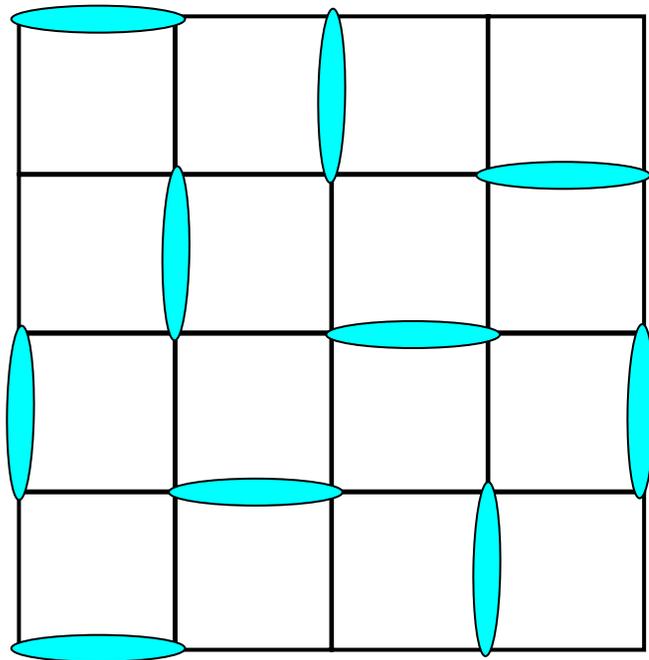


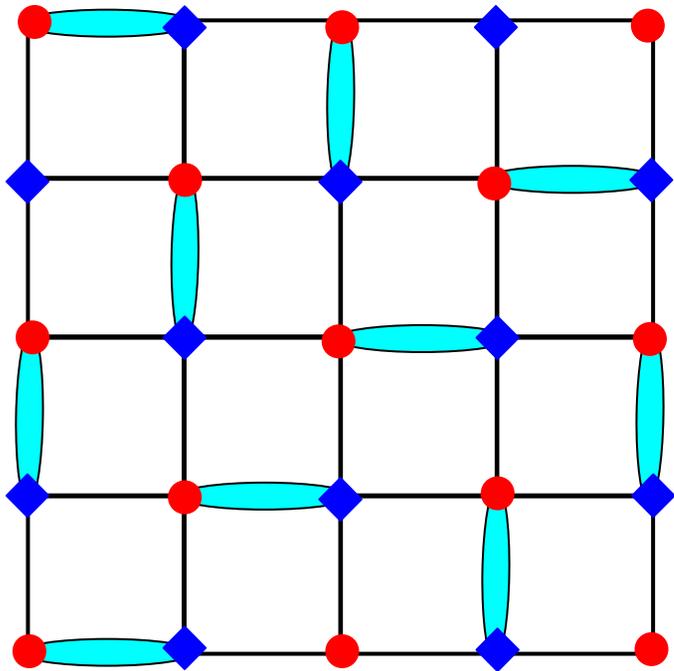
Electron density  $n_e = 1-x$

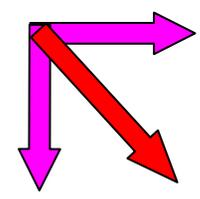
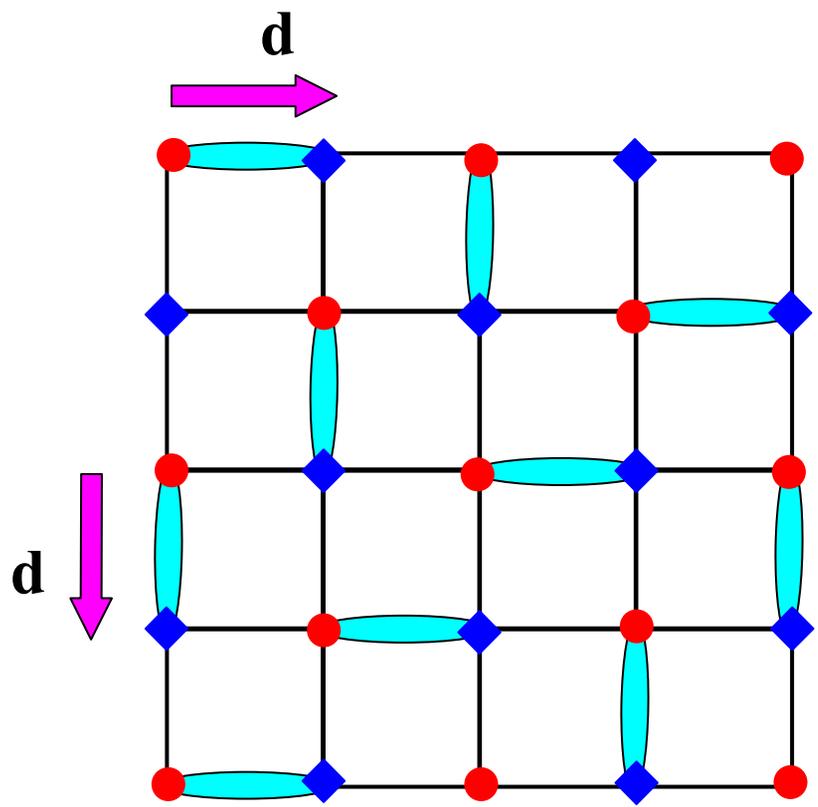
- FM: ferromagnetic phase
- G: antiferromagnetic Neel state
- A: F planes coupled AFM
- C: F chains coupled AFM
- CE: CE-phase
- 120: Jaffet-Kittel state
- FE: Ferroelectric phase



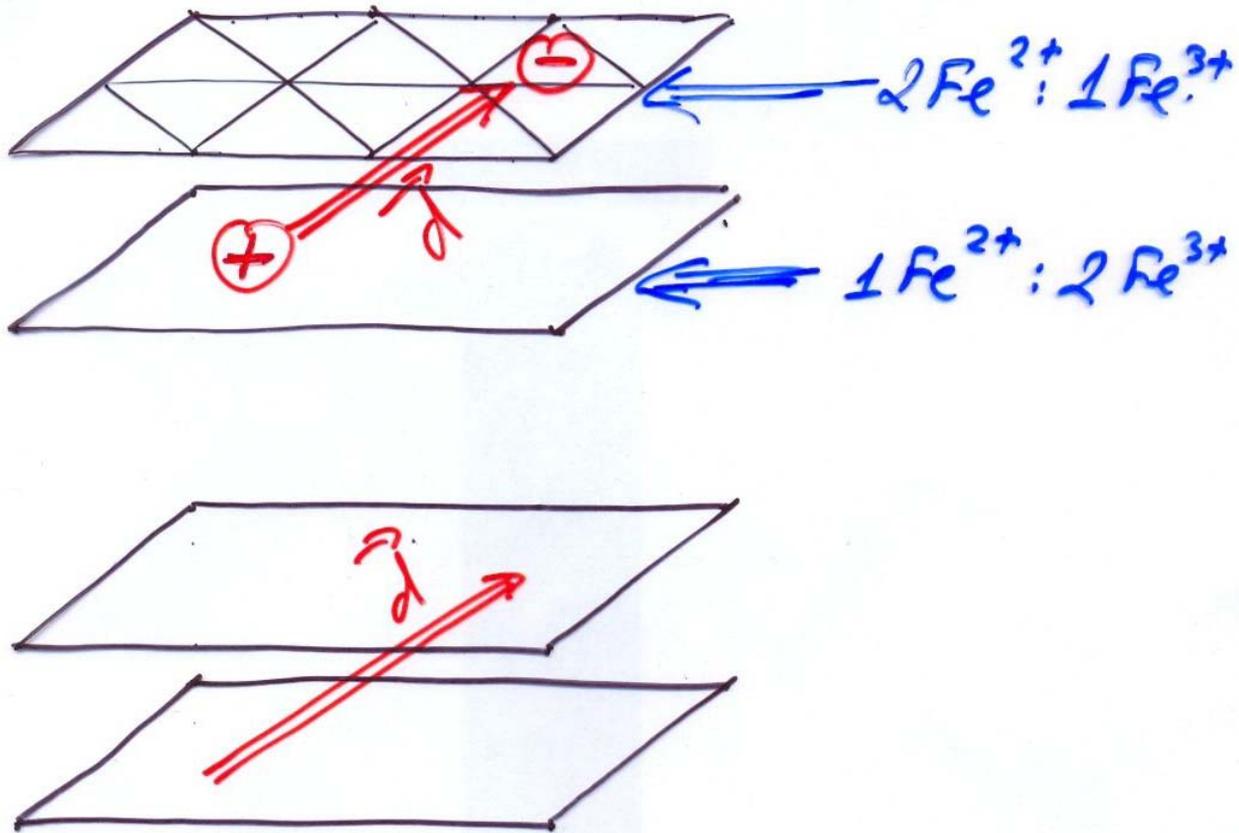








LuFe<sub>2</sub>O<sub>4</sub><sup>2.5+</sup> : "double" triangular layers



# Other similar systems with ferroelectricity due to charge ordering

Some quasi-one-dimensional organic materials (Nad', Brazovskii & Monceau)

**Fe<sub>3</sub>O<sub>4</sub>**: ferroelectric below Verwey transition at 119 K ! Also ferrimagnetic with large magnetization and high T<sub>c</sub>

**RNiO<sub>3</sub>**

PRL 103, 156401 (2009)

PHYSICAL REVIEW LETTERS

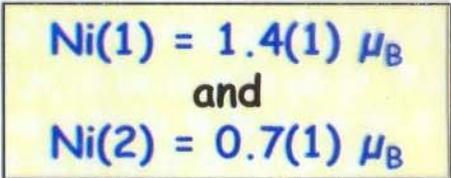
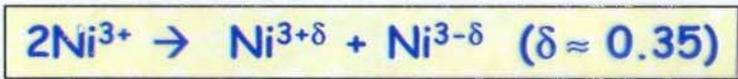
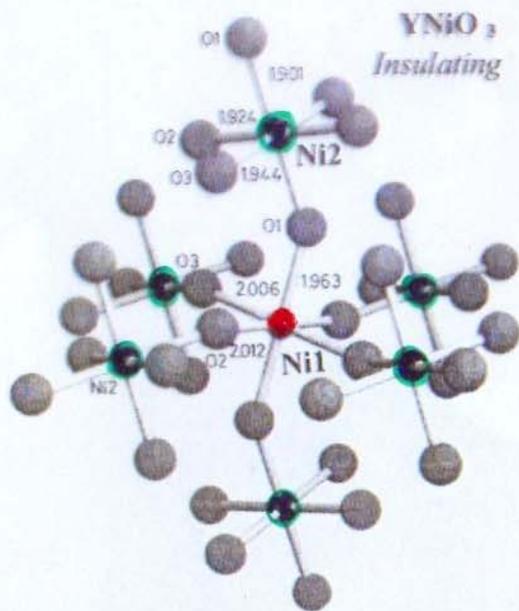
week ending  
9 OCTOBER 2009

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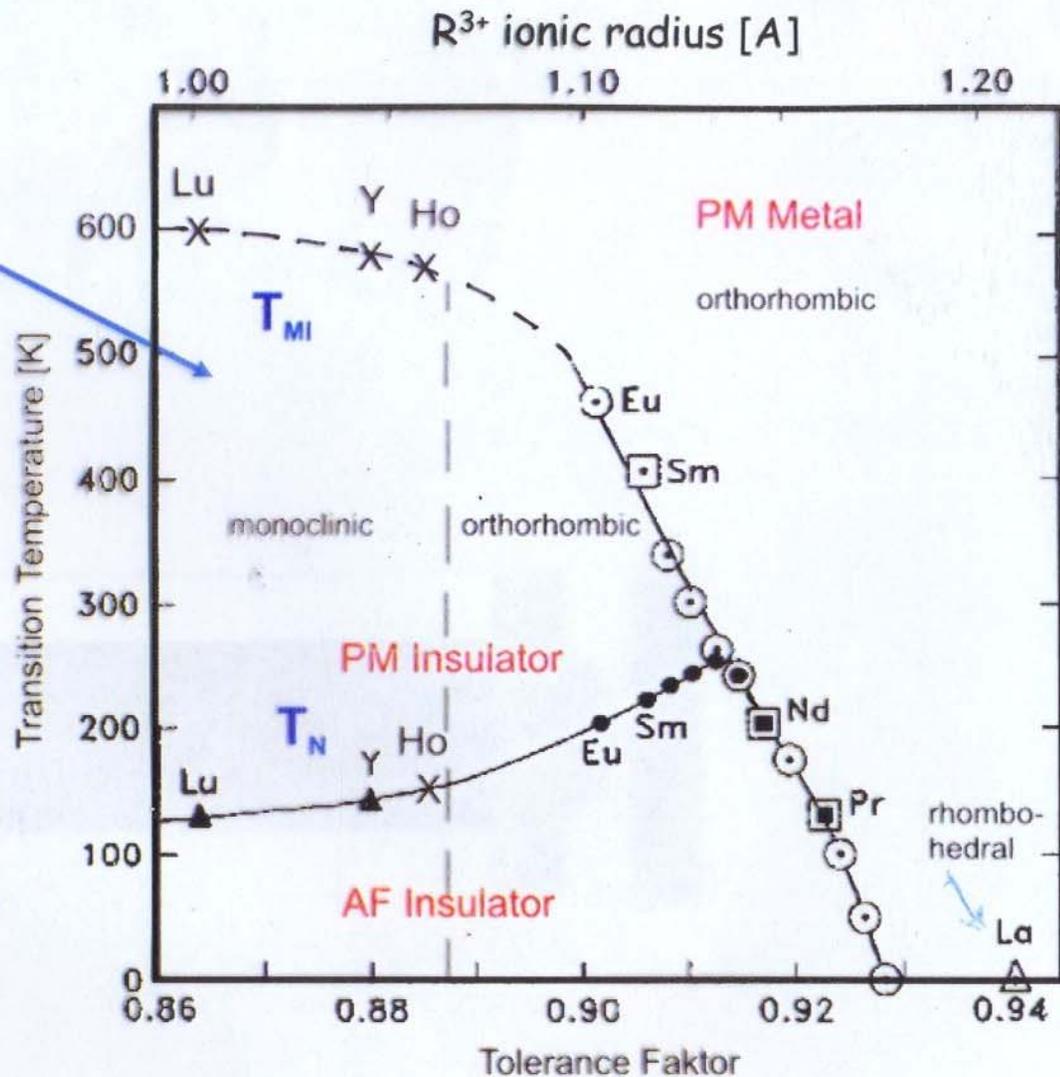
## Multiferroicity in Rare-Earth Nickelates **RNiO<sub>3</sub>**

Gianluca Giovannetti,<sup>1,2,3</sup> Sanjeev Kumar,<sup>1,2</sup> Daniel Khomskii,<sup>4</sup> Silvia Picozzi,<sup>3</sup> and Jeroen van den Brink<sup>1,5,6,7</sup>

# Charge ordering



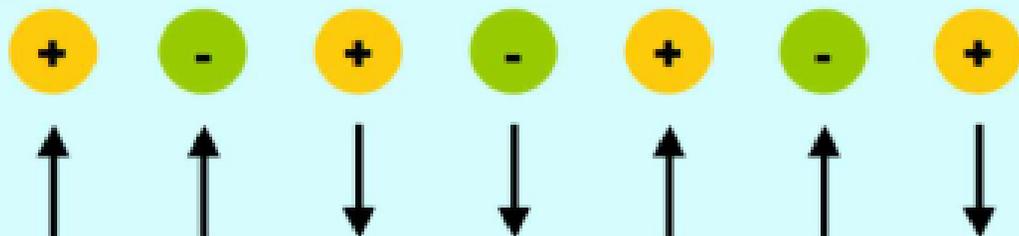
neutron diffraction, J.A. Alonso et al.  
PRL 82, 3871 (99)



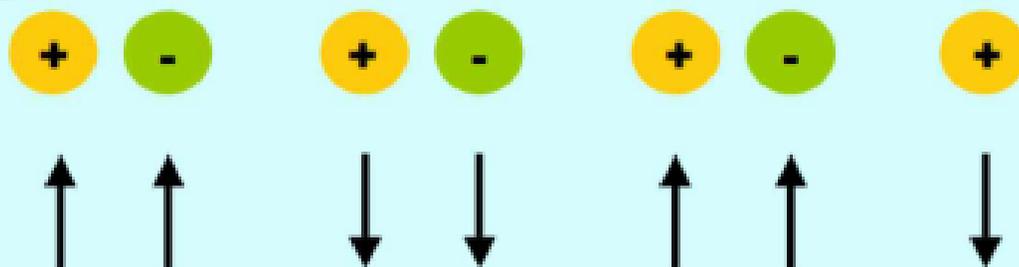
$\sigma$ , Mag.

- △, ▲ Damazeau et al.
- , ■ Lacorre et al.
- , ● Present work
- X Alonso et al.

A



B



● Type-II multiferroics: Ferroelectricity due to magnetic ordering

Coupling of electric polarization to magnetism

Time reversal symmetry  $t \rightarrow -t$

$$\mathbf{P} \rightarrow +\mathbf{P}$$

$$\mathbf{M} \rightarrow -\mathbf{M}$$

Inversion symmetry  $\mathbf{r} \rightarrow -\mathbf{r}$

$$\mathbf{P} \rightarrow -\mathbf{P}$$

$$\mathbf{M} \rightarrow +\mathbf{M}$$

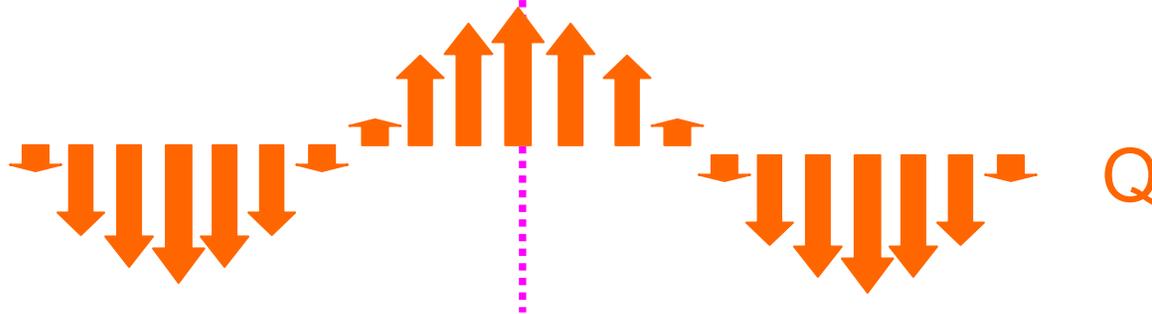
$$E \propto P M \partial M$$

# Polarization induced by SDW

Certain magnetic structures violate inversion symmetry – what is needed for FE  
Typically – magnetic spirals

**Sinusoidal SDW:**

$$M = A \sin Qx$$

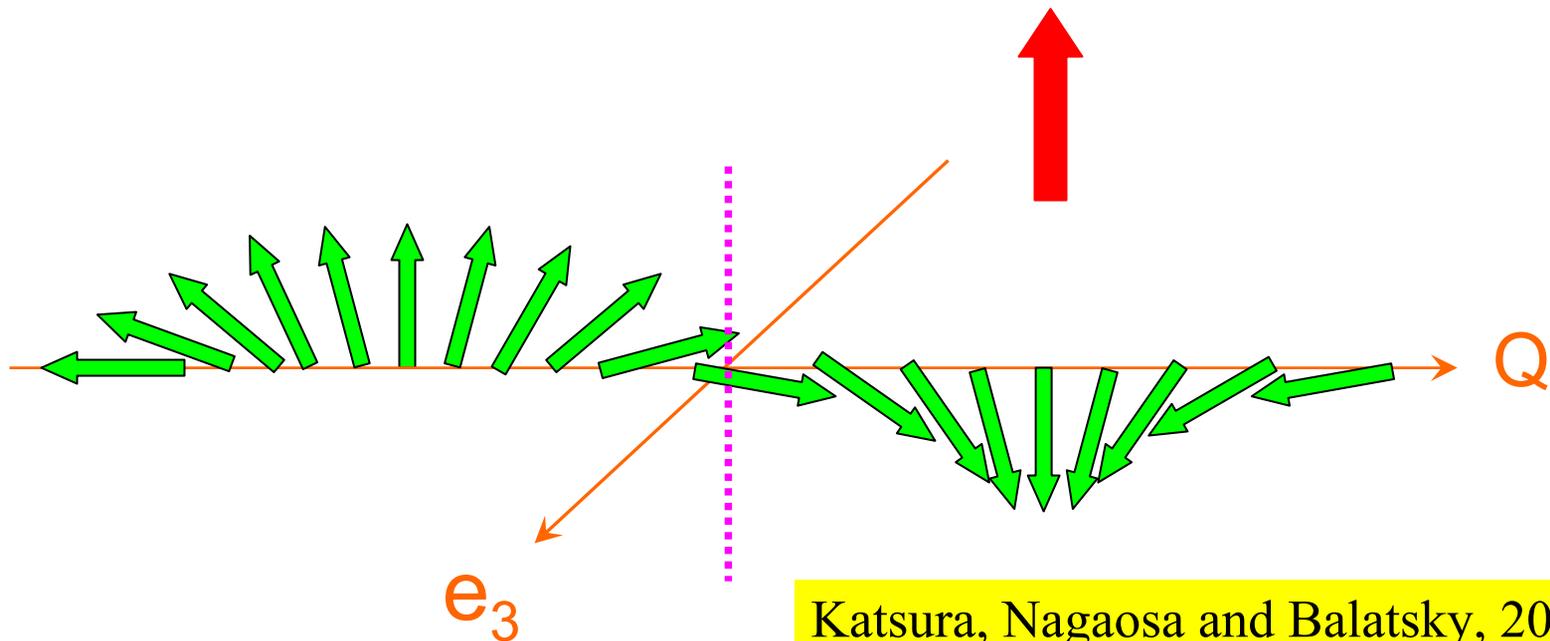


**Mirror plane, no FE!**  $\bar{P} = 0$

# Helicoidal SDW :

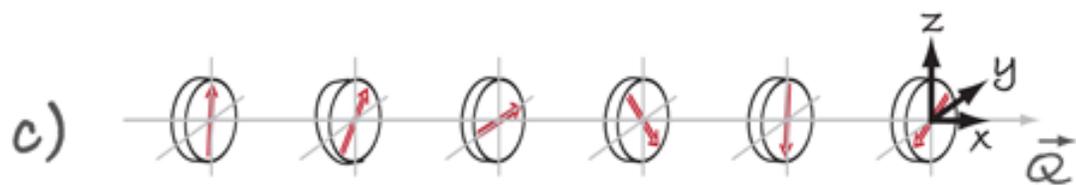
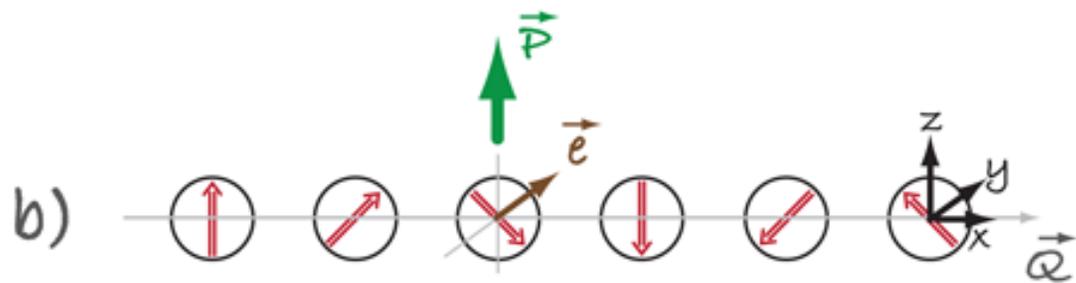
$$\mathbf{M} = A_1 \mathbf{e}_1 \cos Qx + A_2 \mathbf{e}_2 \sin Qx + A_3 \mathbf{e}_3$$

$$\bar{\mathbf{P}} \propto [\mathbf{e}_3 \times \mathbf{Q}]$$

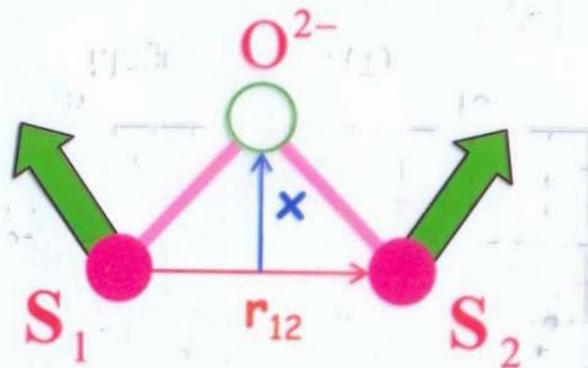


Katsura, Nagaosa and Balatsky, 2005

Mostovoy 2006



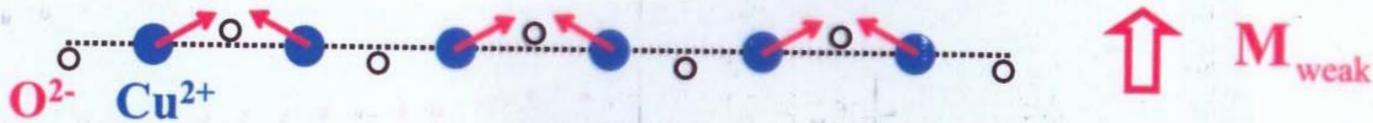
# Effects of Dzyaloshinskii-Moriya interaction



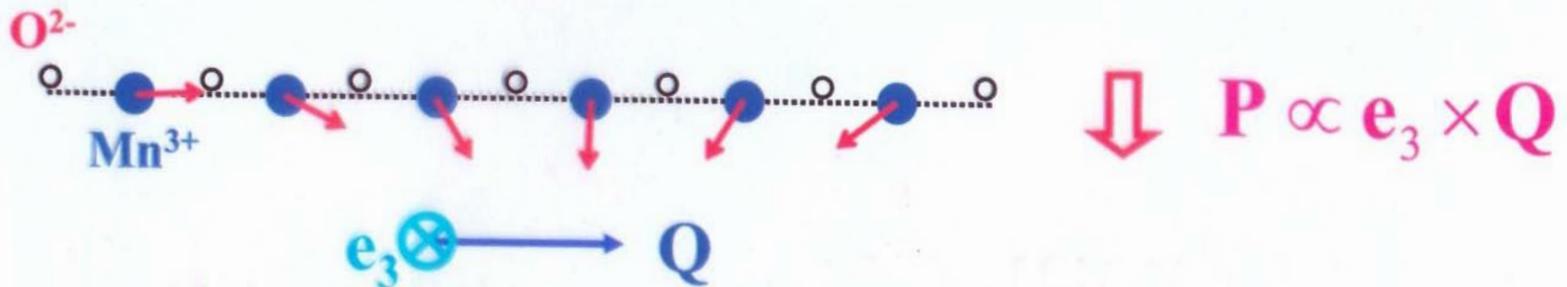
$$E_{DM} = \mathbf{D}_{12} \cdot [\mathbf{S}_1 \times \mathbf{S}_2]$$

$$\mathbf{D}_{12} \propto \lambda \mathbf{x} \times \hat{\mathbf{r}}_{12}$$

Weak ferromagnetism



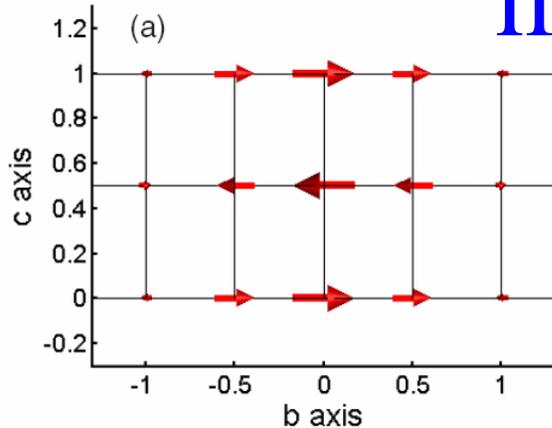
Weak ferroelectricity



# Magnetic ordering in $\text{TbMnO}_3$

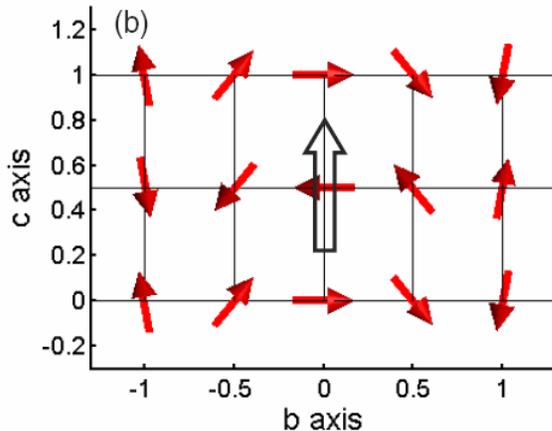
$28\text{K} < T < 41\text{K}$

**Sinusoidal SDW  
spins along b axis**



$T < 28\text{K}$

**Helicoidal SDW  
spins rotating  
in bc plane**



## LETTER TO THE EDITOR

**A new multiferroic material: MnWO<sub>4</sub>**

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J A Mydosh<sup>1</sup>, T Lorenz<sup>1</sup> and D Khomskii<sup>1,3</sup>

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**Abstract**

We report the multiferroic behaviour of MnWO<sub>4</sub>, a magnetic oxide with monoclinic crystal structure and spiral long-range magnetic order. Based upon recent theoretical predictions, MnWO<sub>4</sub> should exhibit ferroelectric polarization coexisting with the spiral magnetic structure. We have confirmed the multiferroic state below 13 K by observing a finite electrical polarization in the magnetically ordered state via pyroelectric current measurements.

(Some figures in this article are in colour only in the electronic version)

Multiferroic materials which combine magnetism and ferroelectricity currently attract considerable attention [1–4]. There are already several multiferroic materials that have been discovered recently among transition metal oxides: TbMnO<sub>3</sub> [5], TbMn<sub>2</sub>O<sub>5</sub> [6], DyMnO<sub>3</sub> [7]. Nevertheless, the search for novel systems with multiferroic properties presents a definite interest. In this letter we report that yet another transition metal oxide, MnWO<sub>4</sub>, belongs to the same class of materials and develops spontaneous electric polarization in a spiral magnetically ordered state<sup>4</sup>.

There exist several different microscopic mechanisms which may cause multiferroic behaviour [3]. One of the most interesting cases is when a spontaneous polarization exists only in a magnetically ordered phase with a particular type of ordering. This is for example the case in TbMnO<sub>3</sub> and TbMn<sub>2</sub>O<sub>5</sub>. Microscopic [10] and phenomenological [11] treatments have shown that this happens particularly in spiral magnetic structures with the spin rotation axis  $\vec{e}$  not coinciding with the magnetic propagation vector  $\vec{Q}$ : theoretical treatment shows that in this case a finite spontaneous polarization perpendicular to the plane spanned by  $\vec{e}$  and  $\vec{Q}$  may appear:

$$\vec{P} \sim \vec{e} \times \vec{Q}. \quad (1)$$

<sup>3</sup> Author to whom any correspondence should be addressed.

<sup>4</sup> As we learned recently, the multiferroic nature of MnWO<sub>4</sub> has also been observed independently [8, 9].

## FAST TRACK COMMUNICATION

# Pyroxenes: a new class of multiferroics

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S V Streltsov<sup>2,4</sup>, D C Hezel<sup>3</sup> and L Bohatý<sup>1,5</sup>

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P  
Y  
R  
O  
X  
E  
N  
E  
S

Spodumene:  
 $\text{LiAlSi}_2\text{O}_6$



Diopside:  
 $\text{CaMgSi}_2\text{O}_6$



Aegirine:  
 $\text{NaFeSi}_2\text{O}_6$



Kosmochlore:  
 $\text{NaCrSi}_2\text{O}_6$



Jade:  
 $\text{NaAlSi}_2\text{O}_6$

**Minerals**



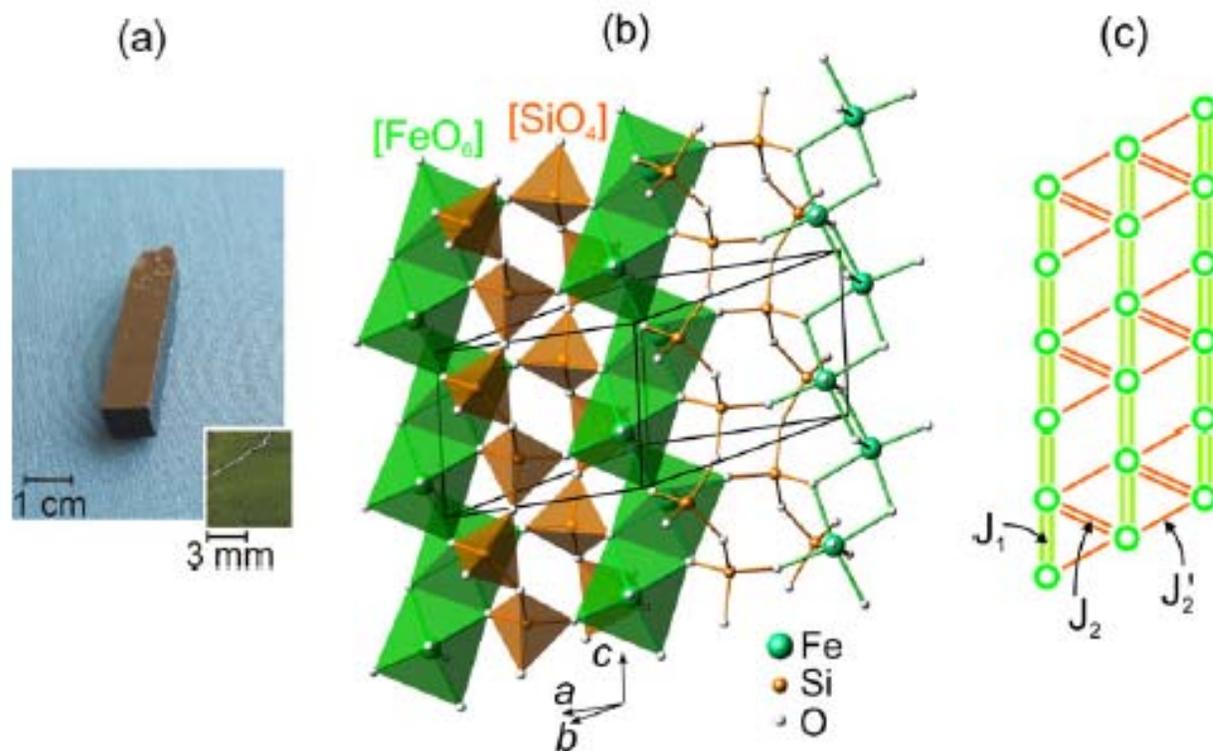
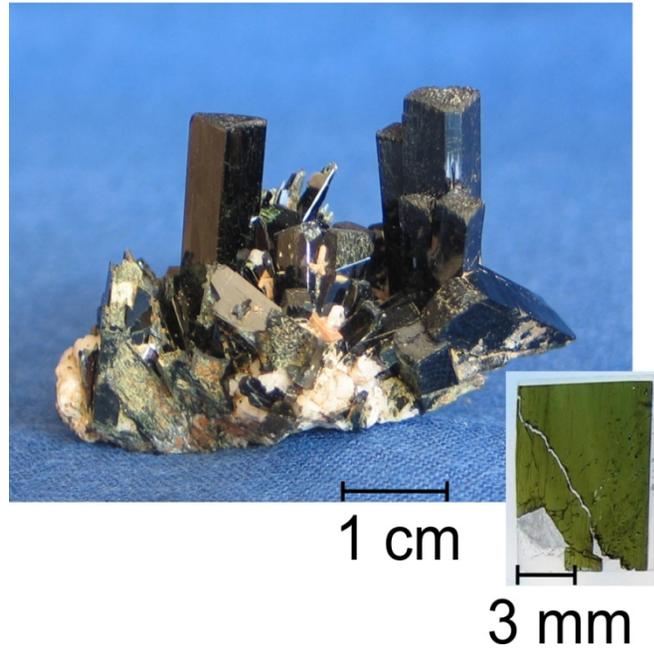


Figure 1. (a) Natural aegirine ( $\text{NaFeSi}_2\text{O}_6$ ) crystal from a pegmatite of alkaline rocks of Mount Malosa, Malawi. In thin sections (see inset) the aegirine crystal is green and transparent. (b) The main features of the crystal structure are chains of edge-sharing  $[\text{FeO}_6]$  octahedra (green) and chains of corner-sharing  $[\text{SiO}_4]$  tetrahedra (orange) running along the  $c$ -direction (structure data from [22]).

(a)



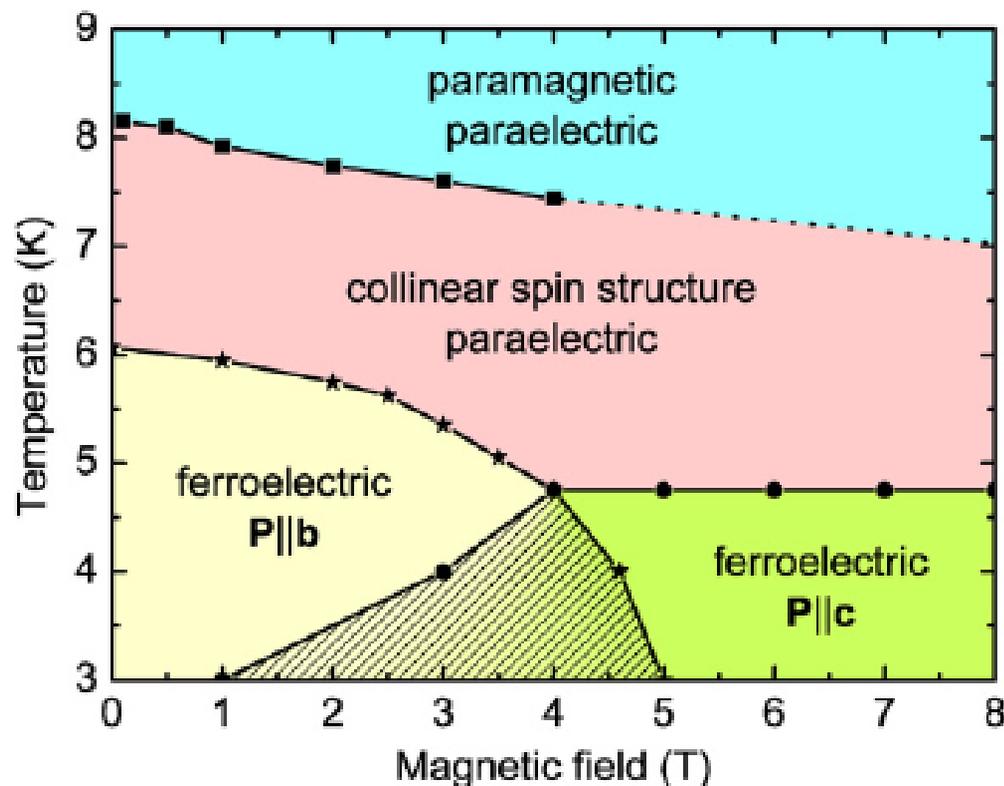
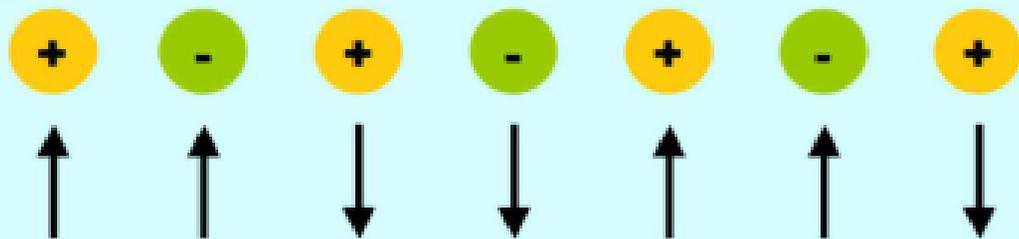
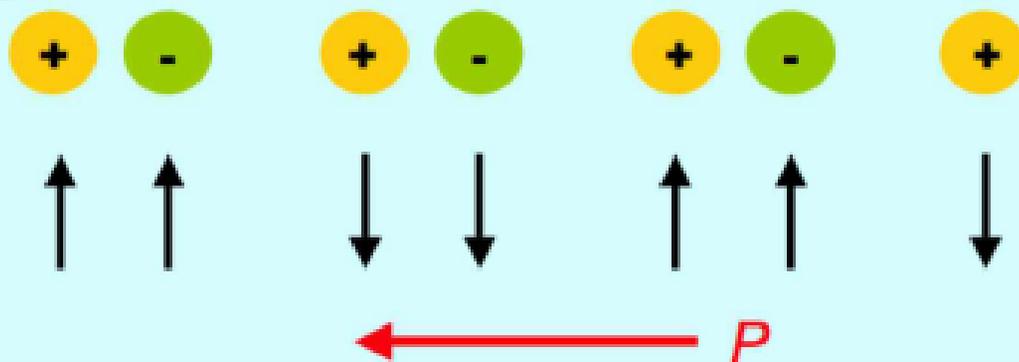


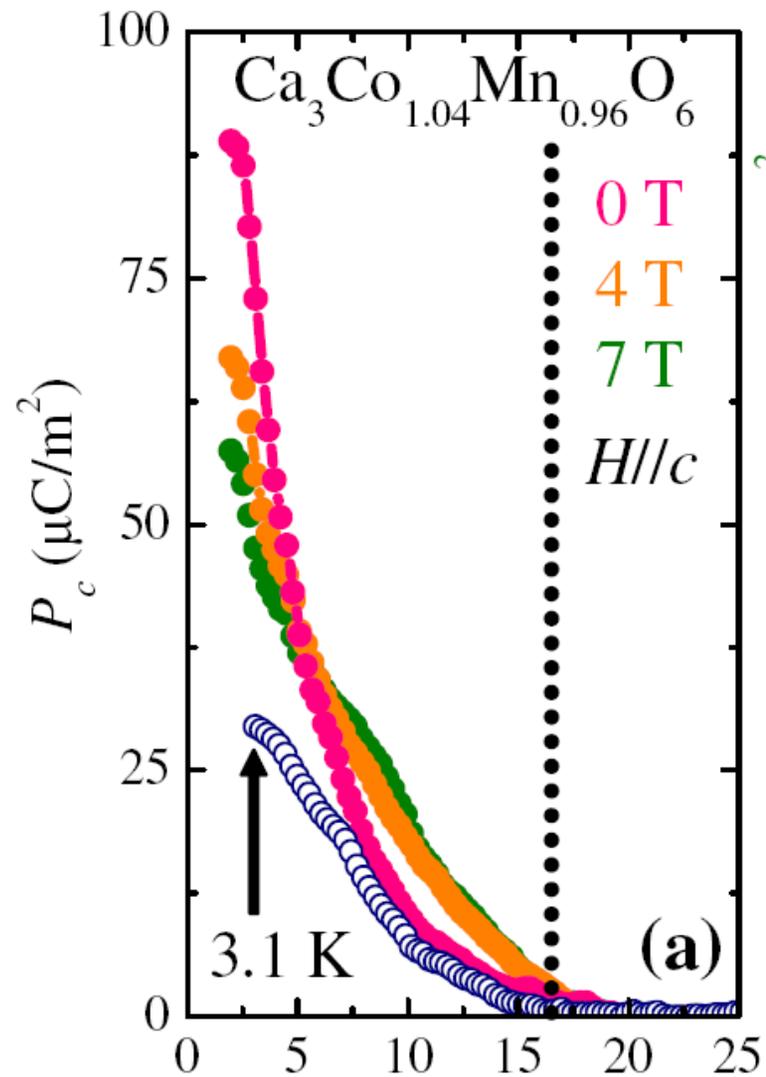
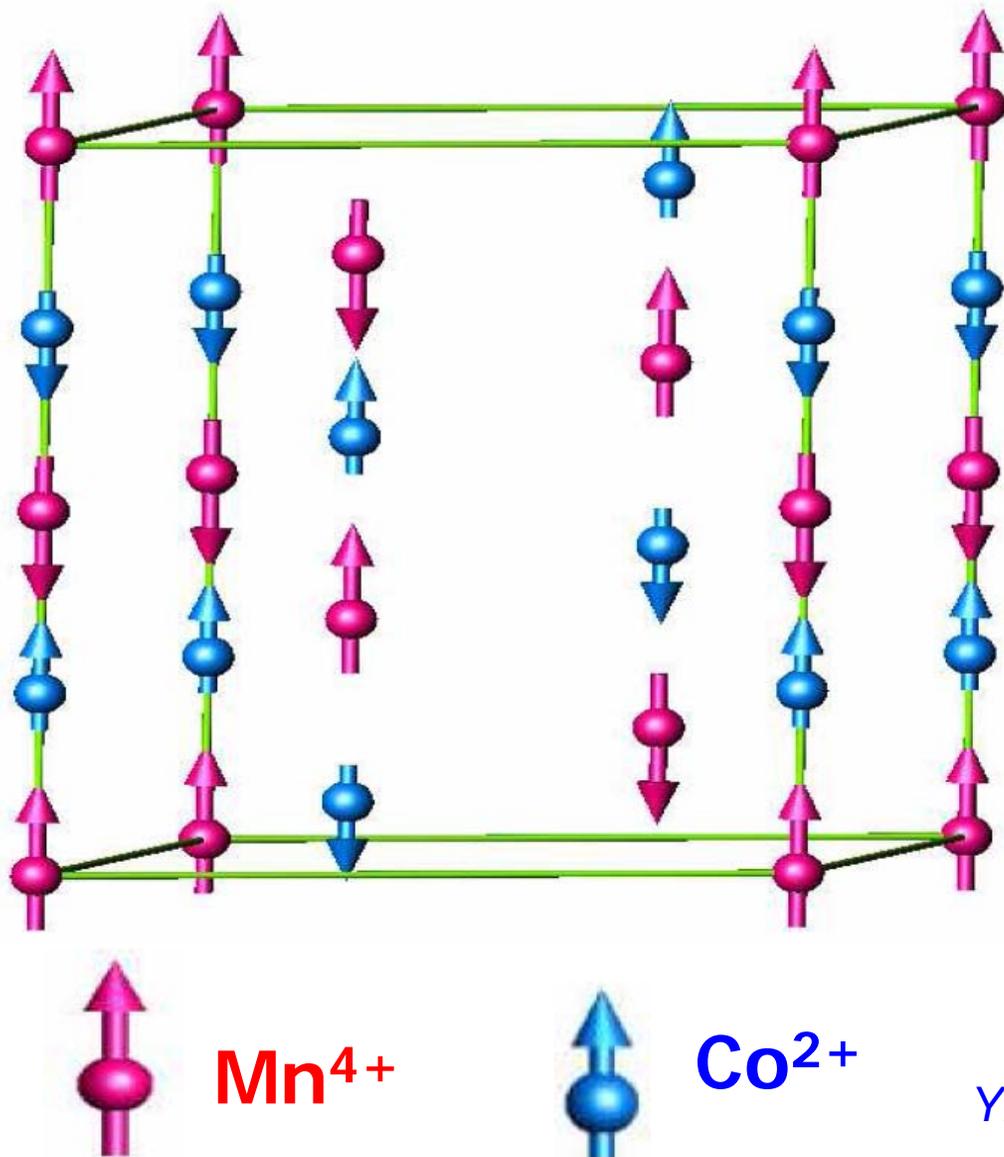
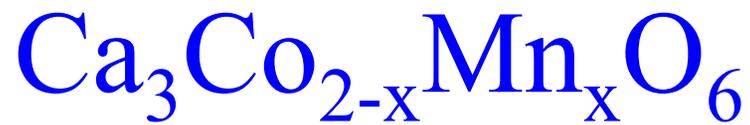
Figure 3. Temperature versus magnetic field (applied in the *ac*-plane) phase diagram for NaFeSi<sub>2</sub>O<sub>6</sub> illustrating the multiferroic behaviour.

A



B



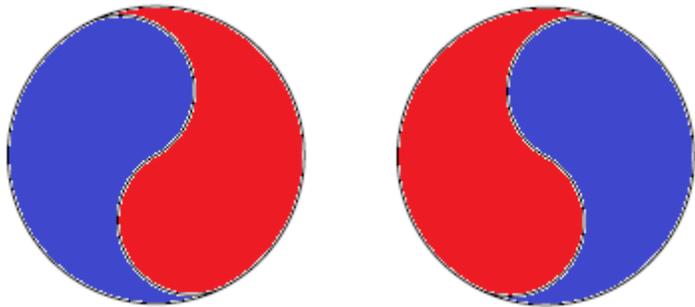


## ● Ferroelectricity in a proper screw

Sometimes also **proper screw** structures can give ferroelectricity

Should not have rotation axis of 2-nd order perpendicular to the helix

Special class of systems: **ferroaxial crystals** (L.Chapon, P.Radaelli)  
crystals with inversion symmetry but existing in two inequivalent modifications, which are mirror image of one another



Characterised by pseudovector (axial vector)  $\mathbf{A}$

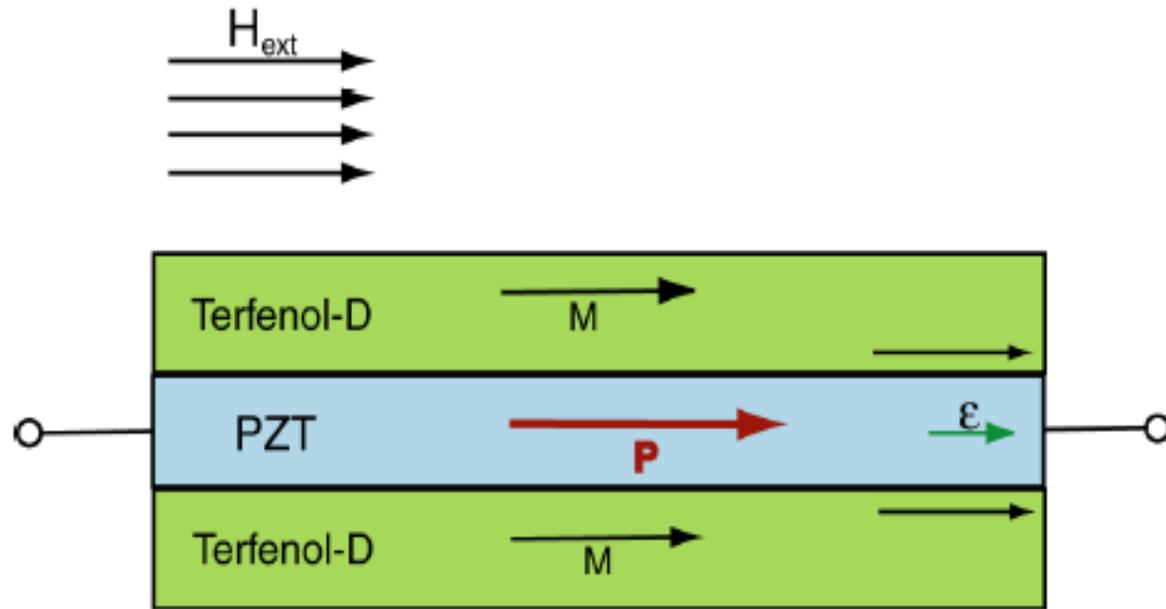
Proper screw may be characterised by chirality  $\kappa = \mathbf{r}_{12} [\mathbf{S}_1 \times \mathbf{S}_2]$

Then one can have polarization  $\mathbf{P} = \kappa \mathbf{A}$  (or have invariant  $(\kappa \mathbf{A} \mathbf{P})$ )

Examples:  $\text{AgCrO}_2$ ,  $\text{CaMn}_7\text{O}_{12}$ ,  $\text{RbFe}(\text{MoO}_4)_2$

# ● Composite multiferroics

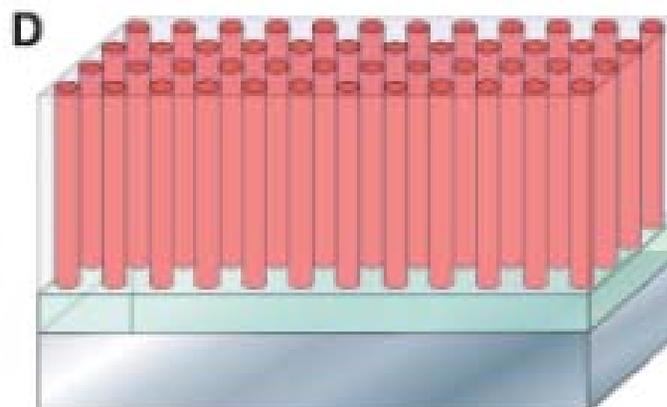
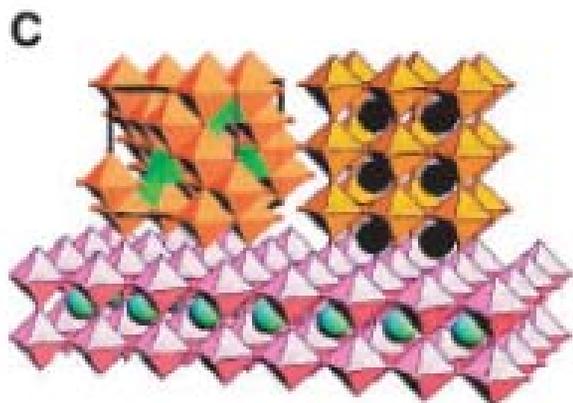
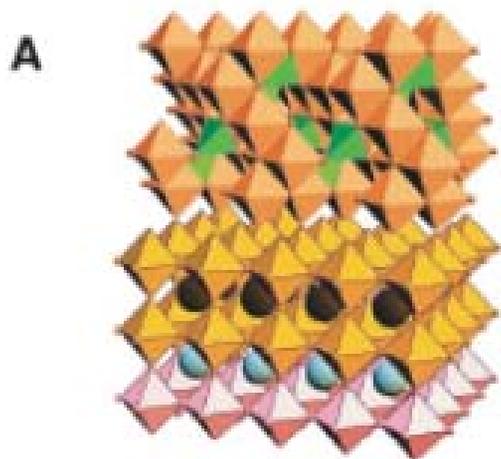
Terfenol-D/PZT-Laminate:



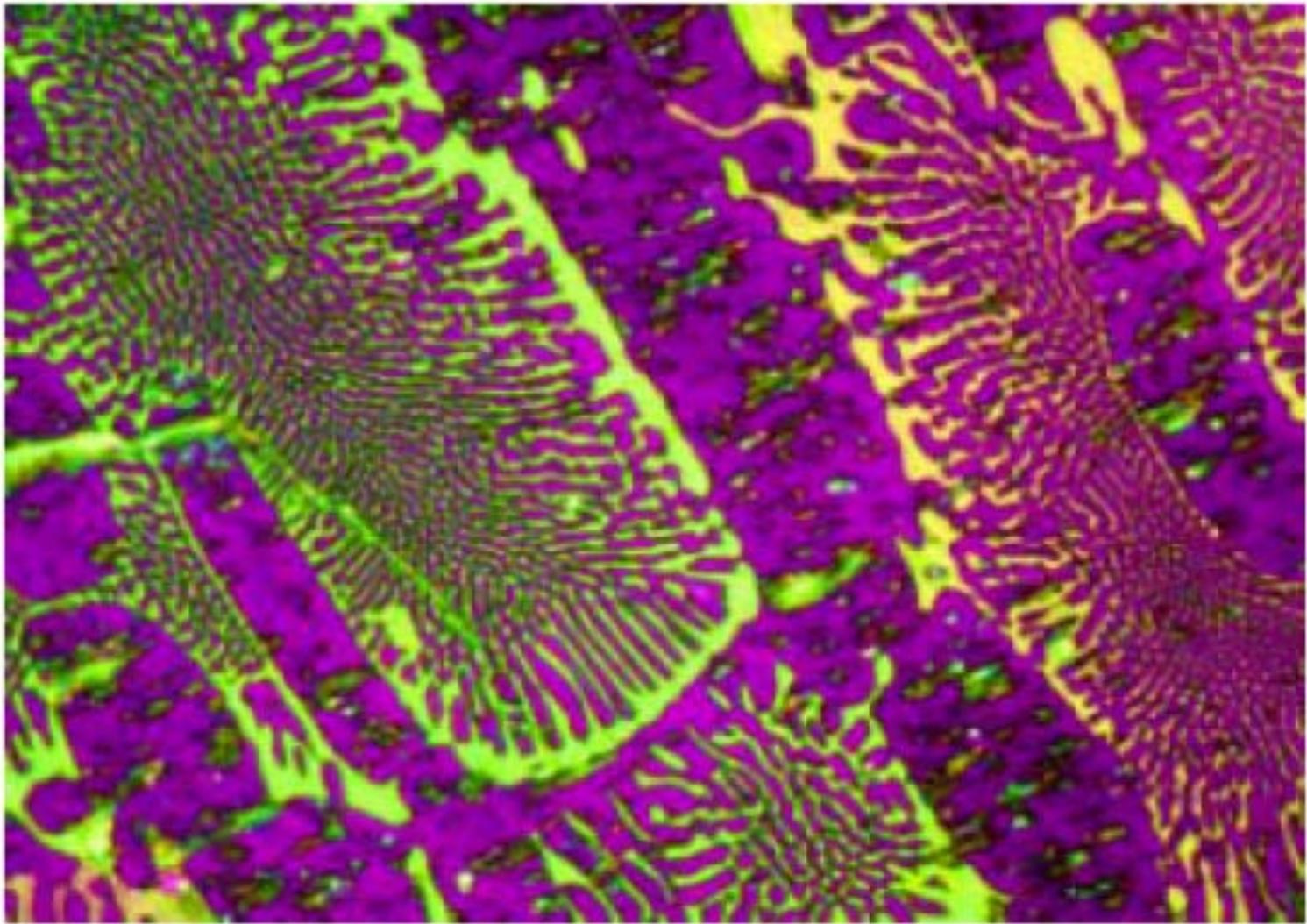
Terfenol-D:  
-  $\text{Tb}_{0,3}\text{Dy}_{0,7}\text{Fe}_2$

PZT:  
-  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$

# Multiferroic $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$ nanocomposites:



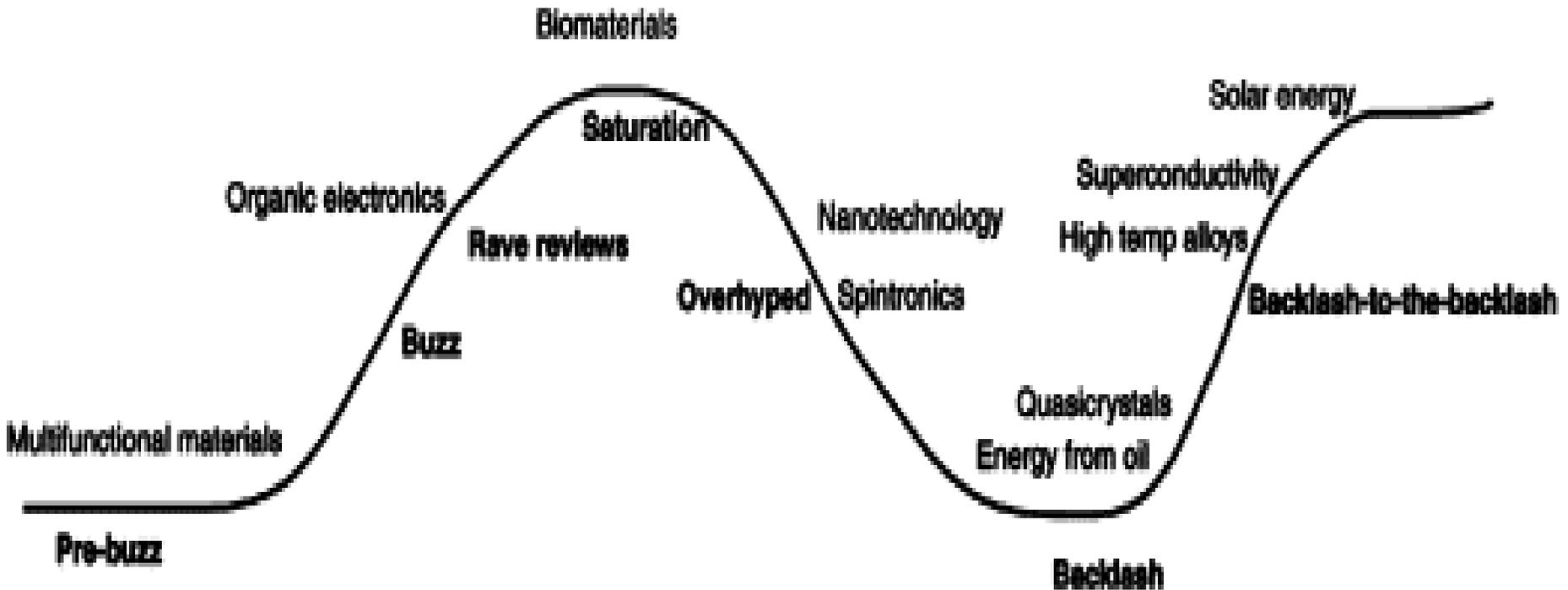
100  $\mu\text{m}$



Violet – ferromagnetic rhombohedral  $(\text{LaSr})\text{MnO}_3$ ,  $T_c=370$  K  
Green – ferroelectric hexagonal  $\text{LuMnO}_3$ ,  $T_c=900$  K  
( Park et al (2005) )

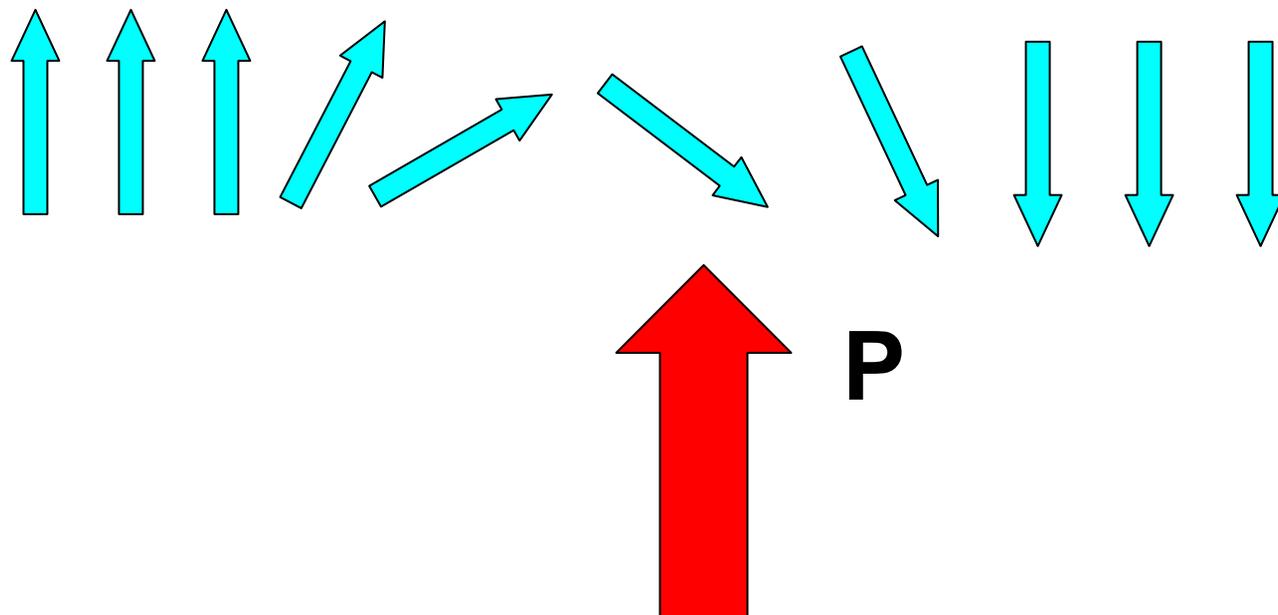
Steve Pearton, Materials Today **10**, 6 (2007)

“The **F**lorida **L**aw of **O**riginal **P**rognostication maps the shifting tide of expectations in materials science.”



**Beyond:**

**Neel domain walls:**





# Magnetoelectricity in ferromagnets

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published online 29 August 2008

PACS 75.50.Dd – Nonmetallic ferromagnetic materials

PACS 75.60.Ch – Domain walls and domain structure

**Abstract** – The creation of Néel domain walls by electric fields in conventional and weak ferromagnets is discussed. In an inhomogeneous electric field the walls move with velocity proportional to the field gradient.

# Magnetoelectric Control of Domain Walls in a Ferrite Garnet Film

*A.S. Logginov, G.A. Meshkov, V.A. Nikolaev, A.P. Pyatakov\**

*Physics Department, M.V. Lomonosov MSU, Moscow, Russia, 119992;*

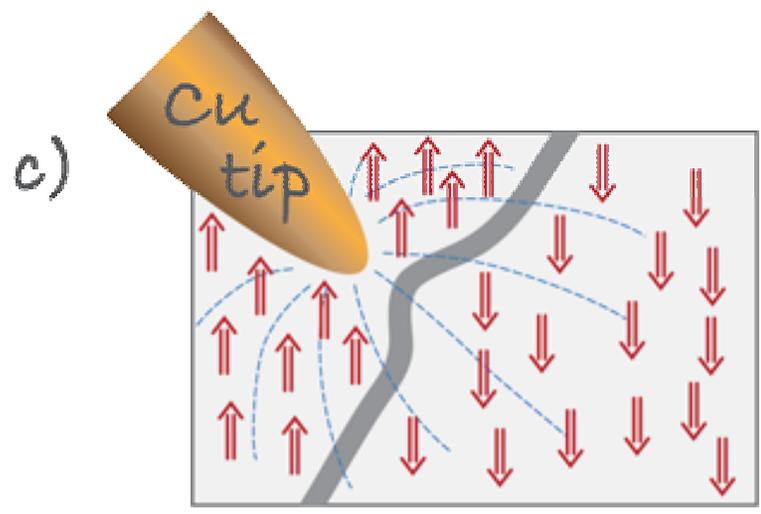
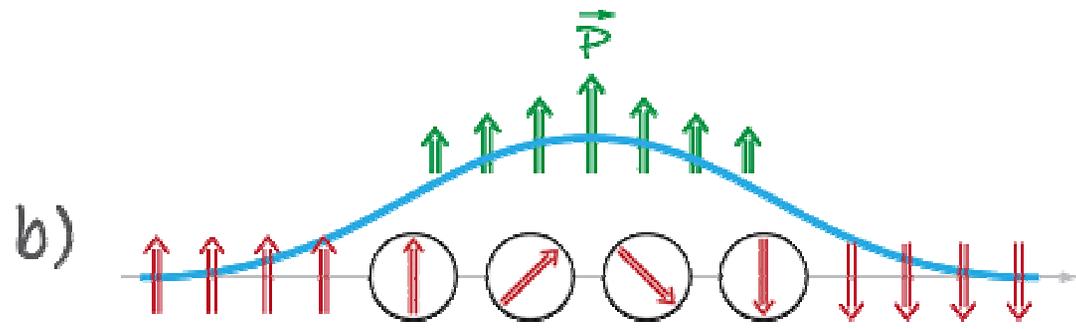
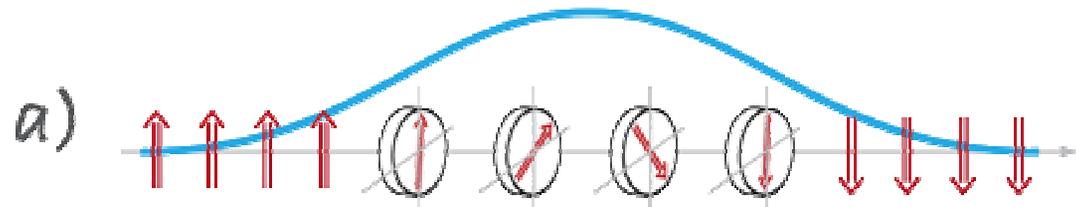
*and A.K. Zvezdin*

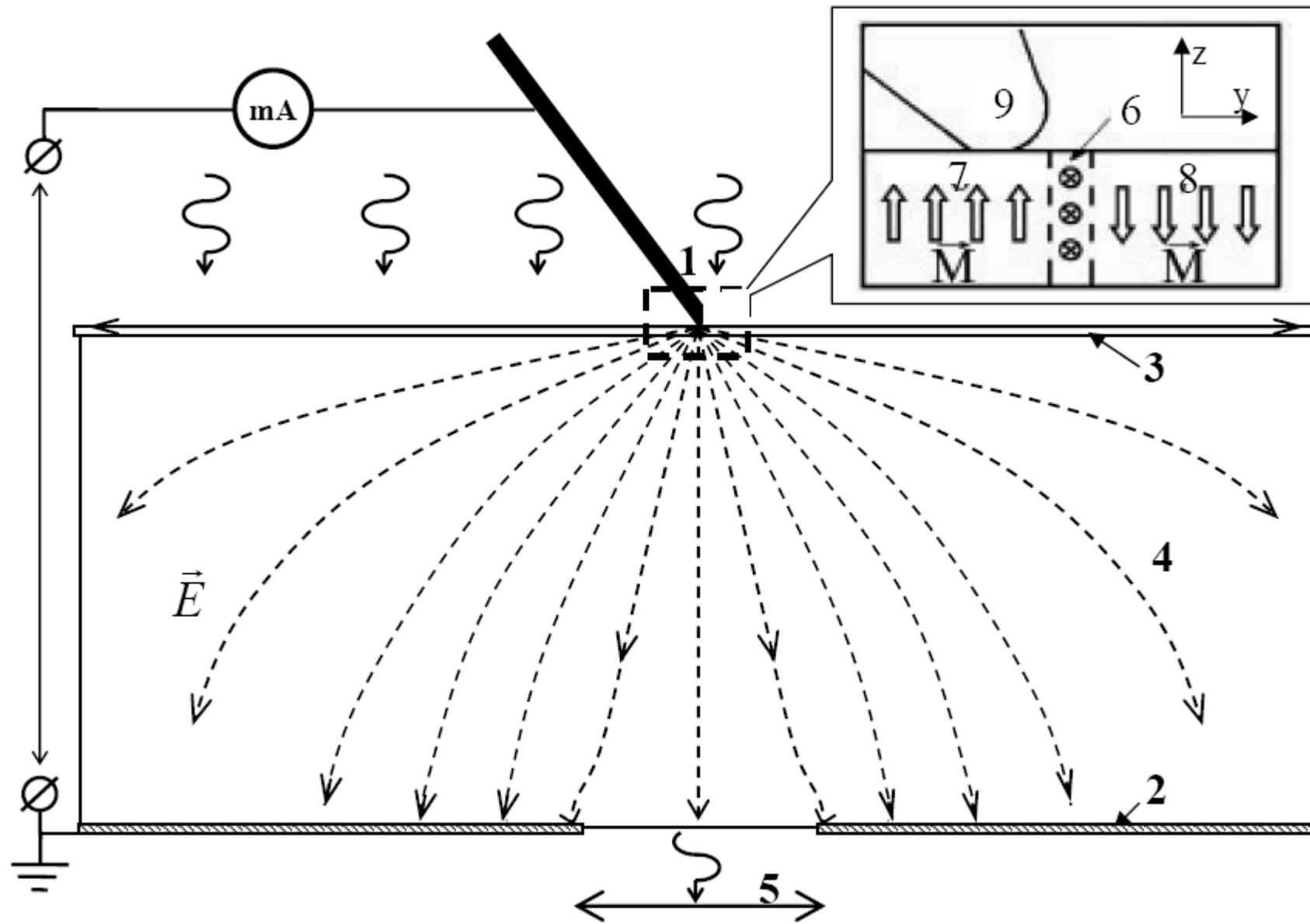
*A.M. Prokhorov General Physics Institute, 38, Vavilova st, Moscow, 119991*

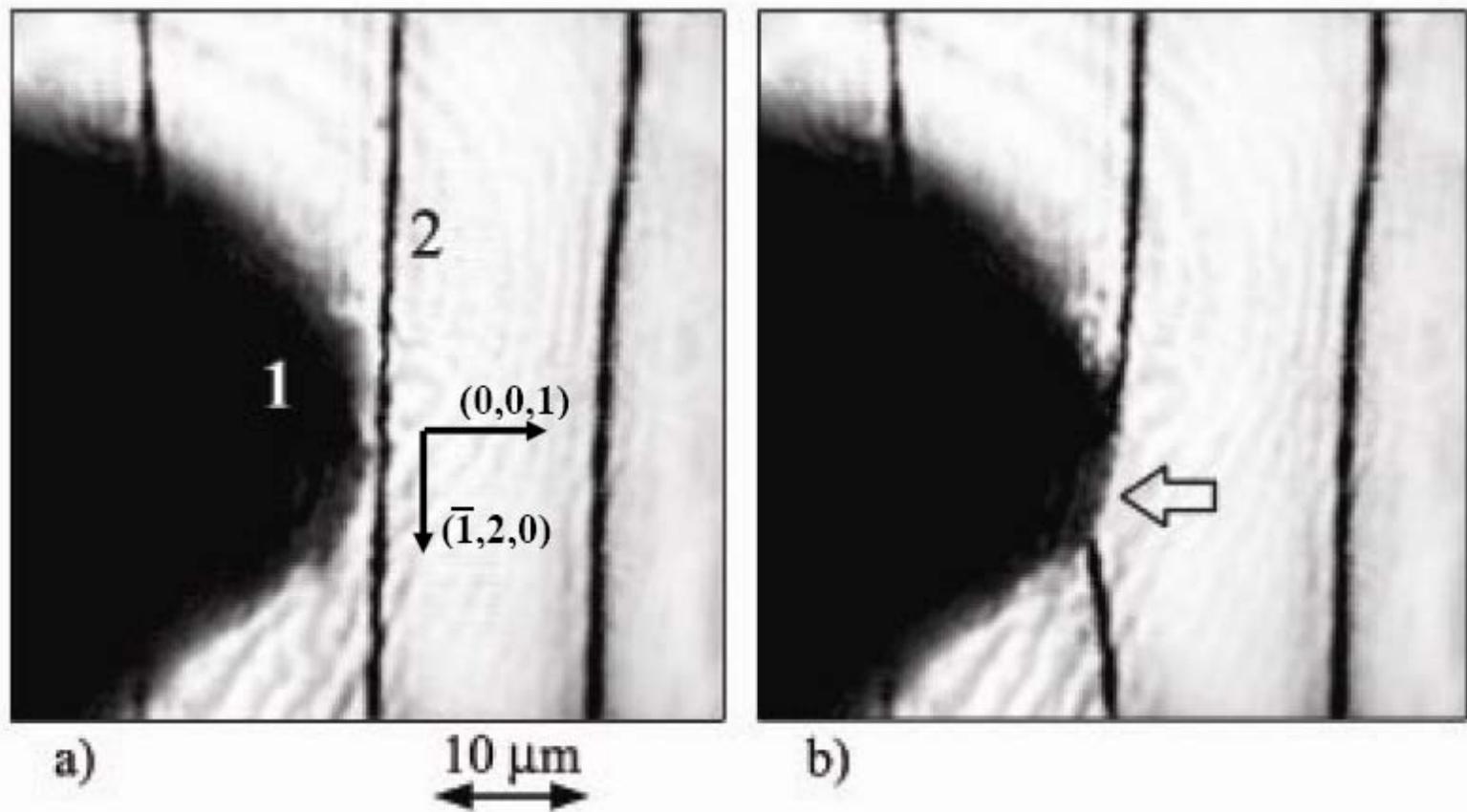
\* Corresponding author: [pyatakov@phys.msu.ru](mailto:pyatakov@phys.msu.ru)

The effect of magnetic domain boundaries displacement induced by electric field is observed in epitaxial ferrite garnet films (on substrates with the (210) crystallographic orientation). The effect is odd with respect to the electric field (the direction of wall displacement changes with the polarity of the voltage) and even with respect to the magnetization in domains. The inhomogeneous magnetoelectric interaction as a possible mechanism of the effect is proposed.

DOI: 10.1134/S0021364007140093







**Fig. 2** The effect of electric field in the vicinity of electrode (1) on magnetic domain wall (2) in the films of ferrite garnets: a) initial state b) at the voltage of +1500 V applied

## LETTERS

# Chiral magnetic order at surfaces driven by inversion asymmetry

M. Bode<sup>1,†</sup>, M. Heide<sup>2</sup>, K. von Bergmann<sup>1</sup>, P. Ferriani<sup>1</sup>, S. Heinze<sup>1</sup>, G. Bihlmayer<sup>2</sup>, A. Kubetzka<sup>1</sup>, O. Pietzsch<sup>1</sup>, S. Blügel<sup>2</sup> & R. Wiesendanger<sup>1</sup>

PRL 101, 027201 (2008)

PHYSICAL REVIEW LETTERS

week ending  
11 JULY 2008



## Atomic-Scale Spin Spiral with a Unique Rotational Sense: Mn Monolayer on W(001)

P. Ferriani,<sup>1,\*</sup> K. von Bergmann,<sup>1</sup> E. Y. Vedmedenko,<sup>1</sup> S. Heinze,<sup>1</sup> M. Bode,<sup>1,†</sup> M. Heide,<sup>2</sup> G. Bihlmayer,<sup>2</sup> S. Blügel,<sup>2</sup> and R. Wiesendanger<sup>1</sup>

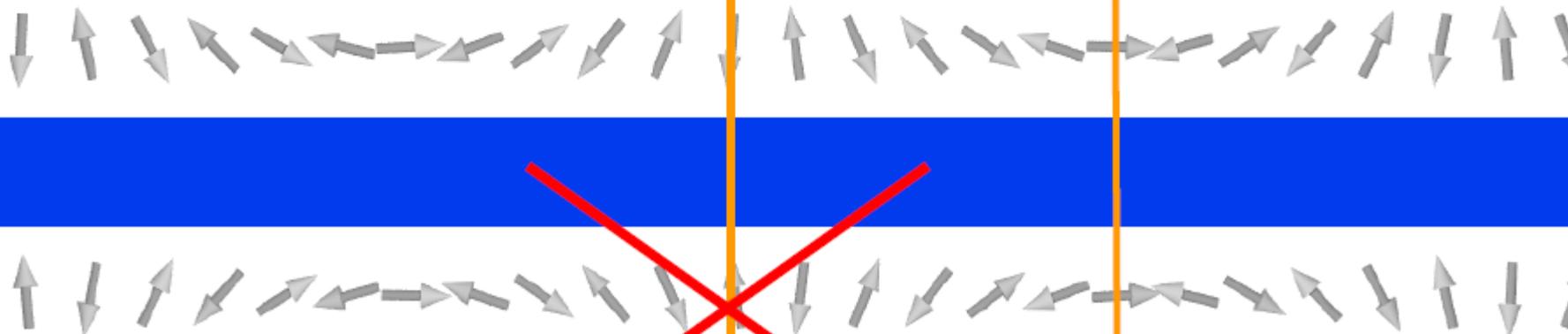
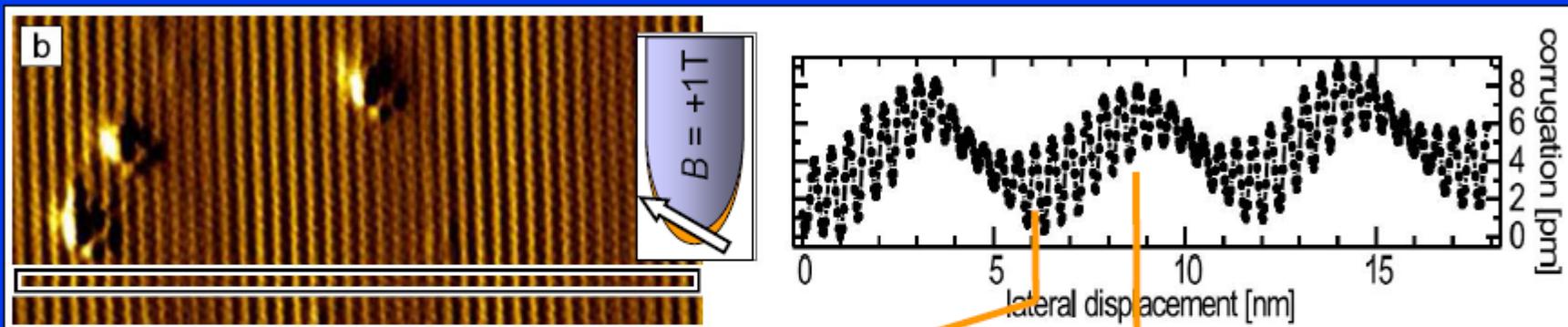
<sup>1</sup>*Institute of Applied Physics, University of Hamburg, Jungiusstrasse 11, 20355 Hamburg, Germany*

<sup>2</sup>*Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany*

(Received 15 April 2008; published 7 July 2008)

Using spin-polarized scanning tunneling microscopy we show that the magnetic order of 1 monolayer Mn on W(001) is a spin spiral propagating along  $\langle 110 \rangle$  crystallographic directions. The spiral arises on the atomic scale with a period of about 2.2 nm, equivalent to only 10 atomic rows. *Ab initio* calculations identify the spin spiral as a left-handed cycloid stabilized by the Dzyaloshinskii-Moriya interaction, imposed by spin-orbit coupling, in the presence of softened ferromagnetic exchange coupling. Monte Carlo simulations explain the formation of a nanoscale labyrinth pattern, originating from the coexistence of the two possible rotational domains, that is intrinsic to the system.

# rotation direction of spin spiral



6 out of 6 independent islands: same rotational sense  
→ DM-driven spin spiral

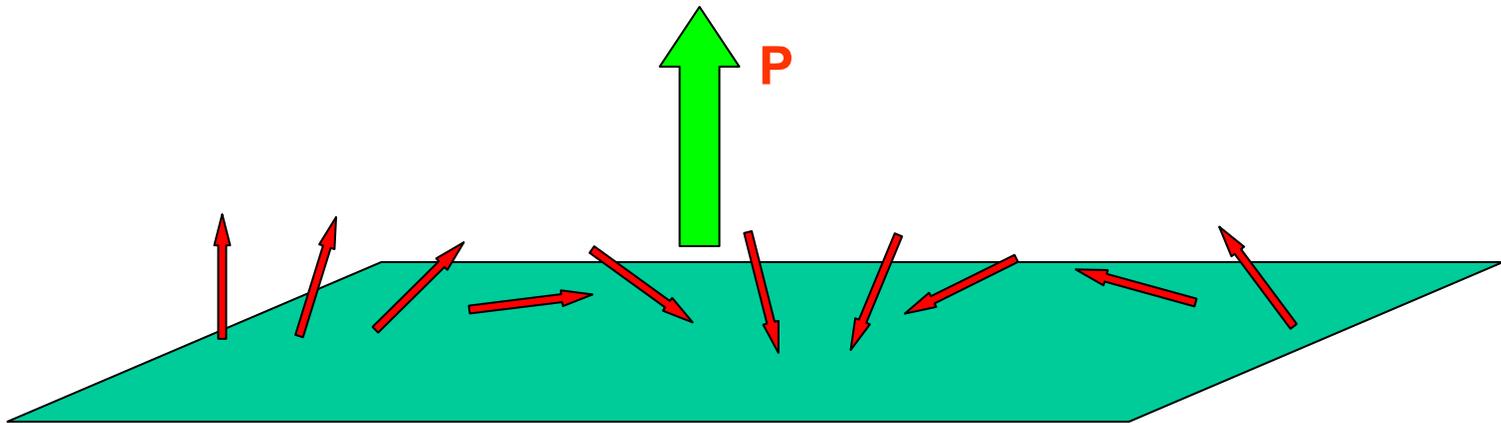
Simple explanation: at the surface there is a drop of a potential (work function, double layer)

I.e. there is an electric field  $\mathbf{E}$ , or polarization  $\mathbf{P}$  perpendicular to the surface

By the relation

$$\bar{\mathbf{P}} \propto [\mathbf{e}_3 \times \mathbf{Q}]$$

there will appear magnetic spiral with certain sense of rotation, determined by  $\mathbf{P}$



# ● Electric dipole carried by the usual spin wave

D.Khomsikii, Physics (Trends) 2, 20 (2009)

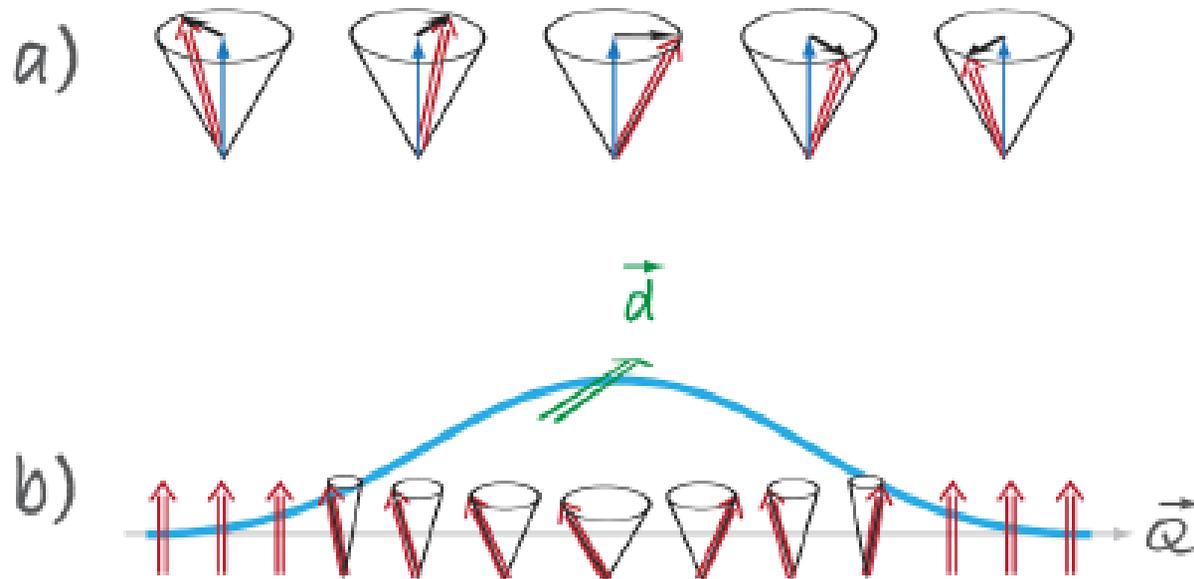


FIG. 5: How polarization emerges in a spin wave (magnon). (a) The classical picture of a spin wave in a ferromagnet: the spin (red arrow) precesses about a fixed axis (blue). The deviation is measured by the black arrows. (b) According to Eq. (1), as a spin-wave packet propagates along  $Q$ , it will also carry an electric dipole moment. (Illustration: Alan Stonebraker)

## Other specific effects?

*Photovoltaic effect*: it exists in ferroelectrics (broken inversion symmetry; motion of electrons and holes in opposite direction in an internal electric field). In ME materials it is also possible (V.V. Men'shenin and E.A. Turov, JETP Lett. **72**, 14 (2000) )

**Photovoltaic effect in magnetic field?**

**Negative refraction in multiferroics or magnetoelectric?** Due to linear coupling between **P** and **M** dielectric function and magnetic susceptibility have common poles (coinciding excitation energies), and above this frequency both are negative (region of anomalous dispersion)

# Low frequency dynamic properties: negative refraction index

---

- Responses to ac electric and ac magnetic field are comparable for  $J \approx 100$  K.

$$\varepsilon_{ik}(\omega) = \varepsilon_0 \delta_{ik} + \frac{8\pi}{V} \sum_n \frac{\omega_{n0} \langle 0 | P_{S,i} | n \rangle \langle n | P_{S,k} | 0 \rangle}{\omega_{n0}^2 - \omega^2 + i\delta},$$

- Spin-orbital coupling may lead to common poles in  $\varepsilon_{ik}(\omega)$  and  $\mu_{ik}(\omega)$   $\rightarrow$
- Negative refraction index if dissipation is weak.

**LHM: negative  $\epsilon(\omega) < 0$  and  $\mu(\omega) < 0$**

$$\text{Maxwell Eqs: } \nabla \times \vec{E} = \frac{i\omega}{c} \vec{B} \quad \nabla \times \vec{H} = -\frac{i\omega}{c} \vec{D}$$

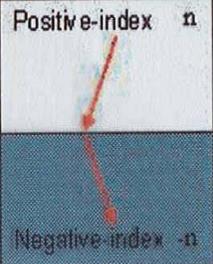
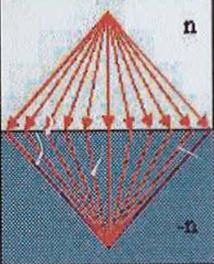
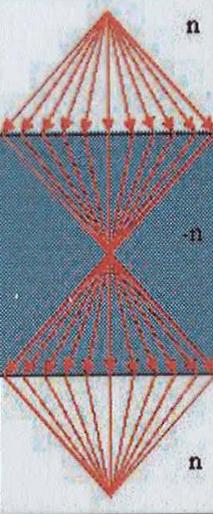
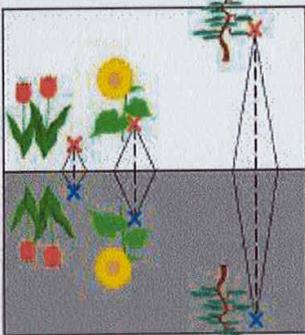
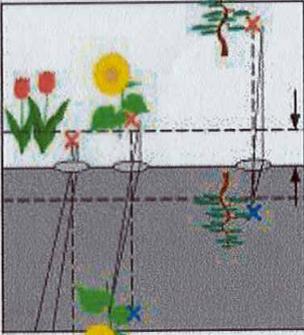
$$\nabla \cdot \vec{D} = 0 \quad \nabla \cdot \vec{B} = 0 \quad \vec{D} = \epsilon(\omega) \vec{E}, \quad \vec{B} = \mu(\omega) \vec{H}$$

$$n^2 = \epsilon\mu > 0$$

Vectors  $\vec{k}, \vec{E}, \vec{H}$

**form a left-handed orthogonal set (LHM)**  
(V. Veselago, 1967).

# Why NR is interesting: Focusing by a slab.

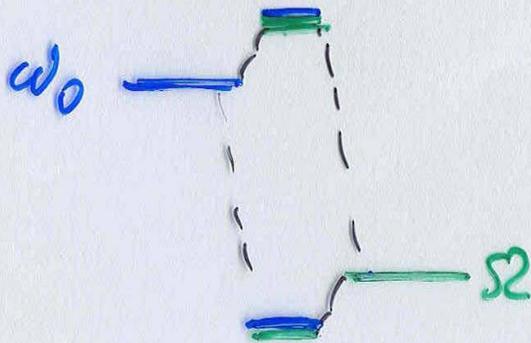
Negative refraction	Imaging	Cascaded Imaging	Imaging by negative PhC	Imaging by lens
<p>Positive-index <math>n</math></p>  <p>Negative index <math>-n</math></p>			<p><math>(x, y, z) \rightarrow (x, y, -z)</math></p>  <p>Mirror-inverted 3D <u>Real</u> Image</p> <p>→ 3D photographing?</p>	<p><math>(x, y, z) \rightarrow (x/z, y/z, -f^2/z)</math></p>  <p>2D image</p>

● Need simultaneously  $\epsilon < 0$ ,  $\mu < 0$

$\epsilon < 0$  close to a resonance (e.g. optical phonon  $\omega_0$ )

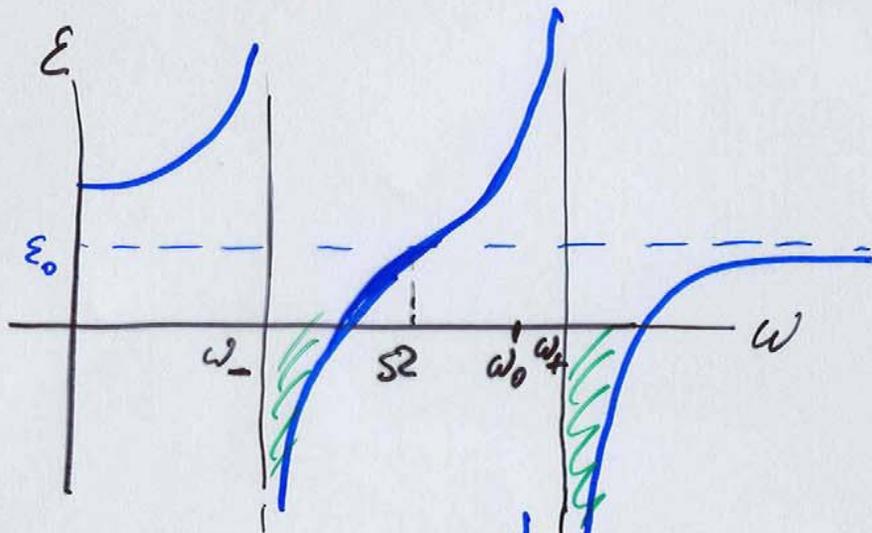
$\mu < 0$  close to magnetic resonance  $\Omega$

[The idea: if there is a linear coupling  
 $\vec{P} \vec{M}$  - mixed resonances, both  $\epsilon, \mu < 0$

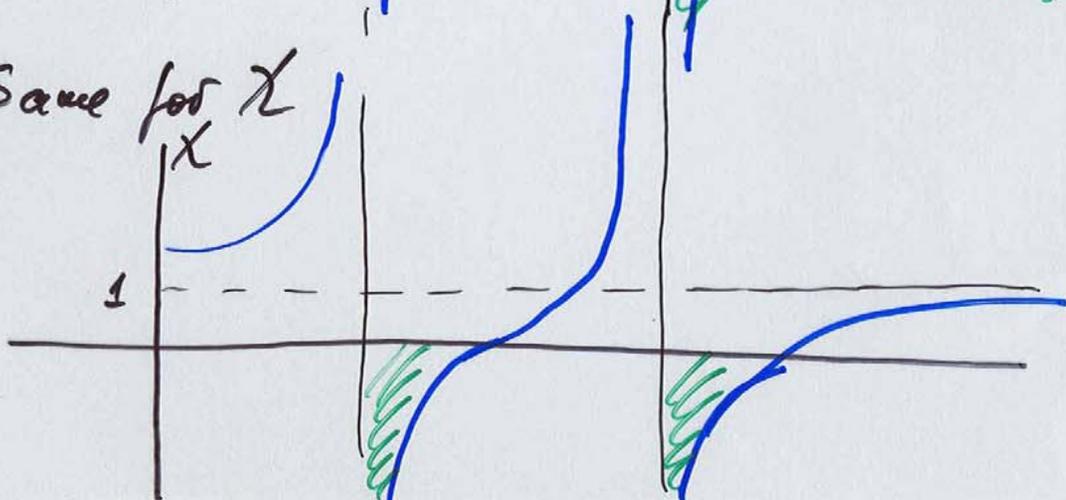


$$\omega_{\pm}^2 = \frac{\omega_0^2 + \Omega^2}{2} \pm \sqrt{\left(\frac{\omega_0^2 - \Omega^2}{2}\right)^2 + \gamma^2} \approx \begin{cases} \omega_0^2 + \frac{\gamma^2}{\omega_0^2 - \Omega^2} \\ \Omega^2 - \frac{\gamma^2}{\omega_0^2 - \Omega^2} \end{cases}$$

(if  $\omega_0^2 > \Omega^2$ )



Same for  $\chi$



For  $\omega \gtrsim \omega_+$   
 $\omega \gtrsim \omega_-$   
 - both  $\epsilon \times \mu < 0$ ,  
 and  $n < 0$

# Beyond multiferroics

- Polarization on domain walls, ways to control it
- Spiral structures at the surfaces
- Electric dipoles carried out by usual spin waves
- Electric dipoles on magnetic monopoles in spin ice
- Magnetic monopoles on charges in magnetoelectric materials

.....

# CONCLUSIONS

**Very nontrivial coupling of electricity and magnetism.**

*Multiferroics* – very interesting physics; potentially very important applications

Two big groups:

- **Materials with independent magnetism and ferroelectricity, with some coupling of them (type-I multiferroics)**
  1. Different structural groups giving magnetism and FE (e.g. boracites)
  2. Mixed perovskites with  $d^0$  and  $d^n$  ions
  3. “Geometric” ferroelectrics ( $\text{YMnO}_3$ )
  4. Lone pairs (systems with  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$  etc)
  5. FE due to coexistence of site- and bond-centered charge ordering
- **Multiferroics with FE due to magnetic ordering (type-II multiferroics)**
  1. Spiral magnets; FE due to spin-orbit interaction ( $\text{TbMnO}_3$ ,  $\text{MnWO}_4$ , ....)
  2. FE due to magnetostriction ( $\text{TbMn}_2\text{O}_5$ ;  $\text{RbFe}(\text{MoO}_4)$ ;  $\text{Ca}_3\text{CoMnO}_6$ )
  3. Electronic mechanism of FE in frustrated systems

# Problems

1) Type-I multiferroics:  $T_c$ 's,  $P$  – OK but:

how to increase the coupling?

2) Type-II multiferroics: coupling OK; but

how to increase  $T_c$  and  $P$  ?

3) Composite MF

4) Novel physical effects (toroics; monopoles,....) ?

5) Novel manifestations; functionality





# ● Electronic mechanism of multiferroic behaviour in frustrated Mott insulators

The Hubbard model: 
$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$E_g \sim U - 2zt$$

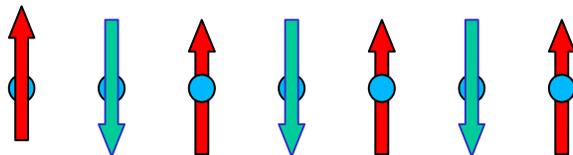


$n=1, U>t$ : **Mott insulator**

Localized electrons/localized magnetic moments

L.Bulaevskii, C.Batista,  
M.Mostovoy and D.Khomskii  
PRB 78, 024402 (2008)

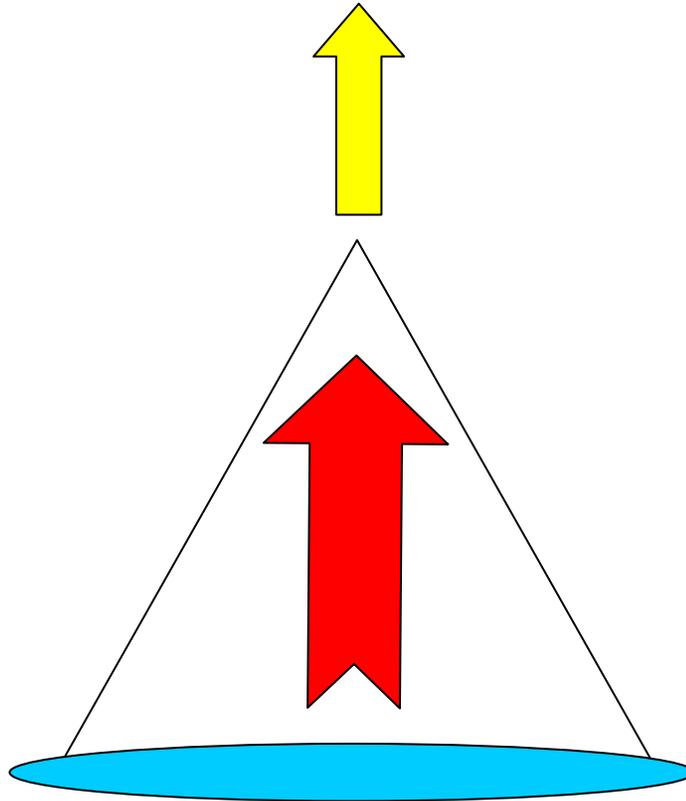
$$H_{eff} = \frac{2t^2}{U} \sum_{\langle ij \rangle} \mathbf{S}_i \mathbf{S}_j.$$



$$\begin{array}{cc} \uparrow & \uparrow \\ \hline \Delta E = 0 \end{array}$$

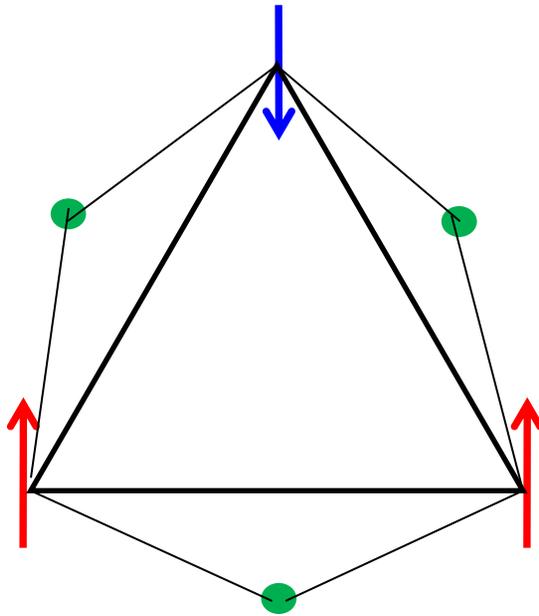
$$\begin{array}{cc} \uparrow & \downarrow \\ \hline \Delta E = -\frac{2t^2}{U} \end{array}$$

$$\mathbf{d} = C_e a (t/U)^3 [\mathbf{S}_1 (\mathbf{S}_2 + \mathbf{S}_3) - 2\mathbf{S}_2 \mathbf{S}_3]$$



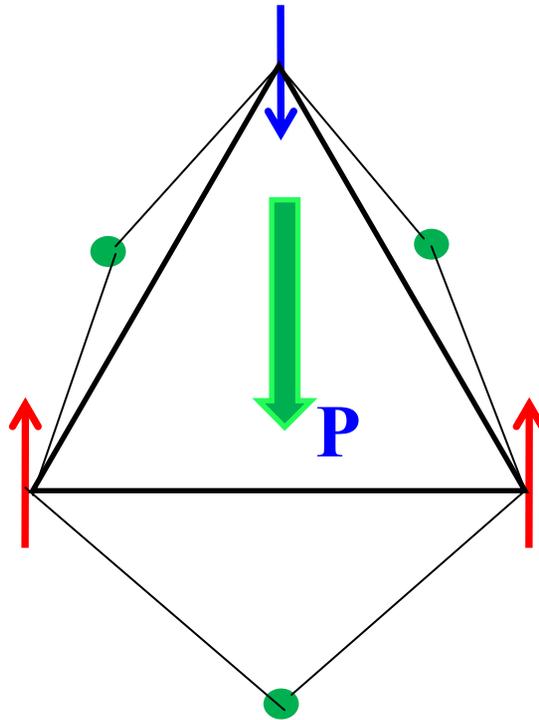
Dipoles are also created by lattice distortions (striction); the expression for

polarization/dipole is the same,  $\mathbf{D} \sim \mathbf{P} \sim \mathbf{S}_1(\mathbf{S}_2 - \mathbf{S}_3) - 2\mathbf{S}_2\mathbf{S}_3$  (M. Mostovoy)



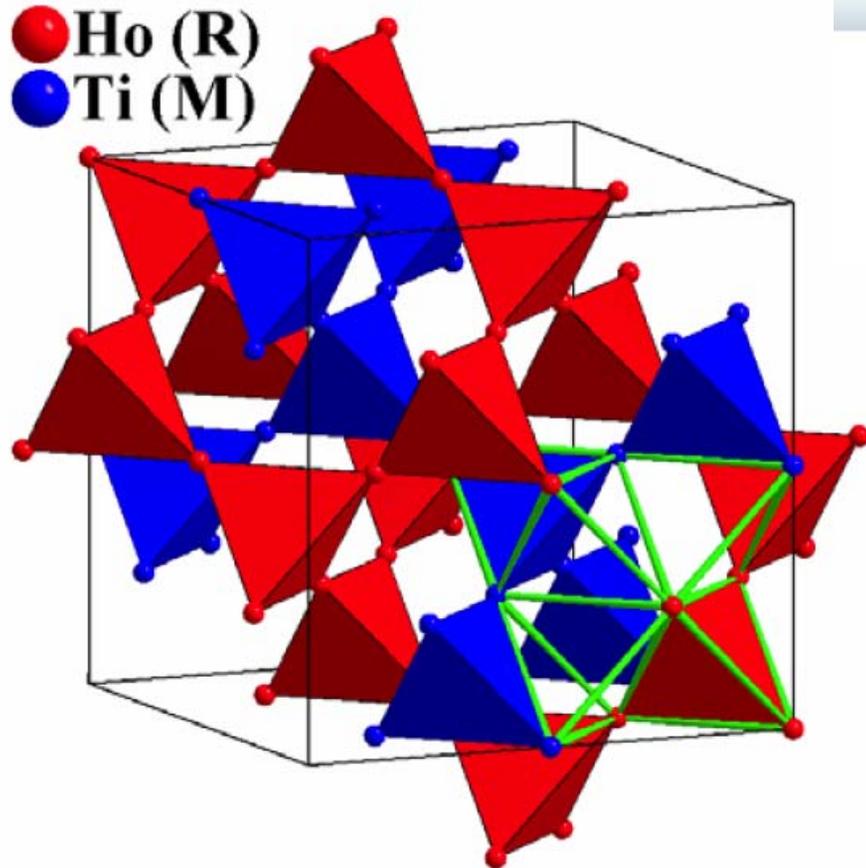
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# ● Monopoles and dipoles in spin ice

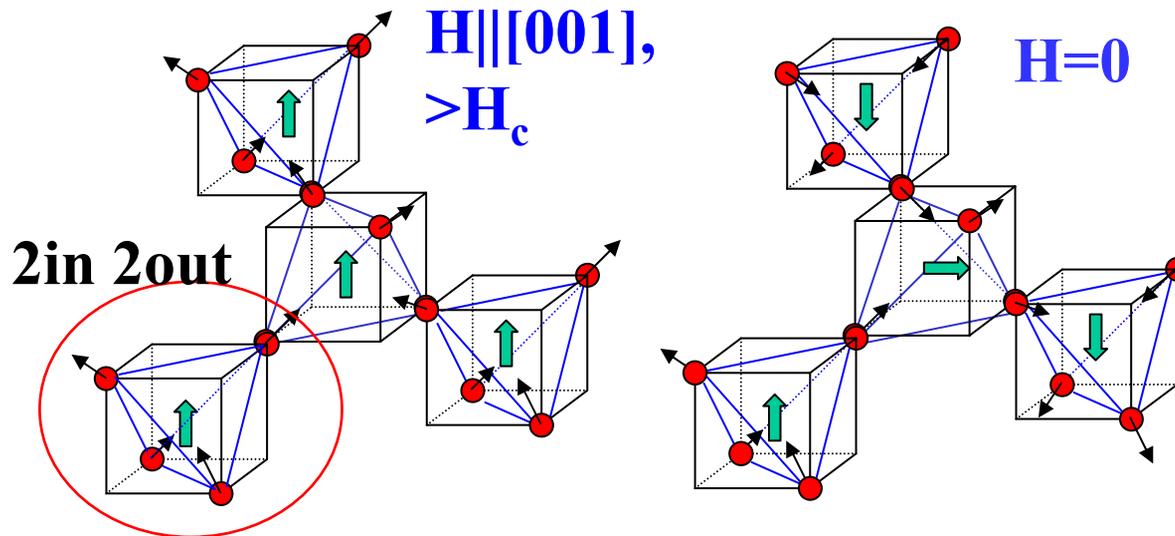
**Pyrochlore: Two interpenetrating metal sub**



# pyrochlore $R_2Ti_2O_7$ □ □ geometrical spin frustration

$R=Ho$

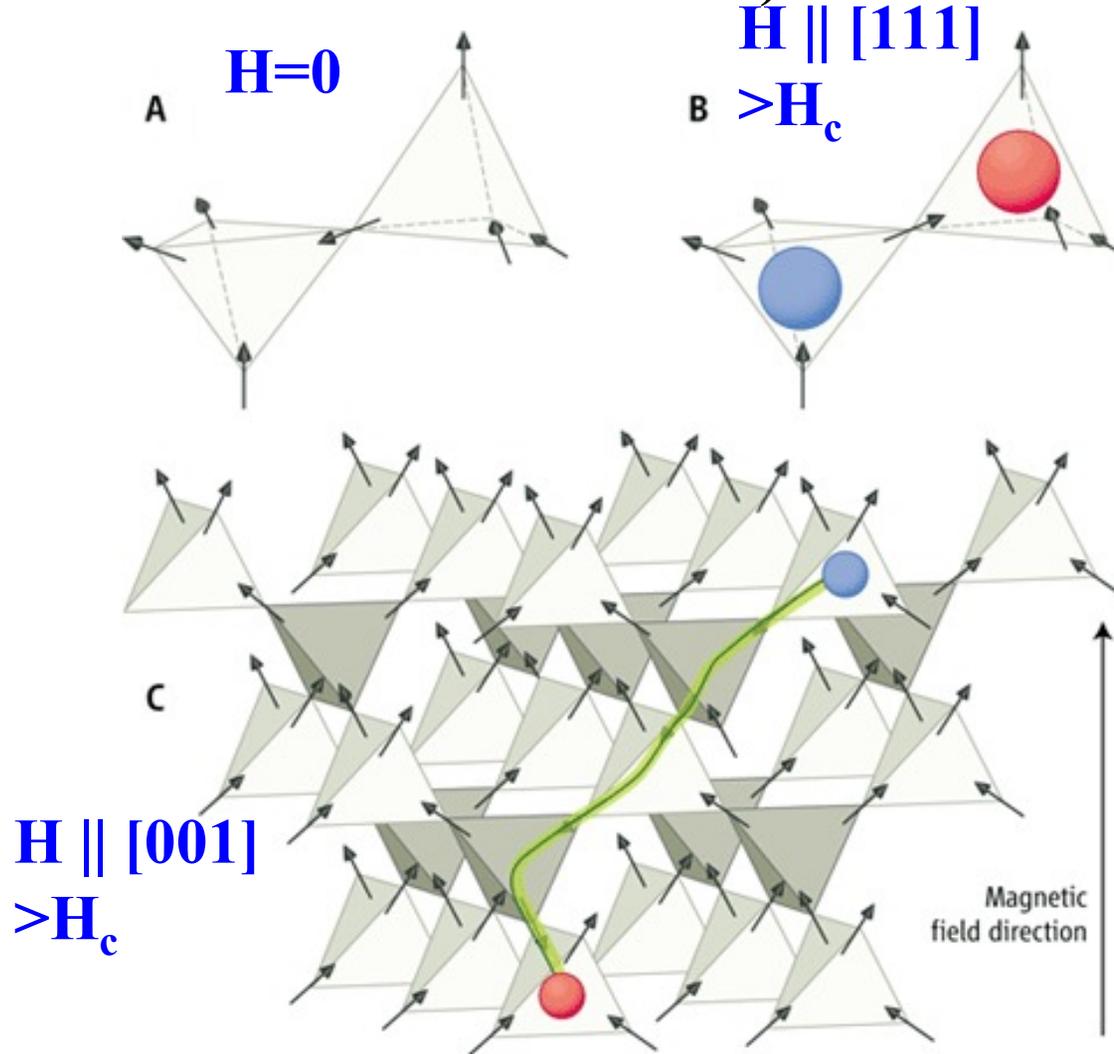
Ferromagnetic interaction, Ising spin (spin ice)



$R=Gd$

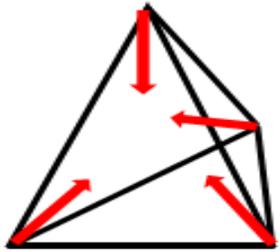
Antiferromagnetic interaction, Heisenberg spin

# Excitations creating magnetic monopole (Castelnovo, Moessner and Sondhi)

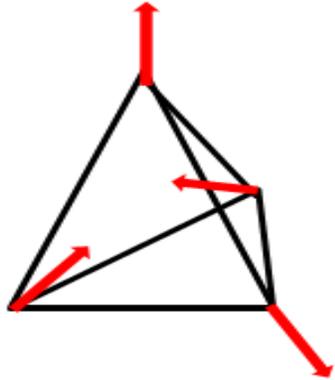


M J P Gingras Science 2009;326:375-376

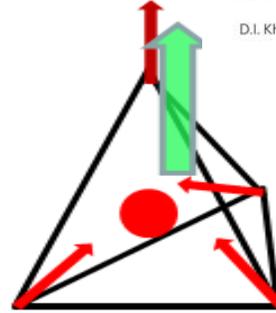
# ★ Dipoles on tetrahedra:



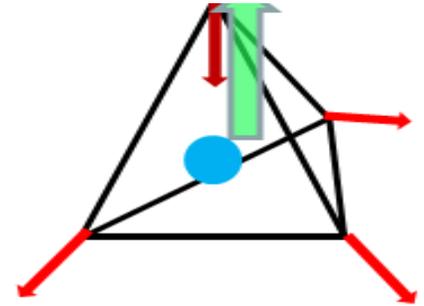
4-in or 4-out:  $\mathbf{d}=0$



2-in/2-out (spin ice):  $\mathbf{d}=0$



3-in/1-out or 1-in/3-out (monopoles/antimonopoles):  $\mathbf{d} \neq 0$



$$\langle n_1 \rangle = 1 + \delta n_1 = 1 - 8 \left( \frac{t}{U} \right)^3 [\mathbf{S}_1 (\mathbf{S}_2 + \mathbf{S}_3) - 2\mathbf{S}_2 \mathbf{S}_3]$$

For 4-in state: from the condition  $\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4 = 0$   $\delta n_1 = 0$ . Change of  $\mathbf{S}_1 \rightarrow -\mathbf{S}_1$  (3-in/1-out, *monopole*) gives nonzero charge redistribution and  $\mathbf{d} \neq 0$ .

Charge redistribution and dipoles are *even* functions of  $\mathbf{S}$ ; inversion of all spins does not change direction of a dipole:  Direction of dipoles on monopoles and antimonopoles is *the same*: e.g. from the center of tetrahedron to a “special” spin

## Dipoles on monopoles, possible consequences:

● “Electric” activity of monopoles; contribution to dielectric constant  $\epsilon(\omega)$

● External electric field:

Decreases excitation energy of certain monopoles

$$\omega = \omega_0 - dE$$

Crude estimate: in the field  $E \sim 10^5$  V/cm energy shift  $\sim 0.1$  K

● Inhomogeneous electric field (tip): will attract some monopoles/dipoles and repel other

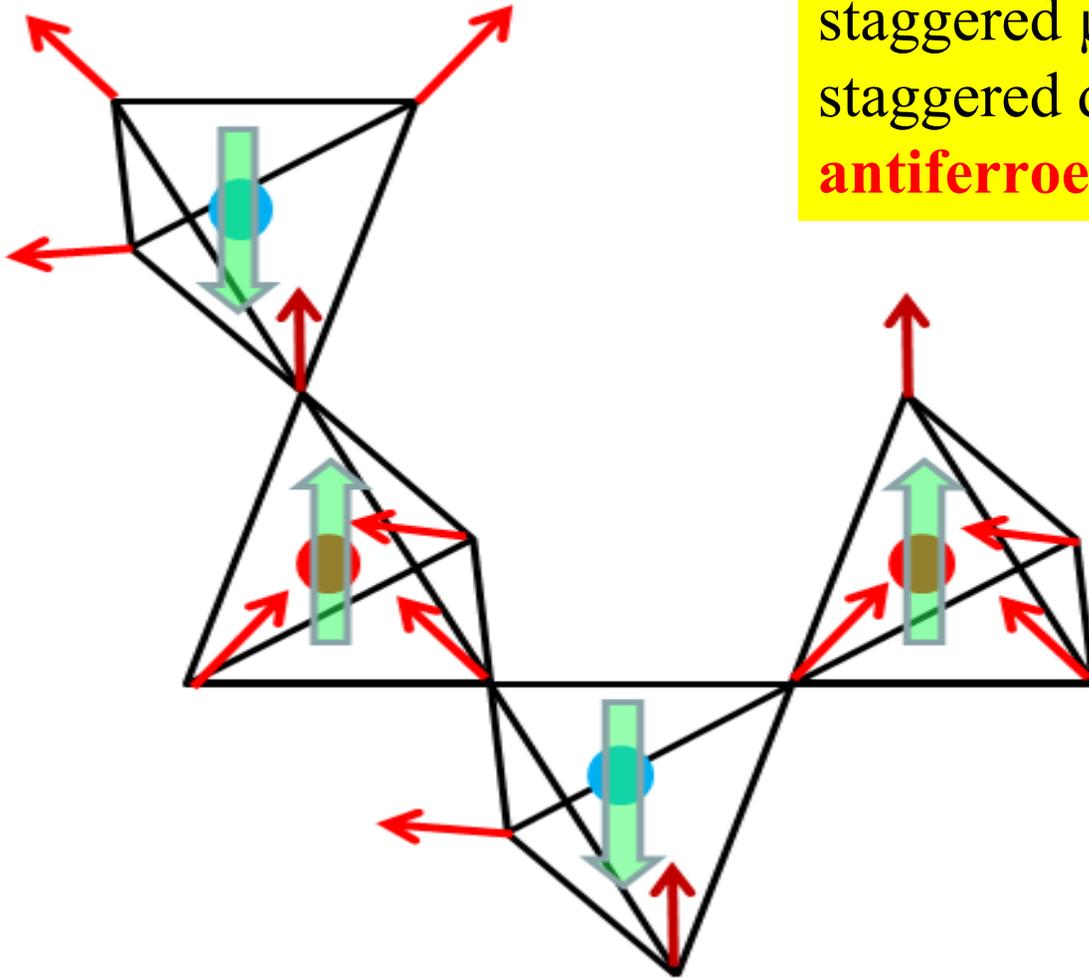
$$\text{Estimates: } \epsilon = dE = eu(\text{\AA})E(\text{V/cm})$$

$$\text{for } u \sim 0.01 \text{\AA} \text{ and } E \sim 10^5 \text{ V/cm } \epsilon \sim 10^{-5} \\ eV \sim 0.1 \text{ K}$$

● In the magnetic field  $H \parallel [001]$   $E$  will promote monopoles, and decrease magnetization  $M$ , and decrease  $T_c$

● In the field  $H \parallel [111]$  – staggered Ising-like dipoles; in  $E_{\perp}$ ?

In strong field  $\mathbf{H} \parallel [111]$  there is a staggered  $\mu/\underline{\mu}$ , and simultaneously staggered dipoles – i.e. it is an **antiferroelectric**



- “Electric” activity of monopoles; contribution to dielectric constant  $\epsilon(\omega)$

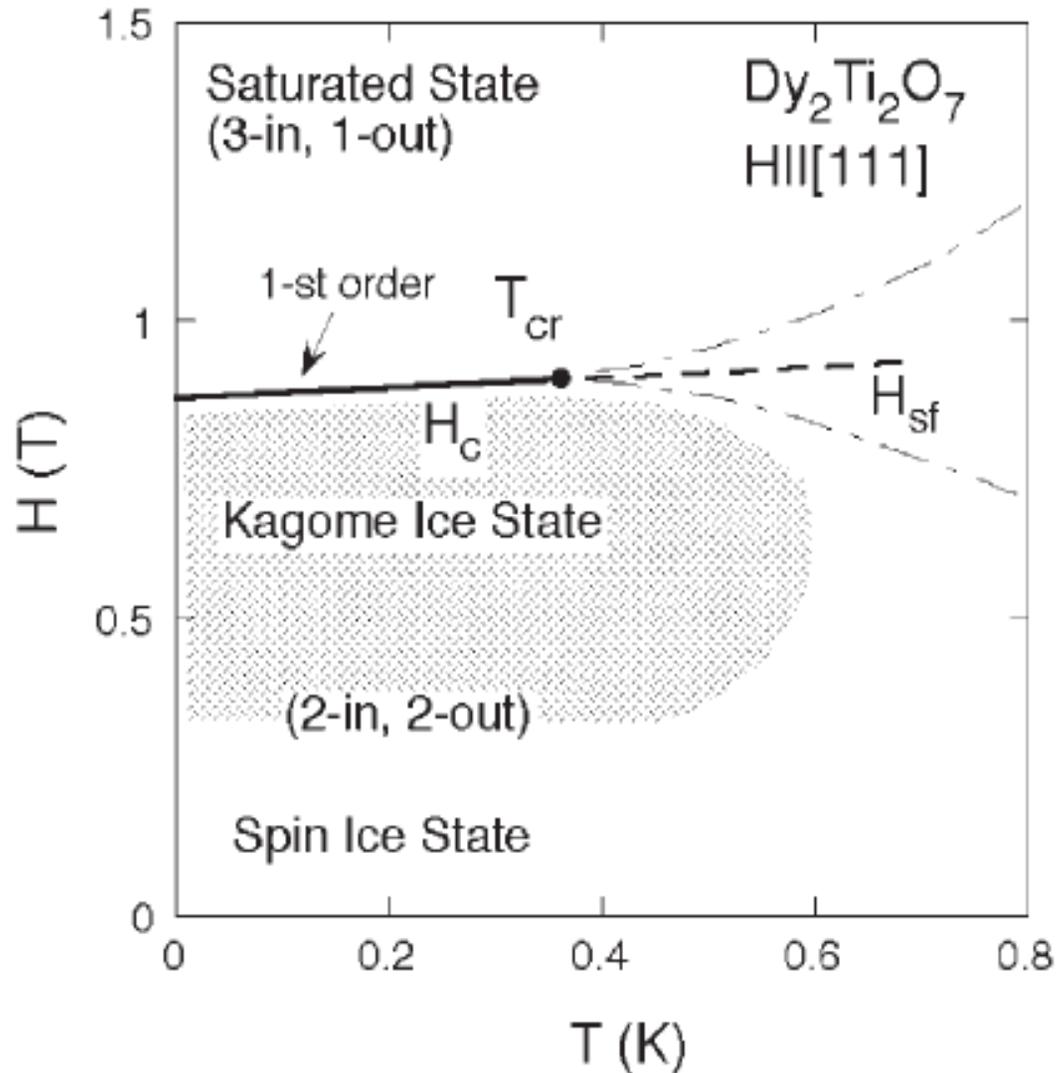
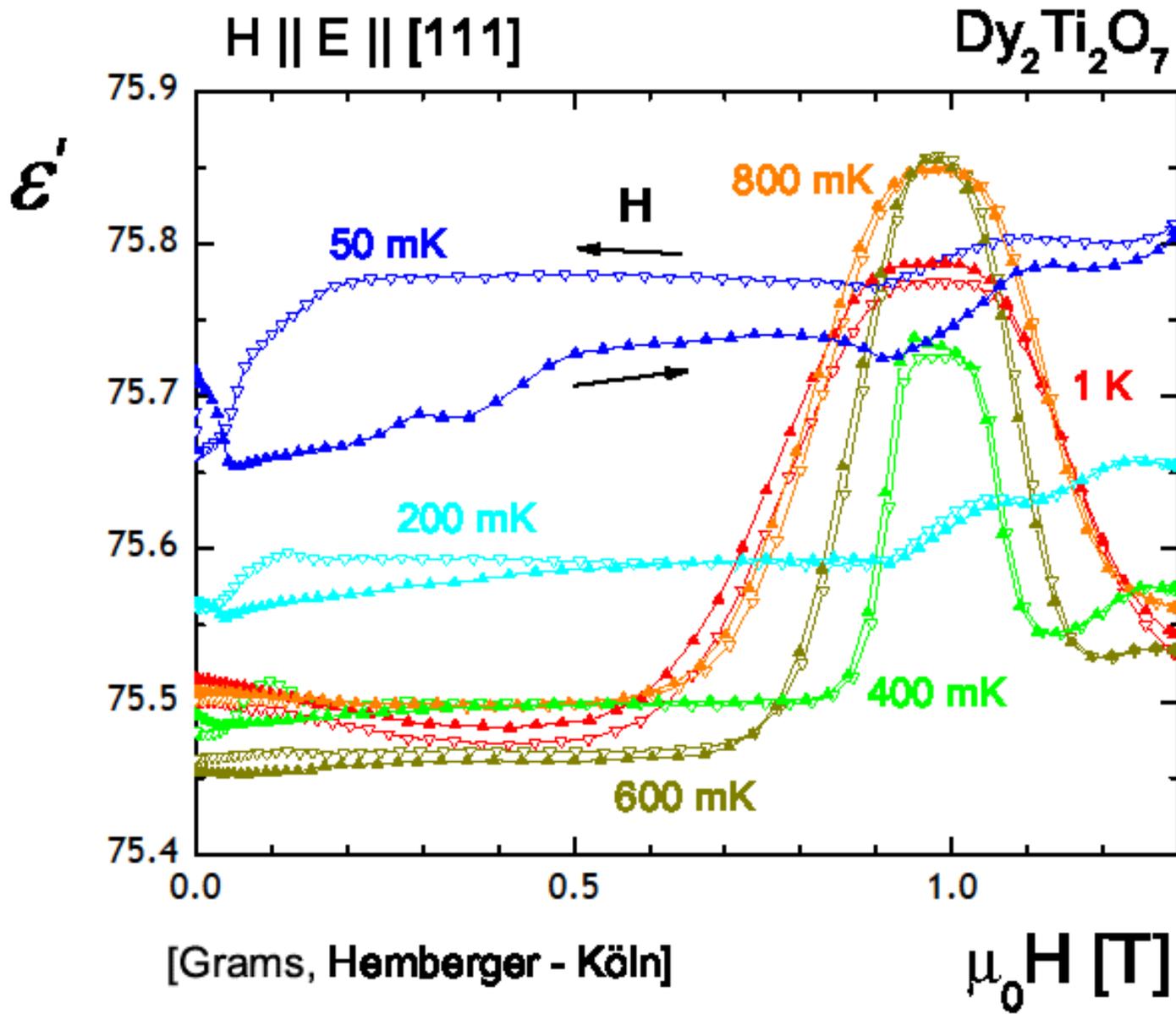
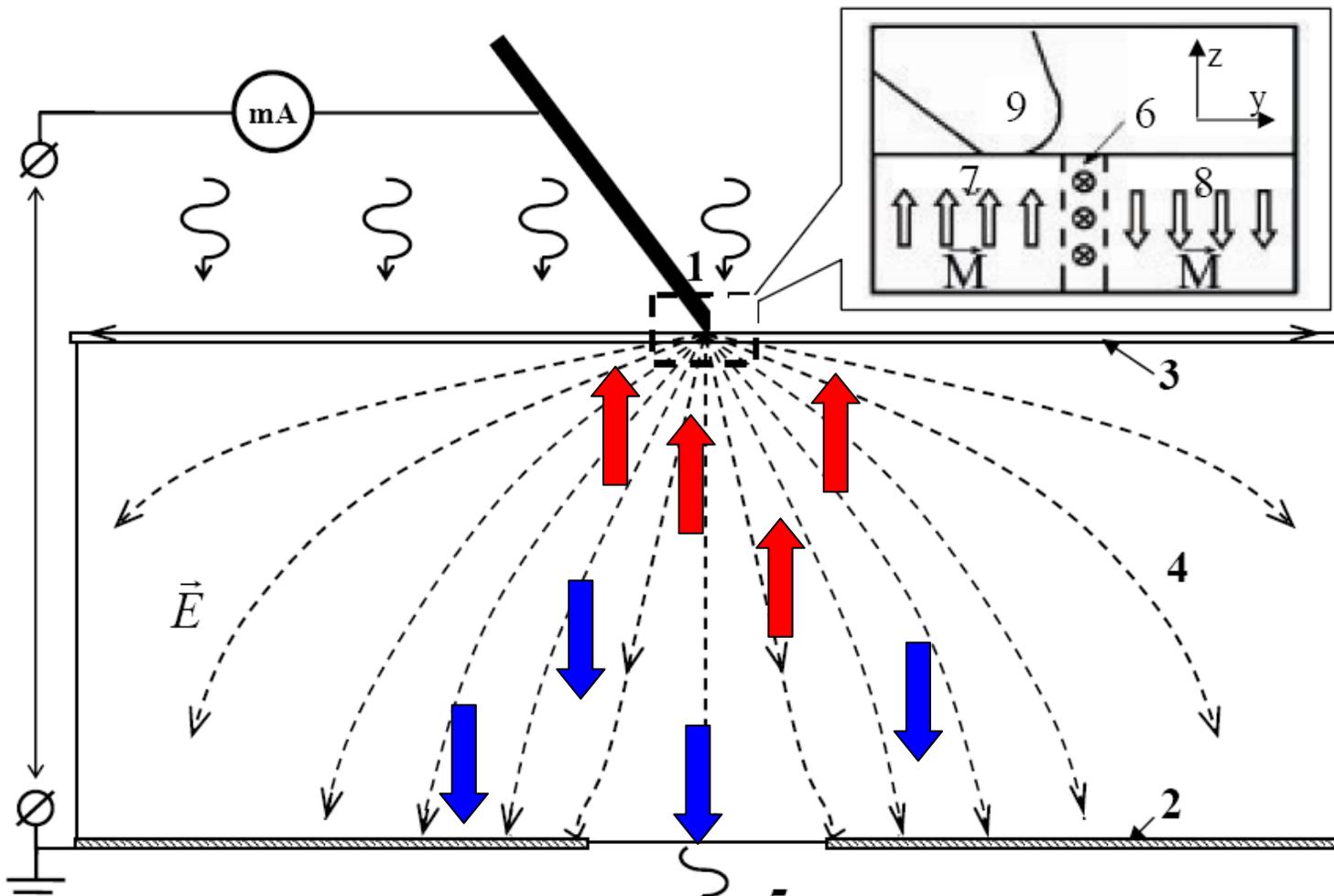


Fig. 1. Phase diagram of  $\text{Dy}_2\text{Ti}_2\text{O}_7$  in a  $[111]$  magnetic field, determined by magnetization and specific heat measurements. The dashed line



● Inhomogeneous electric field



# Monopoles in magnetoelectrics?

**D.Khomskii**

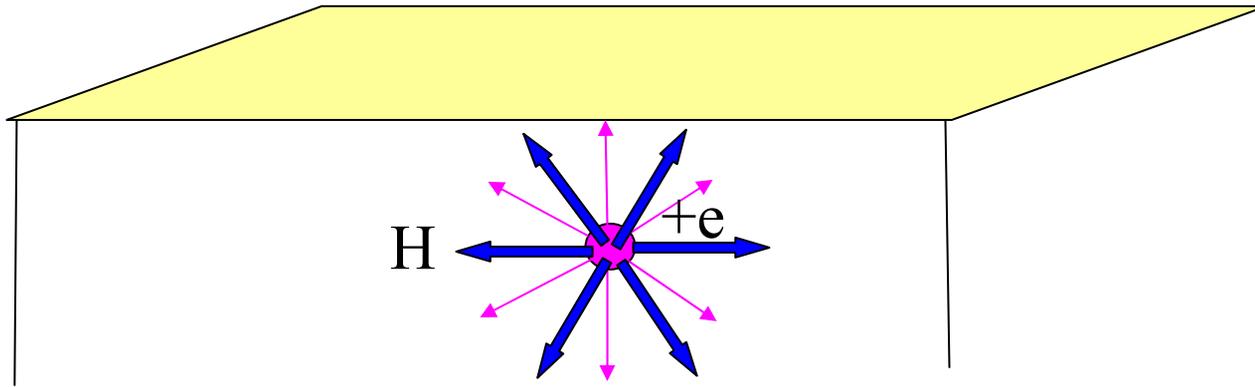
**arXiv:1307.2327**

**(2013)**

# ● Magnetic monopoles in magnetoelectrics

Charge inside of of ME material:  $M_i = \alpha_{ij} E_j$ ,  $H = 4\pi M$

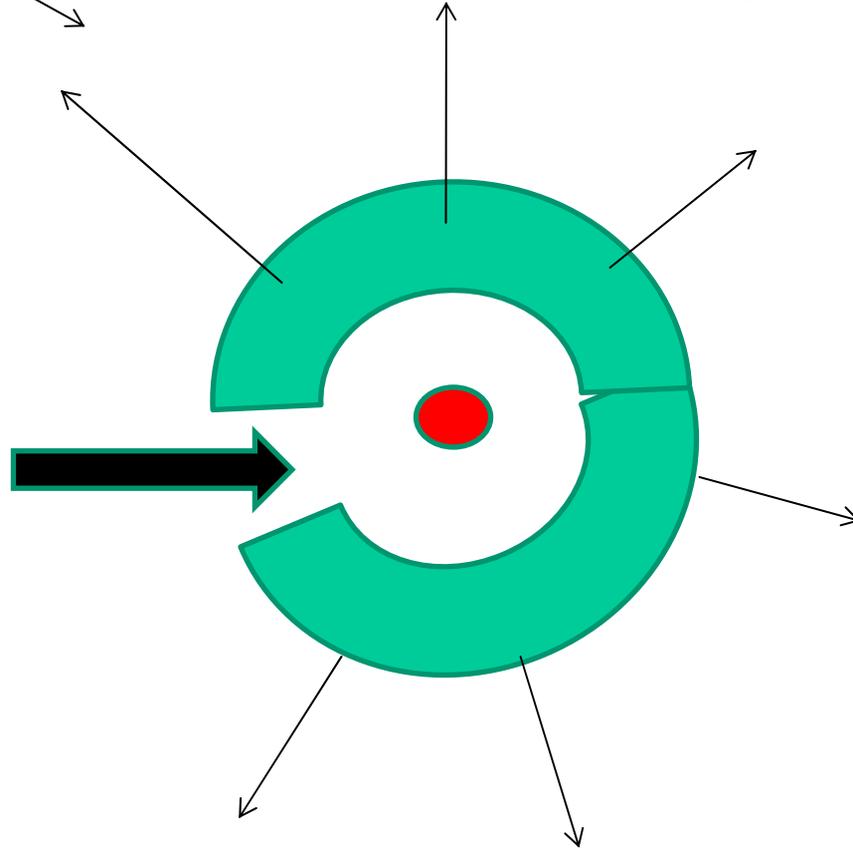
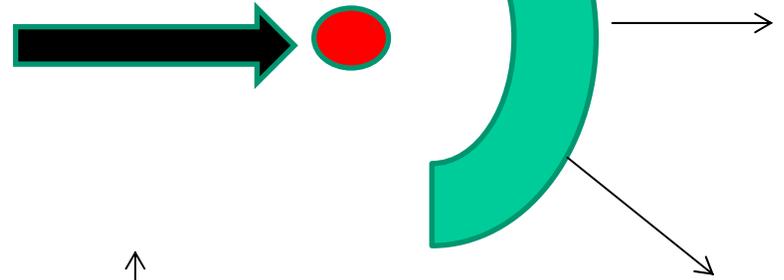
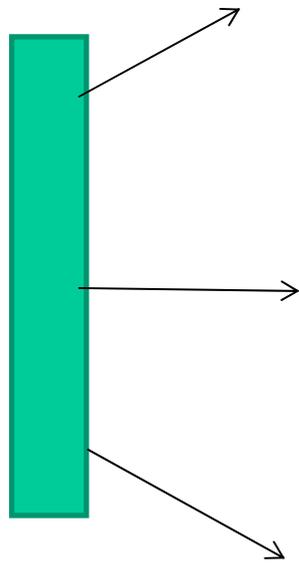
Let  $\alpha_{ij} = \alpha \delta_{ij}$ , diagonal: magnetic field outside of the charge looks like a field of a magnetic monopole  $\mathbf{g} = 4\pi\alpha\mathbf{e}$



Moving electron  $\longrightarrow$  moving monopole.

Electron in a magnetic field: force  $\mathbf{F} = \mathbf{g}\mathbf{H} = 4\pi\alpha\mathbf{e}\mathbf{H}$

(But one can also consider it as an action of the electric field created in magnetoelectric material on the electric charge:  $\mathbf{E} = 4\pi\alpha\mathbf{H}$ ,  $\mathbf{F} = \mathbf{E}\mathbf{e} = 4\pi\alpha\mathbf{e}\mathbf{H}$ )



**Monopole with  
the string!**

## Other possible effects ? (how to find, to measure such monopoles)

**"Electric Hall effect"**: if electric charge  $e$  moving in  $\mathbf{H}$  gives a Hall effect, a monopole moving in electric field will do the same

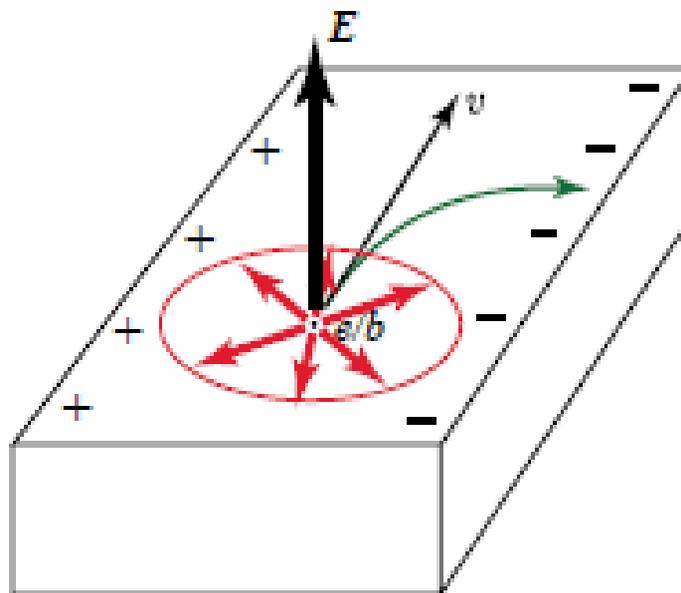


Figure 2: Motion of a magnetic monopole  $b$ , accompanying electric charge  $e$ , in a perpendicular electric field. The force  $b[\mathbf{v} \times \mathbf{E}]$  will bend the trajectory of this object, leading to an "electric Hall effect".

But one can also explain this effect as the usual Hall effect in an effective magnetic field  $\mathbf{B} \sim \alpha \mathbf{E}$

# Charges in magnetoelectrics with toroidal moment (antisymmetric ME tensor)

Magnetolectric coupling in this case is  $\sim \mathbf{T} \cdot [\mathbf{E} \times \mathbf{B}]$ , charge and electric field create  $\mathbf{M} \sim [\mathbf{T} \times \mathbf{E}] \longrightarrow$  *local toroics around charge*

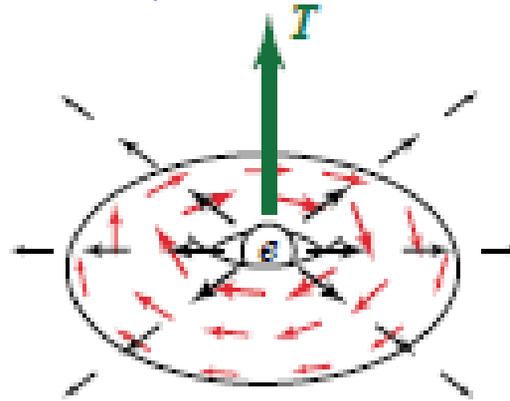
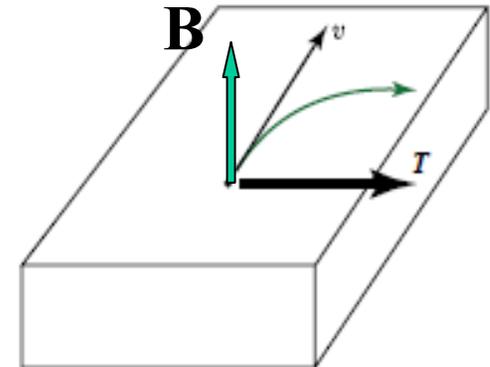


Figure 3: Local toroic (“magnetic donut”) created around charge  $e$  in a magnetoelectric media with antisymmetric magnetoelectric tensor and with magnetic moments  $\mathbf{M}(\mathbf{r}) \sim \mathbf{E}(\mathbf{r}) \times \mathbf{T}$  (close to the core  $\mathbf{M}$  should decrease again).

Toroidal moment couples not to  $\mathbf{B}$  but to  $\text{curl } \mathbf{B}$ ,  $\mathbf{T} \cdot (\text{curl } \mathbf{B}) = \mathbf{T} \cdot 4\pi \mathbf{j}$ . In effect *current will deviate in the direction of  $\mathbf{T}$*  - analog of *Hall effect without magnetic and electric field*.

But one can also explain the effect as a normal Hall effect in a magnetic field  $\mathbf{B} \sim [\mathbf{T} \times \mathbf{E}]$



## Other specific effects?

***Photovoltaic effect:*** it exists in ferroelectrics (broken inversion symmetry; motion of electrons and holes in opposite direction in an internal electric field). In ME materials it is also possible (V.V. Men'shenin and E.A. Turov, JETP Lett. **72**, 14 (2000) )

### **Photovoltaic effect in magnetic field?**

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