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13 - 15 January 2011

MULTIFERROICS: ELECTRONIC DEGREES OF FREEDOM AT PLAY

Silvia Picozzi
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CNR-SPIN, UOS
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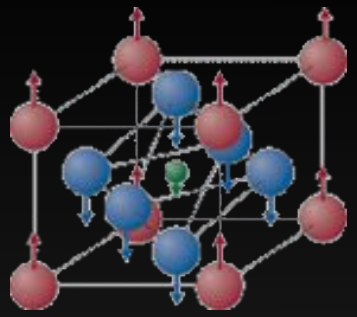
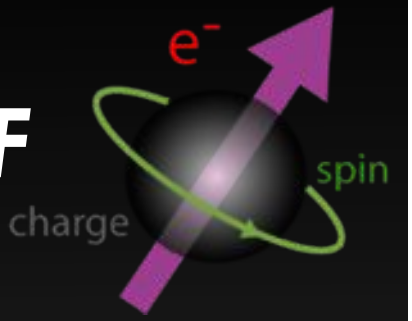
Italy



MULTIFERROICS: *ELECTRONIC DEGREES OF FREEDOM AT PLAY*



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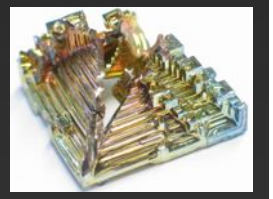
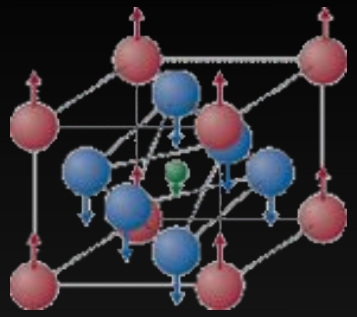
67100 L'Aquila, Italy

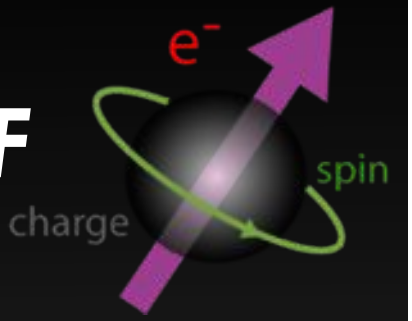
Project "BISMUTH":
Breaking **I**nversion-**S**ymmetry in **M**agnets:
Understand via **TH**eory



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



MULTIFERROICS: *ELECTRONIC DEGREES OF FREEDOM AT PLAY*



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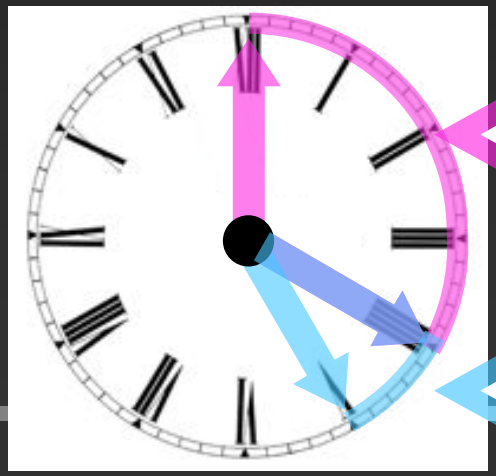
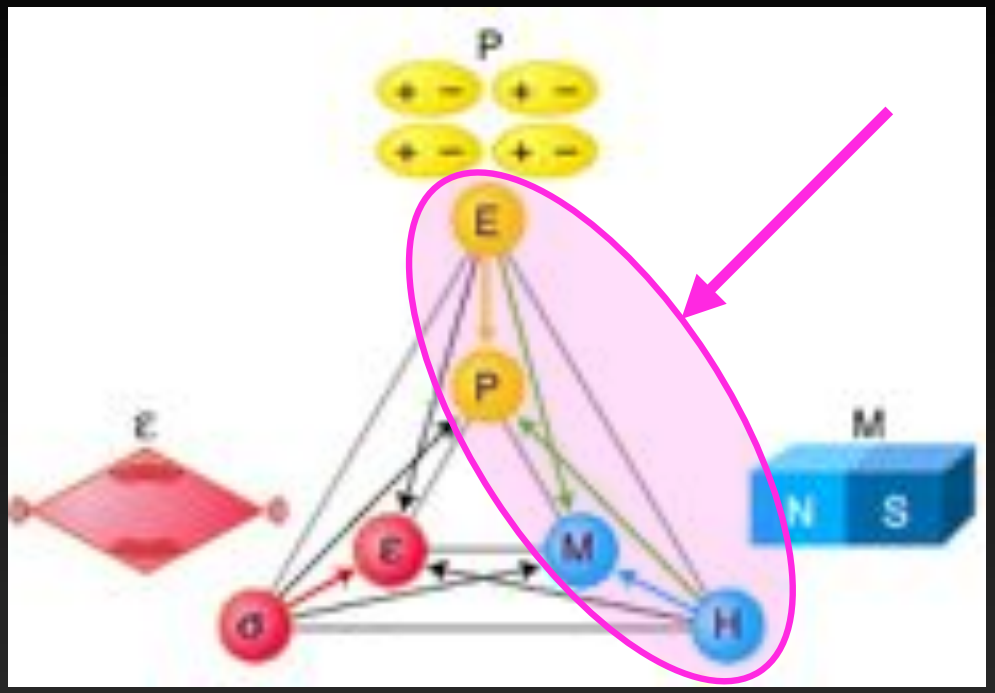
OUTLINE



Magnetically-induced ferroelectrics
Charge-order induced ferroelectrics

Emerging routes to ferroelectricity:
Organics & metal-organic frameworks

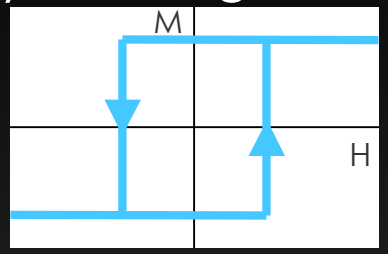
MULTIFERROICS & MAGNETOELECTRICS



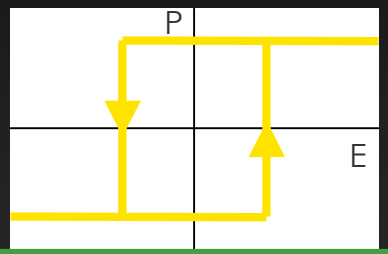
➢ **Ferroic**: P, M or ε are spontaneously formed to produce ferroelectricity, ferromagnetism or ferroelasticity

➢ **Multiferroic**: coexistence of at least two kinds of long-range ordering

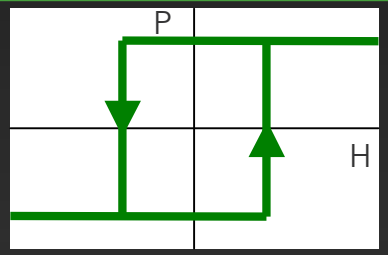
➢**Magnetoelectrics**: Control of P (M) via magnetic (electric) field



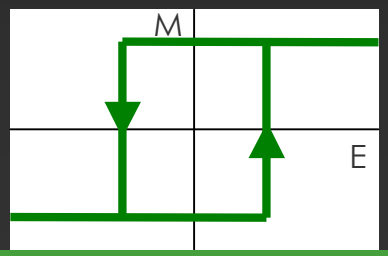
Magnetization vs magnetic field in FMs



Polarization vs electric field in FEs



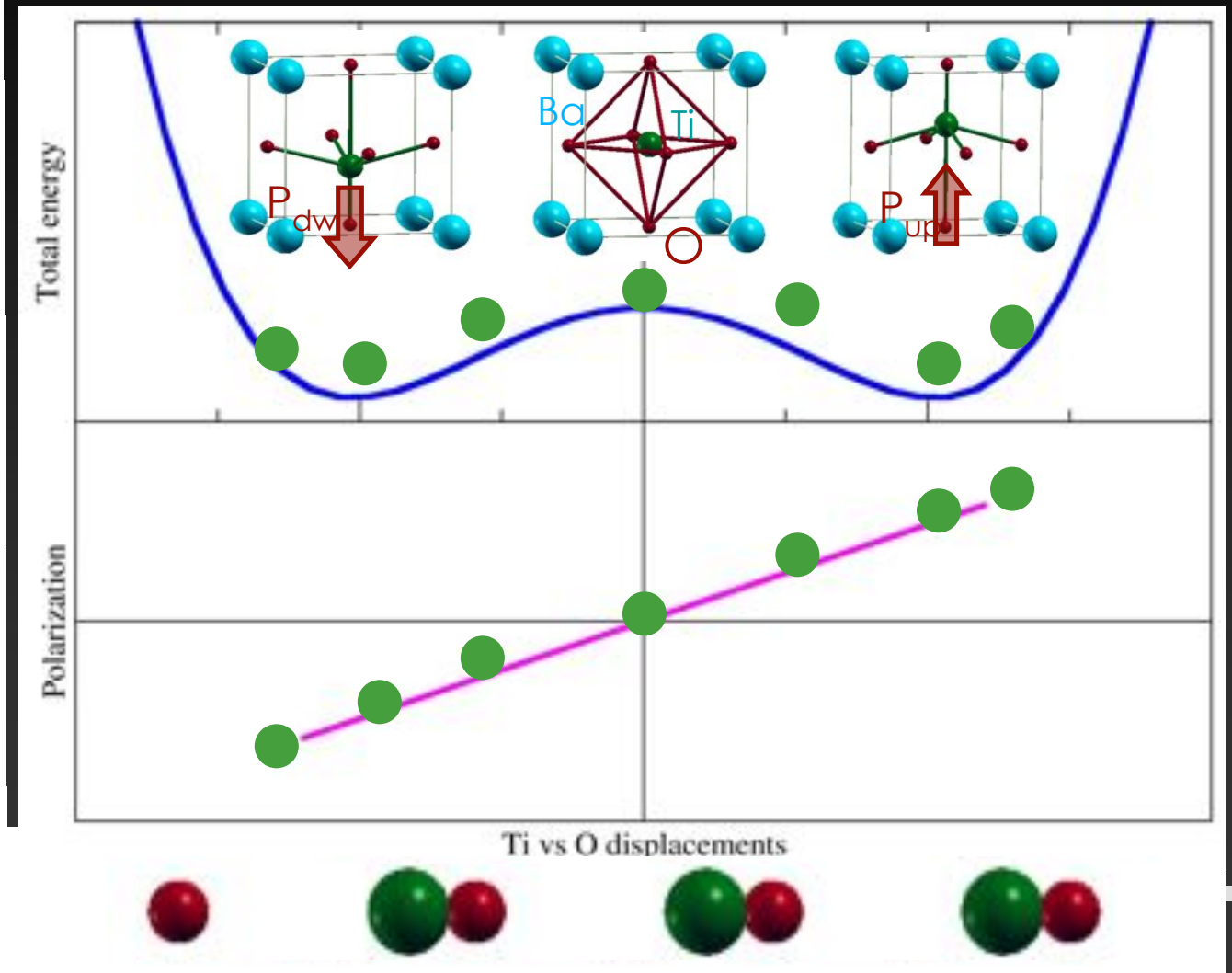
Polarization vs magnetic field in MEs



Magnetization vs electric field in MEs

PROPER DISPLACIVE FERROELECTRICITY

• **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)



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

PROPER DISPLACIVE FERROELECTRICITY

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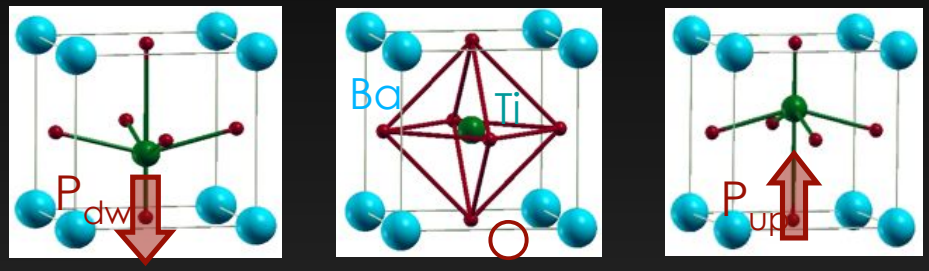
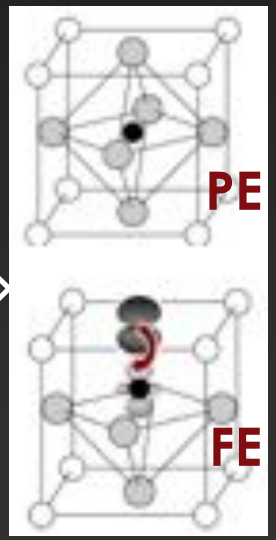


• $BaTiO_3$:
Up or down displacement of B-site cation

NB: B is generally d^0: magnetism and FE contraindicated *(N.Spaldin, D.Khomskii)*

Hybridization: Ti *d* (empty) - O *p* states "covalency-driven"



BREAKING INVERSION SYMMETRY IN MAGNETS

Conventional

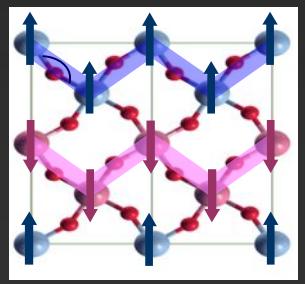
Non-Conventional

FERROELECTRICITY ⟺ no Inversion Symmetry

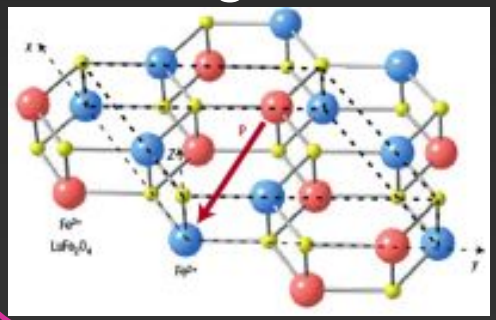
- "Proper"
- **Ionic displac.** break inversion symmetry (IS)
- "**Covalency**"-driven

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

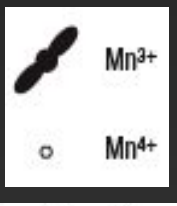
Spin-order (some AFM or "spiral")

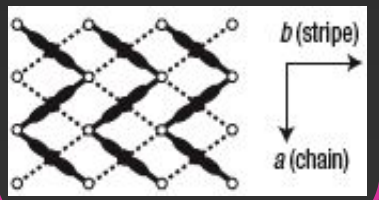


Charge-order

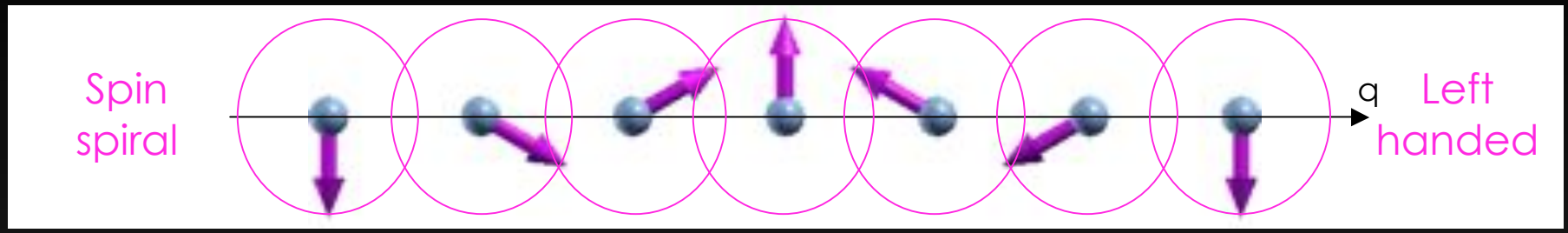


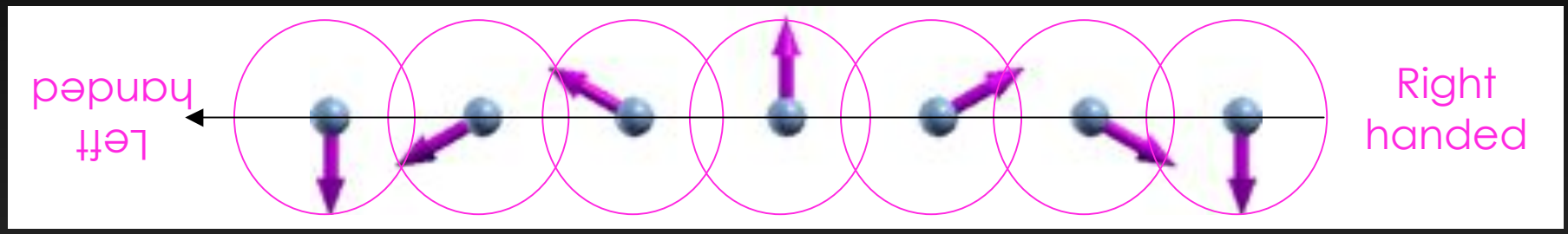
Orbital-order

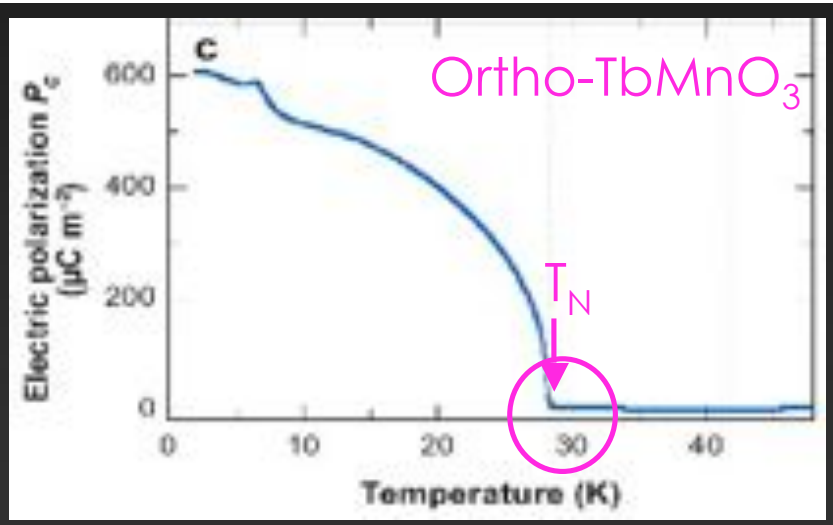


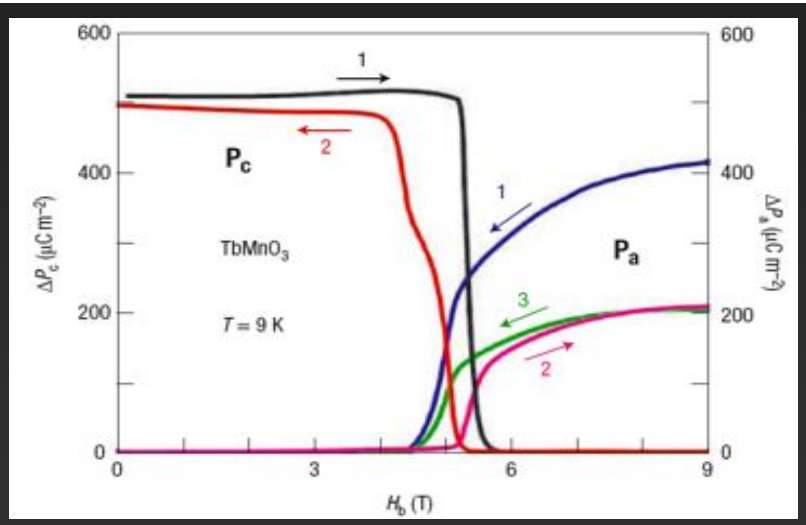


HOW MAGNETIC ORDERING CAN BREAK INV. SYM.?



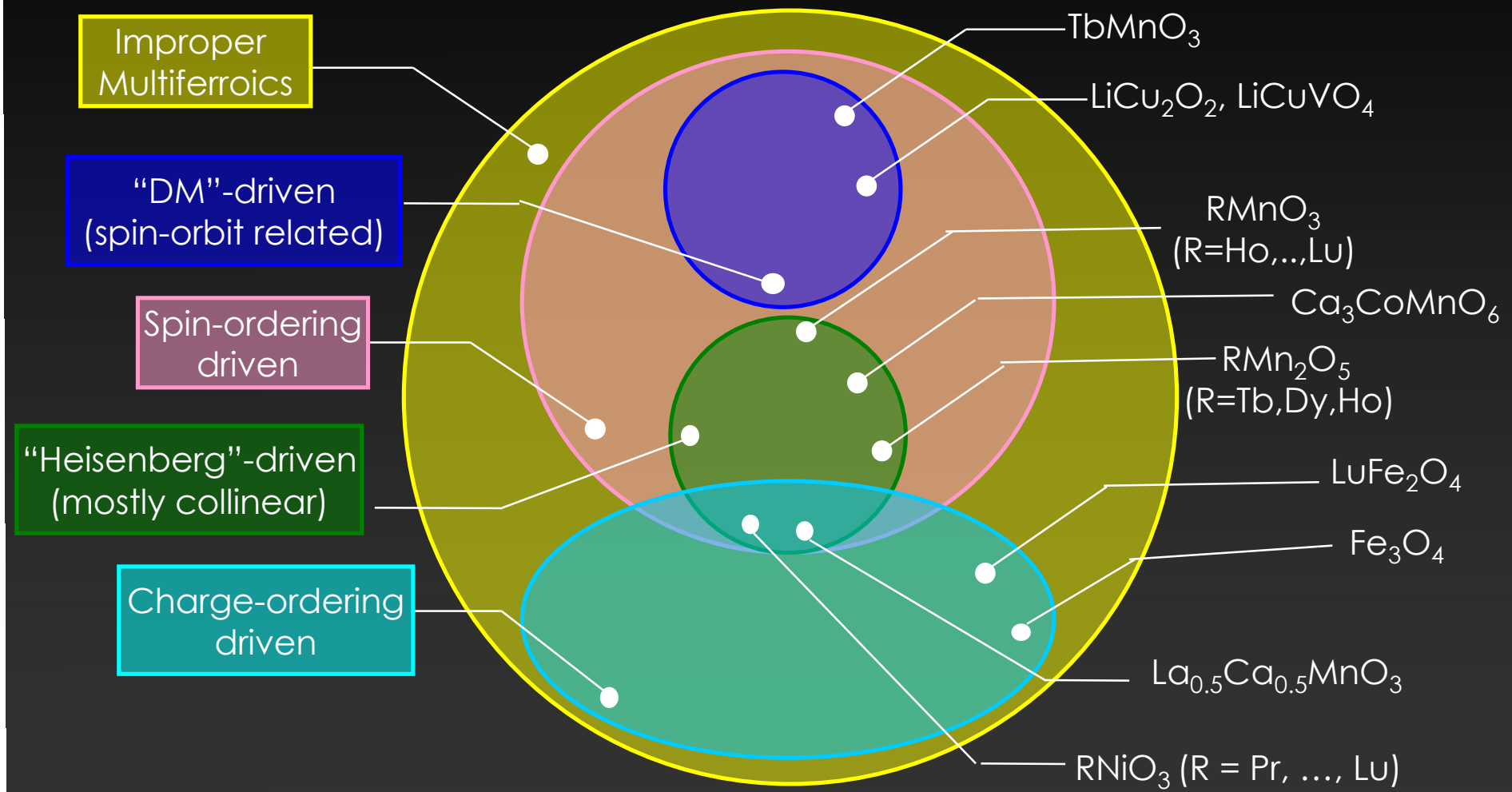


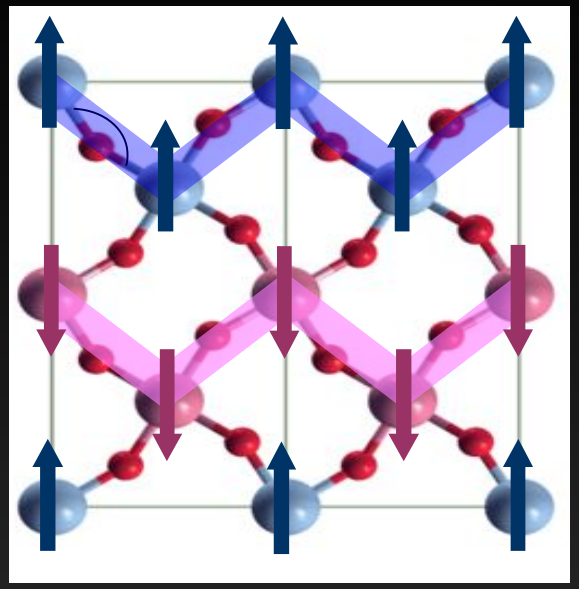




T.Kimura et al., Nature ***425****, 55 (03); S.W.Cheong and M.Mostovoy, Nature Mater.* ***6****, 13 (07)*

CLASSIFICATION OF IMPROPER MULTIFERROICS





E-TYPE MANGANITES: ELECTRONIC AND IONIC FERROELECTRICITY

- In collaboration with:

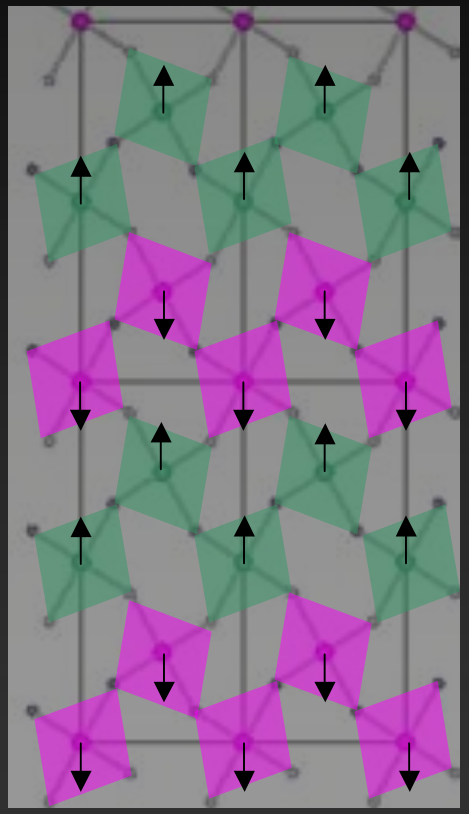
K. Yamauchi *(CNR-INFM)*

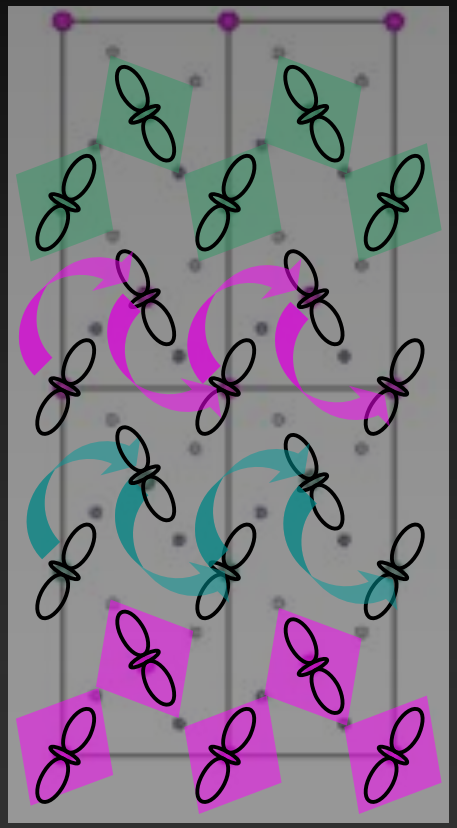
I. A. Sergienko, E. Dagotto
(Oak Ridge Natl. Lab, Univ. Tennessee, TN)

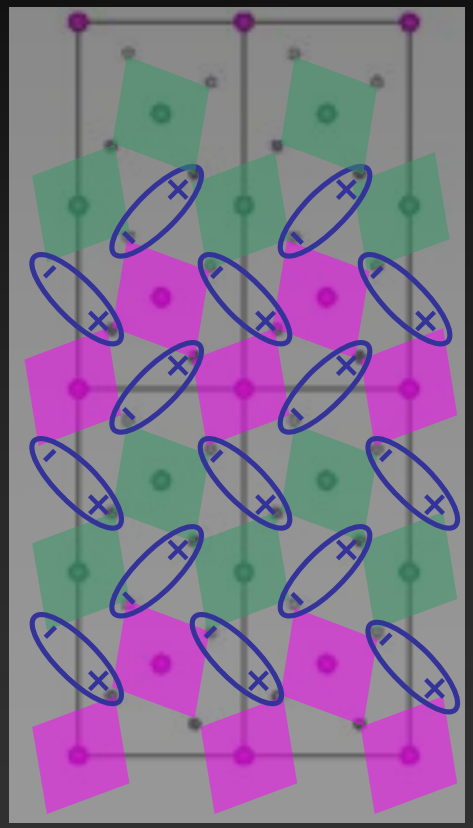
WHY THE AFM-E SHOULD BE FERROELECTRIC ?

- "Electronic" mechanisms

- e_g Orbital Ordering
- Oxygen inequivalency

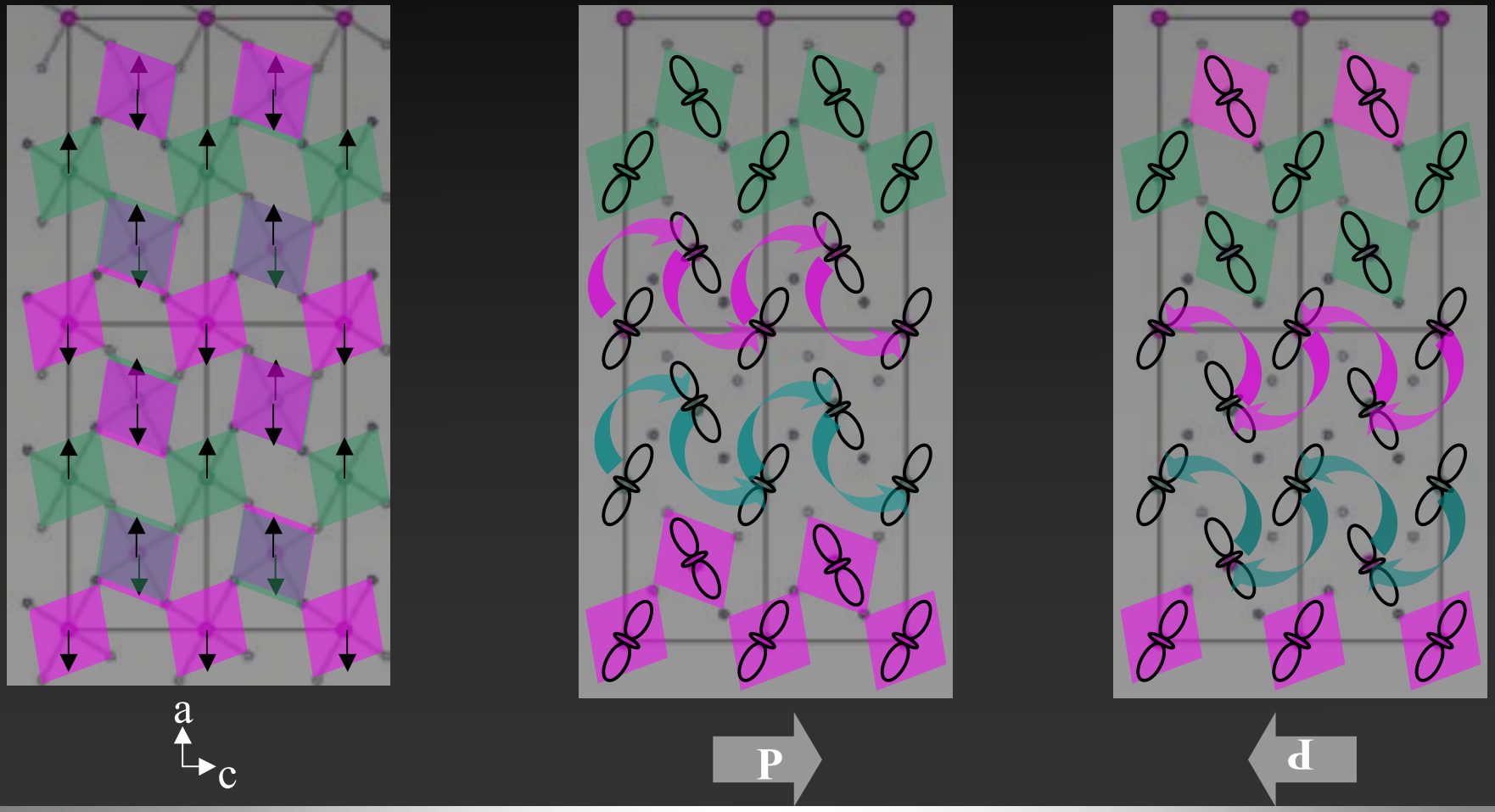






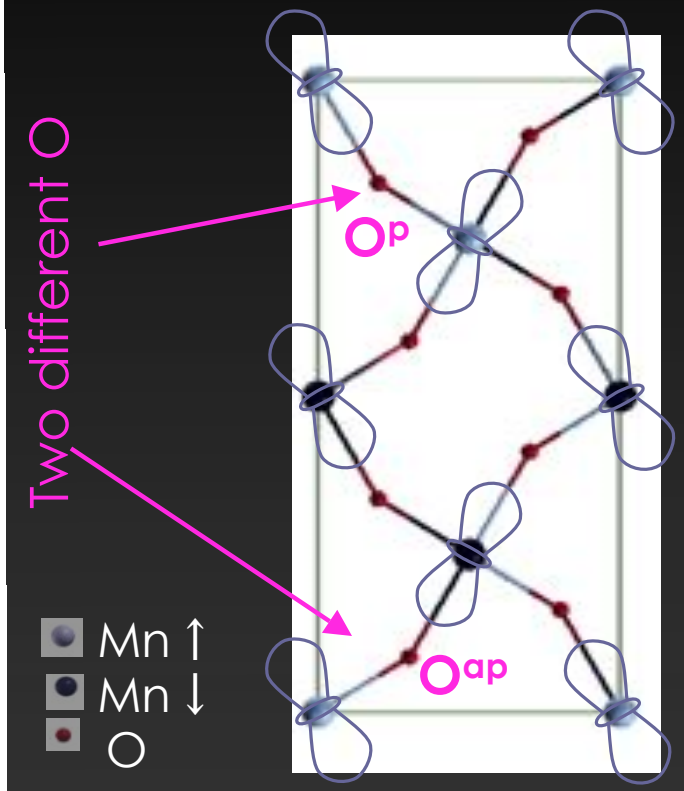
WHY THE AFM-E SHOULD BE FERROELECTRIC ?

- "Switching" mechanisms: change direction of some spins
  - e_g Orbital Ordering

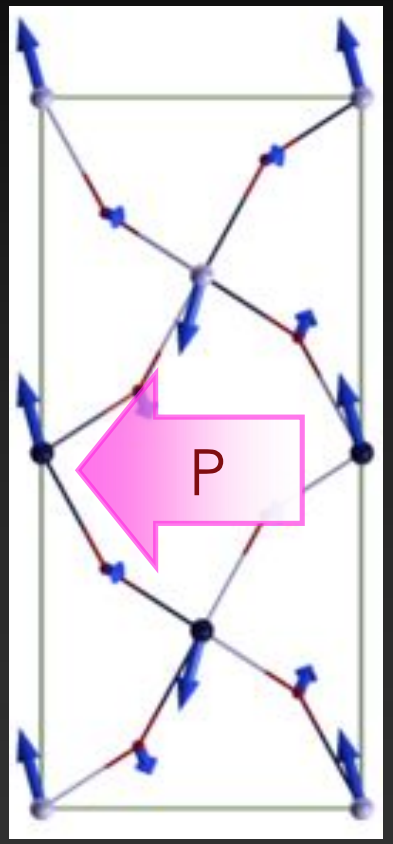


WHY THE AFM-E SHOULD BE FERROELECTRIC ?

- "Structural" contributions: Magnetostriction

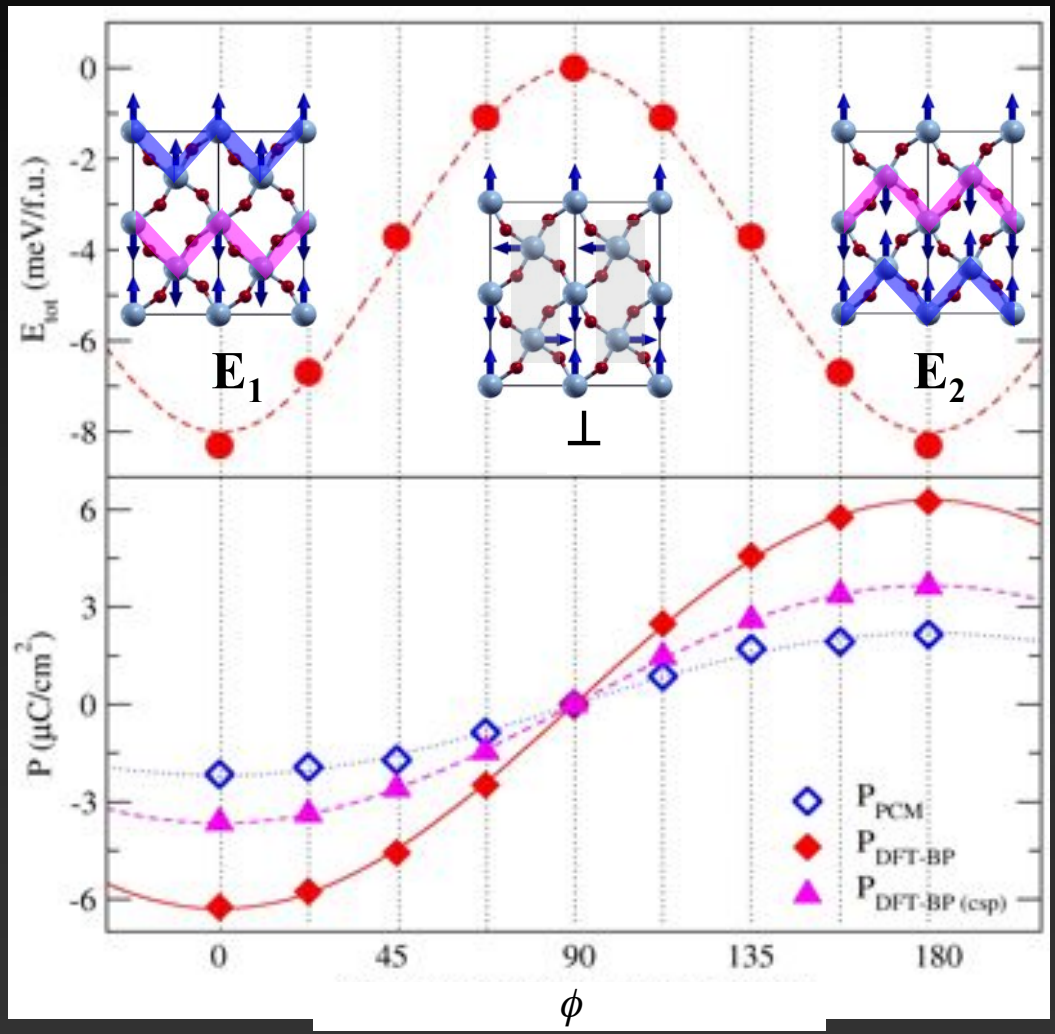


In-plane Mn and O displacements pattern from centrosymmetric AFM-A to non-centrosymmetric AFM-E



ORTHO-HoMnO3 AS A MAGNETICALLY DRIVEN FERROELECTRIC

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



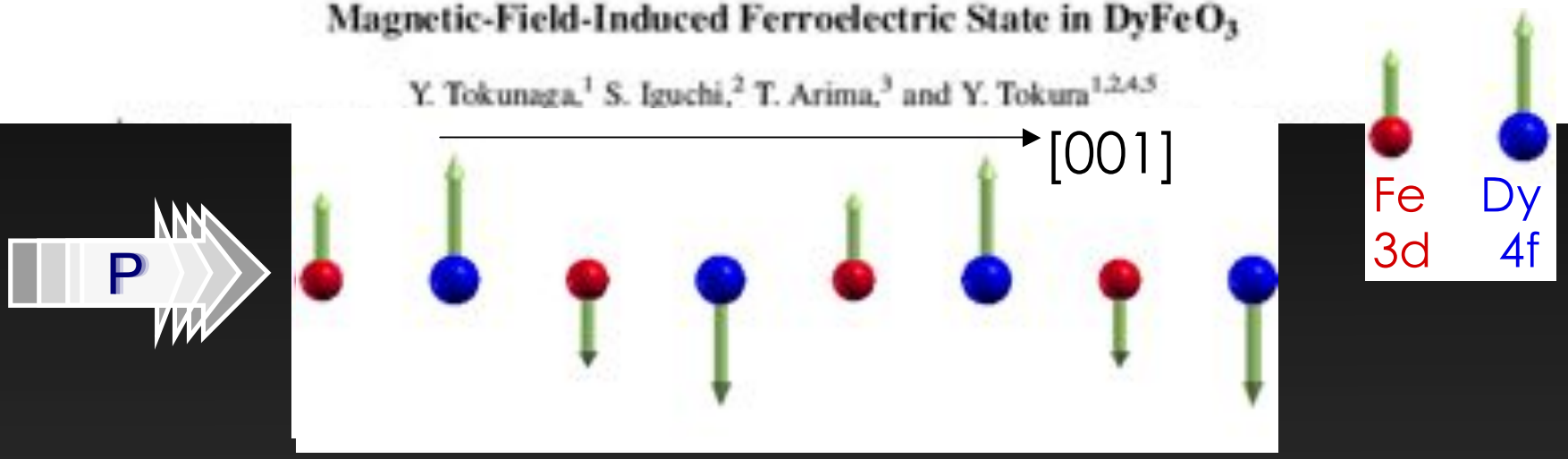
* S. Picozzi, K. Yamauchi, B. Sanyal, I. Sergienko, E. Dagotto, PRL 99, 227201 (2007)

COUPLING BETWEEN f AND d MOMENTS

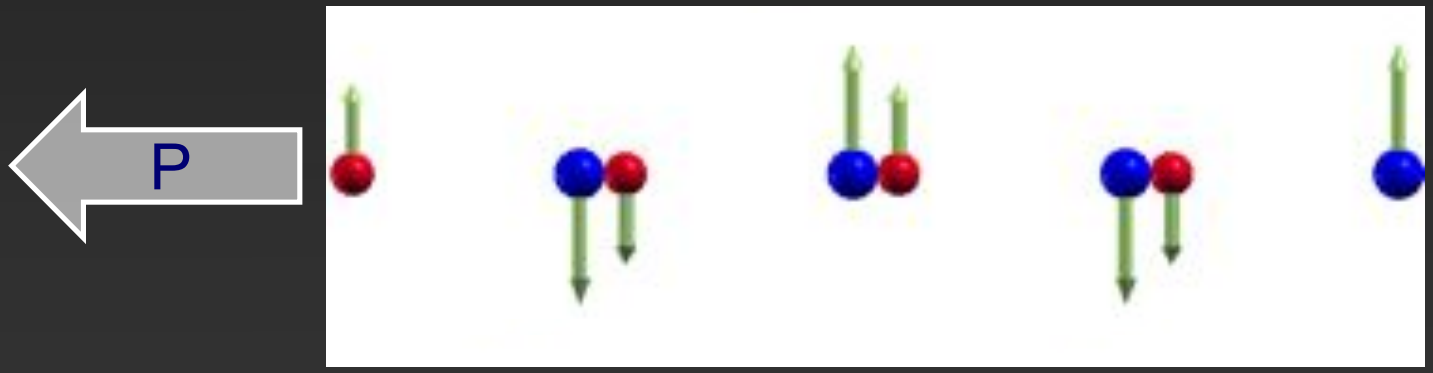
PRL 101, 097205 (2008) PHYSICAL REVIEW LETTERS week ending 29 AUGUST 2008

Magnetic-Field-Induced Ferroelectric State in $DyFeO_3$

Y. Tokunaga,[1] S. Iguchi,[2] T. Arima,[3] and Y. Tokura[1,2,4,5]



HOW TO SWITCH P? REVERSE SIGN OF 4f MOMENT !!

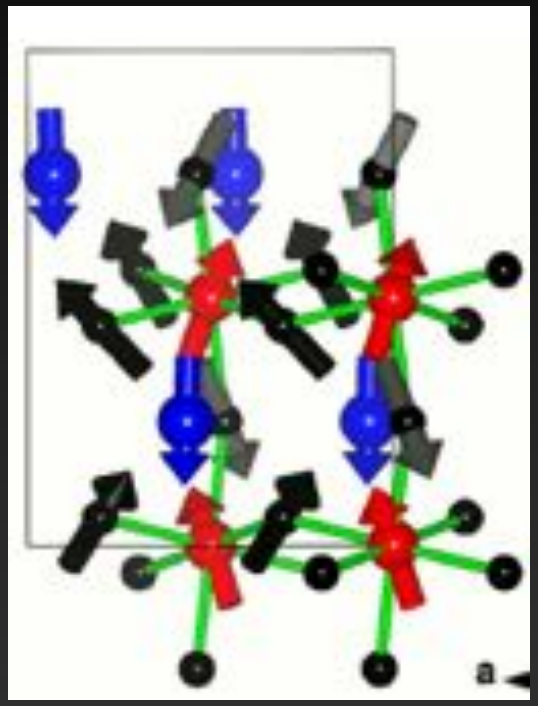


NB: 4f-states included as valence electrons within GGA**+U**

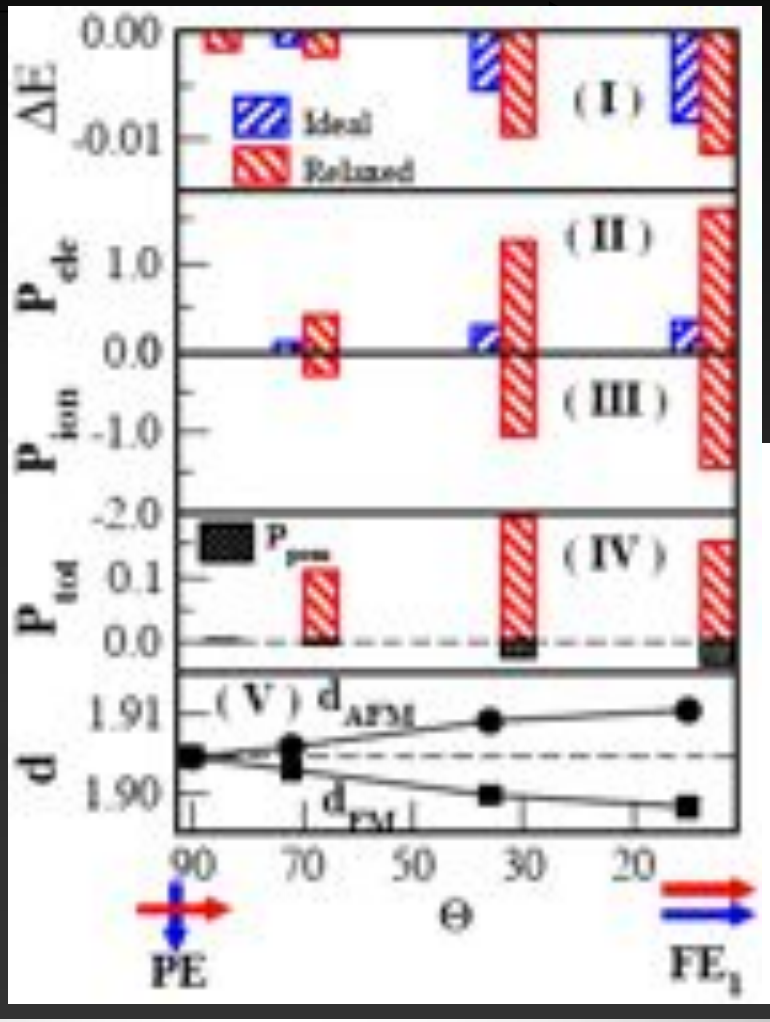
A. Stroppa, …, SP, New J. Phys. **12** , 093026 (2010)

COUPLING BETWEEN f AND d MOMENTS

Exchange striction between Dy 4f and Fe 3d states:

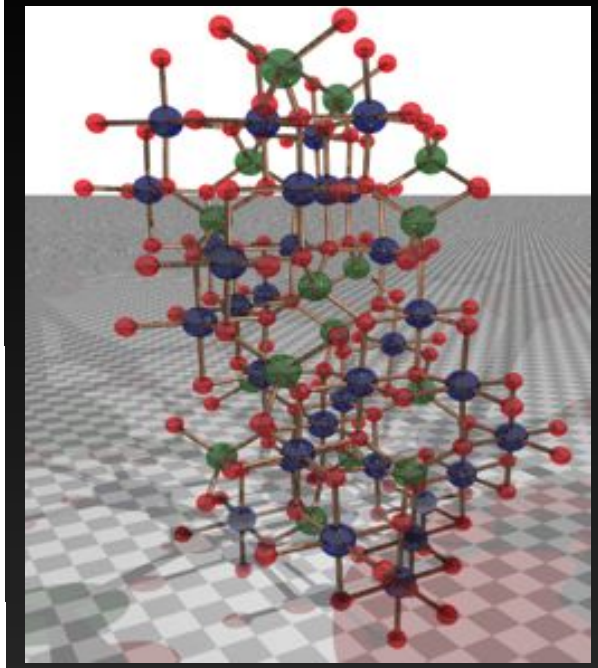


Atomic displacements from PE to FE



Path from -P to P state through paraelectric state by rotating Dy spin

A. Stroppa, …, SP, New J. Phys. **12** , 093026 (2010)



MAGNETITE

- In collaboration with:

K. Yamauchi, T. Fukushima *(CNR-INFM)*

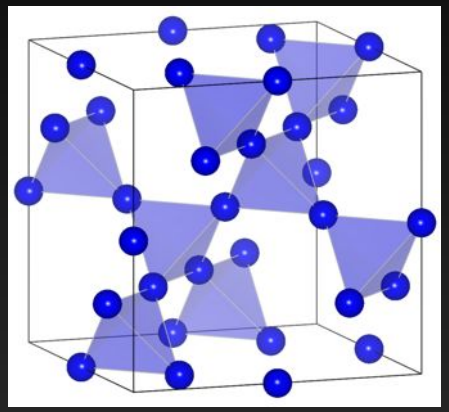
M. Alexe, D. Hesse,U. Gösele *(MPI Halle)*
M. Ziese, P. Esquinazi *(Univ. Leipzig)*

MAGNETITE Fe_3O_4 (AB_2O_4)

Inverse spinel structure *Fd3m*

Ferrimagnetism

$Fe_A^{3+}Fe_B^{2.5+}Fe_B^{2.5+}O_4^{2-}$



$Fe_B^{2.5+}$

Fe_B^{2+} Fe_B^{3+}

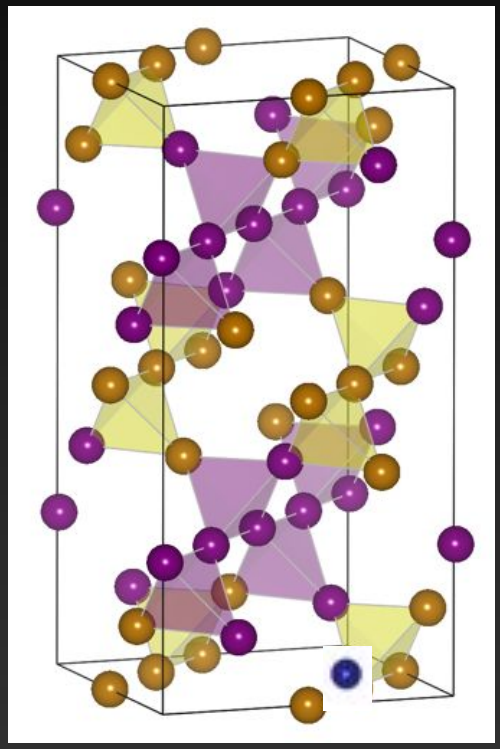
T_V =120 K
Verwey transition

Metal-insulator
Transition **(CO)**

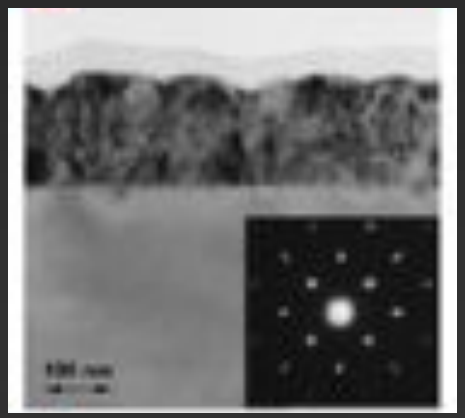
Monoclinic

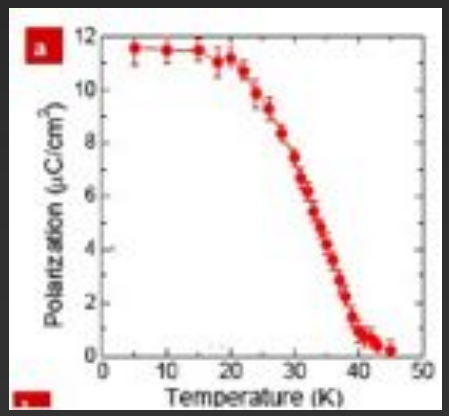
Ferrimagnetism

$Fe_A^{3+}Fe_B^{2+}Fe_B^{3+}O_4^{2-}$



MAGNETITE THIN FILMS: EXPTS*





- Epitaxial Fe3O4 films PLD-deposited on Nb:doped (100) STO
- Real-time FE switching via PUND (positive-up-negative-down)

* *M. Alexe et al., Adv. Mater* ***21****,1 (2009)*

NON-CENTROSYMMETRIC CHARGE ORDERING AS SOURCE FOR FERROELECTRICITY

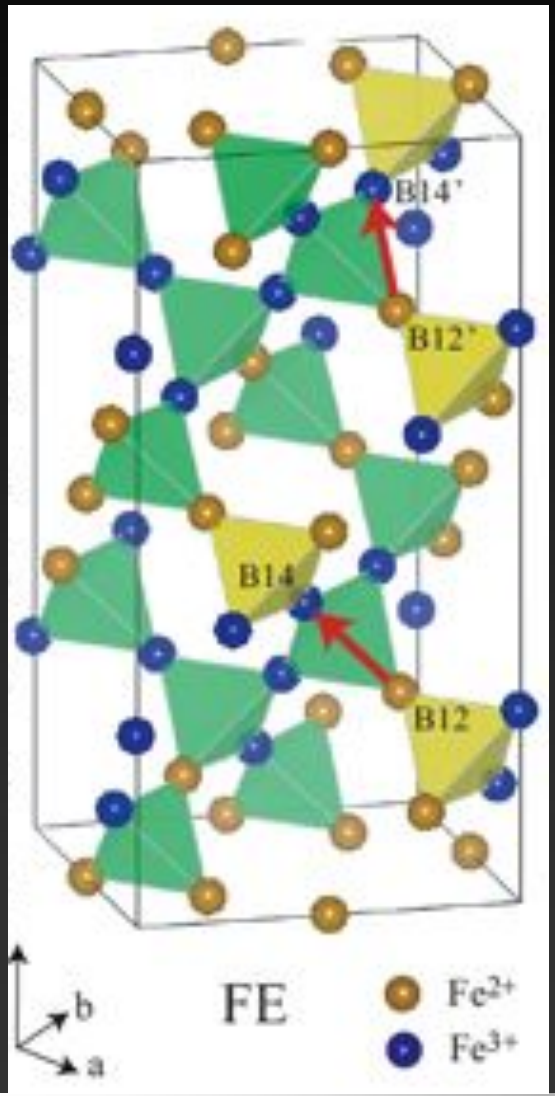
$P_{berry}^{U=4\ eV}$	P_{PCM}	P_{dip}
(-4.4,0,4.1)	(-4.2,0,5.3)	(-4.0,0,5.7)

$P_{berry}^{U=4\ eV}$	$P_{berry}^{U=6.\ eV}$	$P_{berry}^{U=8\ eV}$
(-4.4,0,4.1)	(-4.4,0,4.8)	(-4.3,0,5.1)

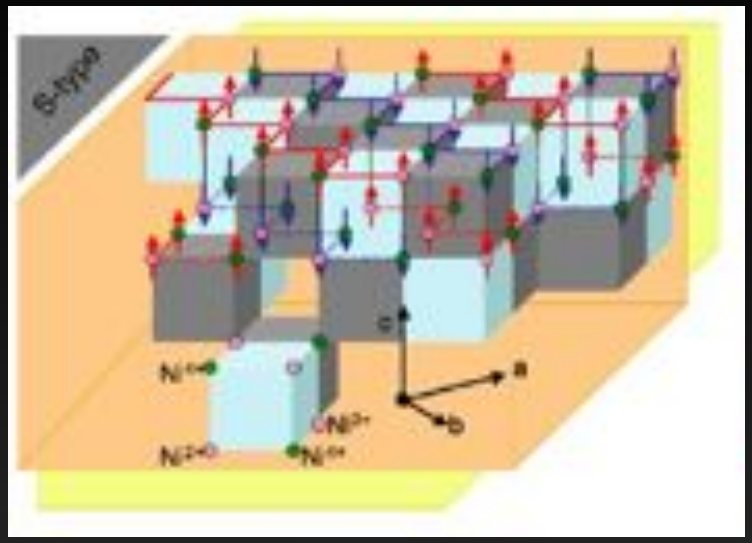
- Good agreement with expts: $P^{exp}_{||} = 5.5\ \mu C/cm^2$

- Most of P comes from local dipoles *i.e.* charge-shifts at selected tetrahedra:

PURELY ELECTRONIC MECHANISM
(ionic contribution negligible)



Cc symmetry (75% 3:1, 25% 2:2)



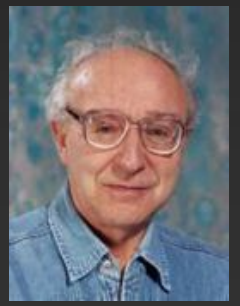
NICKELATES

- In collaboration with:

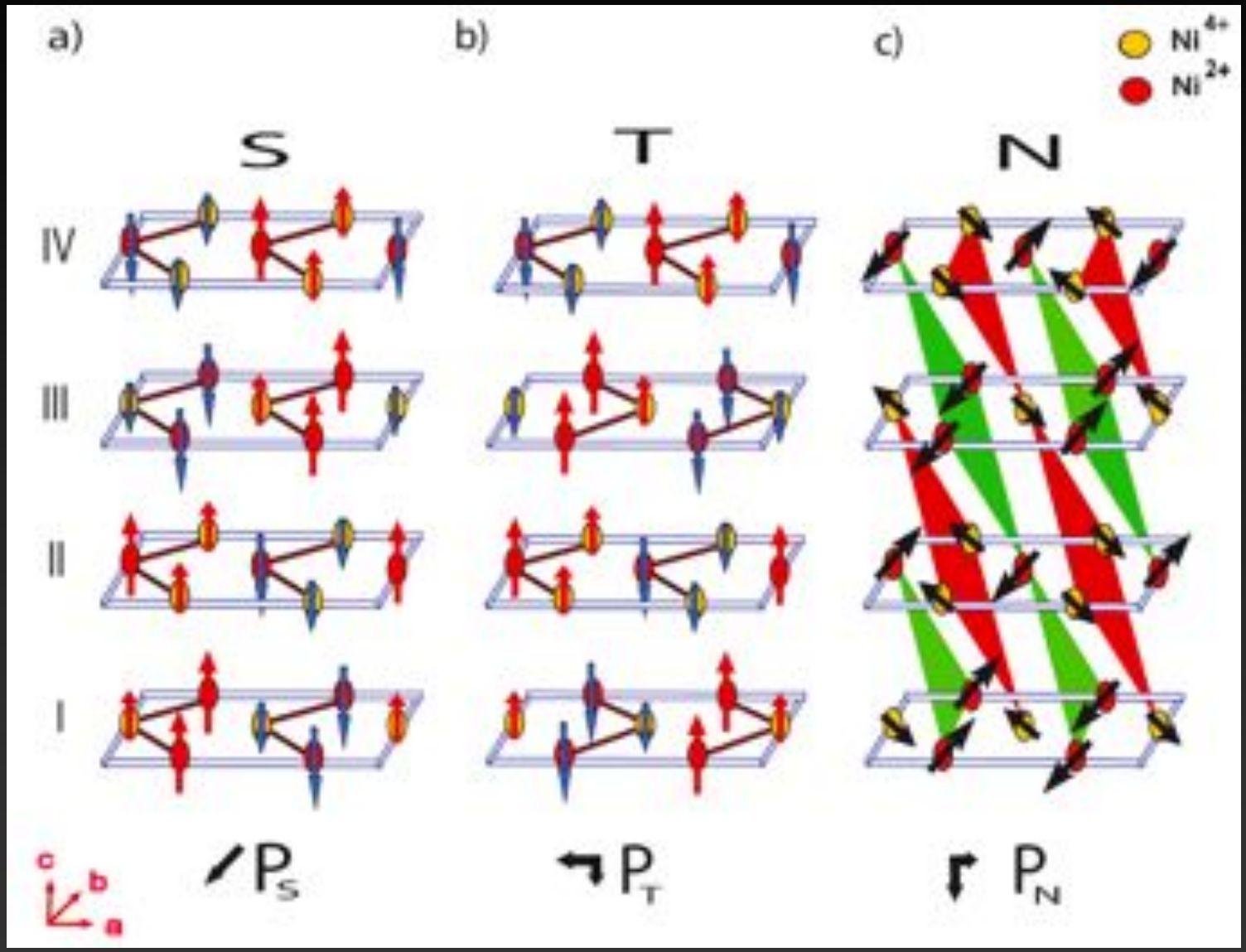
G. Giovannetti *(CNR-INFM)*

D. Khomskii *(Univ. Koeln)*

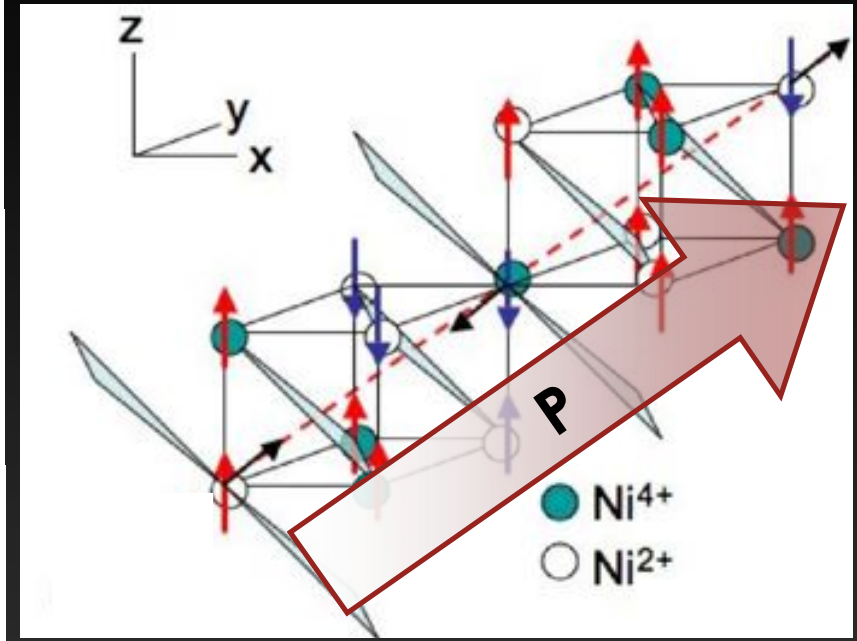
S. Kumar, J. Van den Brink *(Univ. Leiden)*

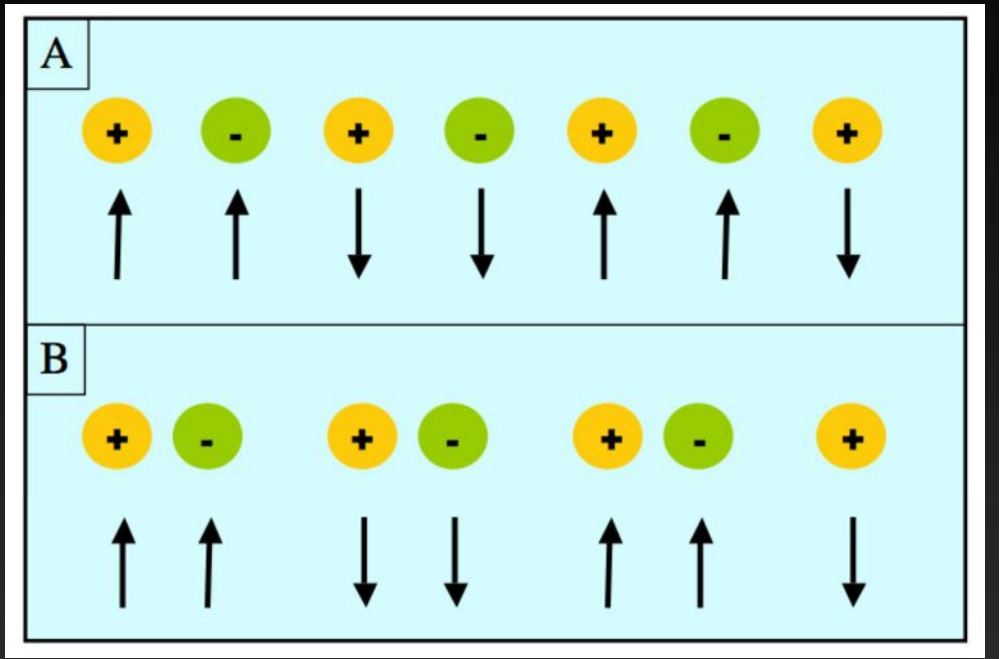


MAGNETISM IN $RNiO_3$



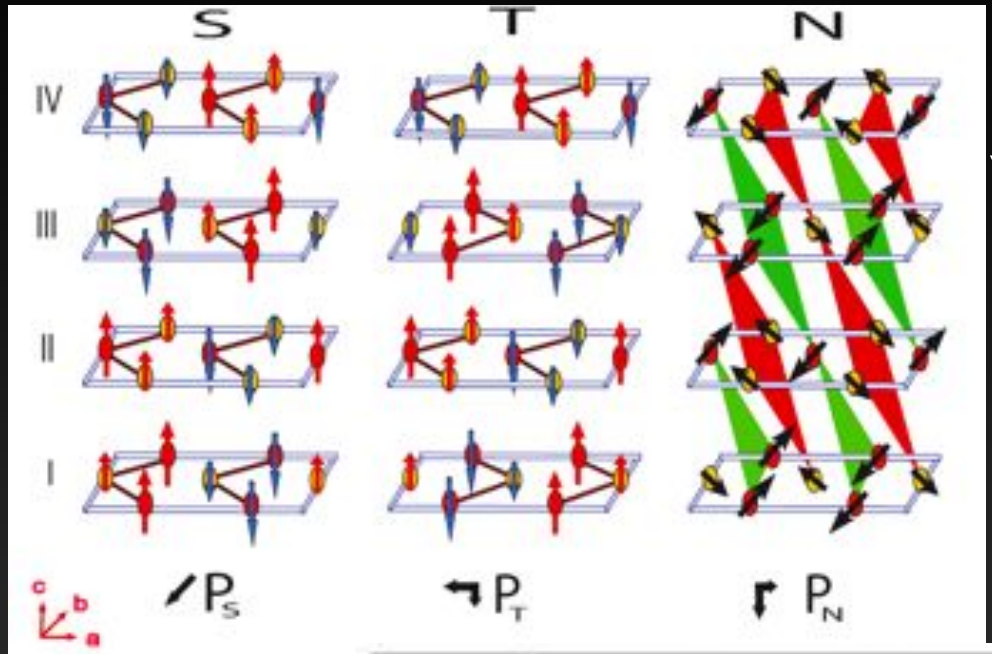
SPIN-DRIVEN FERROELECTRICITY: T-PHASE





Combination of exchange-striction (FM J_1)
in the given "E-like" spin-ordering
and CO should drive FE !

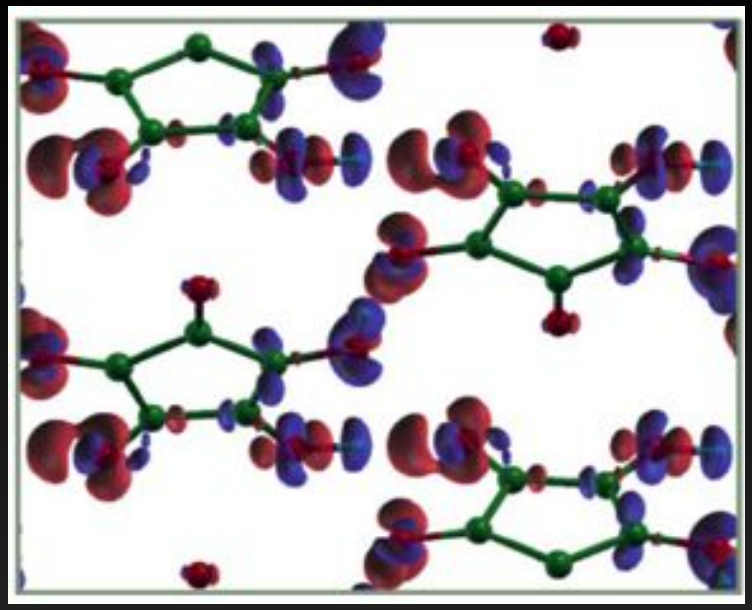
SPIN-DRIVEN FERROELECTRICITY: SUMMARY



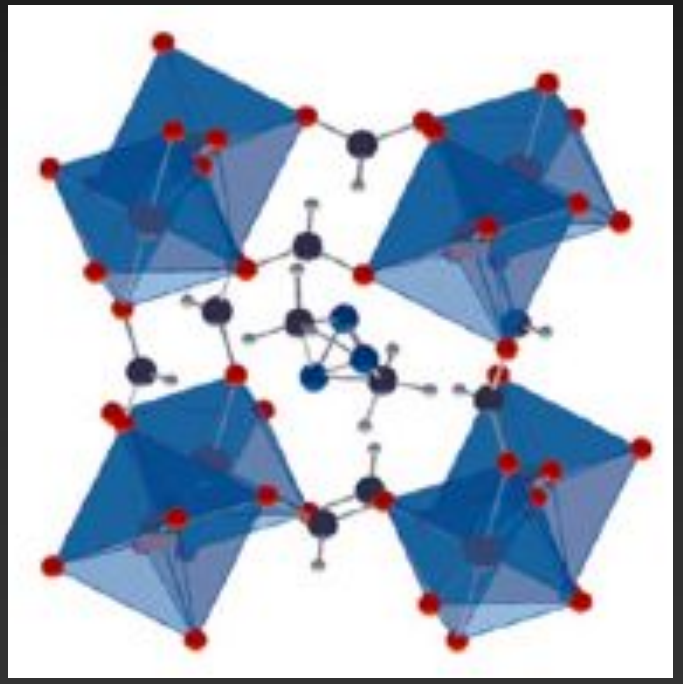
- Magnetic propag. vector: **Q** = [1/2,0,1/2]
- Spiral axis: **e** = [0,1,0] (spins rotate in *ac* plane)
- **P** ~ **e** x **Q** along [1,0,-1]
- **P** = (20,0,-110) nC/cm^2

P (μC/cm^2)

	experimental structure				relaxed structure			
Rare earth	T-type P_{tot}	P_a	P_c	S-type P_b	T-type P_{tot}	P_a	P_c	S-type P_b
Lu	10.31	9.91	2.84	5.21	9.86	9.82	0.76	7.07
Ho	8.66	8.05	3.19	3.60	10.46	10.38	1.39	6.91
Pr	14.80	13.23	6.64	1.81	7.87	7.82	0.94	2.57



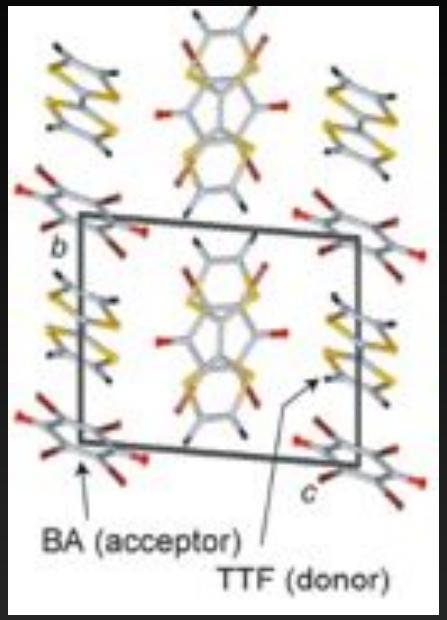
ORGANICS & HYBRIDS

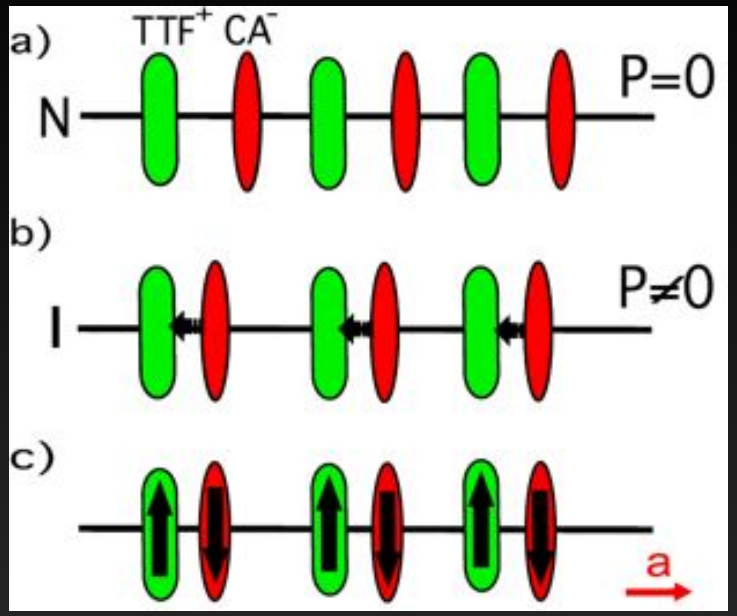


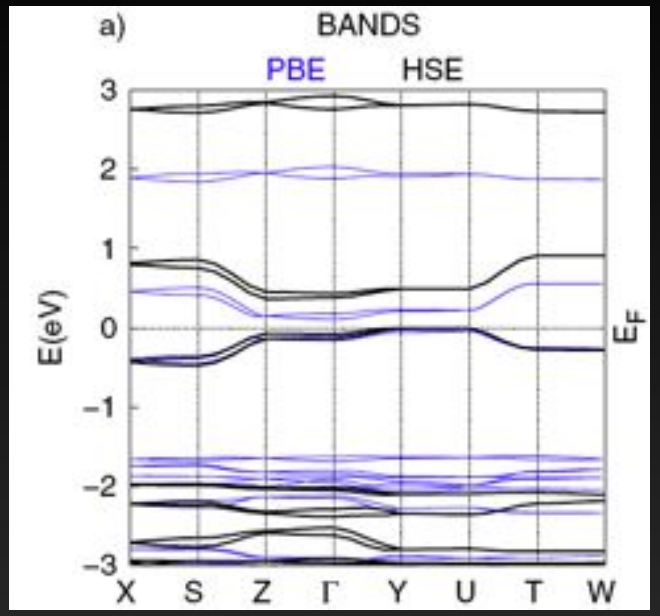
- In collaboration with:

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)*

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

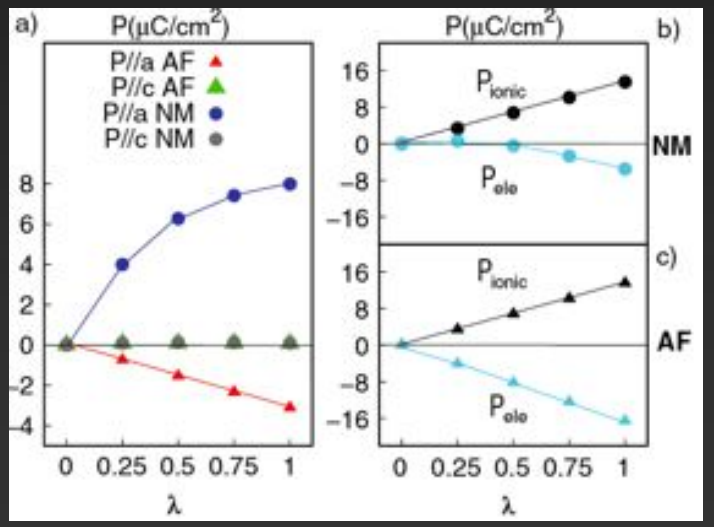






- SPIN PEIERLS: One-dimensional Heisenberg spin 1/2 chain ==>> instability to a dimer-singlet (gain of symmetric exchange)

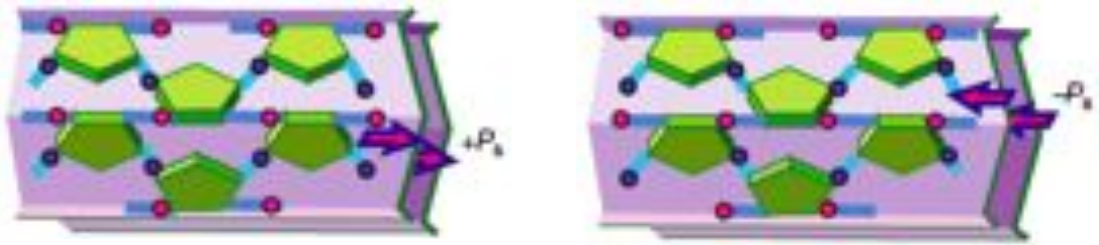
- TTF-CA: Under the neutral-Ionic transition (T_{NIT} = 81 K): long-short bond alternation



*G. Giovannetti et al., PRL **103** 26401 (2009)*

PROTON TRANFER: EFFICIENT SOURCE OF P

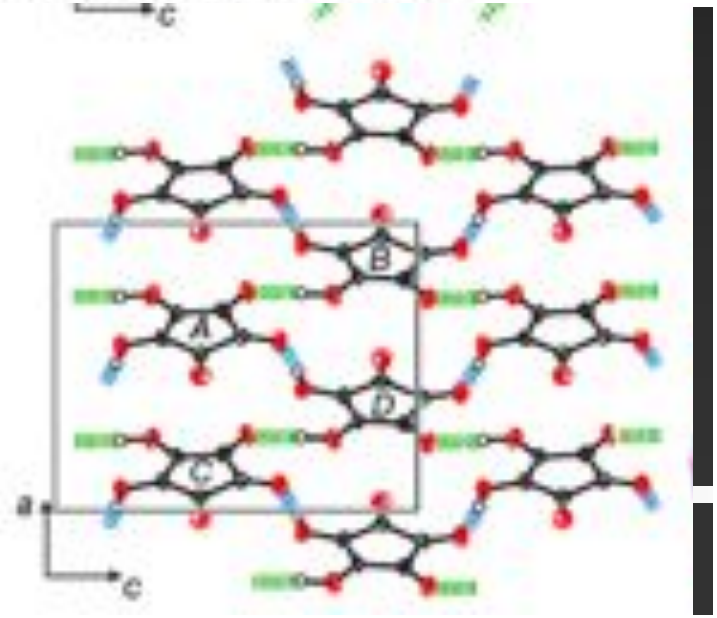
Vol 463|11 February 2010|doi:10.1038/nature08731 nature

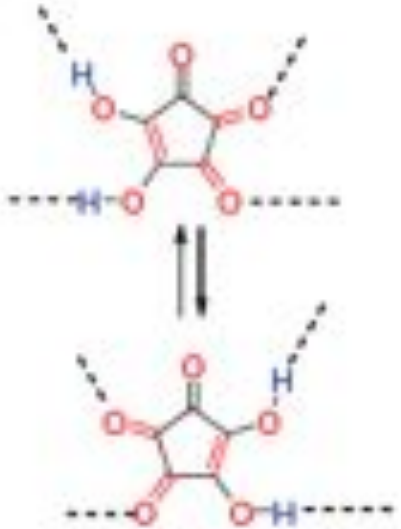


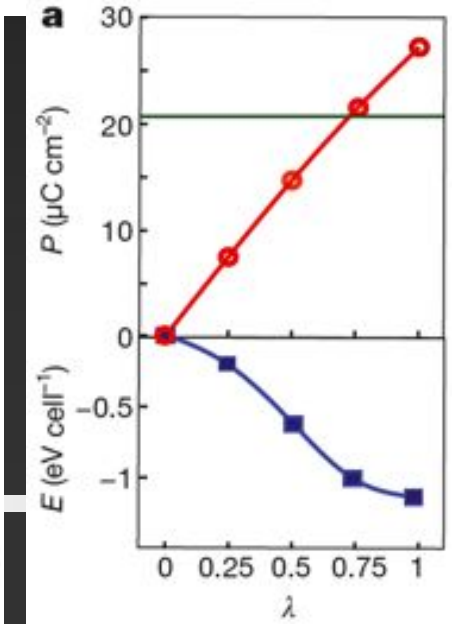
LETTERS

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]







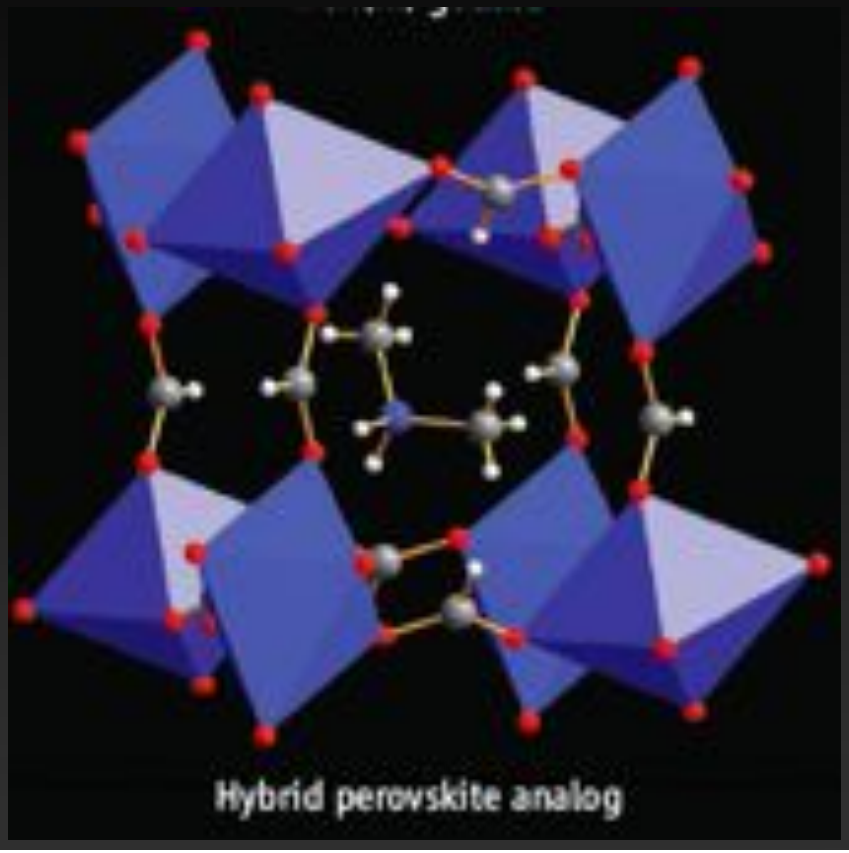
MATERIALS SCIENCE

There's Room in the Middle

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

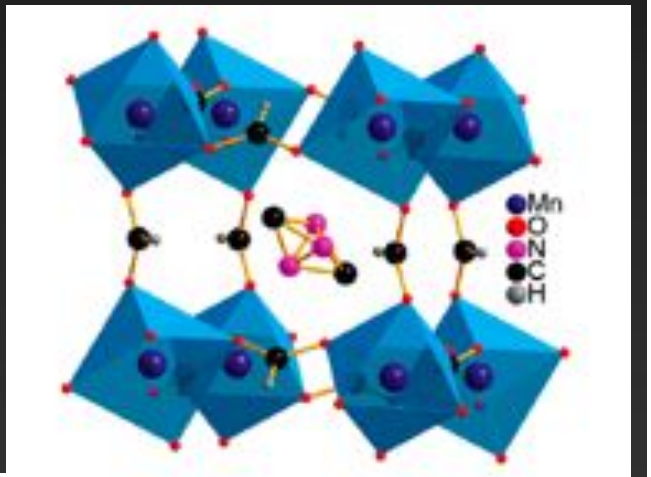
Anthony K. Cheetham and C. N. R. Rao

5 OCTOBER 2007 VOL 318 SCIENCE www.sciencemag.org



Hybrid perovskite analog

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

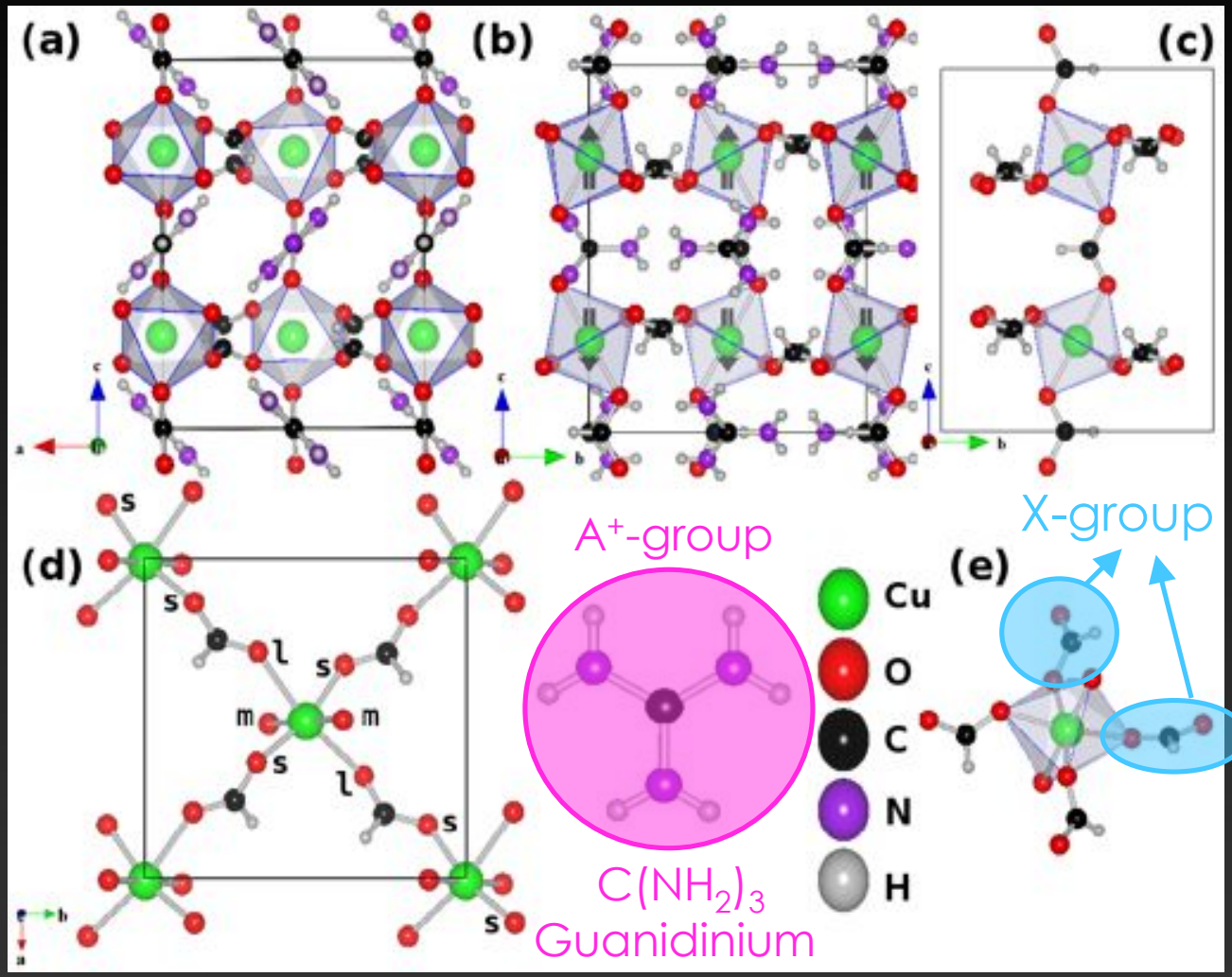


Multiferroic Behavior Associated with an Order–Disorder Hydrogen Bonding Transition in Metal–Organic Frameworks (MOFs) with the Perovskite ABX_3 Architecture

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*[,‡]

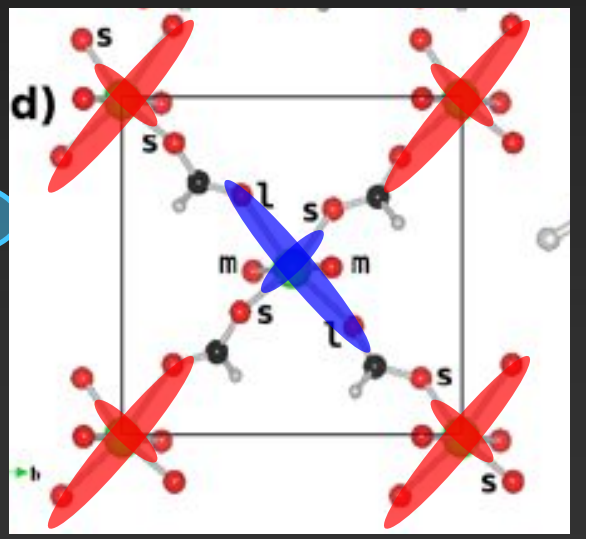
Cu-MOF (ABX_3, $K^+Cu^{+2}F^{-1}_3$ LIKE)



Cu octahedra connected by **HCOO⁻** groups (ligands)

Cu^{+2} Jahn-Teller ion

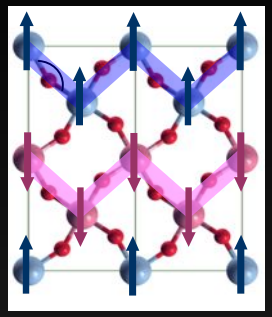
Antiferrodistortive order in the ab plane

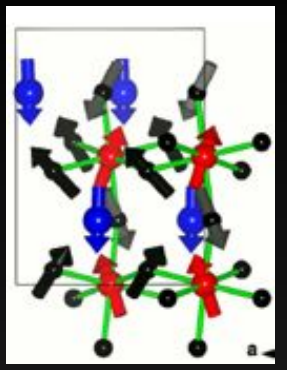


AFM-A magnetic order

TAKE HOME MESSAGES

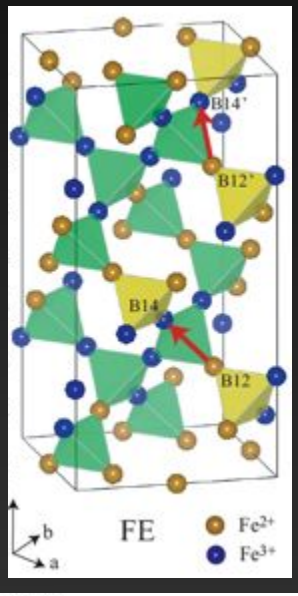
- Dzyaloshinskii-Moriya is not the only mechanism to magnetically induce **P**: **Heisenberg exchange striction can drive a large polarization!**

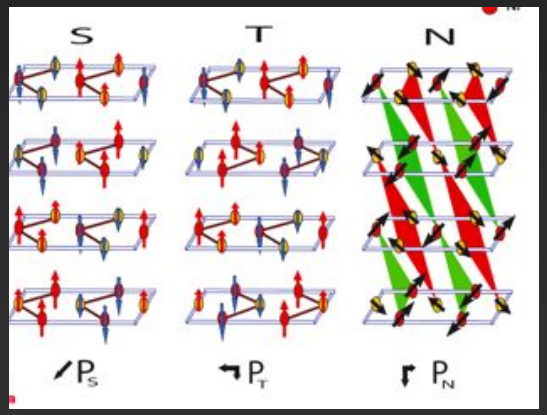




- **Charge ordering** is another efficient mechanism! There are two different ways:

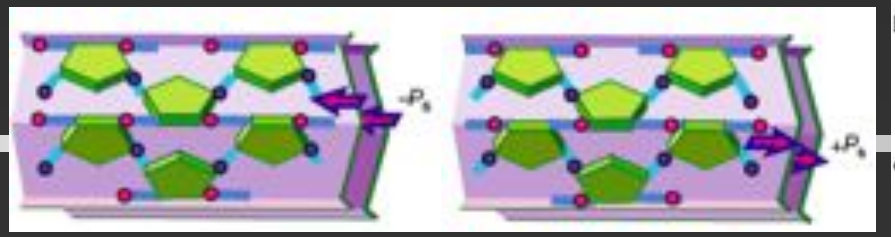
1. **CO alone** can drive P (no matter how large is the charge disproportionation, as long as it is non-centrosymmetric!)

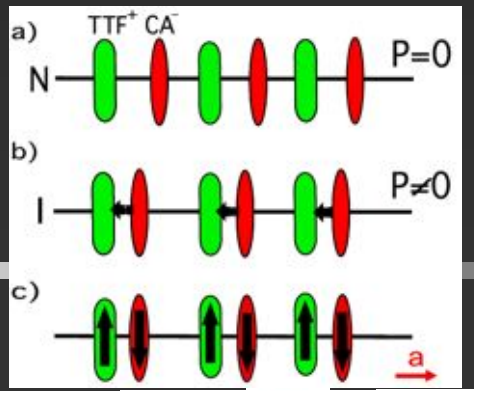




2. **CO combined with spin-ordering** can drive large P!

- Take a look at **organics**!





THE QUAKE: April 6th 2009 3:32 am

- 6.3 Mw Richter
- 8 Km deep
- 300 casualties
- 1500 wounded
- 70.000 evacuees

Collemaggio's church
(XIII century)

From left:
T. Fukushima (now in Osaka)
A. Stroppa (staff researcher),
M. Marsman (visitor),
S. Picozzi (PI),
K. Yamauchi (back to Osaka),
P.Barone (post-doc),
G.Giovannetti (now in Rome)

Physics Dept.

Silvia's house

THANK YOU!

More at:
www.casti.aquila.infn.it/homepages/bismuth/index.html

BISMUTH