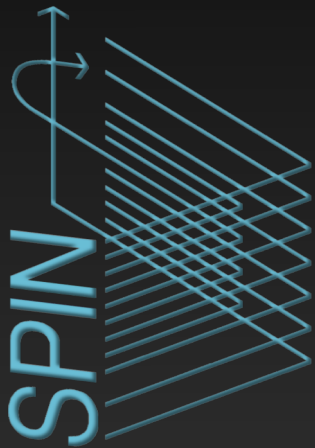


MULTIFERROICS AND MAGNETOELECTRIC EFFECTS

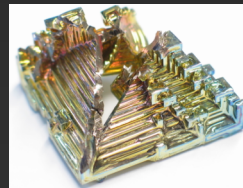


Dr. Silvia Picozzi

*Consiglio Nazionale delle Ricerche,
CNR-SPIN, UOS L'Aquila
67100 L'Aquila, Italy*

Project “BISMUTH”:

Breaking **I**nversion-**S**ymmetry in **M**agnets:
Understand via **T**heory



Sponsored as a Starting Grant 2007 by the
European Research Council - Eu FP7 IDEAS



FERROELECTRICITY: BASICS

What is a ferroelectric?

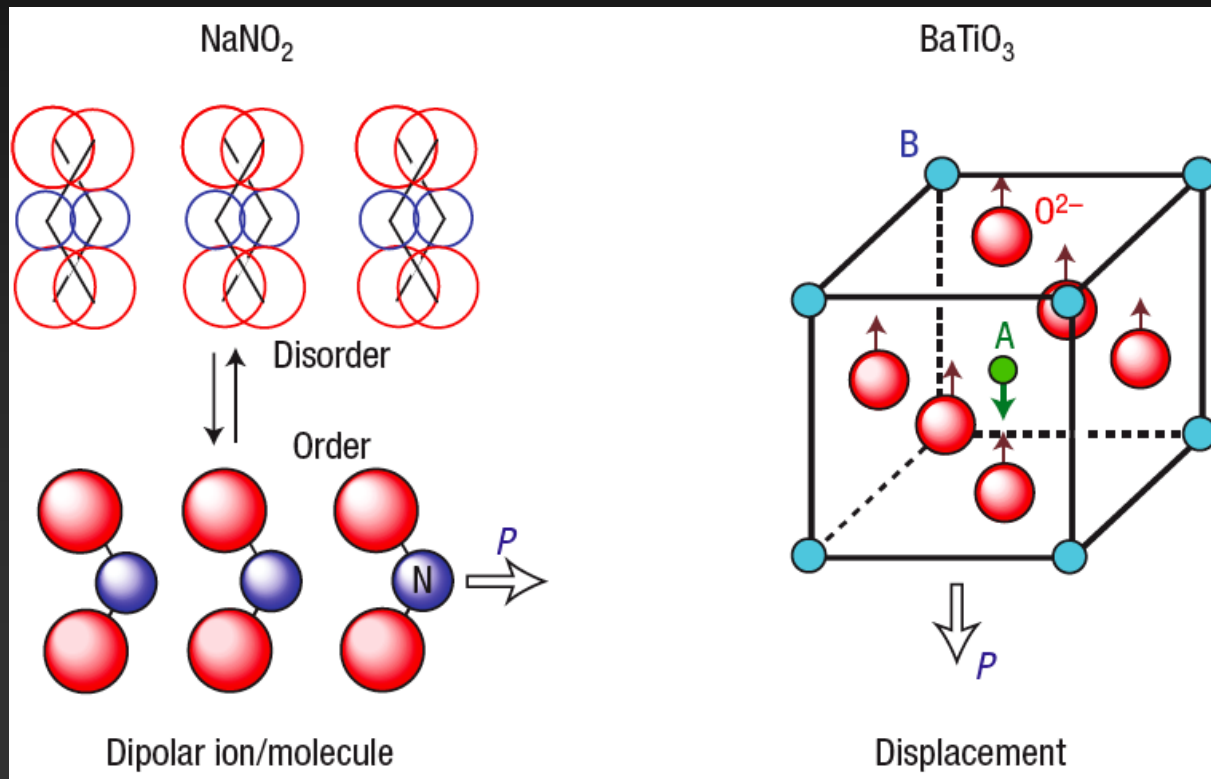
Why is ferroelectric?

Which are the most famous FE materials?

FERROELECTRICITY: BASICS

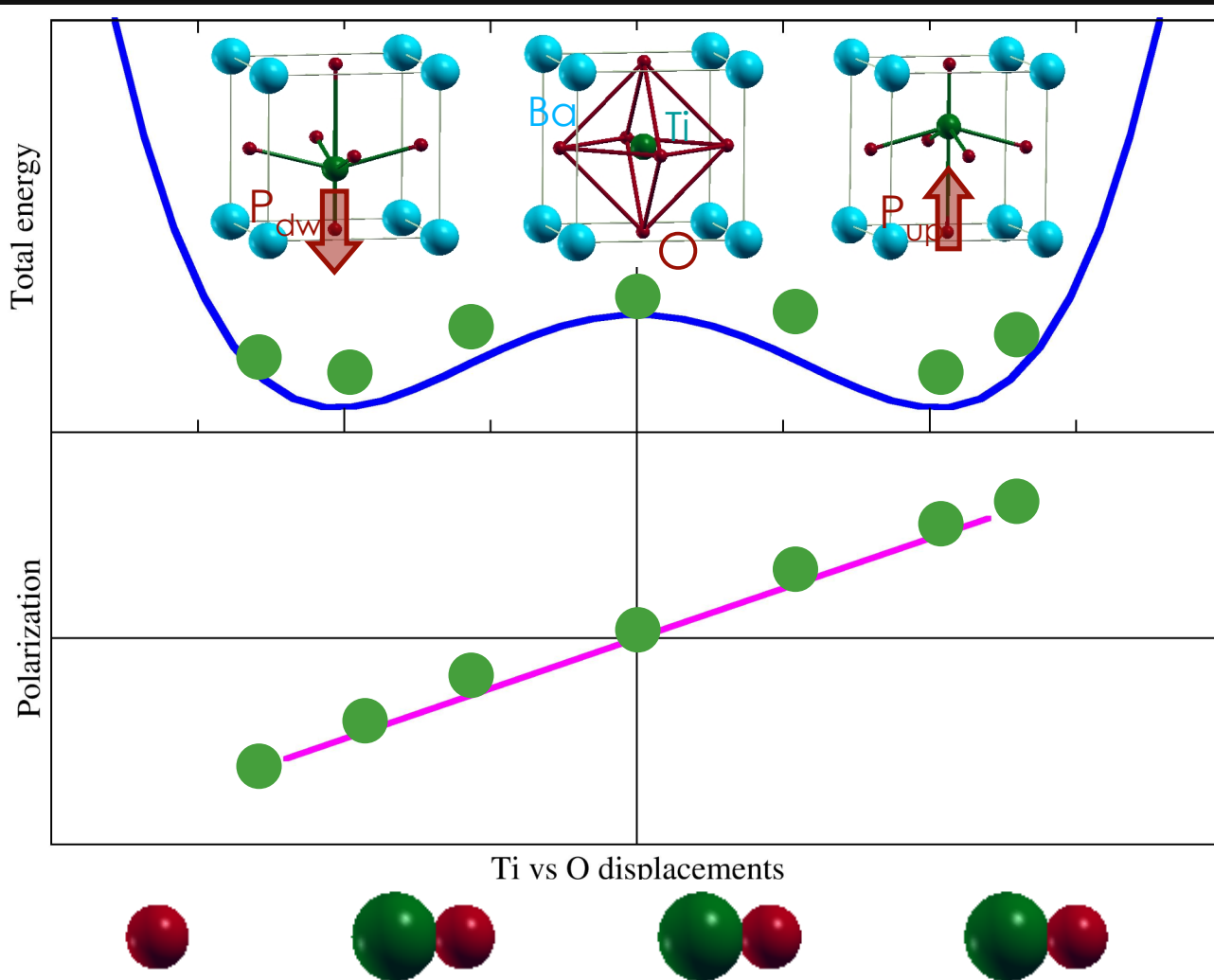
- **Ferroelectrics:** polar materials, in which a spontaneous electric polarization can be switched via an external electric field (P: primary order parameter in the phase transition)

“Order-disorder” vs “displacive”

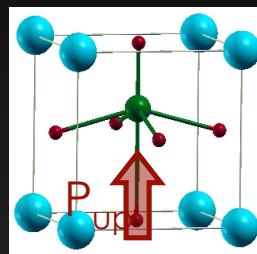
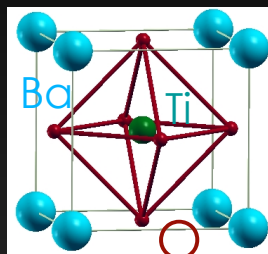
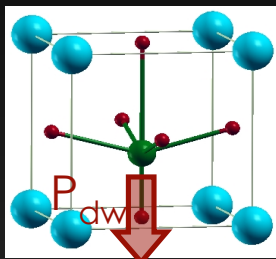


PROPER DISPLACIVE FERROELECTRICITY

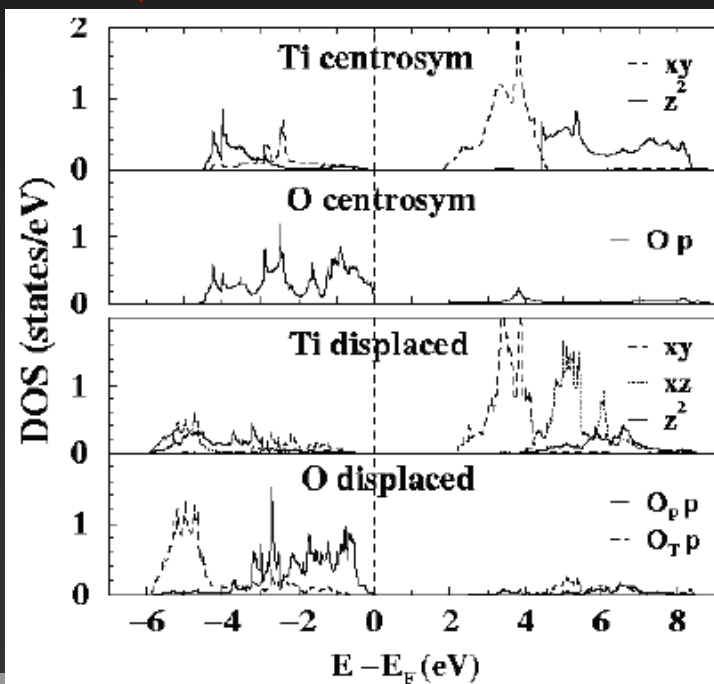
- BaTiO_3 :
Up or down
displacement
of B-site cation



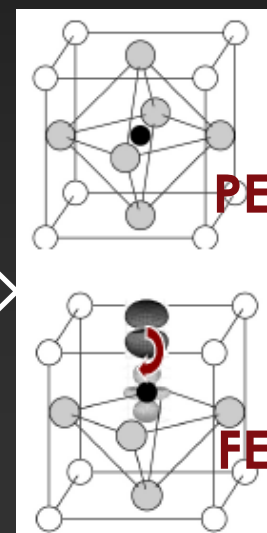
PROPER DISPLACIVE FERROELECTRICITY



- BaTiO_3 :
Up or down
displacement
of B-site cation

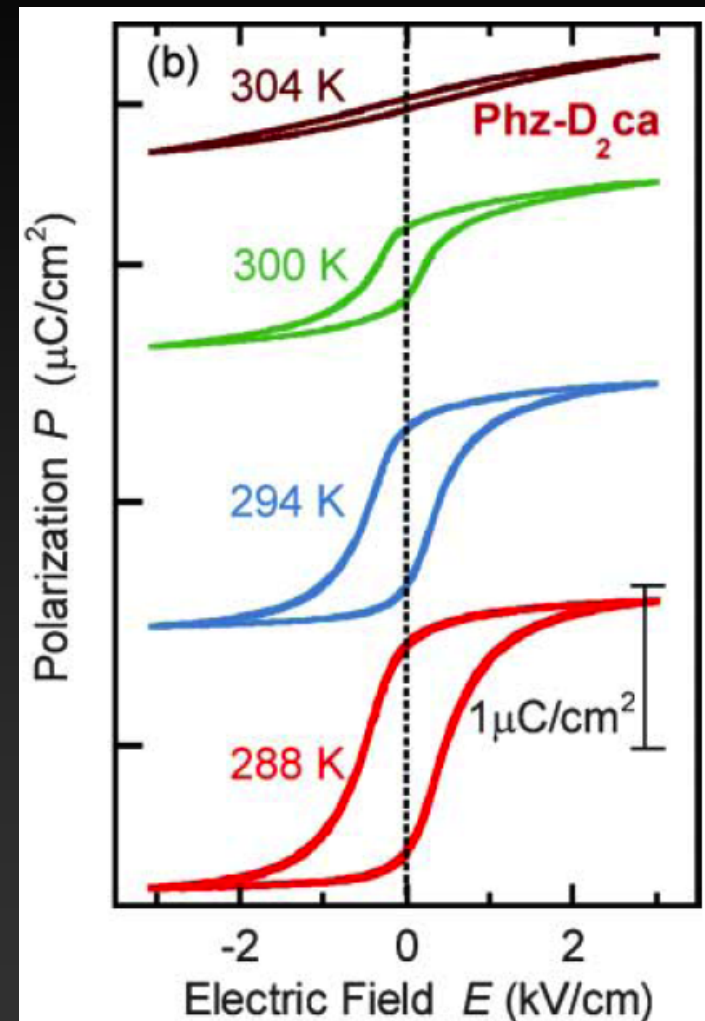
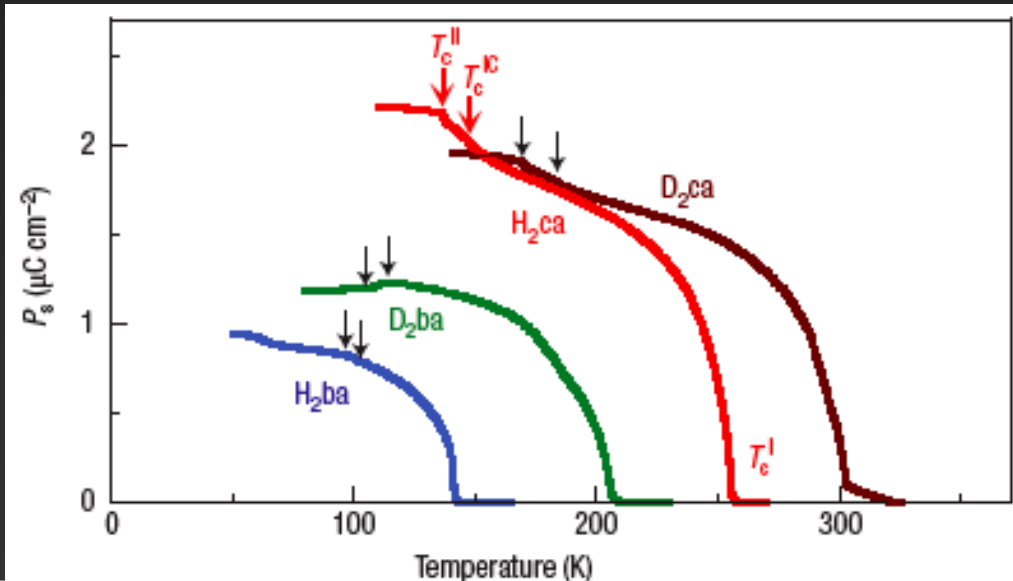


Hybridization:
Ti d (empty) -
O p states
“covalency-
driven”



FERROELECTRICITY: BASICS

- The electric polarization (P) vs field (E) draws a **hysteretic curve** (P - E loop)
- The critical electric field for reversing P is called “**coercive field**”.
- The electric “**bistability**” can be used, i.e, for non-volatile memory elements.
- Ferroelectrics usually have a **Curie temperature** T_c for a paraelectric-to-ferroelectric phase transition.



*S. Horiuchi and Y. Tokura,
Nature Mater. 7, 357 (2008)*

FERROELECTRICS: NUMBERS

Materials	Transition temperature (K)		Dielectric constant	
	T_c	T_c^0	κ_{RT}	κ_{max}
Inorganic compounds				
NaNO ₂	437			4×10^3
BaTiO ₃	381		5×10^3	10^4
PbTiO ₃	763		210	9×10^3
SbSI	293			6×10^4
KH ₂ PO ₄ (KDP)	123	213	30	2×10^4
Organic-Inorganic con				
HdabcoReO ₄	374		6	22
TGS	323	333	45	2×10^3
TSCC	127		5	80
Rochelle salt	297	308		4×10^3

Materials	P_s ($\mu\text{C cm}^{-2}$); temperature	E_c (kV cm ⁻¹)	
NaNO ₂	10; 140 K	5	
BaTiO ₃	26; RT	10	
PbTiO ₃	75; RT	7	
SbSI	20; 270 K	-	
KH ₂ PO ₄ (KDP)	5.0	0.1	
Organic-Inorganic con			
HdabcoReO ₄	16; RT*	>30	
TGS	3.8; 220 K	0.9	
TSCC	0.27; 80 K	3	
Rochelle salt	0.25; 276 K	0.2	

*S. Horiuchi
and
Y. Tokura,
Nature
Mater.
7, 357
(2008)*

COMPLEX OXIDES: BASICS

What is a complex oxide?

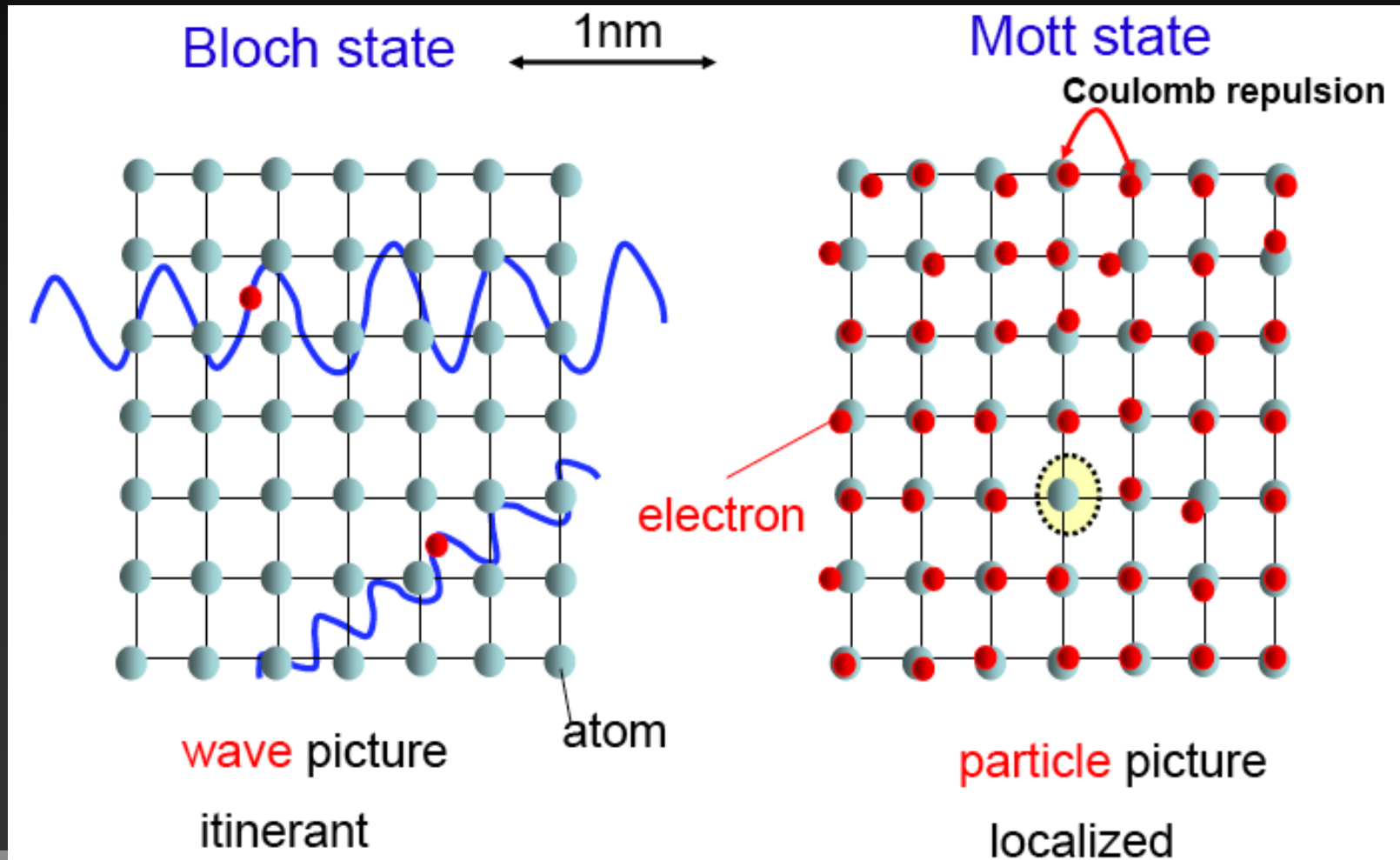
Why are they interesting?

Why are they useful?

How to model them?

WHAT ARE CORRELATED OXIDES?

Systems with correlated electrons:
one electron explicitly influences the others



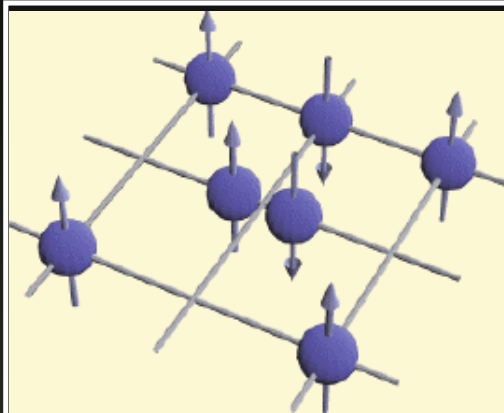
CHARGE, SPIN, ORBITALS AND ALL THAT JAZZ...

Complex oxides as exotic systems

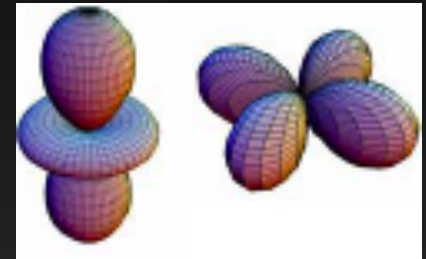
Electron
degrees
of
freedom:



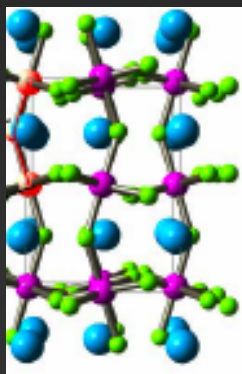
• charge



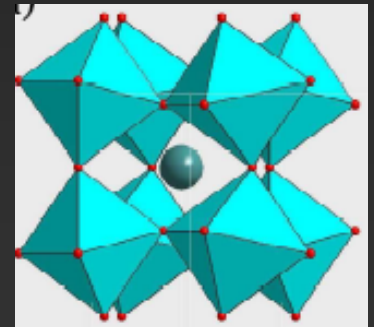
• spin



• orbital



• lattice



COMPARISON WITH SEMICONDUCTORS

Conventional semiconductors

Physics:

- large overlap of s/p orbitals gives extended wavefunctions
- no intrinsic magnetism or other correlations

Technology:

- Quality: high! can be fabricated into complex structures
- Understanding: Semiconductor modeling is straightforward
- Tunability: control charge with modest doping/ E fields

Complex oxides

Physics:

- localization of 3d/2p orbitals gives strong Coulomb interact.
- diverse magnetic and other correlations

Technology:

- Quality: materials chemistry challenging; fabrication less developed
- Understanding: strong correlations challenging to theoretical tools
- Tunability: high! due to competing ordered states

COMPLEX OXIDES: TUNABILITY VS COMPLEXITY

Many “couplings”:

electron-lattice



spin-electron-lattice



Physics phenomena:

ferroelectricity
high-Tc superconductivity

multiferroism
magnetoelectricity
magnetoresistance
spintronics
magnetic frustration

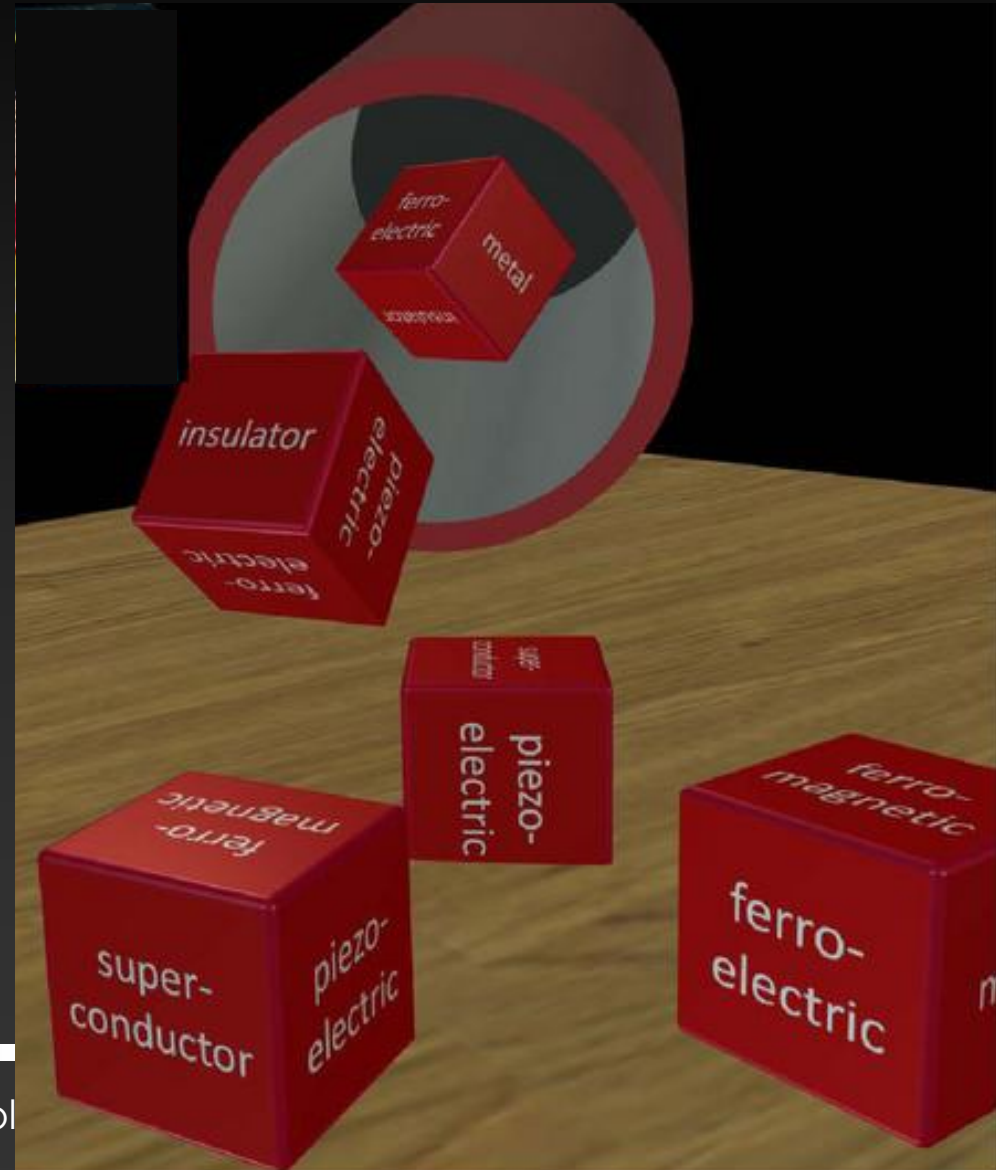
Spin/orbital/lattice couplings with similar energy scales:
small changes (surfaces, interfaces, defects, external perturbations)
can alter the balance between competing large energy interactions
and dramatically change the ground state >> **TUNABILITY!**

COMPLEX OXIDES: TUNABILITY VS COMPLEXITY

Many “couplings”:

electron-lattice

spin-electron-lattice



APPLIED PHYSICS

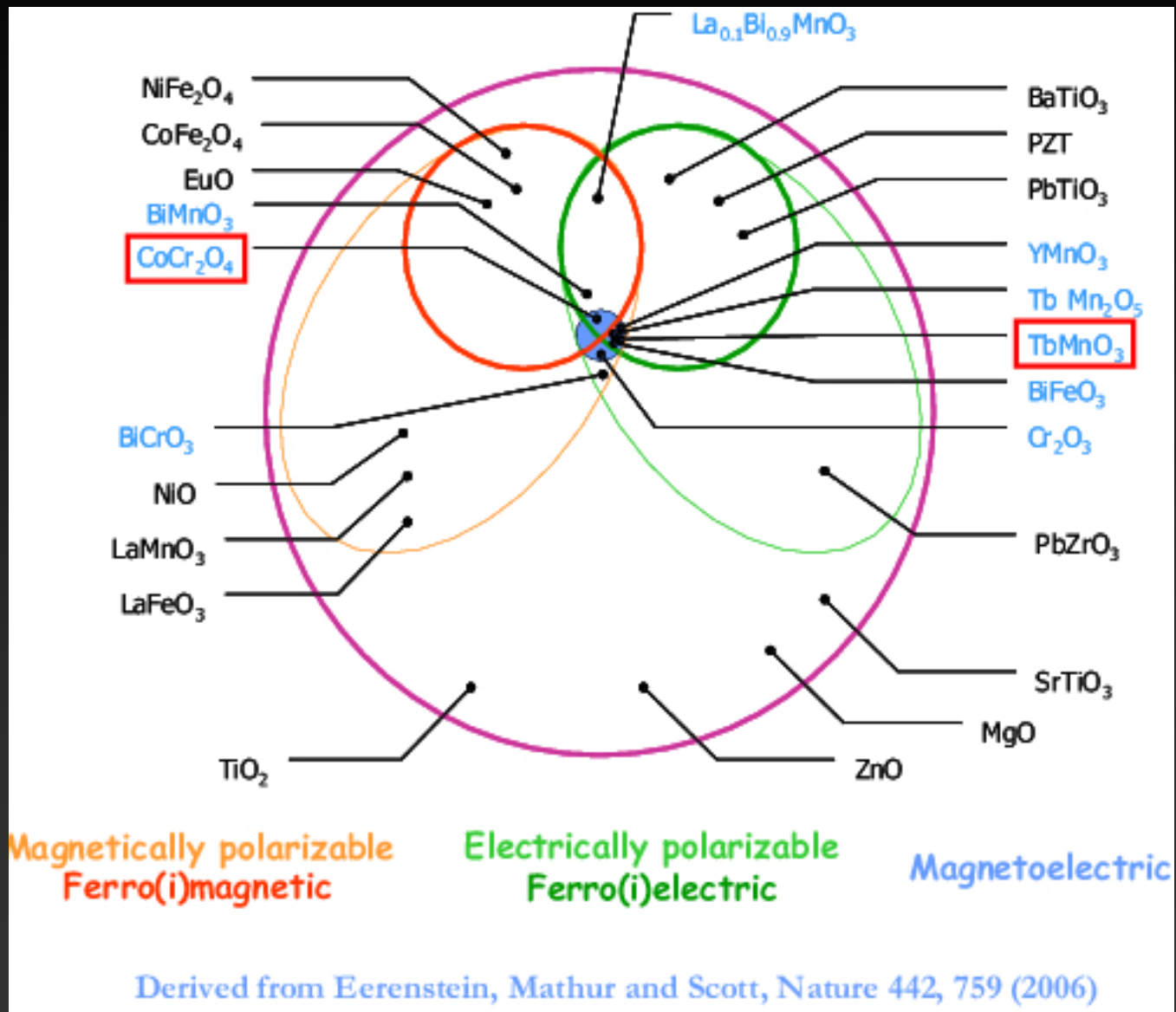
Oxide Electronics Emerge

Arthur P. Ramirez

Microelectronics are built from materials whose electrons interact strongly and can exhibit properties as a group that are not seen in any one particle.

Vastly richer physics suggests entirely new functionalities !

OXIDES CLASSIFICATION



FIRST-PRINCIPLES CALCULATIONS: BASICS

Density functional theory

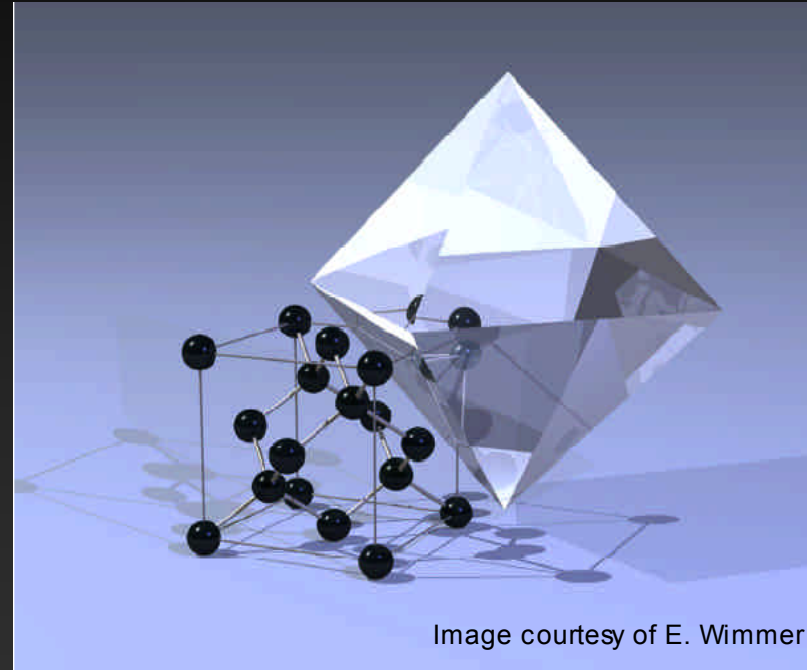
Main theorem

Why are they useful for multiferroics?

Where do they fail?

WHAT ARE FIRST-PRINCIPLES USEFUL FOR?

- **MACRO $\leftrightarrow$ MICRO:** Connect properties with atomic structure
- **MODELLING AND UNDERSTANDING:** Sort out microscopic mechanisms and physical models.
- **COMPUTER-EXPT:** Ask “*what if*” questions.
- **MATERIALS DESIGN:** Screen ideas for new/modified materials
- **THEORY VS EXPERIMENT:** Interpret experimental data, compare spectra, etc
- **ERRORS...** Analyze failures. Ask: Are the approximations used appropriate? Can the models address the essential complexity of the system? Is the theory appropriate for the key properties?

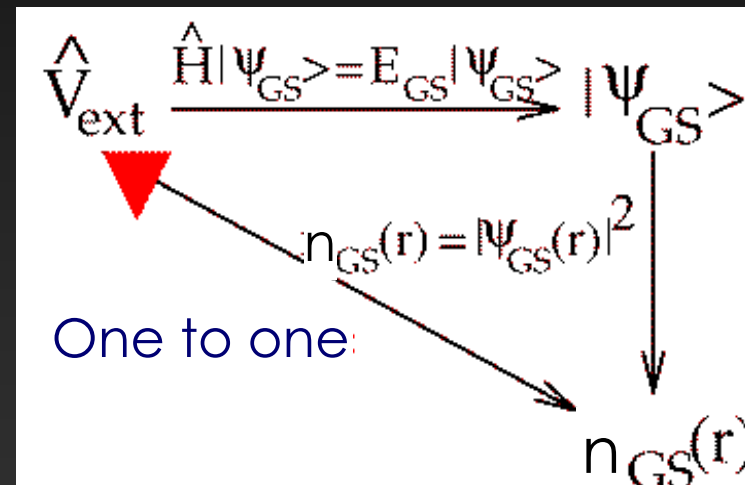


DFT: BASICS

The basic quantity is not the many-body wave-function but the **electronic density $n(\mathbf{r})$**

- **Hohenberg-Kohn theorem (1964)**

- All properties of the many-body system are determined by the ground state density $n_{\text{GS}}(\mathbf{r})$
- Each property is a functional of the ground state density $n_{\text{GS}}(\mathbf{r})$ which is written as $\mathbf{f}[n_{\text{GS}}]$
- In particular, the energy is:

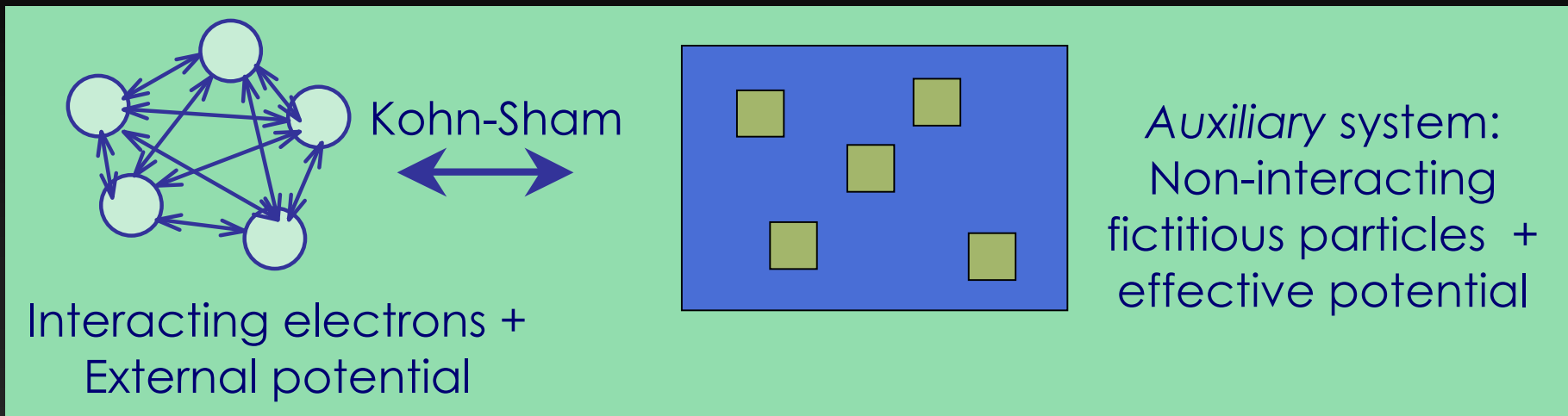


$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V_{\text{ext}} n(\mathbf{r}) d\mathbf{r} = T_e + U_{ee} + \int V_{\text{ext}} n(\mathbf{r}) d\mathbf{r} \geq E[n_{\text{GS}}(\mathbf{r})]$$

and satisfies a **variational principle**

DFT: BASICS

• Kohn-Sham equations (1965)



The ground state density is required to be the same as the exact density

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

Minimization of E leads to one-particle Kohn-Sham equations for independent particles (soluble):

$$[-1/2 \nabla^2 + V_{\text{eff}}[n(\mathbf{r})]] \psi_i = \varepsilon_i \psi_i$$

DFT: BASICS

- **Kohn-Sham equations (1965)**

$$\{-1/2 \nabla^2 + V_{\text{eff}}[n(r)]\} \psi_i = \varepsilon_i \psi_i$$

where: $V_{\text{eff}}[n(r)] = V_{\text{ext}}(r) + V_{\text{H}}(r) + V_{\text{xc}}[n(r)]$

- $V_{\text{ext}}(r)$ is the nuclei (external) potential

- $V_{\text{H}}(r) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ is the Hartree potential

- $V_{\text{xc}}[n(r)] = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}$ is the (*unknown*) exchange-

correlation potential

DFT: BASICS

- **Approximations to the functional E_{xc}**
 - **Local Density Approximation - LDA**
 - ❖ Assume the functional is the same as a model problem –
the *homogeneous electron gas*
 - ❖ E_{xc} has been calculated as a function of density using quantum Monte Carlo methods (Ceperley & Alder)
 - **Gradient approximations - GGA**
 - ❖ Various theoretical improvements for electron density that varies in space

OPERATIVELY...

- Structure, types of atoms, guess for input charge
- Find the potential
- Solve KS Eqs.
- New Density and Potential
- Self-consistent?
- Output:
 - Total energy, force,
 - Eigenvalues

Initial Guess
$n^{\uparrow}(r), n^{\downarrow}(r)$

WHAT CAN WE GET OUT OF THE COMPUTER?

Capabilities, formalism

Predicted quantities

Spin-DFT

Electronic structure (DOS, bands, ...),
magnetism (moments, GS spin configuration, ...)

THE GOOD AND THE BAD OF DFT FOR COMPLEX OXIDES

BUT... $V_{xc}(r)$ is approximated
“Standard” local density approximation (LDA)
designed for a homogeneous electron gas

How to
approach
strong
correlations ?

- **Beyond-LDA methods:**

- LDA+U attempts to incorporate Coulomb repulsions (U)
- Hybrid functionals (mix of “exact-exchange” and LDA)

- **Hamiltonian modelling:**

Extract essential interaction parameters from
LDA and construct a model , but also
provide a fully independent approach to
test the results...

MULTIFERROICS: BASICS

What are they?

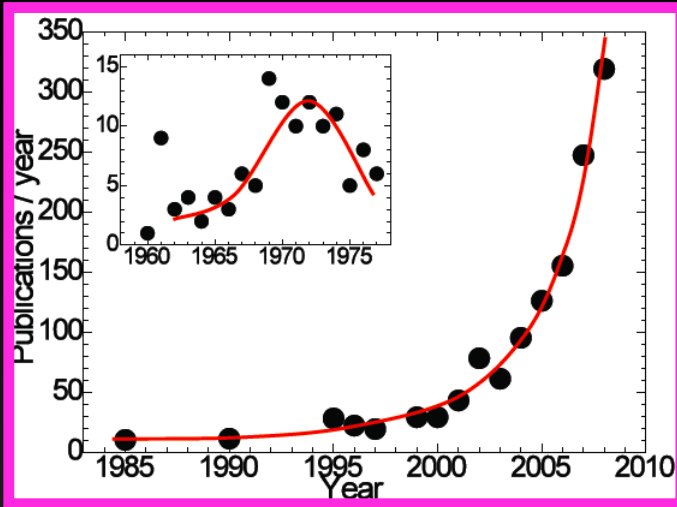
Why are they useful?

Are they many or few?

Lone-pair MFs

Composite MFs

PROPAGANDA



Number of papers listed in
ISI Web of Science
with keyword "multiferroic"

The Science magazine has declared
MFs as an "area to watch" in 2008

Multiferroics. Relatives of ceramic oxide superconductors, the compounds called multiferroics form a group in which single materials display multiple electronic, magnetic, and structural behaviors. Physicists recently used electric fields to manipulate magnetic domains in a multiferroic. Now, they are racing to better control this switching and shape the materials into novel computer chip devices. Success could pave the way for chips that combine the logic functions normally handled by semiconductors with the memory functions now carried out by magnetic materials.



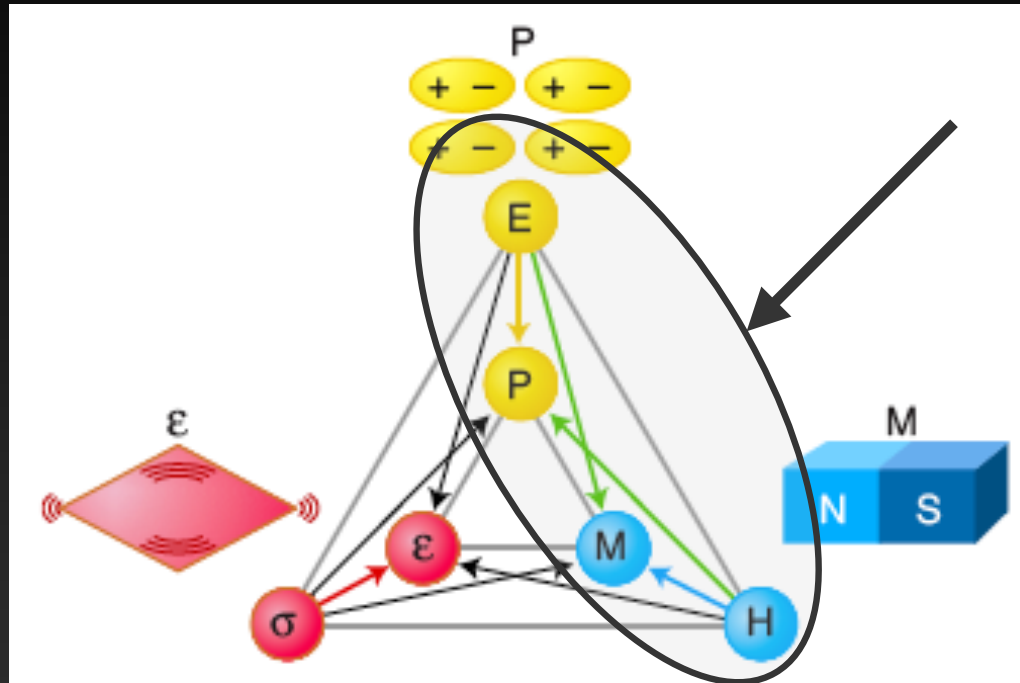
2010 James Mc Groddy Prize
for New Materials

N. A. Spaldin, R. Ramesh and S. W. Cheong

"For groundbreaking contributions in theory and experiment that have advanced the understanding and utility of multiferroic oxides"



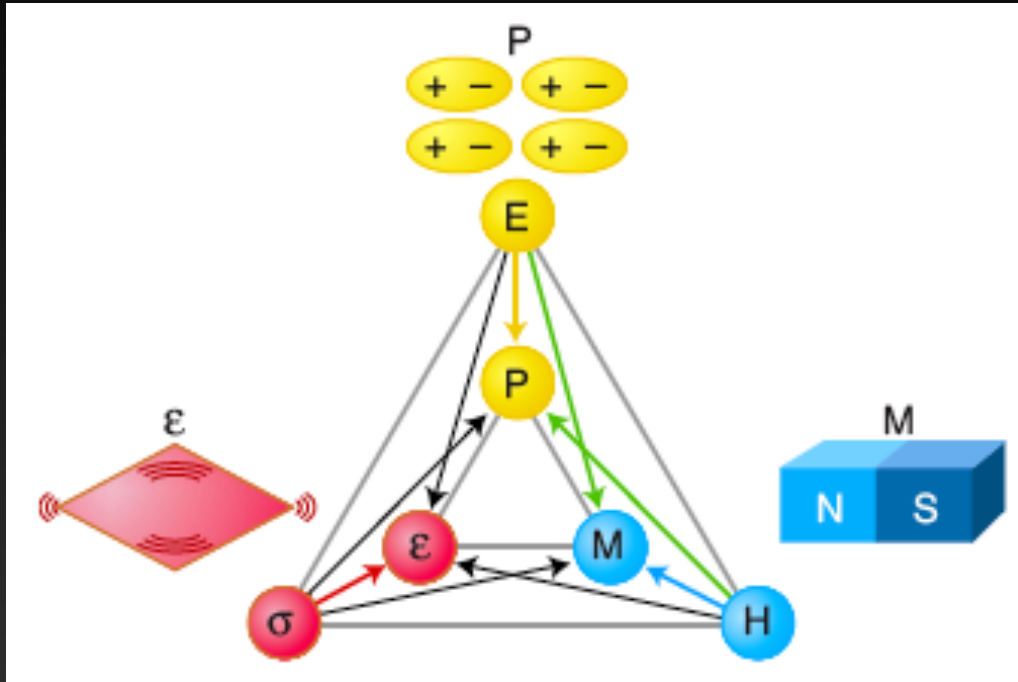
MAGNETOELECTRICS MULTIFERROICS: WHAT ARE THEY?



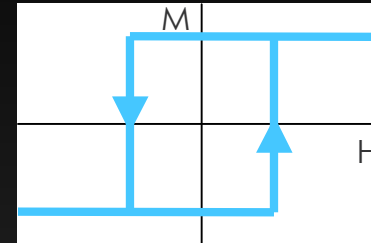
N.A. Spaldin
and M. Fiebig,
Science
309, 391 (2005)

- **Ferroic:** P , M or ϵ are spontaneously formed to produce **ferroelectricity**, **ferromagnetism** or **ferroelasticity**
- **Multiferroic:** coexistence of at least two kinds of long-range ordering

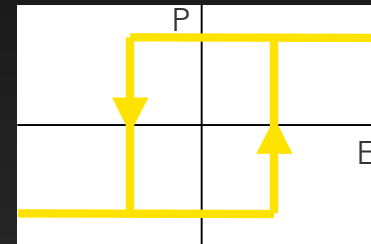
MAGNETOELECTRICS MULTIFERROICS: WHY ARE THEY INTERESTING?



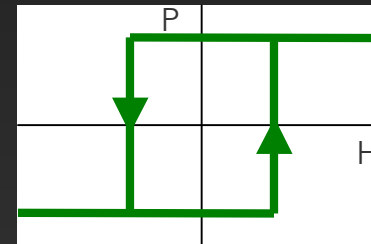
➤ **Magnetoelectrics:** Control of P (M) via a magnetic (electric) field



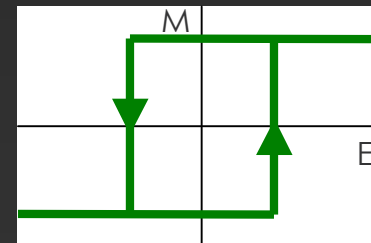
Magnetization
vs magnetic
field in FMs



Polarization vs
electric field in
FEs

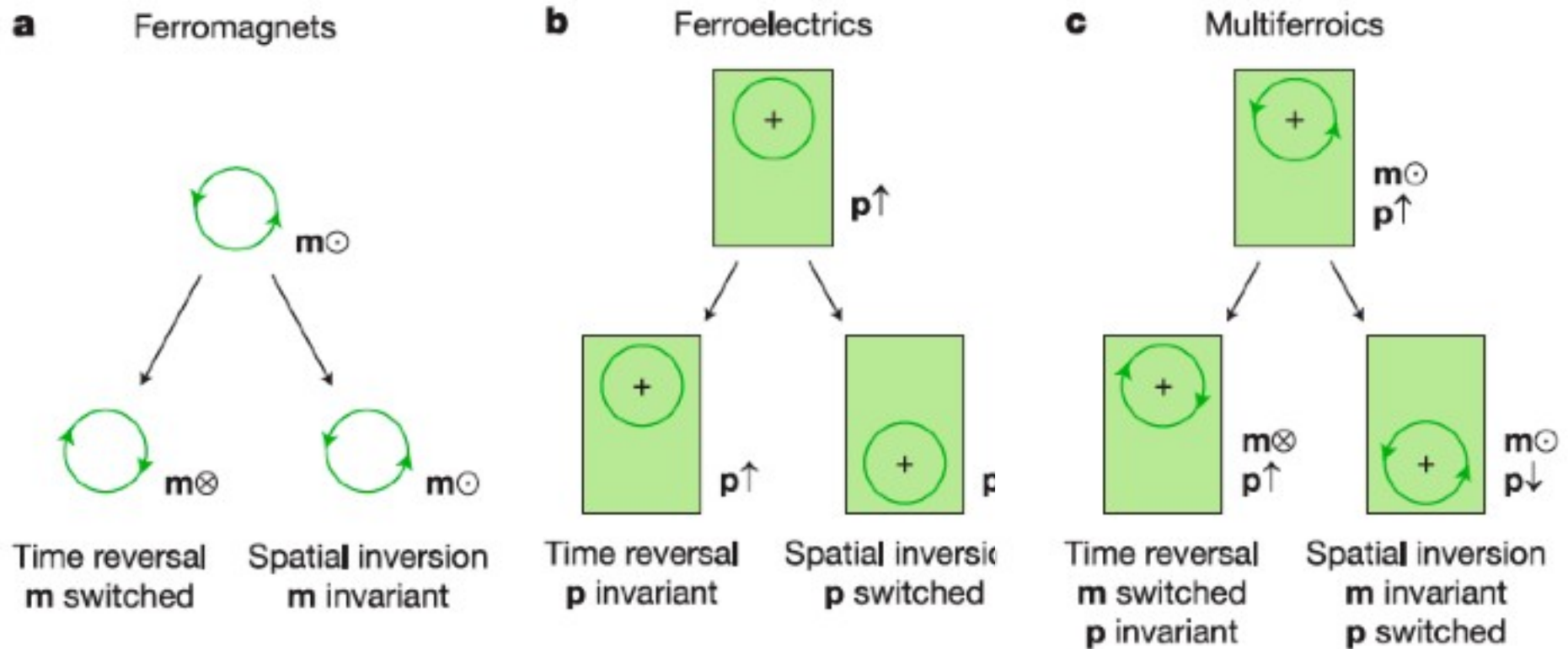


Polarization vs
magnetic field
in MEs



Magnetization
vs electric field
in MEs

(MULTI-) FERROICS: SYMMETRY PROPERTIES



W. Eerenstein, N. D. Mathur and J. F. Scott, *Nature* **442**, 759 (2006)

CRITERIA FOR MAGNETISM AND FERROELECTRICITY

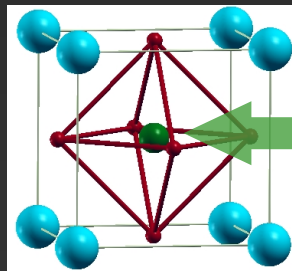
- Uncompensated spins form magnetic moments
- Exchange interaction results from virtual hopping of electrons between ions

➔ In order to stabilize ferro- or ferri- or antiferro-magnetism one needs **partially filled d-shells**!

- Ferroelectricity requires “**d⁰-ness**”
- Ferromagnetism (or FiM- or AFM) requires partially filled d-electrons

➔ CHEMICAL INCOMPATIBILITY!

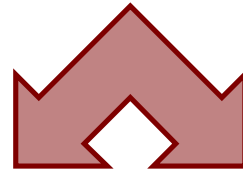
WAY OUT:



➔ Put FE-active ion on A-site

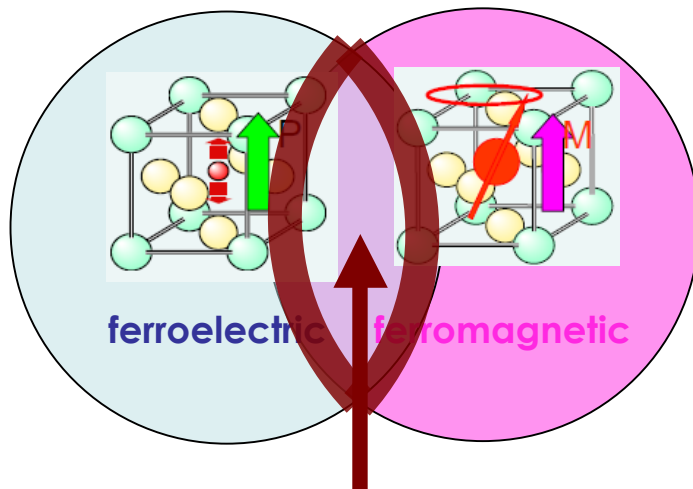
➔ Put magnetic ion on B-site

CLASSIFICATION OF MULTIFERROICS

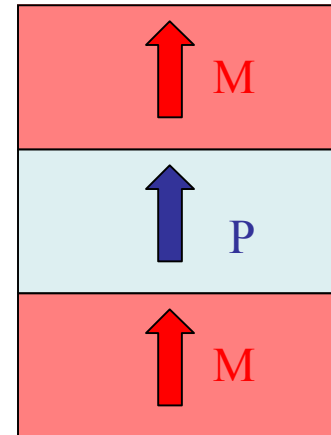
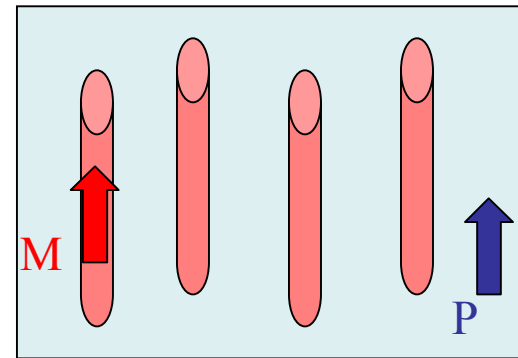


BULK

COMPOSITE

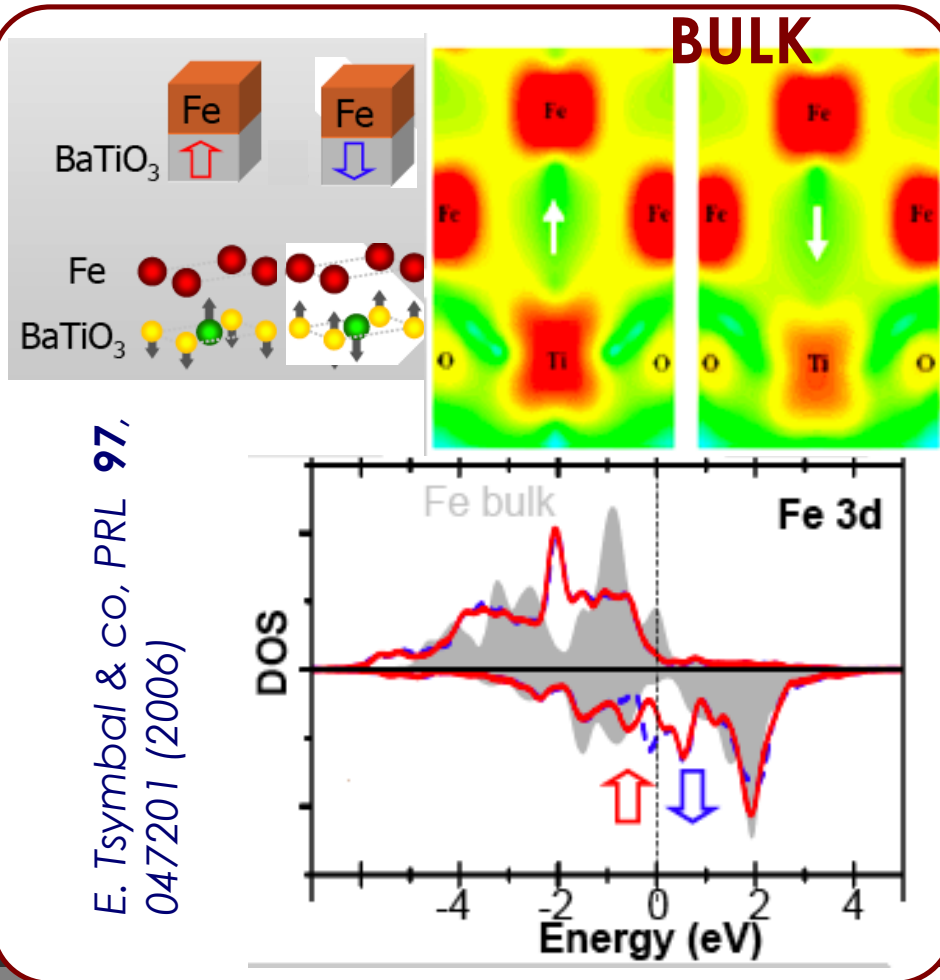
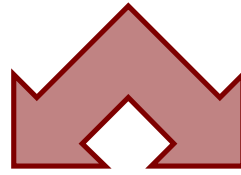


Both magnetic and
dipolar order
in the same
bulk material

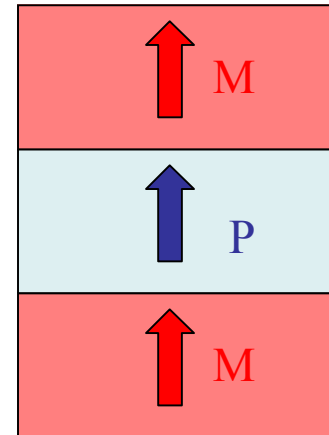
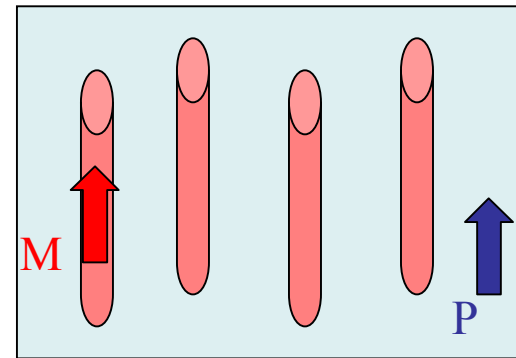


Nanostructures,
heterointerfaces of **two
different materials** (one
FM and the other **FE**)

CLASSIFICATION OF MULTIFERROICS



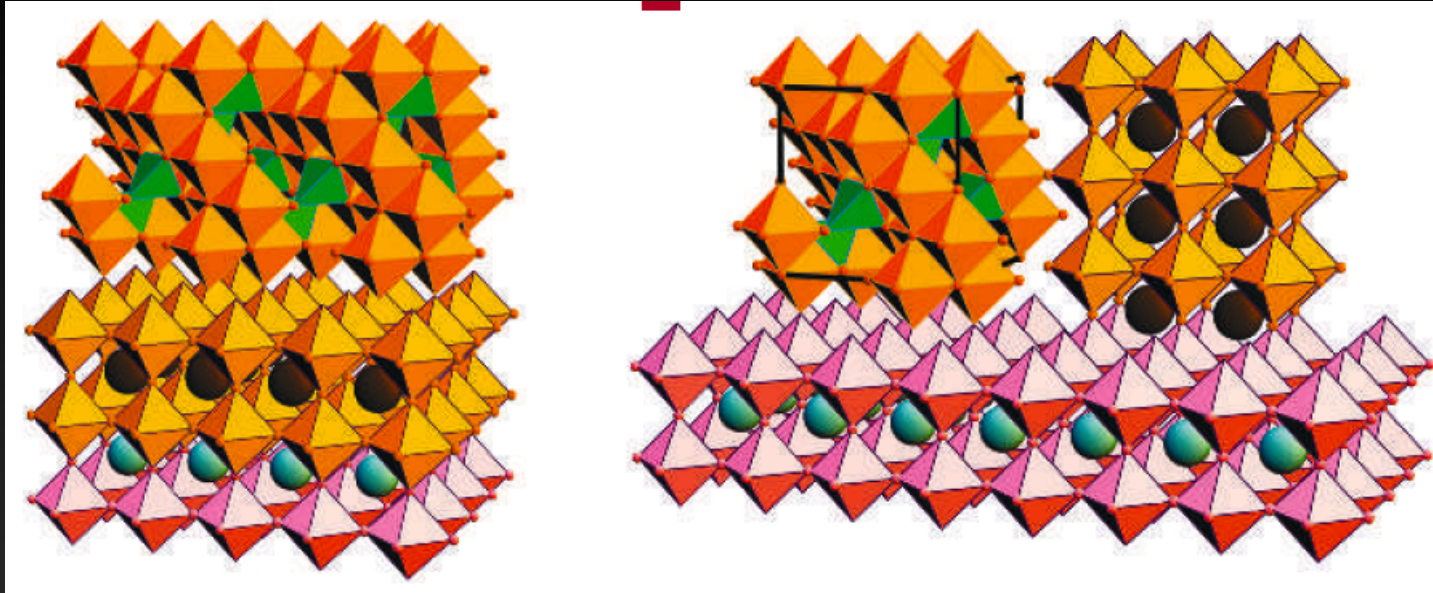
COMPOSITE



Nanostructures,
heterointerfaces of **two
different materials** (one
FM and the other **FE**)

STRAIN-MEDIATED MAGNETOELECTRIC COUPLING

Layered

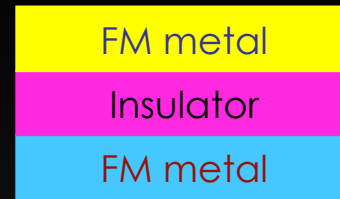


Nano-columns

- Strain coupling requires contact between a piezomagnetic (or magnetostrictive) and a piezoelectric (or electrostrictive) material.
- For nanopillars of CoFe_2O_4 in a BaTiO_3 matrix: observed change in magnetization (around 5%) of the CoFe_2O_4 pillars at the ferroelectric Curie temperature.
- For nanopillars of CoFe_2O_4 in a BiFeO_3 matrix: reported electrically-induced magnetization reversal

Conventional magnetic tunnel junctions (MTJ):

- information stored by the magnetic configuration of the electrodes
- the barrier - a diamagnetic dielectric - is a «passive» element



TUNNEL JUNCTIONS WITH FERROELECTRIC AND/OR FERROMAGNETIC BARRIER

Ferroic insulators bring additional degrees of freedom to MTJs because the barrier can store info

- Ferro(i)magnetic barriers : spin-filtering
- Ferroelectric barriers

Even more, junctions with multiferroic barrier can be used to :

- Store more-than-binary information
- Control the magnetic state by an electric field through the magneto-electric coupling

TUNNEL JUNCTIONS WITH FERROELECTRIC AND/OR FERROMAGNETIC BARRIER

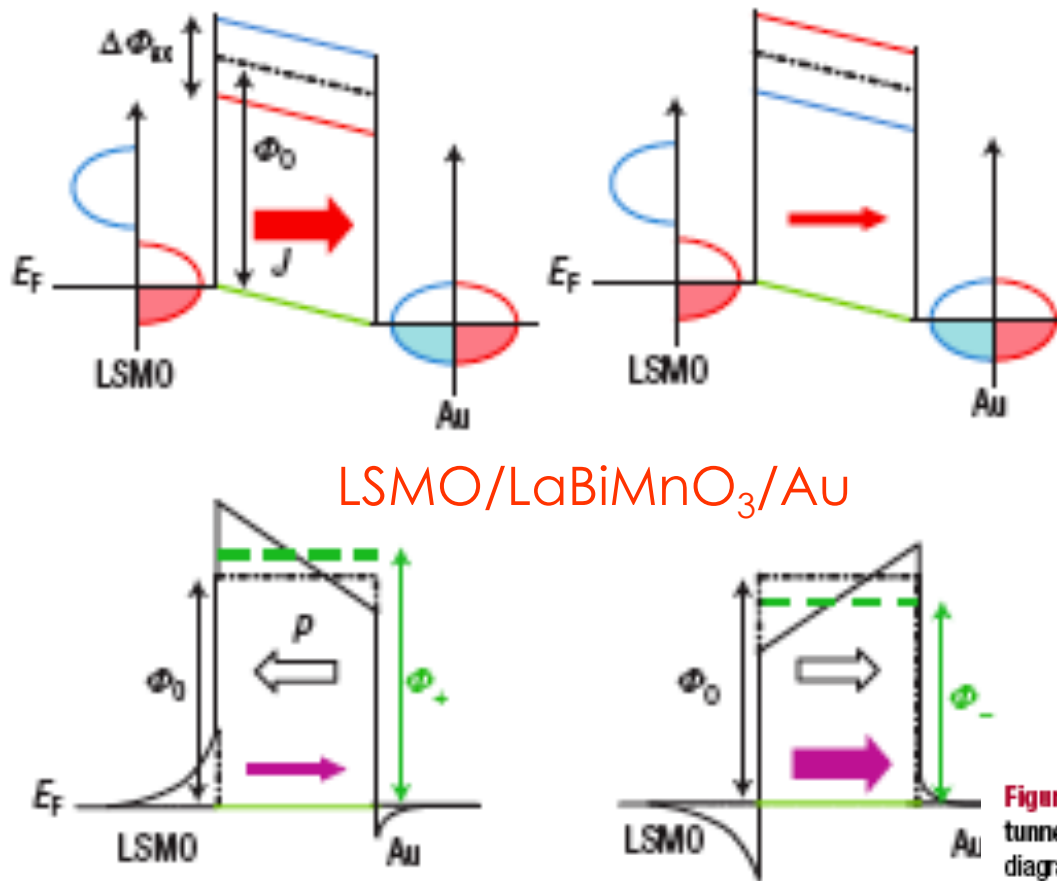
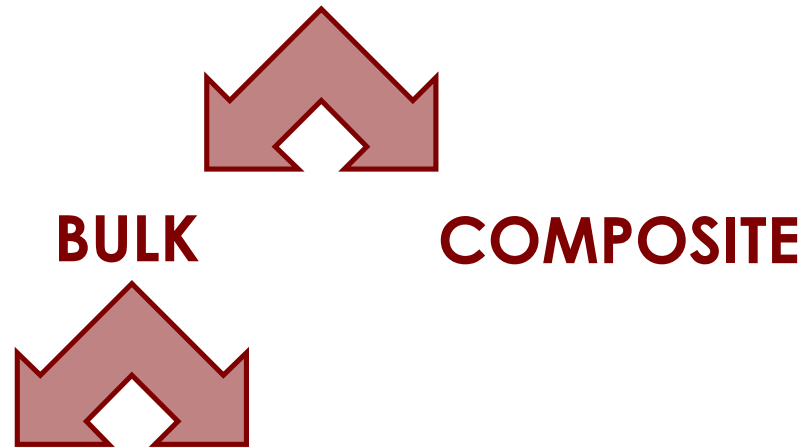


Figure 1 Schematic representation of the tunnel barrier potential profiles and tunnel currents for a ferromagnetic and a ferroelectric barrier. a, Schematic diagram of the spin-dependent tunnelling for parallel (left) or antiparallel (right) configurations of the LBMO and LSMO magnetizations, considering a half-metallic LSMO electrode with only spin-up states at the Fermi level E_F . For simplicity, we assume a non-ferroelectric LBMO barrier. ϕ_0 is the barrier in the absence of ferromagnetism and $\Delta\phi_{xx}$ is the exchange splitting. Spin-up is represented in red and spin-down in blue. In the parallel case, spin-up electrons tunnelling from LSMO experience a small barrier height ($\phi_0 - \Delta\phi_{xx}/2$), which results in a large current density (J , shown by a red arrow) and a low resistance. In the antiparallel case, these electrons tunnel through a larger barrier height ($\phi_0 + \Delta\phi_{xx}/2$), which results in a low current and a large resistance. b, Schematic diagram of the potential profile seen by the tunnelling electrons for the two directions of the barrier electric polarization, according to the model in ref. 13 (assuming a non-magnetic barrier). ϕ_0 is the barrier in the absence of polarization. ϕ_+ and ϕ_- are the average barrier heights seen by the carriers when P points towards LSMO and Au, respectively. The black arrows indicate the direction of the ferroelectric polarization in the barrier. The purple arrows indicate the current density.

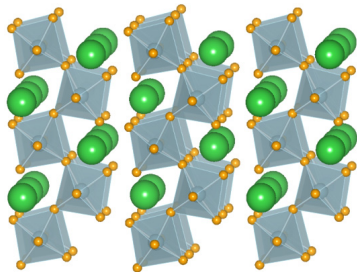
M. Gajek et al., Nature Mat. (2007)

CLASSIFICATION OF MULTIFERROICS



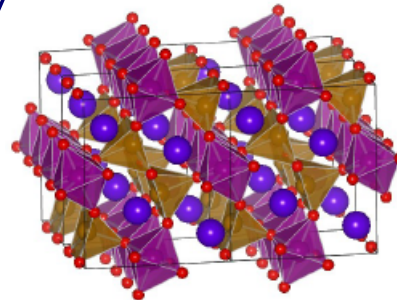
STRUCTURAL MAGNETIC FERROELECTRIC

The primary order parameter related to structural instability (either polar or non-polar)



ELECTRONIC MAGNETIC FERROELECTRIC

The primary order parameter related to electronic degrees of freedom



CLASSIFICATION OF MULTIFERROICS

BULK

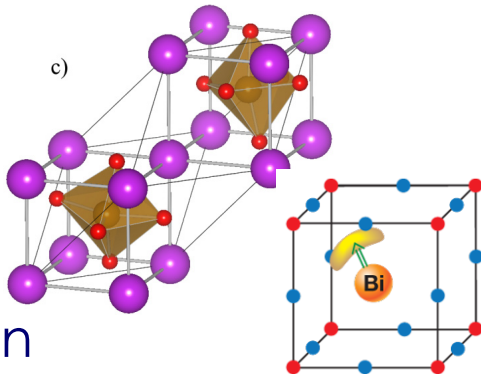
COMPOSITE

**STRUCTURAL
MAGNETIC
FERROELECTRIC**

**ELECTRONIC
MAGNETIC
FERROELECTRIC**

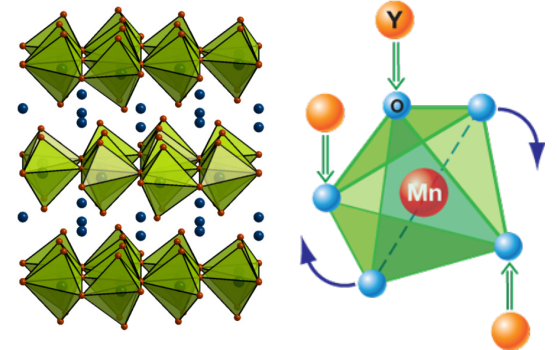
**LONE-
PAIR
DRIVEN**

covalency,
hybridization



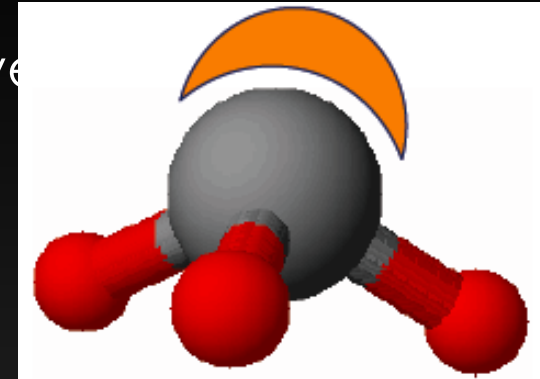
GEOMETRIC

(size-effects, no
significant
rehybridization)



“LONE-PAIR” ACTIVE MULTIFERROICS

- Ferroelectricity from the “stereochemically active lone pair” on Bi^{3+} (cf ammonia, NH_3)
- Magnetism from a 3d transition metal (Mn^{3+} or Fe^{3+})



BiMnO_3 : Ferromagnetic + Polar instability from Bi lone pairs

Anti-polar? (C2/c)  Bi Bi 

P. Baettig, R. Seshadri and N. A. Spaldin, “Anti-polarity in ideal BiMnO_3 ”, JACS 129, 9854-9855 (2007).

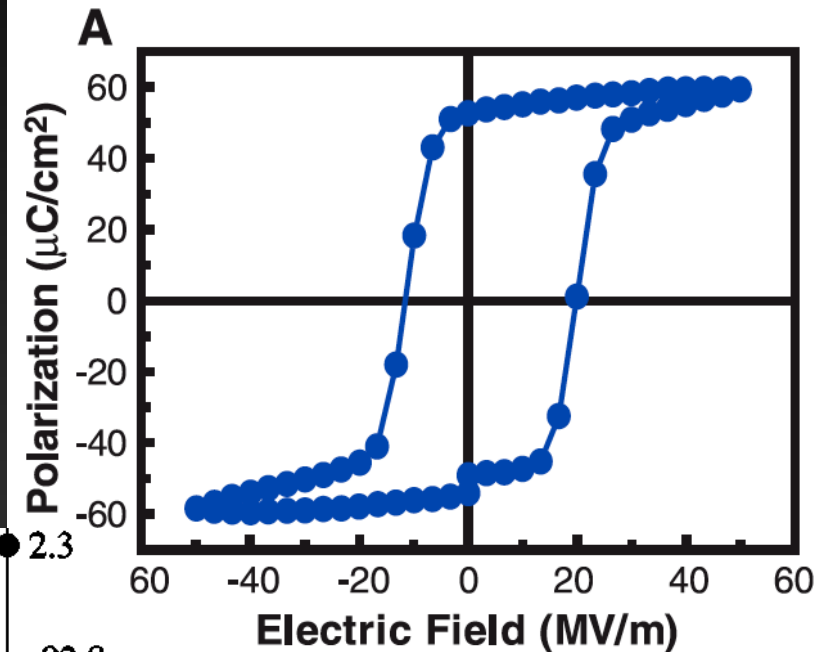
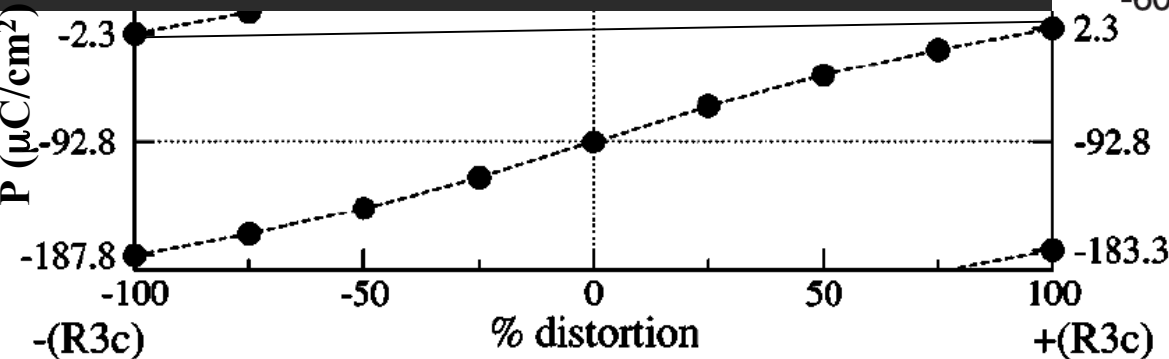
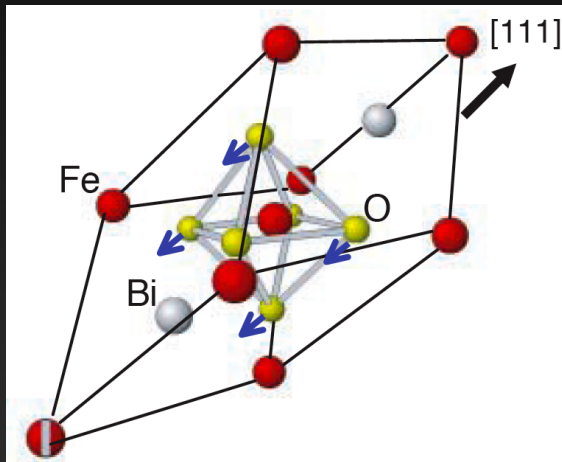
BiFeO_3 : Ferroelectric, $P = 90 \mu\text{C}/\text{cm}^2$ +
Polar instability from Bi lone pairs
Anti-ferromagnetic (weak FM)

*“Epitaxial BiFeO_3 multiferroic thin film heterostructures”,
Wang, Spaldin, Ramesh et al., Science 299, 1719 (2003)*



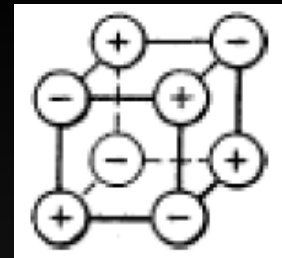
THE “HOLY GRAIL”: BiFeO_3

- A room-temperature multiferroic: FE and AFM (or weak FM)
- Good agreement between theory and experiments for P ($\sim 100 \mu\text{C}/\text{cm}^2$ along $[111]$ or, equivalently, $\sim 60 \mu\text{C}/\text{cm}^2$ along $[001]$)



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

BiFeO₃: MAGNETISM

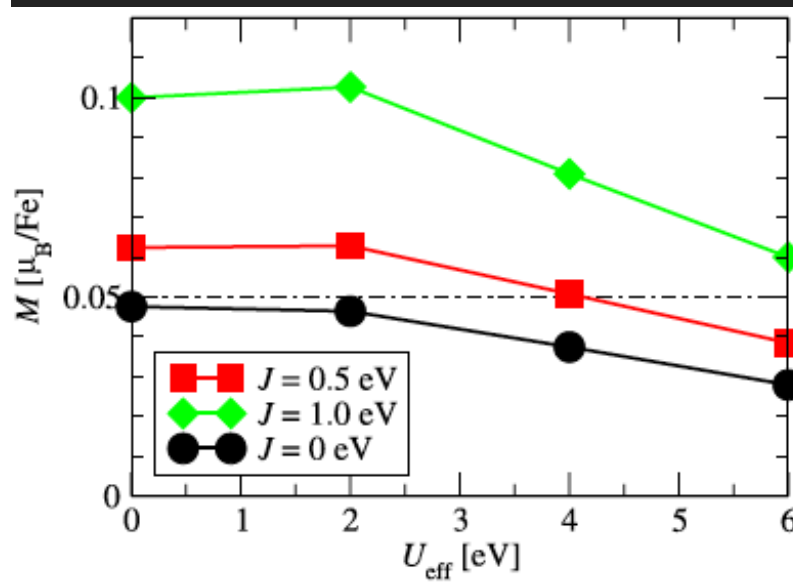
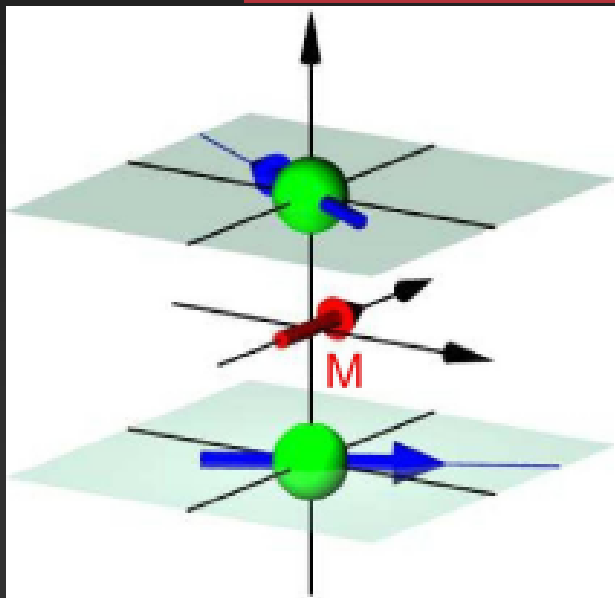


- Bulk: G-type AFM and cycloidal modulation ($\lambda \sim 640$ nm)
- Thin films: the modulation disappears but a weak FM arises

Fe AFM moments are canted by up to $\sim 1^\circ$ due to Dzyaloshinskii-Moriya interaction

$$E_{\text{DM}} = -\frac{1}{2} \vec{D} \cdot (\vec{M}_{\text{Fe1}} \times \vec{M}_{\text{Fe2}}) = -\vec{D} \cdot (\vec{L} \times \vec{M})$$

$$\vec{M} = \vec{M}_{\text{Fe1}} + \vec{M}_{\text{Fe2}} ; \vec{L} = \vec{M}_{\text{Fe1}} - \vec{M}_{\text{Fe2}}$$

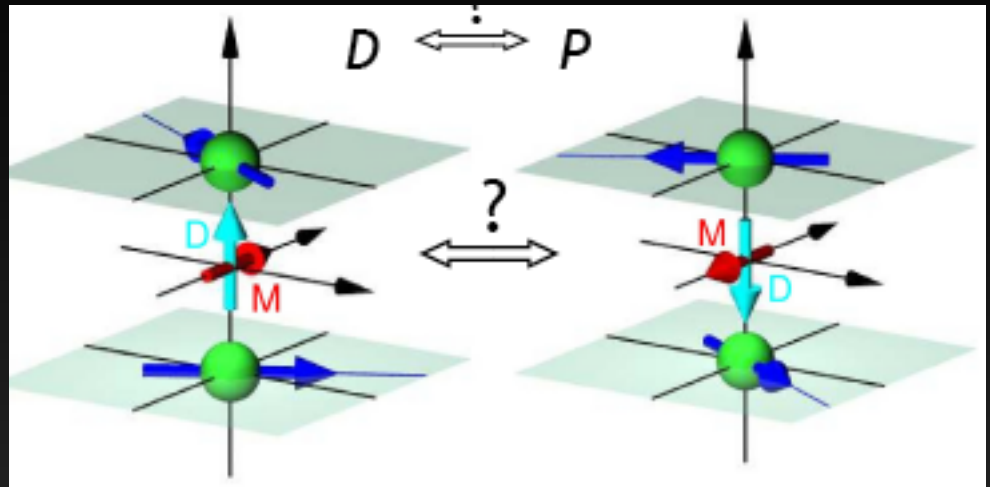


C. Ederer and N.A. Spaldin, PRB 71, 060401 (2005)

BiFeO₃: MAGNETISM

Is the canting
coupled to
polarization ?

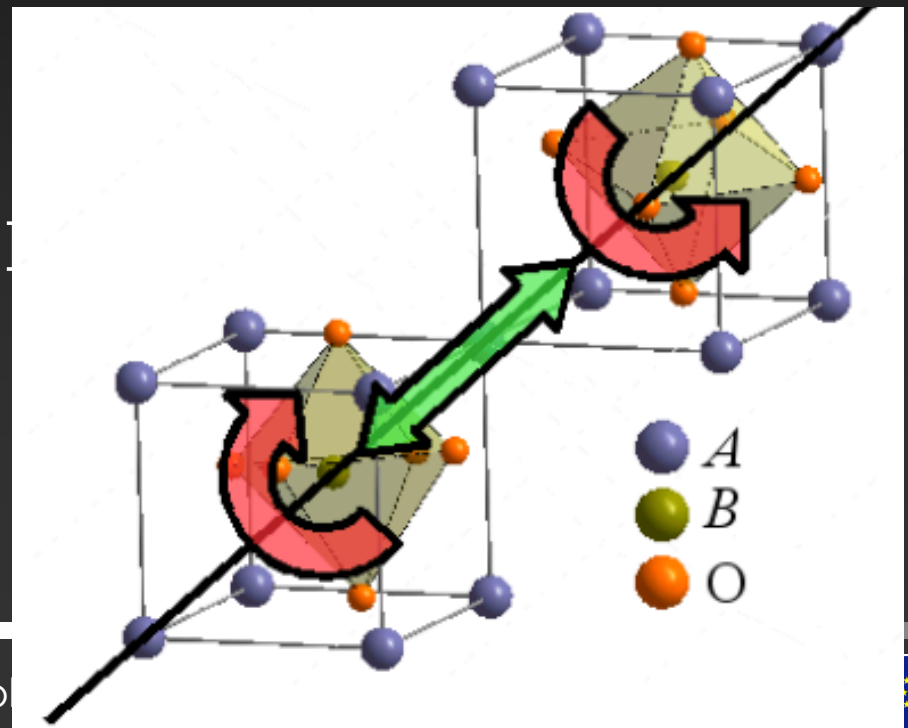
Can I switch the weak
moment by E-field?



No! Two different modes in BFO:

1. Polar displacements along $[111]$
2. Octahedral counter-rotations

.... and DM is related to Oxygen
octahedral rotations



HYBRID FUNCTIONALS

Linear combination of Hartree-Fock-exchange and of DFT (parametrized) exchange:

$$E_{xc}^{\text{Hybrid}} = a E_x^{\text{HF}} + (1-a) E_x^{\text{PBE}} + E_c^{\text{HPBE}}$$

The parameter a can be theoretically derived: $a = 1/4$ for PBE0

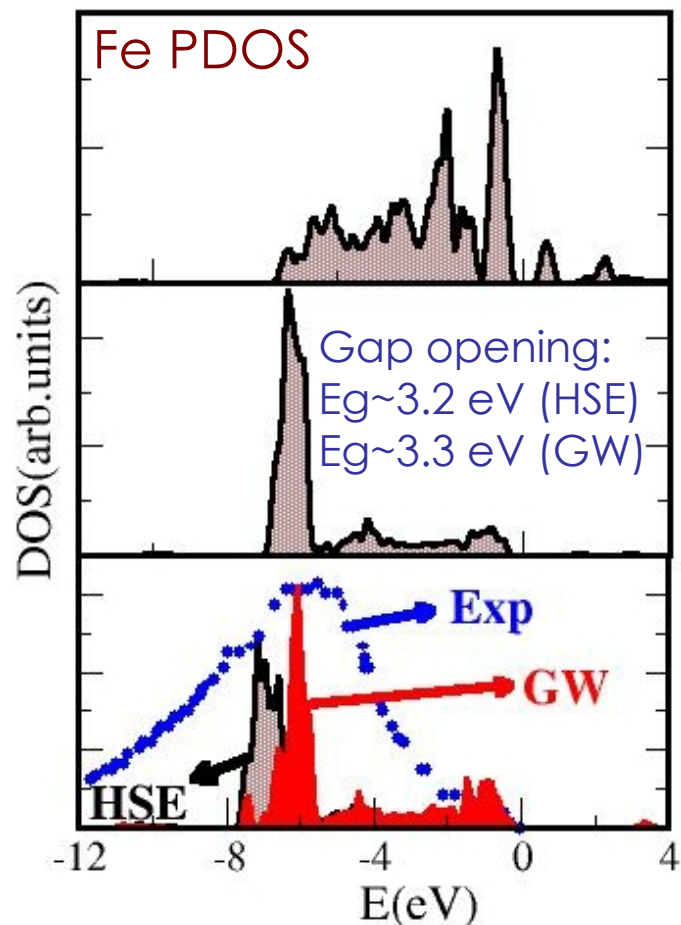
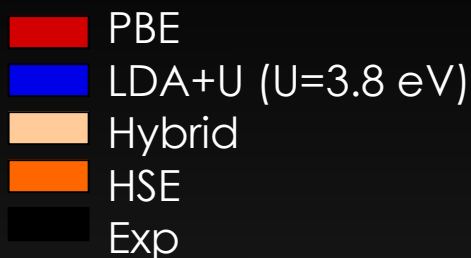
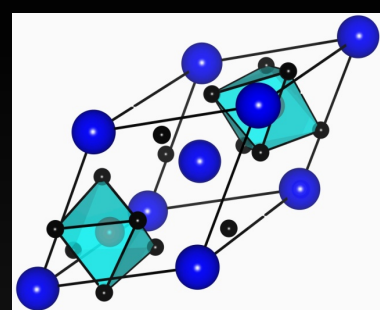
$$E_{xc}^{\text{Hybrid}} = 1/4 E_x^{\text{HF}} + 3/4 E_x^{\text{PBE}} + E_c^{\text{HPBE}}$$

Heyd-Scuseria-Erzenhof (HSE) Functional*: mixing only of the short-range (SR) component of the HF exchange:

$$E_{xc}^{\text{HSE}} = 1/4 E_x^{\text{HF,SR}}(\mu) + 3/4 E_x^{\text{PBE,SR}}(\mu) + E_x^{\text{PBE,LR}} + E_c^{\text{HPBE}}$$

* J. Heyd et al., J. Chem. Phys. **118**, 8207 (2003).

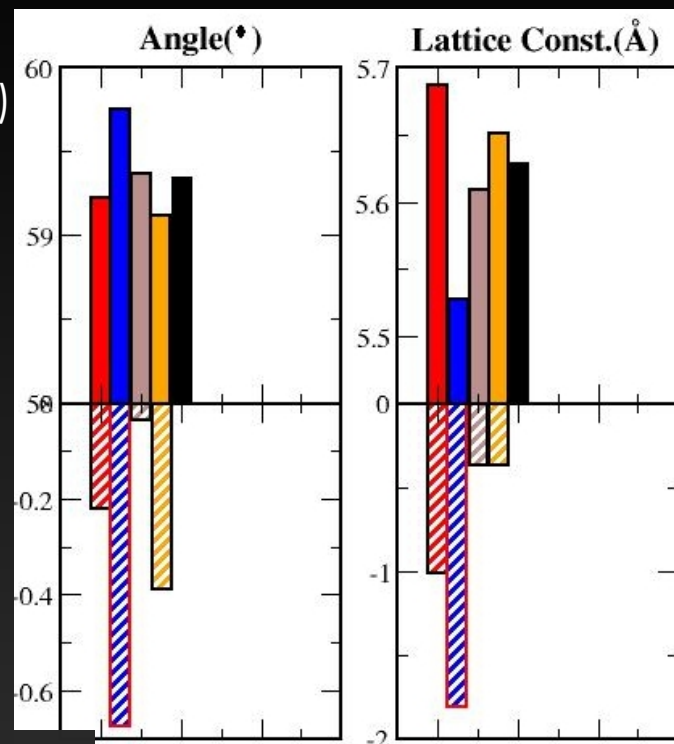
HYBRID FUNCTIONALS FOR BiFeO_3



.... Exp (PRB.78,085106,2008)

___ GW (G. Kresse, priv. comm.)

PROPERTIES:
 ✓ **STRUCTURAL**



Polarization ($\mu\text{C}/\text{cm}^2$)

BiFeO_3	P_{ionic}	P_{ele}	P_{tot}	P_{PCM}
PBE	171.14	-65.56	105.50	87.84
HSE	177.39	-67.09	110.30	103.36

IMPROPER FERROELECTRICITY IN MAGNETS

What do we mean by “improper ferroelectricity”?

Concepts:

how to break inversion symmetry
via spin- or charge-ordering

Frustration

Examples: manganites and metal-organic frameworks

BREAKING INVERSION SYMMETRY IN MAGNETS

Conventional

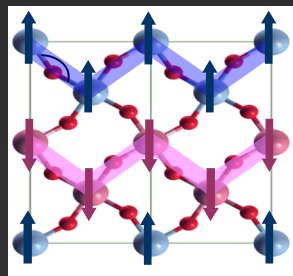
FERROELECTRICITY $\longleftrightarrow$ no Inversion Symmetry

- “Proper”
- **Ionic displac.** break inversion symmetry (IS)
- “**Covalency**”-driven

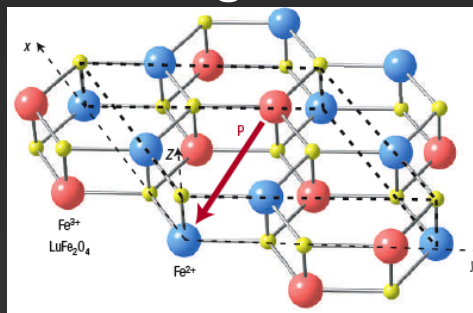
- “Improper”
- **Electron degrees of freedom** break IS
- “**Correlation**”-driven

Non-Conventional

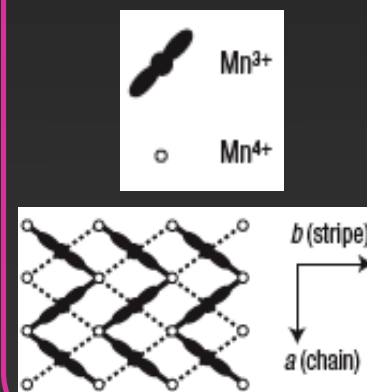
Spin-order
(some AFM or “spiral”)



Charge-order

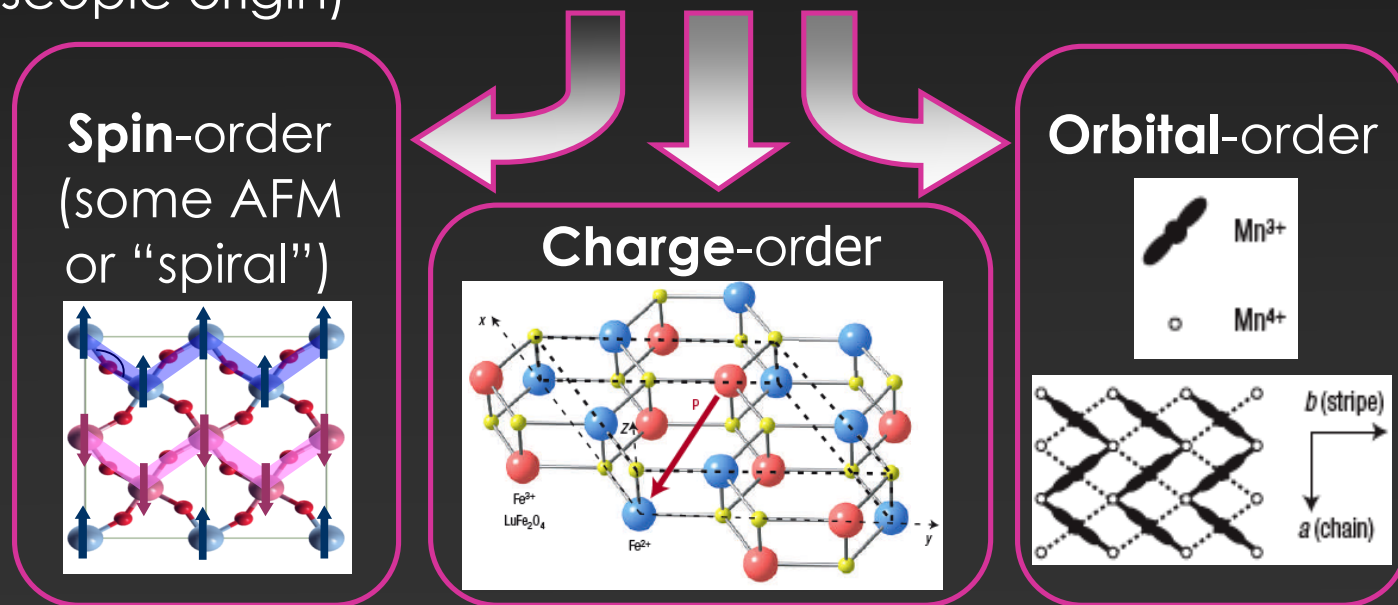


Orbital-order

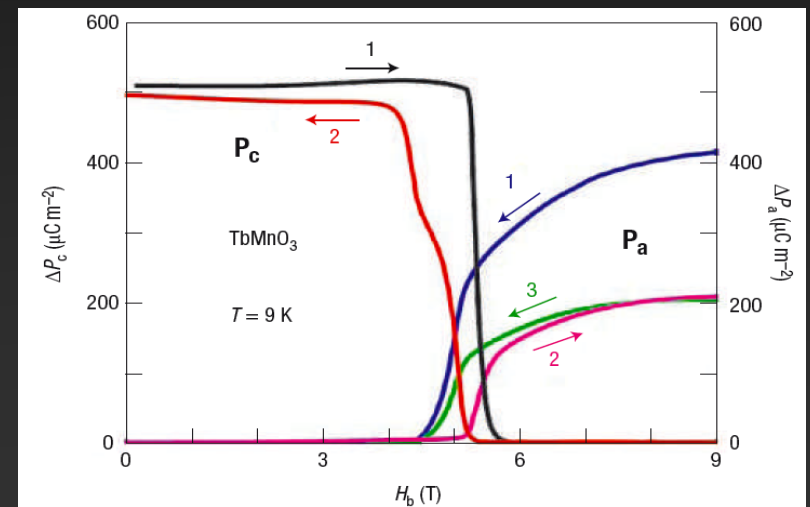
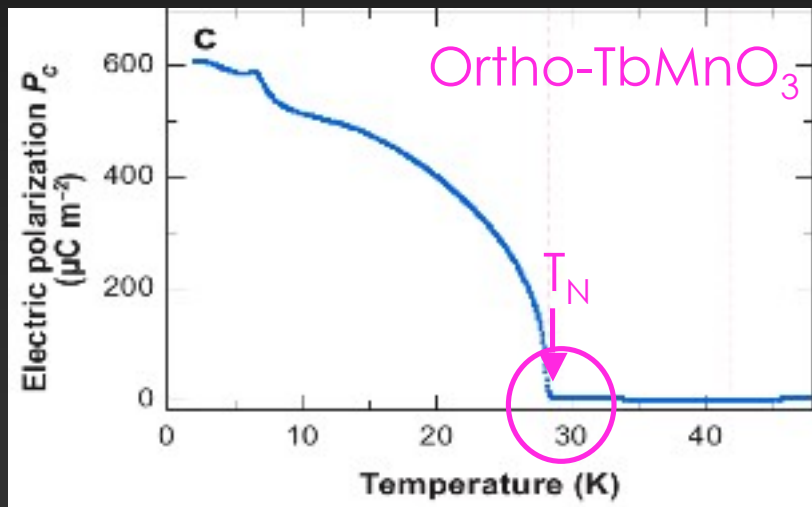
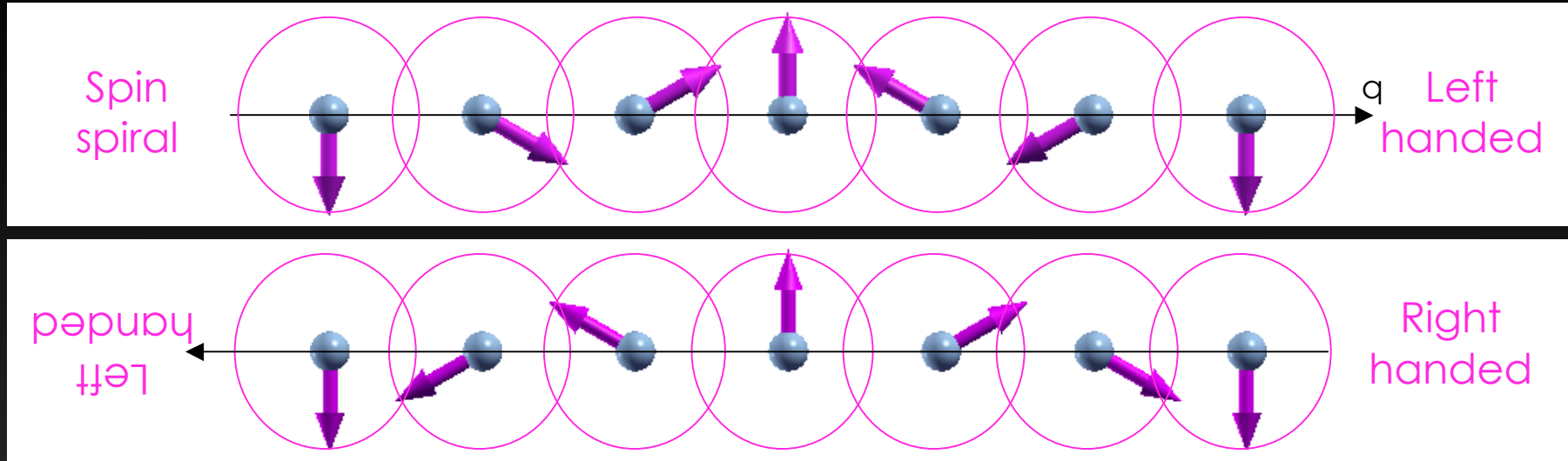


Main **advantages** over **proper multiferroics**:

- displacements/switching involve *electrons* rather than *ions*
⇒ **switching** should be much **faster**
⇒ better as for “fatigue”
- especially for spin-induced ferroelectricity
⇒ **magnetoelectric coupling** should be much **stronger**
(as magnetism and ferroelectricity share the same microscopic origin)



HOW MAGNETIC ORDERING CAN BREAK INV. SYM.?



T.Kimura et al., Nature **425**, 55 (03); S.W.Cheong and M.Mostovoy, Nature Mater. **6**, 13 (07)

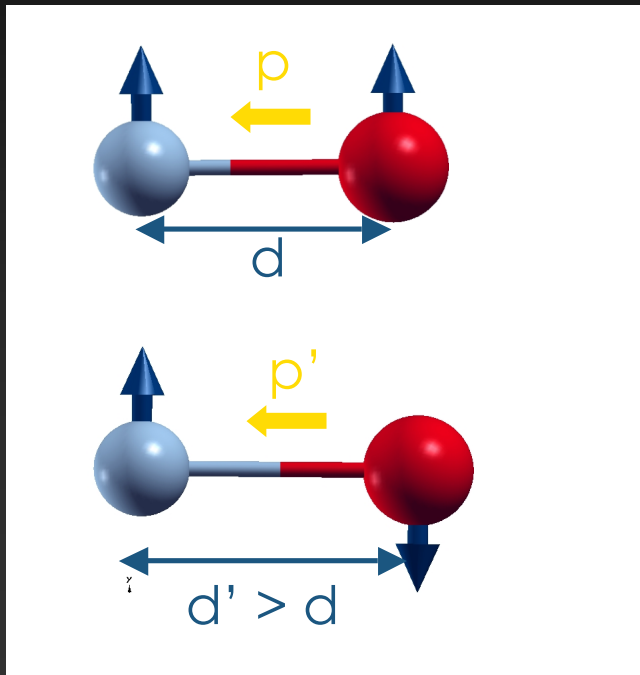
DZYALOSHINSKII-MORIYA VS HEISENBERG

$$\mathbf{p} \propto \mathbf{r}_{ij} \times (\mathbf{S}_1 \times \mathbf{S}_2)$$

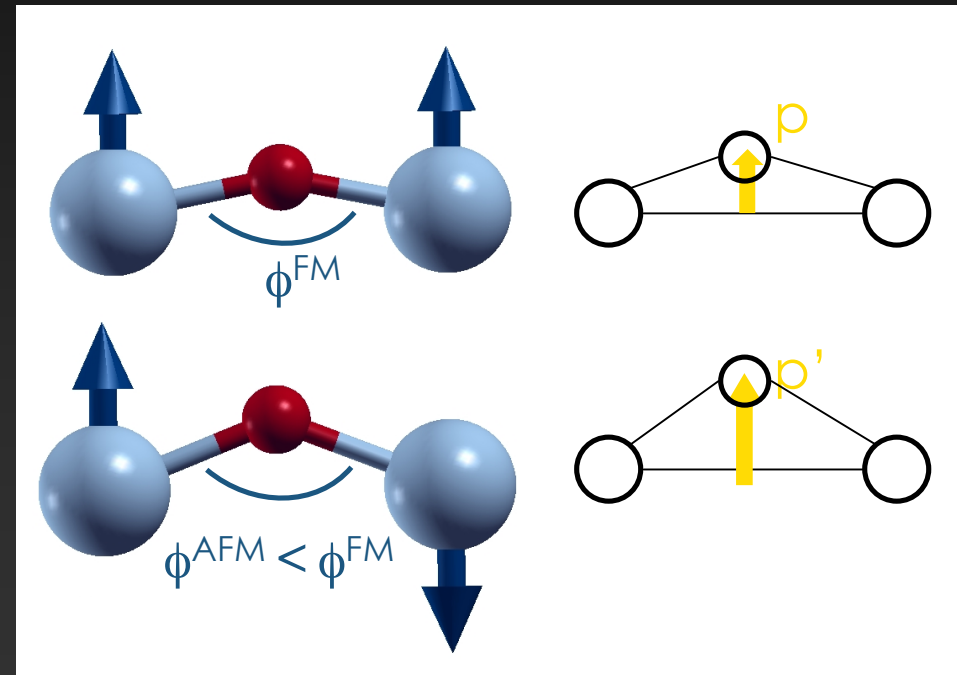
Vector coupling: Requires non-collinear spins

$$\mathbf{p} \propto (\mathbf{S}_1 \cdot \mathbf{S}_2)$$

Scalar coupling: Works with collinear spins



Direct exchange striction



Superexchange striction

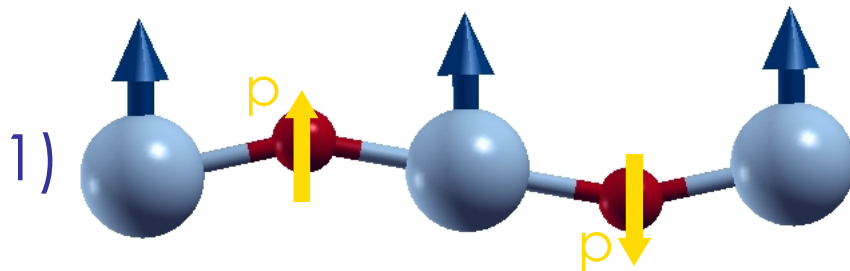
DZYALOSHINSKII-MORIYA VS HEISENBERG

$$\mathbf{p} \propto \mathbf{r}_{ij} \times (\mathbf{S}_1 \times \mathbf{S}_2)$$

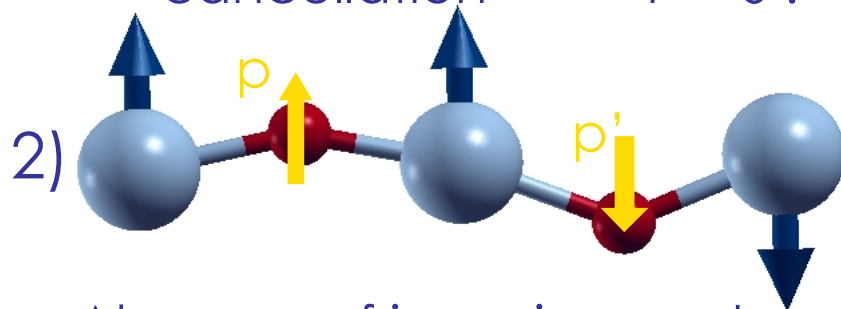
Vector coupling: Requires non-collinear spins

$$\mathbf{p} \propto (\mathbf{S}_1 \cdot \mathbf{S}_2)$$

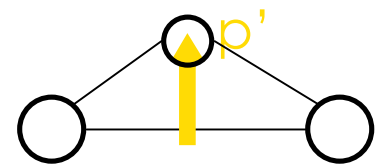
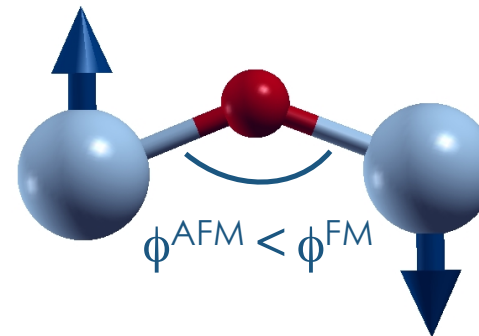
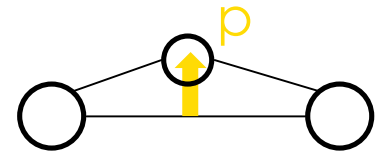
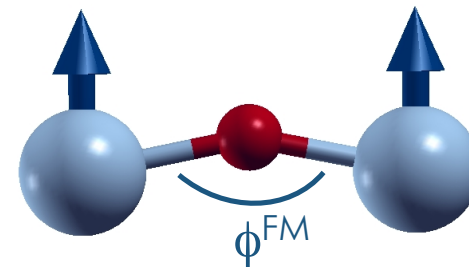
Scalar coupling: Works with collinear spins



Through center of symmetry:
cancellation $\Rightarrow P = 0$!



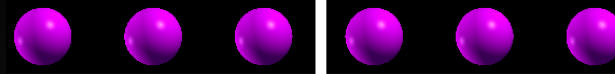
Absence of inversion center:
 P finite!



Superexchange striction

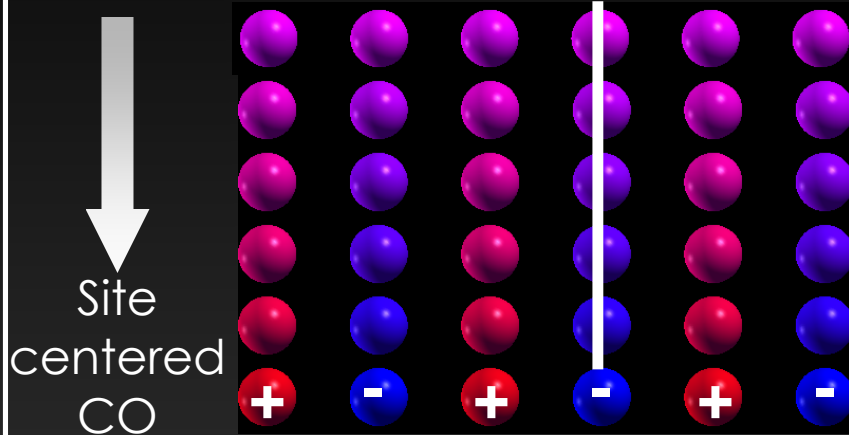
HOW CHARGE ORDERING CAN BREAK INV. SYM.?

Neutral chain



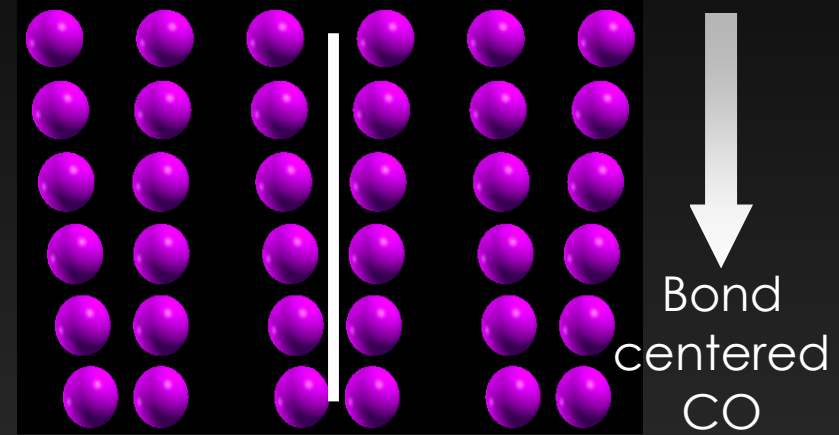
Inversion center: no P

"Pure" charge-ordering



Inversion center: no P

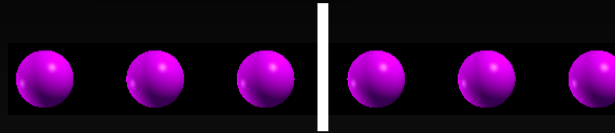
Structural dimerization



Inversion center: no P

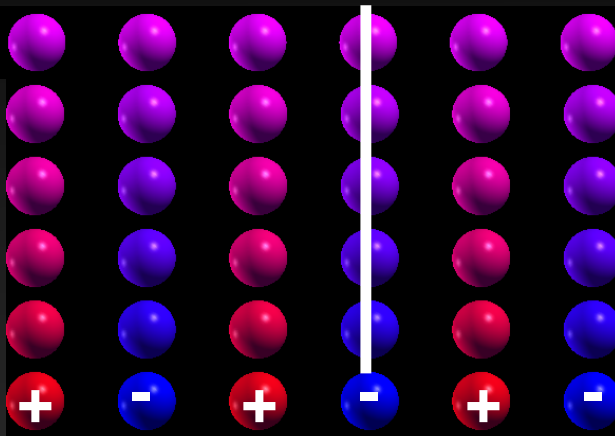
HOW CHARGE ORDERING CAN BREAK INV. SYM.?

Neutral chain

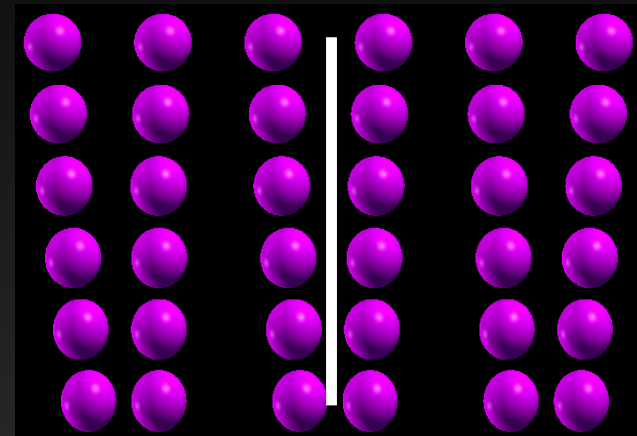


Inversion center: no P

“Pure” charge-ordering

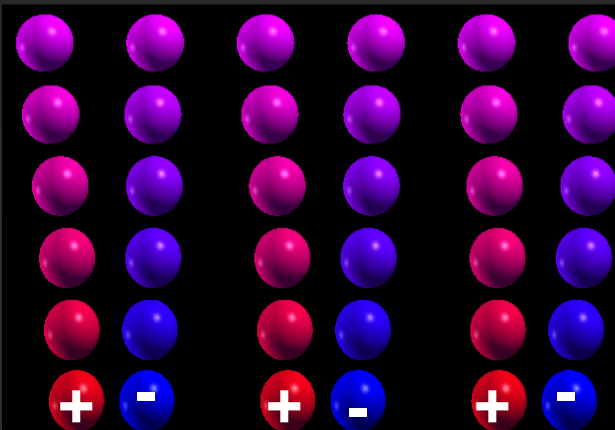


Structural dimerization

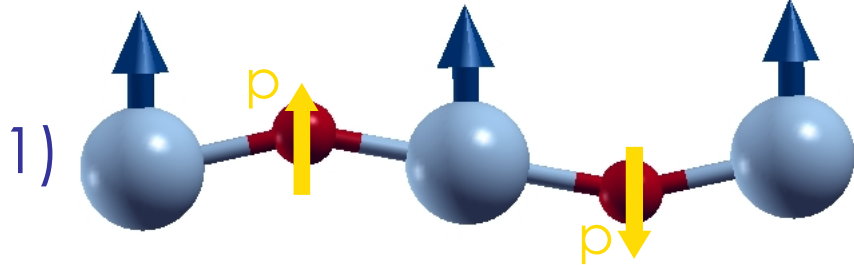


Combination

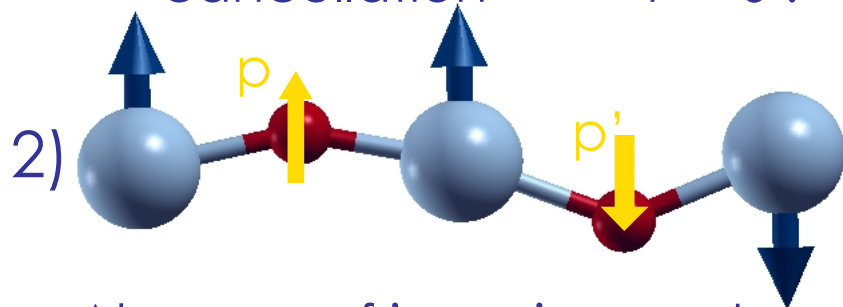
Intermediate
Bond- and site-
centered
CO



Absence of
inversion
center:
**it can be
polar !!**



Through center of symmetry:
cancellation ==>> $P = 0$!



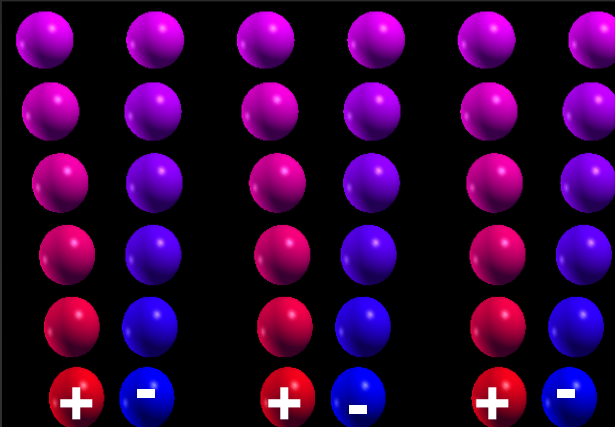
Absence of inversion center:
 P finite!

... but these are
just “*sketches*” ...
In practice we have to find
materials where these
“*local*” dipoles
are periodically repeated

⇒ **polar space groups**

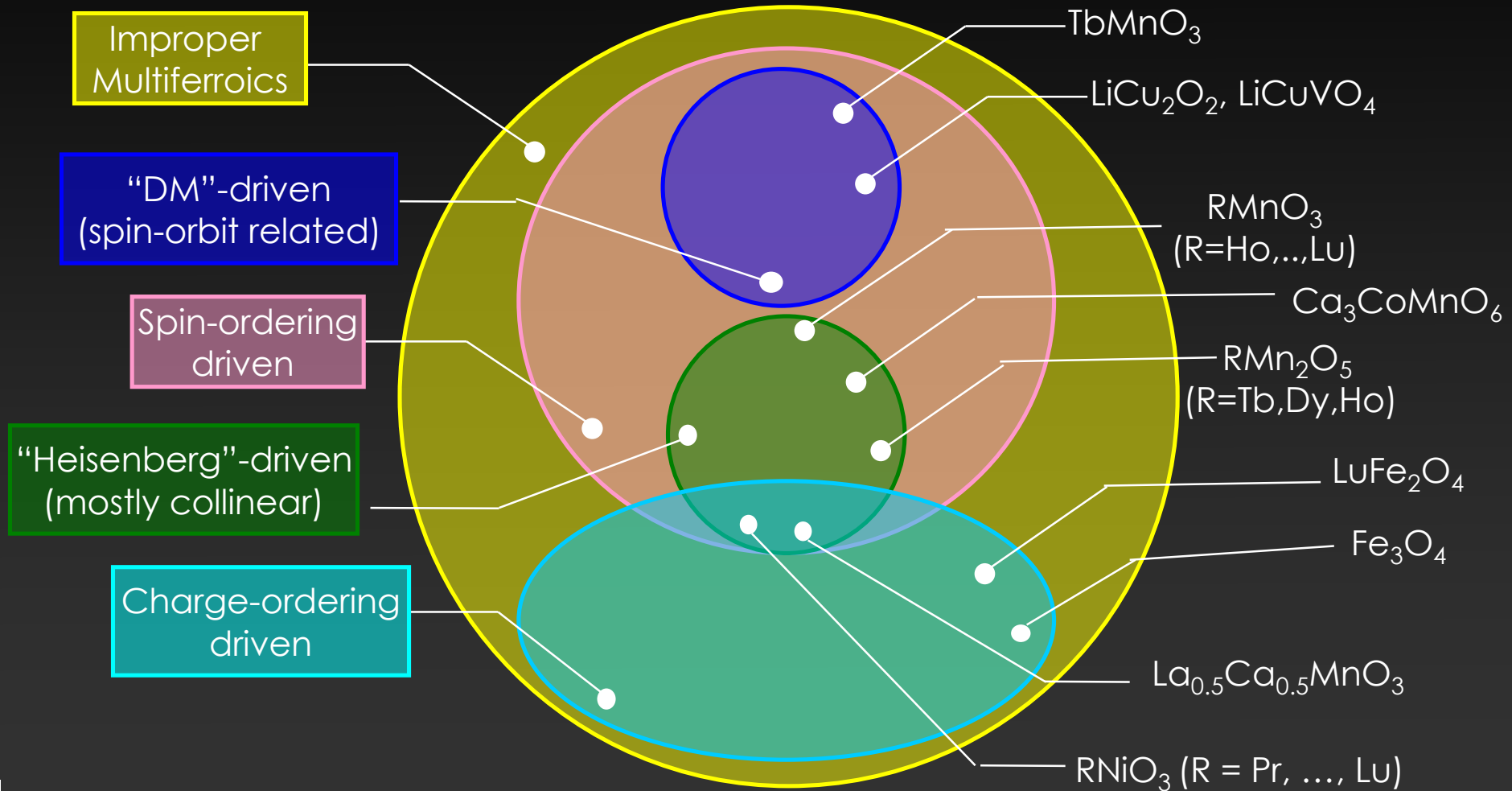
Combination

Intermediate
Bond- and site-
centered
CO

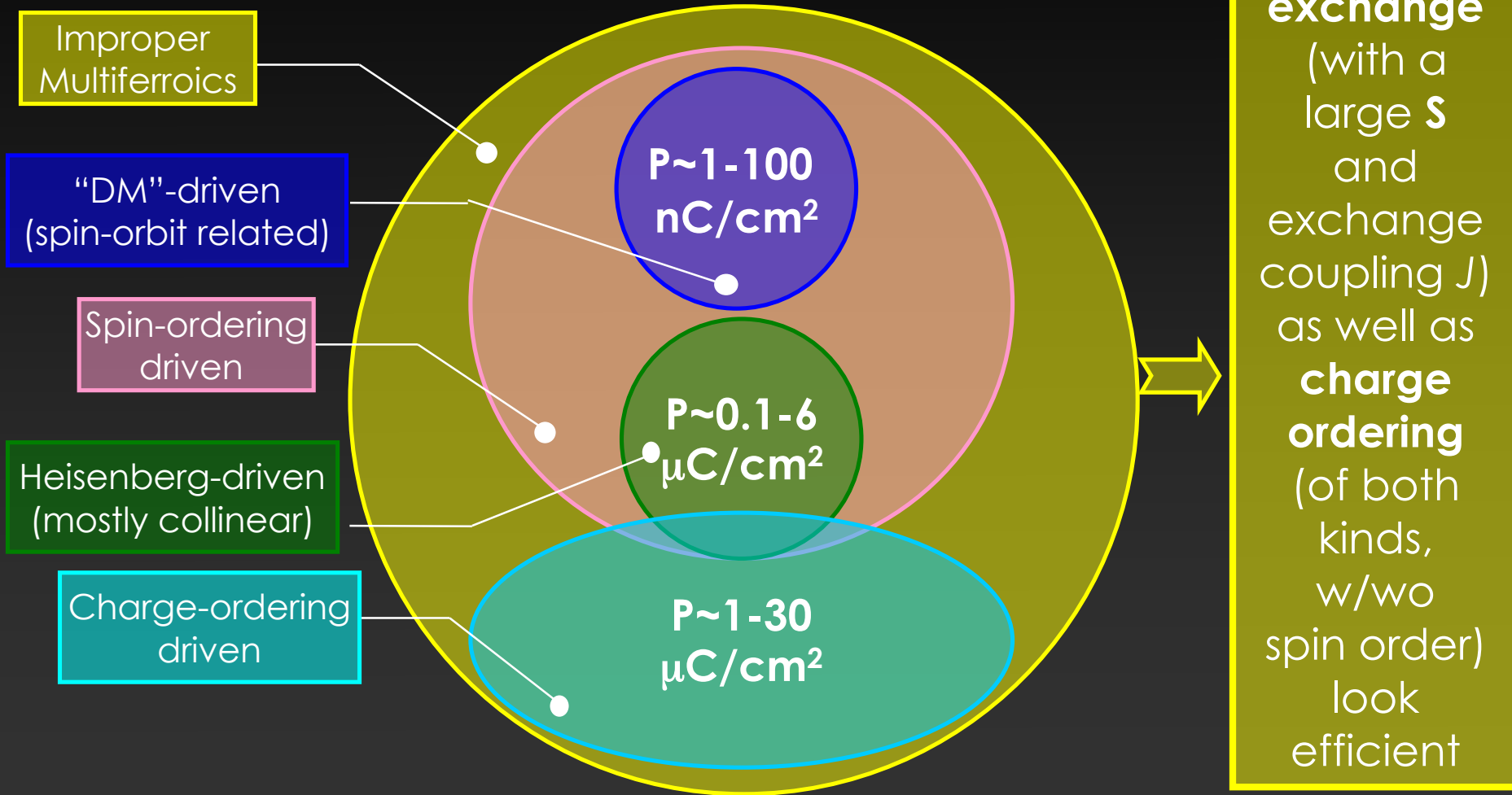


Absence of
inversion
center:
**it can be
polar !!**

CLASSIFICATION OF IMPROPER MULTIFERROICS

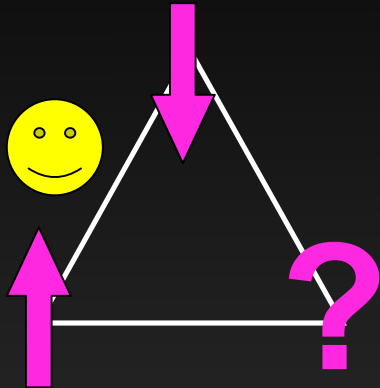


WHAT ABOUT THE SIZE OF P?

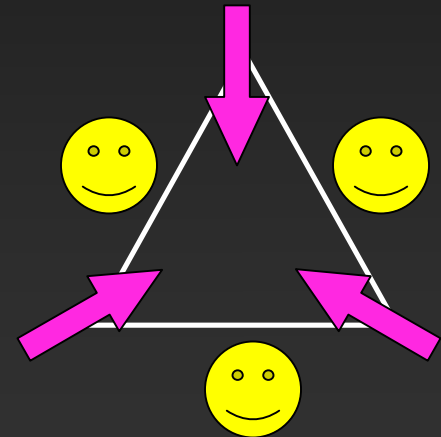
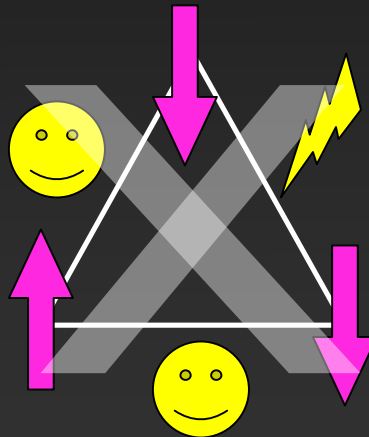
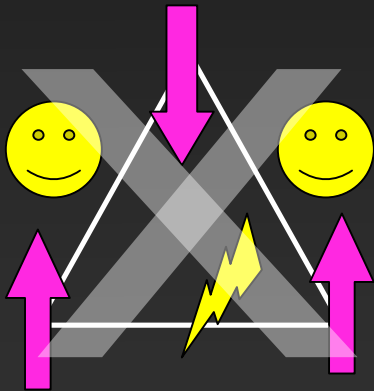


FRUSTRATION IN MAGNETS

Spins on a triangular lattice with AFM coupling

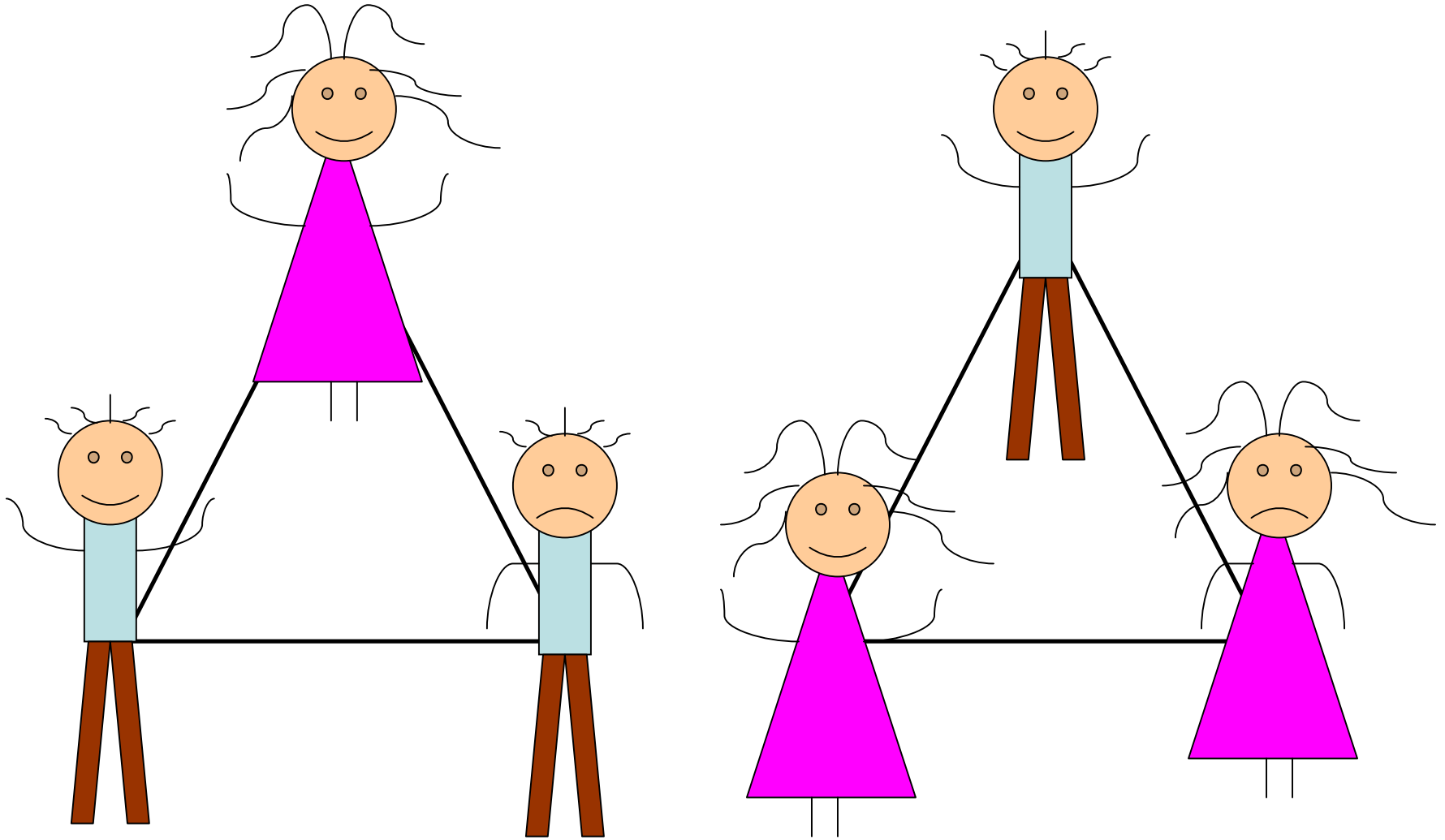


What about the third spin ????



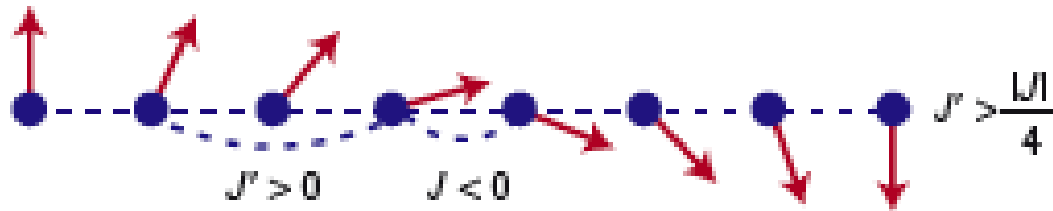
=>> Complex non-collinear spin configurations !!

FRUSTRATION IN MAGNETS



FRUSTRATION IN MAGNETS

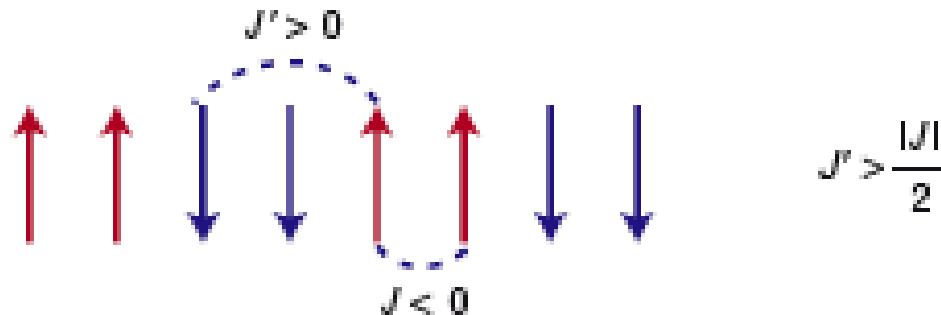
Frustrated spin chains with the nearest-neighbour FM and next-nearest-neighbour AFM interactions J and J' .



The spin chain with isotropic (Heisenberg)

$$H = \sum_n [J \mathbf{S}_n \cdot \mathbf{S}_{n+1} + J' \mathbf{S}_n \cdot \mathbf{S}_{n+2}].$$

For $J' / |J| > 1/4$ its classical ground state is a **magnetic spiral**.



The chain of Ising spins $\sigma_n = \pm 1$, with energy

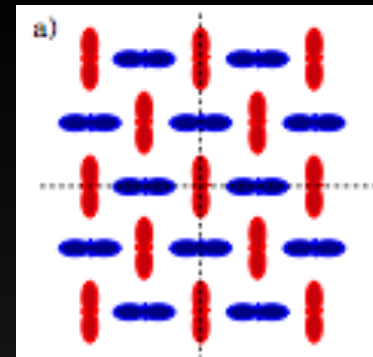
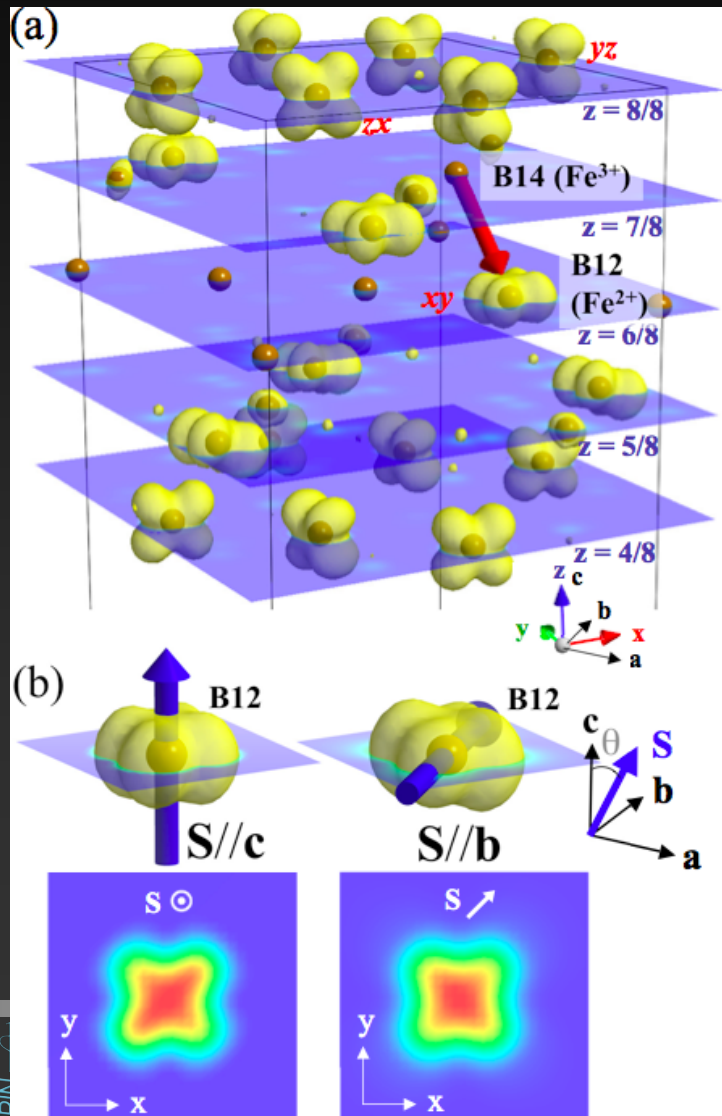
$$H = \sum_n [J \sigma_n \sigma_{n+1} + J' \sigma_n \sigma_{n+2}]$$

has the **up-up-down-down** ground state for $J' / |J| > 1/2$.

ROLE OF ORBITAL ORDERING

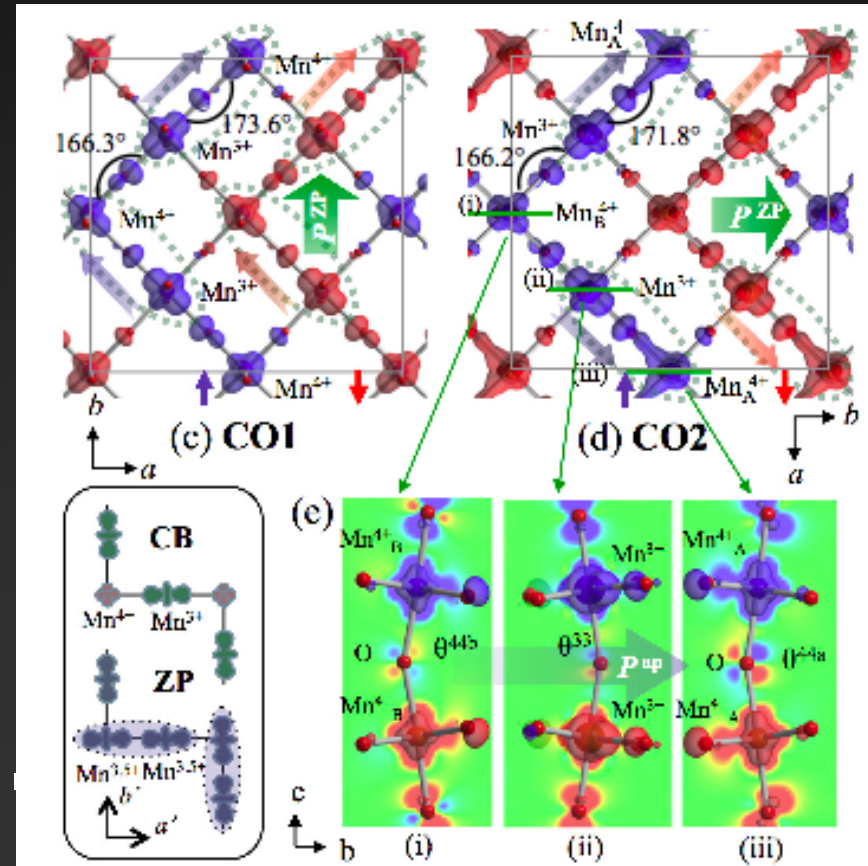
It does not break inversion symmetry by itself, but it is a needed ingredient in many cases !

MAGNETITE



- Mn^{3+} in RMnO_3
- Cu^{2+} in Cu-MOF

HALF-DOPED MANGANITES



TWO “OLD” EXAMPLES OF MULTIFERROICS

PRL 99, 227201 (2007)

PHYSICAL REVIEW LETTERS

week ending
30 NOVEMBER 2007

1

Dual Nature of Improper Ferroelectricity in a Magnetoelectric Multiferroic

S. Picozzi,¹ K. Yamauchi,¹ B. Sanyal,² I. A. Sergienko,^{3,4} and E. Dagotto^{3,4}

¹*Consiglio Nazionale delle Ricerche–Istituto Nazionale di Fisica della Materia (CNR-INFM), CASTI Regional Laboratory, 67010 L'Aquila, Italy*

²*Theoretical Magnetism Group, Department of Physics, Uppsala University, Box-530, SE-75121, Uppsala, Sweden*

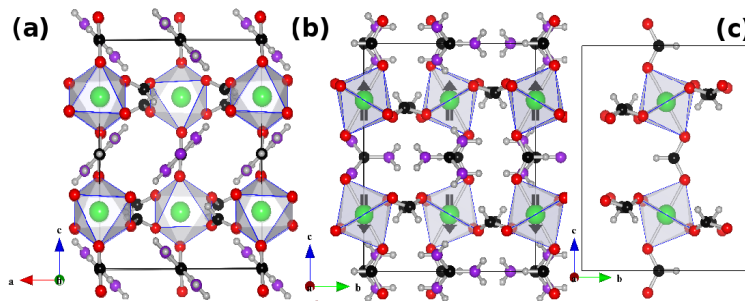
³*Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

⁴*Department of Physics & Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA*

(Received 8 May 2007; published 26 November 2007)

2

Multiferroics



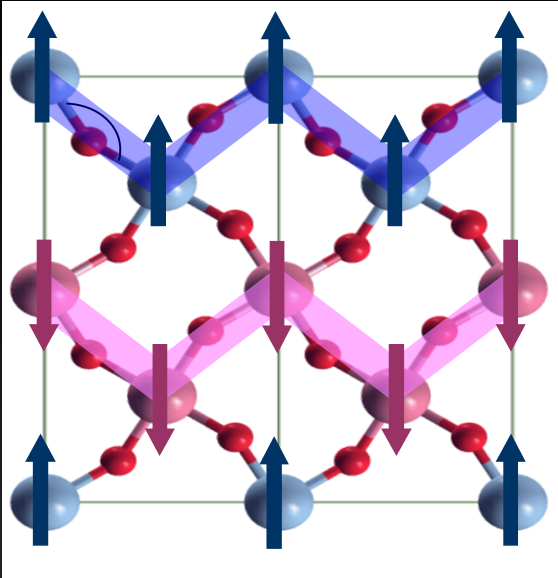
Angewandte
50 International Edition
Chemie

DOI: 10.1002/anie.201101405

Electric Control of Magnetization and Interplay between Orbital Ordering and Ferroelectricity in a Multiferroic Metal–Organic Framework**

Alessandro Stroppa,* Prashant Jain,* Paolo Barone, Martijn Marsman, Juan Manuel Perez-Mato, Anthony K. Cheetham, Harold W. Kroto, and Silvia Picozzi

E-TYPE MANGANITES: ELECTRONIC AND IONIC FERROELECTRICITY



• In collaboration with:

K. Yamauchi (*now at Osaka*)



I. A. Sergienko, E. Dagotto
(*Oak Ridge Natl. Lab, Univ. Tennessee, TN*)

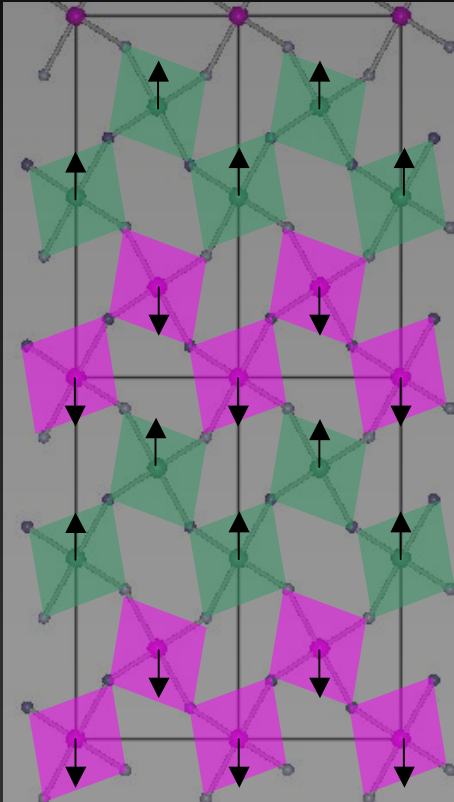


WHY THE AFM-E SHOULD BE FERROELECTRIC ?

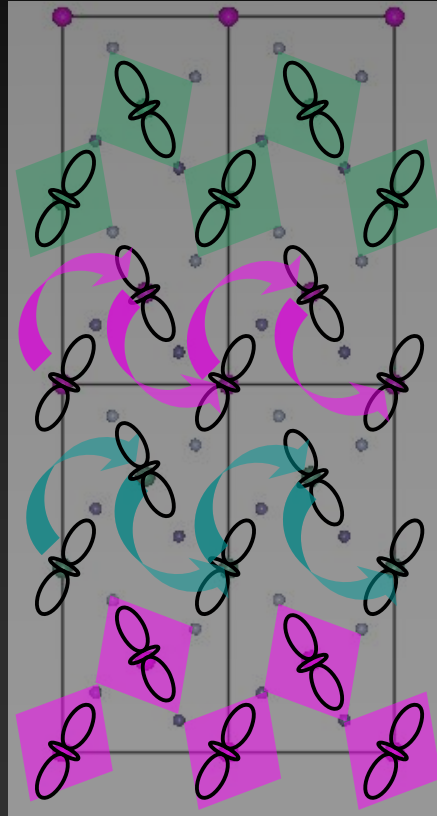
- “Electronic” mechanisms

- e_g Orbital Ordering

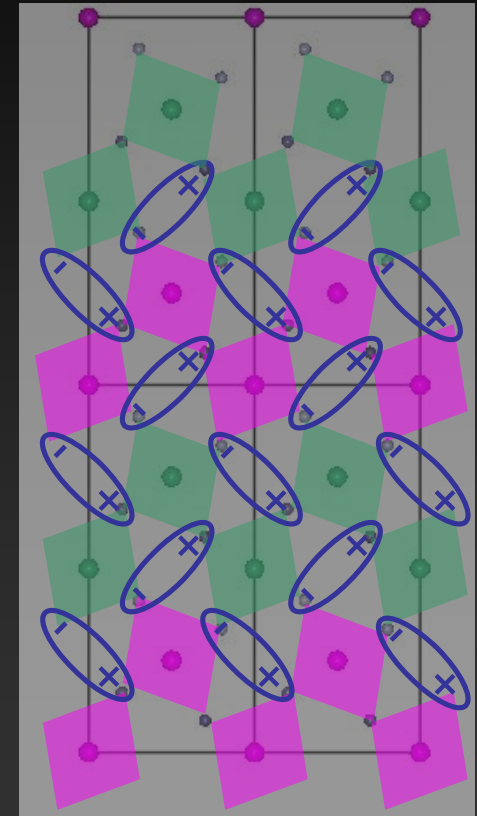
- Oxygen inequivalency



a
c



P

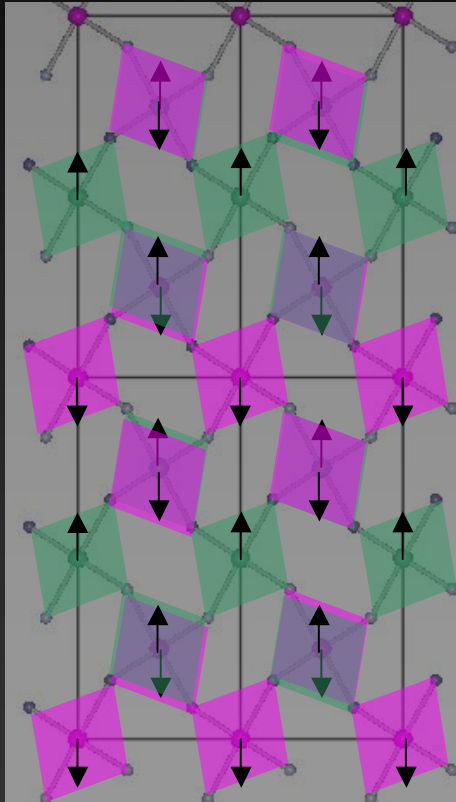


P

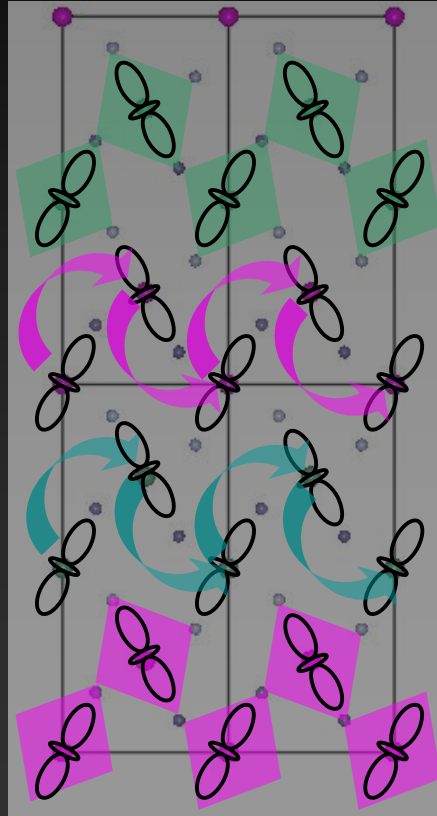
WHY THE AFM-E SHOULD BE FERROELECTRIC ?

- “Switching” mechanisms: change direction of some spins

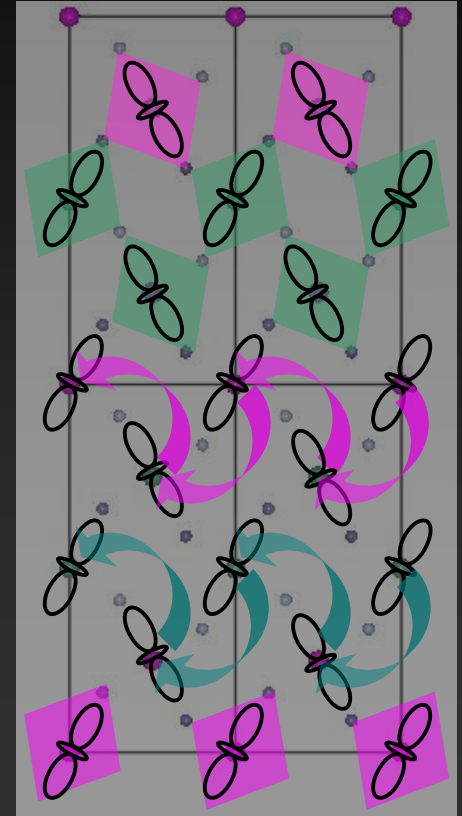
- e_g Orbital Ordering



a
c



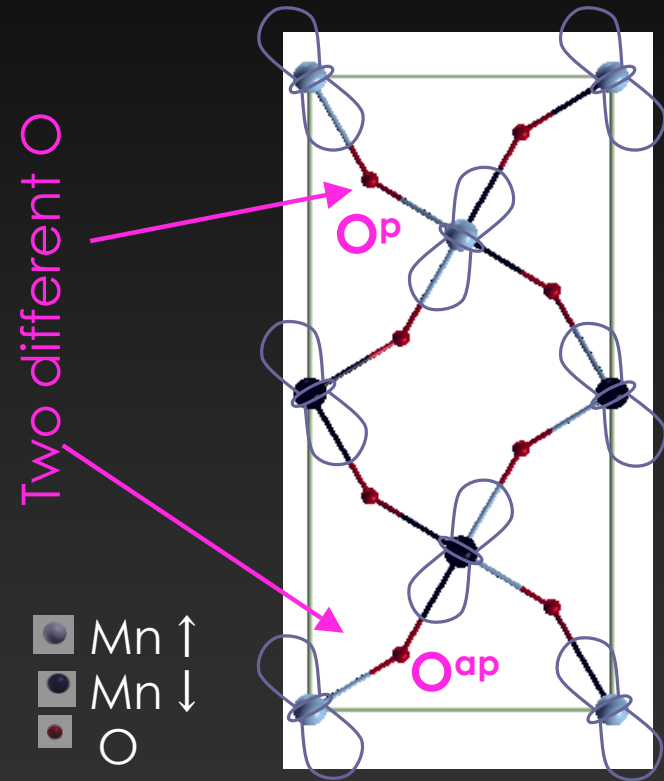
P



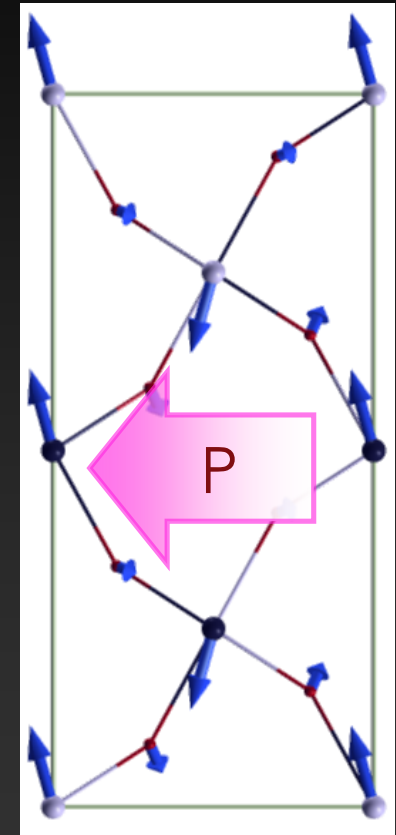
d

WHY THE AFM-E SHOULD BE FERROELECTRIC ?

- “Structural” contributions: Magnetostriction



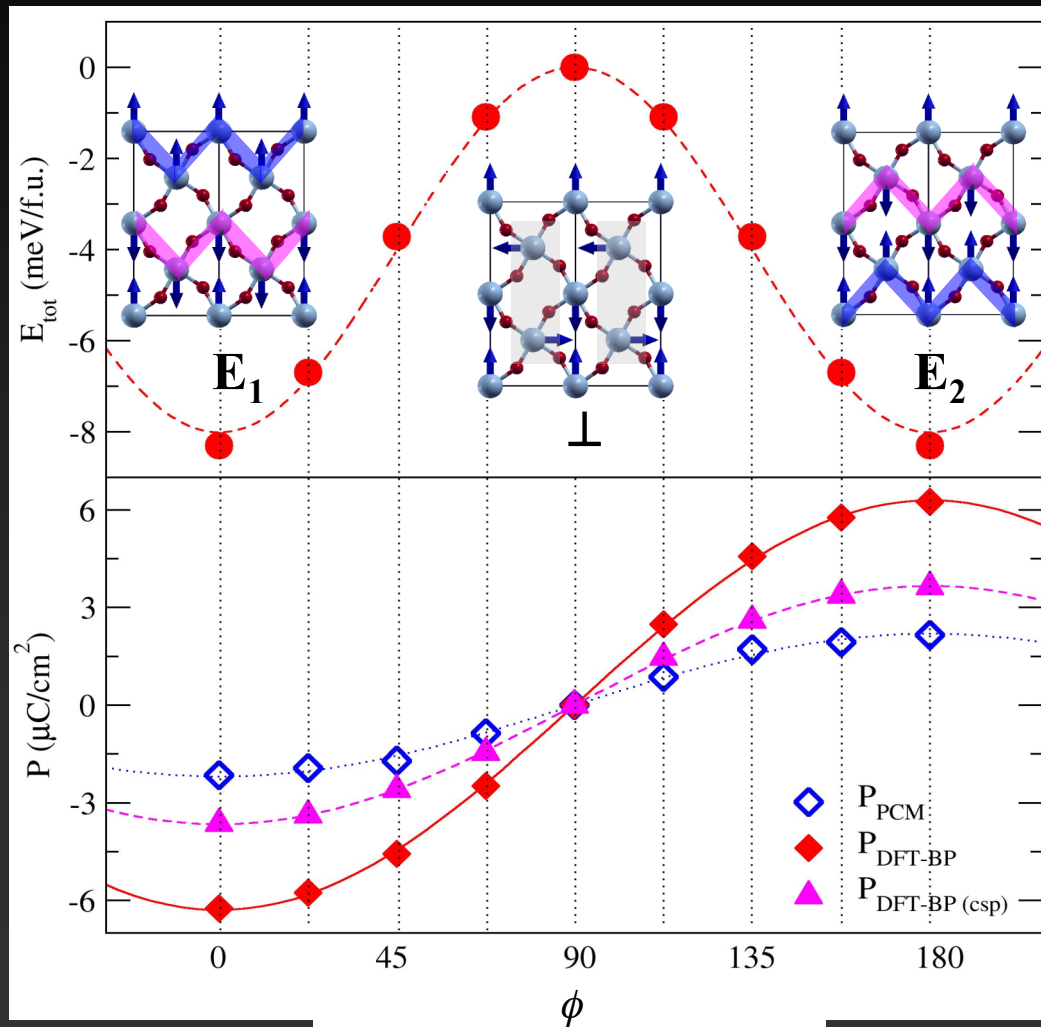
In-plane Mn and O displacements pattern from centrosymmetric AFM-A to non-centrosymmetric AFM-E

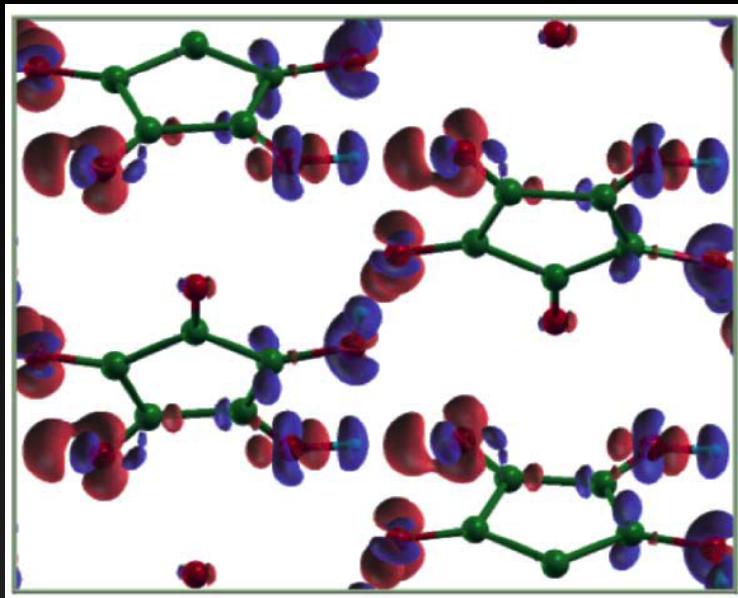


ORTHO-HoMnO3 AS A MAGNETICALLY DRIVEN FERROELECTRIC

- First *ab-initio* calculation of P driven by AFM*
- P is $\sim$ few $\mu\text{C}/\text{cm}^2$ (highest among magnetic improper ferroelectrics)
- FE switching path via spin-rotations
- Dual nature of P in real compounds: ionic displacements *and* electronic/magnetic effects are both important

* S. Picozzi, K. Yamauchi, B. Sanyal, I. Sergienko, E. Dagotto, PRL 99, 227201 (2007)

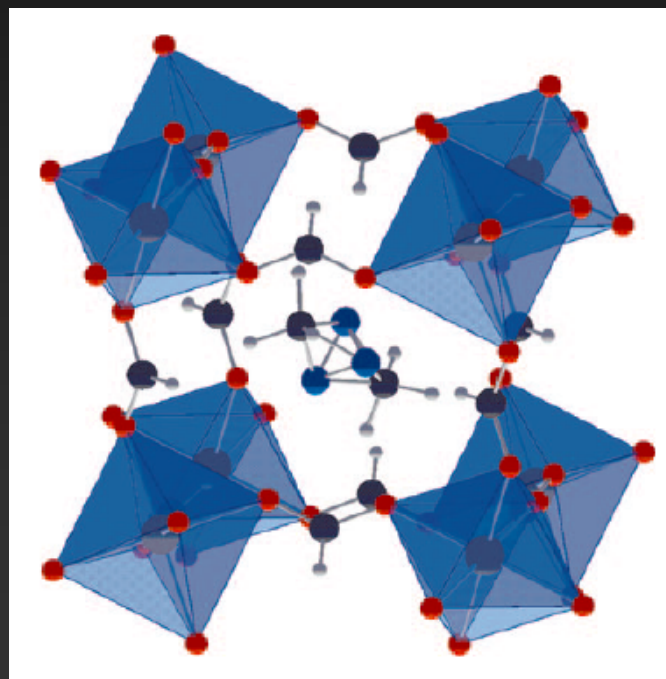


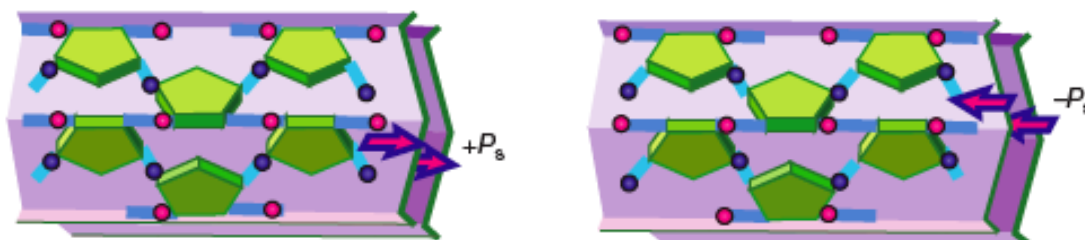


ORGANICS & HYBRIDS

• In collaboration with:

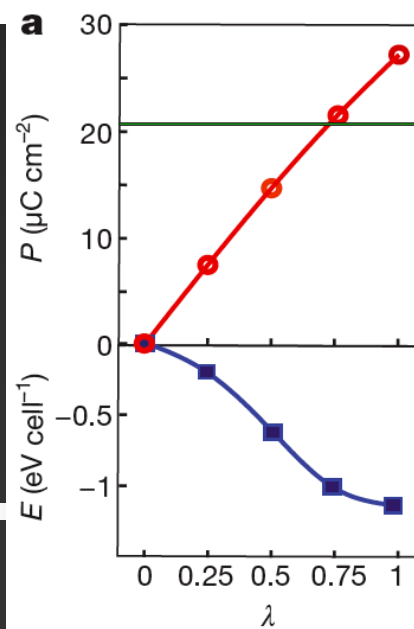
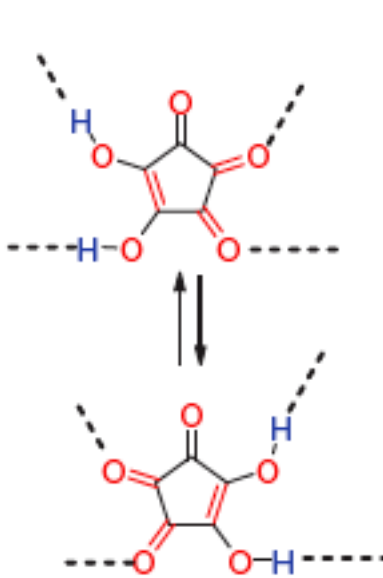
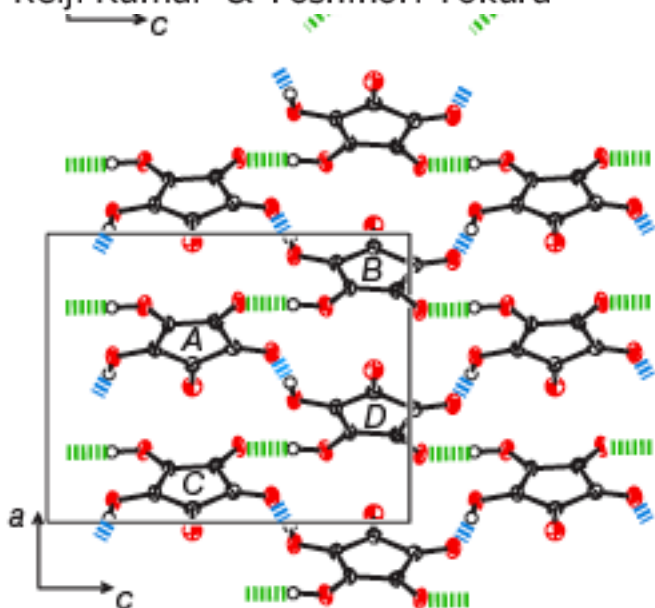
A. Stroppa (*CNR-SPIN*)
 S. Horiuchi, Y. Tokura (*Univ. Tokyo*)
 S. Kumar, J. Van den Brink (*IFW Dresden*)
 A.K. Cheetham (*Univ. Cambridge*)
 P. Jain, H. W. Kroto (*Florida State Univ*)



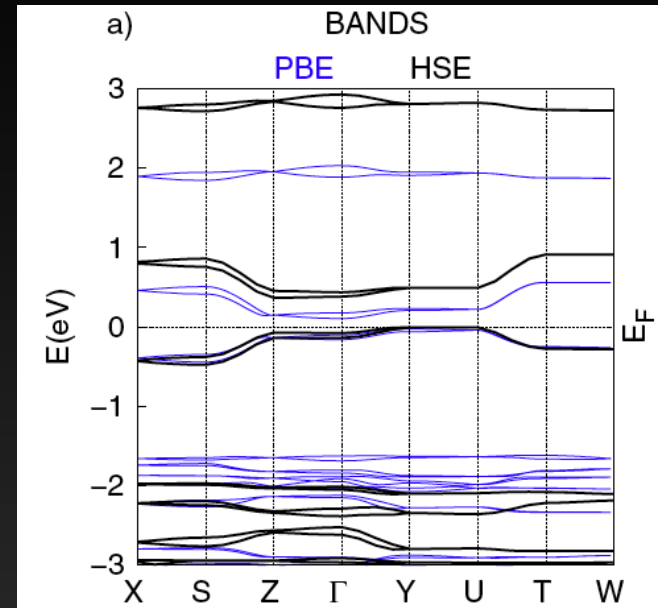
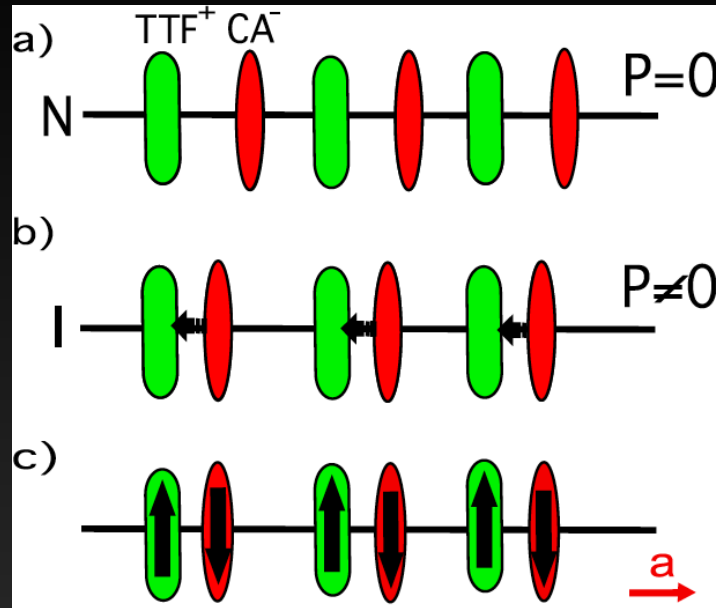
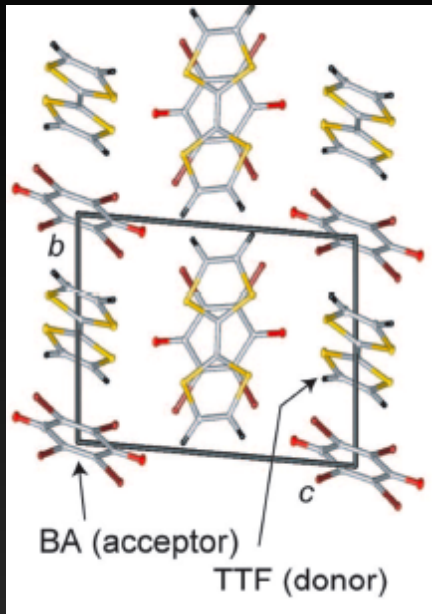


Above-room-temperature ferroelectricity in a single-component molecular crystal

Sachio Horiuchi¹, Yusuke Tokunaga², Gianluca Giovannetti^{3,4}, Silvia Picozzi³, Hirotake Itoh², Ryo Shimano^{2,5}, Reiji Kumai¹ & Yoshinori Tokura^{1,2,6}

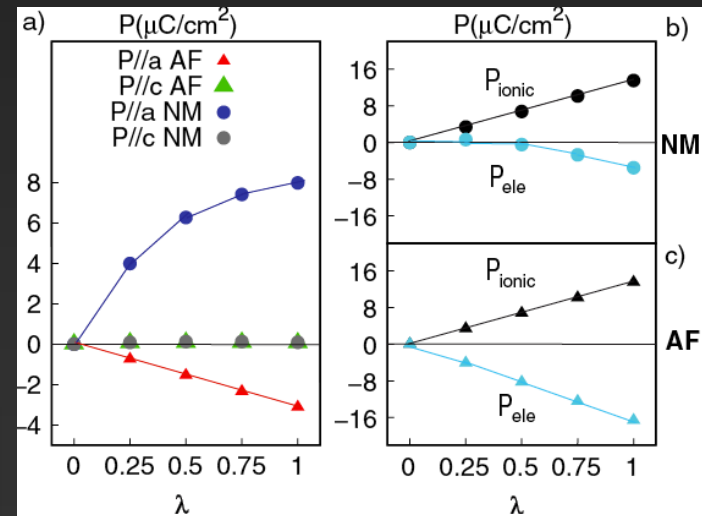


TTF-CA: SPIN-PEIERLS AS A SOURCE OF P ?



• SPIN PEIERLS: One-dimensional Heisenberg spin 1/2 chain $\Rightarrow$ instability to a dimer-singlet (gain of symmetric exchange)

• TTF-CA: Under the neutral-ionic transition ($T_{\text{NIT}} = 81 \text{ K}$): long-short bond alternation

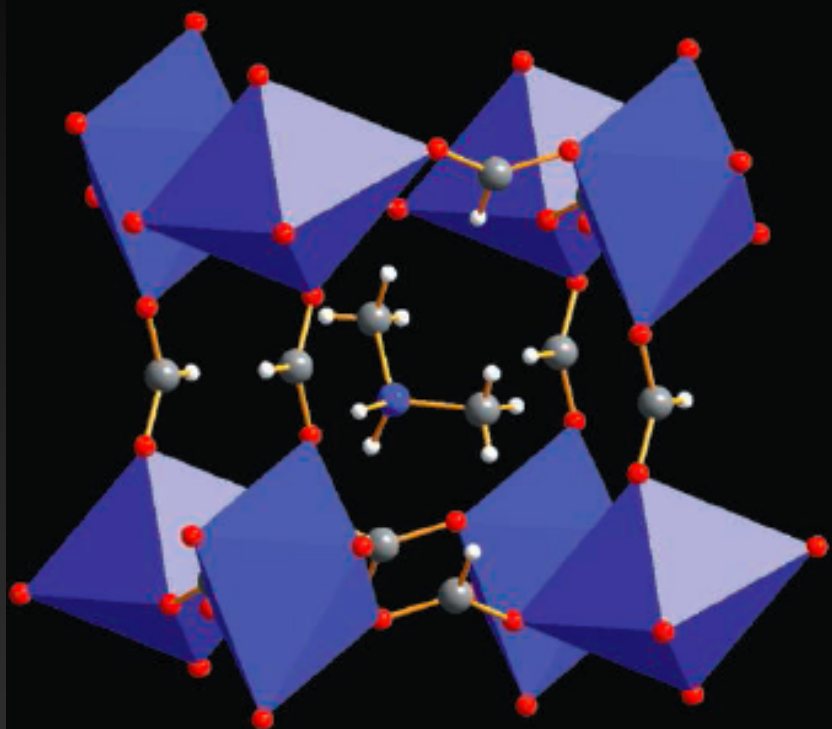


There's Room in the Middle

Anthony K. Cheetham and C. N. R. Rao

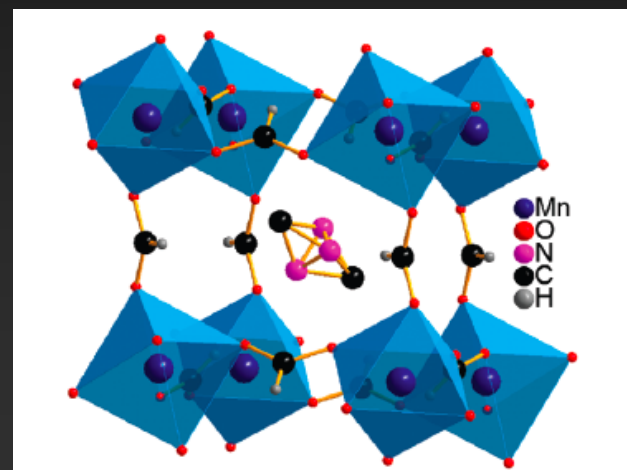
5 OCTOBER 2007 VOL 318 SCIENCE www.sciencemag.org

Dense inorganic-organic hybrid materials offer opportunities for creating unusual properties or combinations of properties.



Hybrid perovskite analog

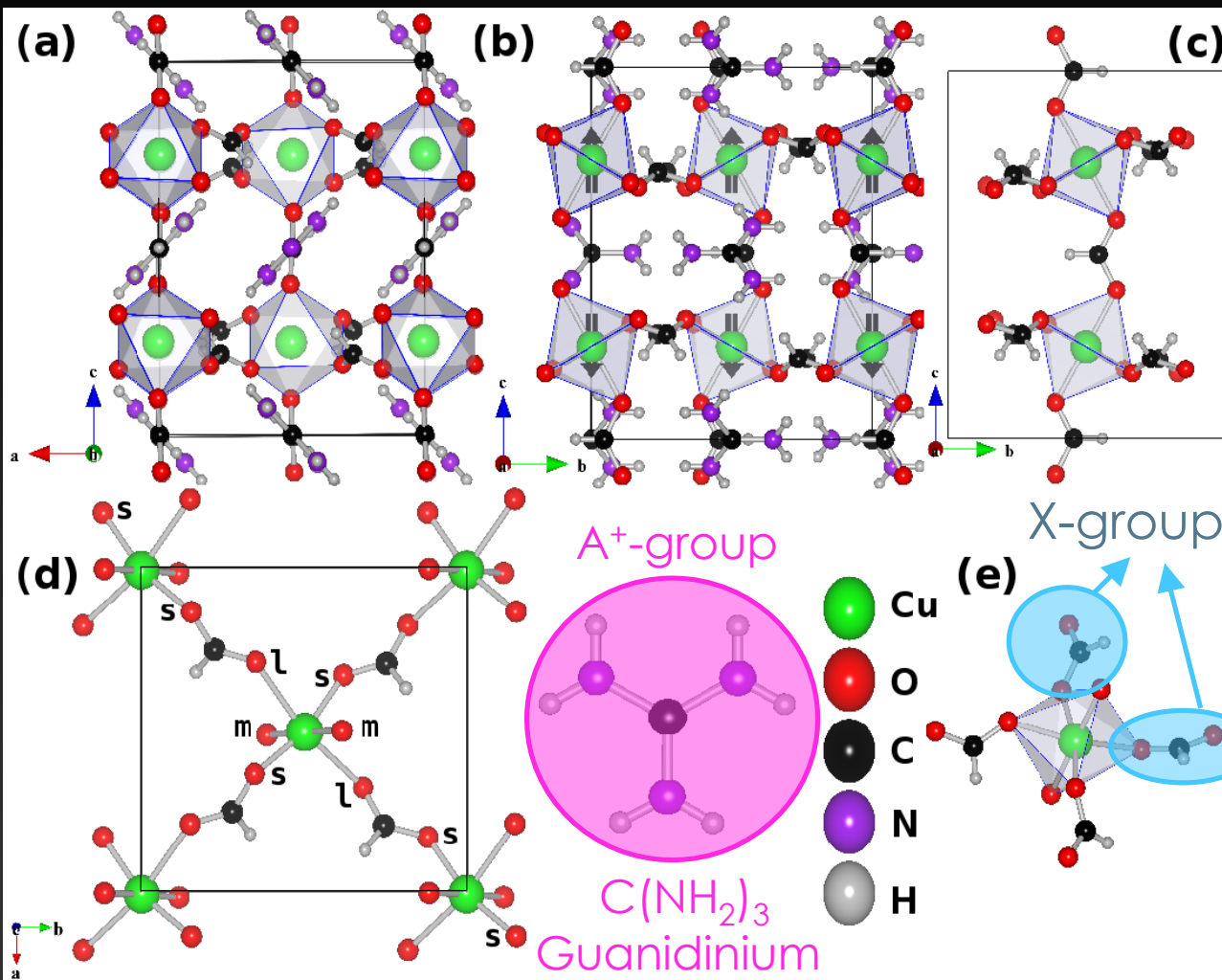
Crystalline hybrid materials like **Metal Organic Frameworks (MOFs)** are very attractive materials for gas storage, drug delivery, catalysis, optics, and magnetism



Multiferroic Behavior Associated with an Order–Disorder Hydrogen Bonding Transition in Metal–Organic Frameworks (MOFs) with the Perovskite ABX_3 Architecture J. AM. CHEM. SOC. 2009, 131, 13625–13627

Prashant Jain,^{†,‡,§} Vasanth Ramachandran,[†] Ronald J. Clark,[†] Hai Dong Zhou,[§] Brian H. Toby,^{||} Naresh S. Dalal,^{†,§} Harold W. Kroto,[†] and Anthony K. Cheetham^{*,‡}

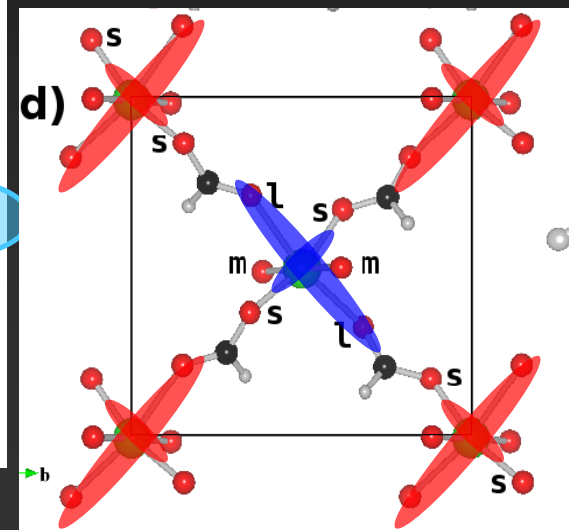
Cu-MOF (ABX_3 , $K^+CuF^{-1}_3$ LIKE)



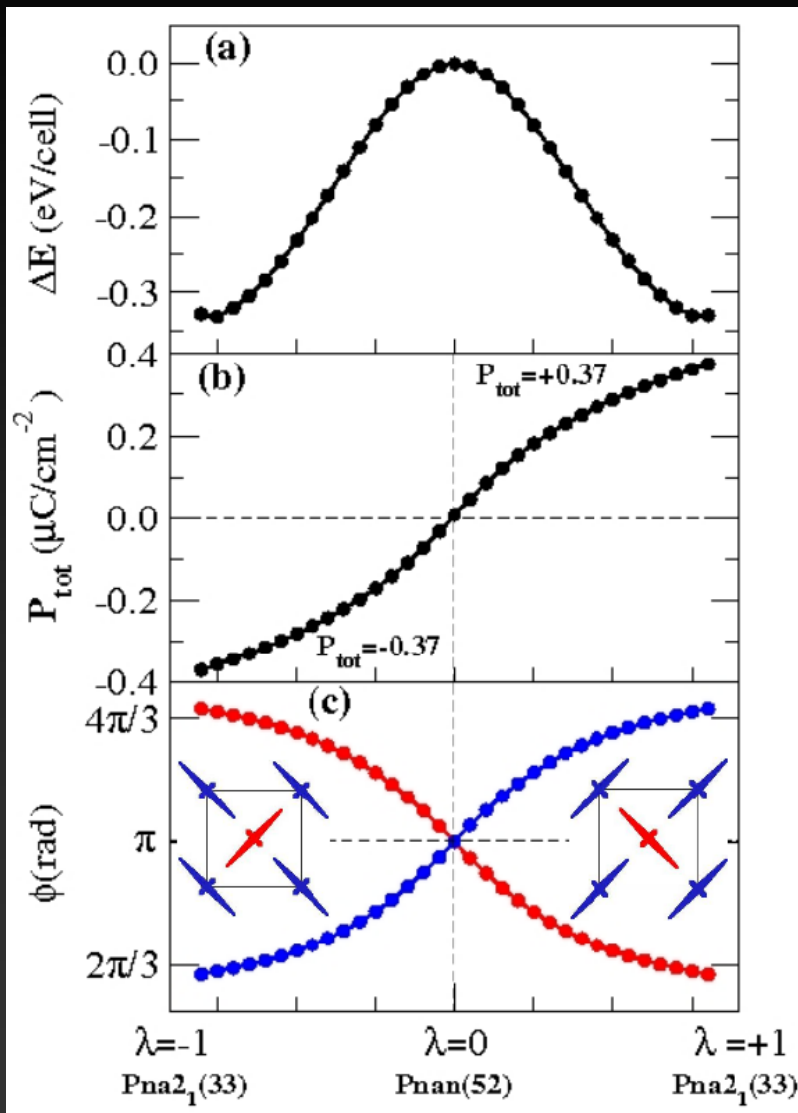
Cu octahedra
connected
by $HCOO^-$ groups
(ligands)

Cu^{+2} Jahn-Teller ion

Antiferrodistortive
order in the ab plane



Cu-MOF: FERROELECTRICITY



λ amplitude of the polar distortion:

$\lambda=0$ paraelectric state ($P=0$);
 $\lambda=\pm 1$ ferroelectric (FE) state
($P=0.37 \mu C/cm^2$).

NB.: The AFD order is non-polar in usual inorganic compound (like $KCuF_3$)

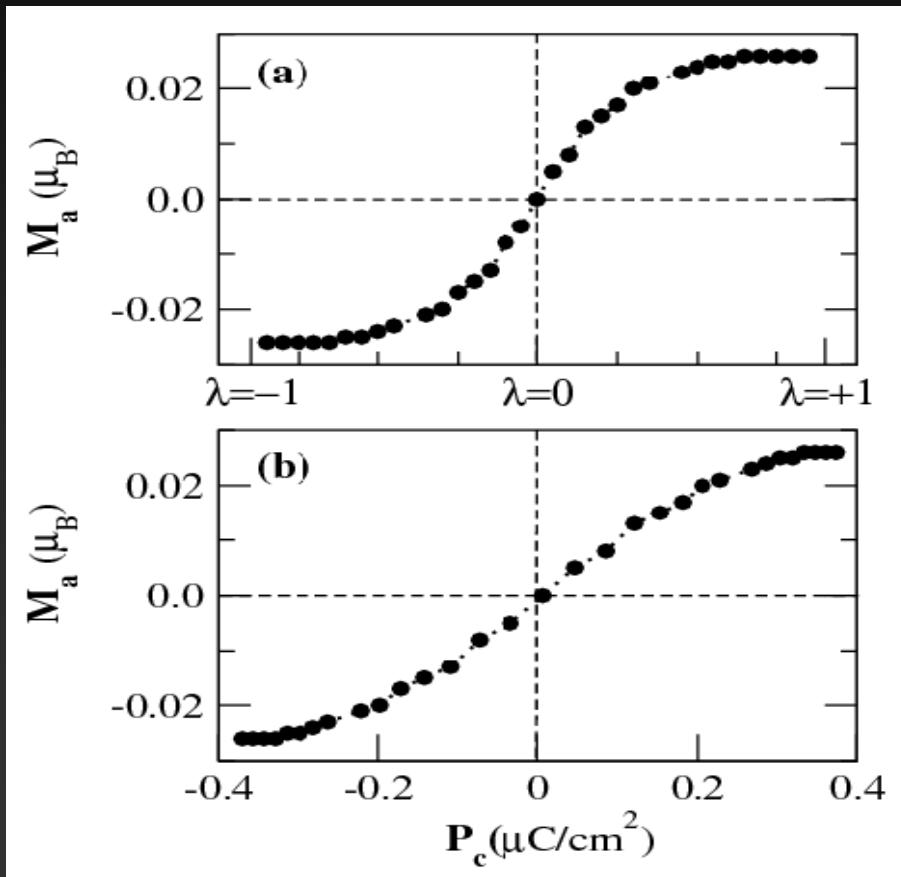
ϕ = amplitude of the
antiferrodistortive (AFD) order

**In Cu-MOF AFD and FE
are clearly correlated!**

Cu-MOF: MAGNETOELECTRICITY

Symmetry analysis: Coupling of the type $M_a P_c L_c$
⇒ Weak-FM component is allowed in Cu-MOF
and coupled to the Ferroelectric order!

Ab-initio calculations fully confirm
what expected by symmetry

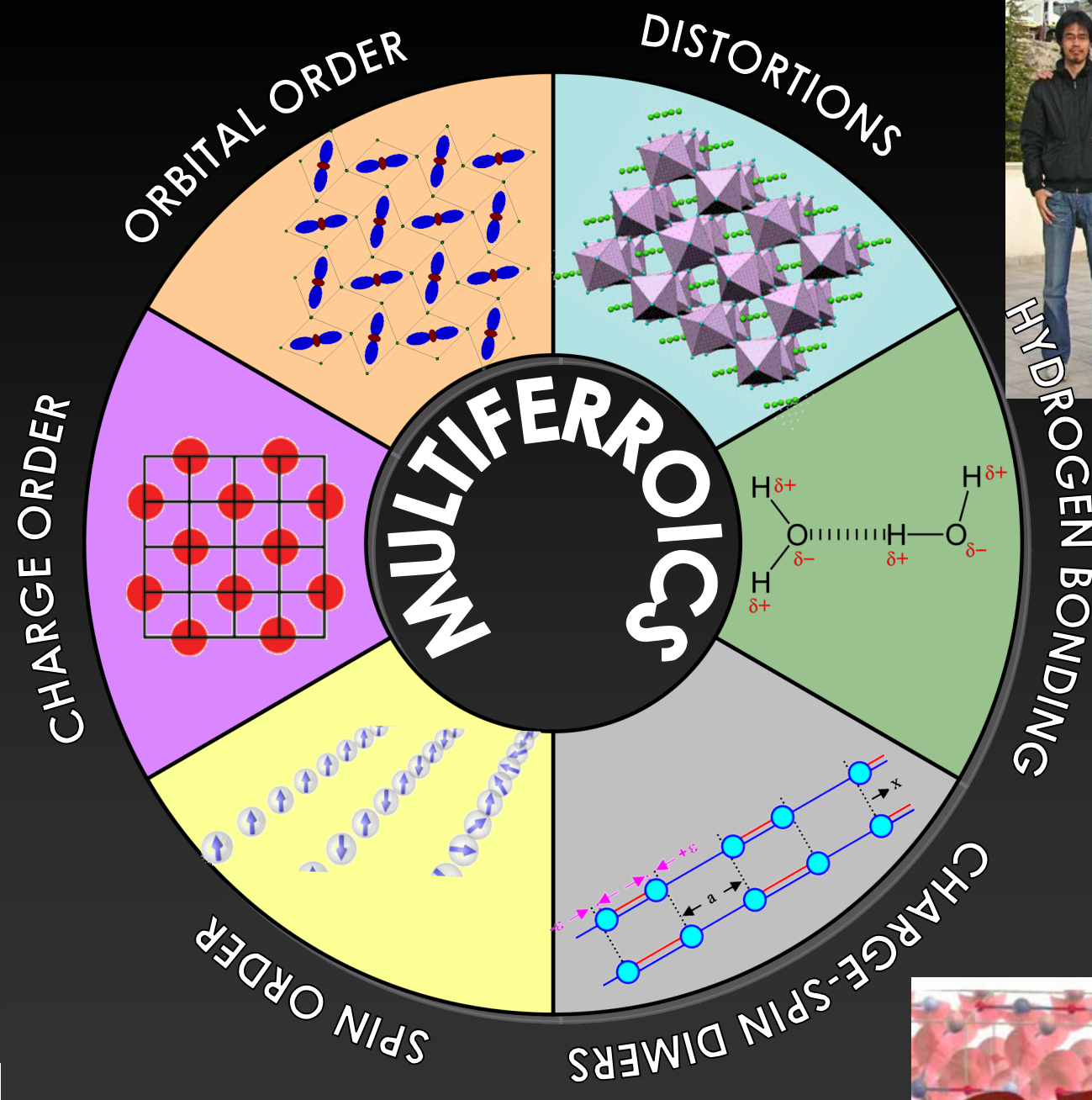


In Cu-MOF, a magnetic field can couple to the weak-FM component and can reverse the FE polarization (and viceversa: an electric field can switch the weak-moment)

ELECTRICAL CONTROL OF MAGNETIZATION !

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**THANK
YOU!**



Silvia Picozzi

European School on Magnetism