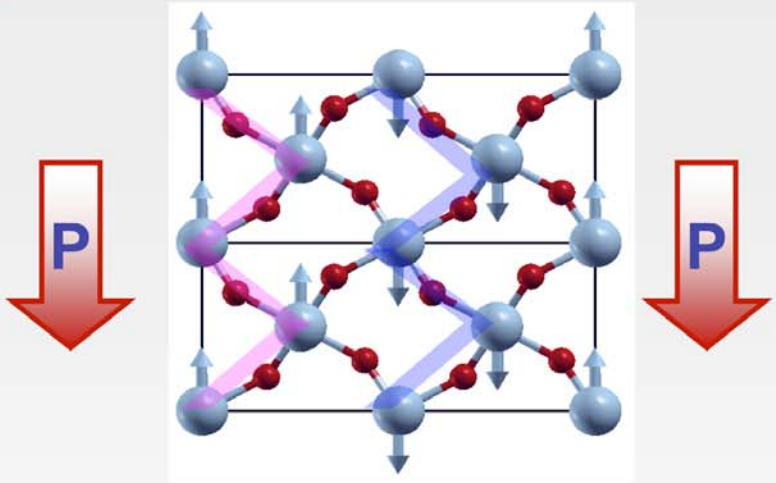
Dual nature of improper ferroelectricity in a magnetoelectric multiferroic



Silvia Picozzi

Consiglio Nazionale delle Ricerche - Istituto Nazionale di Fisica della Materia (CNR-INFM), 67100 L'Aquila, Italy

K. Yamauchi *(CNR-INFM, L'Aquila)*, **B. Sanyal** *(Uppsala Univ., Sweden),*

I. A. Sergienko and E. Dagotto

(Oak Ridge Natl Lab and Univ. Tennessee,TN, USA)

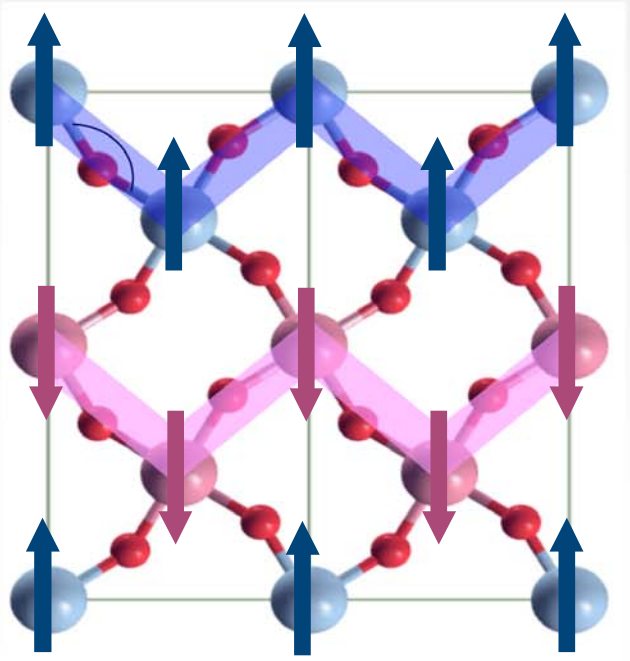
How can we induce ferroelectricity in magnets ?

Our approach: look at "improper ferroelectricity" in magnets (i.e. **P** appears as a consequence or concomitantly with some other kind of orderings).

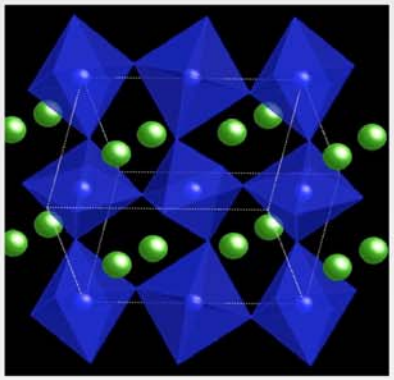
For ferroelectricity, we need to break **inversion symmetry.**
How to do that in magnets via electronic degrees of freedom?

1. **Spin** degree of freedom:

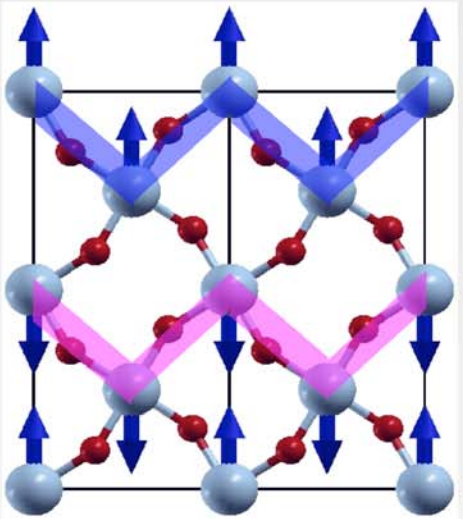
- **Spirals** (see previous talks)
- Some kinds of **collinear commensurate antiferromagnetic** spin ordering (e.g. AFM-E)



Starting point: the AFM-E spin configuration

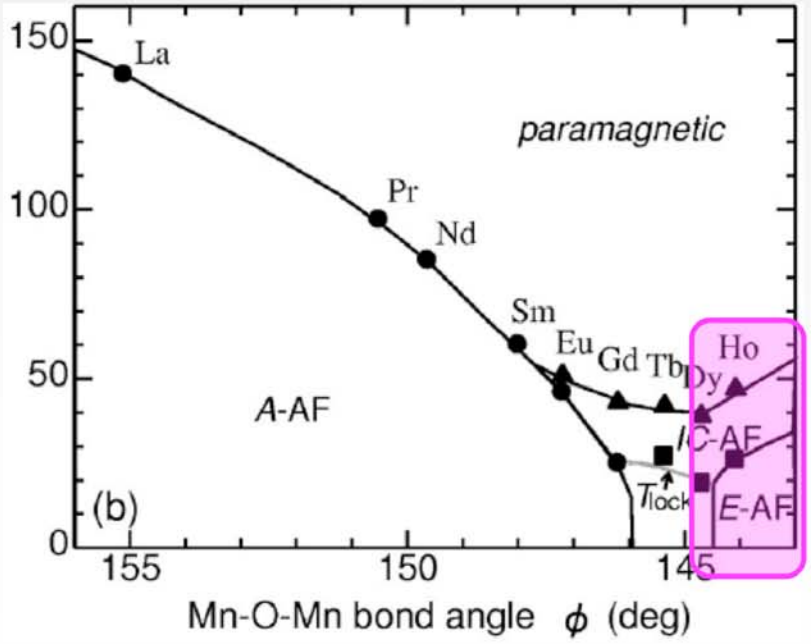


1. Distorted ortho-manganites: Jahn-Teller and $GdFeO_3$-like tilting
2. *Pnma* space group
3. Double along *a* and form zig-zag FM spin chains AFM coupled with respect to neighboring chains



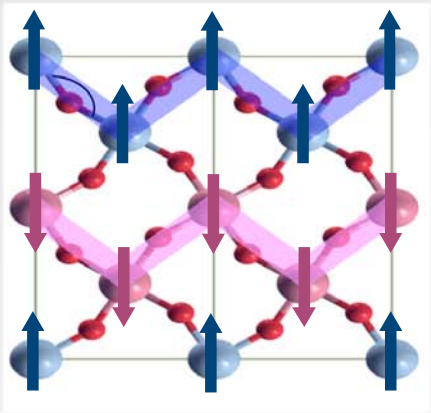
When does the AFM-E occur?

- Transition from AFM-A to AFM-E with octahedral $GdFeO_3$-like distortions[1,3]
- AFM-E: expts in $HoMnO_3$ + model-hamiltonian-studies[2]



1. *T. Kimura et al., PRB 68, 060403 (2003).*
2. *T. Hotta et al., PRL 90, 247203 (2003).*
3. *J. Zhou and J. B. Goodenough, PRL 96, 247202 (2006).*

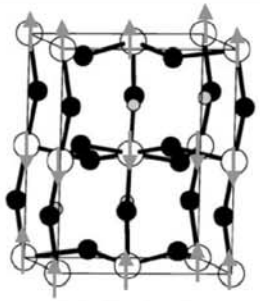
Magnetic ordering:
AFM-E as ground state in distorted $RMnO_3$



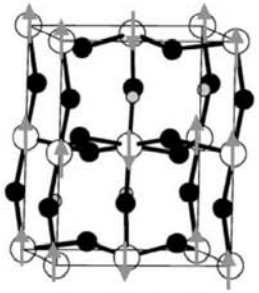
In-plane spin ordering for AFM-E and AFM-E* (with AFM and FM interplanar stacking, resp.)

Table: energy difference (in meV/Mn) with respect to FM

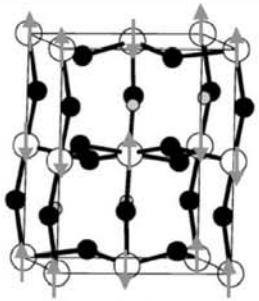
	$YMnO_3$	$TbMnO_3$ ($7\uparrow,1\downarrow$)	$LaMnO_3$
FM	0	0	0
AFM-E	-45	-32	-2
AFM-E*	-23	-11	+2
AFM-A	-29	-8	-17
AFM-C	-10	17	58
AFM-G	-24	4	64



AFM-A



AFM-C



AFM-G

S. Picozzi, K. Yamauchi, G. Bihlmayer and S. Bluegel, PRB 74, 094402 (2006)

Outline/Questions on Ferroelectricity AND Magnetism

AFM-E ortho-$HoMnO_3$: is this a novel multiferroic?

First-principles density-functional calculations

- **Electric polarization from "displacement" mechanism: is it effective?**
- **Which is the mechanism for polarization induced by AFM-E magnetic ordering?**
- **Ferroelectric switching path: how can we achieve it?**
- **Conclusions**

Computational details

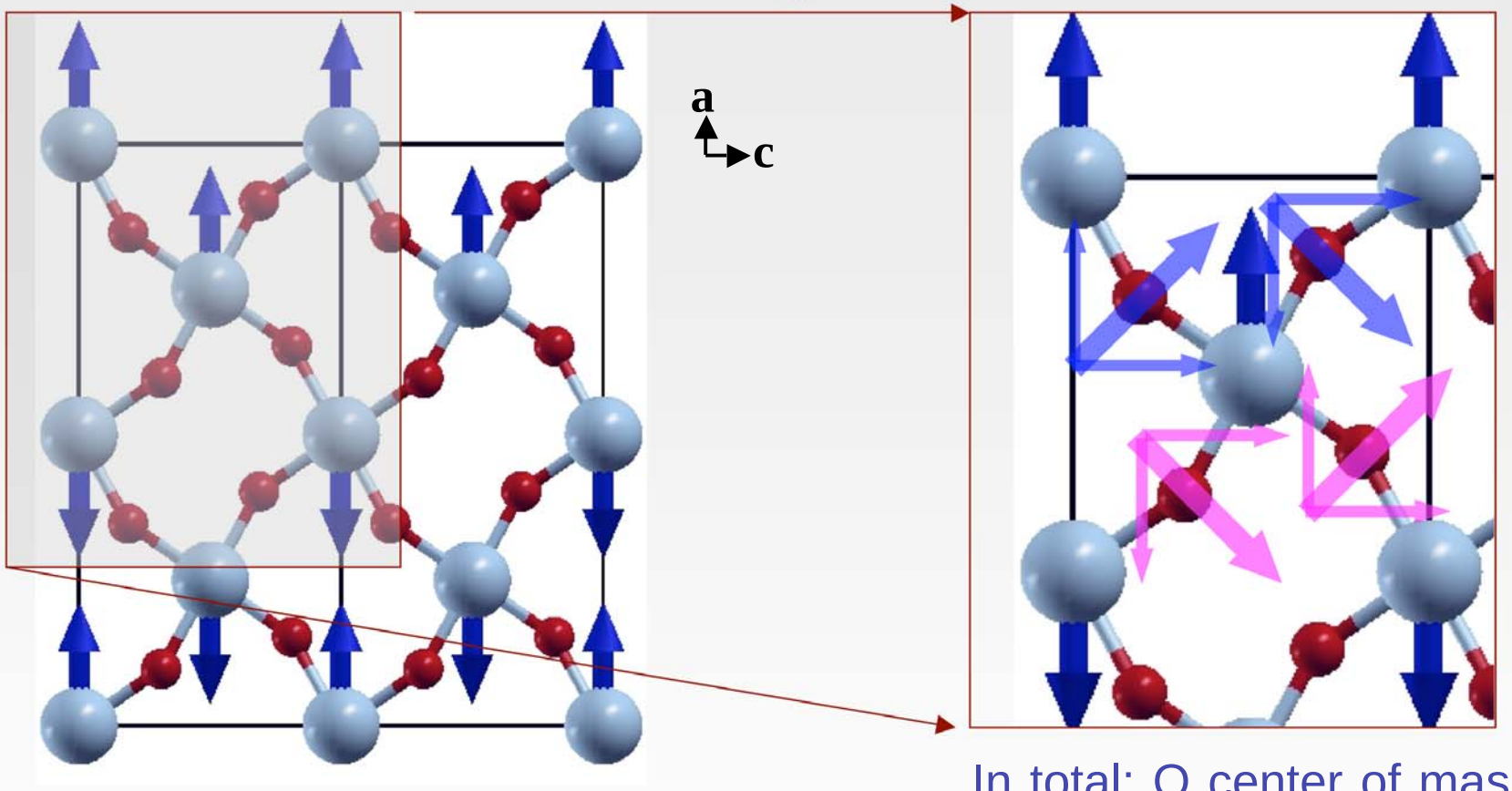
- VASP[1] simulations with Projector Augmented Wave pseudopotentials
- Generalized Gradient Approx. (PBE exch.-corr.)
- Ho pseudopotential: 4f “frozen”
- Monkhorst-Pack shell: [3,4,6]
- Hubbard potential[2] on Mn d: GGA +U (for various U and J = 0.15*U)
- Berry phase approach to polarization[3]
- Non-collinear magnetism[4]
- Spin-orbit neglected

1. *G. Kresse and J. Furthmueller, Phys. Rev. B 54, 11169 (1996)*
2. *V.I. Anisimov, et al., J. Phys.: Condens. Matter. 9, 767 (1997).*
3. *R.D.King-Smith and D.Vanderbilt, PRB 47,1651 (1993); R. Resta, RMP 66, 899 (1994).*
4. *D. Hobbs, G. Kresse and J. Hafner, Phys. Rev. B 62, 11556 (2000).*

Structural details

- Experimental lattice constants for paramagnetic $HoMnO_3$
- Extremely high $GdFeO_3$-like distortions
- Internal atomic positions fully relaxed (forces < 0.01 meV/Å)

Polarization from “Displacement” mechanism *



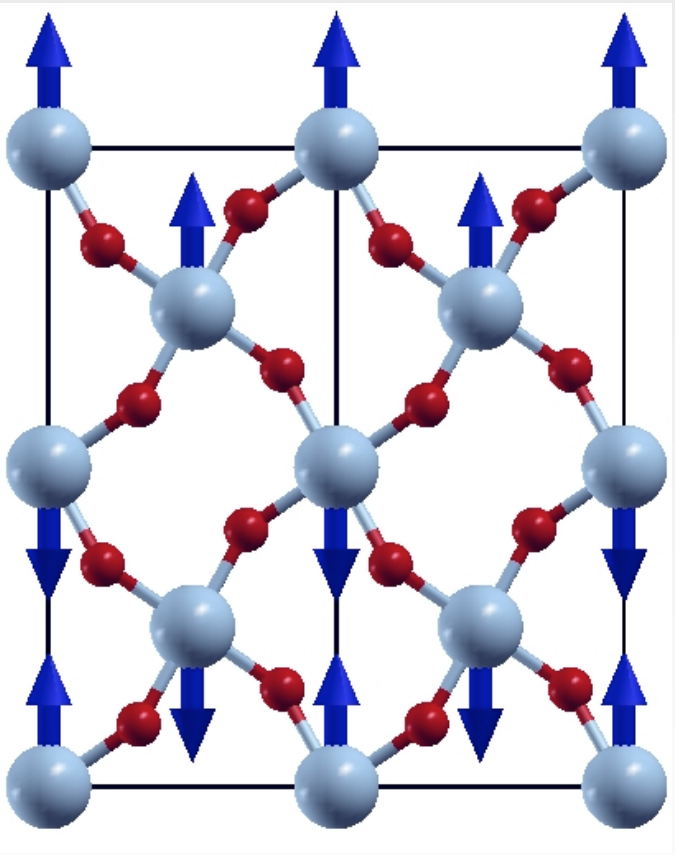
Simple model:

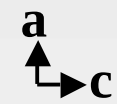
- start from centro-symmetric atomic positions
- only O atoms can move and they are forced in the MnO_2 planes

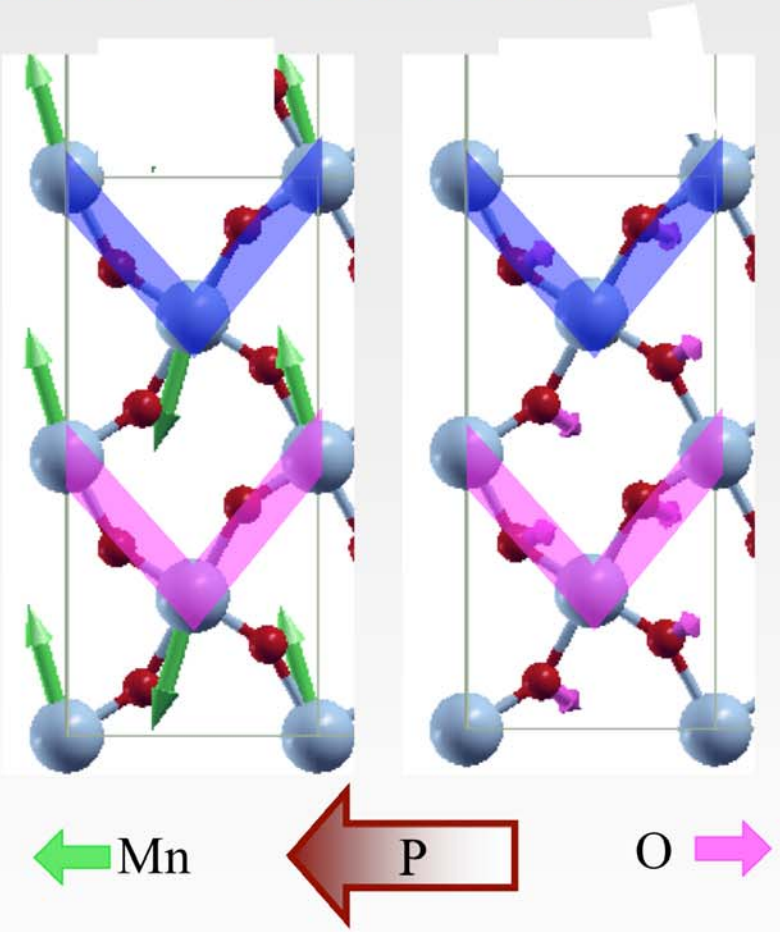
In total: O center of mass move “right”: Polarization directed along *c* axis

**** I.A. Sergienko, C. Sen and E. Dagotto, PRL 97, 227204 (2006).***

Polarization from“Displacement” mechanism





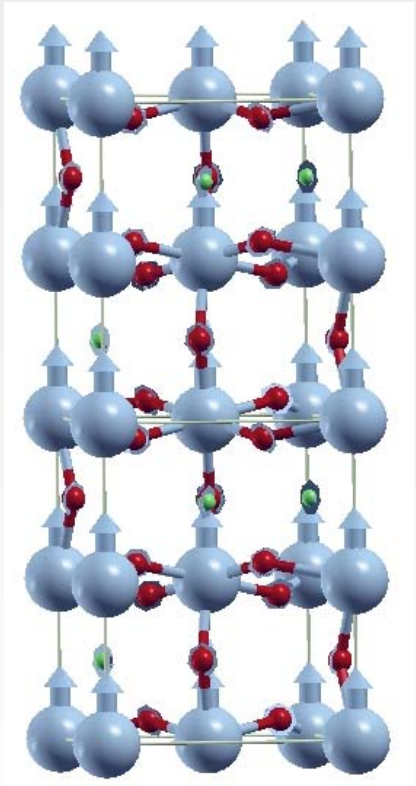


Simple model:

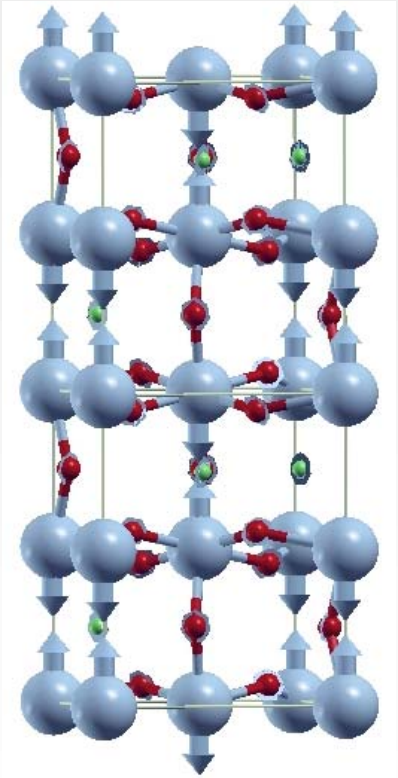
- start from centro-symmetric atomic positions
- only O atoms can move and they are forced in the MnO_2 planes

… But…. actually the displacement pattern is not so simple (also Mns move), but the polarization is indeed directed along c

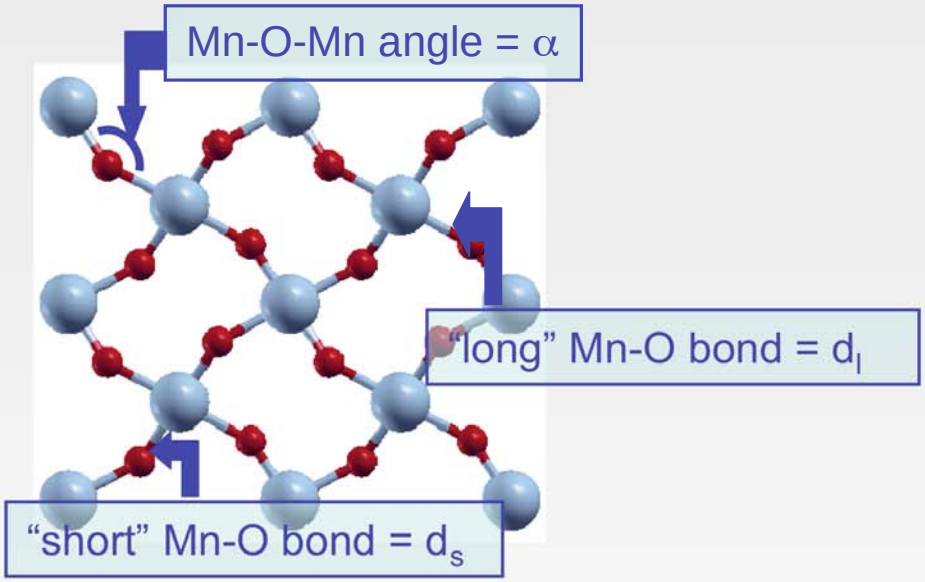
Does the Mn-O-Mn angle depend on Mn-Mn spin configuration?



FM

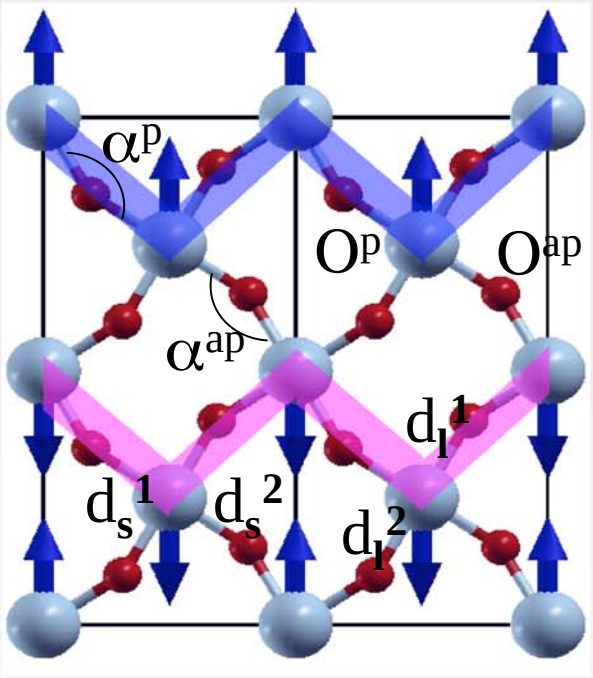


AFM-G



	α (°)	d_l (Å)	d_s (Å)
FM	143.9	2.19	1.93
AFM-G	142.8	2.24	1.90

In-plane FM (AFM) interactions ⟷ Larger (Smaller) angles



$HoMnO_3$ AFM-E: in-plane structural parameters

NB: Zig-zag chains and symmetry reduction:

- 2 different Mn-O-Mn angles (FM and AFM)
- 2 different Mn-O "long" bond lengths
- 2 different Mn-O "short" bond lengths

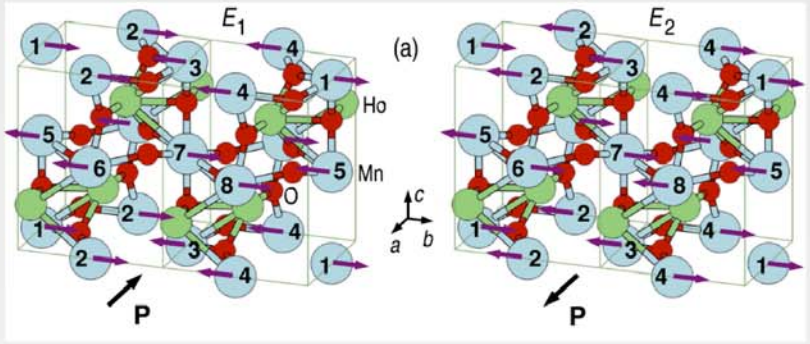
	α^p	α^{ap}	d^l_1	d_l^2	d_s^1	d_s^2
FM	143.9	-	2.19	2.19	1.93	1.93
AFM-G	-	142.8	2.24	2.24	1.90	1.90
AFM-E	145.3	141.9	2.25	2.18	1.92	1.92

Very different Mn-O-Mn α and Mn-O d_l : displacement mechanism active!

Ferroelectric switching

Sergienko et al.[1] :

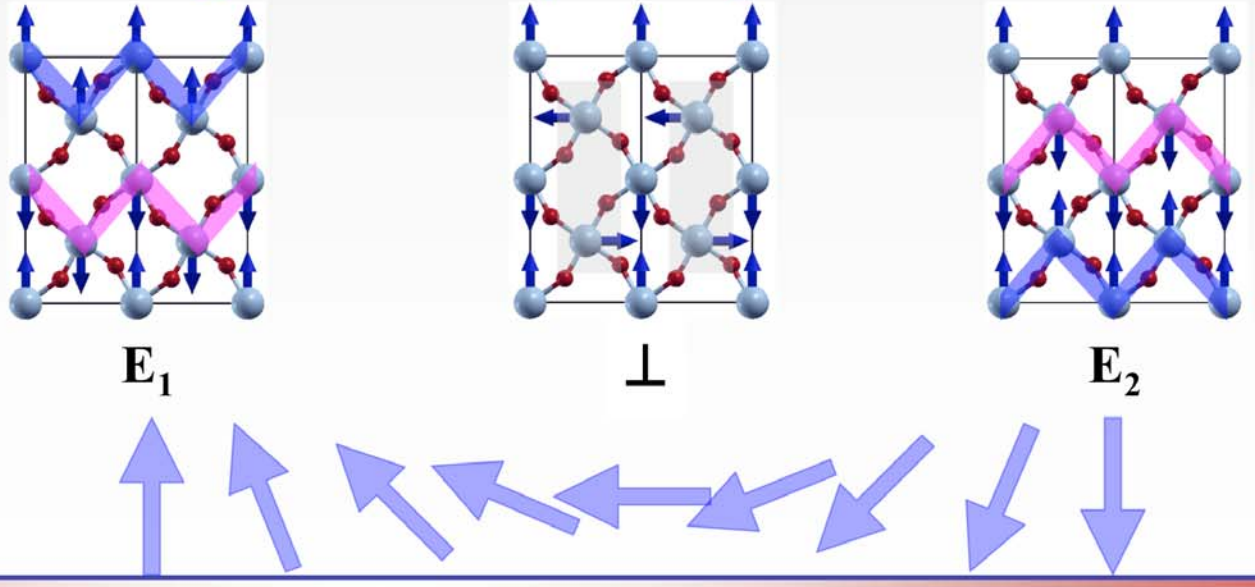
- Model calculations using Landau theory
- two E-phase domains differing for orientation of half of the Mn spins and giving opposite P



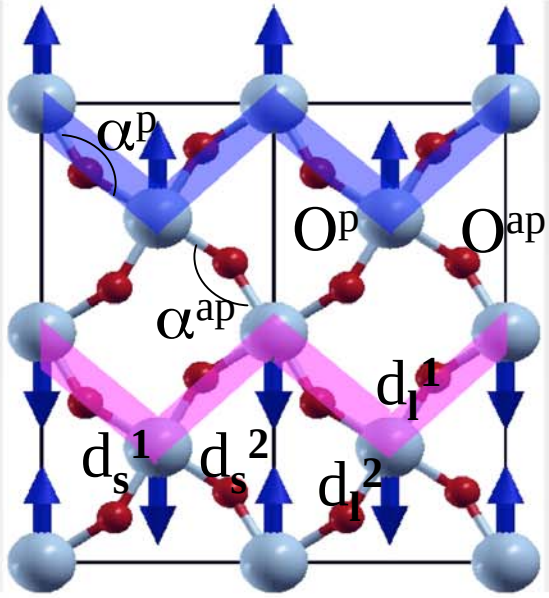
1. I.A. Sergienko, C. Sen and E. Dagotto, PRL 97, 227204 (2006).

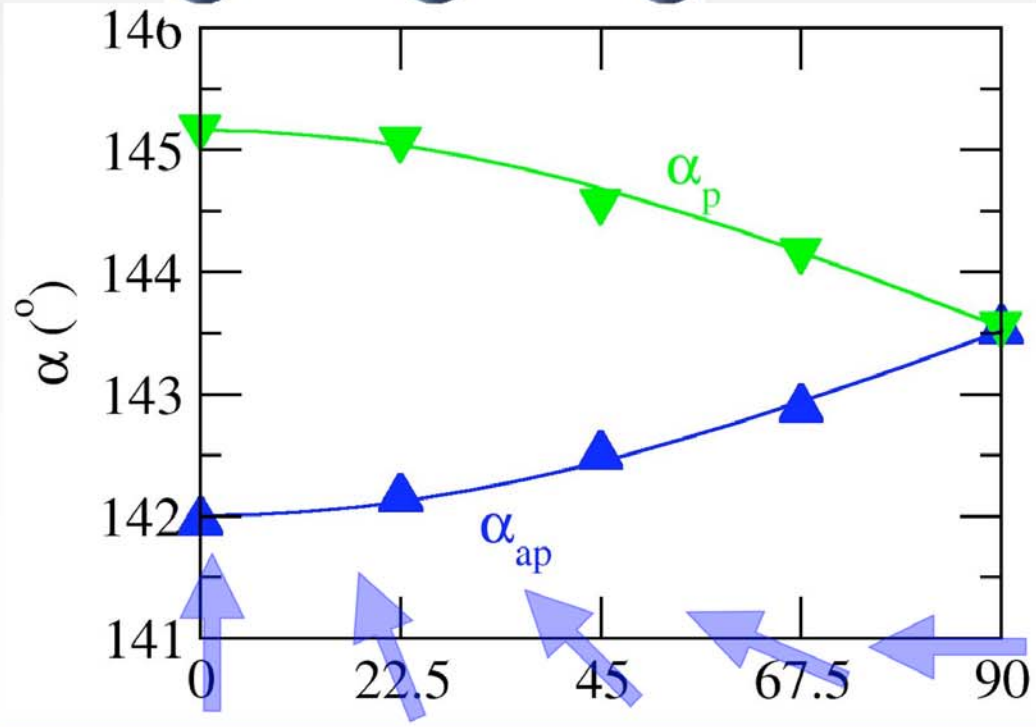
How to go from E_1 to E_2?

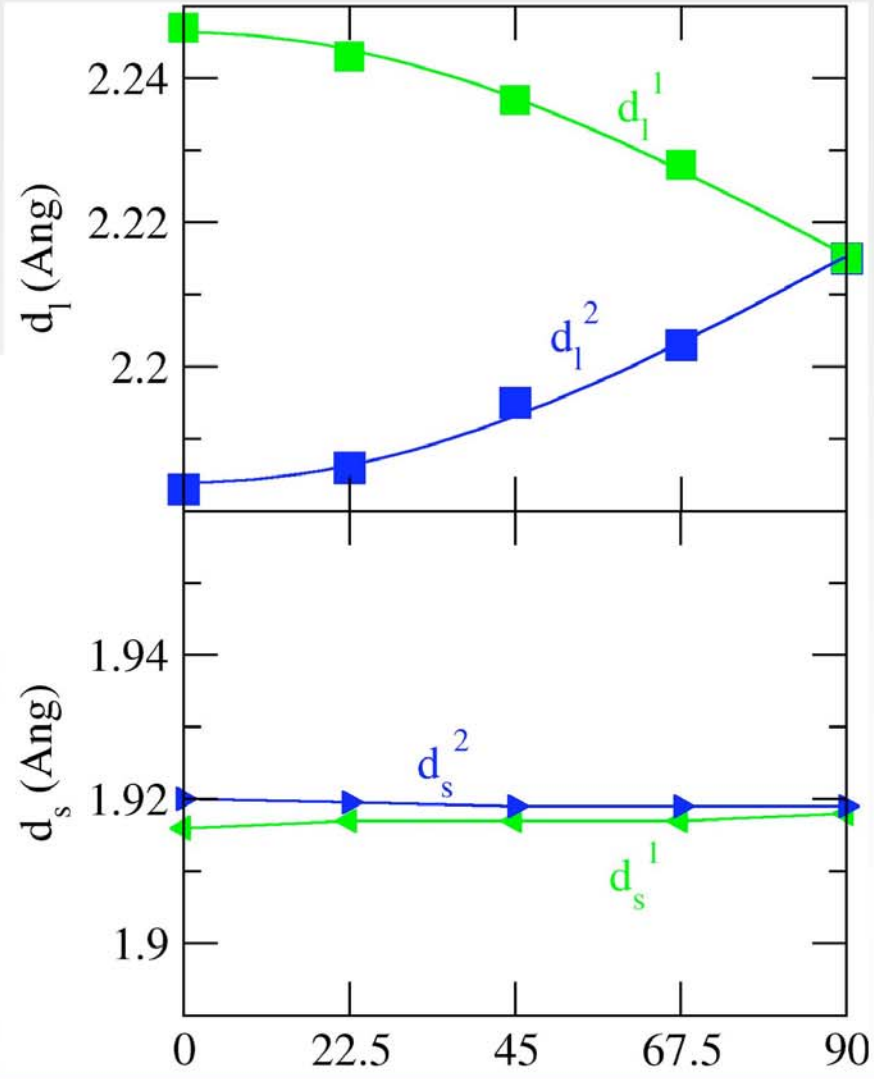
- Via progressive rotation of "central" spins
- Non collinear VASP calculations constraining the direction of local moments



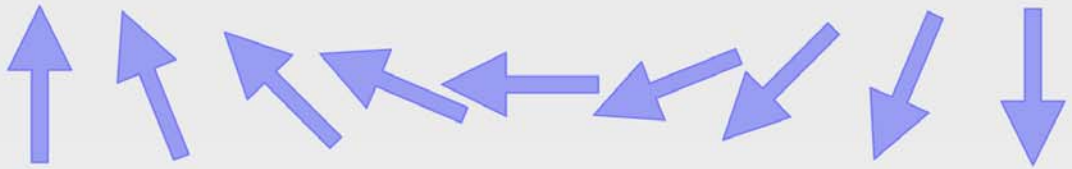
Structural changes along the switching path





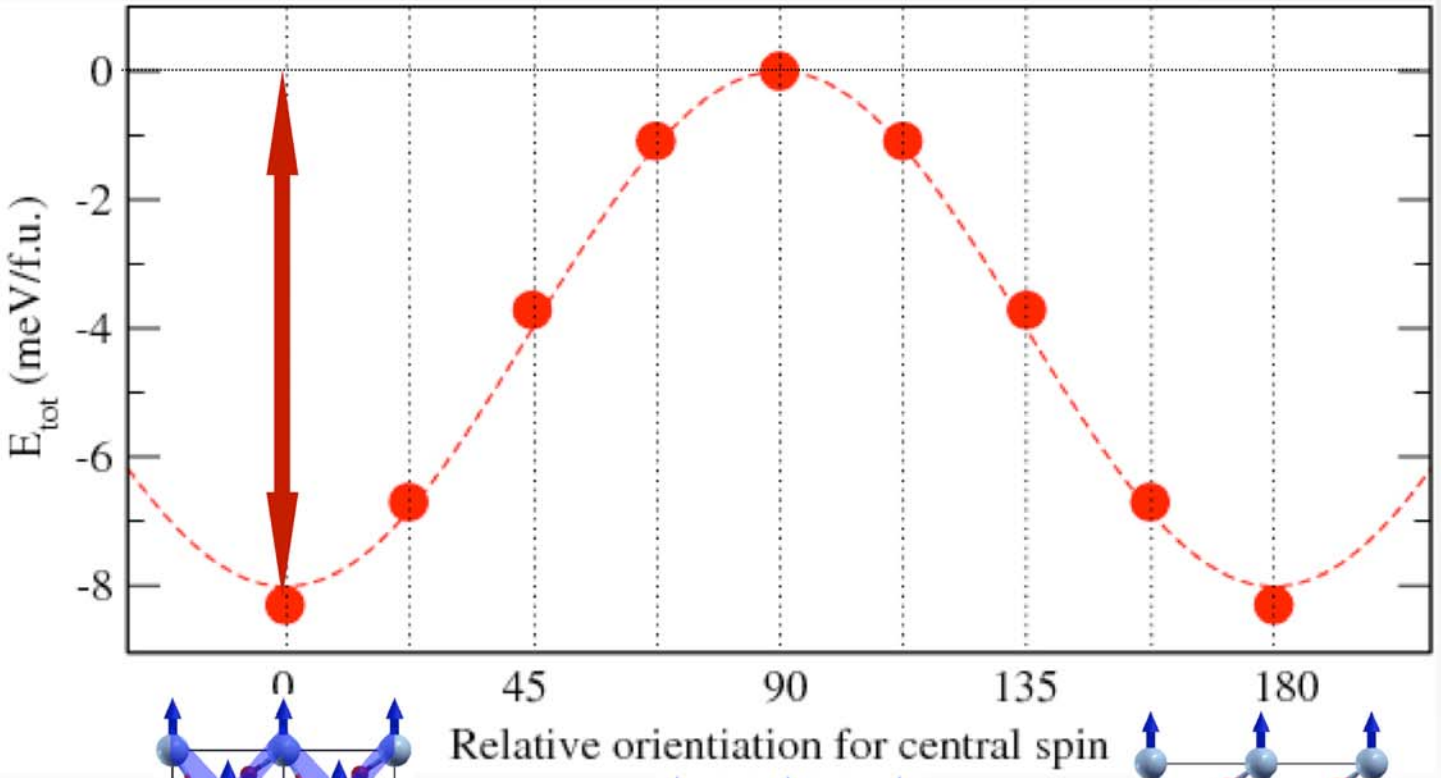


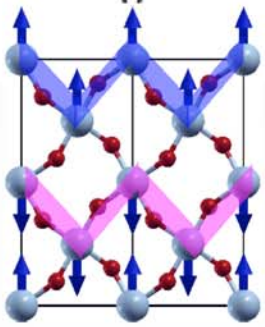
Ferroelectric switching



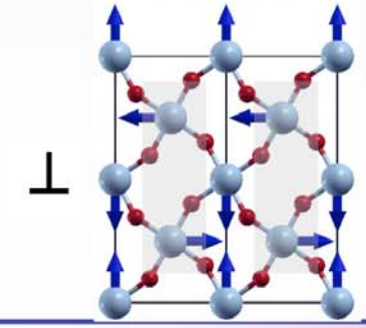
Depth of the well
~ 8 meV/f.u.

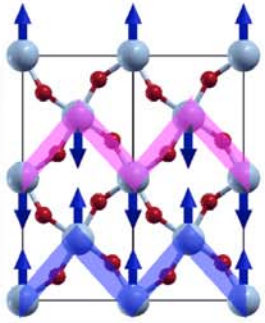
(cfr
18 meV/f.u.
in $BaTiO_3$)





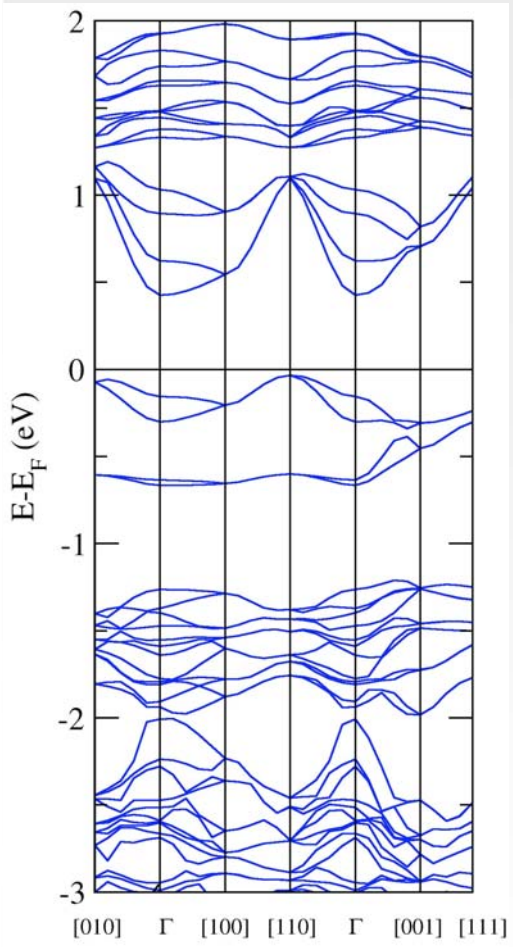
E_1



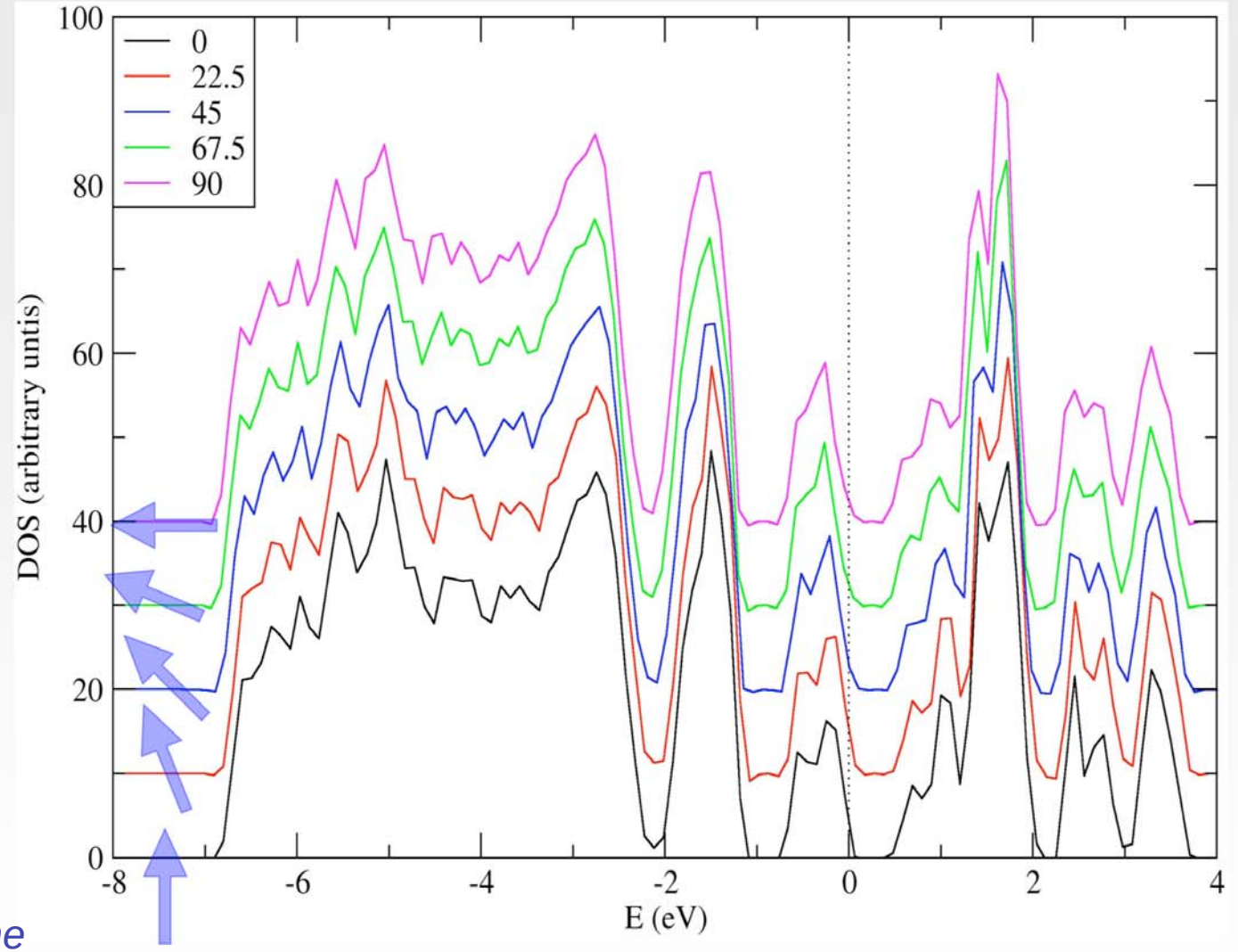


E_2

Insulating character along the switching path

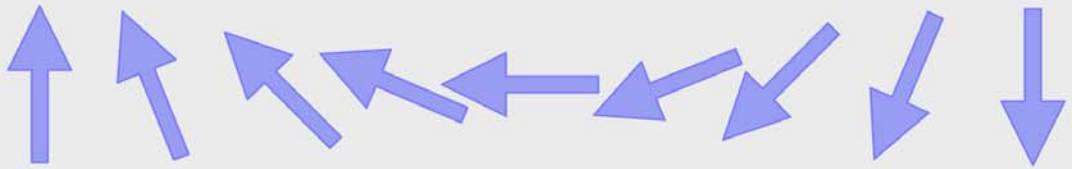


Band structure along the main symmetry lines for relaxed AFM-E1



NB: the DOS look pretty much unaltered along the path: no drastic charge rearrangement…

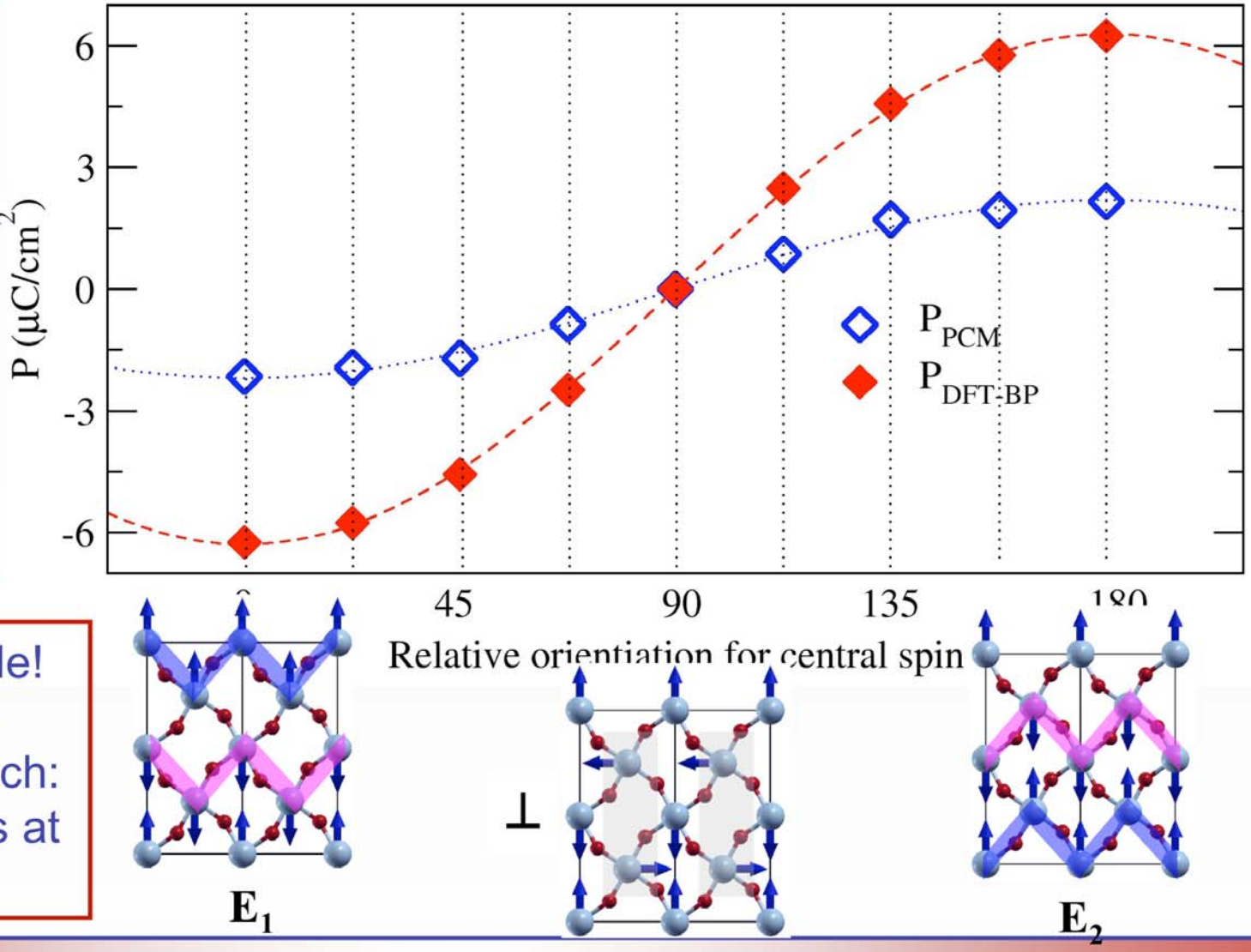
What about polarization?



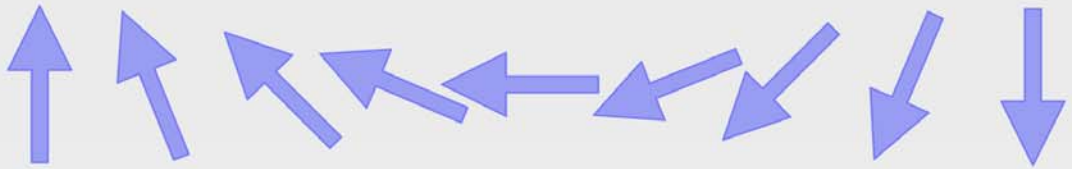
Electrical control of AFM domains

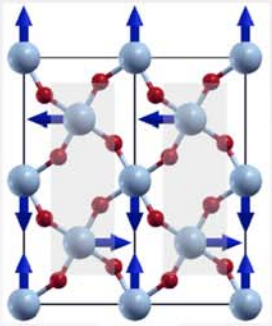
P much higher than other multiferroic manganites (in $TbMnO_3$ P~0.1 $\mu C/cm^2$)

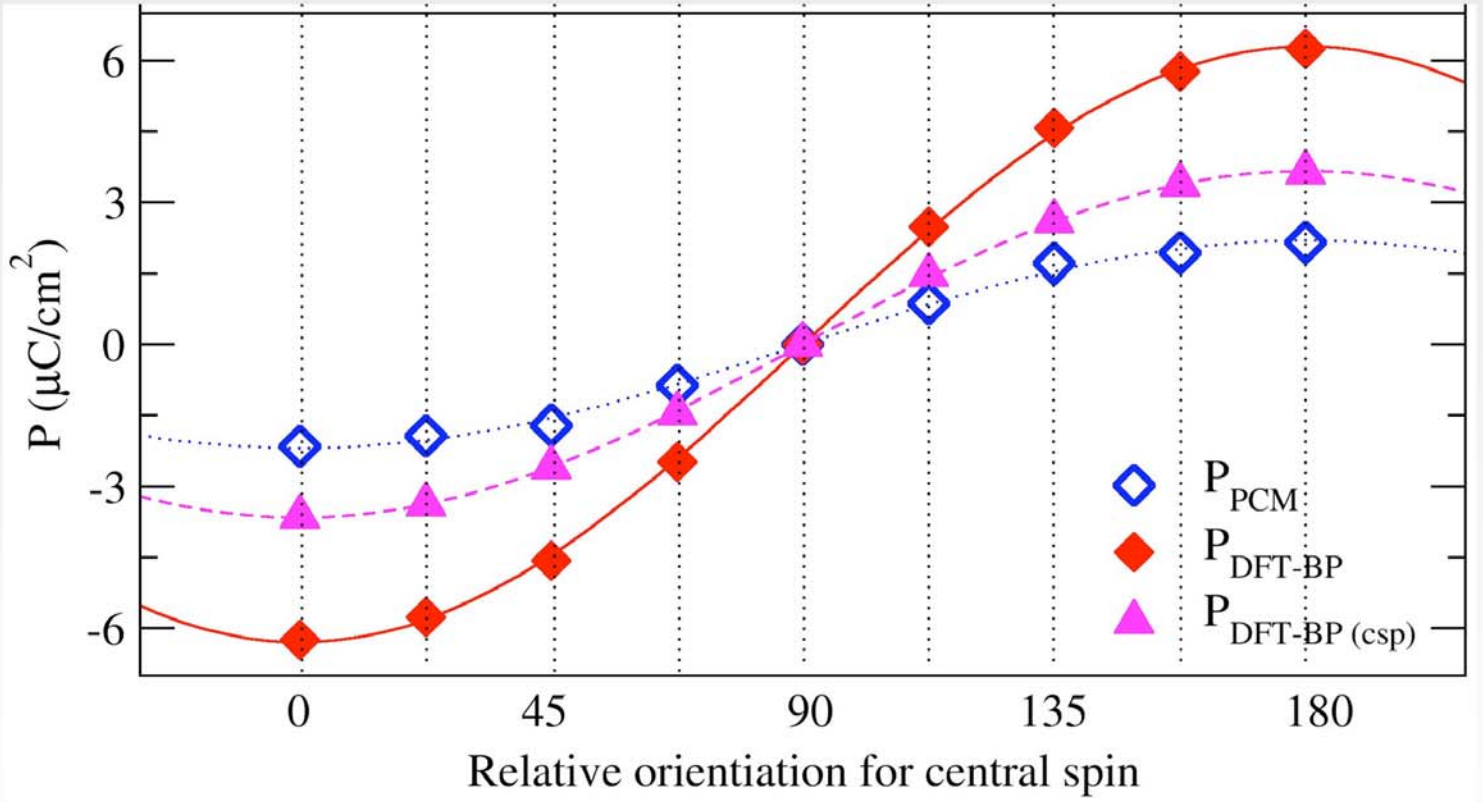
P_{PCM} not reliable! Need for fully quantum approach: electronic effects at play!



What about polarization?







Take centro-symmetric positions from ⊥ and switch the AFM-E1 or AFM-E2 spin-configurations: P ~ 3 μC/cm² (with opposite sign):

Magnetism breaks the symmetry and gives P !!!

Model study:
Landau theory of phase transitions

$P_c = \chi_z (c_{xz} \sin\phi - c_0 \cos\phi)$ $P_a = c'_{xz}\, \chi_x \sin\phi$ $P_b = 0$

χ_z (χ_x) = *z* (*x*) component of dielectric susceptibility

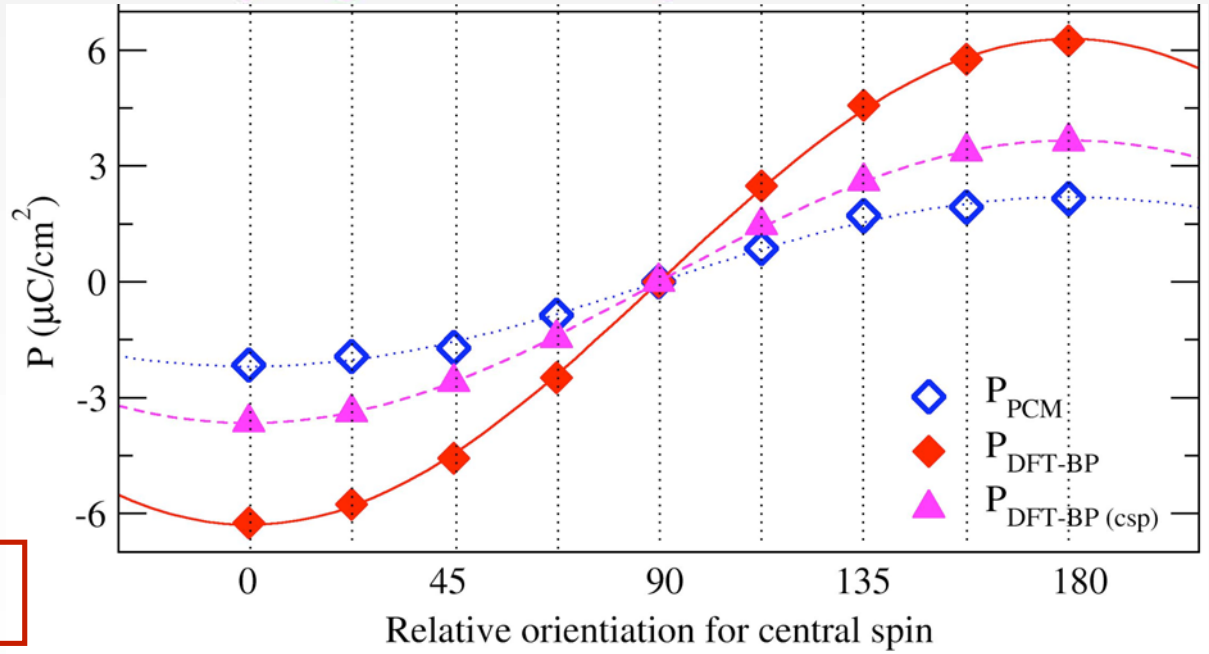
ϕ = rotation angle of the central spins

NB: c_{xz} and c'_{xz} originate from coupling of **P** to the product of the *a* and *c* components of the magnetic moments (relativistic origin)

No SOC => Only *c* component of P left:

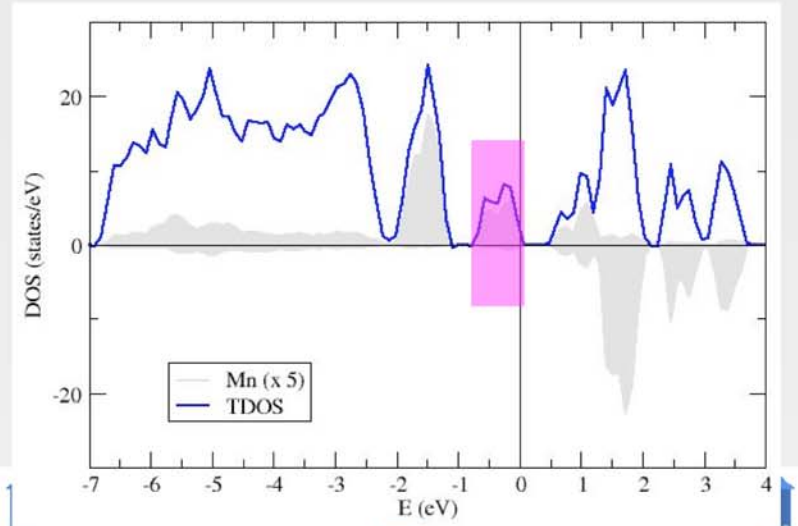
$P_c = - \chi_z c_0 \cos\phi$

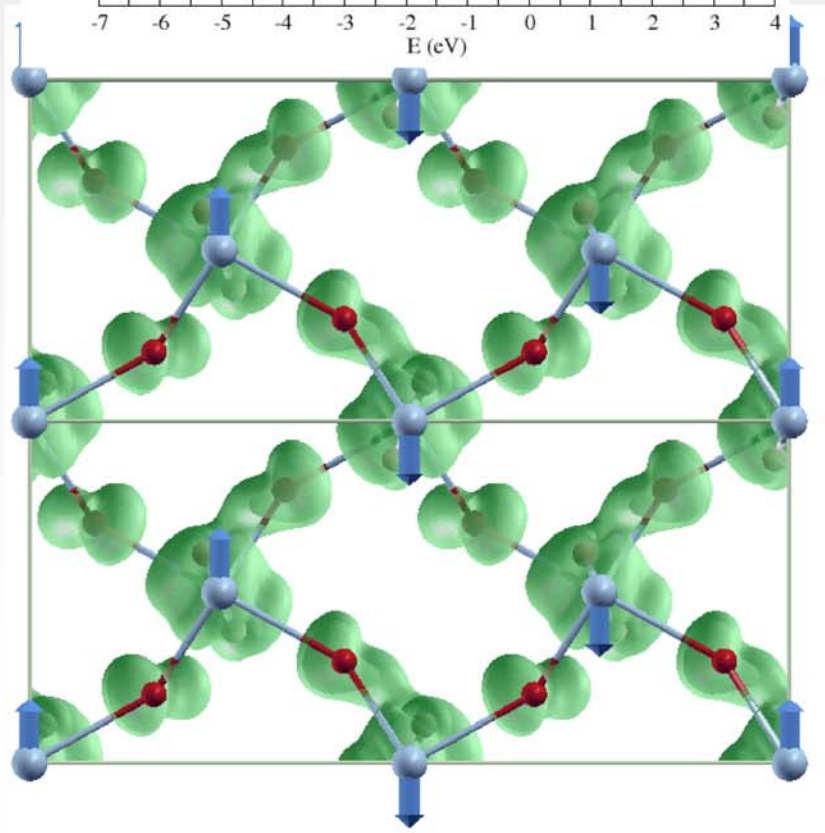
Excellent agreement!



Symmetry-breaking induced by magnetic ordering

- "Centro-symmetric positions" with AFM-E_1 ordering
- Plot charge density for Mn e_g + O *p* orbitals





- O atom bonded to AFM Mn is different from O bonded to two FM spins
- More charge on the "short" compared to the "long" bond:

relevance of magnetic ordering, Jahn-Teller and $GdFeO_3$ tilting

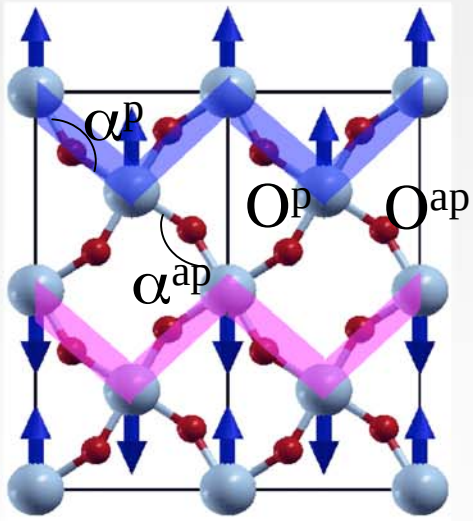
In-plane Mn and O Born effective charges

$$Z^*_{\kappa,\alpha\beta} = \Omega\,(\Delta P)_\alpha / |e| u_{\kappa,\beta}$$

- $(\Delta P)_\alpha$ = change of polarization along direction α
- $u_{\kappa,\beta}$ = displacement of atom κ in direction β
- Ω = unit cell volume
- NB: calc. only the (3,3) comp. of the Z* tensor

$Z^*_{\kappa,33}$

	Mn	O^{ap}	O^{p}
"⊥"	3.9 *e*	-3.1 *e*	-3.1 *e*
AFM-E	3.8 *e*	-2.6 *e*	-3.5 *e*



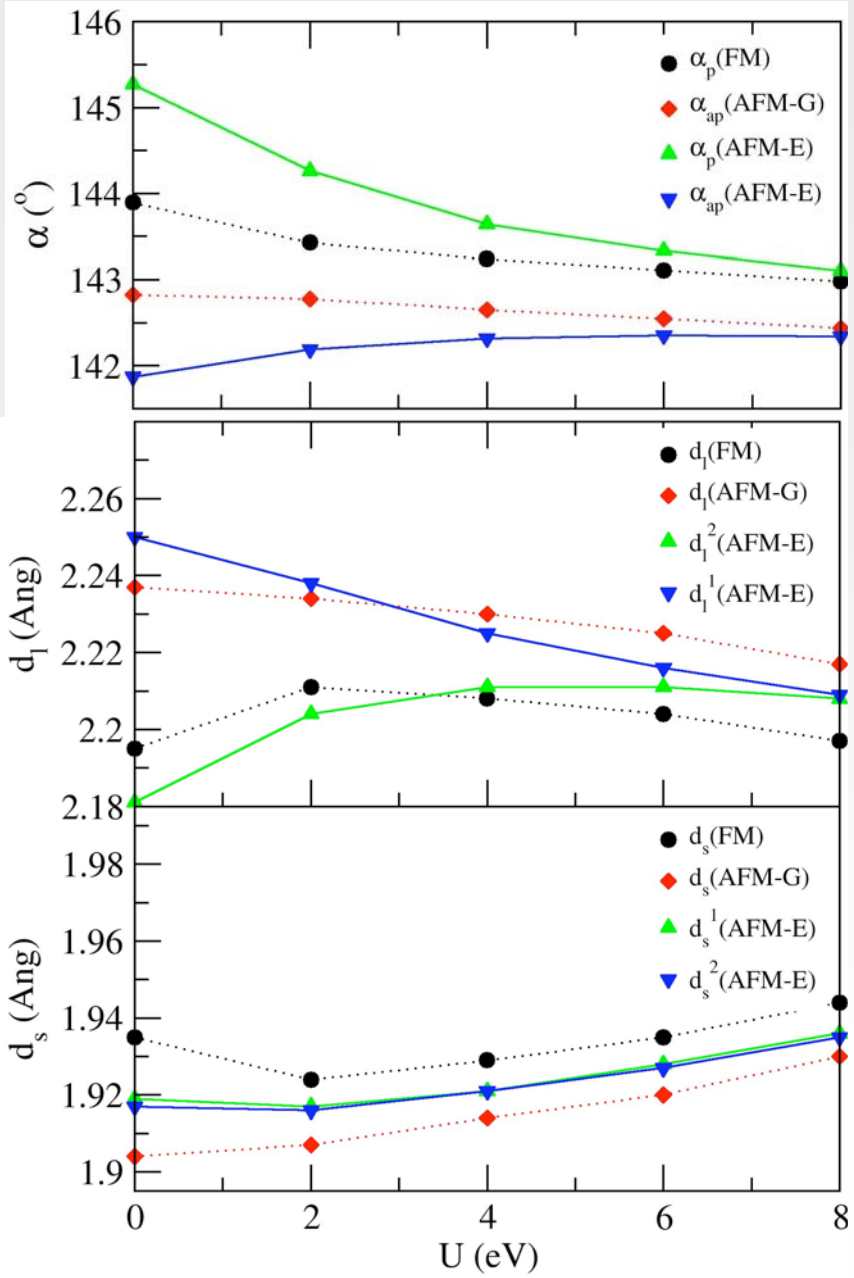
- Z* values not so "*anomalous*" : rather "*ionic*" picture
- Polarization in centrosymmetric structure comes from inequivalency of the oxygens

How about correlations? "GGA+U"

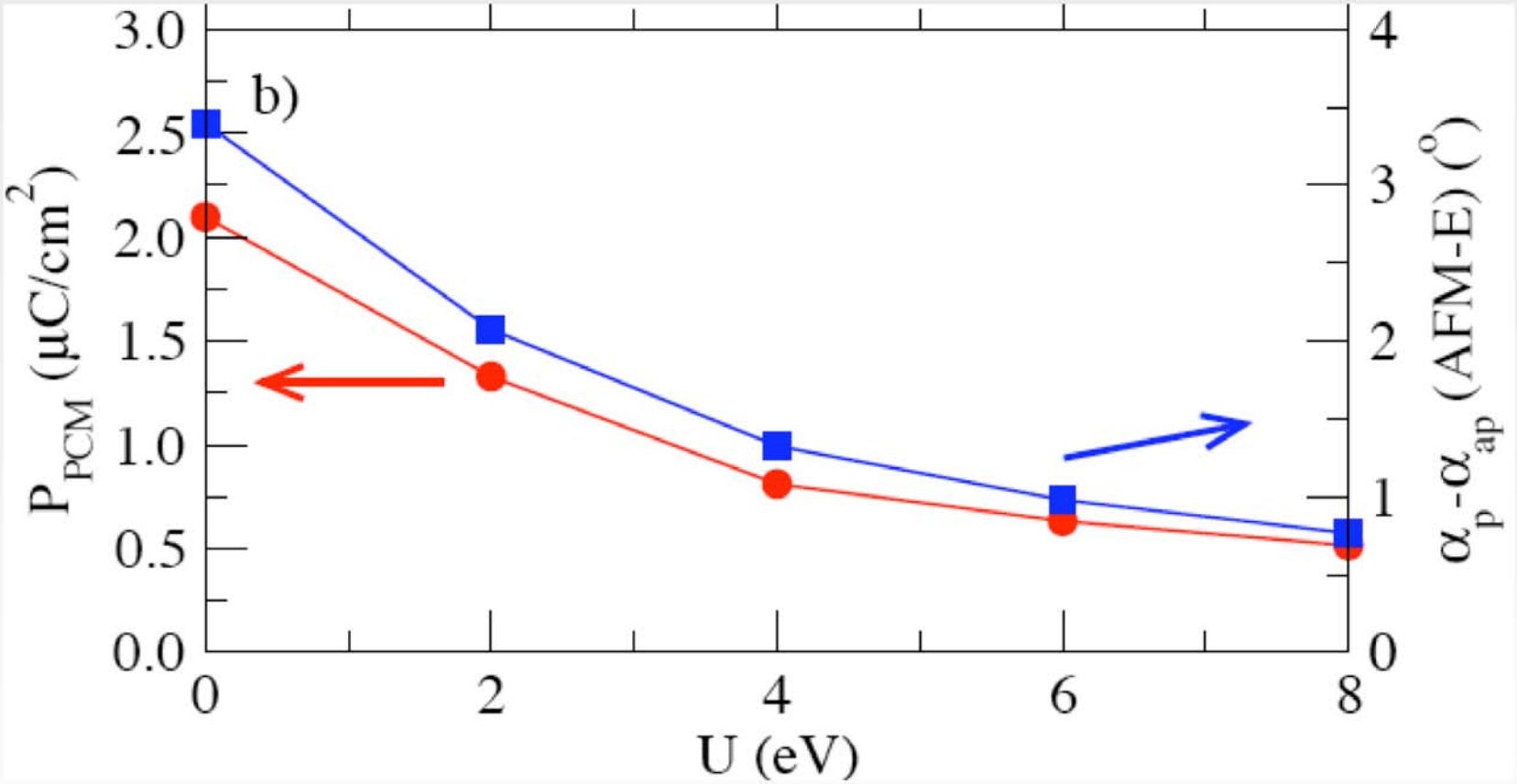
- Difference between Mn-O-Mn angles for FM and AFM Mn decreases with U

- The two "short" Mn-O bond lengths are very similar
- The two "large" Mn-O bond lengths become closer with U ⇨

  Smaller distortions!



What about P vs U?



- P follows the displacement trend and decreases with U. It makes sense:

  U = energy penalty paid for adding an extra-*e* on Mn ⇨ If U increases, hopping is less favourable, therefore α^p- α^{ap} (and eventually P) decreases
- However, P > 0.5 μC/cm^2 in the whole U range

Theory vs Experiment*

Polarization from integrating pyroelectric current on $HoMnO_3$ poly-cristalline samples (single crystals not available)

- P small (although it is a lower bound…)
- P increases at ordering temperature of Ho spins!

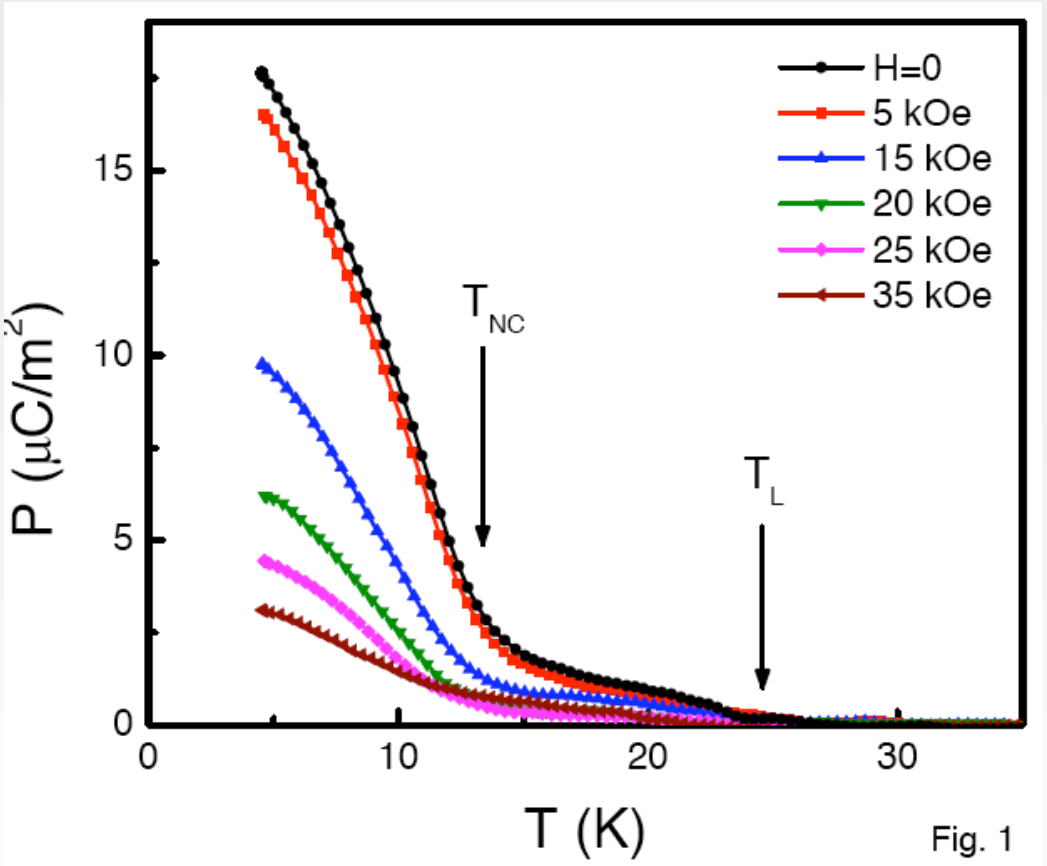


Fig. 1

1. Expt: Make better *samples* ???? Deposit thin films ???
2. Theory: Make better *simulations* ??? Ho 4f spins ???

* *B. Lorenz, YQ. Wang and C.W.Chu, cond-mat/0608195*

Summary#

AFM-E ortho-$HoMnO_3$: is this a novel multiferroic?
First-principles density-functional calculations

- **Electric polarization from "displacement" mechanism**

  Largest P predicted so far for an "improper ferroelectric" where P is induced by antiferromagnetism

- **Ferroelectric switching path**

  Via spin-rotations: Electrical control of AFM domains

- **Polarization induced by AFM-E magnetic ordering**

  1. **P** has a both of "*ionic*" and "*electronic/magnetic*" origin.This solves controversy in model Hamiltonian studies
     + we believe it is rather *general* in the class of IMF
  2. It is possible to achieve "large" P (i.e. few $\mu C/cm^2$) with centrosymmetric positions

 # S.Picozzi, K.Yamauchi, B.Sanyal,I.A.Sergienko and E.Dagotto, arXiv/0704.3578

Take-home message:

"Dual nature" of P in real compounds:

- **displacements of ions**

and

- **electronic/magnetic effects**

can both sizably contribute to P

How can we induce ferroelectricity in magnets ?

For ferroelectricity, we need to break **inversion symmetry.**

How to do that in magnets via the electronic degrees of freedom?

1. **Spin** degree of freedom ✓
2. **Charge** degree of freedom
3. **Orbital** degree of freedom

Any good candidates?