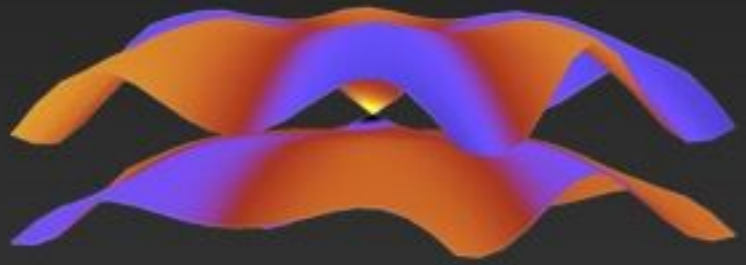
MULTIFERROICS FROM FIRST PRINCIPLES

Dr. Silvia Picozzi
Consiglio Nazionale delle Ricerche,
Istituto Superconduttori, Materiali e Dispositivi Innovativi
CNR-SPIN *66100 Chieti, Italy*
https://sites.google.com/site/silviapicozzi/



GROUP INTRODUCTION

LOCATION

MATERIALS

Multifunctional/ Coupling between degrees of freedom:

- Oxides

- Organics, hybrid
- Interfaces/surf.
- .....

METHODS

- Density Functional Theory

... but also:

- Symmetry analysis
- Model Hamilt.

FIRST-PRINCIPLES CALCULATIONS: BASICS

Density functional theory
Main theorems
Why are they useful for multiferroics?
Where do they fail?

WHAT ARE FIRST-PRINCIPLES USEFUL FOR?

- **MACRO ⟺ 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

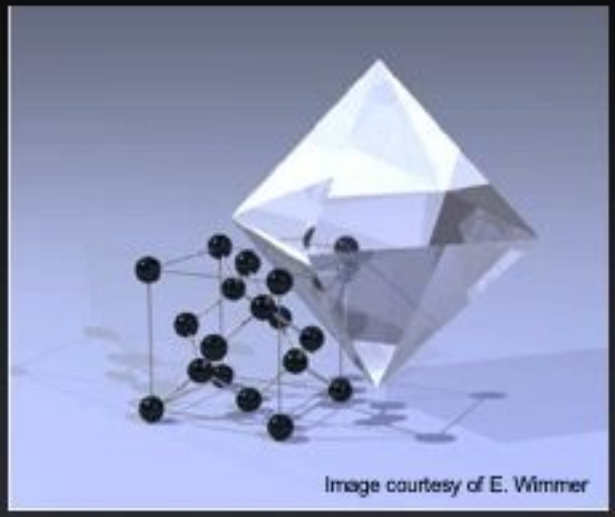


Image courtesy of E. Wimmer

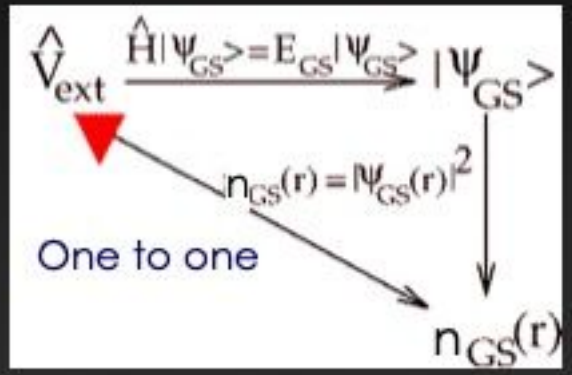
- **ERRORS...** Analyze failures. Ask: Are the approximations appropriate? Can the models address the complexity of the system? Is the theory appropriate for the key properties?

DFT: BASICS

The basic quantity is not the many-body wave-function but the **electronic density n(r)**

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

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



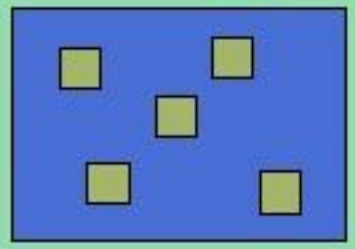
$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V_{ext}\, n(\mathbf{r})\, d\mathbf{r} = \mathbf{T_e + U_{ee}} + \int V_{ext}\, n(\mathbf{r})\, d\mathbf{r} \geq E[n_{GS}(r)]$$

and satisfies a variational principle

DFT: BASICS

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

Kohn-Sham



Auxiliary system: Non-interacting fictitious particles + effective potential

Interacting electrons + External potential

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):

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

DFT: BASICS

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

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

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

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

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

- $V_{xc}[n(r)] = \frac{\delta E_{xc}}{\delta n(r)}$ 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…

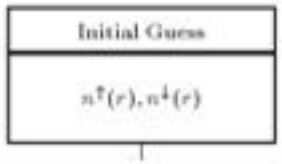
- Structure, types of atoms, guess for input charge

- Solve KS Eqs.

- New Density and Potential

- Self-consistent?
- Output:
  - Total energy, force, ….
  - Eigenvalues

Self-Consistent Kohn-Sham Equations



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…

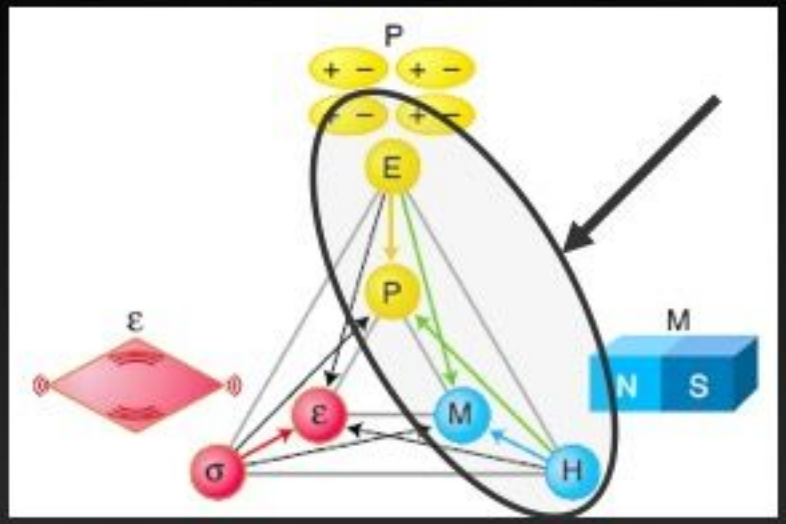
WHAT CAN WE GET OUT OF THE COMPUTER?

Capabilities, formalism	Predicted quantities
Spin-DFT	Electronic structure (DOS, bands, …), magnetism (moments, GS spin configuration, …)

MULTIFERROICS: EXAMPLES FROM FIRST-PRINCIPLES

- Introduction and Classification
- Lone-pair driven
- (Structurally) Improper FE
- (Electronically) Improper FE

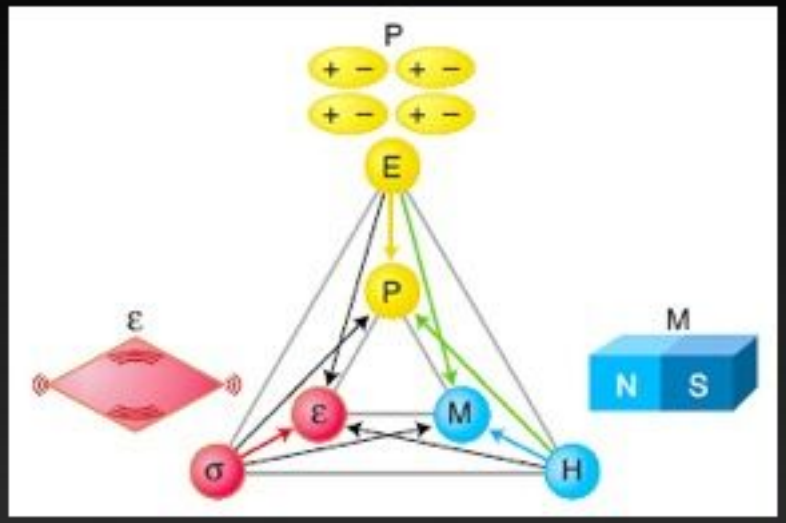
MAGNETOELECTRICS MULTIFERROICS: WHAT ARE THEY?



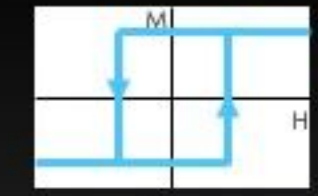
N.A. Spaldin and M. Fiebig, Science ***309****, 391 (2005)*

- **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

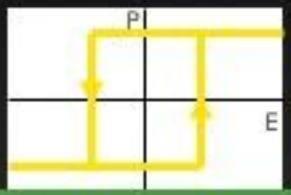
MAGNETOELECTRICS MULTIFERROICS: WHY ARE THEY INTERESTING?



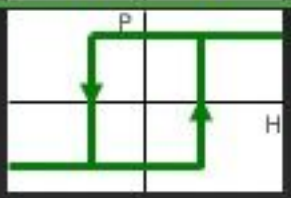
➢ **Magnetoelectrics**: Control of P (M) via a magnetic (electric) field



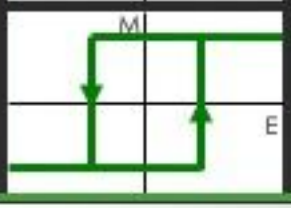
Magnetization vs magnetic field in FMs



Polarization vs electric field in FEs

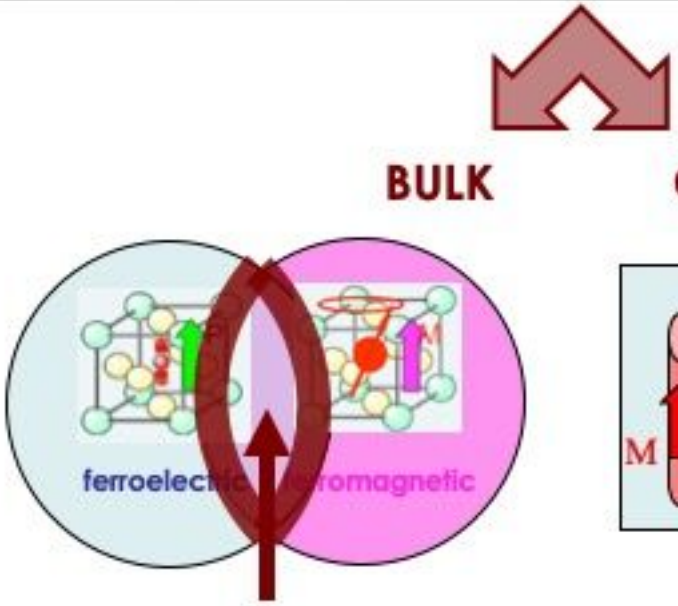


Polarization vs magnetic field in MEs



Magnetization vs electric field in MEs

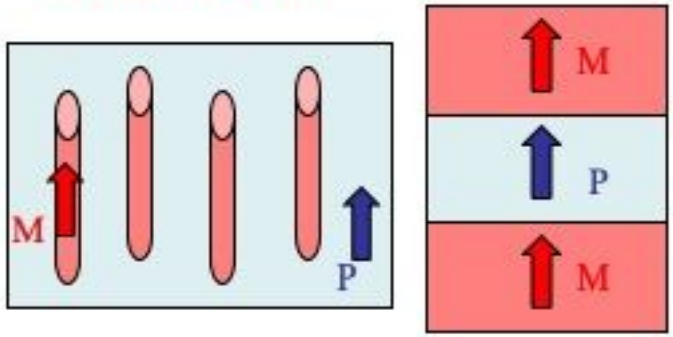
CLASSIFICATION OF MULTIFERROICS



BULK

Both magnetic and dipolar order in the same ***bulk*** material

COMPOSITE



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

CLASSIFICATION OF MULTIFERROICS

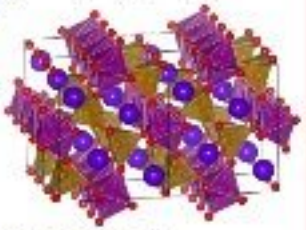
BULK **COMPOSITE**

STRUCTURAL MAGNETIC FERROELECTRIC

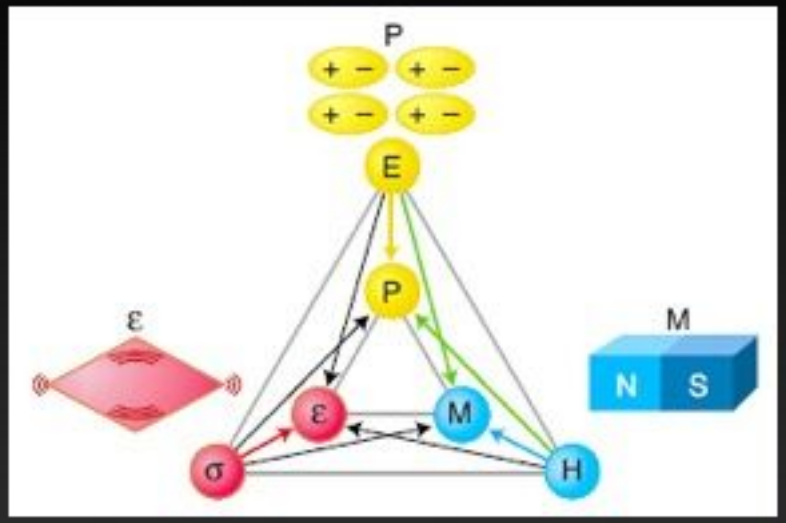
The primary order parameter related to structural instability (either polar or non-polar)

ELECTRONIC MAGNETIC FERROELECTRIC

The primary order parameter related to electronic degrees of freedom



MAGNETOELECTRICS MULTIFERROICS: WHY ARE THEY INTERESTING?



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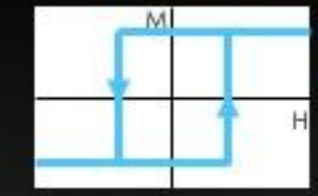
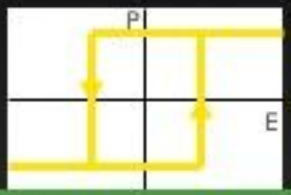
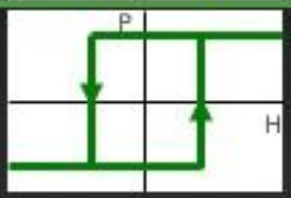


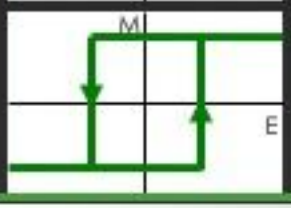
Magnetization vs magnetic field in FMs



Polarization vs electric field in FEs



Polarization vs magnetic field in MEs



Magnetization vs electric field in MEs

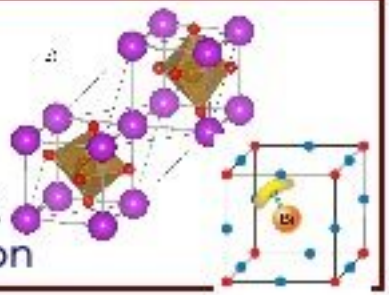
CLASSIFICATION OF MULTIFERROICS

BULK **COMPOSITE**

STRUCTURAL MAGNETIC FERROELECTRIC

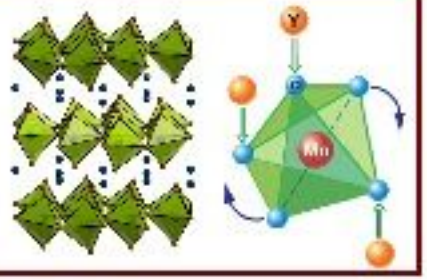
ELECTRONIC MAGNETIC FERROELECTRIC

LONE-PAIR DRIVEN
covalency, hybridization



GEOMETRIC

(size-effects, no significant rehybridization)



CRITERIA FOR MAGNETISM AND FERROELECTRICITY

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

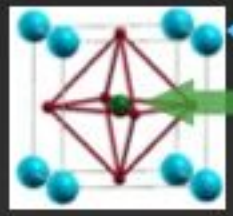
➡ To have FM or FiM or AFM, one needs ***partially filled d-shells***!

- Ferroelectricity requires "***d^0-ness***"
- Ferromagnetism (or FiM- or AFM) requires partially filled d-electrons

➡ **CHEMICAL INCOMPATIBILITY!**

- *B.T. Matthias, New ferroelectric crystals, Phys. Rev. (1949)*
- *N.A. Hill, Why are there so few magnetic ferroelectrics? J. Phys. Chem. B 104, 6694 (2000)*

WAY OUT:



Put FE-active ion on A-site

Put magnetic ion on B-site

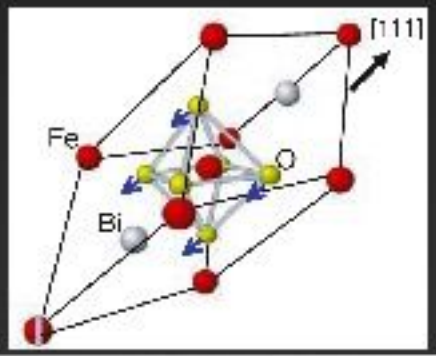
LONE-PAIR DRIVEN MF: THE "HOLY GRAIL, $BiFeO_3$

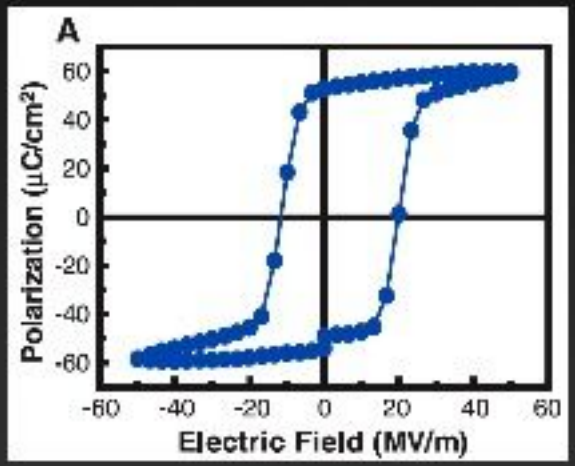
- A room-temperature multiferroic: FE and AFM (or weak FM)

- Ferroelectricity from the "stereochemically active lone pair" on Bi^{3+} (cf ammonia, NH_3)

- Magnetism from a 3d transition metal (Fe^{3+}, d^5)
- Good agreement between theory and expts

for P (~100 μC/cm² along [111], ~60 μC/cm² along [001])



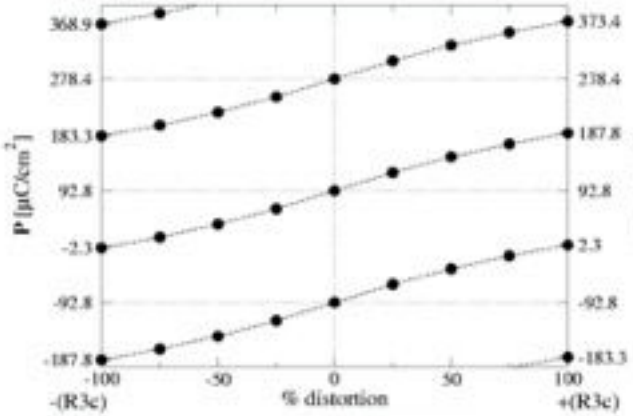


J. Wang et al., Science ***299****, 1719 (2003).*

THE "HOLY GRAIL": $BiFeO_3$

Beyond LDA methods: Centrosymmetric reference structure metallic in LSDA

Modern theory of polarization: Non-zero P in centrosymmetric structure

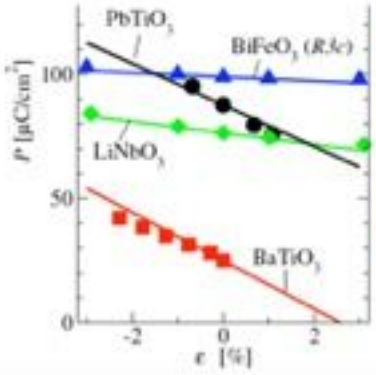


Calculate P = 95 μC/cm² along [111]

J.B. Neaton, U.V. Waghmare, C. Ederer, N.A. Spaldin and K.M. Rabe, *First-principles study of spontaneous polarization in multiferroic $BiFeO_3$*, PRB **71**, 014113 (2005)

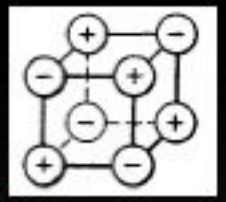
Absence of strain dependence:

Effect of epitaxial strain on the spontaneous polarization of thin film ferroelectrics, C. Ederer and N.A. Spaldin, Phys. Rev. Lett. **95**, 257601 (2005)



Nicola A. Spaldin's contri-butions

BiFeO3: MAGNETISM

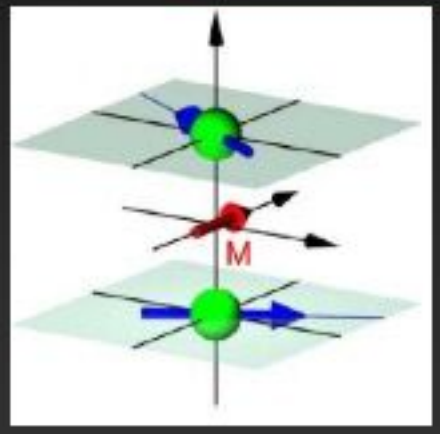


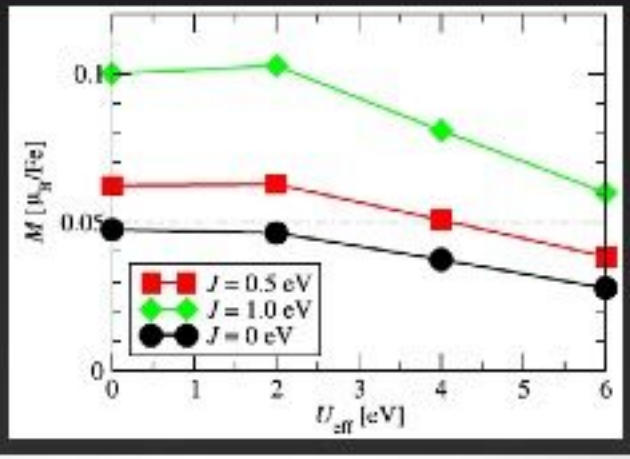
- Bulk: G-type AFM and cycloidal modulation (λ~640 nm)
- Thin films: the modulation disappears but a weak FM arises

Fe AFM moments are canted by up to ~1° due to Dzyaloshinskii-Moriya interaction

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

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



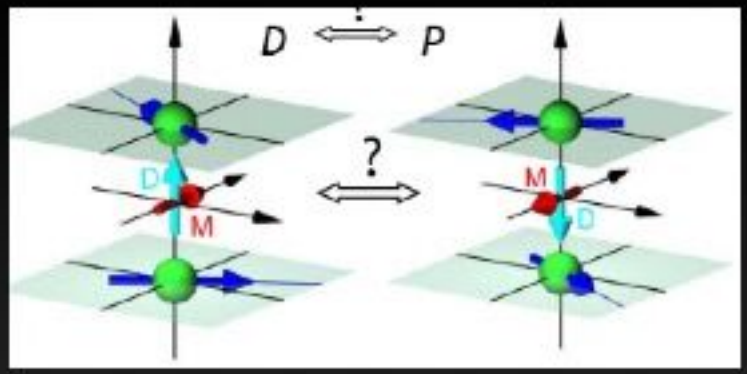


C. Ederer and N.A.Spaldin, PRB 71, 060401 (2005)

BiFeO3: MAGNETISM

Is the canting coupled to polarization ?

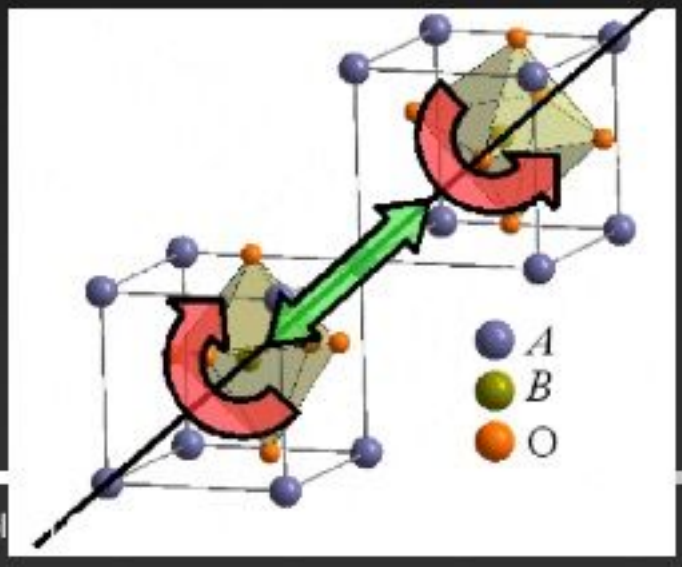
Can I switch the weak moment by E-field?



No! Two different modes in BFO:

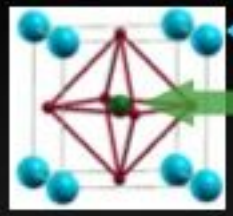
1. Polar displacements along [111]
2. Octahedral counter-rotations

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



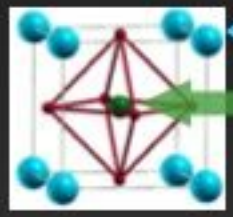
COMBINE FE AND FM: WAY OUT (II)

$BiFeO_3$:



Put FE-active ion on A-site

Put magnetic ion on B-site

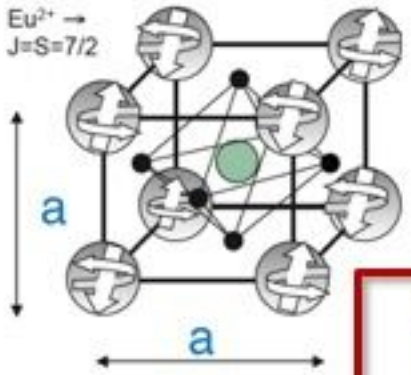


Put FM-active ion on A-site

Leave Ferroelectric ion on B-site

WAY OUT (II): EuTiO3

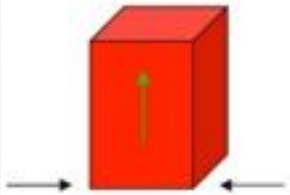
C.J. Fennie and K.M. Rabe, *Physical Review Letters* **97** (2006) 267602



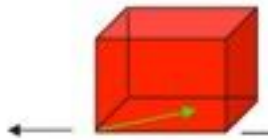
$Eu^{2+}Ti^{4+}O_3$

- In bulk: paraelectric (PE) and antiferromagnetic (AFM)
- Epitaxially strained thin film: ferroelectric (FE) and ferromagnetic (FM)

Fennie's, Rabe's contri-butions

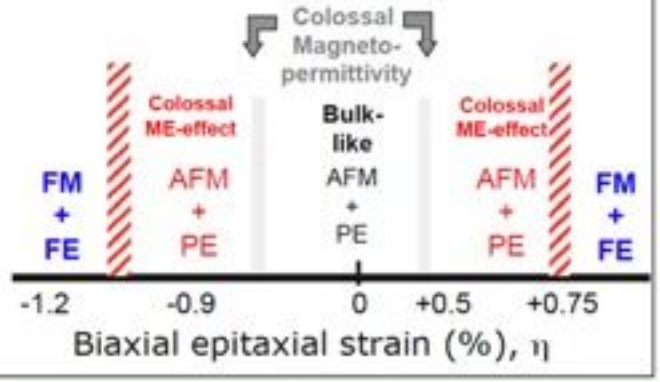


Compressive
Ferroelectric c-phase



Tensile
Ferroelectric aa-phase

Epitaxially strained film
Rich magnetoelectric phase diagram due to spin-lattice coupling predicted from first principles



IMPROPER FERROELECTRICITY IN MAGNETS

What do we mean by "improper ferroelectricity"?

Concepts:

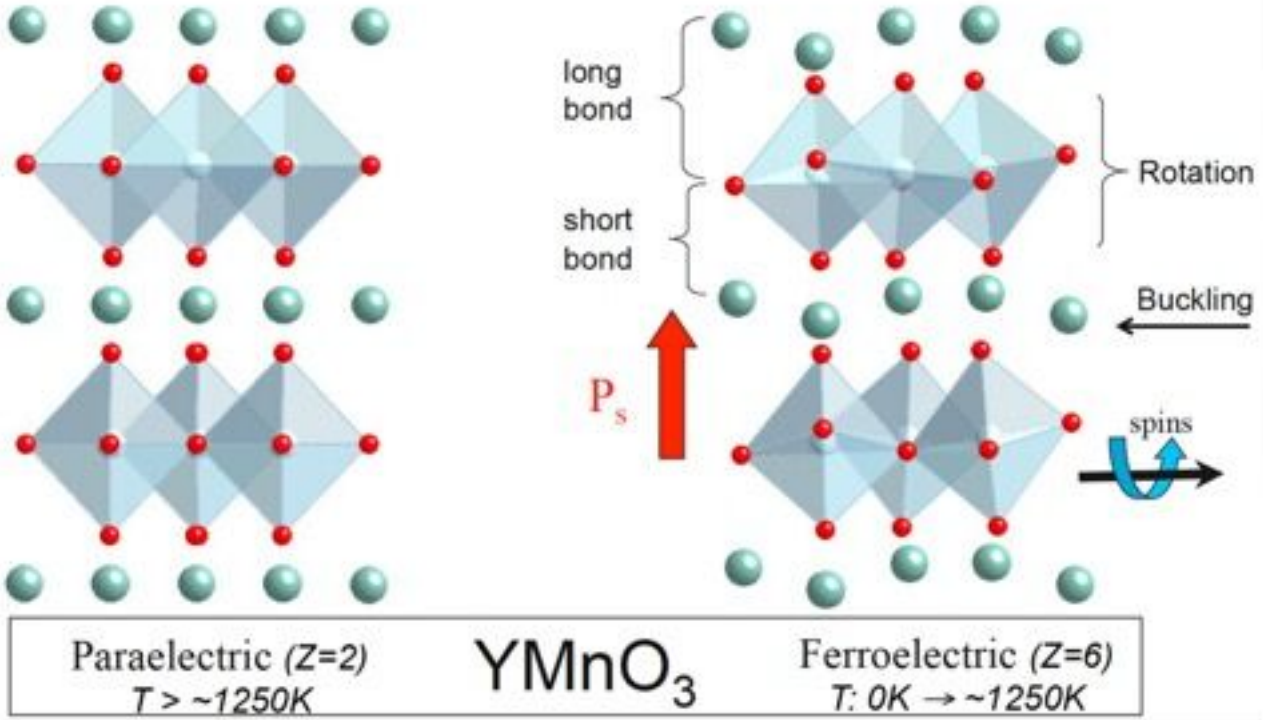
how to break inversion symmetry via coupled structural distortions, spin- or charge-ordering

Examples: manganites (hexagonal vs orthorhombic)

IMPROPER STRUCTURAL FERROELECTRICITY: HEXAGONAL MANGANITES

$RMnO_3$, R = Y, Sc, Ho-Lu

vanAken, Palstra, Fillipetti, Spaldin, Nature Materials 2004.

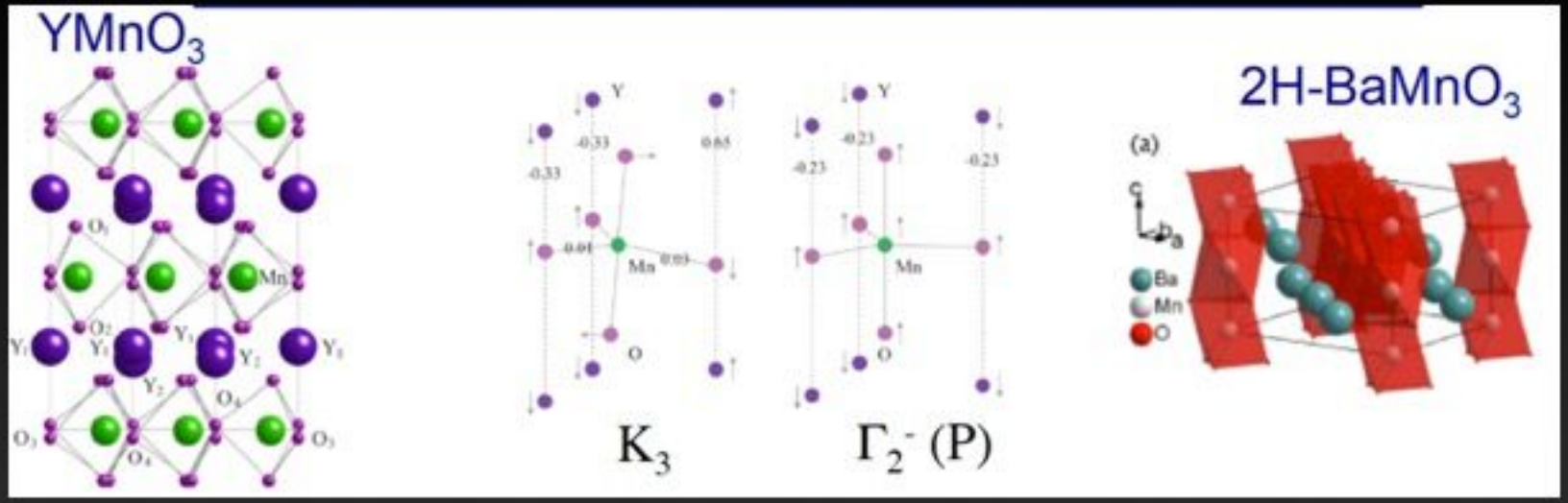


Paraelectric *(Z=2)*
T > ~1250K

$YMnO_3$

Ferroelectric *(Z=6)*
T: 0K → ~1250K

IMPROPER STRUCTURAL FERROELECTRICITY: HEXAGONAL MANGANITES

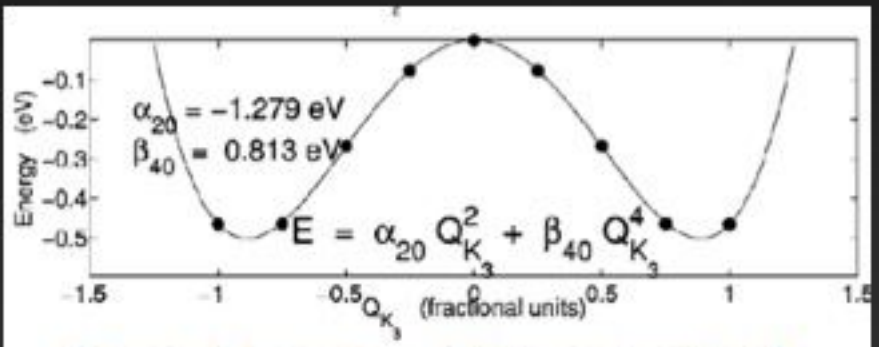


MnO5 (trigonal bi-pyramids)
are rotated
and trimerize in the FE state

- *C. Fennie & KM Rabe,*
PRB **72**, 110103 (2005)
- *J. Varignon and P. Ghosez,*
PRB **87**, 140403 (2013)

IMPROPER STRUCTURAL FERROELECTRICITY: HEXAGONAL MANGANITES

⇨ WHY IS IT FERROELECTRIC ?!??!??



Zone-boundary (trimerization) mode is unstable

RATIONALIZATION WITH LANDAU THEORY

Primary order parameter ≡ η

where η is "some other mode", e.g. zone-boundary lattice instability, *magnetic chiral vector*, etc.

Secondary order parameter

Spontaneous polarization **P**

$$\mathcal{F}(\eta, P) = \alpha_P P^2 + \alpha_\eta \eta^2 + \gamma_\eta P \eta^n + \beta P^4$$

n ≡ faintness index

$$\partial \mathcal{F}/\partial P = 2\alpha_p P + \gamma_\eta \eta^n + 4\,\beta P^3 = 0$$

$P_{eq} \sim -\eta^n$

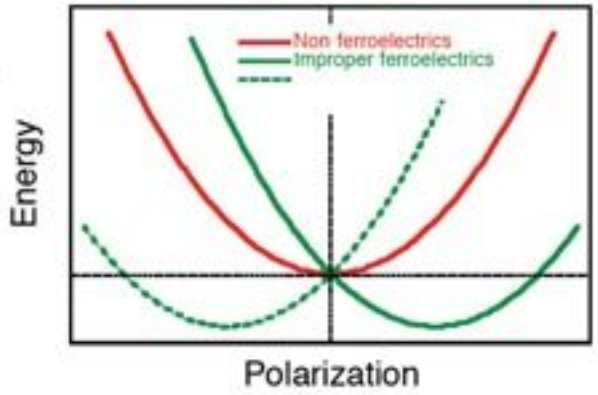
Once primary OP becomes nonzero, a polarization is induced

C. Fennie & KM Rabe, PRB **72**, 110103 (2005)
J. Varignon and P. Ghosez, PRB **87**, 140403 (2013)

IMPROPER FERROELECTRICITY : RECAP

$$\mathcal{F}(\eta, P) = \alpha_P P^2 + \alpha_\eta \eta^2 + \\ + \gamma_\eta P \eta^n + \beta P^4$$

n = faintness index



- P not intrinsically unstable but slave of another unstable degree of freedom (structural or other) ϕ.
- P coupling at **linear** order with ϕ ➔ **shift** of the well.
- Other exponent *n* (« faintness ») possible (*n* = 1 : pseudo-proper)
- No anomalous Born Effective Charges
- **Ferroelectric** ? Yes, but switching P requires switching ϕ ...
- No divergence of the dielectric constant

IMPROPER FERROELECTRICITY IN HEXAGONAL MANGANITES

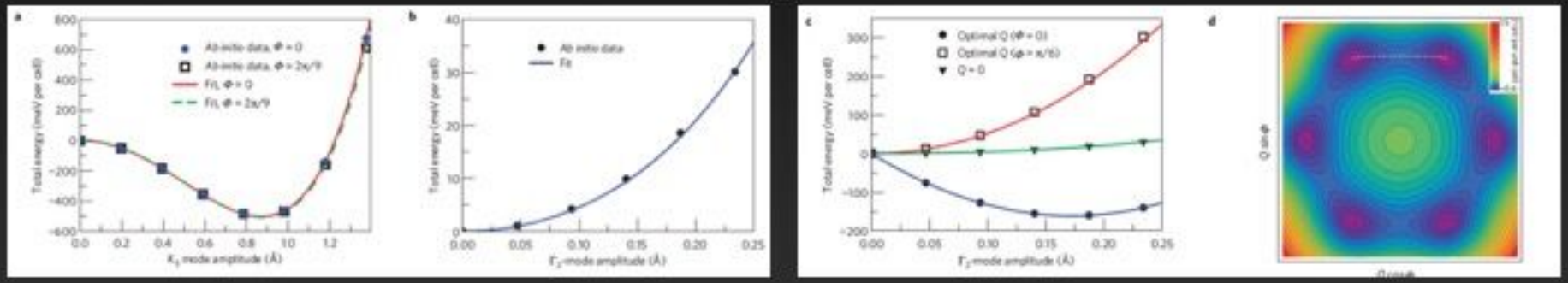
Expand energy to fourth order in the primary K_3 and secondary $\mathbf{P}$ order parameters:

Fennie and Rabe, Physical Review B 72, 100103 2005

(note energy expansion simplified for pedagogy)

$$\mathcal{F}(K_3, \mathbf{P}) = \alpha_P \mathbf{P}^2 + \alpha_k K_3^2 + \gamma_\eta \mathbf{P} K_3^3 + \beta \mathbf{P}^4$$

$$\Rightarrow P \sim \gamma_\eta K_3^3$$



Extraction of model parameters from ab-initio (K_3: trimerization mode, Γ_2: polar mode).
S. Artyukhin et al, Nat. Mater. 13, 42 (2014).

BREAKING INVERSION SYMMETRY IN MAGNETS

FERROELECTRICITY ⟺ no Inversion Symmetry

Conventional

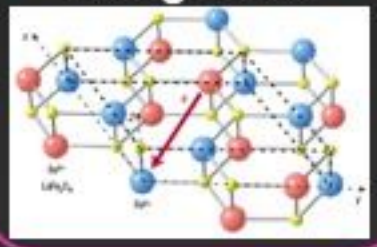
- "Proper"
- **Ionic displac.** break inversion symmetry (IS)
- "**Covalency**"-driven

Non-Conventional

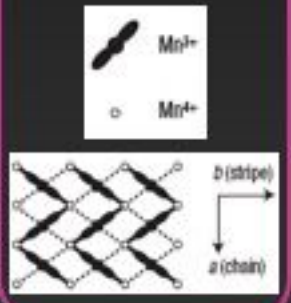
- "Improper"
- **Electron degrees of freedom** break IS
- "**Correlation**"-driven

Spin-order (some AFM or "spiral")

Charge-order



Orbital-order



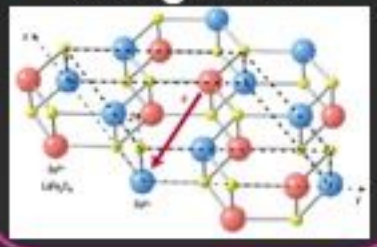
Main **advantages** over **proper multiferroics:**

- displacements/switching involve *electrons* rather than *ions*
  ⇒ **switching** should be much **faster**
  ⇒ better as for "fatigue"

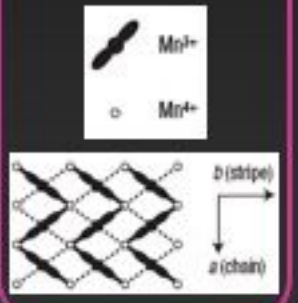
- especially for spin-induced ferroelectricity
  ⇒ **magnetoelectric coupling** should be much **stronger** (as magnetism and ferroelectricity share the same microscopic origin)

Spin-order (some AFM or "spiral")

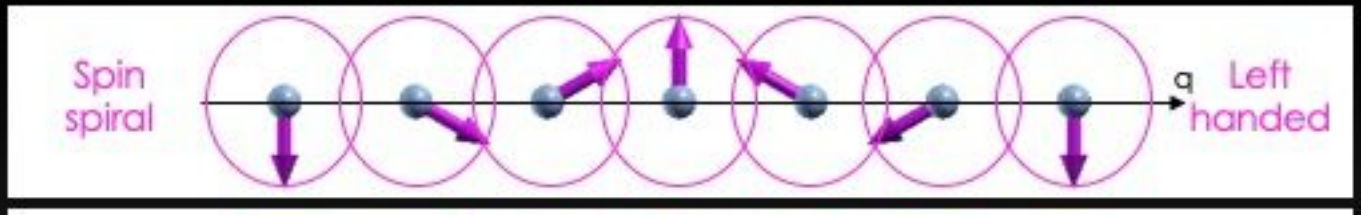
Charge-order

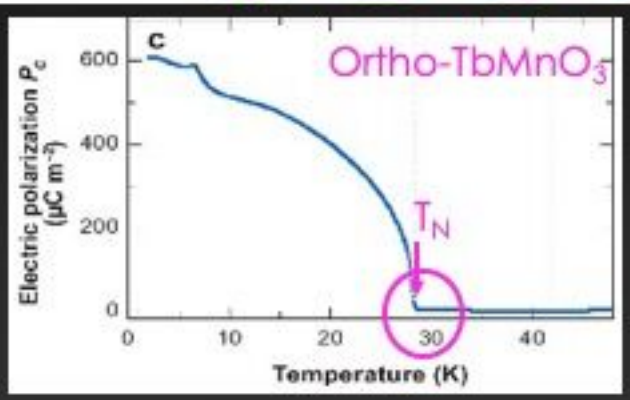


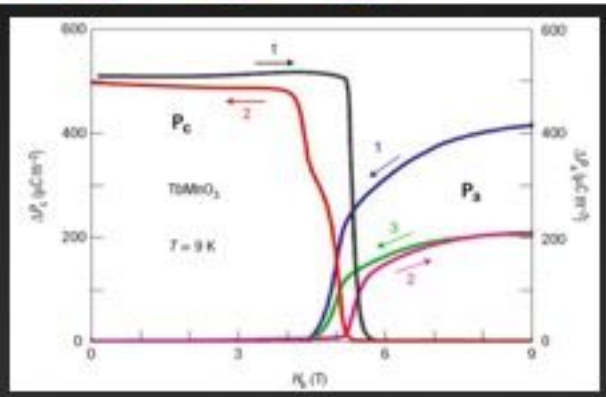
Orbital-order



HOW MAGNETIC ORDERING CAN BREAK INV. SYM.?

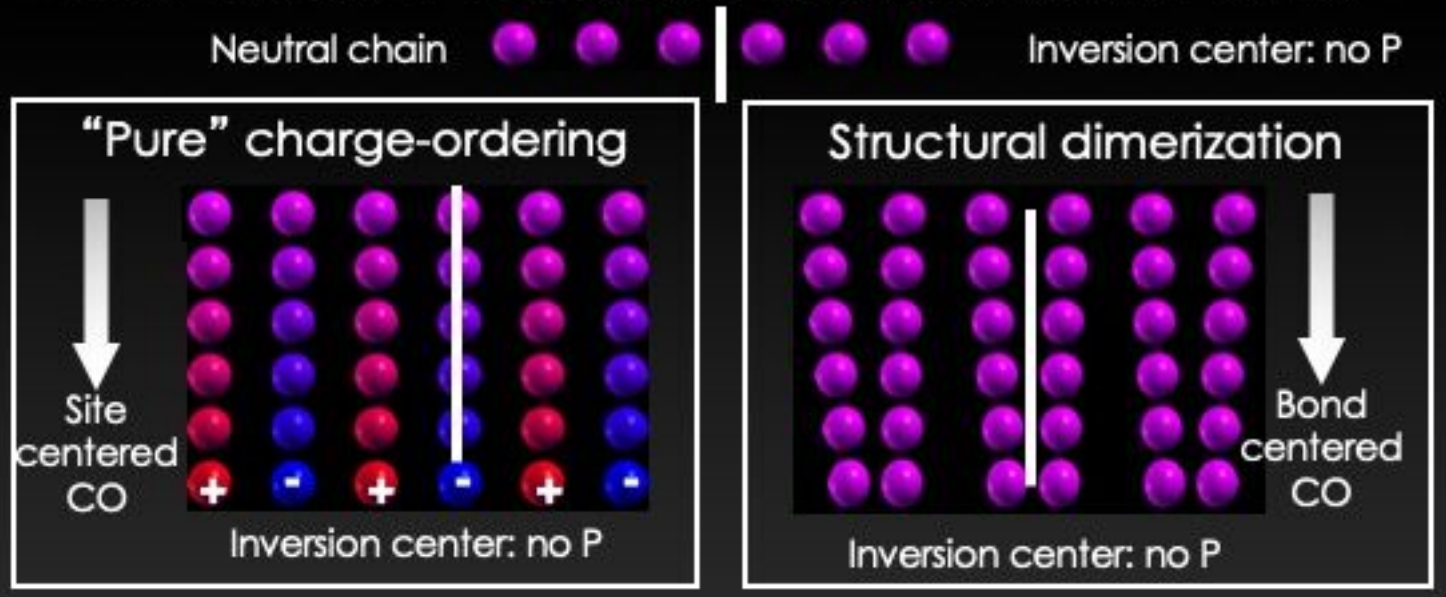






*T.Kimura et al., Nature **425**, 55 (03); S.W.Cheong and M.Mostovoy, Nature Mater. **6**, 13 (07)*

HOW CHARGE ORDERING CAN BREAK INV. SYM.?

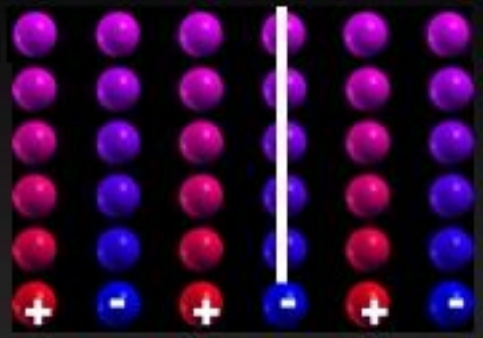


HOW CHARGE ORDERING CAN BREAK INV. SYM.?

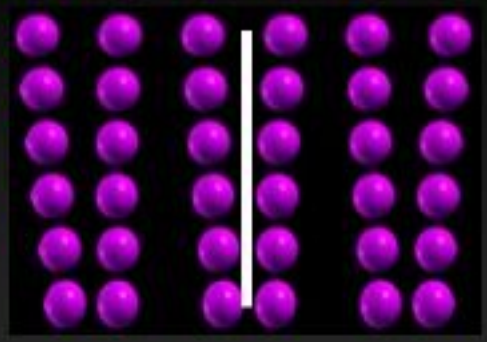
Neutral chain

Inversion center: no P

"Pure" charge-ordering

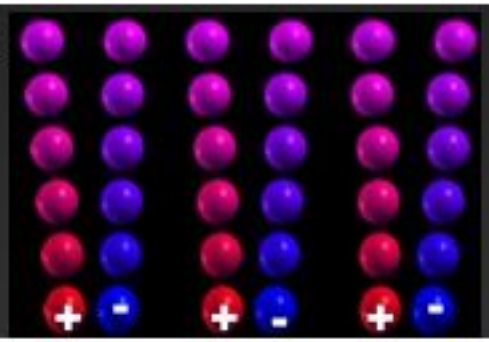


Structural dimerization

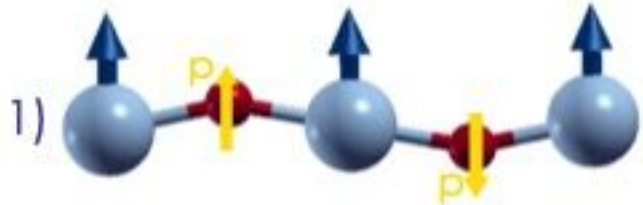


Combination

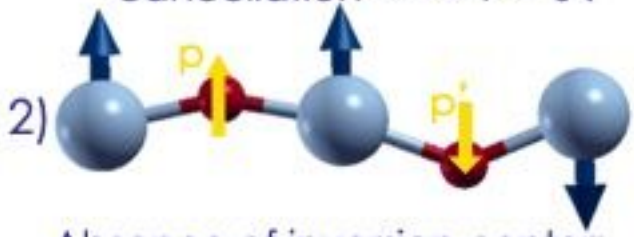
Intermediate Bond- and site-centered CO



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



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



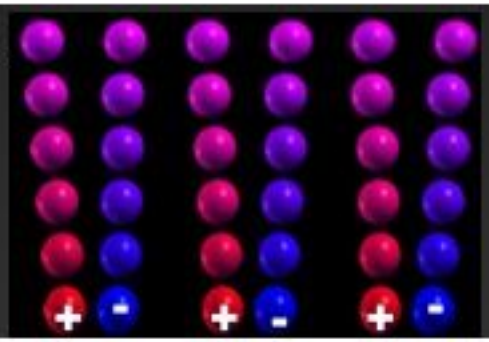
Absence of inversion center:
P finite!

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

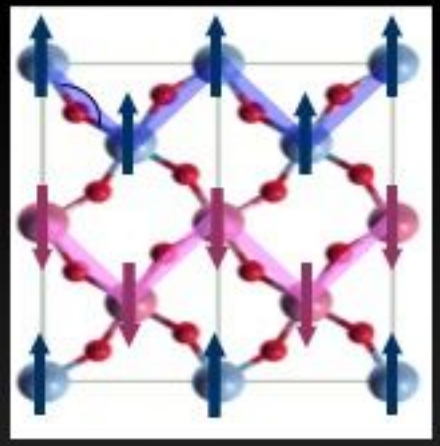
⇒ **polar space groups**

Combination

Intermediate
Bond- and site-
centered
CO



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



E-TYPE MANGANITES: ELECTRONIC AND IONIC FERROELECTRICITY

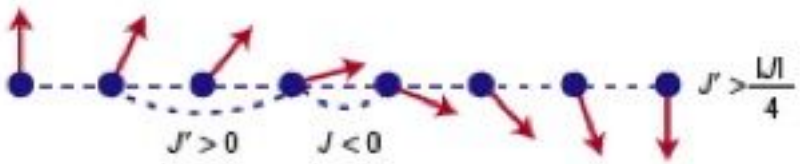
- In collaboration with:

K. Yamauchi *(now at Osaka)*

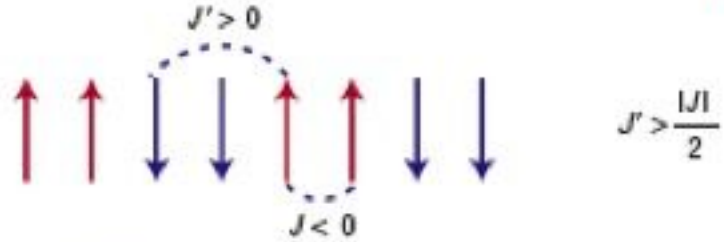
I. A. Sergienko, E. Dagotto
(Oak Ridge Natl. Lab, Univ. Tennessee, TN)

FRUSTRATION IN MAGNETS

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



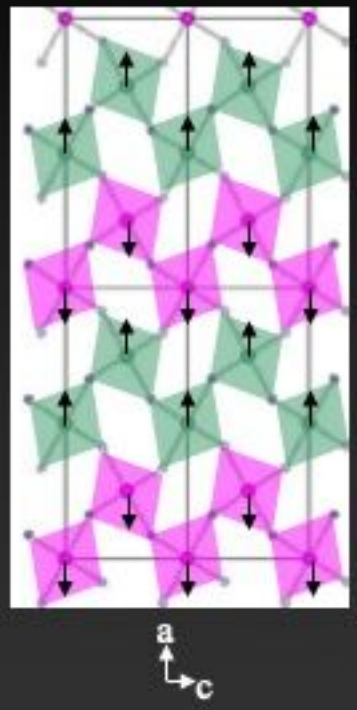
The spin chain with isotropic (Heisenberg)
$H = \Sigma_n [J\, S_n \cdot S_{n+1} + J' S_n \cdot S_{n+2}]$.
For $J' / |J| > 1/4$ its classical ground state is a **magnetic spiral**.



The chain of Ising spins $\sigma_n = \pm 1$, with energy
$H = \Sigma_n [J\, \sigma_n \sigma_{n+1} + J' \sigma_n \sigma_{n+2}]$
has the **up–up–down–down** ground state for $J' / |J| > 1/2$.

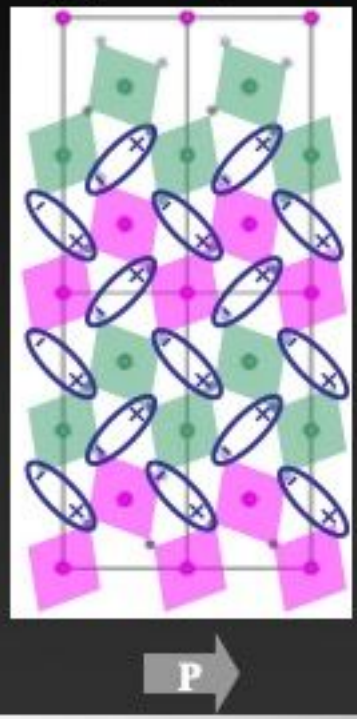
WHY THE AFM-E SHOULD BE FERROELECTRIC ?

- "Electronic" mechanisms



- e_g Orbital Ordering

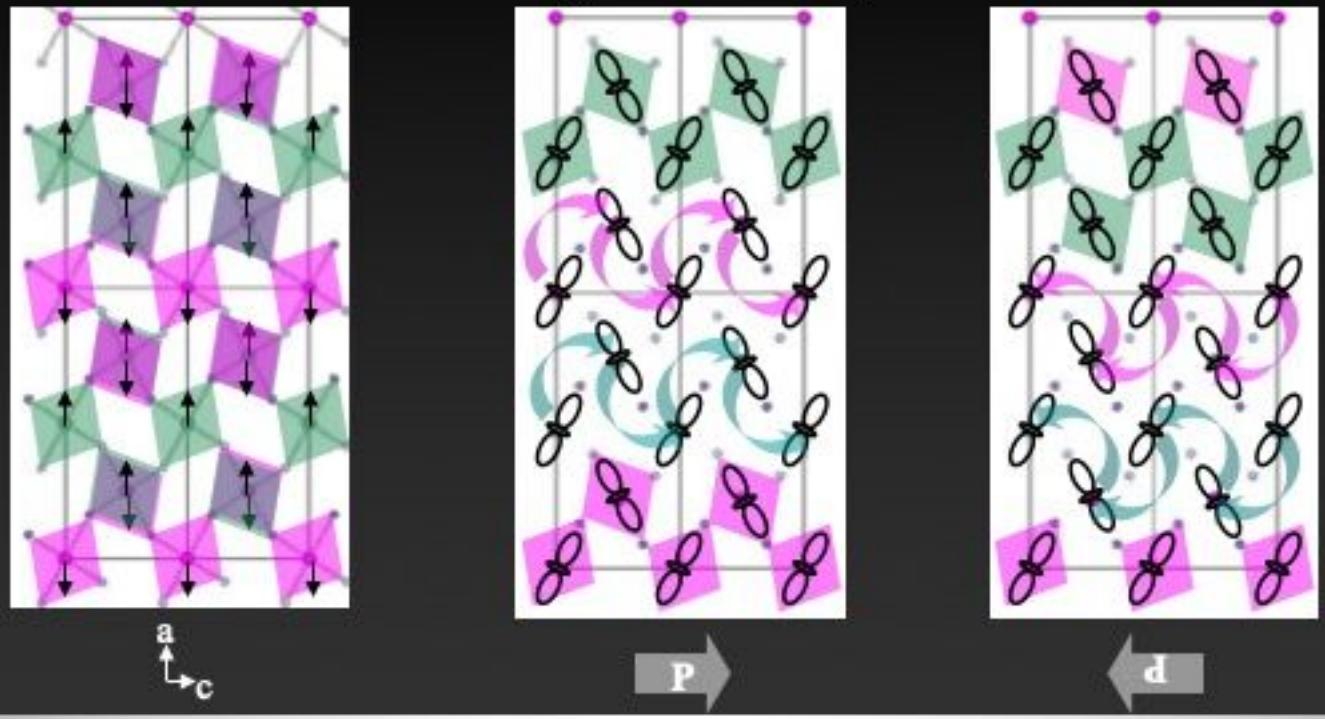
- Oxygen inequivalency



WHY THE AFM-E SHOULD BE FERROELECTRIC ?

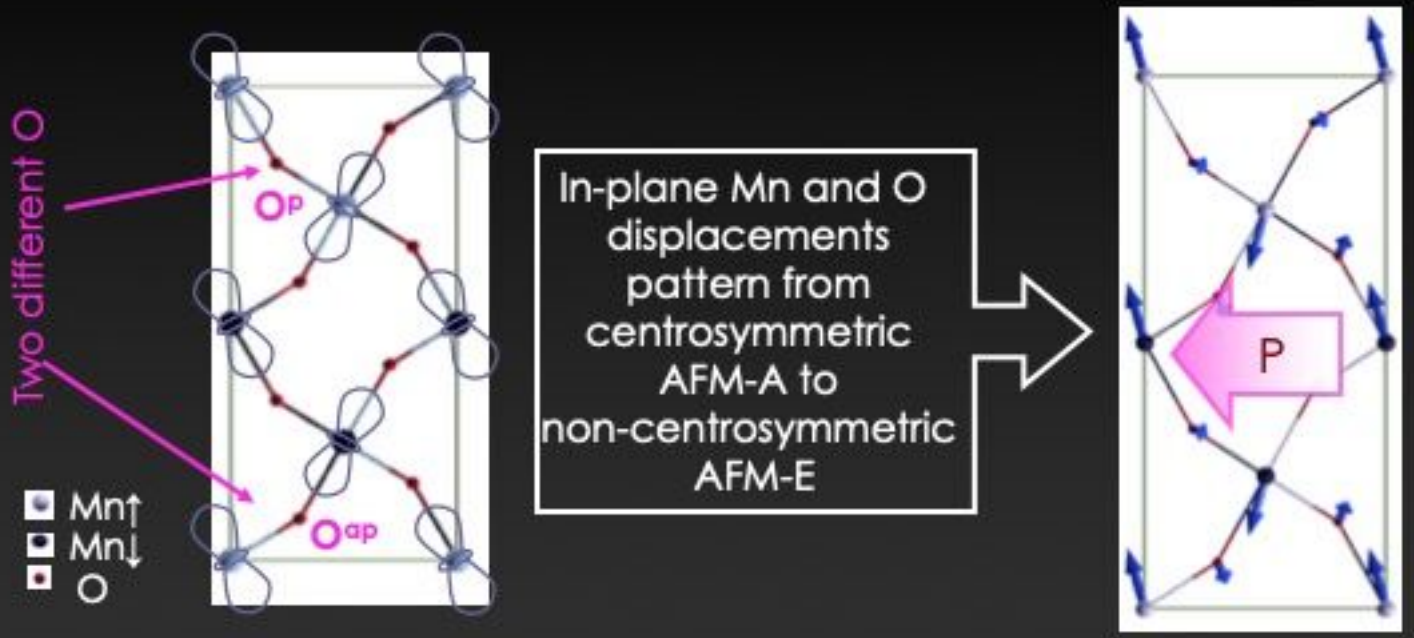
- "Switching" mechanisms: change direction of some spins

- e_g Orbital Ordering



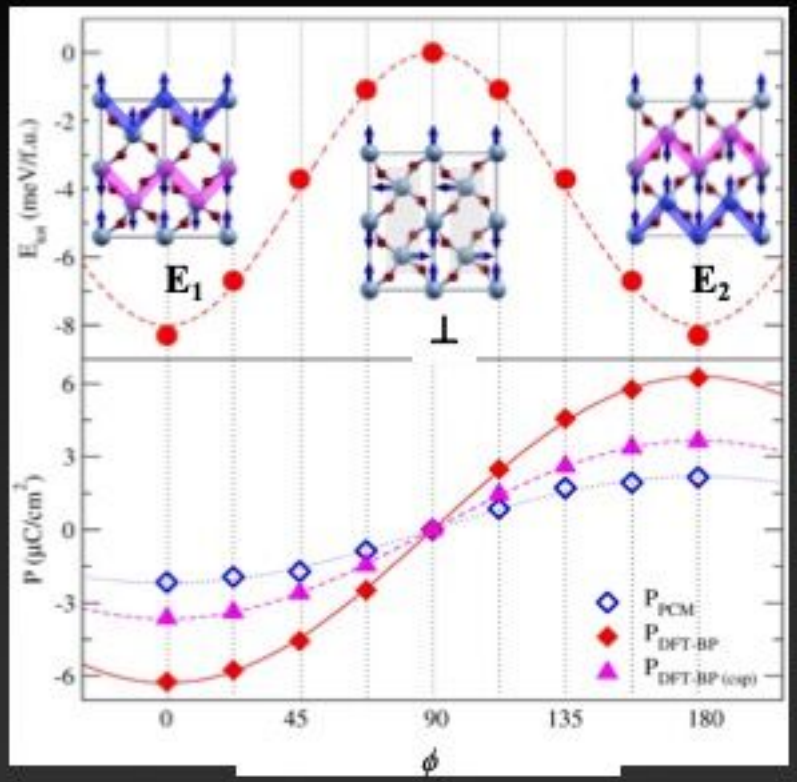
WHY THE AFM-E SHOULD BE FERROELECTRIC ?

- "Structural" contributions: Magnetostriction



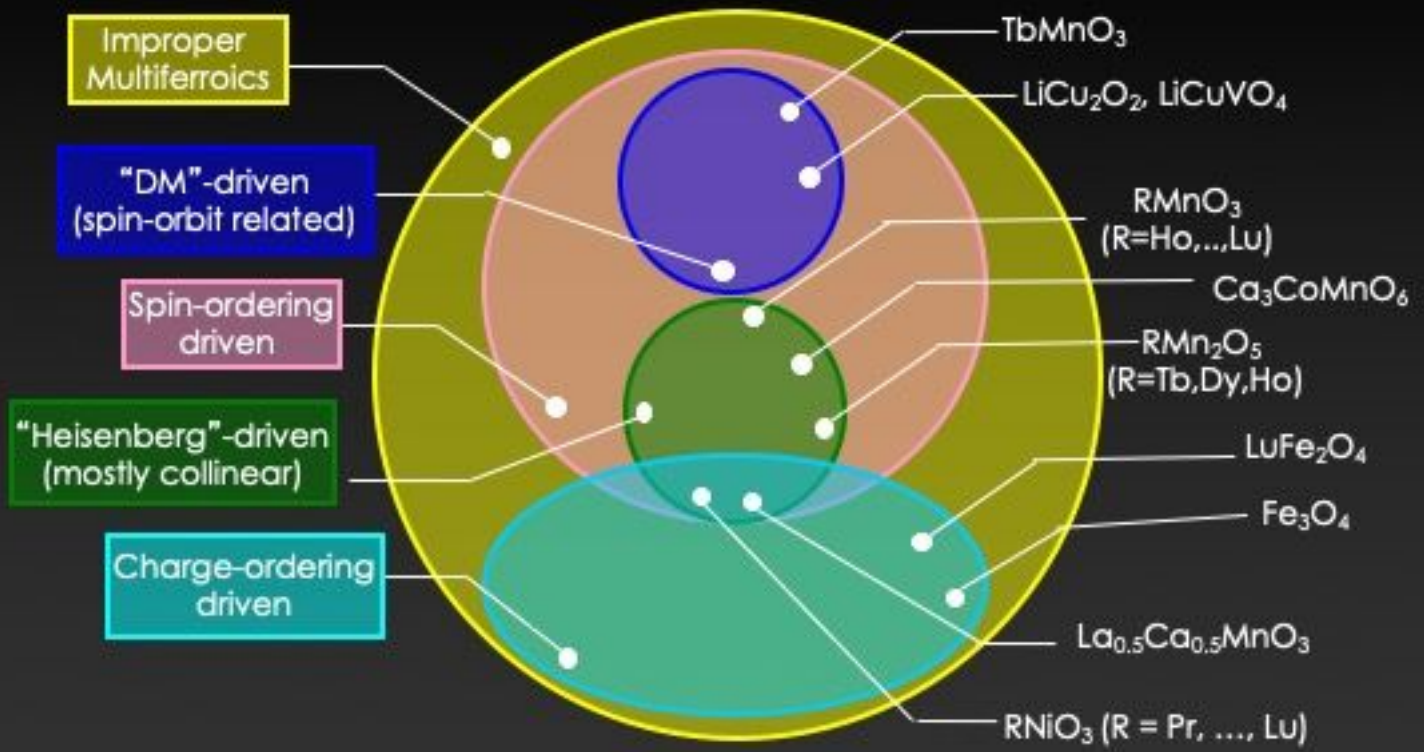
ORTHO-HoMnO3 AS A MAGNETICALLY DRIVEN FERROELECTRIC

- First *ab-initio* calculation of P driven by AFM*
- P is ~few μC/cm² (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

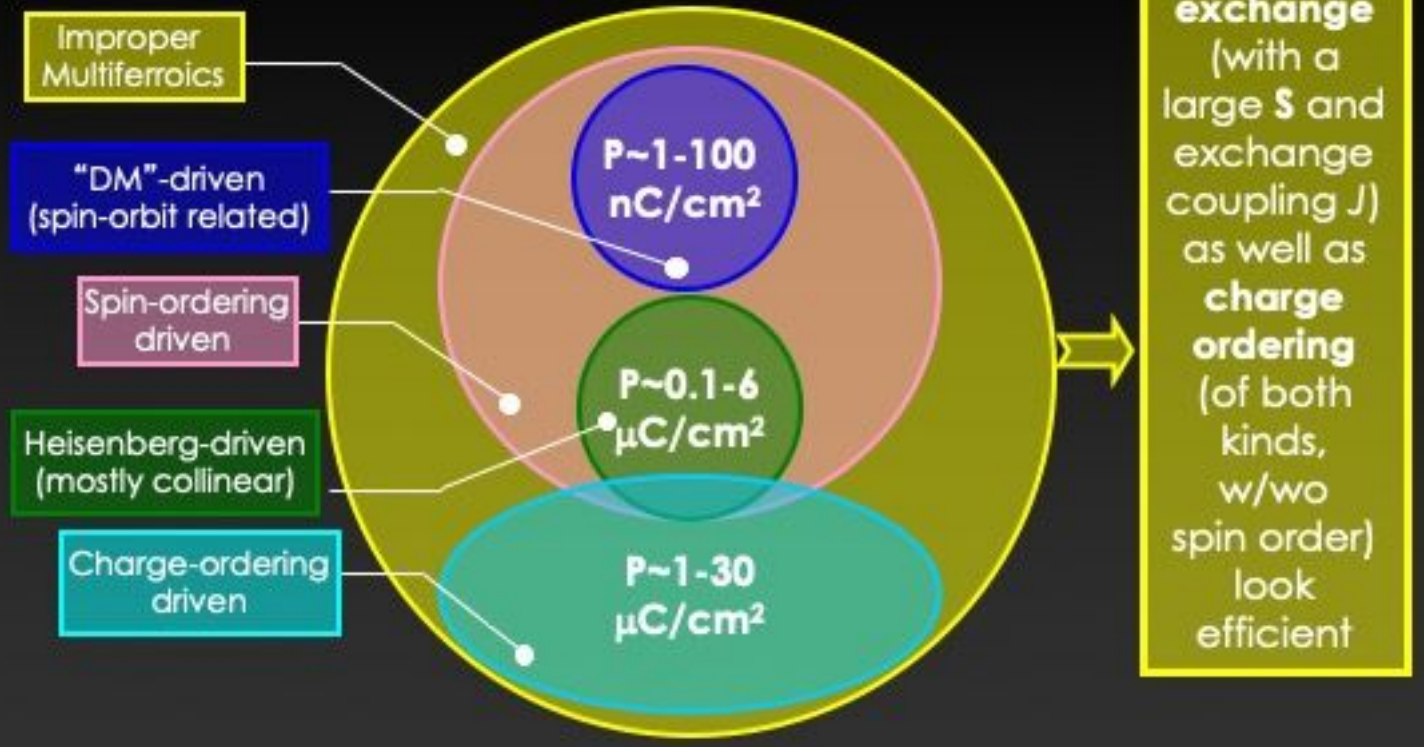


* S. Picozzi, K. Yamauchi, B. Sanyal, I. Sergienko, E. Dagotto, PRL 99, 227201 (2007)

CLASSIFICATION OF IMPROPER MULTIFERROICS



WHAT ABOUT THE SIZE OF P?

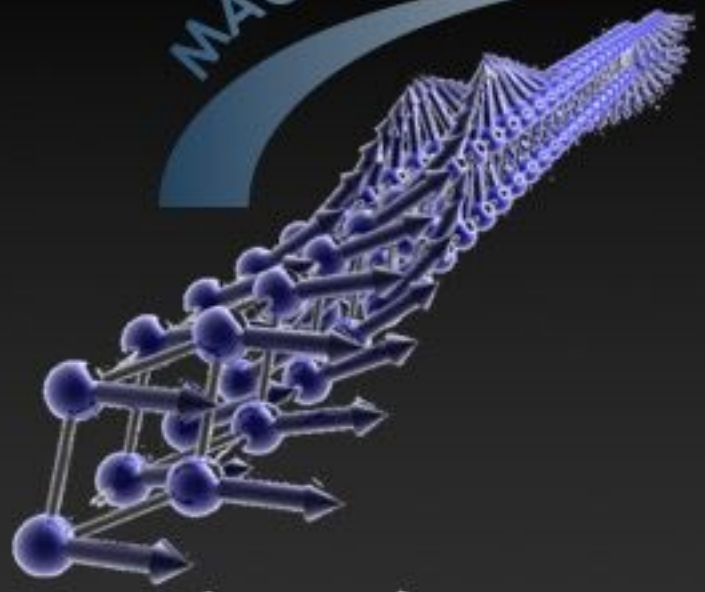


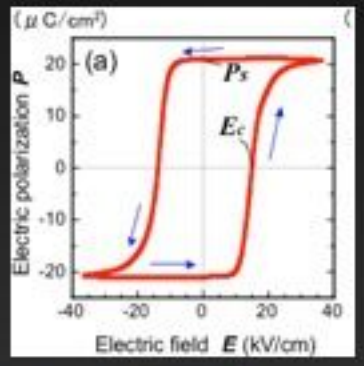
OTHER MECHANISMS
OTHER MATERIALS

1. Can we drive magnetism with an electric field?
2. Can we use organic or metal-organic frameworks?

MAGNETOELECTRICITY: SIMPLE ARGUMENTS

MAGNETISM DRIVES POLARIZATION





CAN POLARIZATION DRIVE MAGNETISM ?

X-ray imaging of cycloidal magnetic domains in ferroelectric monodomain $BiFeO_3$

R. D. Johnson,[1,2] P. Barone,[3] A. Bombardi,[4] R. J. Bean,[5] S. Picozzi,[3]
P. G. Radaelli,[1] Y. S. Oh,[6] S-W. Cheong,[6] and L. C. Chapon[7]

Hard X-ray Magnetic Scattering (DIAMOND, UK):
High space and momentum resolution

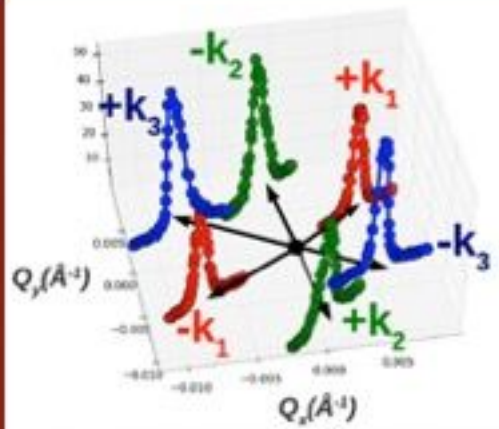
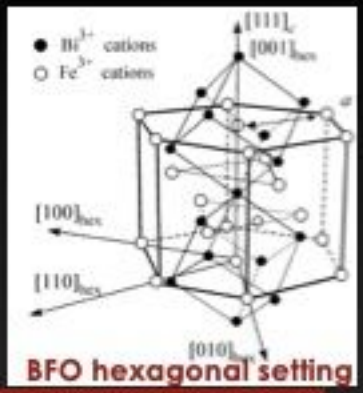


Fig: Magnetic Bragg intensities of the six satellites

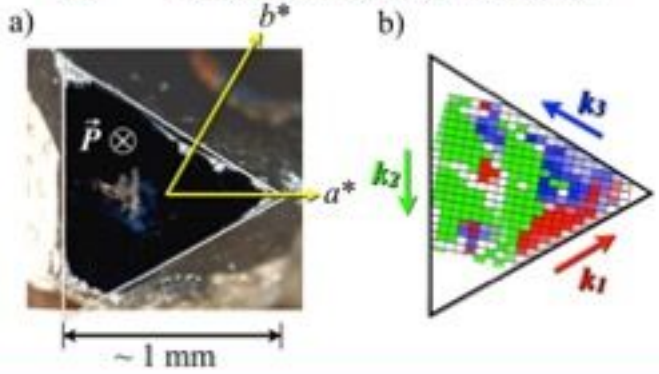
$k_1 = 2\pi\ (\delta, \delta, 0)$
$k_2 = 2\pi\ (\delta, -2\delta, 0)$
$k_1 = 2\pi\ (-2\delta, \delta, 0)$
$\delta = 0.0045$



BFO hexagonal setting

Imaging of 3 large (up to 500 μm) magnetic domains for k_1, k_2, k_3

a) Photograph of the crystal
b) Distribution of AFM domains



DETERMINATION OF MAGNETIC POLARITY λ

X-ray Magnetic Scattering with circ. pol. Light
⇒ Determination of absolute rotation direction of magnetization

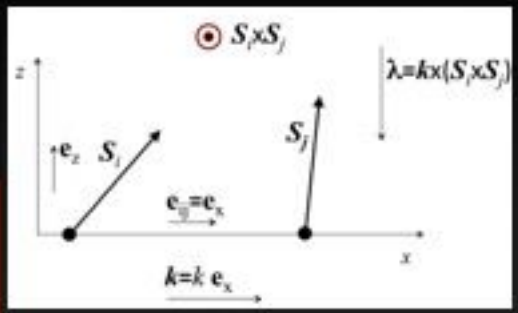
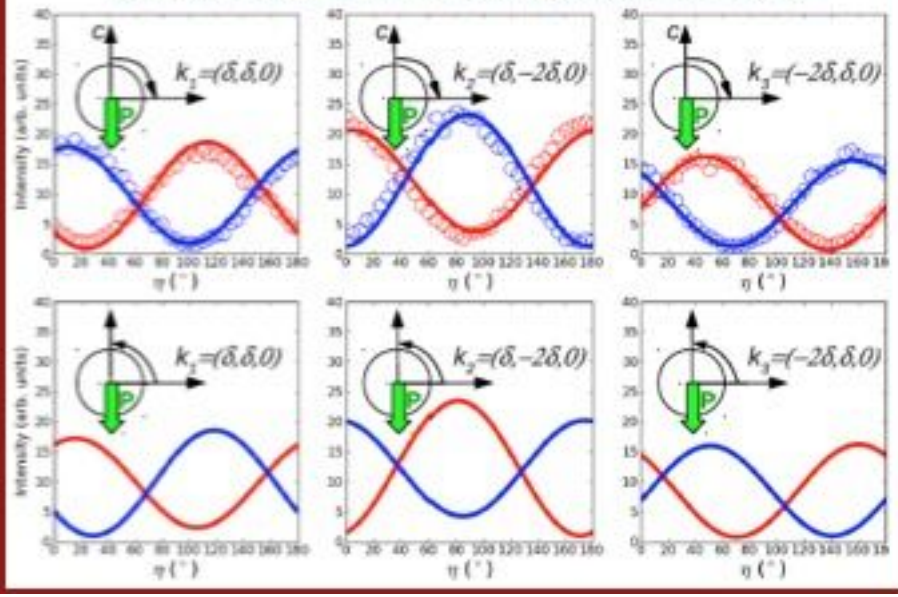


Fig: Variation of the scattered X-ray intensity vs analyser angle for three magnetic reflections



β= -1 (CW)

β= +1 (CCW)

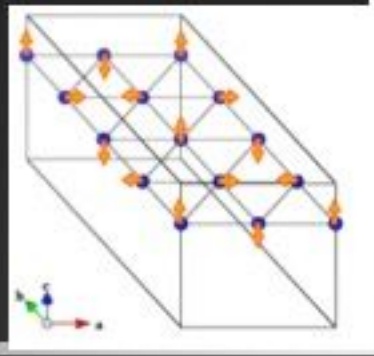
All magnetic configurations rotate clockwise !!

MICROSCOPIC ORIGIN: DFT

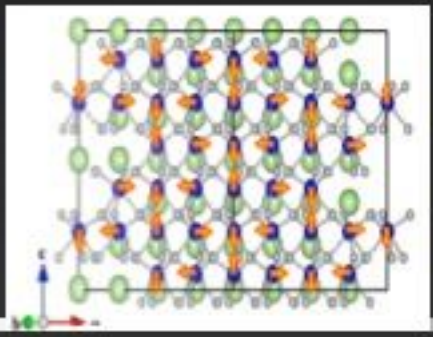
(Real) Cycloid modulation 640 Å ⇒ Reduce unit cell in DFT: 2**a** x 4**b** x **c** (240 atoms)

	τ (Å)	P_c ($\mu C/cm^2$)	ΔE (meV/Fe)
FE↑	0.668	105.17	-2.34
PE	0	0	0
FE↓	-0.668	-105.17	2.34

TABLE I. DFT results obtained for U=5 eV, J=1 eV. The energy difference is defined as $\Delta E = E_{CW} - E_{CCW}$. FE↑ and FE↓ are characterized by opposite collective displacements, τ, respectively upward and downward, of Bi sublattice with respect to O layers perpendicular to c axis.



The sign of FE polarization stabilizes the magnetic polarity of the cycloid. For PE, CW and CCW states are degenerate



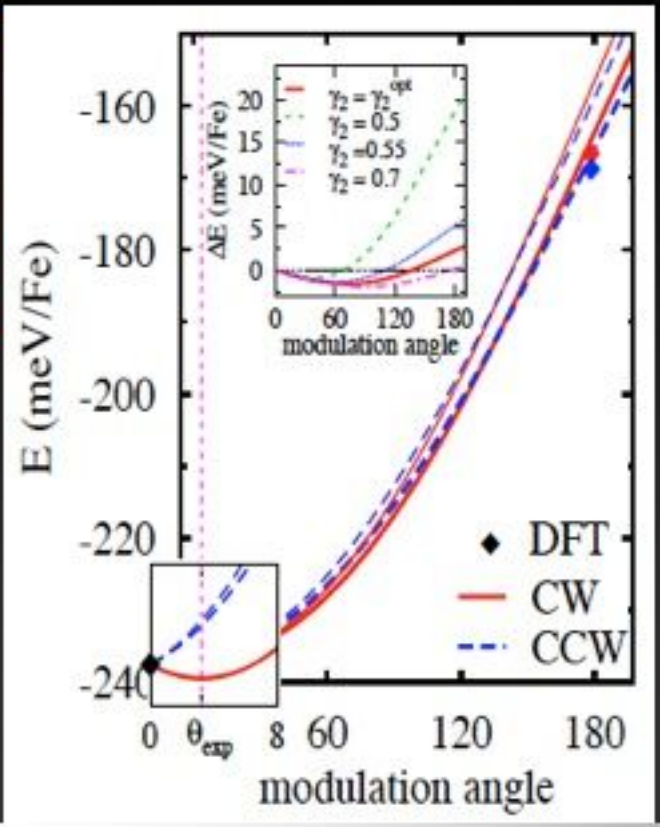
MODEL HAMILTONIAN STUDY

$$H = \frac{1}{2}\left(\sum_{ij}^{nn} J_{nn} + \sum_{ij}^{nnn} J_{nnn}\right) \boldsymbol{S}_i \cdot \boldsymbol{S}_j +$$

$$-\gamma P_e \left(\sum_{ij}^{nn} + \gamma_2 \sum_{ij}^{nnn}\right) \frac{1}{l_{ij}^z} (\boldsymbol{e}_z \times \boldsymbol{e}_{ij}) \cdot (\boldsymbol{S}_i \times \boldsymbol{S}_j)$$

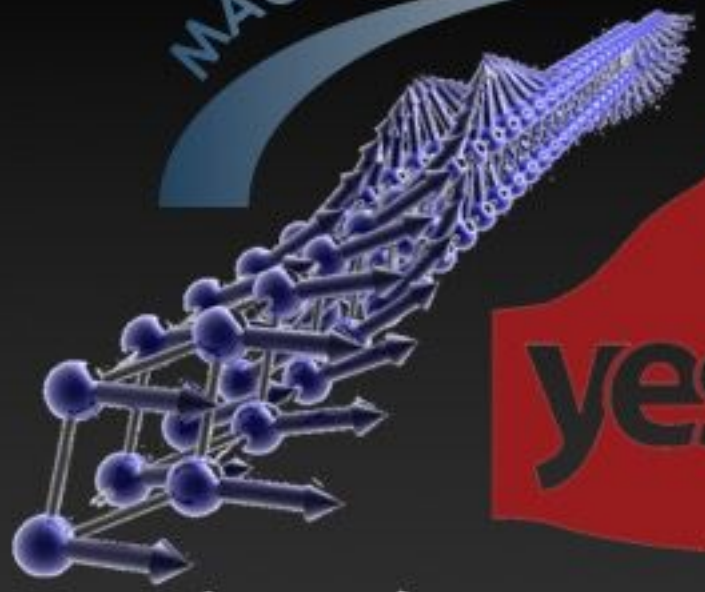
COUPLING TERM:
DZIALOSHINSKII-MORIYA LIKE

The energy favored magnetic polarity depends on modulation angle
⇒ Importance of 2nd *nn* to reproduce expts
⇒ $\gamma \sim 2.4 \times 10^{-4}$ V



MAGNETOELECTRICITY: SIMPLE ARGUMENTS

MAGNETISM DRIVES POLARIZATION

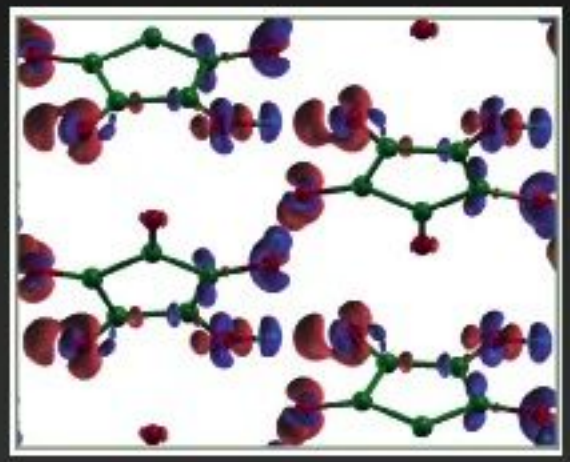


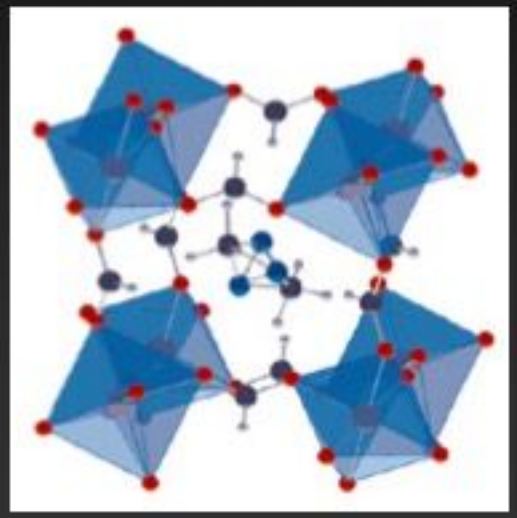
MAGNETIC CYCLOIDS in each domain propagate with a UNIQUE ROTATION direction imposed by the ELECTRIC POLARITY of the crystal

CAN POLARIZATION DRIVE MAGNETISM ?

R.D. Johnson et al,
PRL **110**, 217206 (2013)

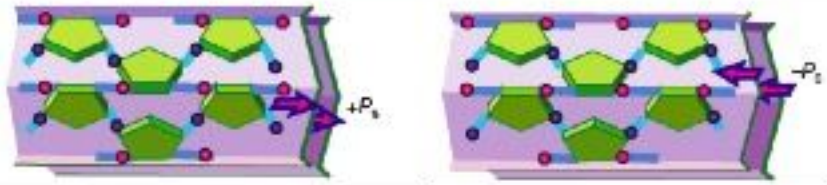
… NOT ONLY OXIDES: ORGANICS & HYBRIDS





PROTON TRANFER: EFFICIENT SOURCE OF P

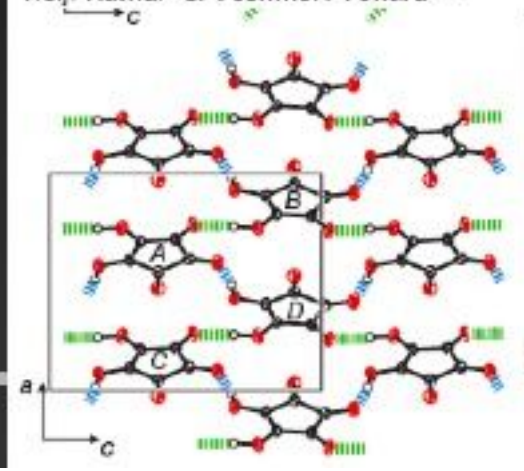
Vol 463|11 February 2010|doi:10.1038/nature08731 nature

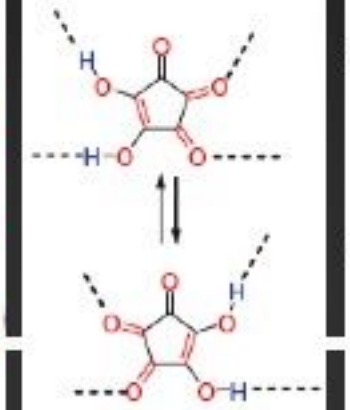


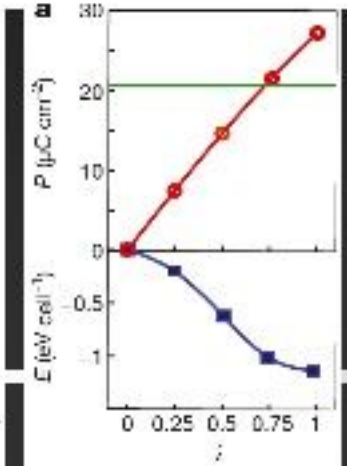
LETTERS

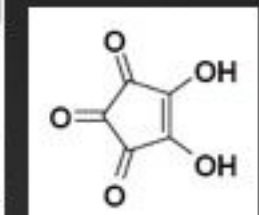
Above-room-temperature ferroelectricity in a single-component molecular crystal

Sachio Horiuchi[1], Yusuke Tokunaga[2], Gianluca Giovannetti[3,4], Silvia Picozzi[3], Hirotake Itoh[2], Ryo Shimano[2,5], Reiji Kumai[1] & Yoshinori Tokura[1,2,6]



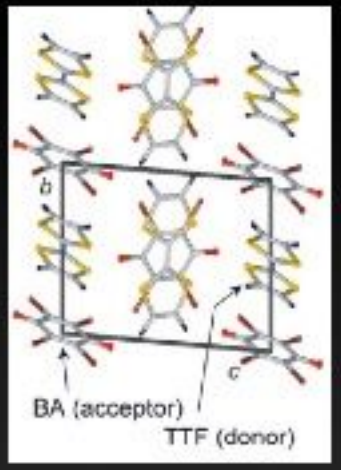


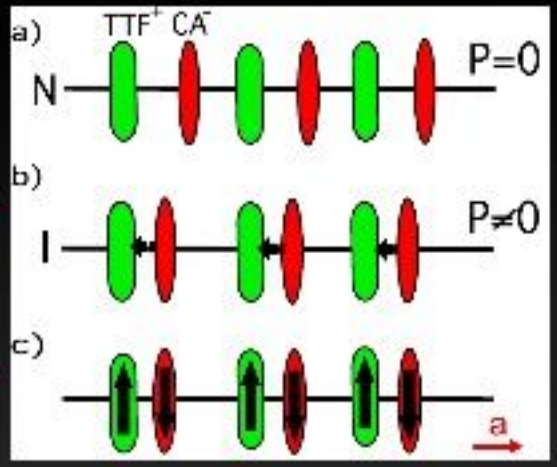


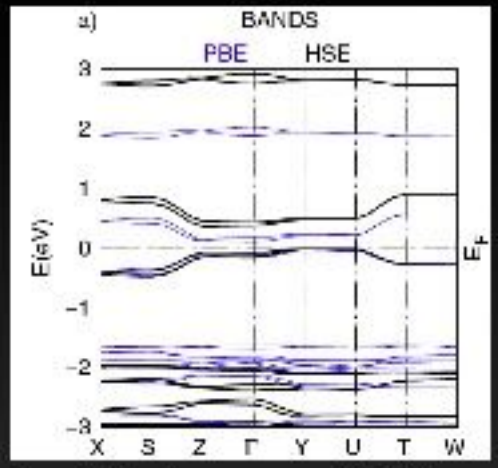


Croconic Acid

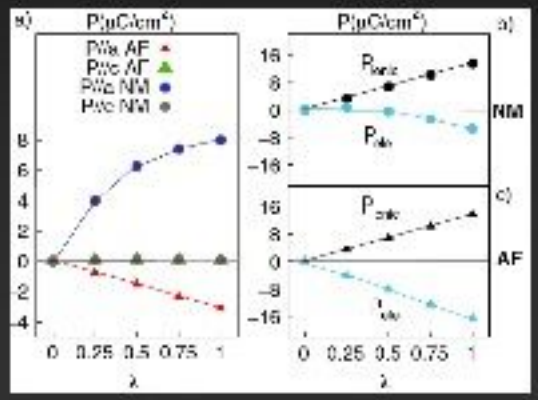
TTF-CA: SPIN-PEIERLS AS A SOURCE OF P ?



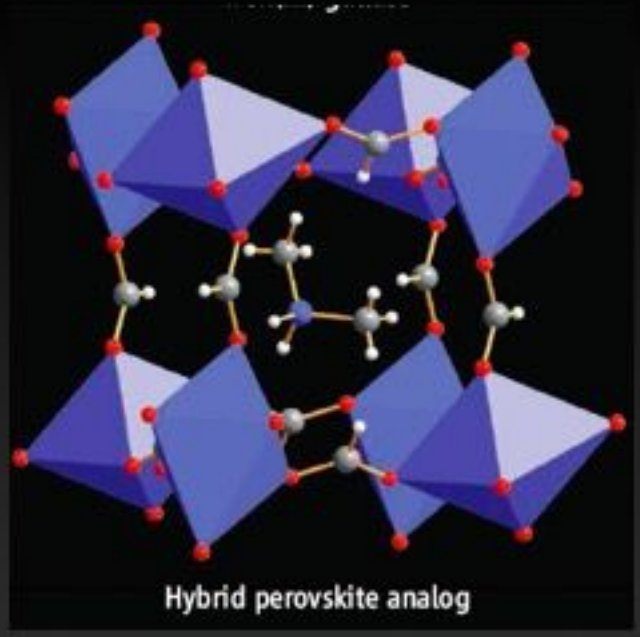




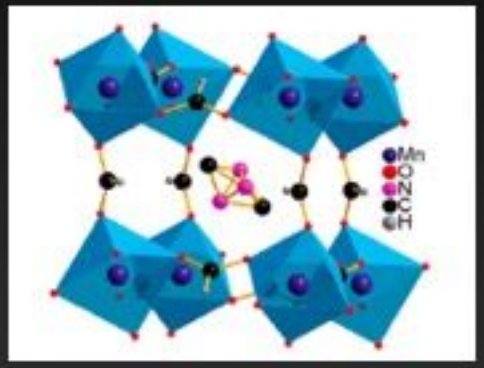
- SPIN PEIERLS: One-dimensional Heisenberg spin 1/2 chain ==>> instability to a dimer-singlet (gain of symmetric exchange)
- TTF-CA: Under the neutral-Ionic transition



METAL-ORGANIC FRAMEWORKS



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

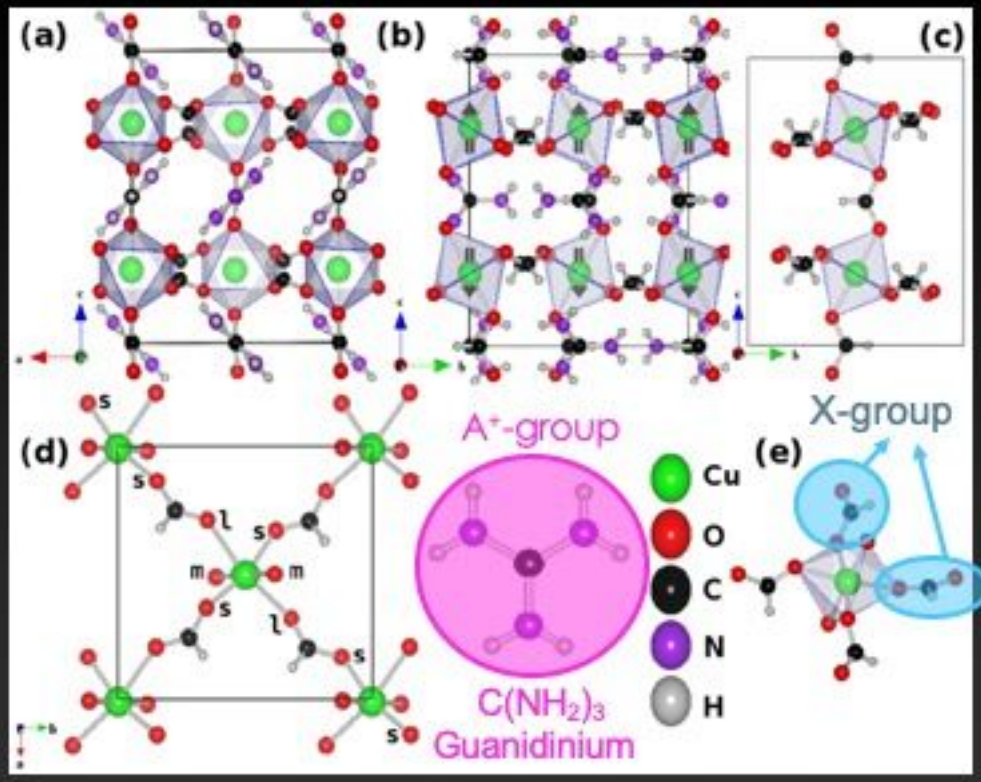


Hybrid Improper Ferroelectricity in a Multiferroic and Magnetoelectric Metal-Organic Framework

Adv. Mater. **2013**, *25*, 2284–2290

A. Stroppa, P. Barone, P. Jain, J. M. Perez-Mato, and S. Picozzi*

METAL-ORGANIC FRAMEWORKS

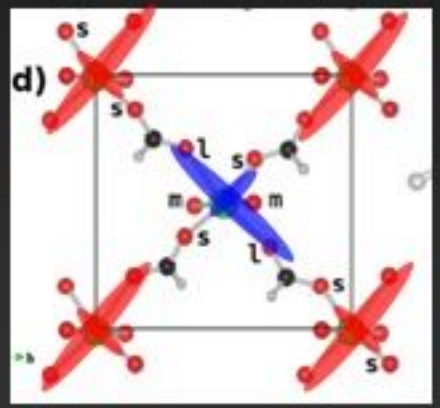


AFM-A magnetic order

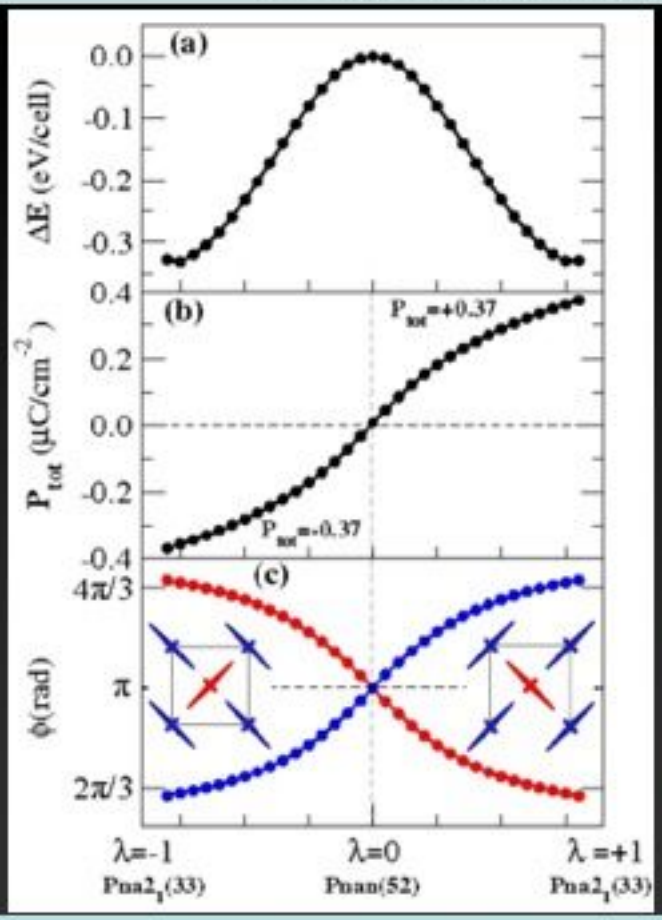
Cu octahedra connected by **HCOO**$^{-}$ groups (ligands)

Cu^{+2} Jahn-Teller ion

Antiferrodistortive order in the ab plane



Cu-MOF AS A NEW MULTIFERROIC



λ amplitude of the polar distortion:

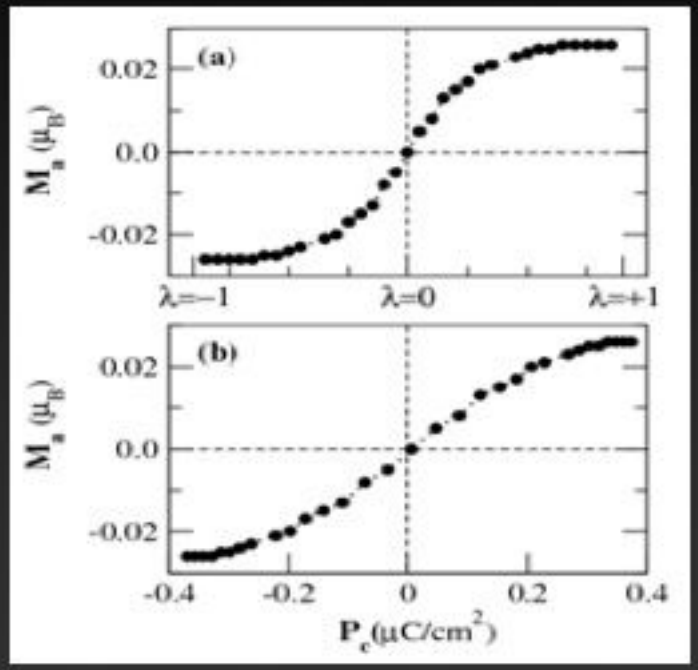
λ=0 paraelectric state (P=0);
λ=+/- 1 ferroelectric (FE) state
(P=0.37 μC/cm2).

NB: The AFD order is non-polar in usual inorganic compound (like KCuF3)

In Cu-MOF AFD and FE are clearly correlated!

Cu-MOF AS A NEW MULTIFERROIC

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



Ab-initio calculations fully confirm what expected by symmetry

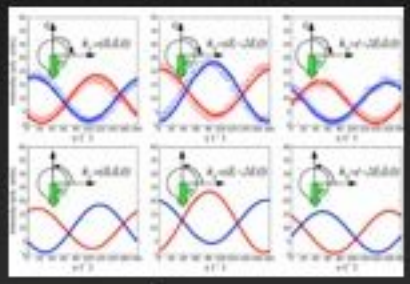
In Cu-MOF, a magnetic field can couple to **weak-FM component** and can **reverse FE polarization** (and viceversa: an **electric Field** can **switch weak-moment**)

ELECTRICAL CONTROL OF MAGNETIZATION !

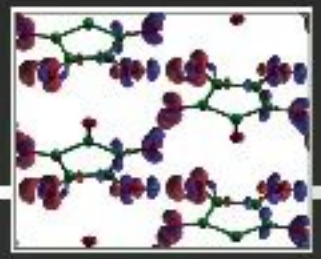
TAKE HOME MESSAGES

- **First principles calculations can give valuable insights into mechanisms and quantitative reliable estimates for different materials**
- Very different microscopic origins for improper ferroelectricity

- **Heisenberg exchange striction** seems a mechanism able to drive a large polarization !
- **Charge ordering** is an efficient mechanism!

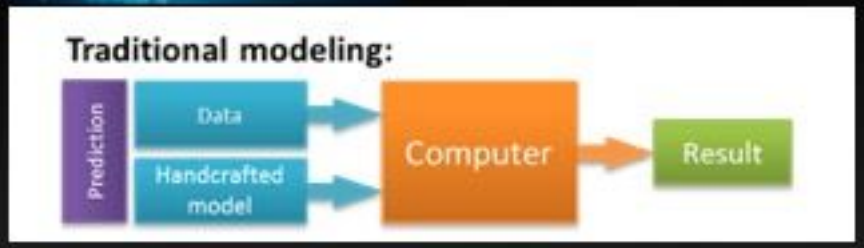


- **MAGNETOELECTRICITY:** can polarization drive magnetism?
  The case of $BiFeO_3$ spin cycloid



- Take a look at **organics/hybrids**!

FUTURISTIC OUTLOOK: MACHINE LEARNING ?



Can we use DFT data to train a **Machine Learning Algorythm** to predict when a material is FE or AFE,to go to **high time/space scales**, to **design room temperature MF ?**

1 PhD and 1 post-doc position opening: pls contact me!