Multiferroics: different ways to combine magnetism and ferroelectricity

D.Khomskii
Cologne University, Germany

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MULTIFERROICS

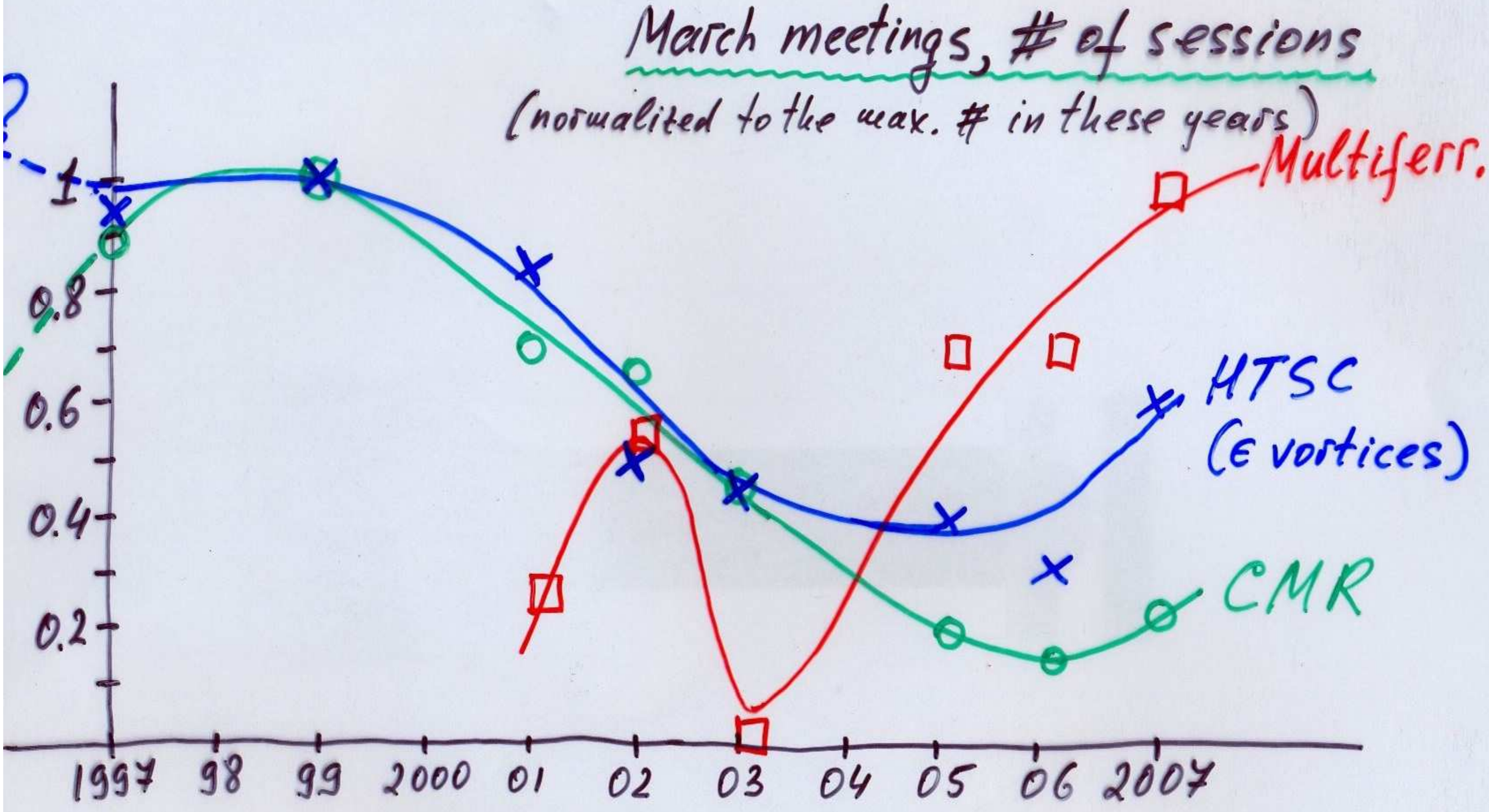
Materials combining ferroelectricity, (ferro)magnetism and (ferro)elasticity

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

D.Kh. JMMM **306**, 1 (2006)

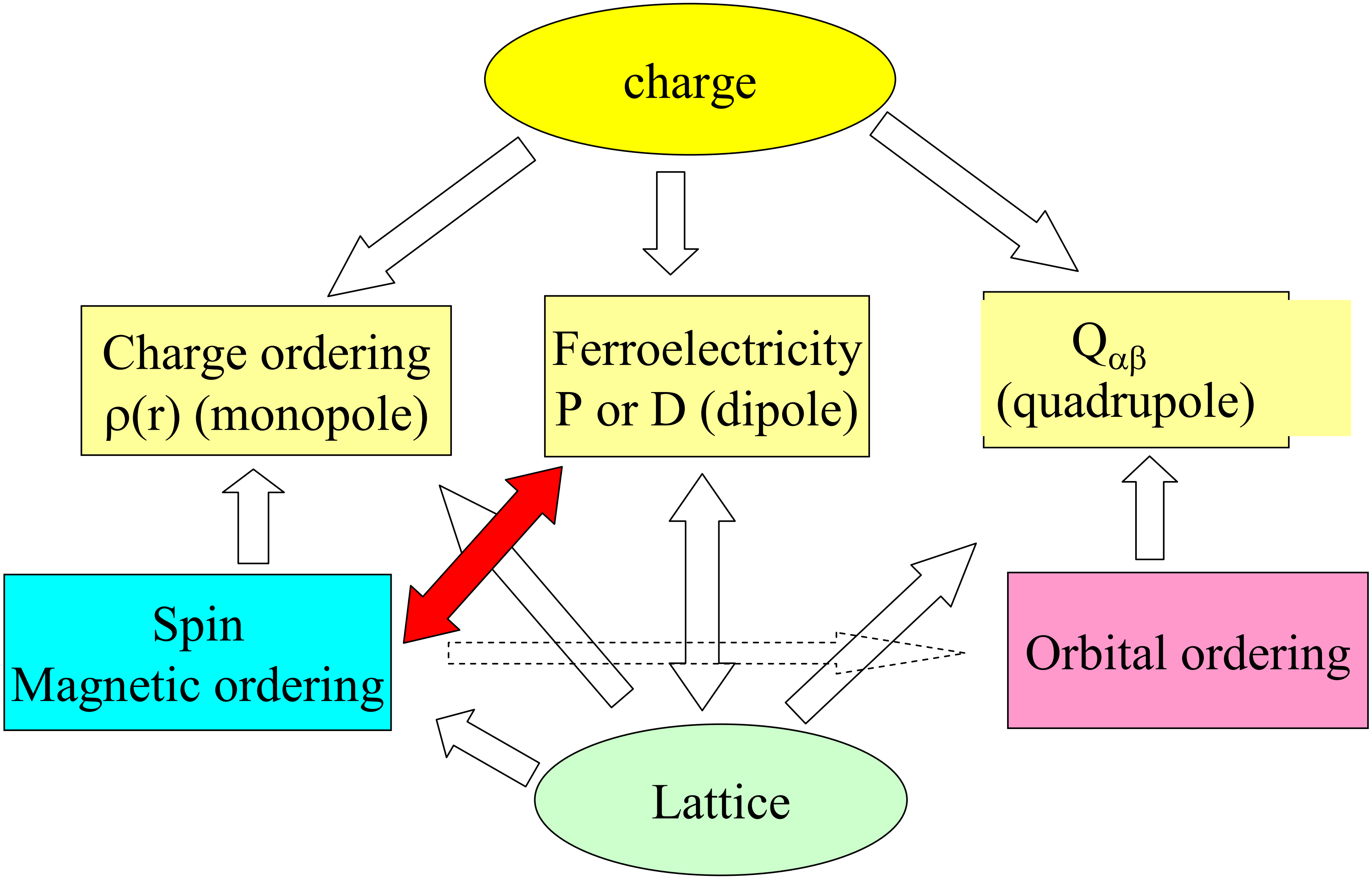


March meetings, # of sessions

(normalited to the max. # in these years)

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

Degrees of freedom



charge

Charge ordering
$\rho(r)$ (monopole)

Ferroelectricity
P or D (dipole)

$Q_{\alpha\beta}$
(quadrupole)

Spin
Magnetic ordering

Orbital ordering

Lattice

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_{FE} (K)	T_M (K)	P(μC cm^{-2})
$BiFeO_3$	1103	643	6.1
$YMnO_3$	914	76	5.5
$HoMnO_3$	875	72	5.6
$TbMnO_3$	28	41	0.06
$TbMn_2O_5$	38	43	0.04
$Ni_3V_2O_8$	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

1) Perovskites: d^0 vs d^n
2) “Geometric” multiferroics (YMnO3)
3) Lone pairs (Bi; Pb, ….)
4) FE due to charge ordering

5) FE due to magnetic ordering

Perovskites: d^0 vs d^n

Empirical rule:FE for perovskites with empty d-shell
($BaTiO3$, $PbZrO3$; $KNbO3$)
contain Ti^{4+}, Zr^{4+}; Nb^{5+}, Ta^{5+}; Mo^{6+}, W^{6+}, etc.

Magnetism – partially filled d-shells, d^n, n>o

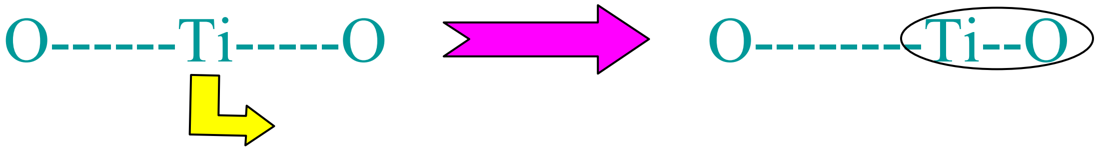
Why such mutual exclusion?

Not quite clear. Important what is the mechanism of FE in perovskites like $BaTiO3$

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

Real microscopic reason: **chemical bonds**

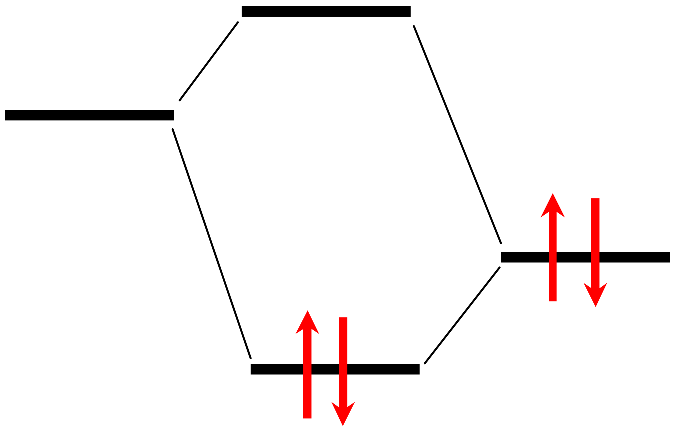
Ti^{4+}: establishes *covalent bond* with oxygens (which “donate” back the electrons), using empty d-levels


O------Ti-----O

O-------Ti--O

Better to have one strong bond with one oxygen that 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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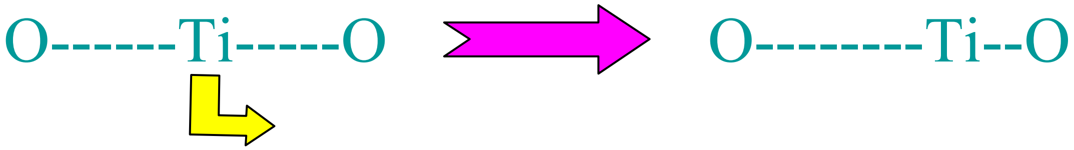
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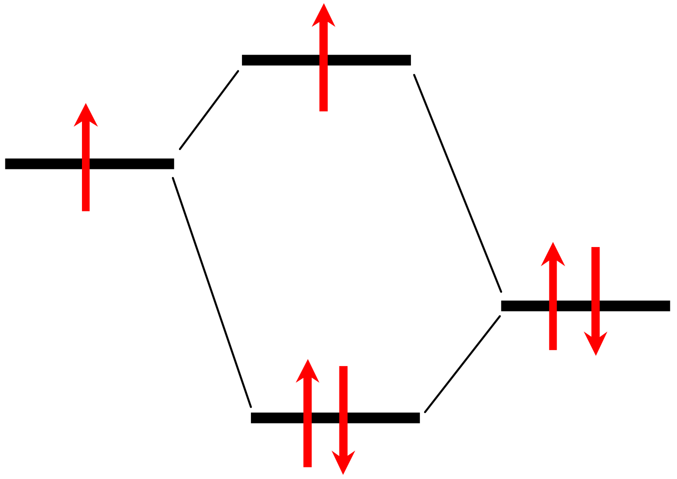
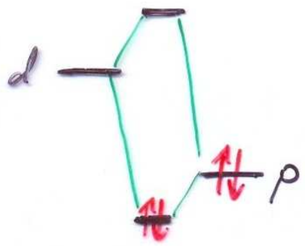


Other localized d-electrons break *singlet* chemical bond by Hund’s rule pair-breaking (a la pair-breaking of Cooper pairs by magnetic impurities)

- Back to the problem of why finite occupation of d-shell is bad for FE?

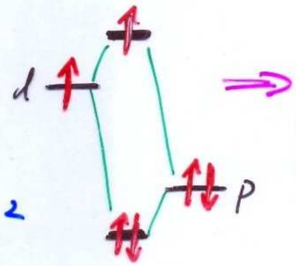
At least two reasons:

① d^0-configuration: only bonding orbitals are occupied



In MO: $E = -\frac{t^2}{u} \cdot \underset{\substack{\uparrow \\ \text{two electrons}}}{2}$

d^1-configuration:



⇒ antibonding orbitals are occupied!

$E = -\frac{t^2}{u} \cdot 2 + \frac{t^2}{u} \cdot 1 = -\frac{t^2}{u}$

- lost half of the energy gain!

② Presence of other d-electrons hinders the formation of (strong) covalent bond

! (a la pairbreaking of Cooper pairs by magnetic impurities)

Strong covalent bond: $|\Psi_0\rangle = \frac{1}{\sqrt{2}}(d\uparrow p\downarrow - d\downarrow p\uparrow)$

⇒ Both $d\uparrow$ and $d\downarrow$ are present

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

Always strong Hund's rule coupling

$$-J_H\, d^{+}\hat{\vec{\sigma}}d \cdot \tilde{d}^{+}\hat{\vec{\sigma}}\tilde{d} = -J_H\, \vec{S}_d\, \vec{S}_{\tilde{d}}$$

Spin $\tilde{d}\uparrow$ – „does not like" the component $d\downarrow p\uparrow$ of the valence bond wave function $|\Psi_0\rangle$

$\Longrightarrow$ we lose half of the energy gain δE

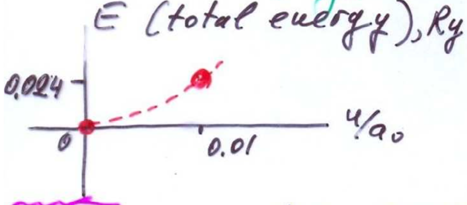
Thus the Hund's rule decoupling may be destructive for FE

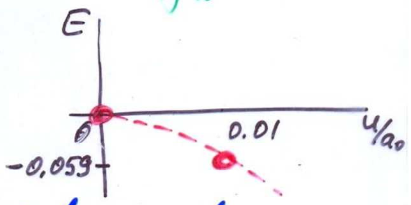
- To check this:

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

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

$CaMnO_3$, $J_H \neq 0$ $\qquad$ $J_H = 0$





$\Rightarrow$ If we switch off Hund's rule coupling – $CaMnO_3$ ($Mn^{4+}(d^3)$) would become unstable wrt ferroelectric displacement

The ways out:

(x) "Mixed" systems, with both d^0 and d^n ion
($PbFe_{1/2}Nb_{1/2}O_3$; $PbCo_{1/2}W_{1/2}O_3$, ….)

(x) Independent magnetic and FE subsystems, different subgroups responsible for FE and magnetism.
E.g. Ni-J boracite $Ni_3B_7O_{13}J$

(x) "Geometric" FE: $YMnO_3$, etc

(x) Lone pairs: Bi^{3+} ($BiFeO_3$; $BiMnO_3$); Pb^{2+} ($PbVO_3$) ;
Aurivillius phases with magnetic ions?

(x) Charge ordering (organics; $LuFe_2O_4$; Fe_3O_4; $(PrCa)MnO_3$? $RNiO_3$?)

→ coupling usually weak!

(x) **FE due to magnetic ordering**

1) Magnetics with spiral magnetic structure ($TbMnO_3$, $Ni_3V_2O_8$; $MnWO_4$, $CuFeO_2$; $LiCuV_2O_4$)

2) Magnetics with FE due to magnetostriction ($TbMn_2O_5$? ; $RbFe(MoO_4)_2$

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 RMnO3

YMnO3: T_{FE}~900 K; T_N~70 K

The origin (T.Palstra, N. Spaldin): tilting of MnO5 trigonal bipiramids – a la tilting of MO6 octahedra in the usual perovskites leading to orthorombic distortion.

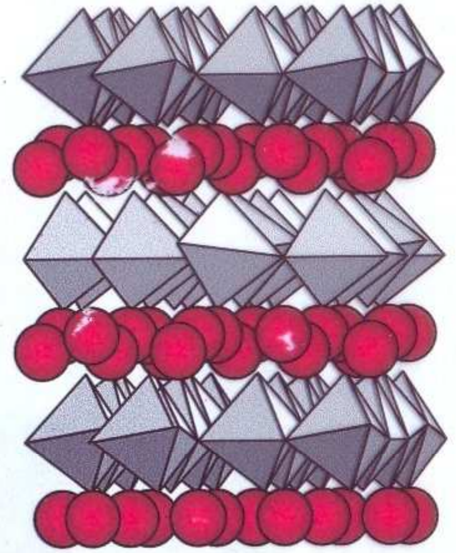
In perovskites one AMO3 one A-O distance becomes short, but no total dipole moment – dipole moments of neighbouring cells compensate.

In YMnO3 – total dipole moment, between Y and O; Mn plays no role!

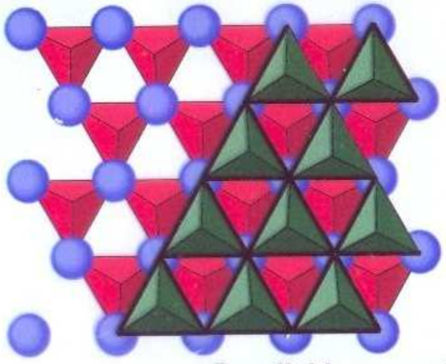
Crystal structure of $YMnO_3$

Ferroelectric distortion

Displacements from:
centrosymmetric high temp
to ferroelectric room temp

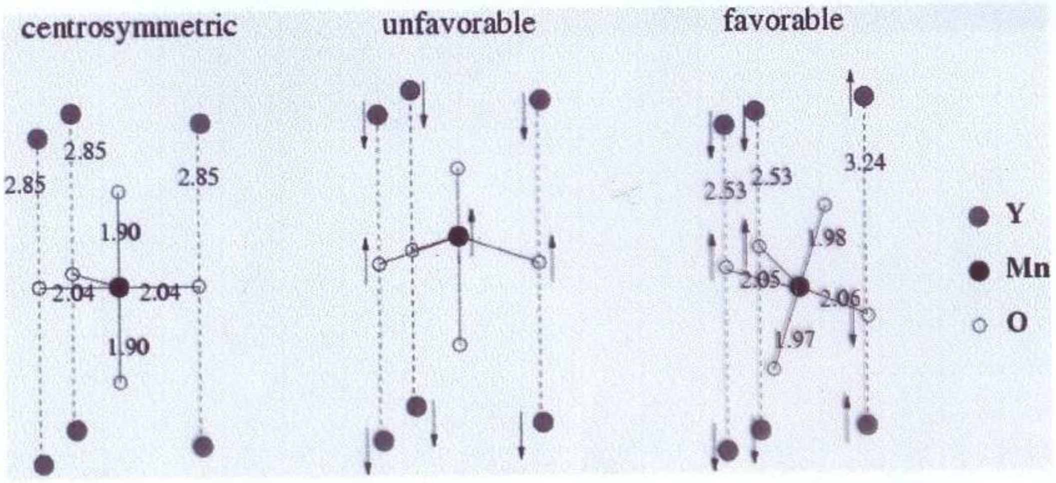


Perpendicular hexagonal axis



Parallel hexagonal axis

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



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

Lone pairs and ferroelectricity

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

Many nonmagnetic ferroelectrics with Bi^{3+}; Pb^{2+} . – e.g. PZT [Pb(ZrTi)O3]

Some magnetic:

Aurivillius phases: good ferroelectrics, layered systems with perovskite slabs/Bi_2O_2 layers ($SrBi_2Nb_2O_9$; $SrBi_4Ti_4O_{15}$, etc). Exist with magnetic ions, but not really studied.

PbVO3 – a novel compound. Distortion so strong that probably impossible to reverse polarization – i.e. it is probably not ferroelectric, but rather pyroelectric

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Synthesis, Structure, and Properties of New Perovskite $PbVO_3$

Roman V. Shpanchenko,* Viktoria V. Chernaya, Alexander A. Tsirlin,
Pavel S. Chizhov, Dmitry E. Sklovsky, and Evgeny V. Antipov

Department of Chemistry, Moscow State University, 119992 Moscow, Russia

Evgeny P. Khlybov

Institute for High-Pressure Physics, 142092 Troitsk, Russia

Vladimir Pomjakushin

*Laboratory for Neutron Scattering, ETH Zurich & PSI Villigen,
CH-5232 Villigen PSI, Switzerland*

Anatoly M. Balagurov

Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Russia

Julia E. Medvedeva

Institute of Solid State Chemistry, 620249 Ekaterinburg, Russia

Enrique E. Kaul and Christoph Geibel

Max-Planck Institute CPfS, Nöthnitzer Street 40, 01187 Dresden, Germany

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The new perovskite $PbVO_3$ 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_5 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 $[VO_2]$-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_3, 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_3 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_6 octahedra. Octahedra in these structures are regular or slightly distorted and no formation of a short vanadyl bond is observed. Thus, $SrVO_3$ is an ideal cubic perovskite[1,2] and $CaVO_3$ is an orthorhombically distorted perovskite ($GdFeO_3$-type)[1,3] while $BaVO_3$ forms trigonal 5H close-packing in a wide range of oxygen nonstoichiometry.[4] Stoichiometric $CaVO_3$ and $SrVO_3$ compounds exhibit metallic-like conductivity down to 2−4 K and Pauli paramagnetic behavior. These properties can be changed by variation of oxygen content.[2,5−7]

Until now no information is available on the existence of $PbVO_3$ despite Pb^{2+} cation crystal radius (1.63 Å) being very close to that for Sr^{2+} (1.58 Å). The synthesis of this compound looks very attractive, taking into account the influence of the lone pair of the Pb^{2+} 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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* To whom correspondence should be addressed. E-mail: shpanchenko@icr.chem.msu.ru.

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10.1021/cm049310x CCC: $27.50

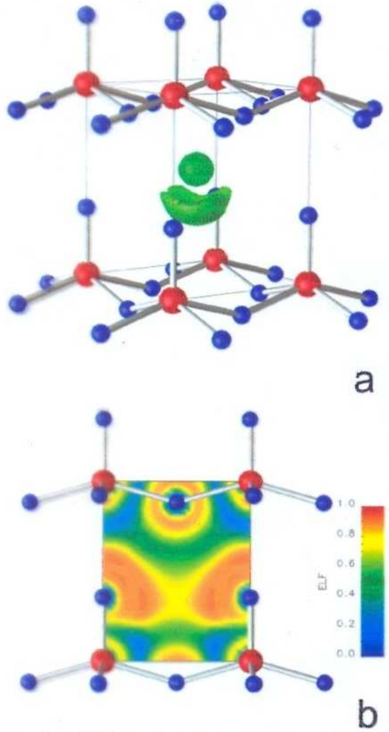

Figure 3. (a) Valence electrons ELF isosurface (η = 0.85) around Pb. (b) ELF distribution in the (100) plane.

consequently of the physical properties of the material. In the case of PbVO$_3$ 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$_3 \pm \delta$ (δ = 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(ρ) 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$_6$O$_{11}$ foreign phase.[19] However, the neutron experiment allows some estimations to be made for magnetic properties of PbVO$_3$. 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 μ_B, assuming a ferromagnetic alignment of the V^{4+} 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 μ_B.

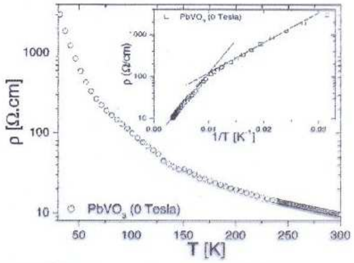

Figure 4. Temperature dependence of the resistivity of a polycrystalline PbVO$_3$ sample. Inset: Log ρ versus $1/T$ plot, showing the two regions with activated behavior (lines are guide to the eyes).

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

First, we performed calculations using local spin density approximation (LSDA) considering both ferromagnetic (FM) and antiferromagnetic (AFM) ordering models for PbVO$_3$. The electronic band structure was calculated using the linearized muffin-tin (MT) orbitals method within the atomic-spheres approximation.[22] 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 (μ = 0.38 μB inside the vanadium MT sphere). The character of the states near E_F evidences significant Vd−O2p hopping and suggests

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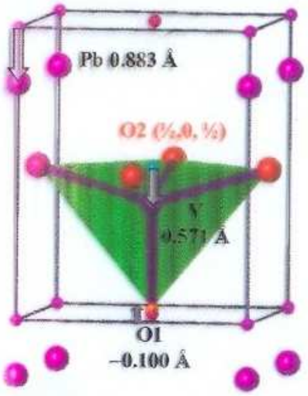
Pb^{2+} lone pairs: Pb^{2+}/Pb^{4+} Pb^{2+}+2e

Alexei A. Belik,[*] Masaki Azuma, Takashi Saito, Yuichi Shimakawa, and Mikio Takano

Chem. Mater. **2004**,

Crystallographic features and tetragonal phase stability of $PbVO_3$ - a New Member of $PbTiO_3$ Family

Crystallographic features and stability of the tetragonal phase of $PbVO_3$ were investigated and compared with those of $PbTiO_3$. The tetragonality of $PbVO_3$ is the largest among $PbTiO_3$-type compounds and increases from 12 K to the decomposition temperature of 570 K. At high pressure, the tetragonal-to-cubic accompanied by insulator-to-metal phase transition was observed.



$a = 3.80391$ Å
$c = 4.67680$ Å
$c/a = 1.229$

Problems with Bi perovskites:

$BiMnO_3$: ferromagnetic insulator; Jahn-Teller distorted perovskite; ferroelectric?

$BiFeO_3$: rombohedral; good ferroelectric; spiral magnetic structure

$BiCoO_3$: very strong tetragonal distortion! a la $PbVO_3$ (pyroelectric)

$BiNiO_3$: Ni^{2+}, Bi^{4+} → charge segregates into $Bi^{3+} + Bi^{5+}$

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

DMITRY V. EFREMOV[1], JEROEN VAN DEN BRINK[2*] AND DANIEL I. KHOMSKII[1,3]
[1]Laboratory of Solid State Physics, Material Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[2]Instituut-Lorentz for Theoretical Physics, Leiden University, PO Box 9506, 2300 RA Leiden, The Netherlands
[3]II Physicalisches Institut, Universität zu Köln, Zuelpicher Strasse 77, 50937 Köln, Germany
*e-mail: brink@ilorentz.org

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$_3$, colossal magnetoresistance manganites and the high-T_c superconductors. Hundreds of these compounds are magnetic[1], and hundreds of others are ferroelectric[2], 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$_6$ 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^0 configuration), for example Ti^{4+}, Nb^{5+} and W^{6+}. Apparently the presence of the d^0 plays an important role in formation of a ferroelectric state[3,4]. In all of these systems ferroelectricity originates from a shift of the transition metal ion from the centre of the O$_6$ octahedron. In this way a stronger covalent bond with one (or three) instead of six weaker bonds with neighbouring oxygen atoms is formed[5].

The problem of why magnetism and ferroelectricity seem to be mutually exclusive has received some attention[3,4]. 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[3].

There are apparently three exceptions to the empirical assertion of the incompatibility of magnetism and ferroelectricity in perovskites: BiFeO$_3$, BiMnO$_3$ and RMnO$_3$ (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$_3$ and in BiMnO$_3$ ferroelectricity is due to the lone pairs of non-magnetic[6] Bi, and in YMnO$_3$ it is due to tilting of almost rigid MnO$_5$ trigonal bipyramids[7]. This last example shows that the shift of the transition metal ion from the centre of the O$_6$ octahedron is not the only feasible mechanism of ferroelectricity. Recently ferroelectricity was observed in TbMnO$_3$, and was attributed to magnetic frustration in this system[8]; a similar mechanism seems to operate[9] in TbMn$_2$O$_5$. 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.

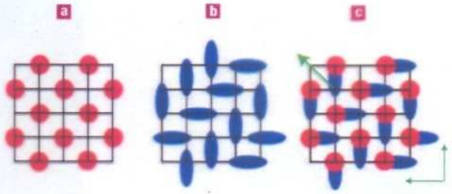
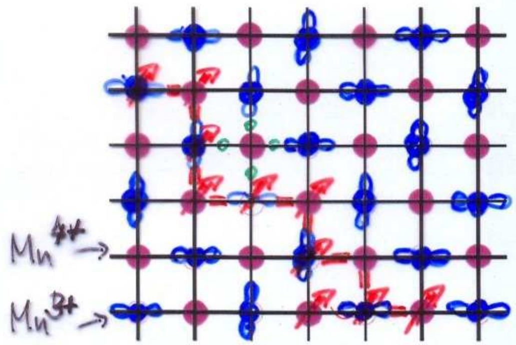


Figure 1 Three types of charge ordering. a, Site-centred charge order; **b**, bond-centred charge order (the Zener polaron state); and **c**, a ferroelectric intermediate state. The charge-ordered structure in **c** lacks inversion symmetry. Thin green arrows indicate the dipole moments of horizontal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

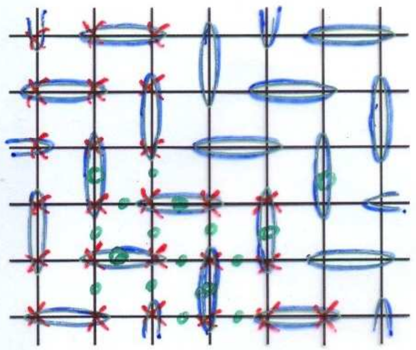
We consider doped manganites of the type R$_{1-x}$Ca$_x$MnO$_3$, with R = La, Pr. Different types of magnetic, charge and orbital orderings are observed in this class of compounds. It becomes more and more clear (see for example, ref. 10) that the charge and orbital

- Charge density waves :
  - manganites
  - magnetite Fe_3O_4 (Vervey transition at 119K)

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



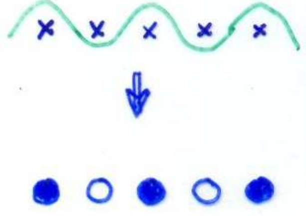
SCDW



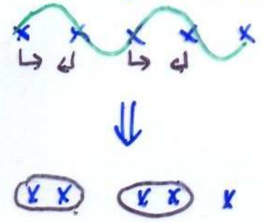
BCDW (Zener polarons)

(Daoud-Aladine et al., PRL 2002)

1d:

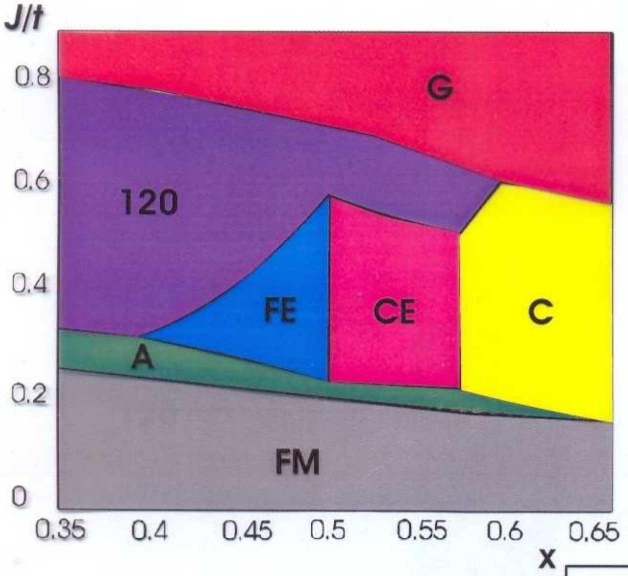


CO

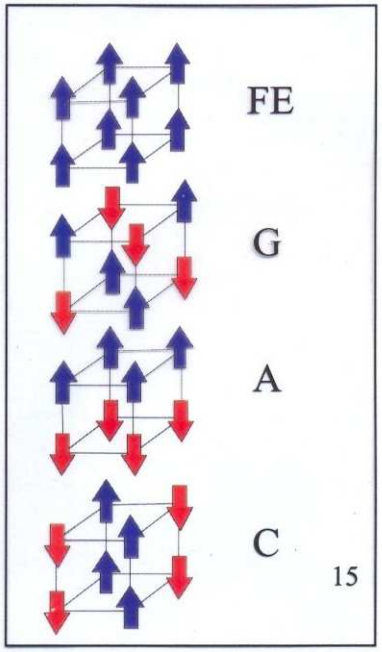


Peierls state

Phase diagram of manganites near x=0.5



Electron density $n_e = 1\text{-}x$



FM: ferromagnetic phase

G: antiferromagnetic Neel state

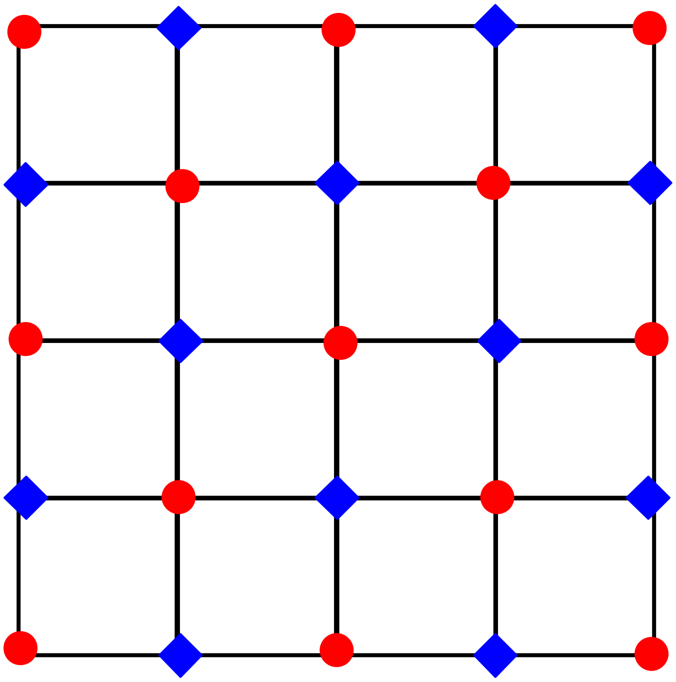
A: F planes coupled AFM

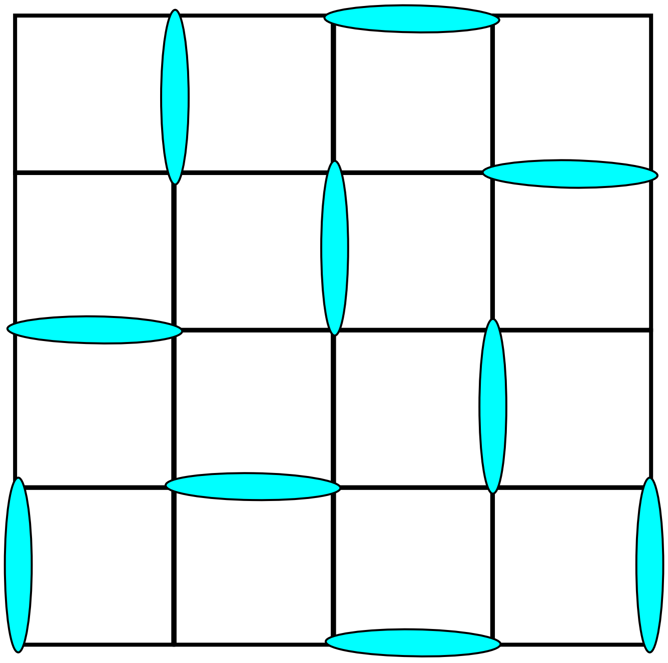
C: F chains coupled AFM

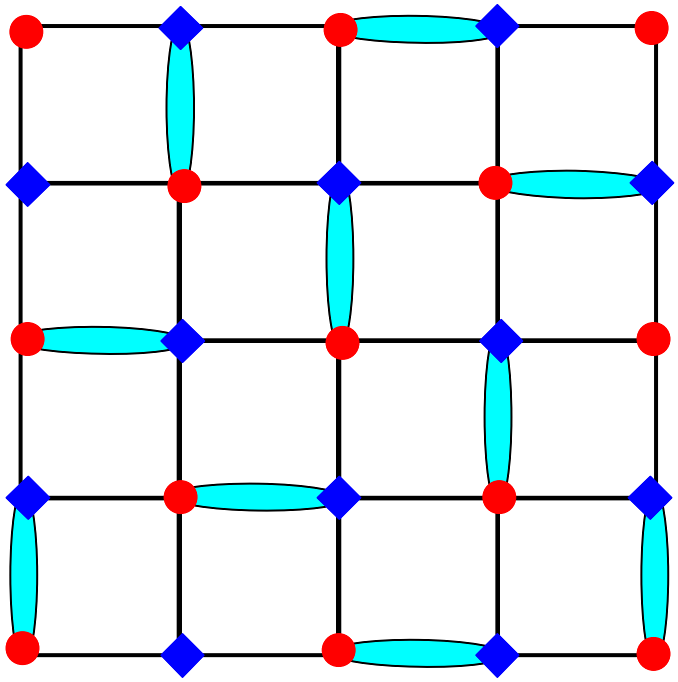
CE: CE-phase

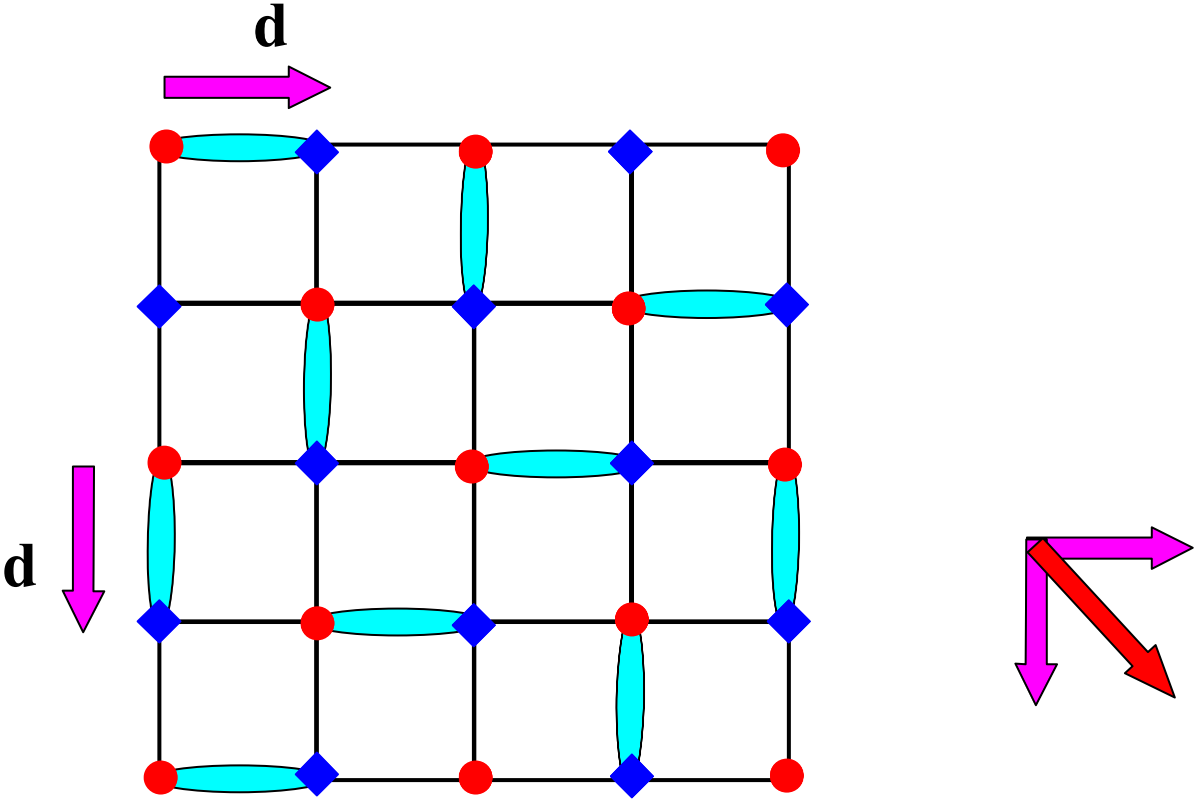
120: Jaffet-Kittel state

FE: Ferroelectric phase

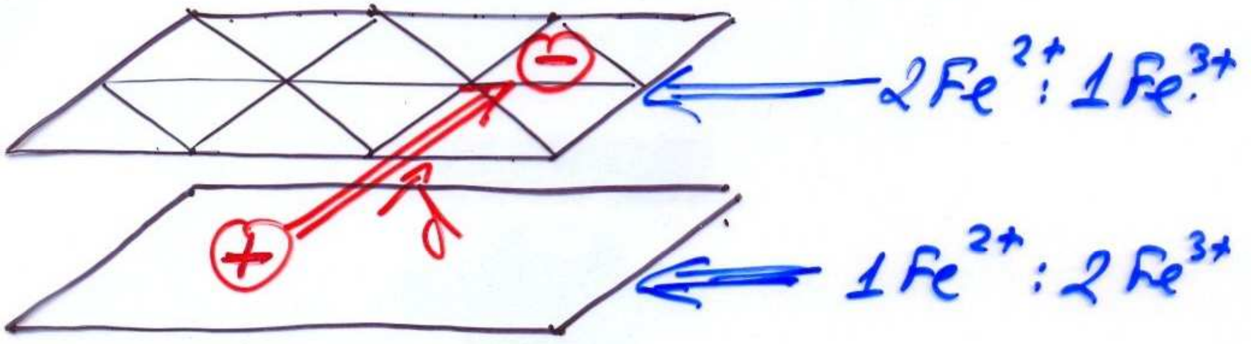


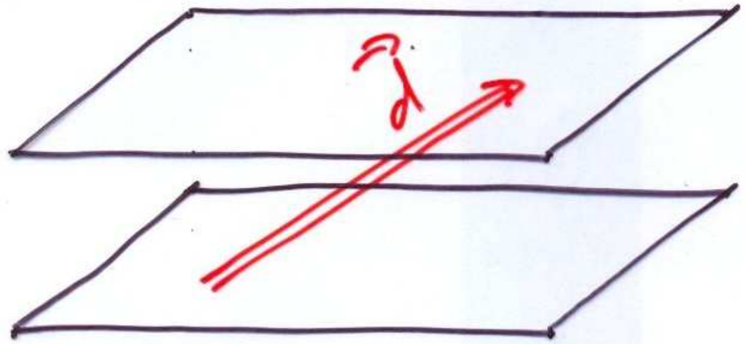




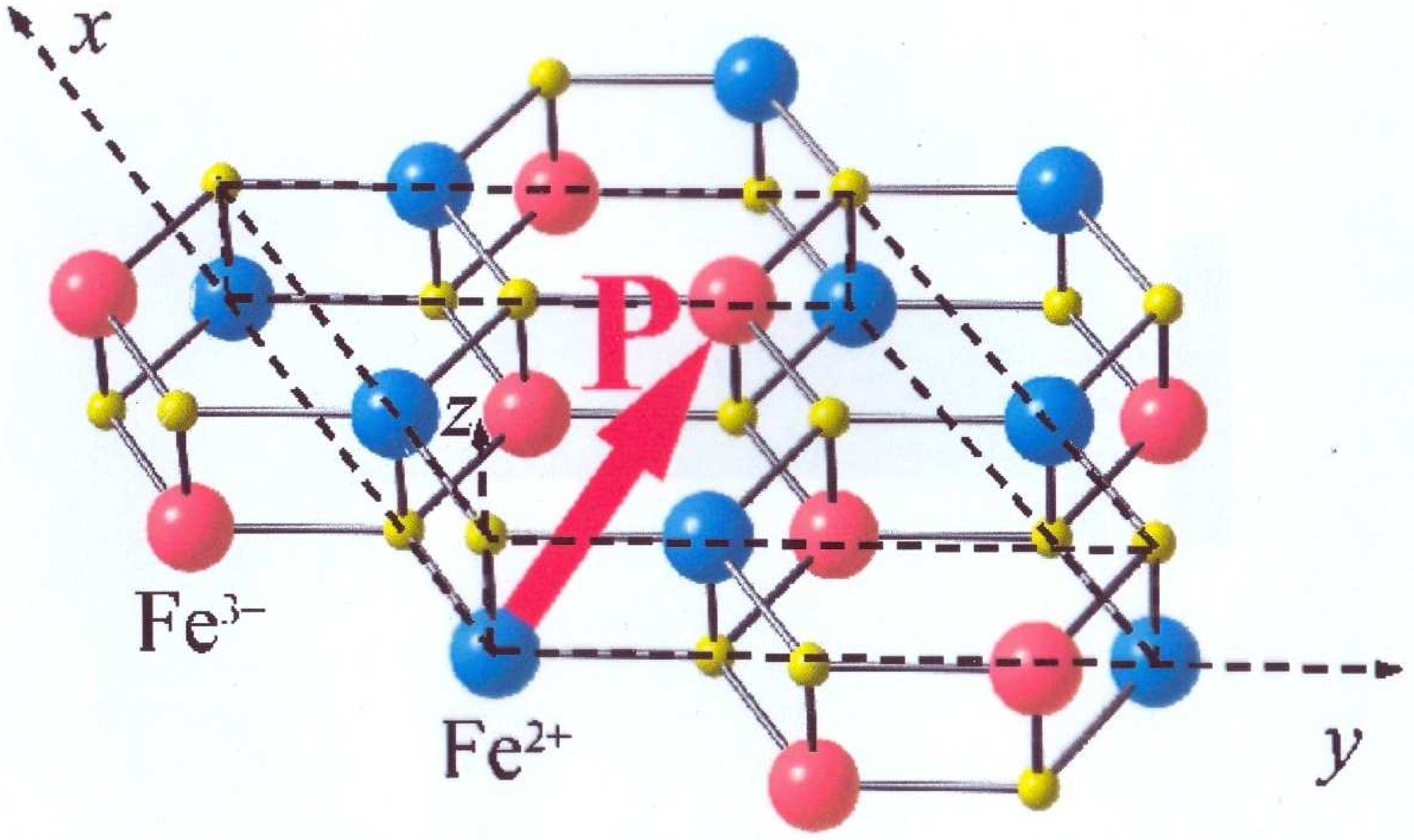

d
d

$LuFe_2^{2.5+}O_4$: „double" triangular layers





$LuFe_2O_4$



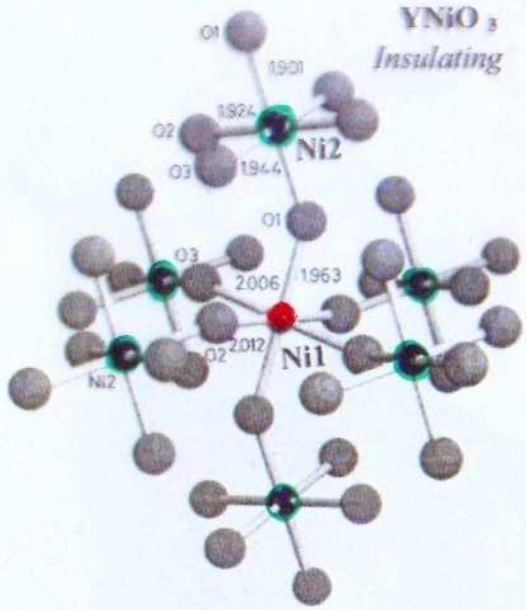
Other similar systems with ferroelectricity due to charge ordering

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

Fe_3O_4: ferroelectric below Verwey transition at 119 K ! Also ferrimagnetic with large magnetization and high Tc

$RNiO_3$?

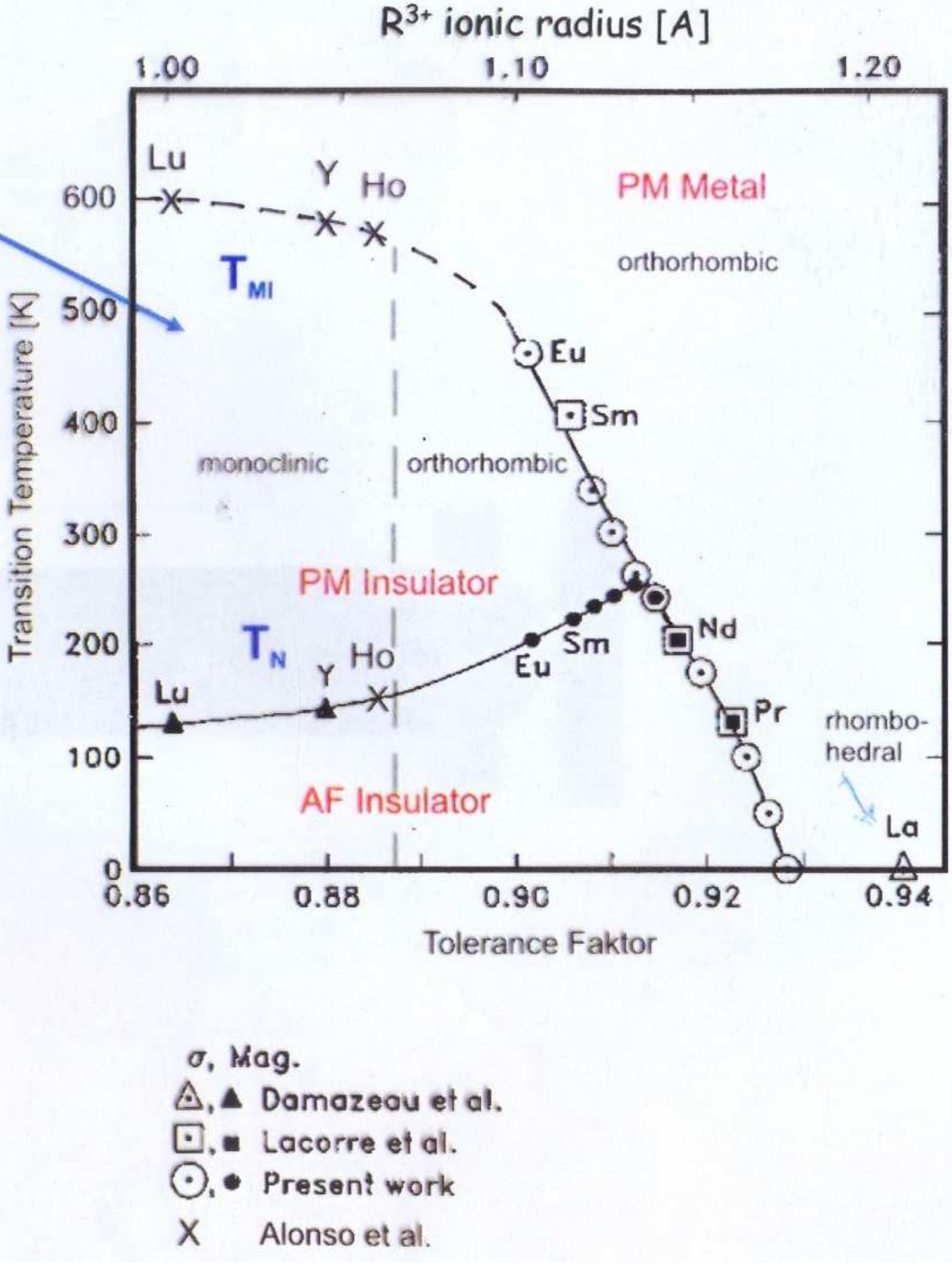
Charge ordering



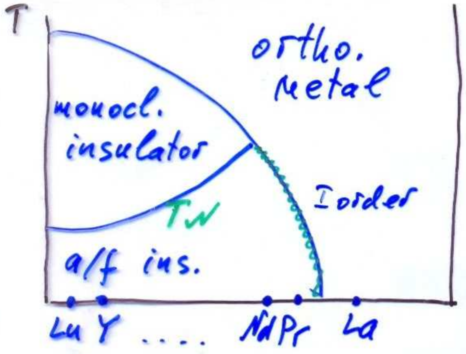
$2Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$ ($\delta \approx 0.35$)

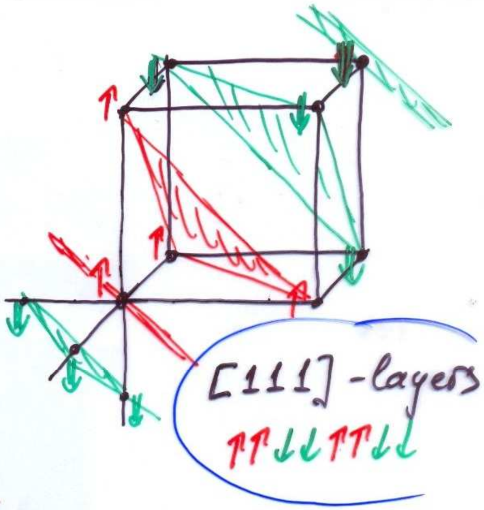
$Ni(1) = 1.4(1)\ \mu_B$
and
$Ni(2) = 0.7(1)\ \mu_B$

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



(Site + bond)-centered CO in $RNiO_3$



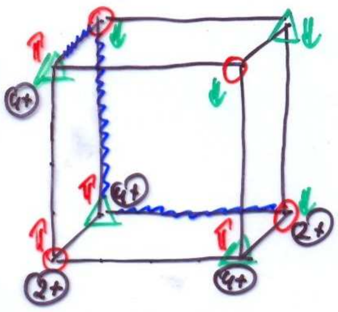


Monoclinic distortion
(at least for small RE = Lu, Y, ...) :
charge disproportionation

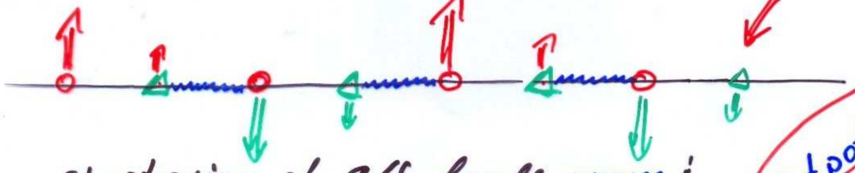
$$2\,Ni^{3+} \Rightarrow Ni^{2+} + Ni^{4+}$$

$(t_{2g}^6 e_g^1)$ $(t_{2g}^6 e_g^2)$ (t_{2g}^6)

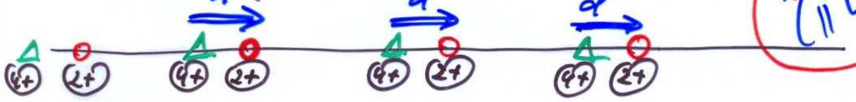
$s = \frac{1}{2}$ $s = 1$ $s = 0$



Similar situation
in RMn_2O_5
(L. Chapon - P. Radaelli)



shortening of a/f bonds 〰 :



Net polarization
(∥[111])!

Ferroelectricity due to magnetic ordering

Coupling of electric polarization to magnetism

Time reversal symmetry $t \to -t$

$$\mathbf{P} \to +\mathbf{P}$$

$$\mathbf{M} \to -\mathbf{M}$$

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

$$\mathbf{P} \to -\mathbf{P}$$

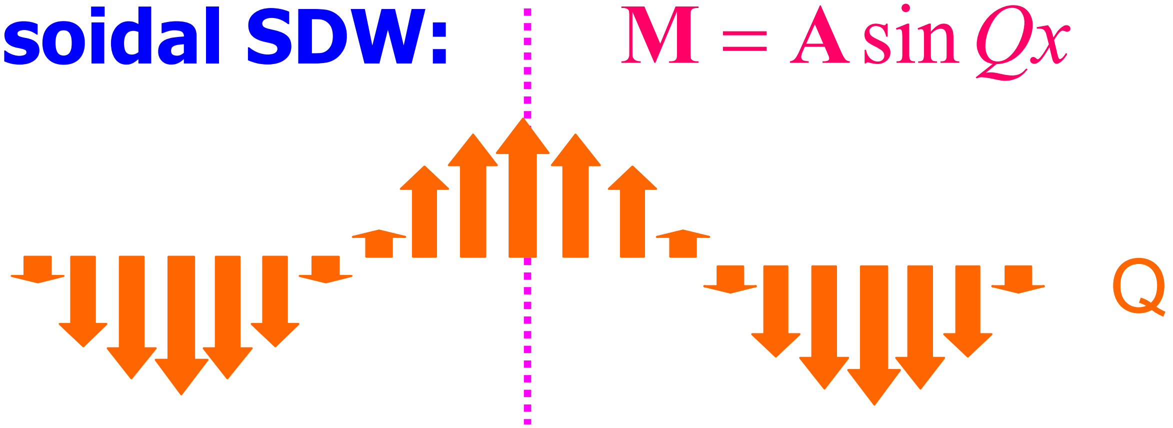
$$\mathbf{M} \to +\mathbf{M}$$

$$\Bigg\} \; E \propto P M \partial M$$

Polarization induced by SDW

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

Sinusoidal SDW: $\mathbf{M} = \mathbf{A} \sin Qx$

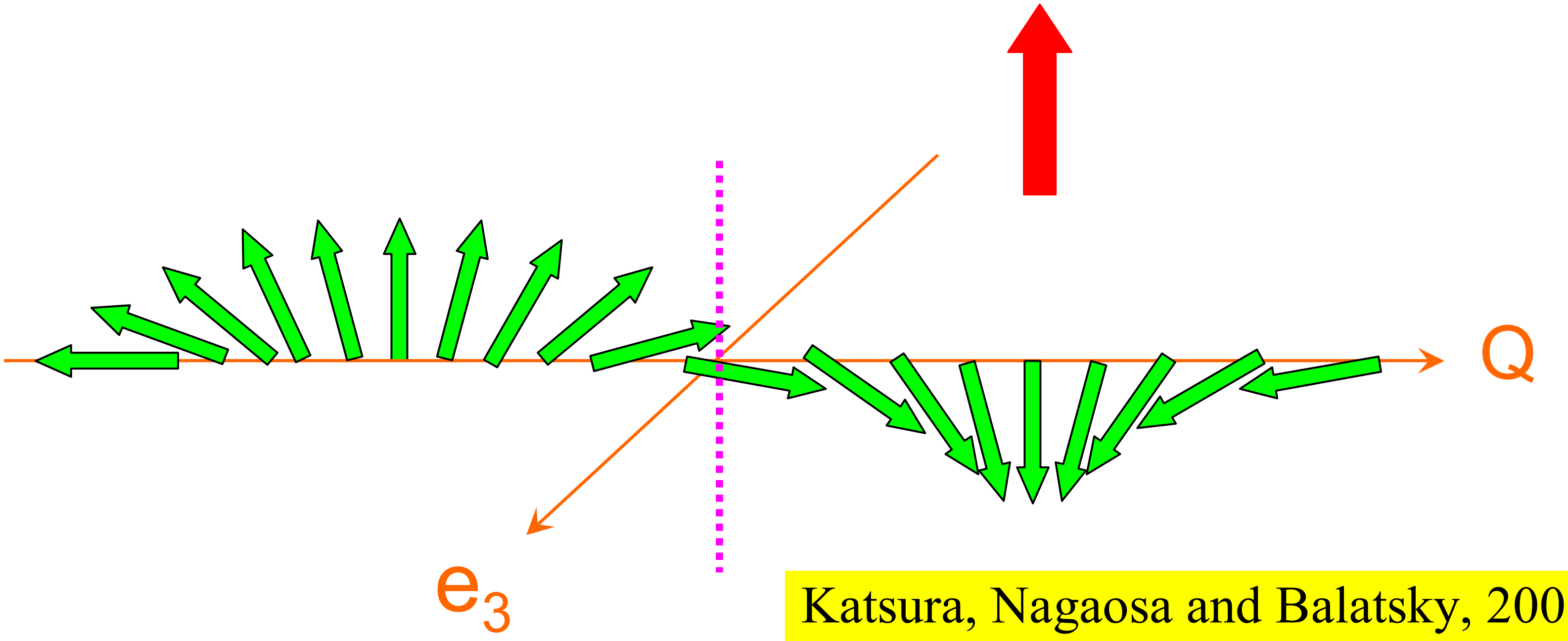


Mirror plane, no FE! $\overline{\mathbf{P}} = 0$

Helicoidal SDW :

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

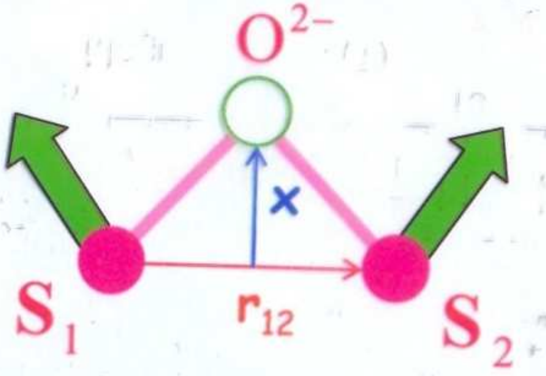
$$\overline{\mathbf{P}} \propto [\mathbf{e}_3 \times \mathbf{Q}]$$



Katsura, Nagaosa and Balatsky, 2005

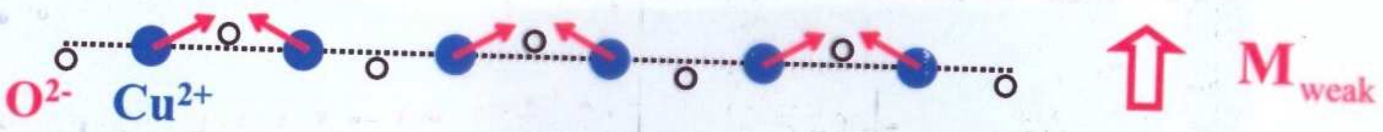
Mostovoy 2006

Effects of Dzyaloshinskii-Moriya interaction



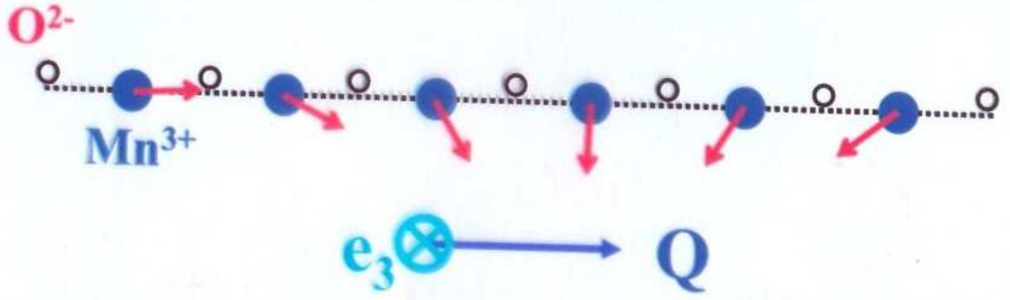
$$E_{DM} = \mathbf{D}_{12} \cdot [\mathbf{S}_1 \times \mathbf{S}_2]$$
$$\mathbf{D}_{12} \propto \lambda\, \mathbf{x} \times \hat{\mathbf{r}}_{12}$$

Weak ferromagnetism



$\Uparrow$ $\mathbf{M}_{\text{weak}}$

Weak ferroelectricity

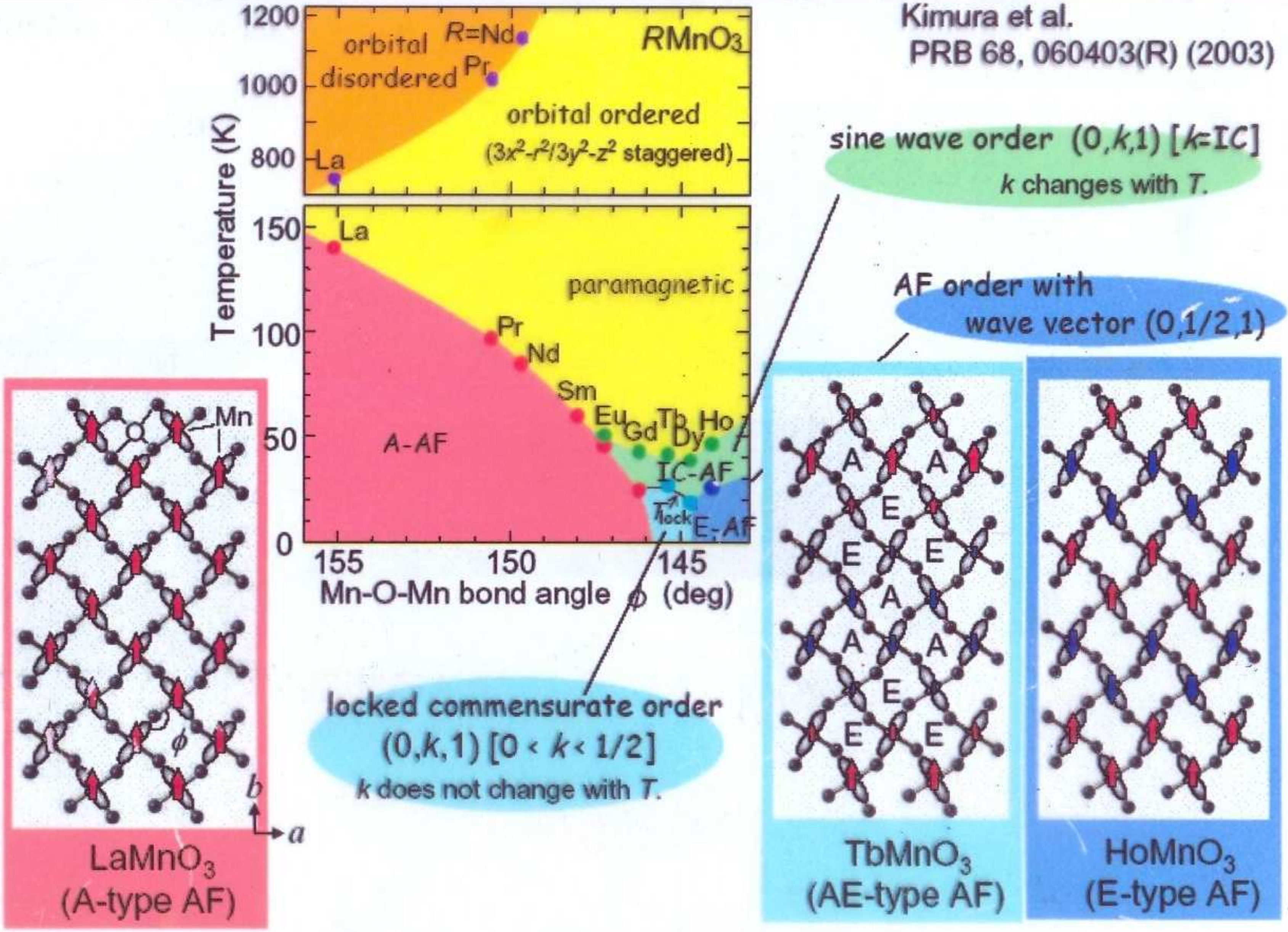


$\Downarrow$ $\mathbf{P} \propto \mathbf{e}_3 \times \mathbf{Q}$

H. Katsura et al PRL (2005), Sergienko&Dagotto PRB (2006)

orthorhombic RMnO3

Evolution of spin structure against Mn-O-Mn bond angle in RMnO$_3$



Kimura et al.
PRB 68, 060403(R) (2003)

sine wave order $(0,k,1)$ [k=IC]
k changes with T.

AF order with
wave vector (0,1/2,1)

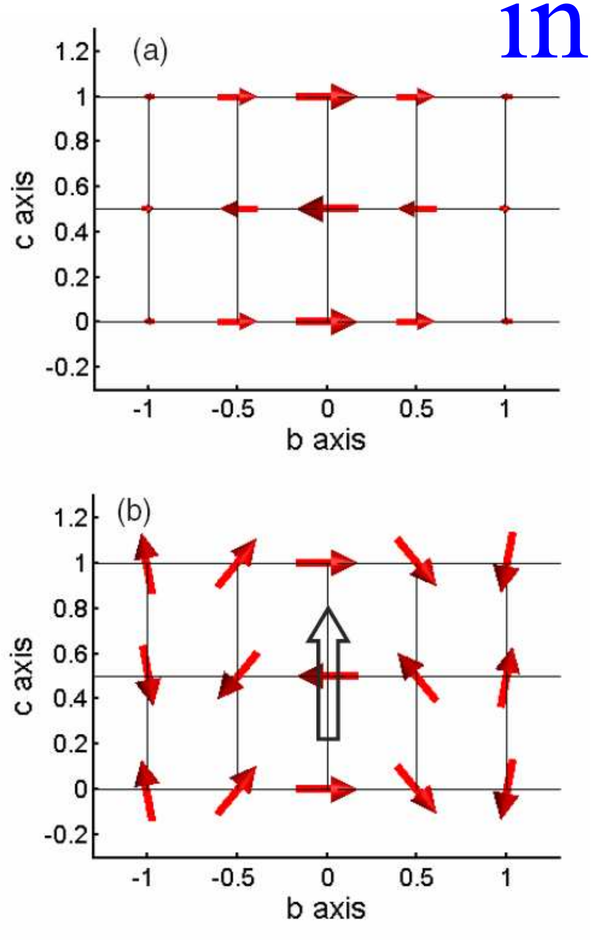
locked commensurate order
$(0,k,1)$ [$0 < k < 1/2$]
k does not change with T.

LaMnO$_3$
(A-type AF)

TbMnO$_3$
(AE-type AF)

HoMnO$_3$
(E-type AF)

Magnetic ordering in $TbMnO_3$



28K < T < 41K

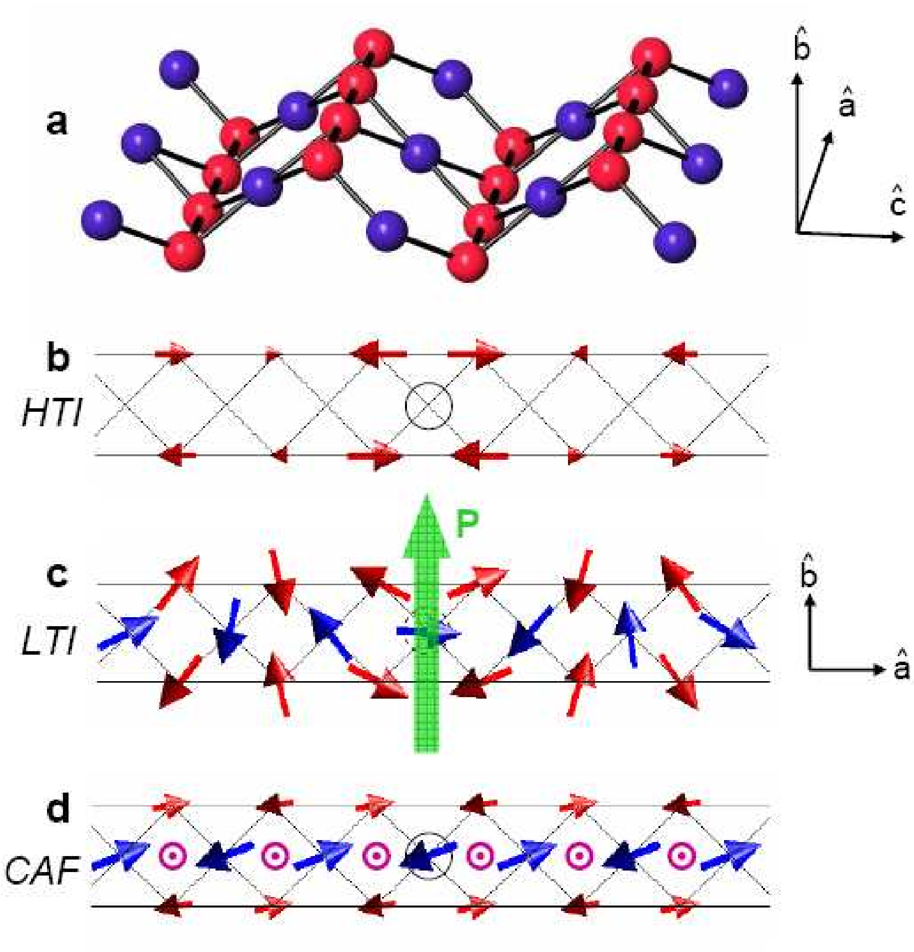
Sinusoidal SDW spins along b axis

T < 28K

Helicoidal SDW spins rotating in bc plane

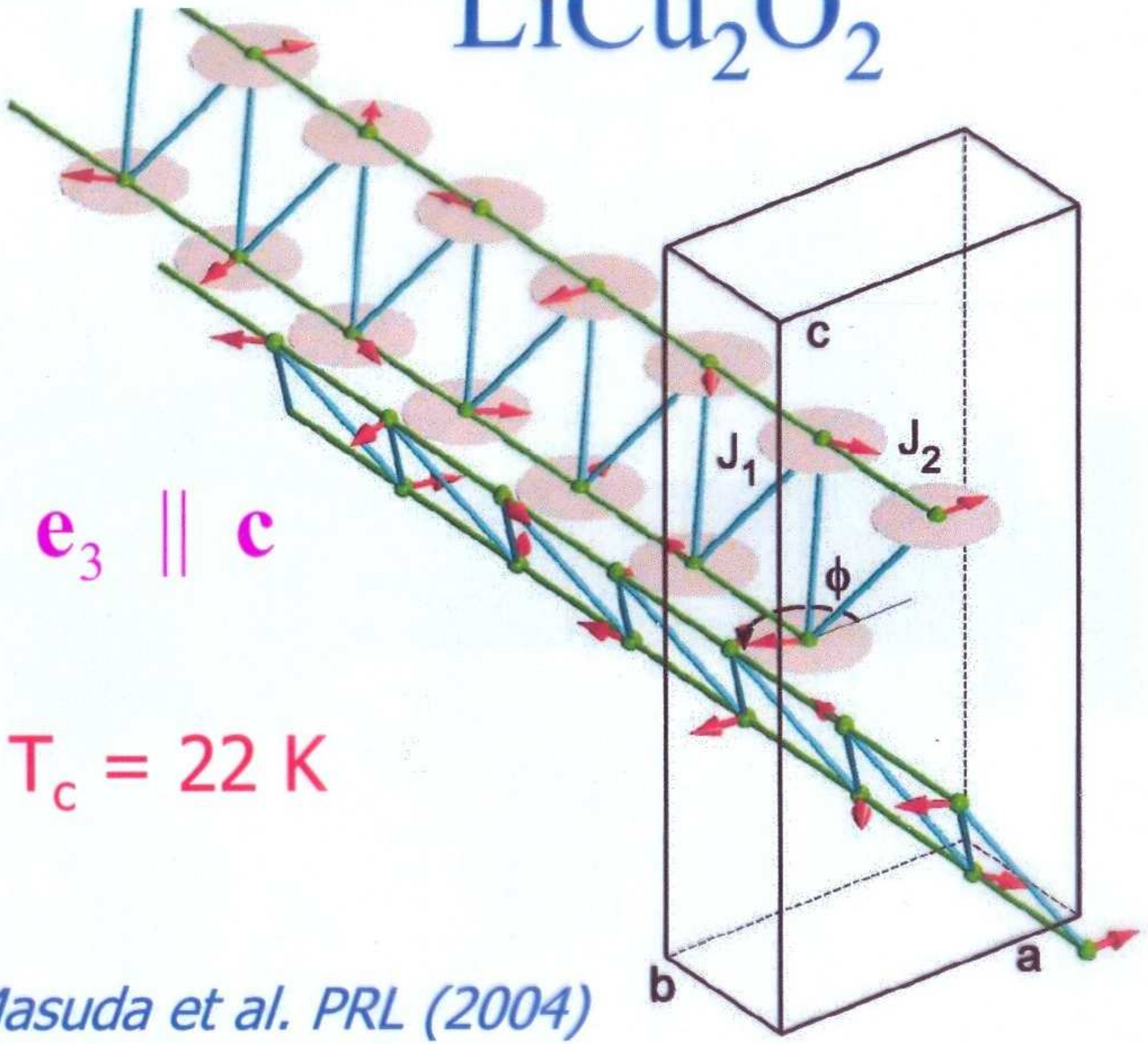
M. Kenzelmann et al (2005)

Kagome staircase material $Ni_3V_2O_8$



G. Lawes et al (2005)

$LiCu_2O_2$



$e_3 \parallel c$

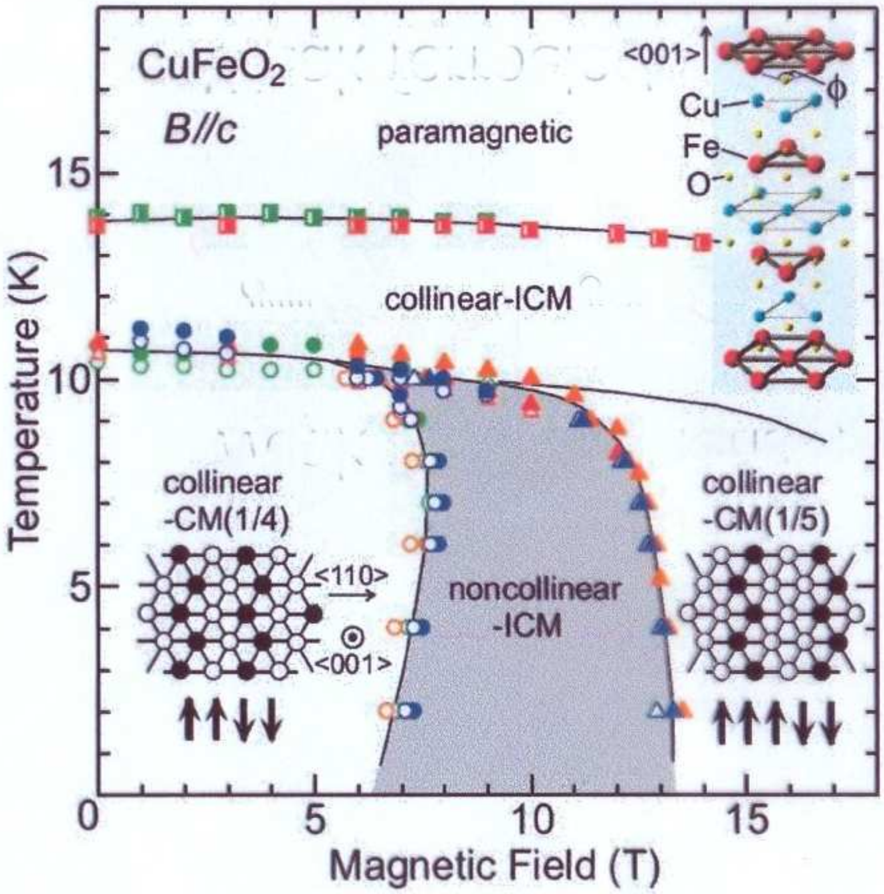
$T_c = 22$ K

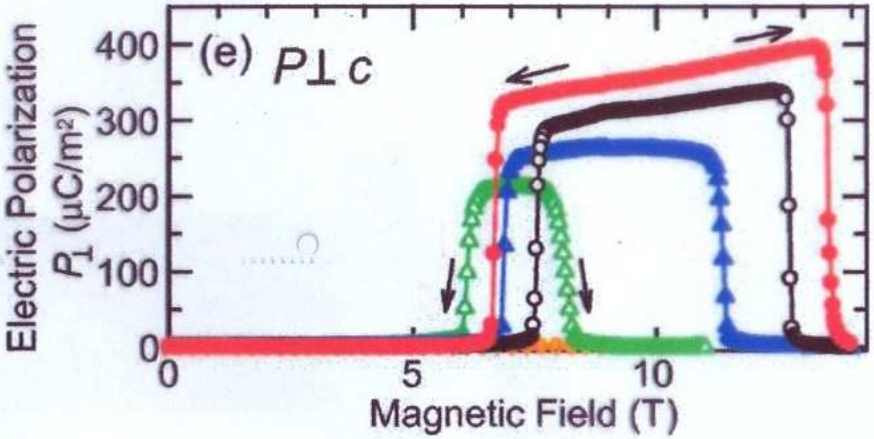
$P \parallel a$

$Q \parallel b$

T. Masuda et al. PRL (2004)

Field-induced ferroelectricity in $CuFeO_2$





T.Kimura et al
PRB (2006)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter 18 (2006) L471–L475 doi:10.1088/0953-8984/18/39/L01

LETTER TO THE EDITOR

A new multiferroic material: $MnWO_4$

O Heyer[1], N Hollmann[1], I Klassen[1], S Jodlauk[2], L Bohatý[2], P Becker[2], J A Mydosh[1], T Lorenz[1] and D Khomskii[1,3]

[1] II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, 50937 Köln, Germany
[2] Institut für Kristallographie, Universität zu Köln, Zülpicher Strasse 49b, 50674 Köln, Germany

E-mail: khomskii@ph2.uni-koeln.de

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Abstract
We report the multiferroic behaviour of $MnWO_4$, a magnetic oxide with monoclinic crystal structure and spiral long-range magnetic order. Based upon recent theoretical predictions, $MnWO_4$ 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: $TbMnO_3$ [5], $TbMn_2O_5$ [6], $DyMnO_3$ [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, $MnWO_4$, belongs to the same class of materials and develops spontaneous electric polarization in a spiral magnetically ordered state[4].

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 $TbMnO_3$ and $TbMn_2O_5$. 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:

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

---

[3] Author to whom any correspondence should be addressed.
[4] As we learned recently, the multiferroic nature of $MnWO_4$ has also been observed independently [8, 9].

0953-8984/06/390471+05$30.00

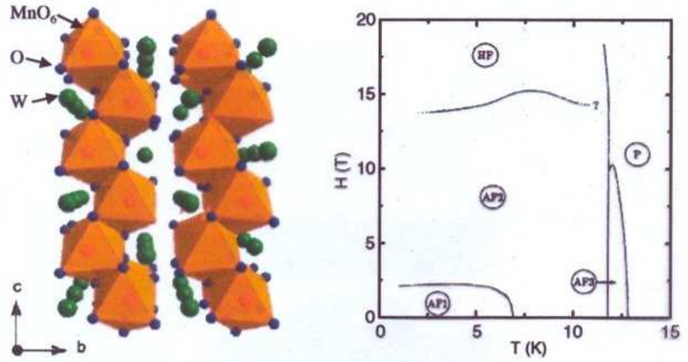

Figure 1. Crystal structure of MnWO$_4$ and schematic H–T phase diagram for a magnetic field applied along the easy axis according to references [14] and [15], respectively.

This is not the only source for a magnetically driven ferroelectricity [12, 13], but perhaps the most common one. Accordingly, one strategy to search for new multiferroic materials is to look for magnetic systems with proper magnetic structures. MnWO$_4$ (also known as the mineral hübnerite) appears to be just such a system. Detailed studies of the magnetic ordering in this material have shown [14, 15] that below 12.3 K a spiral magnetic ordering develops which seems to satisfy the criterion of equation (1). In order to test this we carried out measurements of the dielectric response and of spontaneous polarization of MnWO$_4$ using single-crystalline samples.

The crystals of MnWO$_4$ were grown from melt solution. On the basis of earlier work [16] we applied a modified flux technique, using a melt solvent from the system Na$_2$WO$_4$–WO$_3$. The resulting crystals are of dimensions up to $15 \times 5 \times 3$ mm^3 and of dark brown colour. The crystal structure of MnWO$_4$ is monoclinic (the space group of the paramagnetic phase is $P2/c$) and consists of edge-sharing [MnO$_6$] and [WO$_6$] octahedra that form zigzag chains along the c-axis; see figure 1. Tungsten atoms and manganese atoms are arranged in alternating sheets parallel to (100) [17].

There is apparently also a finite interchain coupling causing the observed magnetic ordering below $\simeq$13 K (see figure 1) [14, 15]. According to the previous results there are two separate transitions at 13.5 and 12.3 K. The upper one is from the paramagnetic state to an incommensurate spin-density wave state, with wavevector $\vec{Q} = (-0.214, 1/2, 0.457)$. The spins are collinear in the ac plane with an angle of about 35° with respect to the a axis. For later use, this direction is termed the easy axis. In the so-called AF2 phase below 12.3 K the wavevector hardly changes, but a finite spin component along the b axis develops and, as a consequence, an elliptical spiral structure evolves. Finally, a transition to a commensurate magnetic structure with $Q = (\pm 1/4, 1/2, 1/2)$ is found around 8 K, in which the spins are again collinear. Our magnetic measurements, see below, confirm the presence of at least two magnetic transitions, one around 13 K and a second one around 6 K, but we were unable to resolve two separate transitions at 12.3 and 13.5 K. According to references [14, 15] the separate transitions around 13 K can probably be much better resolved by for example specific heat measurements than in magnetic data. Moreover, it is reported that the transition to the AF1 phase is of first order and is found between 6.8 and 8 K for different samples and measurement techniques.

IOP FTC

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter 19 (2007) 432201 (9pp) doi:10.1088/0953-8984/19/43/432201

FAST TRACK COMMUNICATION

Pyroxenes: a new class of multiferroics

S Jodlauk[1], P Becker[1], J A Mydosh[2], D I Khomskii[2], T Lorenz[2], S V Streltsov[2,4], D C Hezel[3] and L Bohatý[1,5]

[1] Institut für Kristallographie, Universität zu Köln, Zülpicher Straße 49 b, 50674 Köln, Germany
[2] II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany
[3] Institut für Geologie und Mineralogie, Universität zu Köln, Zülpicher Straße 49 b, 50674 Köln, Germany

E-mail: ladislav.bohaty@uni-koeln.de

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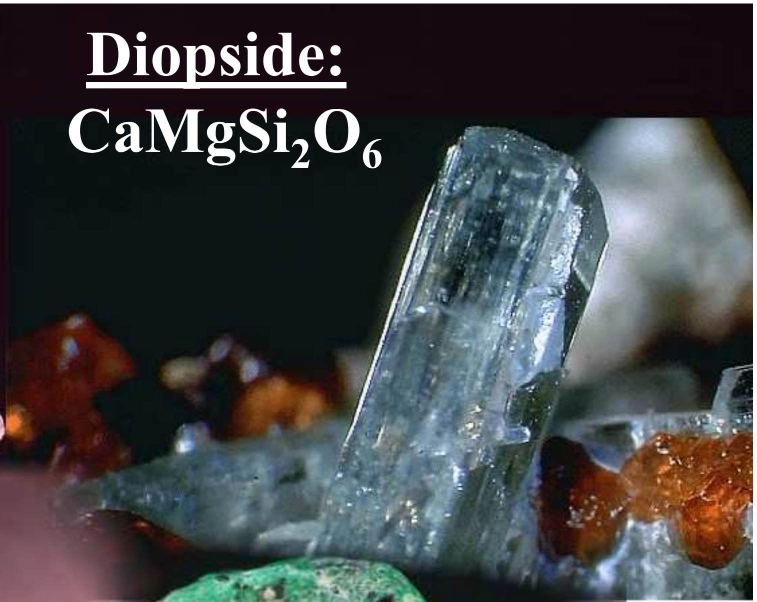
Published 26 September 2007

PYROXENES

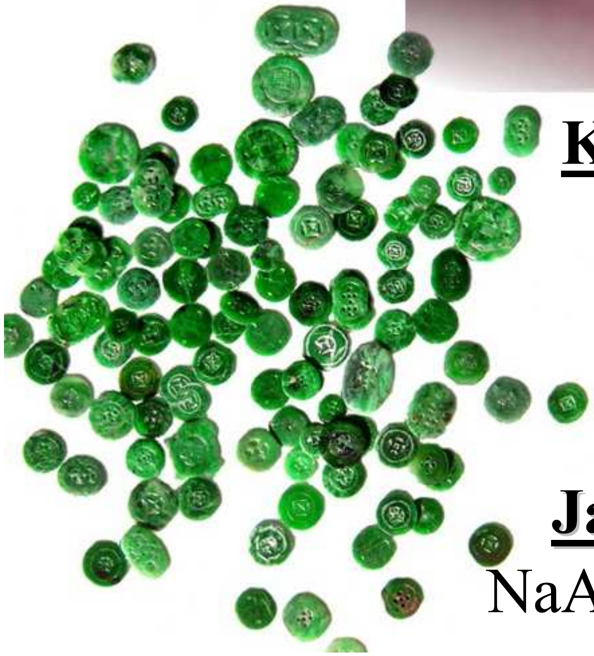
Spodumene:
$LiAlSi_2O_6$



Diopside:
$CaMgSi_2O_6$

Aegirine:
$NaFeSi_2O_6$

Kosmochlore:
$NaCrSi_2O_6$



Jade:
$NaAlSi_2O_6$

Minerals

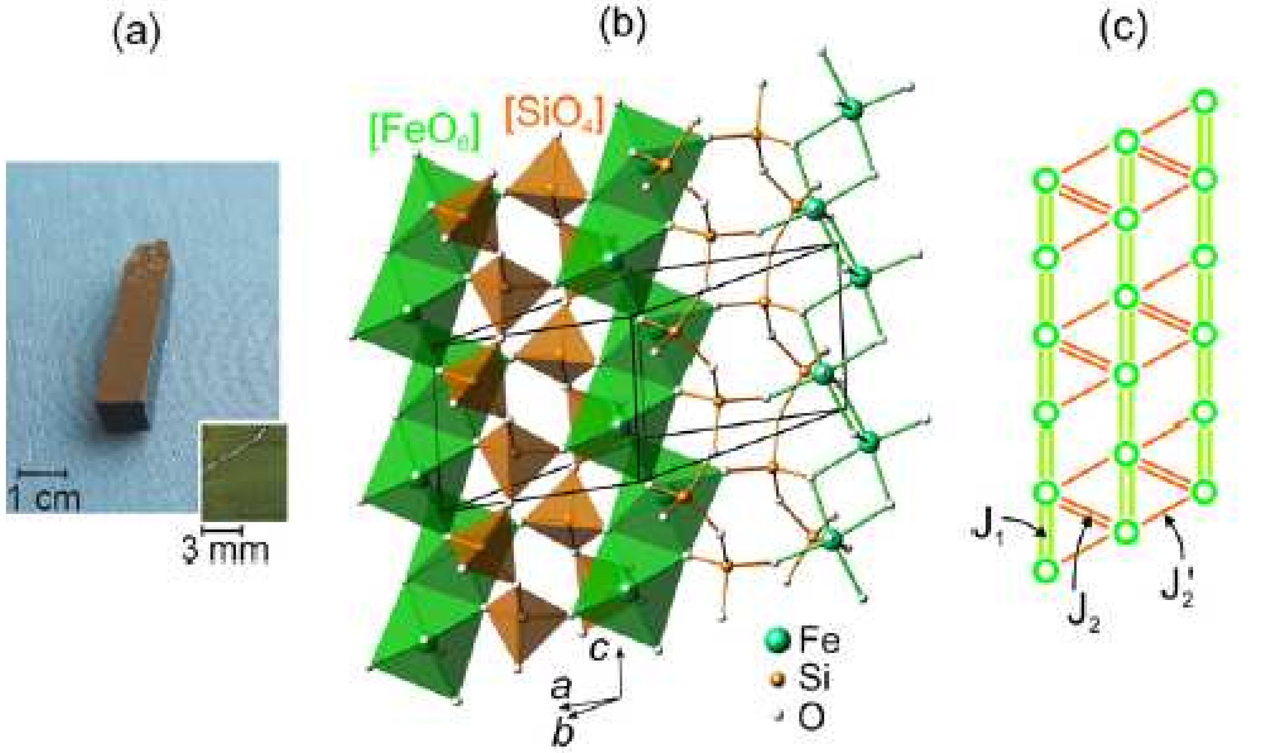
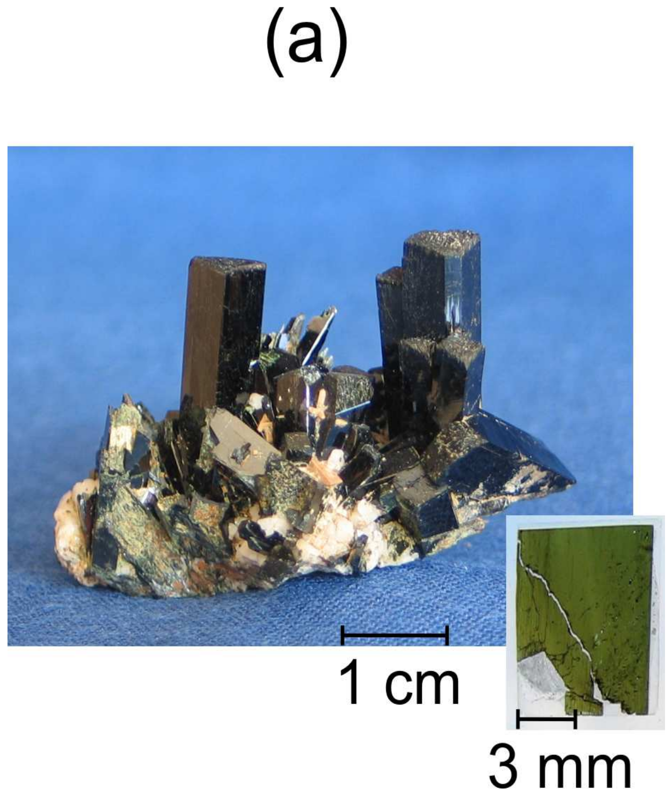


Figure 1. (a) Natural aegirine ($NaFeSi_2O_6$) crystal from a pegmatite of alkaline rocks of Mount Malosa, Malawi. In thin sections (see inset) the aegirine crystal is green and transparent. (b) The main features of the crystal structure are chains of edge-sharing [FeO_6] octahedra (green) and chains of corner-sharing [SiO_4] tetrahedra (orange) running along the *c*-direction (structure data from [22]).


(a)
1 cm
3 mm

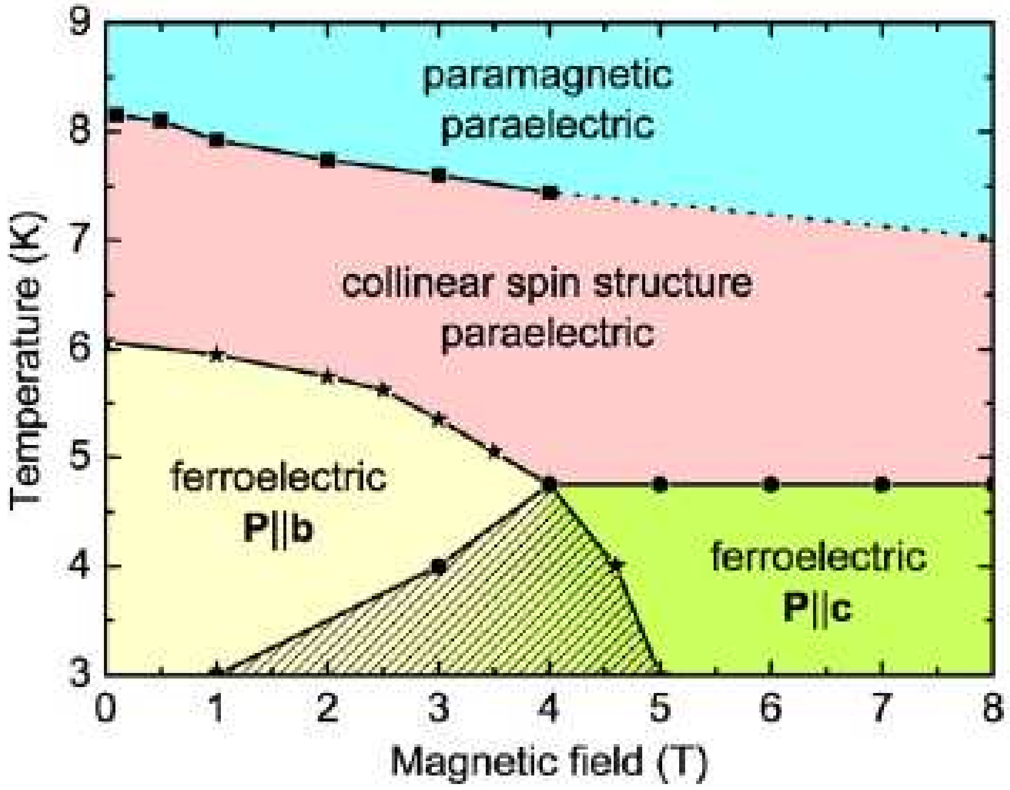
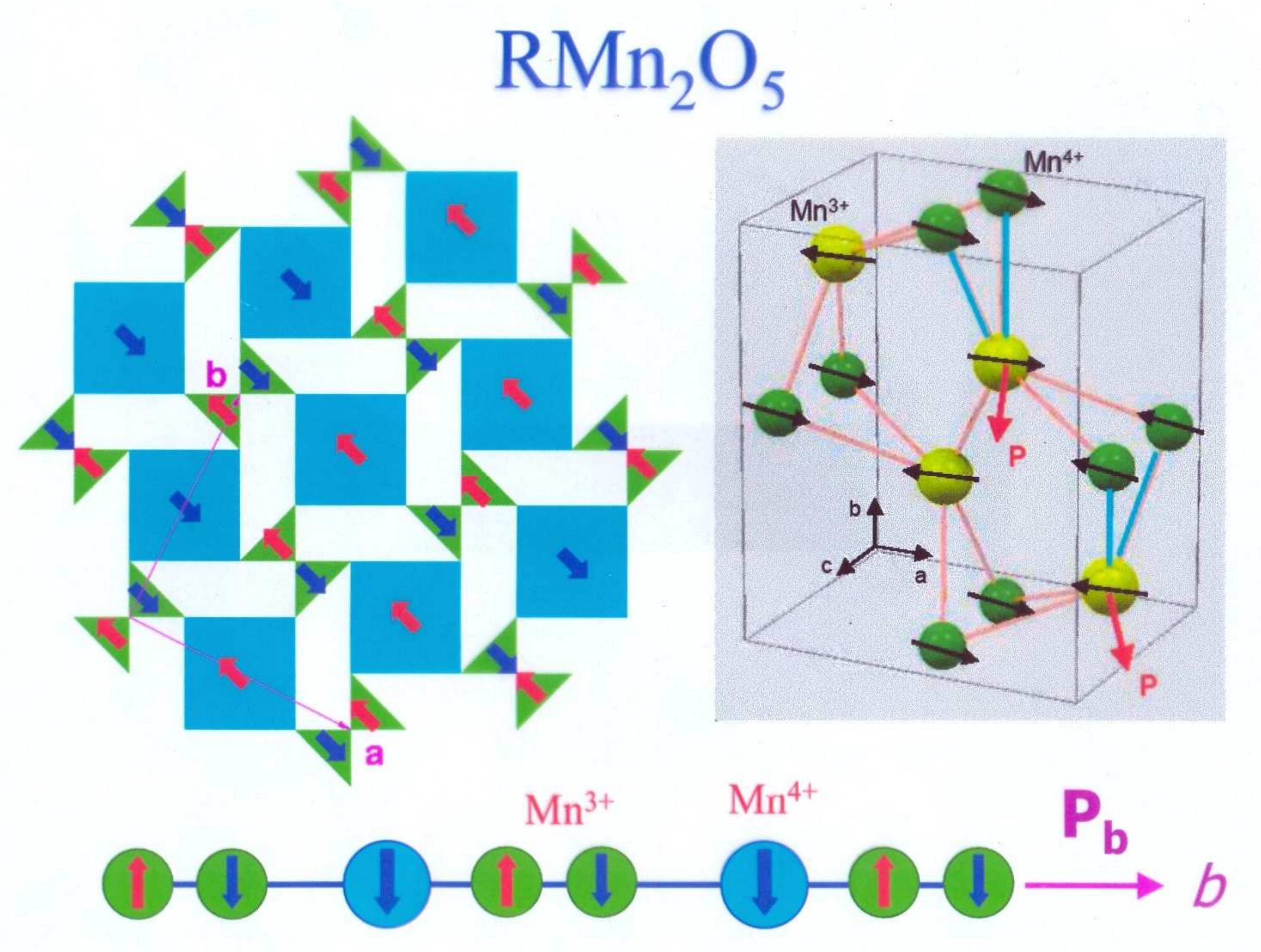
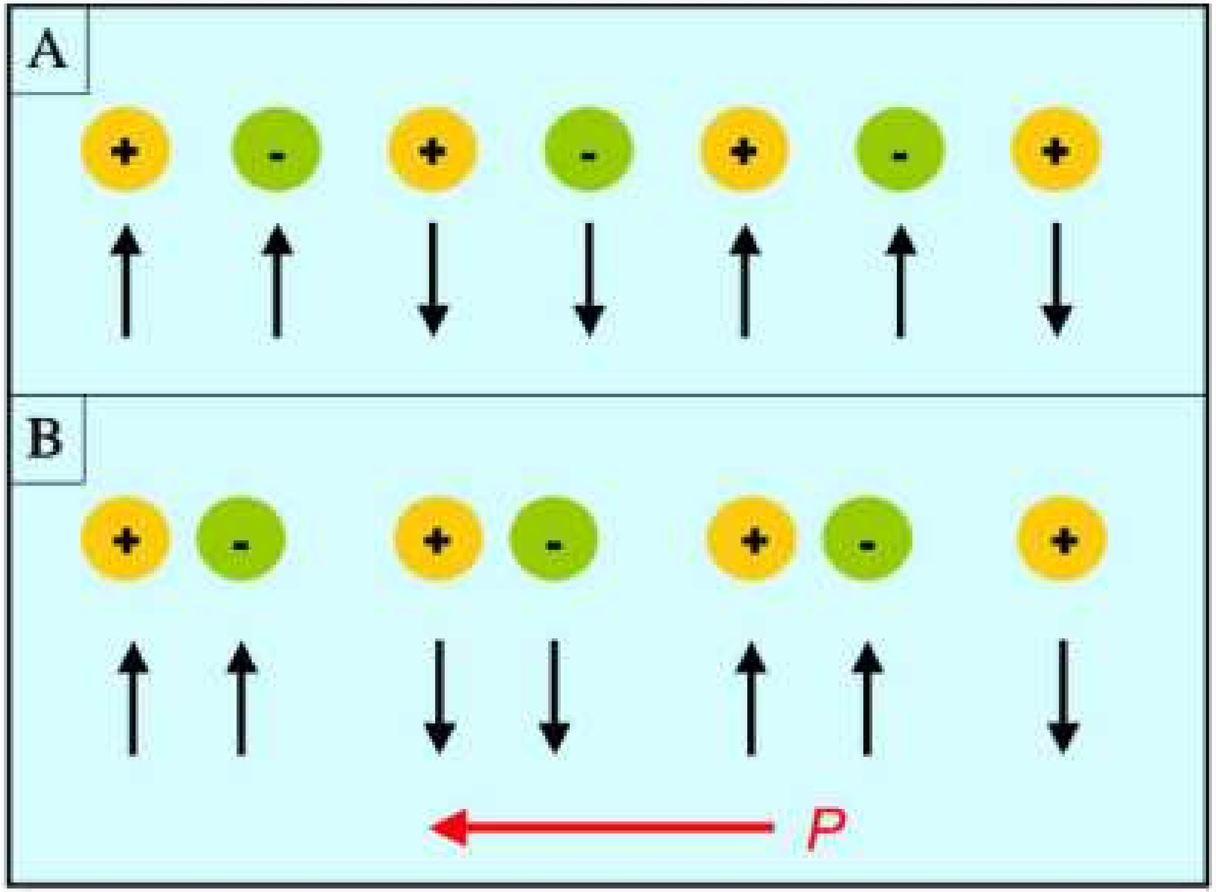


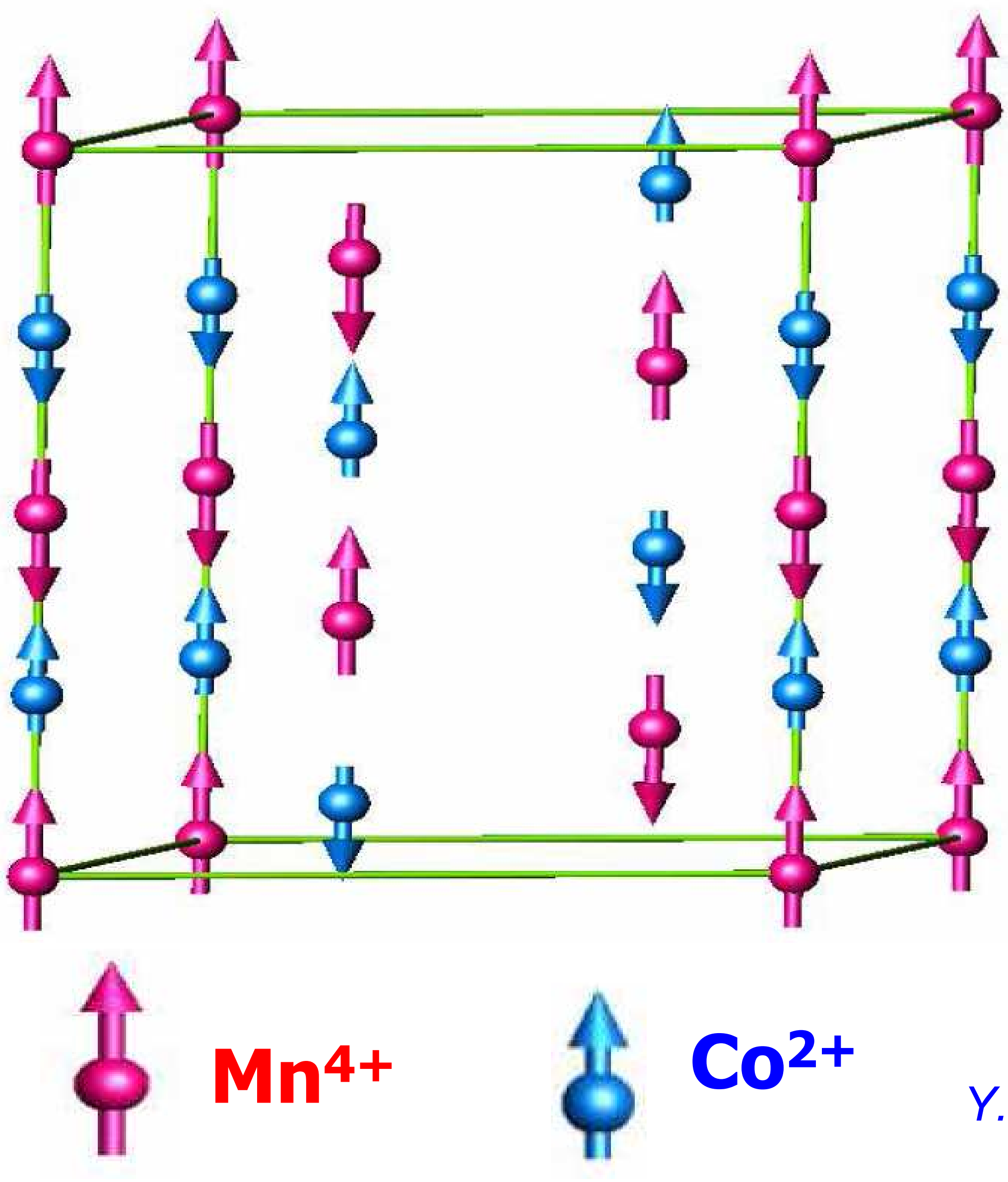
Figure 3. Temperature versus magnetic field (applied in the *ac*-plane) phase diagram for $NaFeSi_2O_6$ illustrating the multiferroic behaviour.

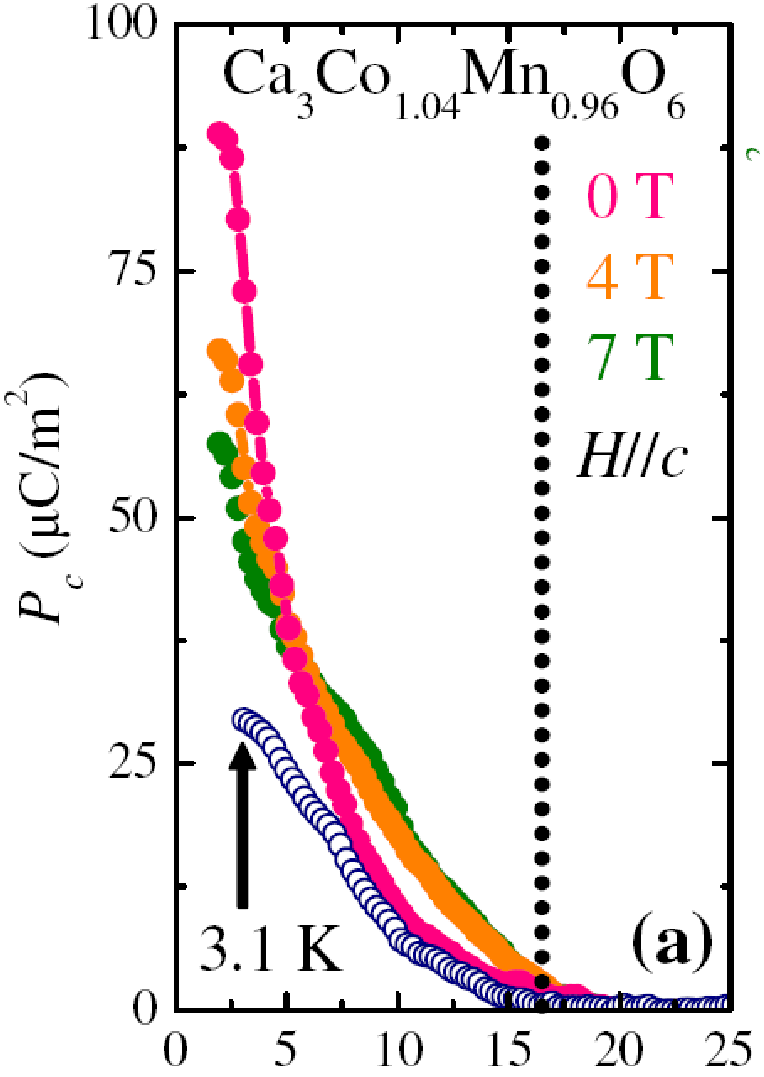
Magnetostriction mechanism




A
+
-
B
P

$Ca_3Co_{2-x}Mn_xO_6$



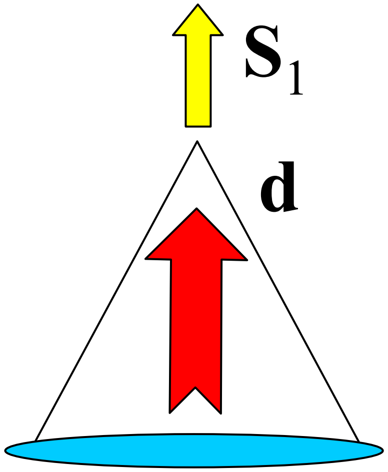


*Y.J. Choi et al PRL **100** 047601 (2008)*

Electronic mechanism of ferroelectricity in magnetic systems

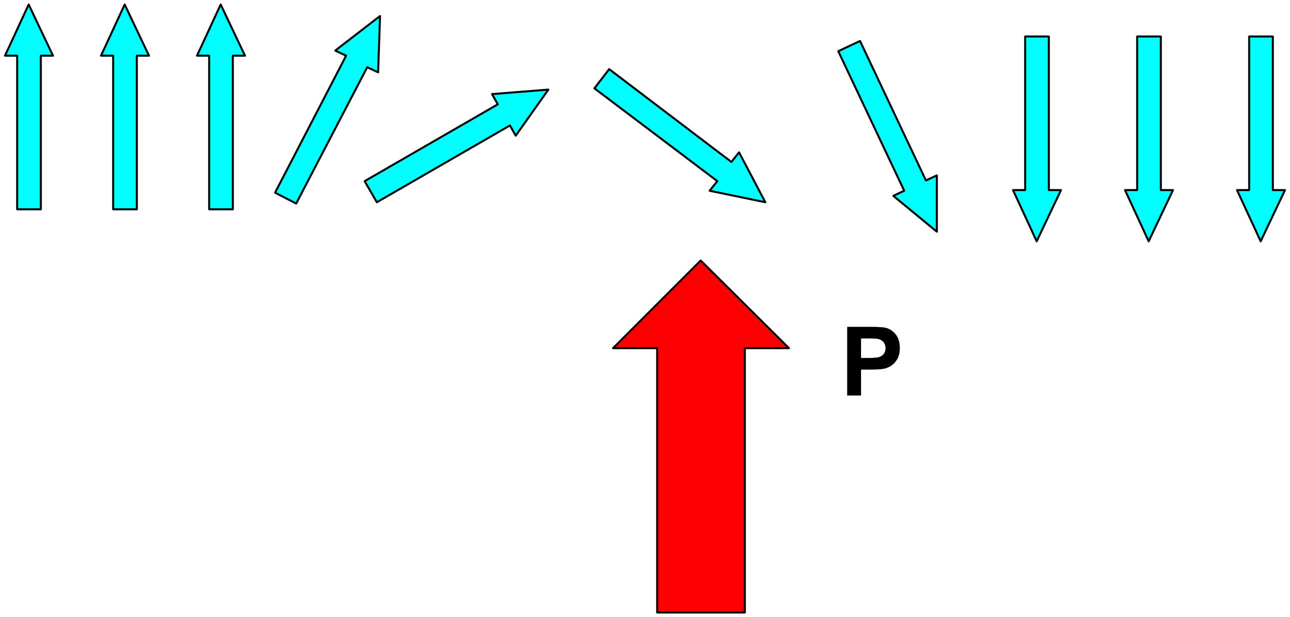
L.Bulaevskii, Ch.Batista, M.Mostovoy and D.Khomskii,

Phys.Rev.B 78, 024402 (2008)



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

Neel domain walls:



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Magnetoelectricity in ferromagnets

I. Dzyaloshinskii(a)

Institut Laue-Langevin - 6 r. Jules Horowitz, 38042 Grenoble, France, EU and
Department of Physics and Astronomy, University of California Irvine - Irvine, CA 92697, USA

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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

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.

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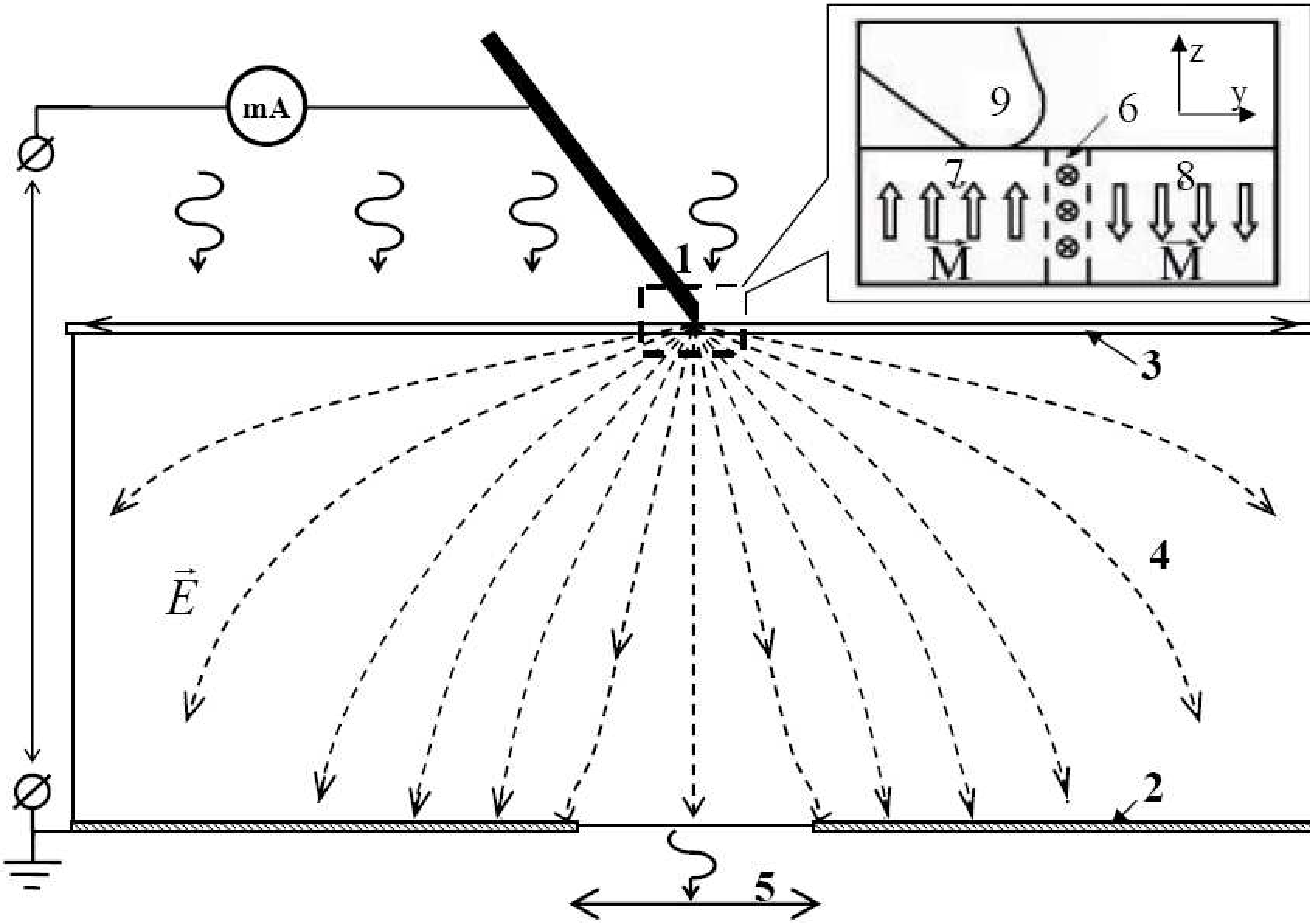
mA
9
6
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$\vec{M}$
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2
5

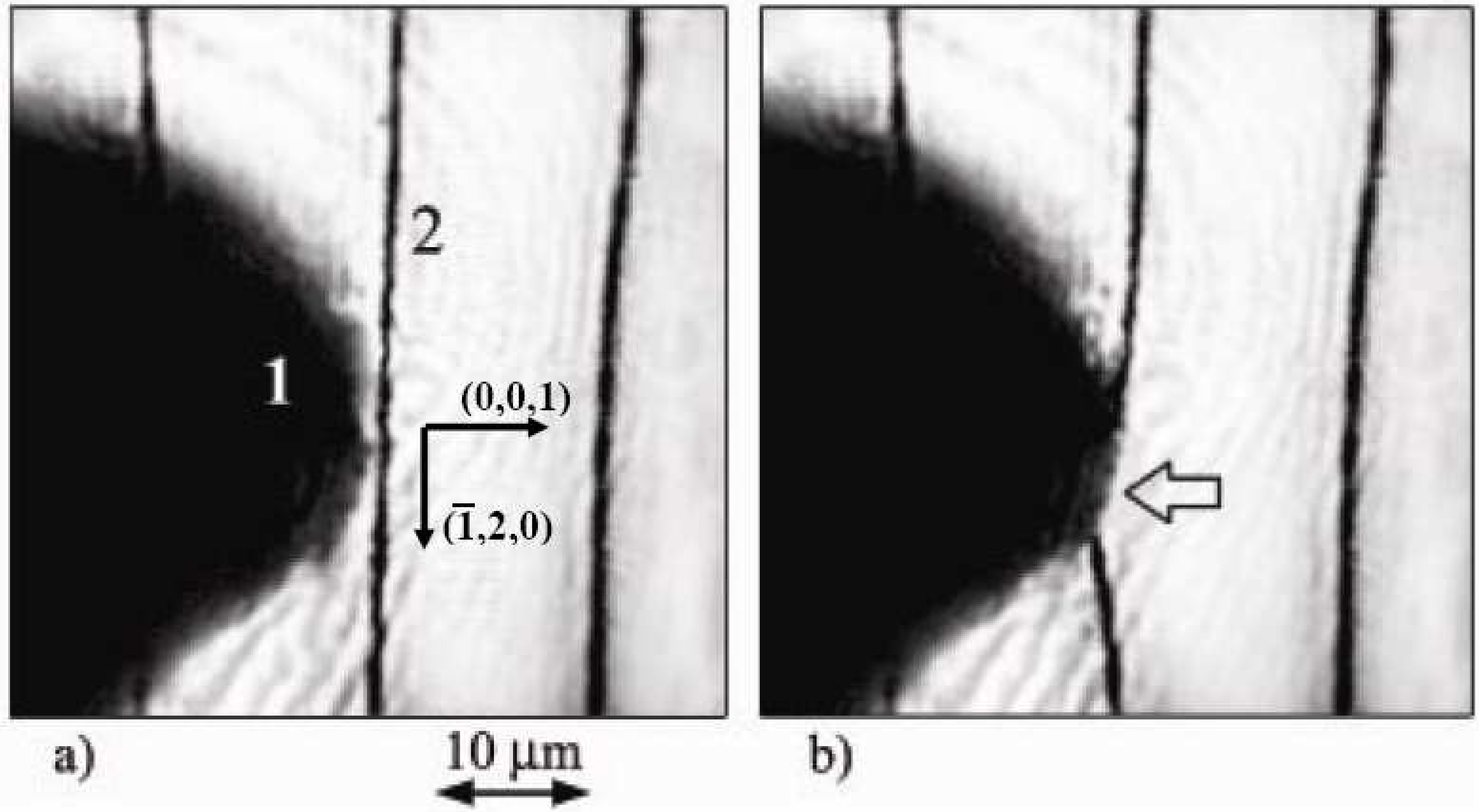
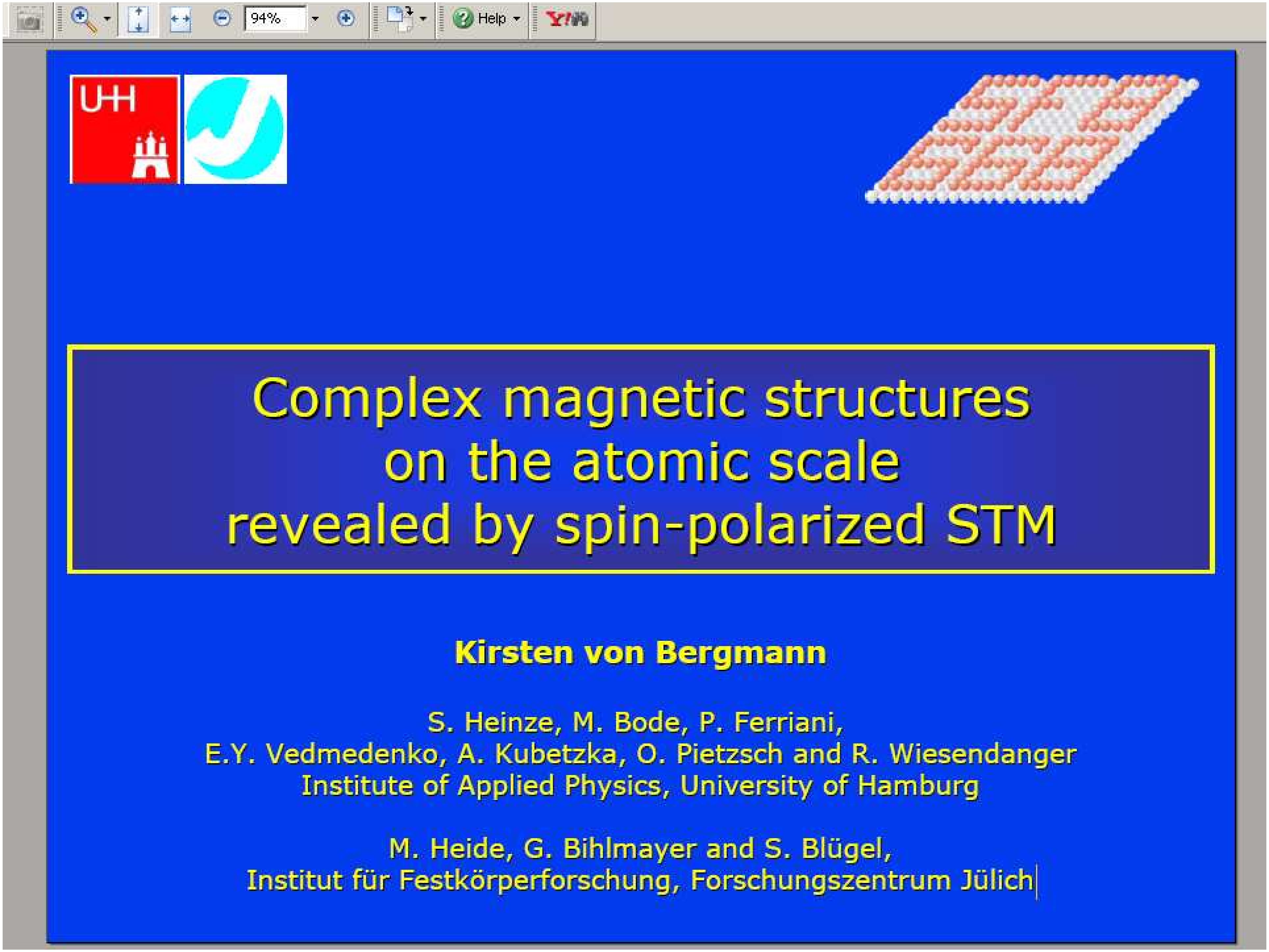


Fig. 2 The effect of electric field in the vicinity of electrode (1) on magnetic domain wall (2) in the films of ferrite garnets: a) initial state b) at the voltage of +1500 V applied

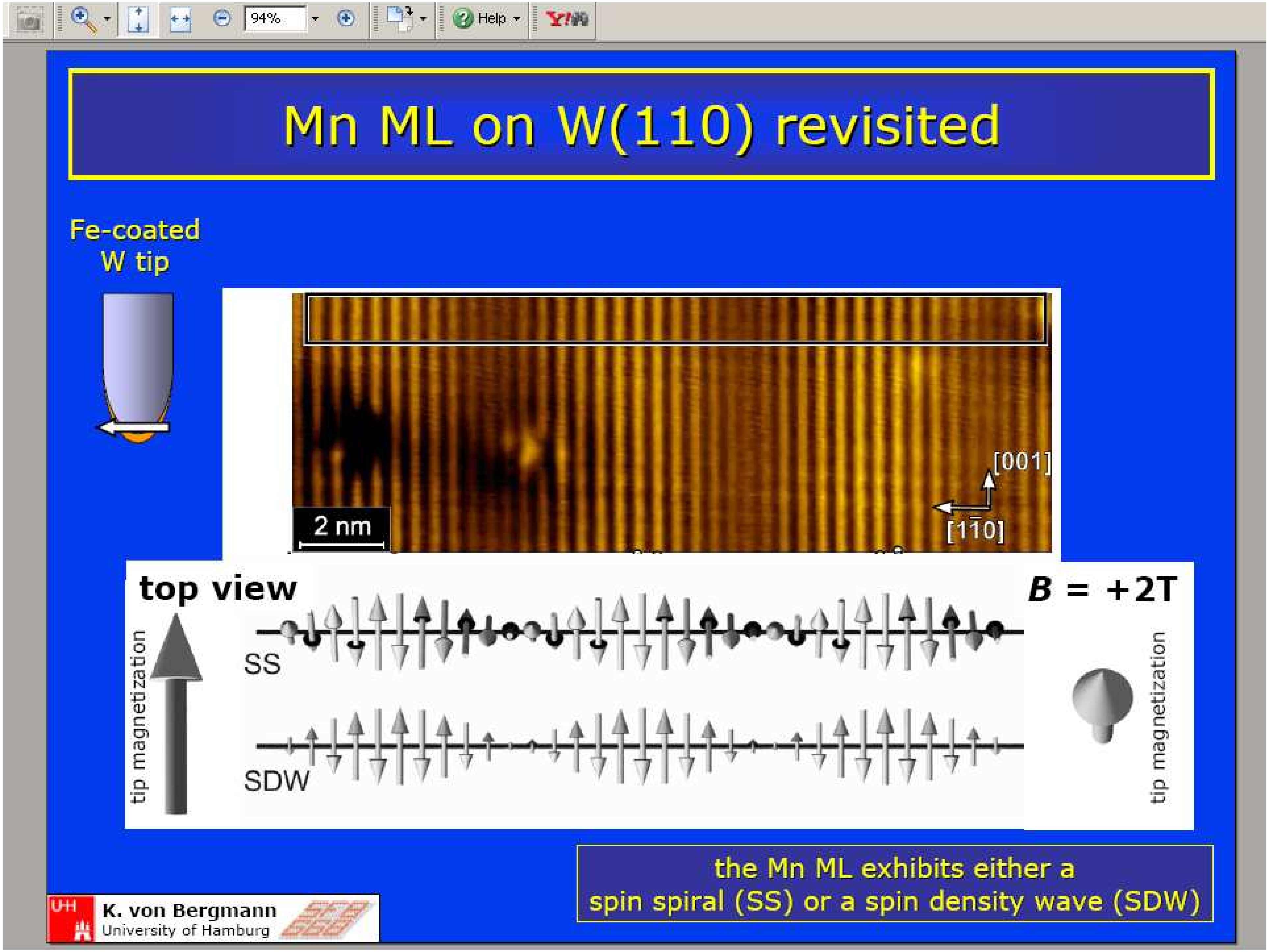


Complex magnetic structures on the atomic scale revealed by spin-polarized STM

Kirsten von Bergmann

S. Heinze, M. Bode, P. Ferriani,
E.Y. Vedmedenko, A. Kubetzka, O. Pietzsch and R. Wiesendanger
Institute of Applied Physics, University of Hamburg

M. Heide, G. Bihlmayer and S. Blügel,
Institut für Festkörperforschung, Forschungszentrum Jülich

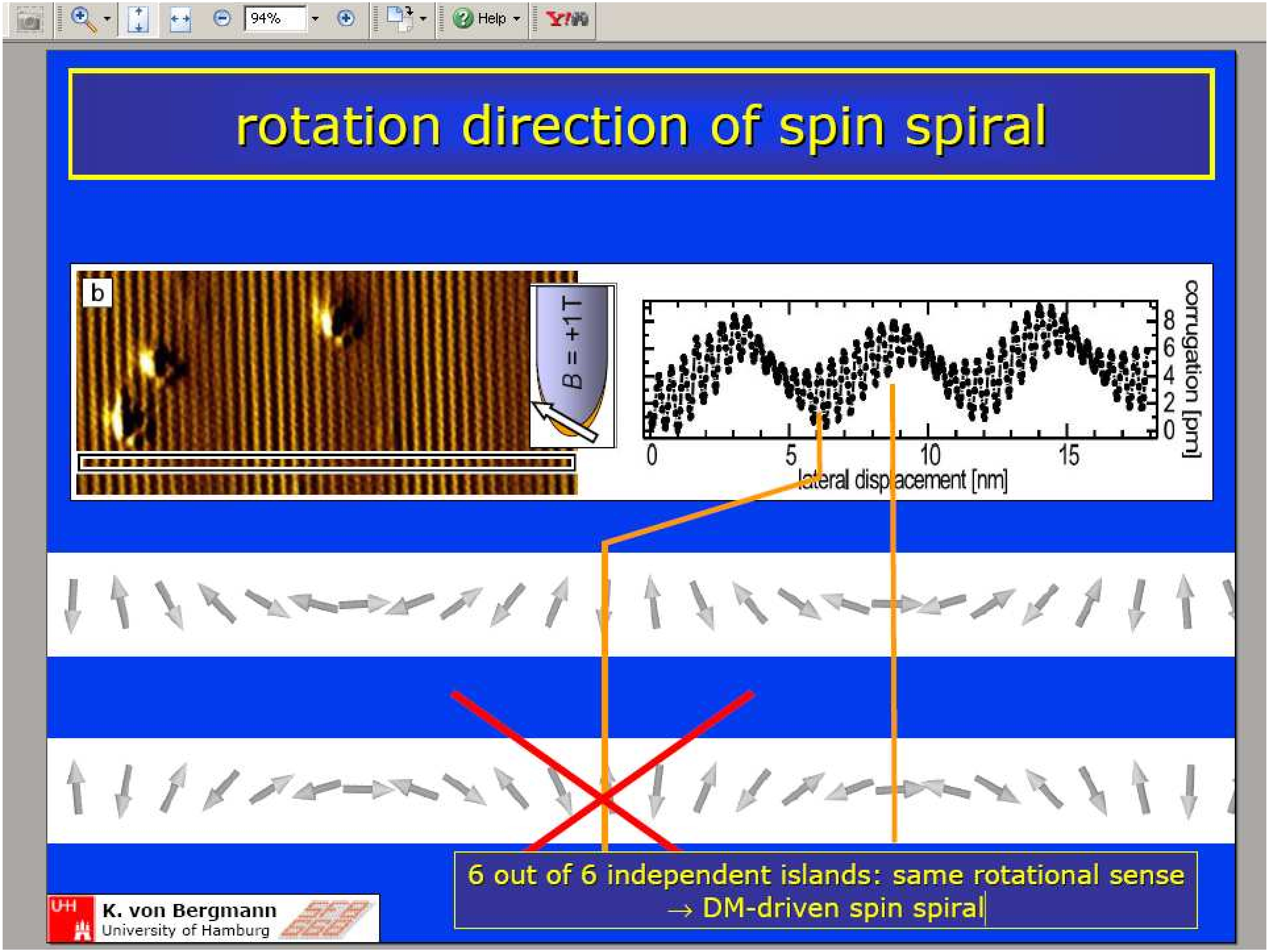


Mn ML on W(110) revisited

Fe-coated
W tip

the Mn ML exhibits either a
spin spiral (SS) or a spin density wave (SDW)

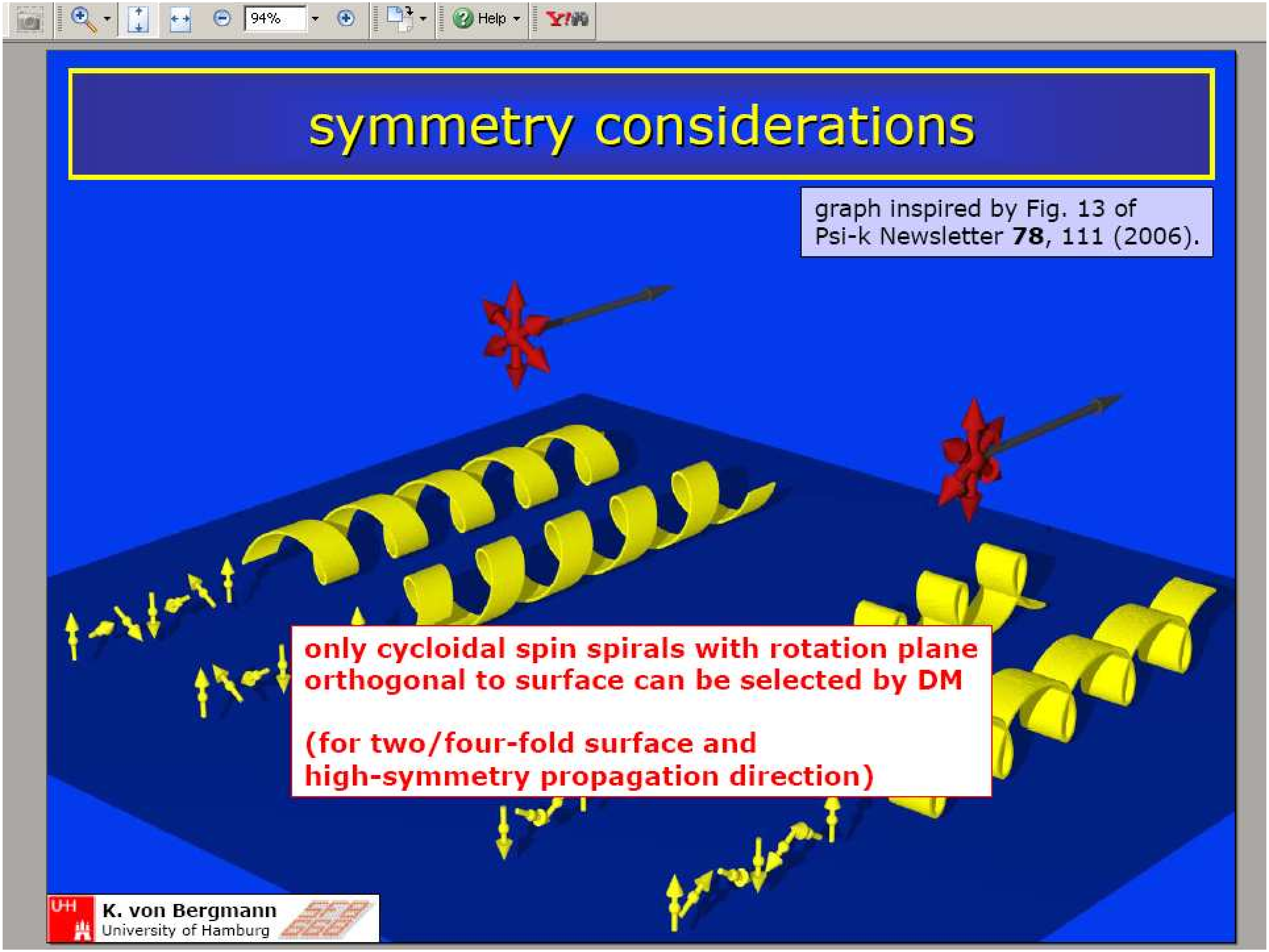
K. von Bergmann
University of Hamburg



rotation direction of spin spiral

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

K. von Bergmann
University of Hamburg



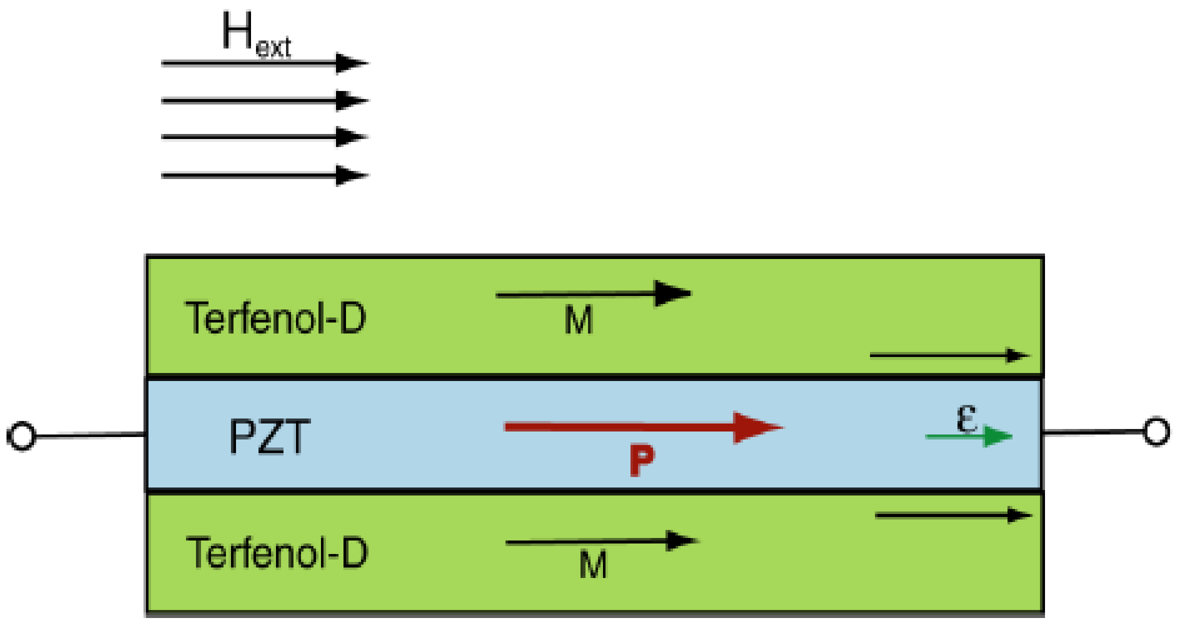
symmetry considerations

graph inspired by Fig. 13 of
Psi-k Newsletter **78**, 111 (2006).

only cycloidal spin spirals with rotation plane orthogonal to surface can be selected by DM

(for two/four-fold surface and high-symmetry propagation direction)

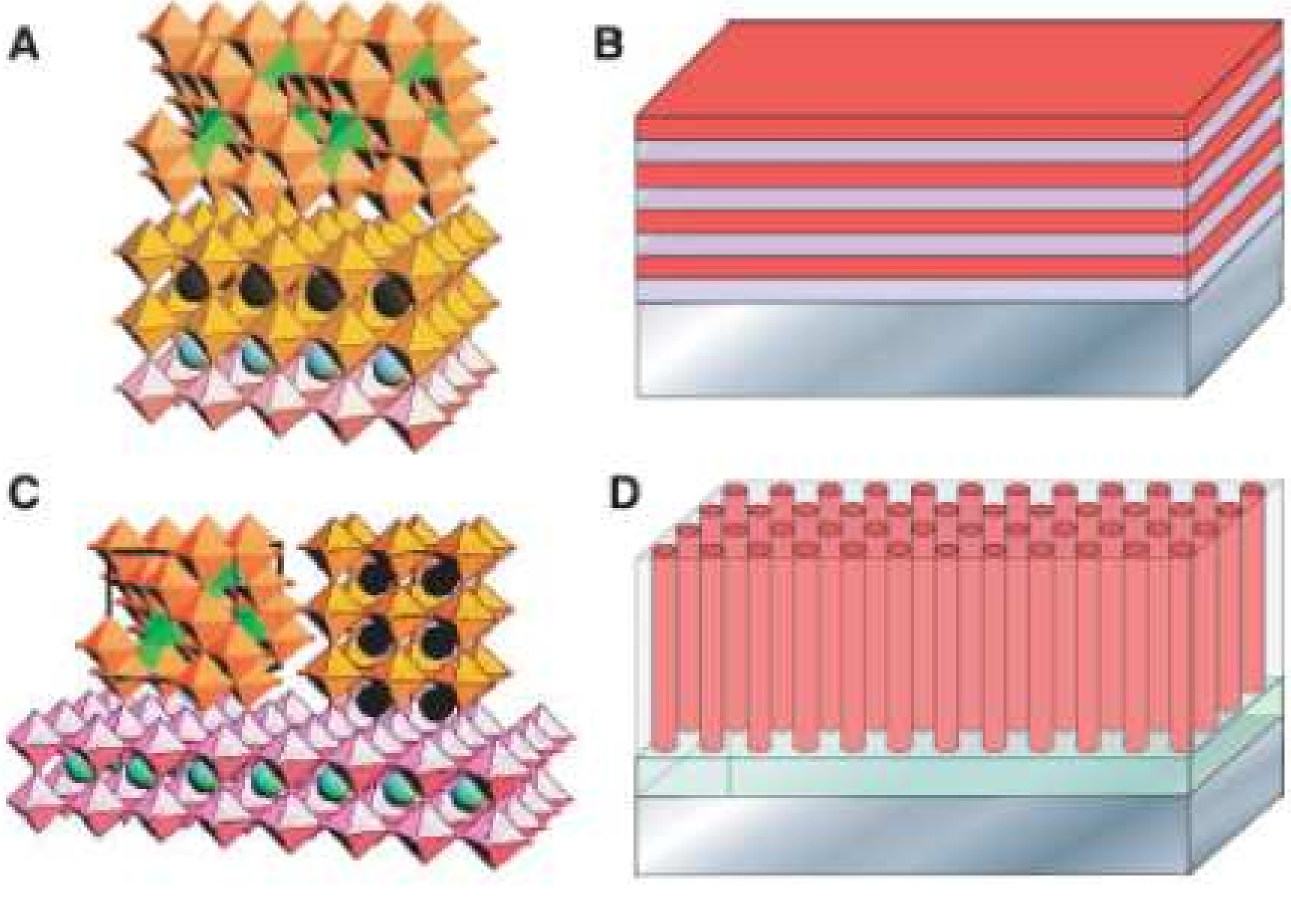
Terfenol-D/PZT-Laminate:

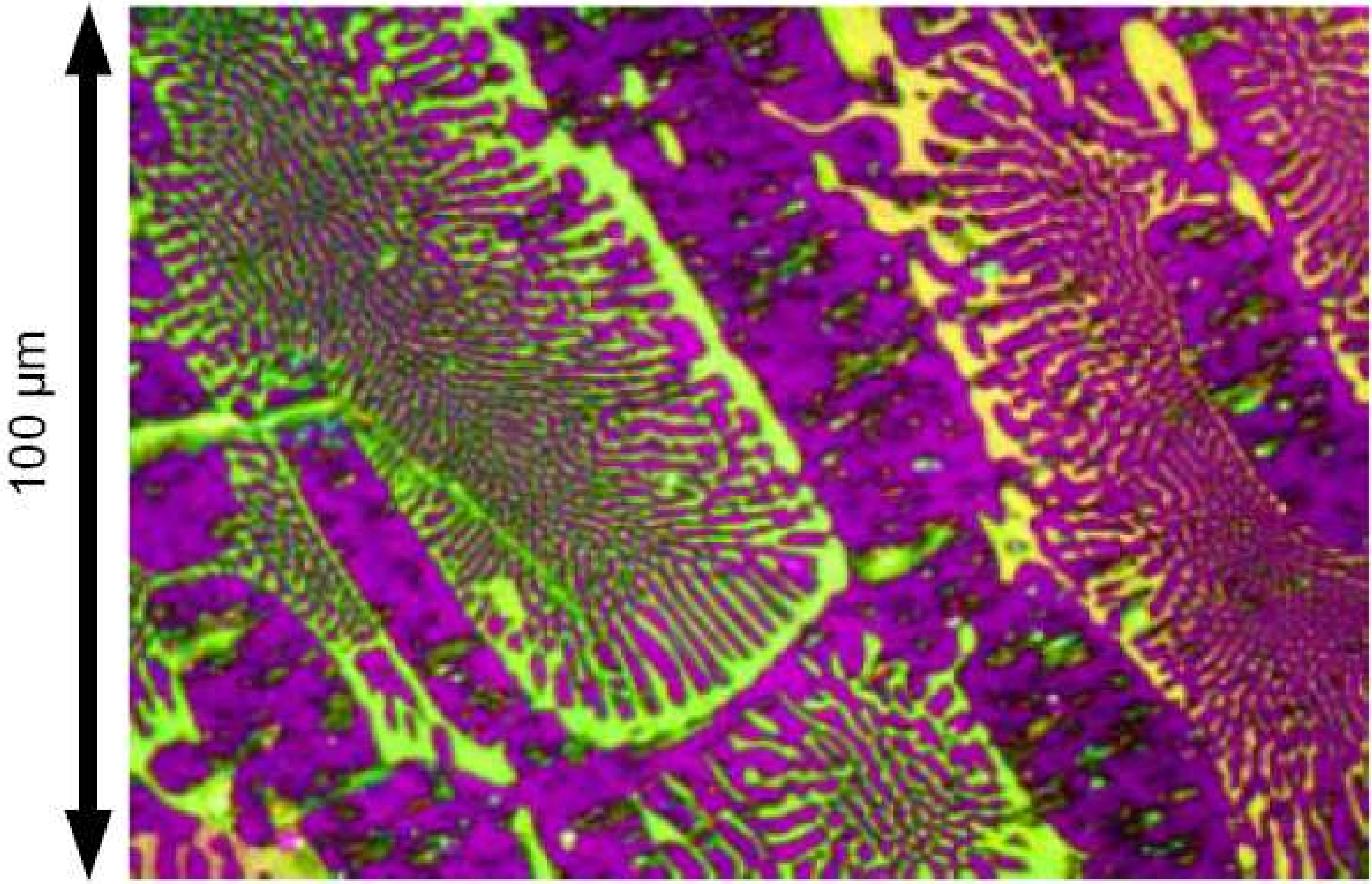


Terfenol-D:
- $Tb_{0,3}Dy_{0,7}Fe_2$

PZT:
- $PbZr_{1-x}Ti_xO_3$

Multiferroic $BaTiO_3/CoFe_2O_4$ nanocomposites:

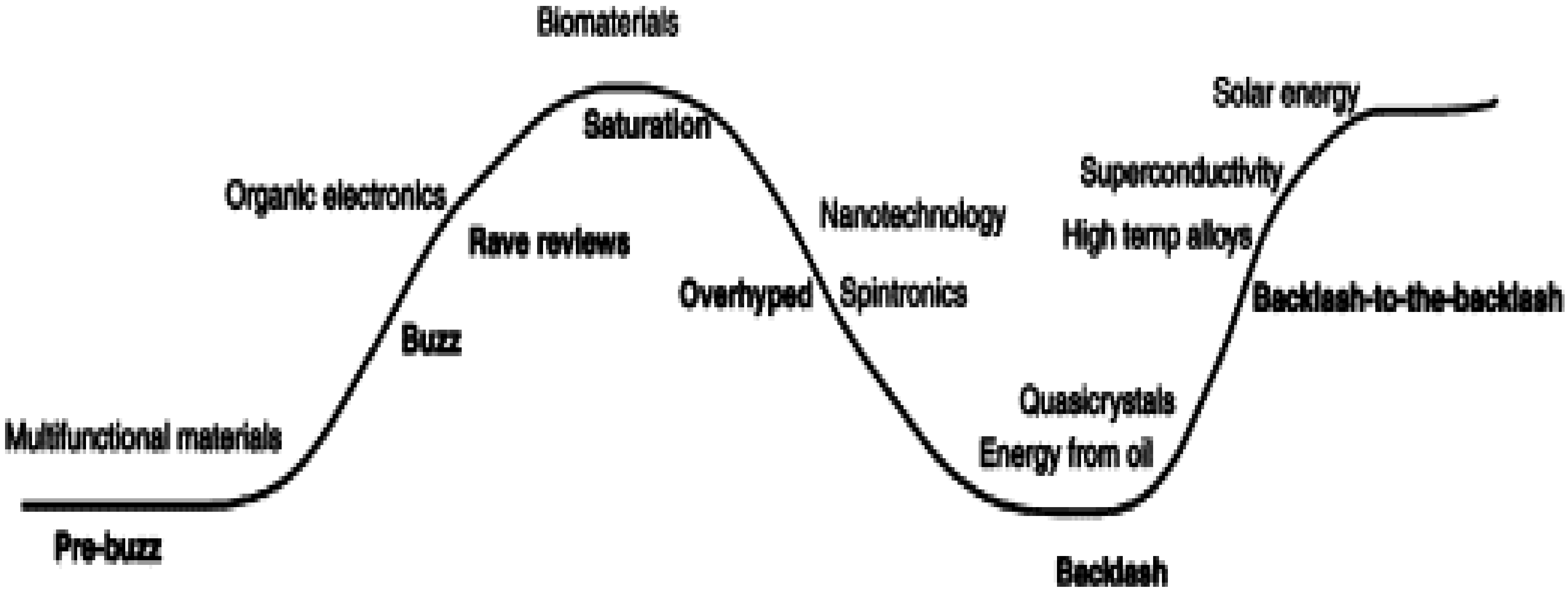




Violet – ferromagnetic rhombohedral (LaSr)MnO3, Tc=370 K
Green – ferroelectric hexagonal LuMnO3, Tc=900 K
(Park et al (2005))

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."



CONCLUSIONS

- 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 ($YMnO_3$)
4. Lone pairs (systems with Bi^{3+}, Pb^{2+} etc)
5. FE due to coexistence of site- and bond-centered charge ordering
6. #########

Multiferroics with FE due to magnetic ordering (**type-II multiferroics**)

1. Spiral magnets; FE due to spin-orbit interaction ($TbMnO_3$, $MnWO_4$, ….)
2. FE due to magnetostriction ($TbMn_2O_5$?; $RbFe(MoO_4)_2$)
3. Electronic mechanism of FE in frustrated systems

Problems

1)Type-I multiferroics: Tc’s, P – OK   but:

how to increase the coupling?

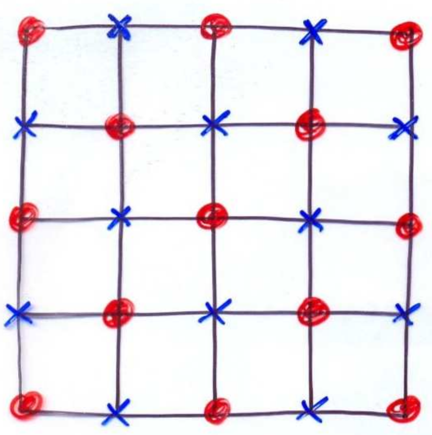
2) Type-II multiferroics: coupling OK; but

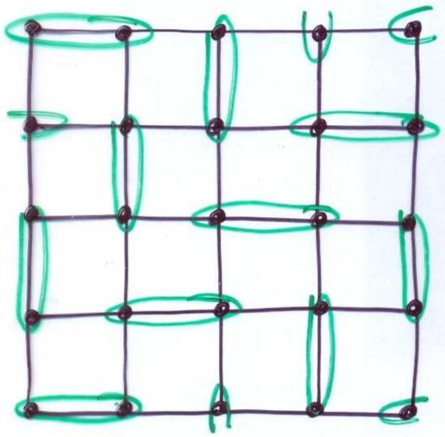
how to increase Tc and P ?

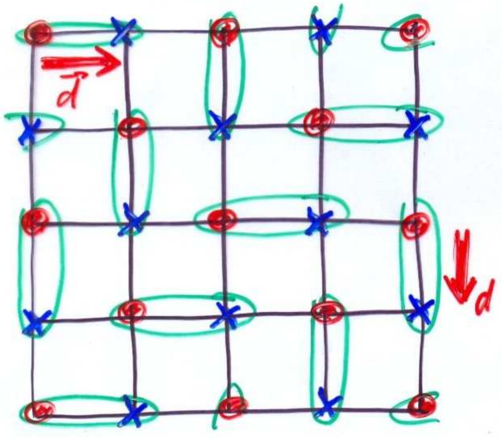
3) Composite MF

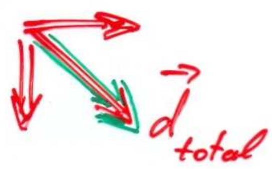
Novel physical effects? (toroics; ….)

Novel manifestations; functionality





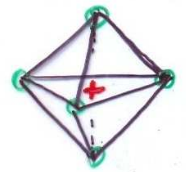




⇒ Ferroelectric phase!

- Hexagonal manganites $RMnO_3$, $YMnO_3$

$T_{ferroel} \sim 900\,K$, $T_N \sim 100\,K$

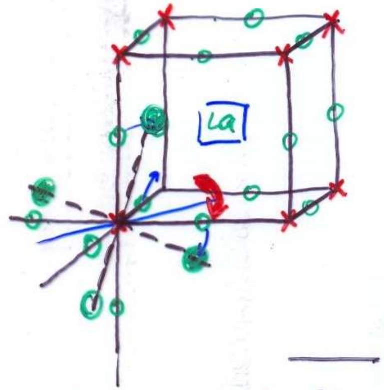


Ferroelectricity has nothing to go with Mn!

⇒ Tilting of rigid MnO_5 trigonal bipyramids

(T. Palstra et al., Nature Materials)

Well-known case of perovskites:



e.g. $LaMnO_3$

Tilting of MnO_6-octahedra leads to a cubic → orthorombic transition, 1 very short La – O bond

— • —

Similar tilting of rigid MnO_5 in the structure of hexagonal manganites like $YMnO_3$ gives short Y – O bond – dipole moment, and in this structure – ferroelectricity