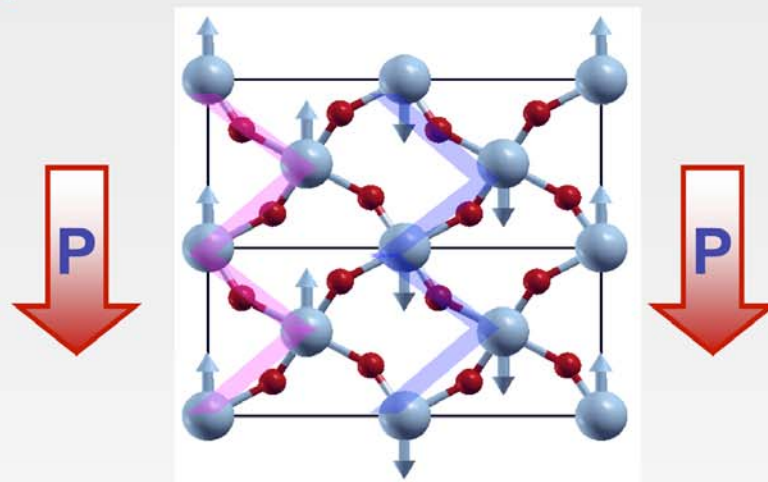
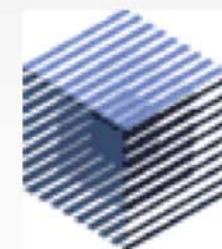


Dual nature of improper ferroelectricity in a magnetoelectric multiferroic



Silvia Picozzi

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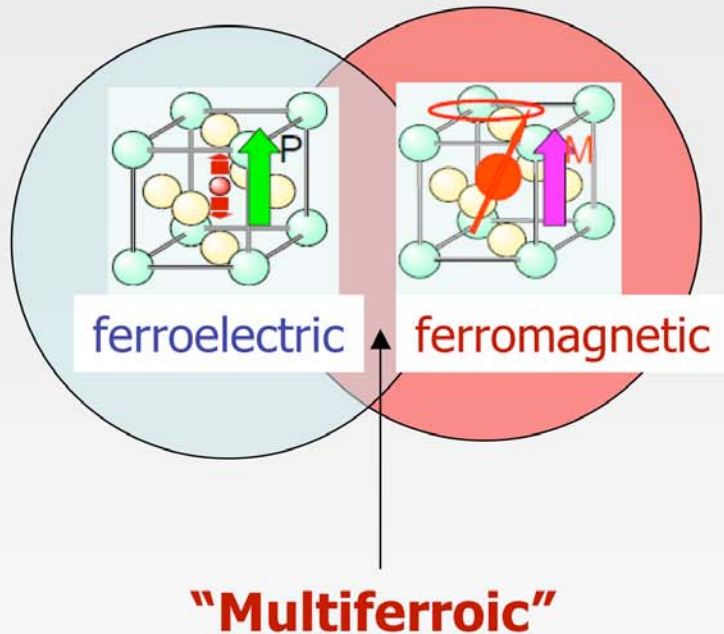
K. Yamauchi (CNR-INFM, L'Aquila), **B. Sanyal** (Uppsala Univ., Sweden),

I. A. Sergienko and E. Dagotto

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



Introduction on Bulk Multiferroics



.....But:

“**d⁰-ness**”: standard ferroelectrics show an **empty** d-shell (Ti^{4+} , Nb^{5+}) whereas magnetism requires **partially filled** d-shells ☹️

... One needs new mechanisms... ☹️

Our approach:

looking at “**improper ferroelectricity**” in **magnets** (i.e. where polarization appears as a consequence or concomitantly with some other kind of orderings)



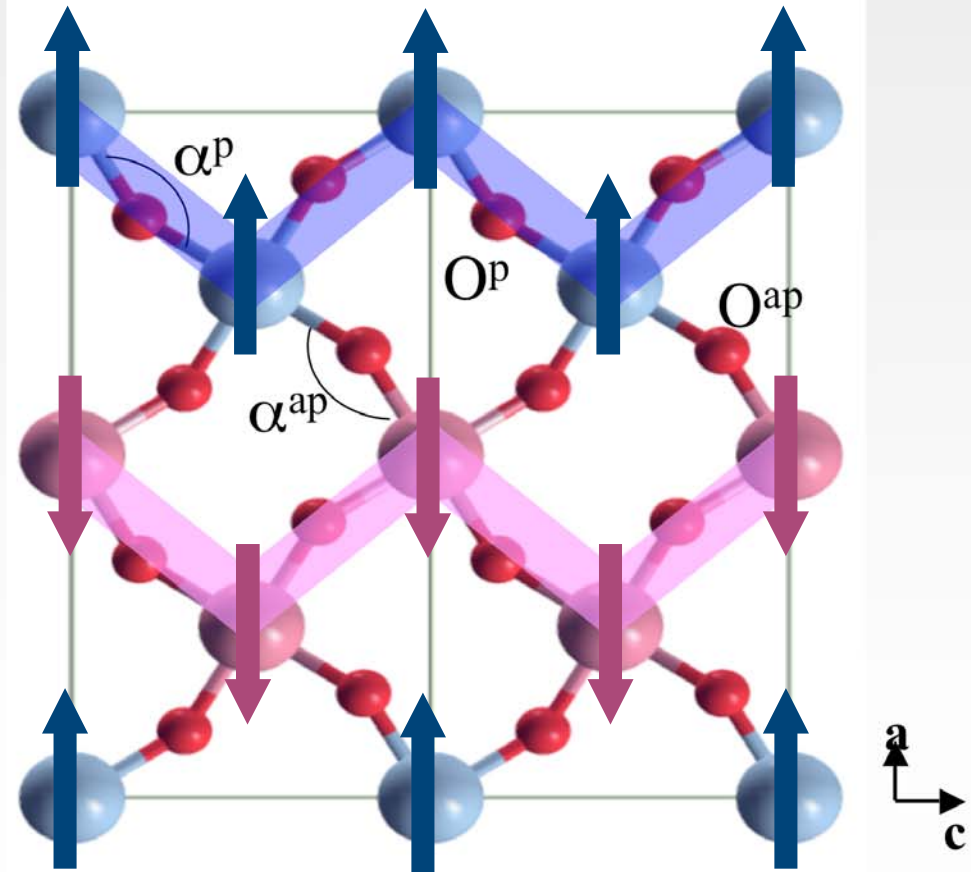
How can we induce ferroelectricity in magnets ?

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 talk by M. Mostovoy)
- Some kinds of **anti-ferromagnetism** (see for example AFM-E)



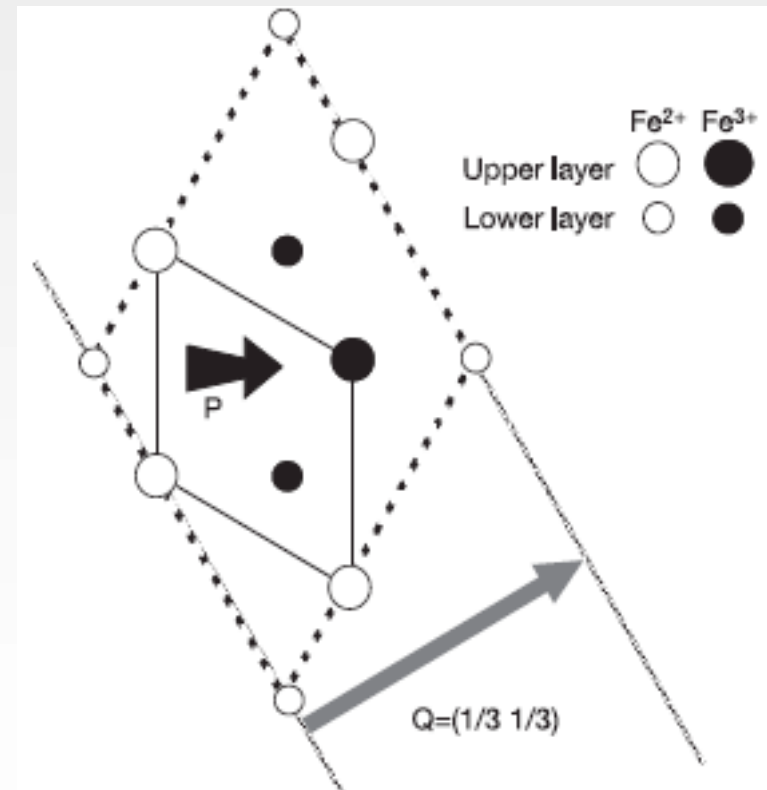
How can we induce ferroelectricity in magnets ?

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

1. **Spin** degree of freedom:
2. **Charge** degree of freedom:

- **LuFe₂O₄**
*N. Ikeda et al.,
Nature* **436**, 1136 (2005)

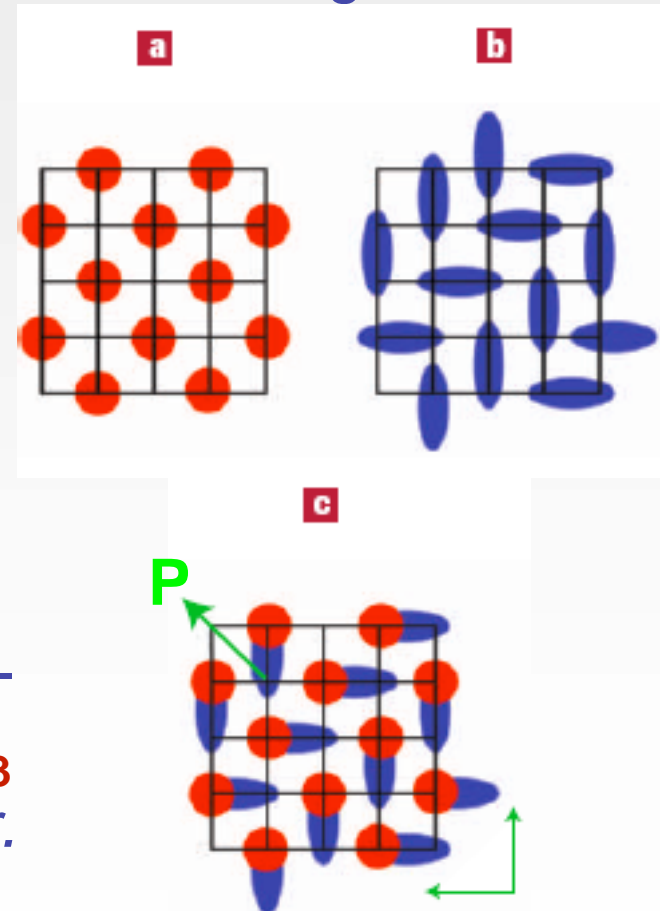


How can we induce ferroelectricity in magnets ?

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:
- **LuFe_2O_4**
*N. Ikeda et al.,
Nature 436, 1136 (2005)*
 - Intermediate bond- and site-centered ordering in **PrCaMnO_3**
D. Efremov et al., Nature Mater. 3, 853 (2004)



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?

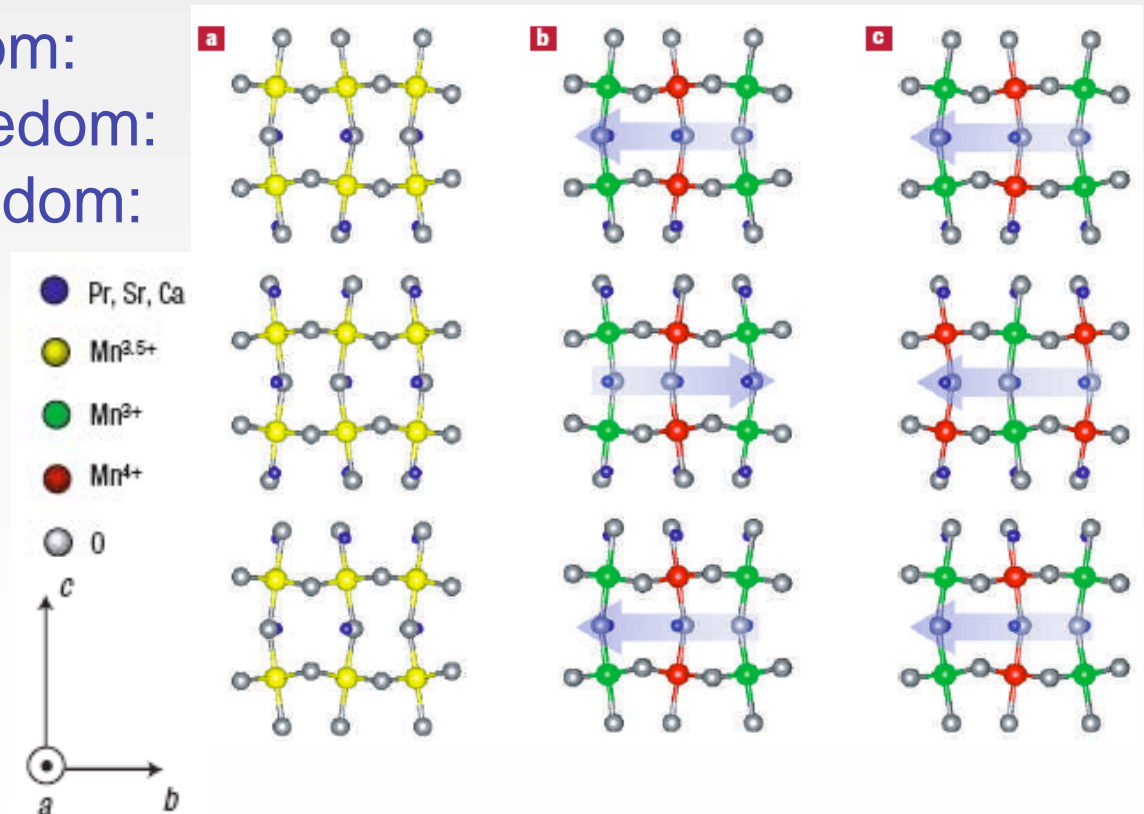
1. **Spin** degree of freedom:
2. **Charge** degree of freedom:
3. **Orbital** degree of freedom:

Bilayer manganite



Tokura's group

Nature Mater. **5**, 937
(2006)

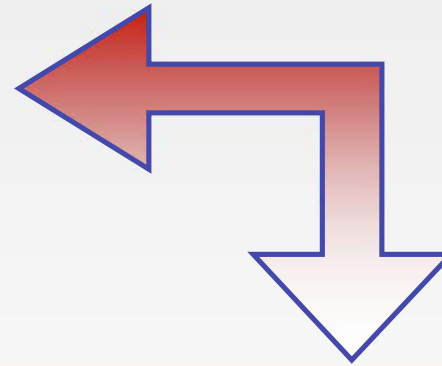


How can we induce ferroelectricity in magnets ?

For ferroelectricity, we need to break
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How to do that in magnets via the electronic degrees of freedom?

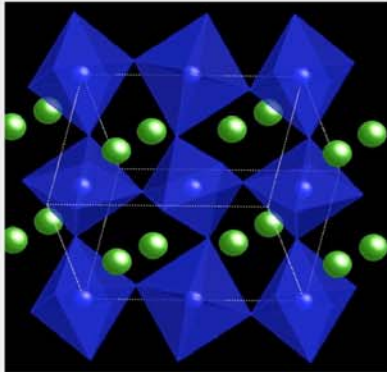
1. **Spin** degree of freedom:
2. **Charge** degree of freedom:
3. **Orbital** degree of freedom:



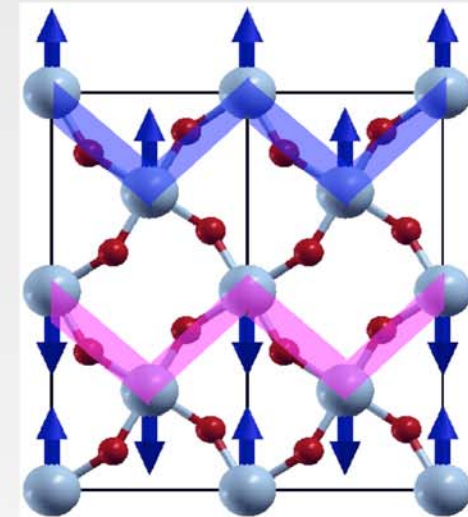
So far:
Is antiferromagnetism
enough to induce
ferroelectricity and how big?
Let's look at
AFM-E HoMnO₃



Starting point: the AFM-E spin configuration



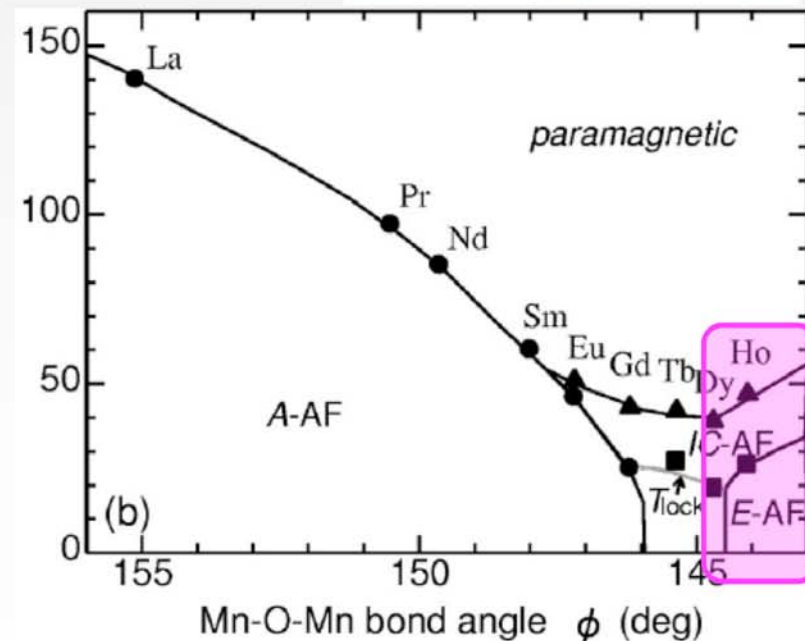
1. Distorted ortho-manganites: Jahn-Teller and GdFeO_3 -like tilting
2. $Pnma$ space group
3. Double along a and form zig-zag FM spin chains AFM coupled with respect to neighboring chains



When does the AFM-E occur?

- Transition from AFM-A to AFM-E with octahedral GdFeO_3 -like distortions¹
- AFM-E: expts in HoMnO_3 + model-hamiltonian-studies²

1. T. Kimura et al., *PRB* 68, 060403 (2003).
2. T. Hotta et al., *PRL* 90, 247203 (2003).



Magnetic ordering:

AFM-E as ground state in distorted RMnO_3

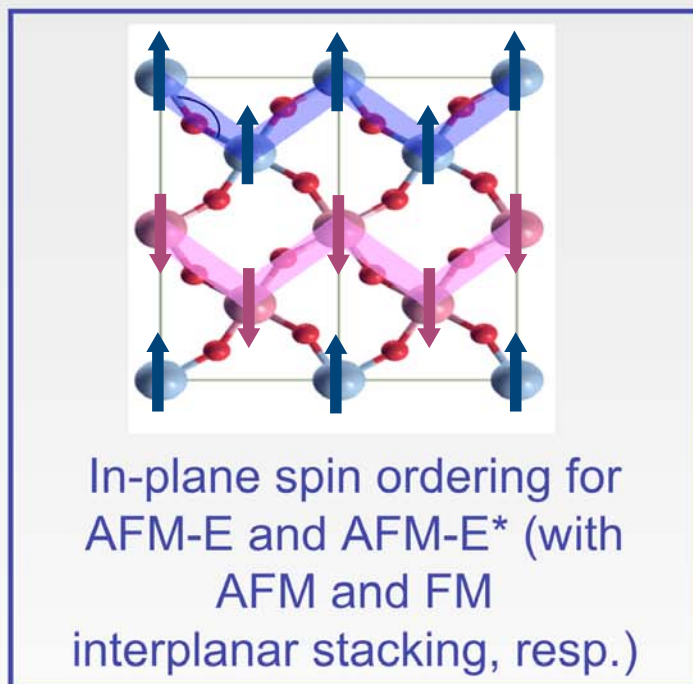
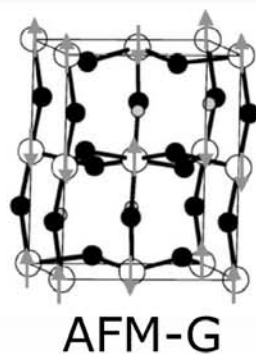
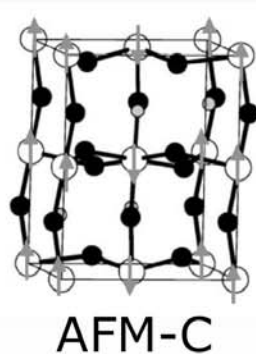
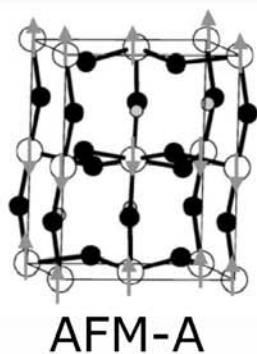


Table: energy difference (in meV/Mn) with respect to FM

	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



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



Computational details

- VASP¹ simulations with Projector Augmented Wave pseudopotentials
- Generalized Gradient Approx. (PBE exch.-corr.)
- Ho pseudopotential: 4f not-pseudized
- Monkhorst-Pack shell: [3,4,6]
- Hubbard potential² on Mn d: GGA +U (for various U and $J = 0.15*U$)
- Berry phase approach to polarization³
- Non-collinear magnetism⁴
- Spin-orbit neglected

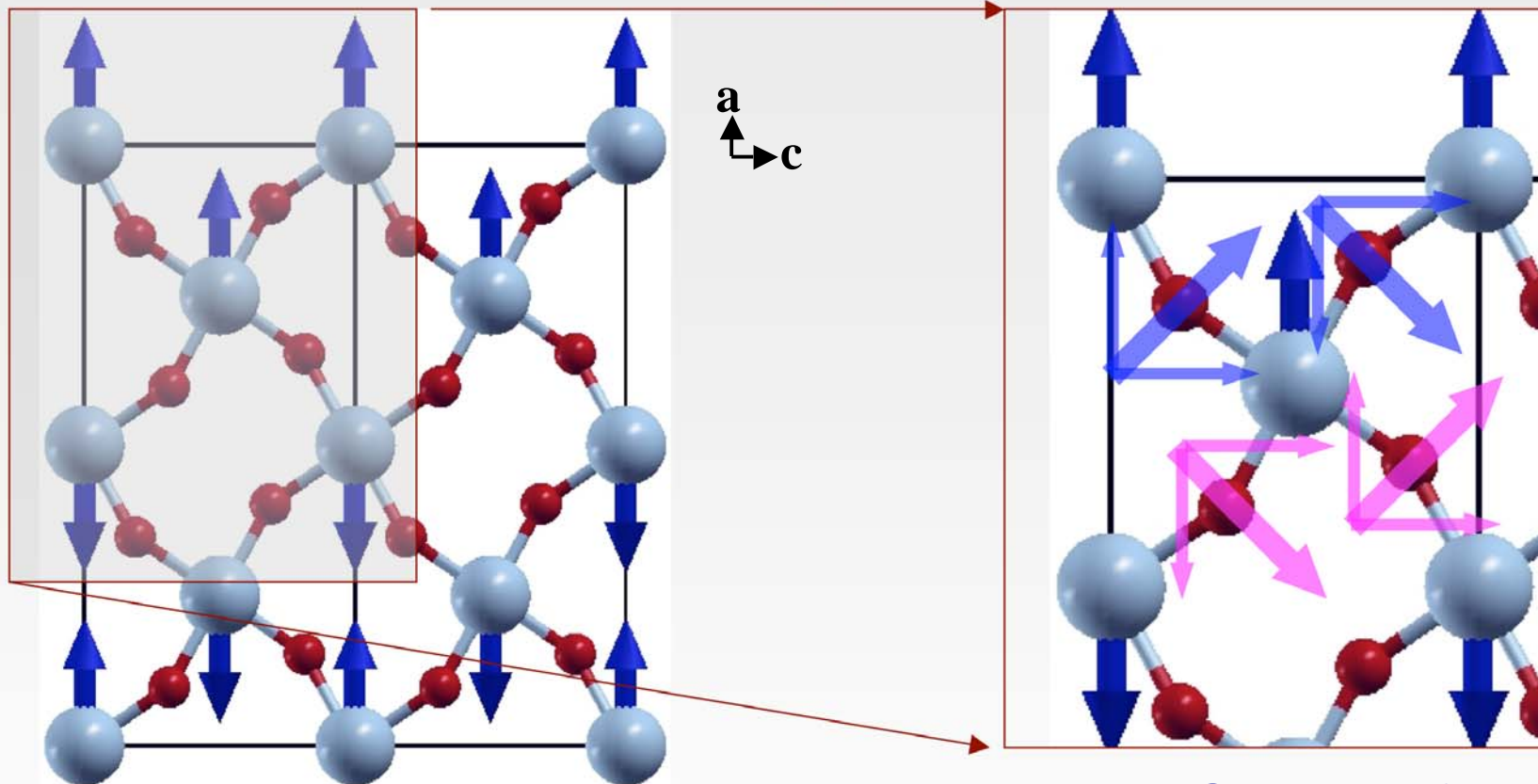
1. G. Kresse and J. Furthmüller, *Phys. Rev. B* 54, 11169 (1996)
2. V.I. Anisimov, et al., *J. Phys.: Condens. Matter.* 9, 767 (1997).
3. R.D.King-Smith and D.Vanderbilt, *PRB* 47,1651 (1993); R. Resta, *RMP* 66, 899 (1994).
4. D. Hobbs, G. Kresse and J. Hafner, *Phys. Rev. B* 62, 11556 (2000).

Structural details

- Experimental lattice constants for paramagnetic HoMnO₃
- Extremely high GdFeO₃-like distortions
- Internal atomic positions fully relaxed (forces < 0.01 meV/Å)



Polarization from “Displacement” mechanism *



Simple model:

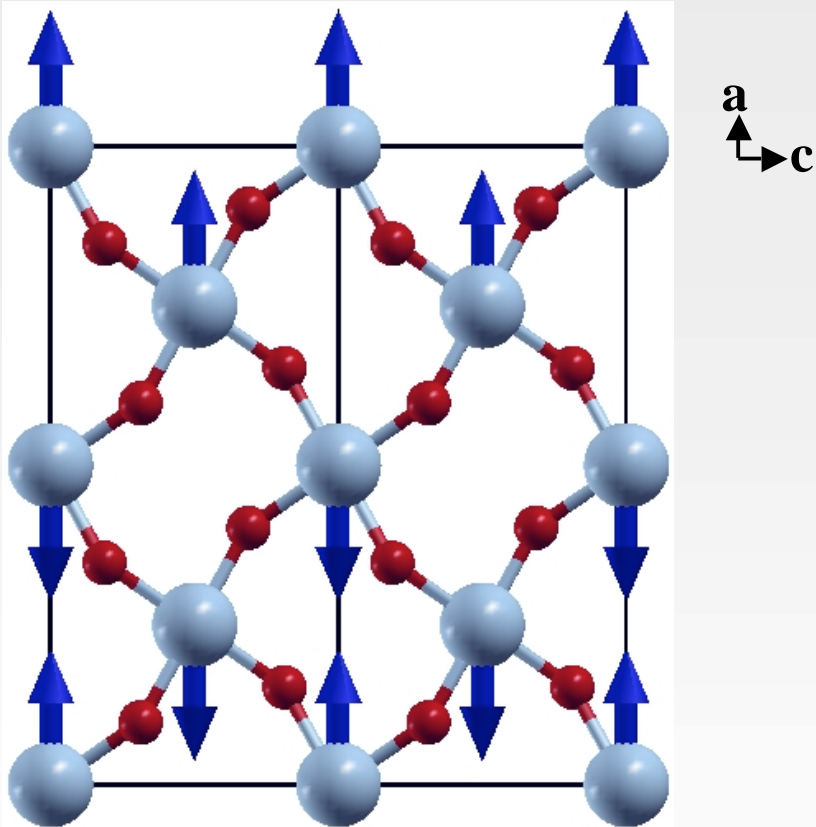
- start from centro-symmetric atomic positions
- only O atoms can move and they are forced in the MnO₂ planes

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).*

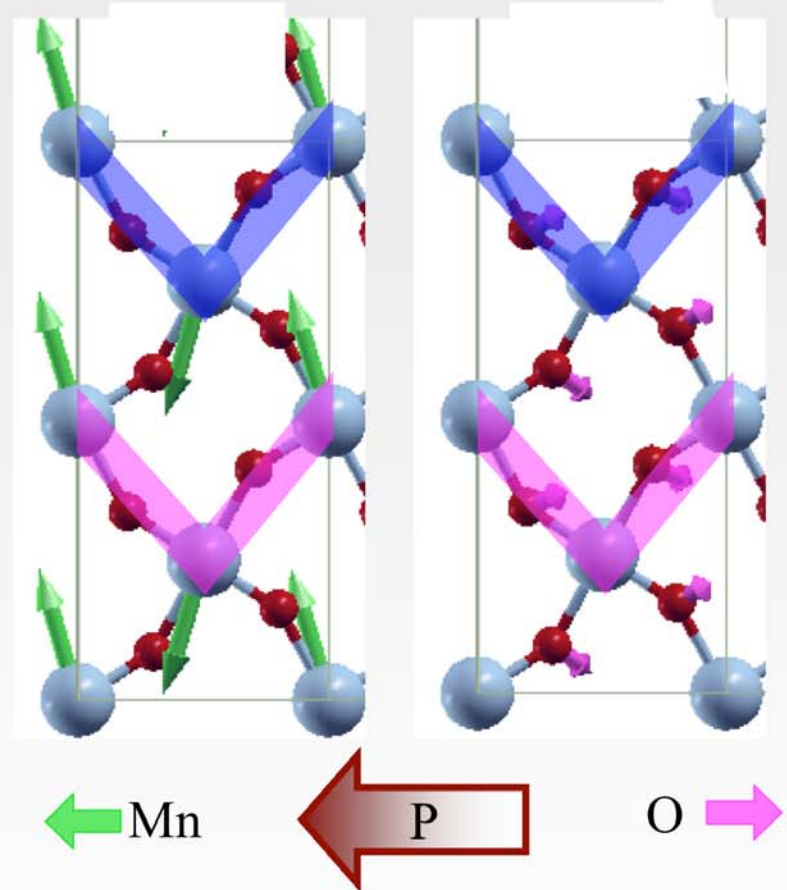


Polarization from "Displacement" mechanism



Simple model:

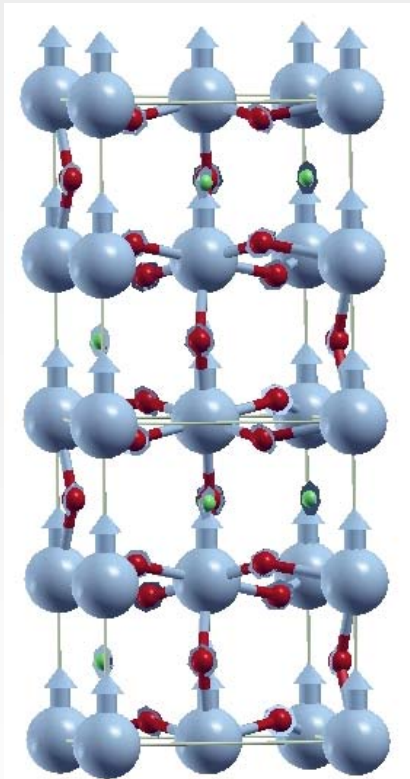
- start from centro-symmetric atomic positions
- only O atoms can move and they are forced in the MnO₂ planes



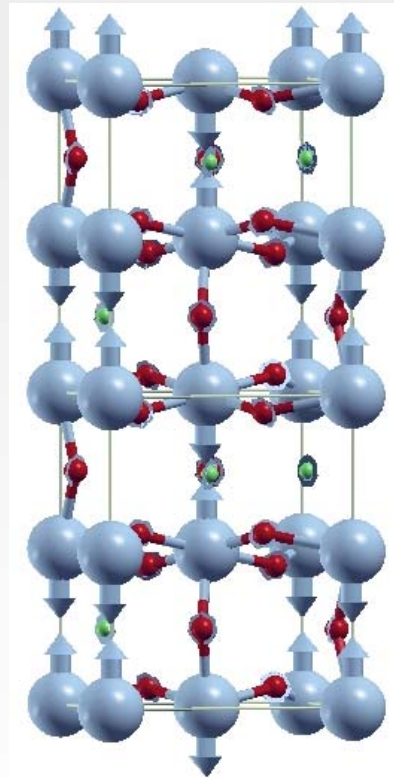
... But.... actually the displacement pattern is not so simple (also Mns move), but the polarization is indeed directed along c



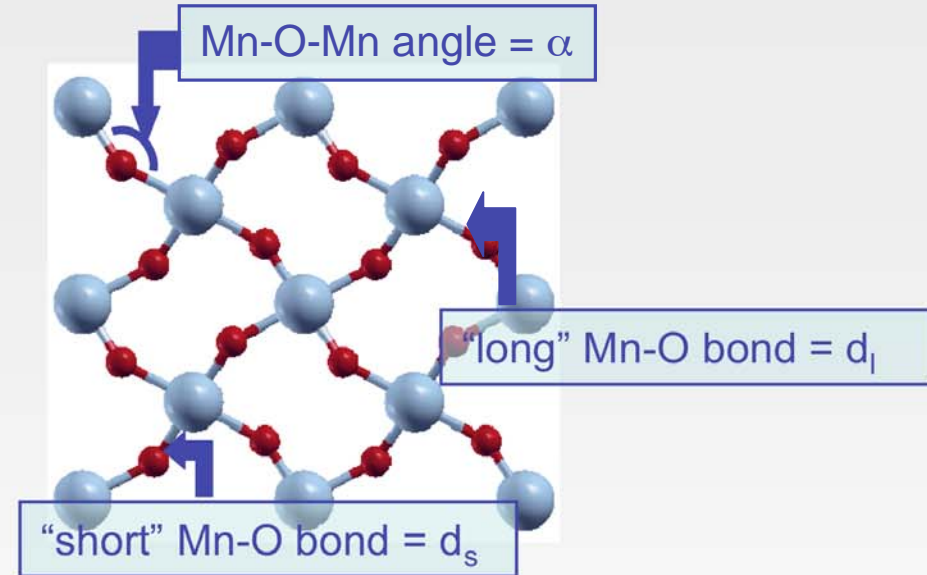
Does the Mn-O-Mn angle depend on Mn-Mn spin configuration?



FM



AFM-G

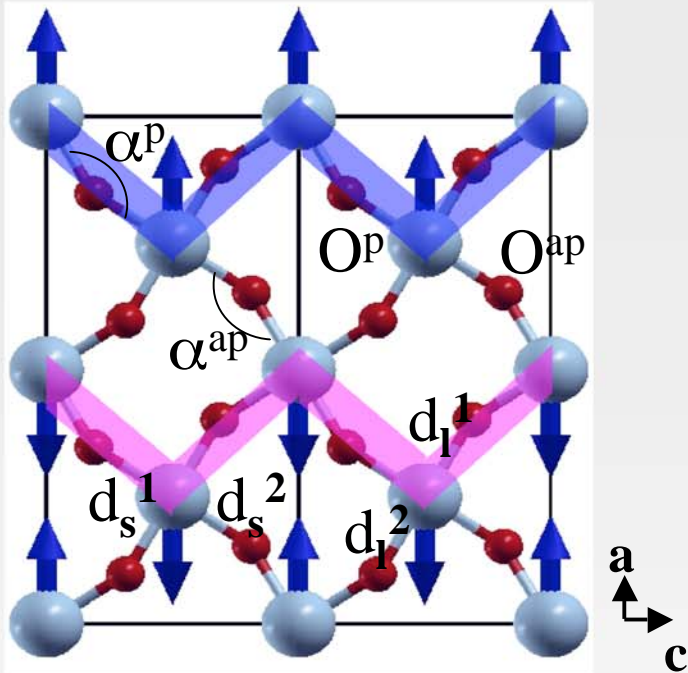


	α ($^\circ$)	d_l (\AA)	d_s (\AA)
FM	143.9	2.19	1.93
AFM-G	142.8	2.24	1.90

In-plane FM (AFM) interactions \longleftrightarrow Larger (Smaller) angles



HoMnO₃ 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

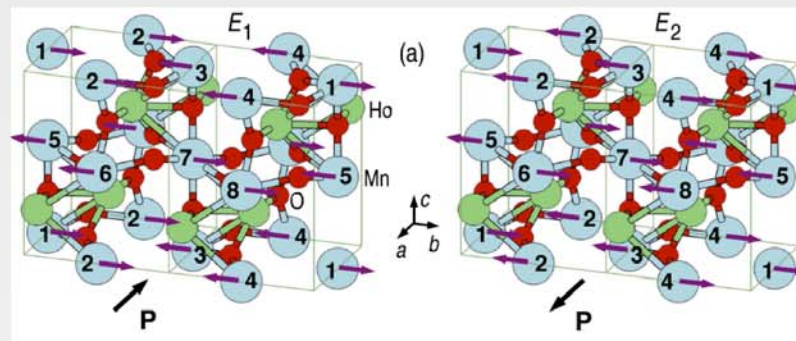
Very different Mn-O-Mn α and Mn-O d_l : displacement mechanism active!



Ferroelectric switching

Sergienko et al.¹ :

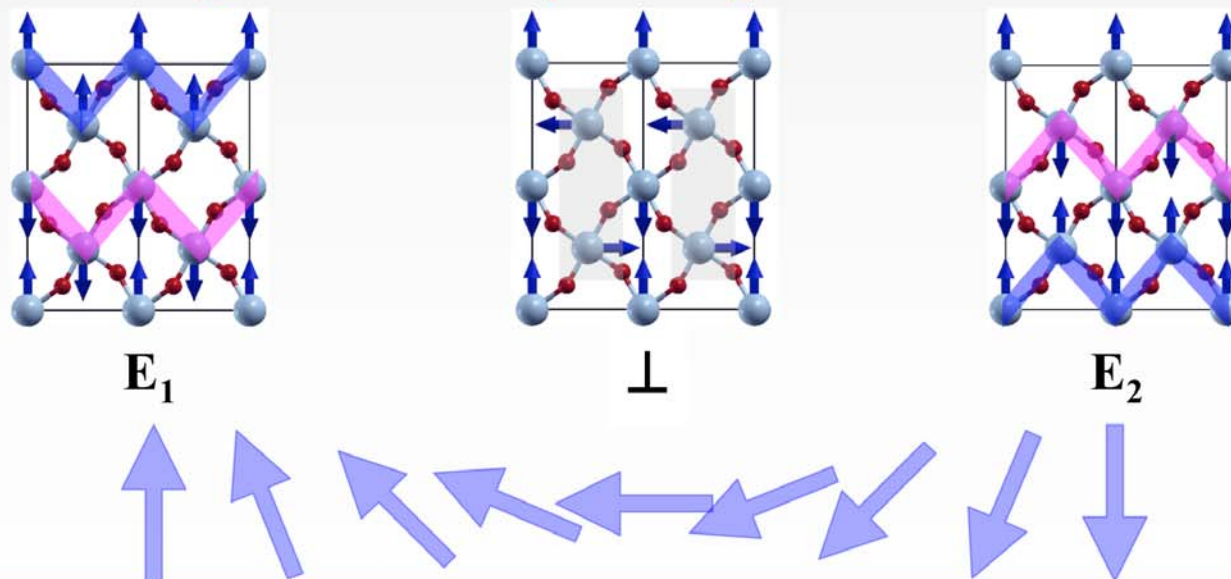
- Model calculations using Landau theory
- two E-phase domains differing for orientation of half of the Mn spins and giving opposite P



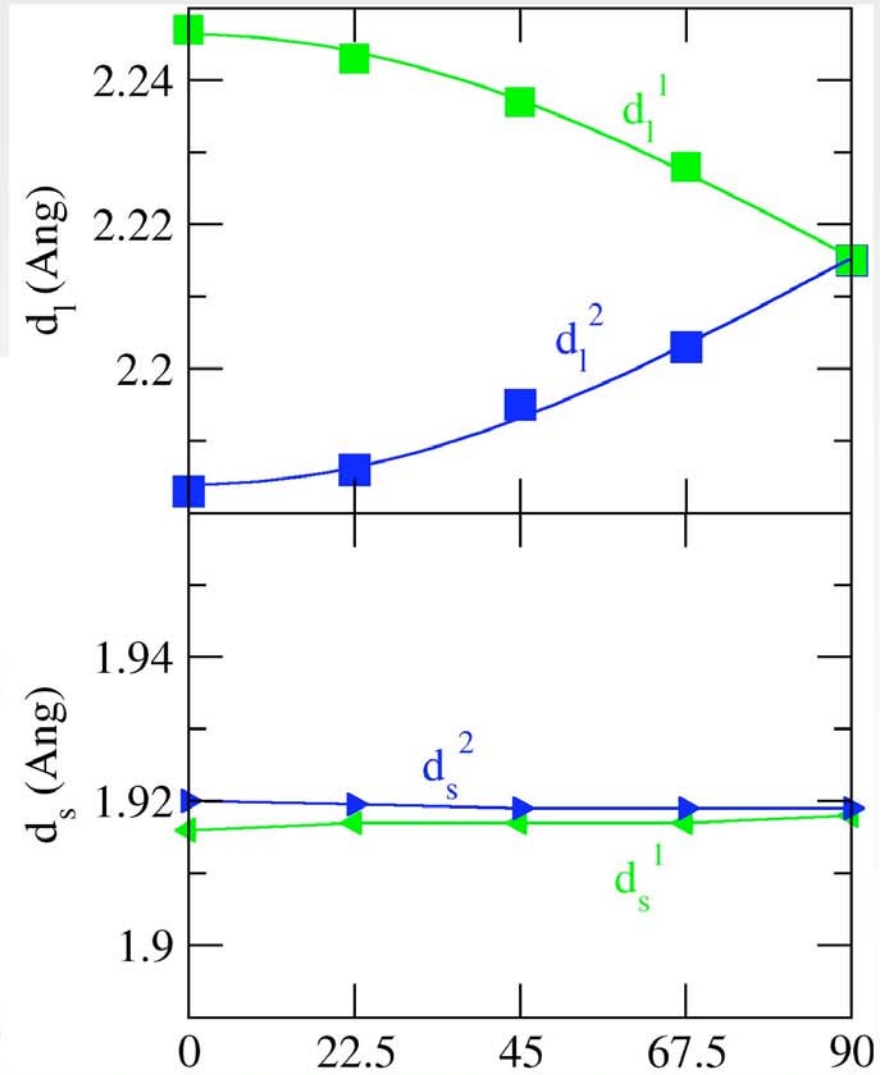
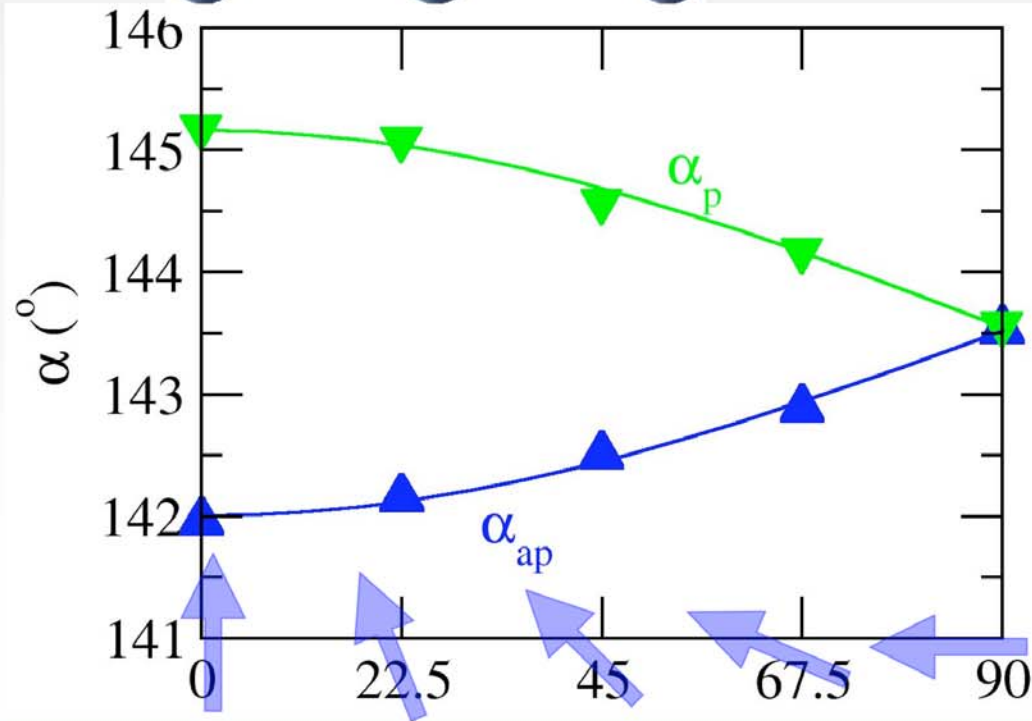
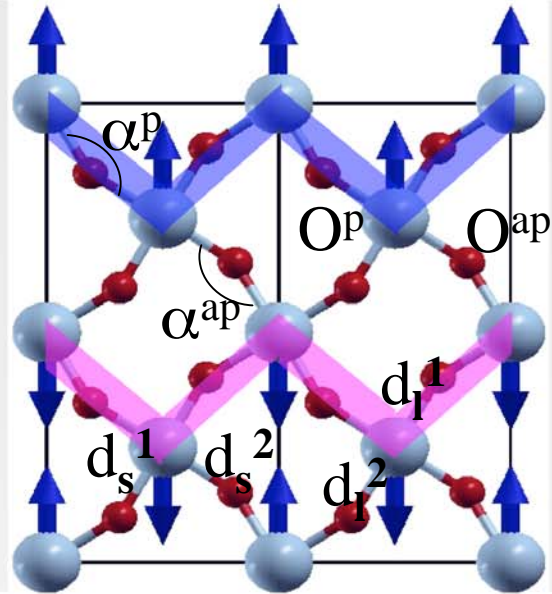
1. I.A. Sergienko, C. Sen and E. Dagotto, *PRL* 97, 227204 (2006).

How to go from E_1 to E_2 ?

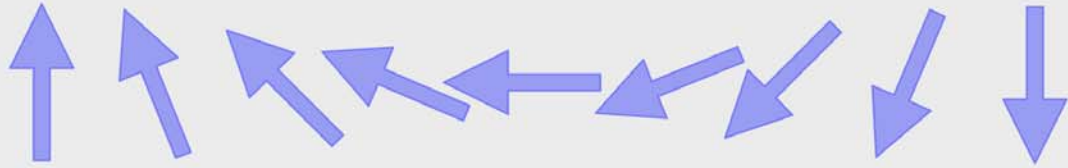
- Via progressive rotation of “central” spins
- Non collinear VASP calculations constraining the direction of local moments



Structural changes along the switching path

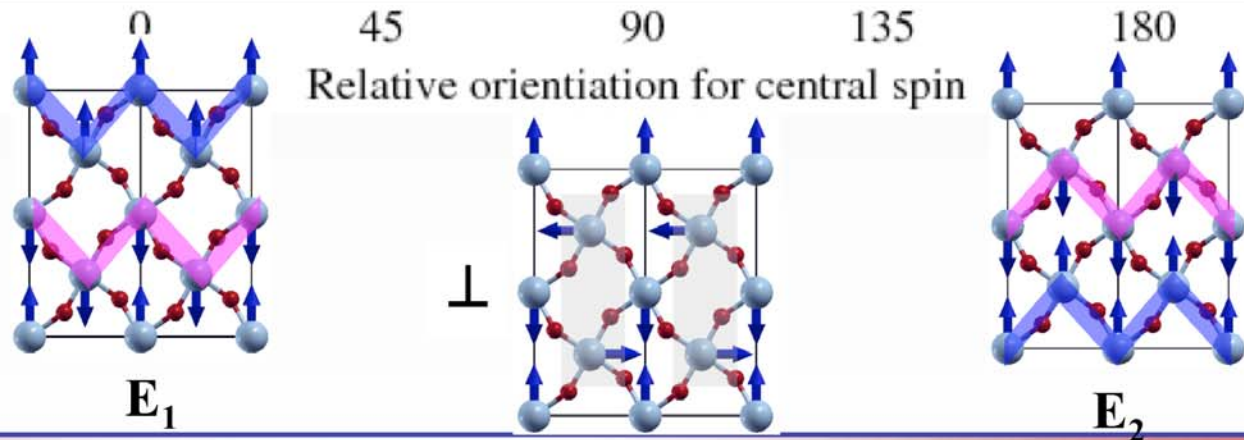
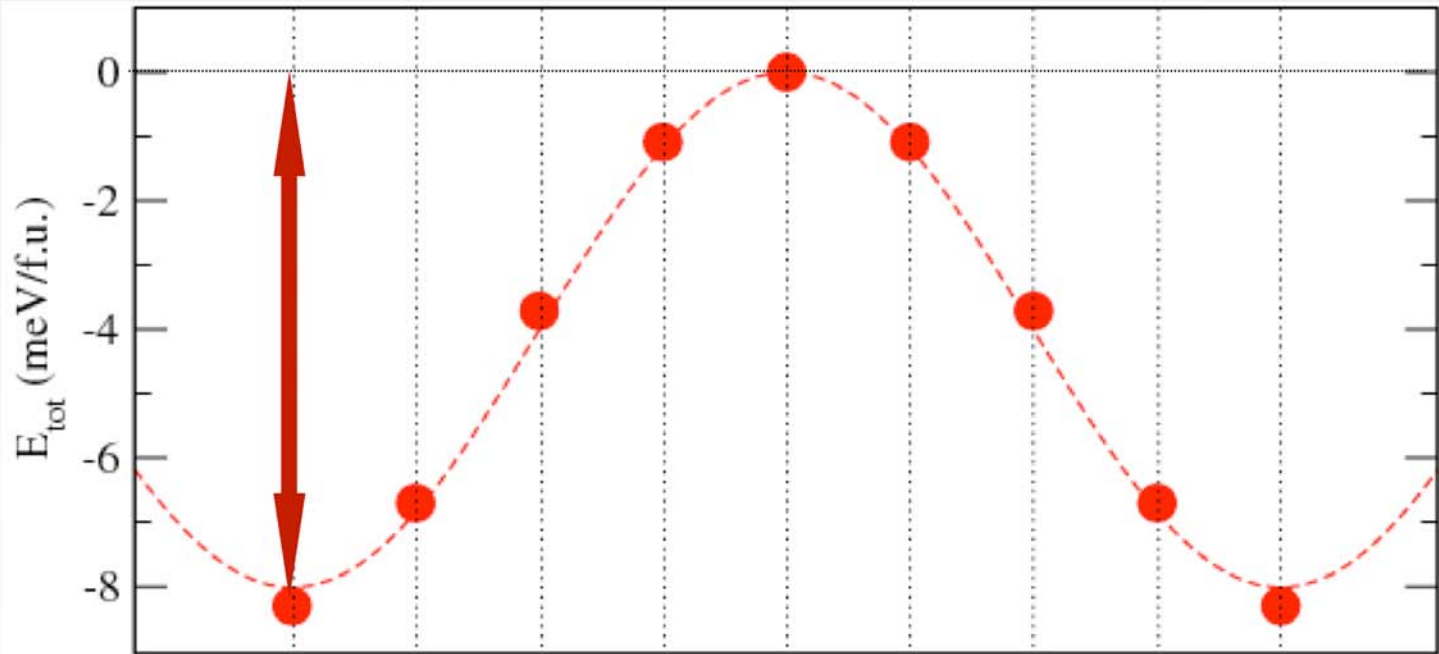


Ferroelectric switching

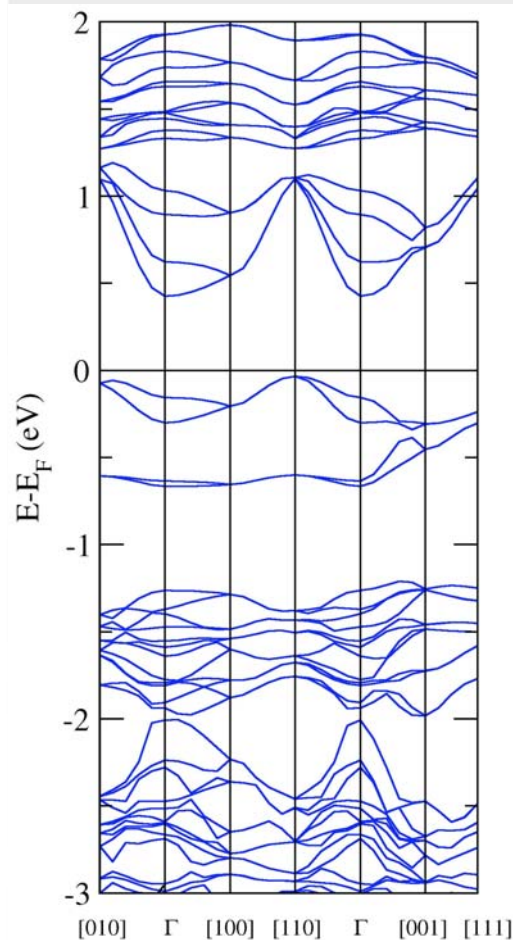


Depth of the well
 ~ 8 meV/f.u.

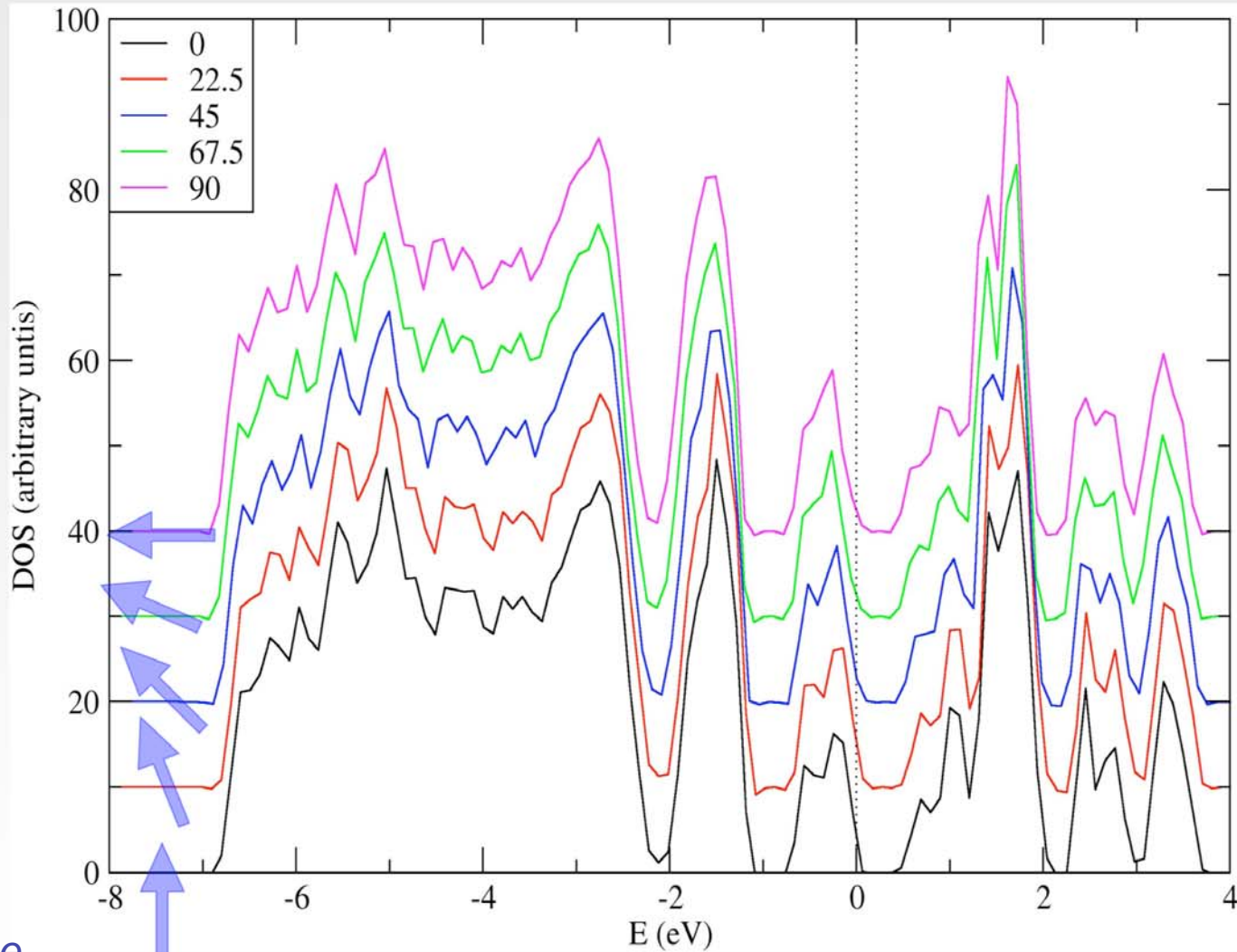
(cfr
18 meV/f.u.
in BaTiO₃)



Insulating character along the switching path



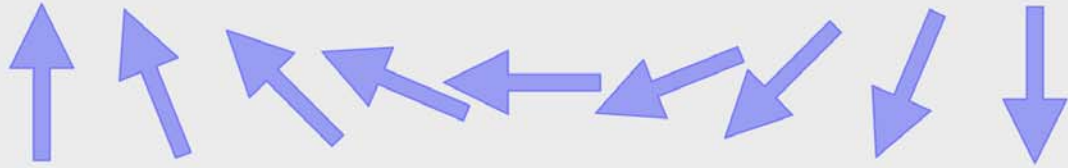
Band structure along the main symmetry lines for relaxed AFM-E1



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



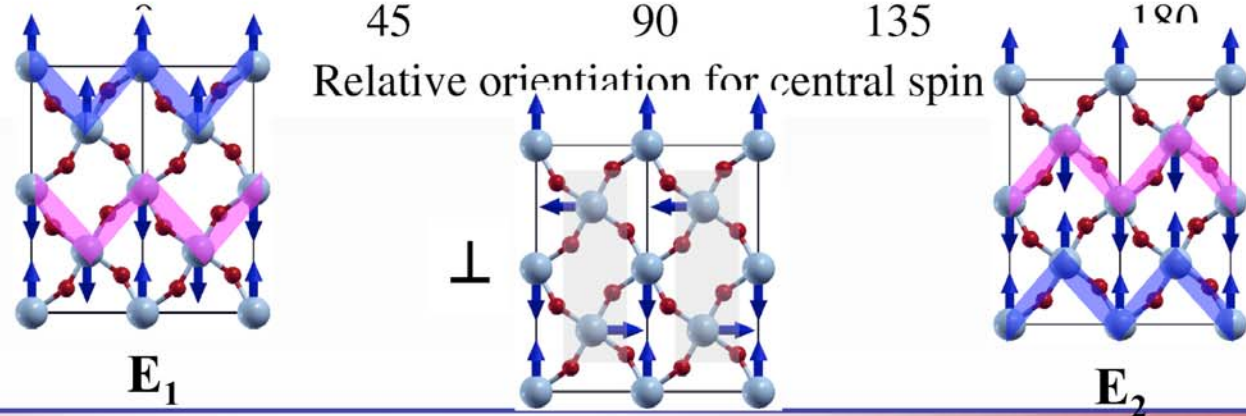
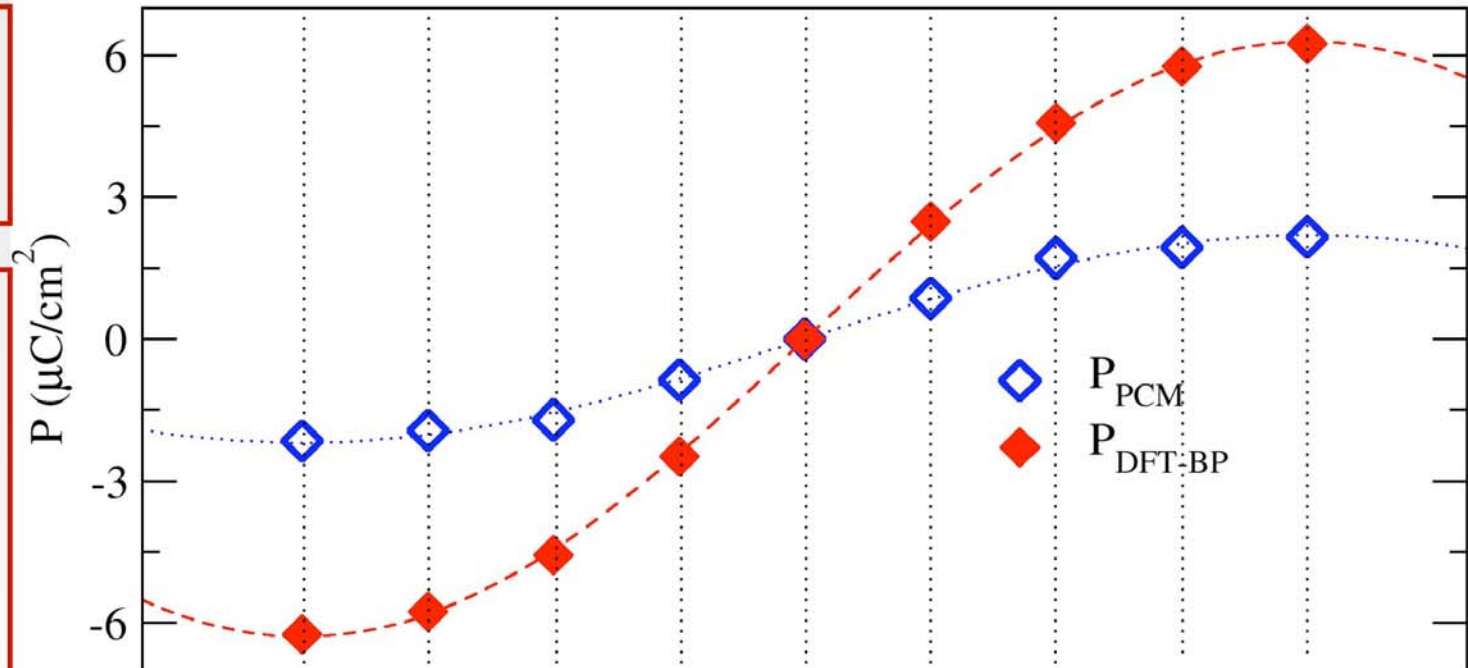
What about polarization?



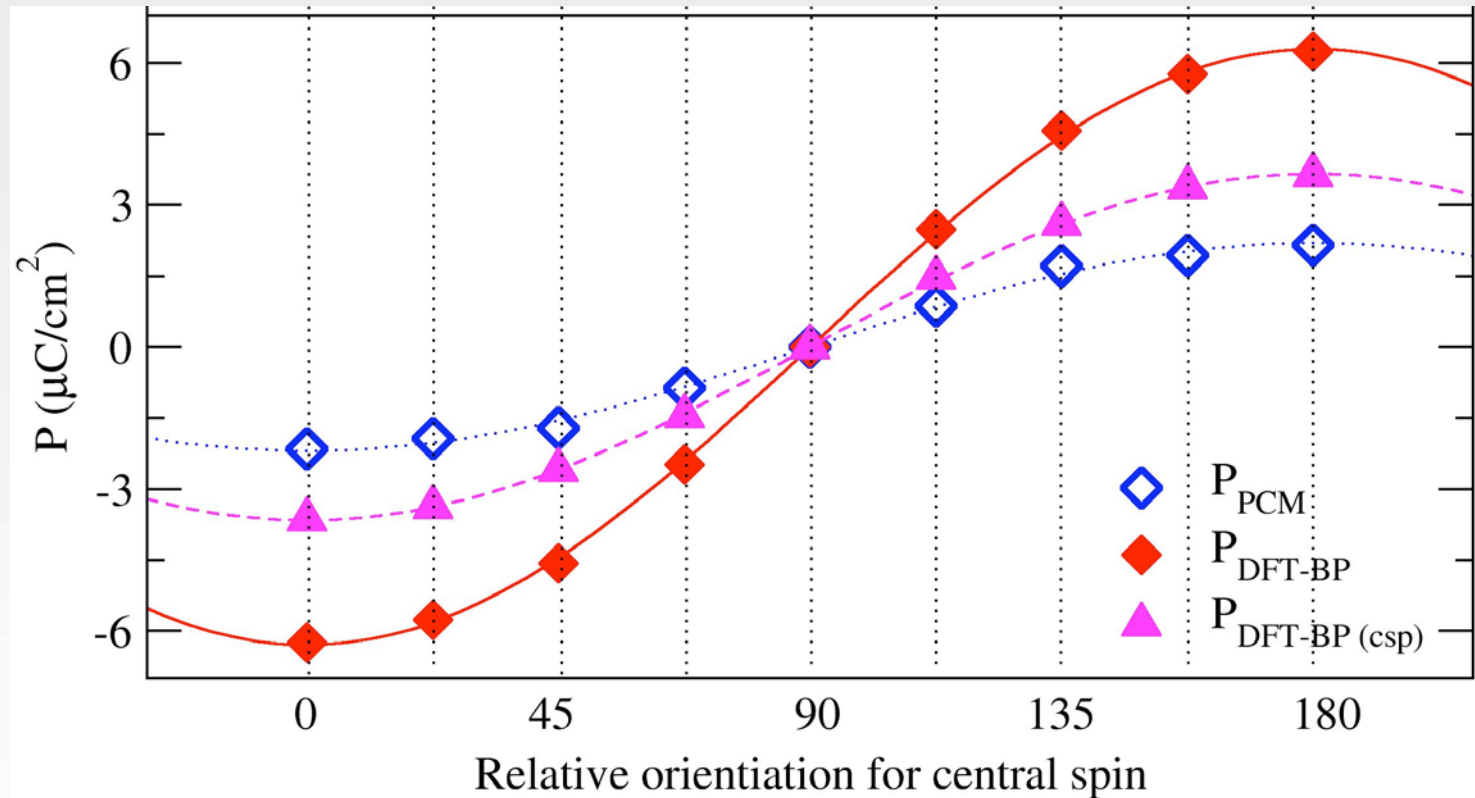
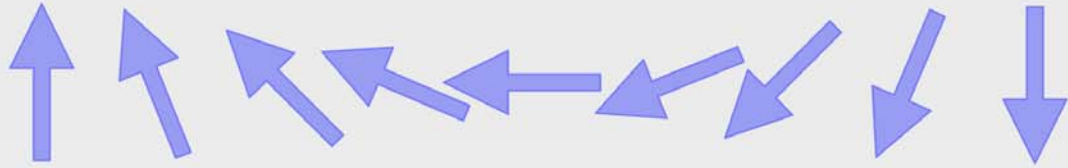
Electrical control of AFM domains

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

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



What about polarization?



Take **centro-symmetric positions** from \perp and switch the AFM-E1 or AFM-E2 spin-configurations:
 $P \sim 3 \mu\text{C}/\text{cm}^2$ (with opposite sign):
Magnetism breaks the symmetry and gives P !!!



Model study: Landau theory of phase transitions

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

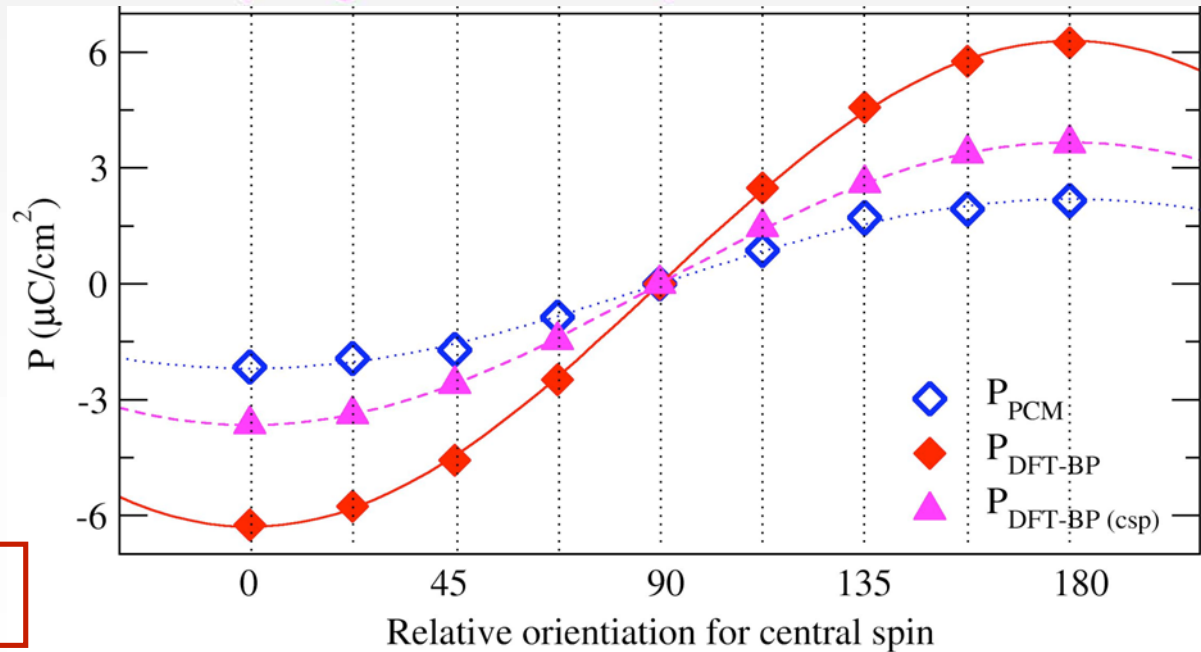
χ_z (χ_x) = z (x) component of dielectric susceptibility
 ϕ = rotation angle of the central spins

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

No SOC => Only c component of \mathbf{P} left:

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

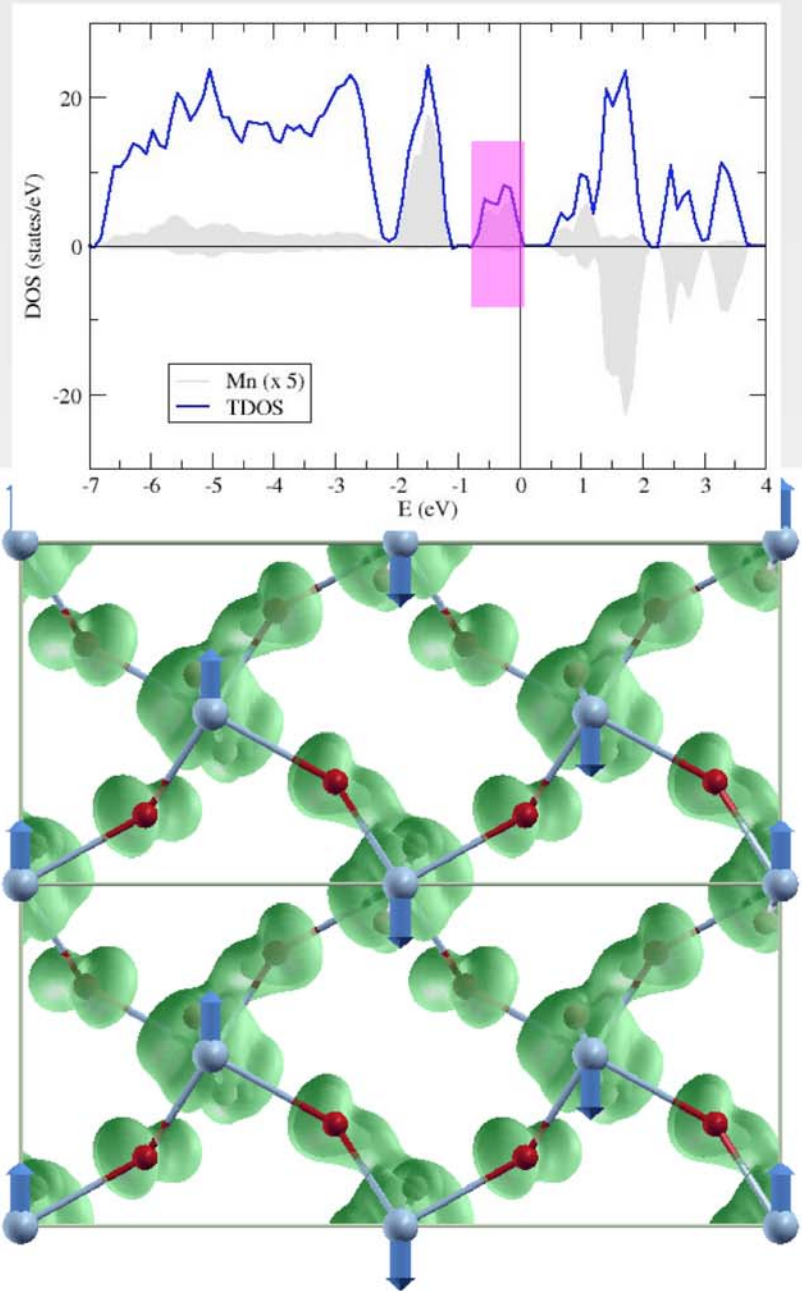
Excellent agreement!



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



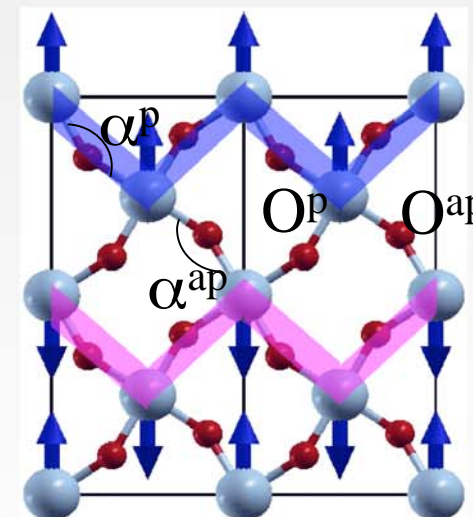
In-plane Mn and O Born effective charges

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

- $(\Delta P)_{\alpha}$ = 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
" \perp "	3.9 e	-3.1 e	-3.1 e
AFM-E	3.8 e	-2.6 e	-3.5 e

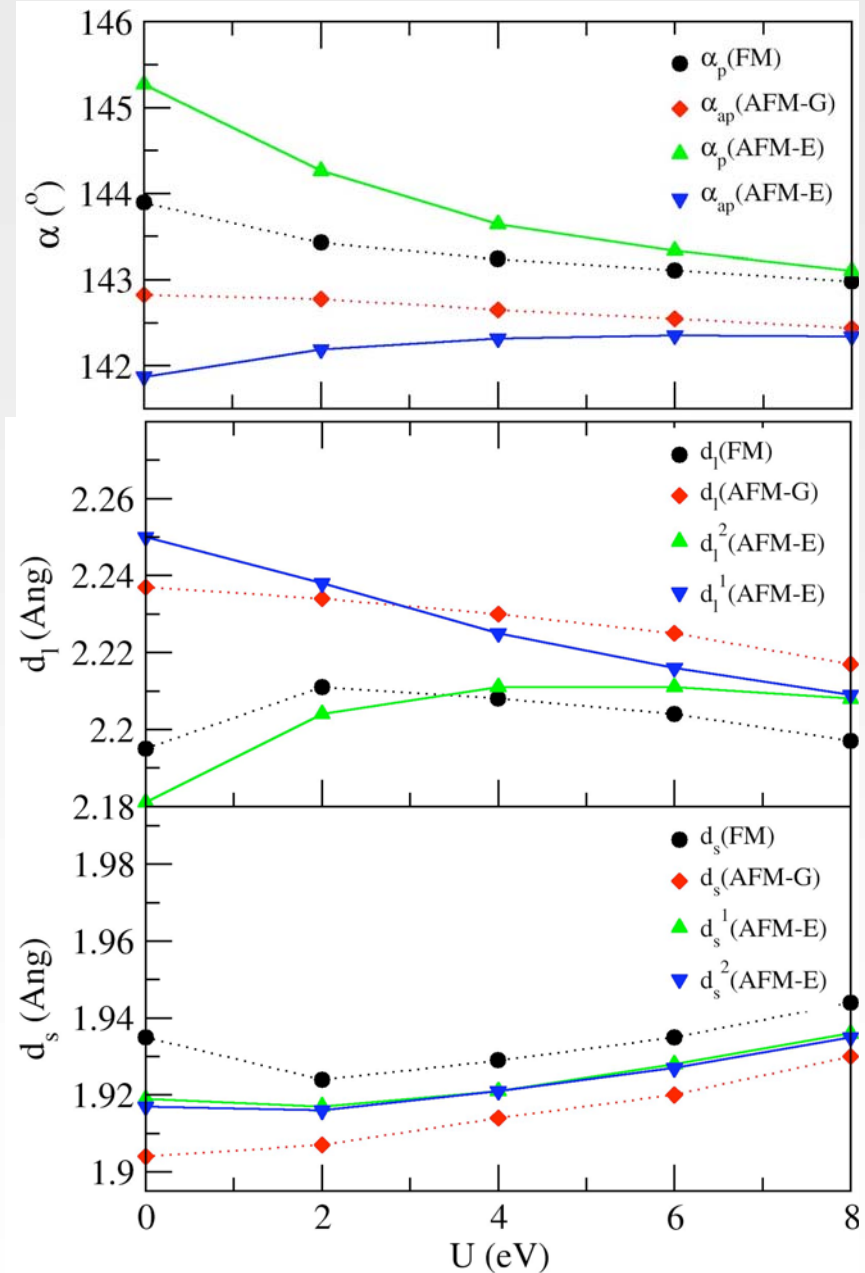


- Z^* values not so "anomalous" : rather "ionic" picture
- Polarization in centrosymmetric structure comes from inequivalency of the oxygens

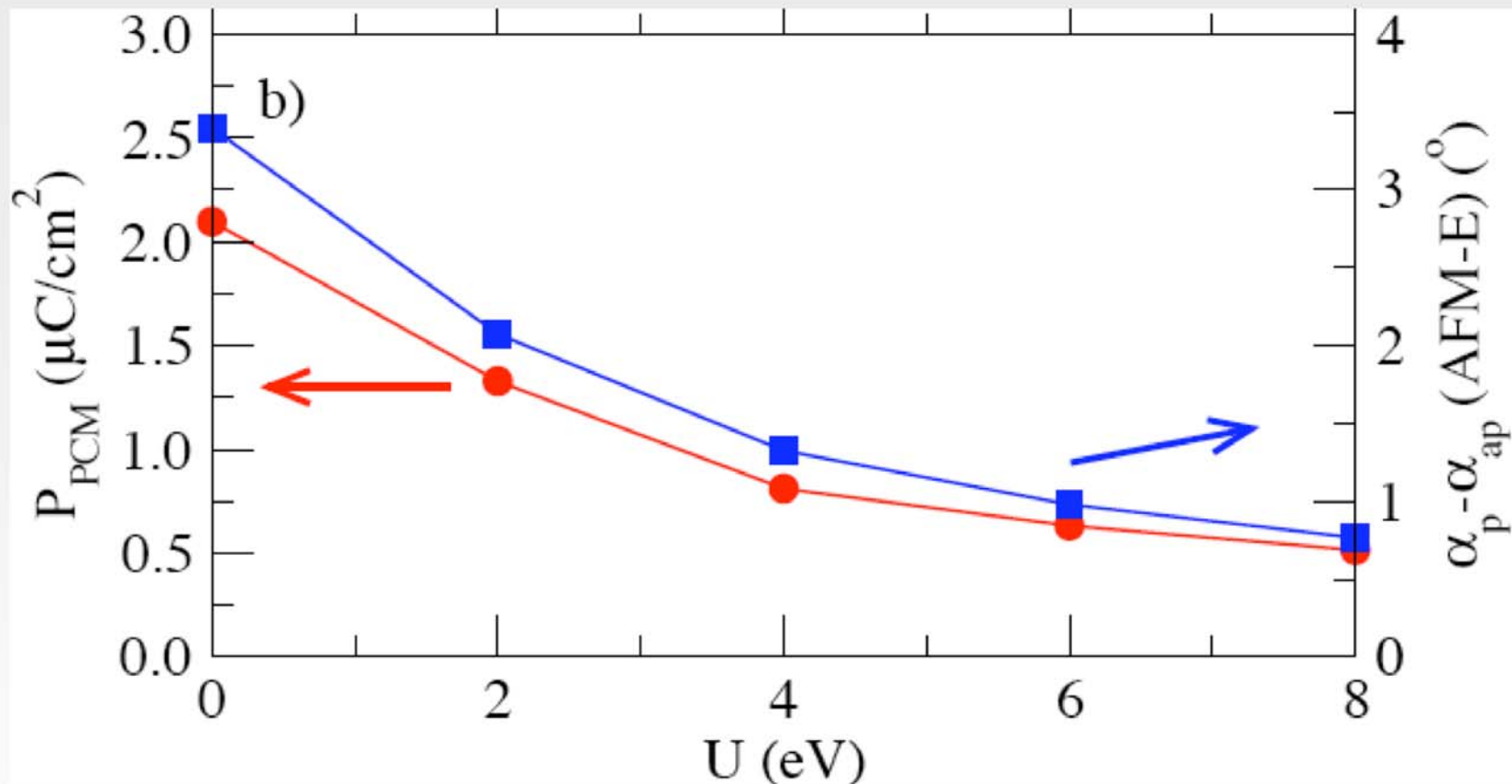


How about correlations? “GGA+U”

- 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?



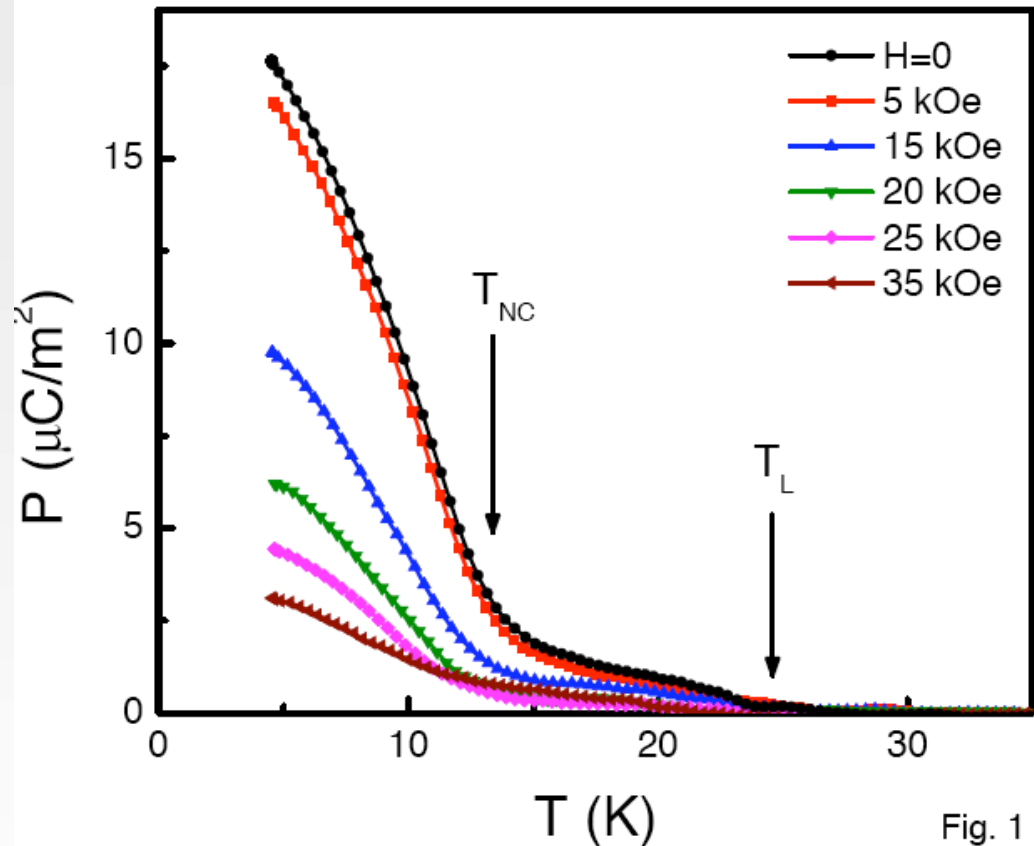
- P follows the displacement trend and decreases with U. It makes sense: U = energy penalty paid for adding an extra-e on Mn \rightarrow If U increases, hopping is less favourable, therefore $\alpha^p - \alpha^{ap}$ (and eventually P) decreases
- However, $P > 0.5 \mu\text{C}/\text{cm}^2$ in the whole U range



Theory vs Experiment*

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

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



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-HoMnO₃: is this a novel multiferroic?
First-principles density-functional calculations

- **Electric polarization from “displacement” mechanism**

Largest P predicted so far for an “improper magnetic ferroelectric” (IMF)

- **Ferroelectric switching path**

Via spin-rotations: Electrical control of AFM domains

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

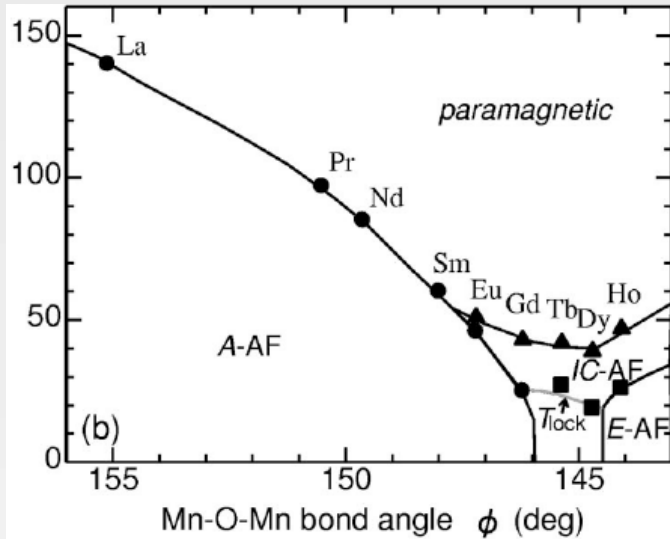
1. **Dual nature of P**: both of “*ionic*” and “*electronic/magnetic*” origin. This solves controversy in model Hamiltonian studies + we believe it is rather *general* in the class of IMF

2. It is possible to achieve “large” P (i.e. few $\mu\text{C}/\text{cm}^2$) with centrosymmetric positions

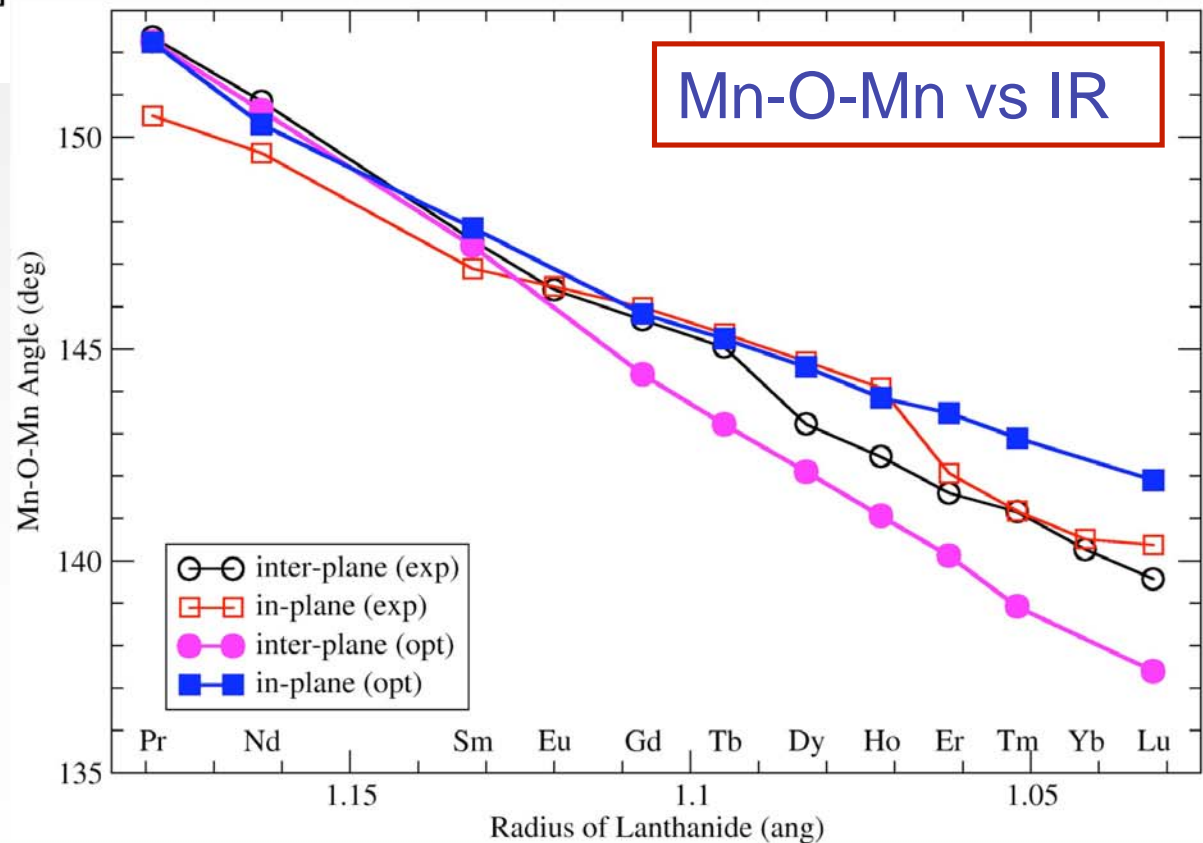
S.Picozzi, K.Yamauchi, B.Sanyal, I.A.Sergienko and E.Dagotto, arXiv/0704.3578



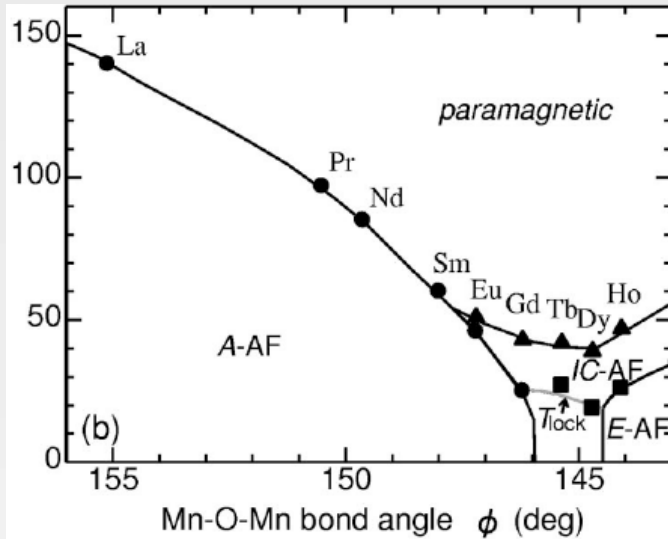
Work in progress: what happens for other rare-earth manganites ?



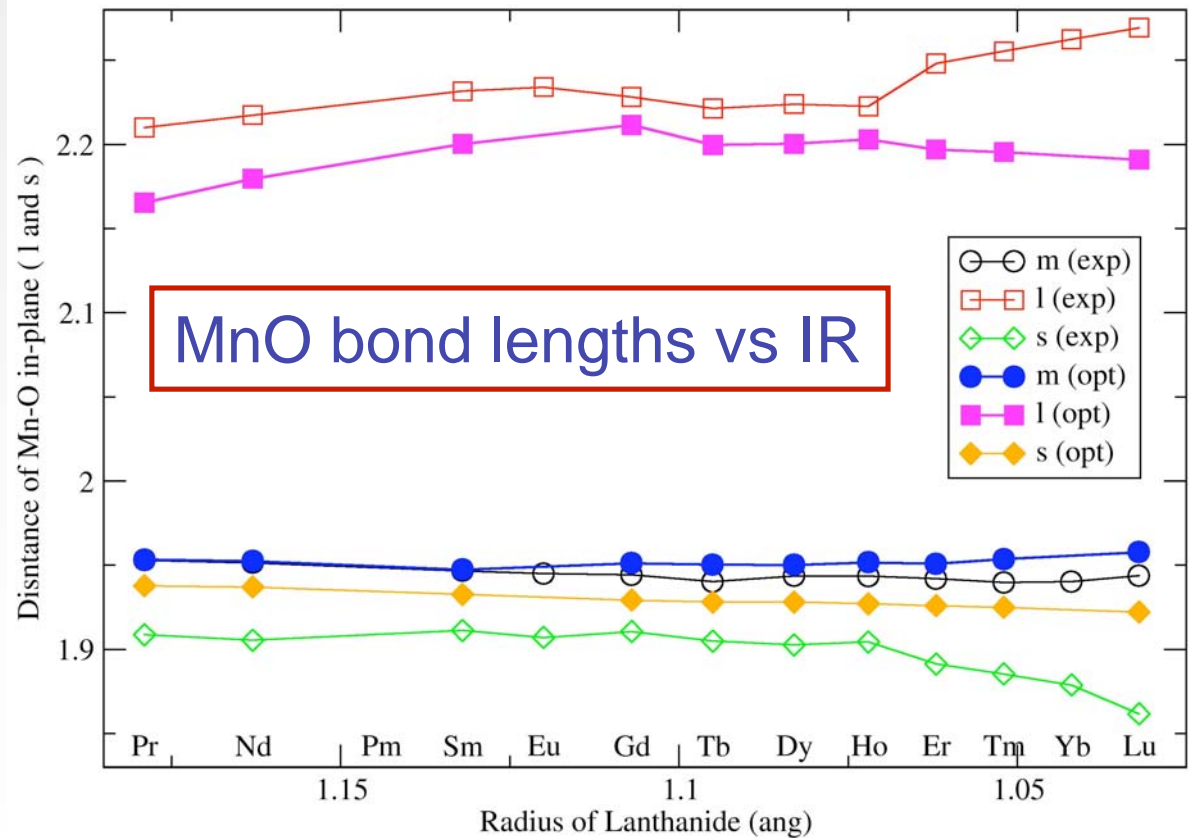
- Both in-plane and out-of-plane Mn-O-Mn angles decrease with the R ionic radius (IR): agreement with expts.



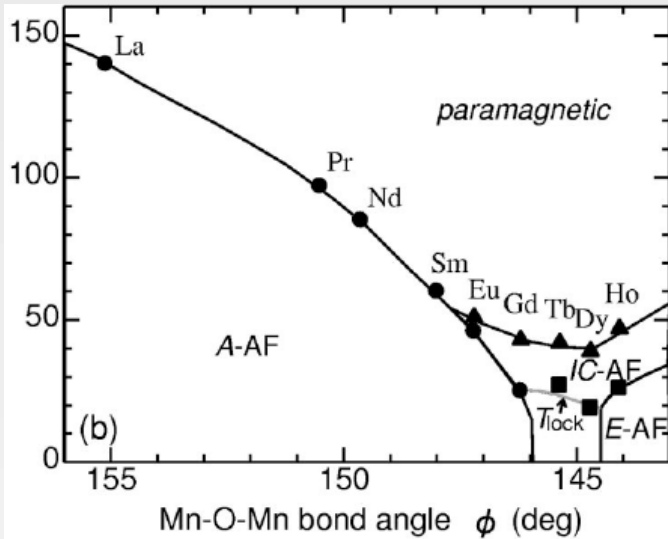
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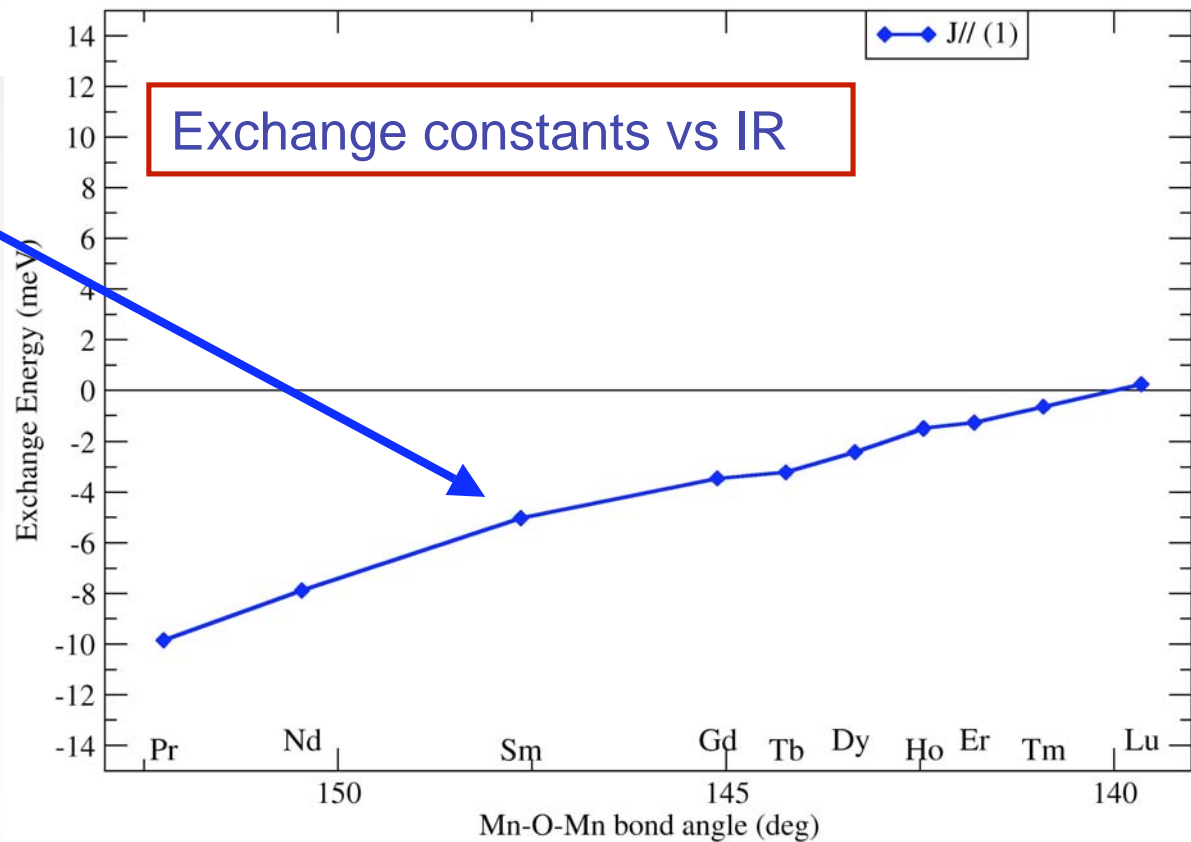
- Both in-plane and out-of-plane Mn-O-Mn angles decrease with the R ionic radius: agreement with expts.
- Broad maximum of l (and s) around Gd-Tb



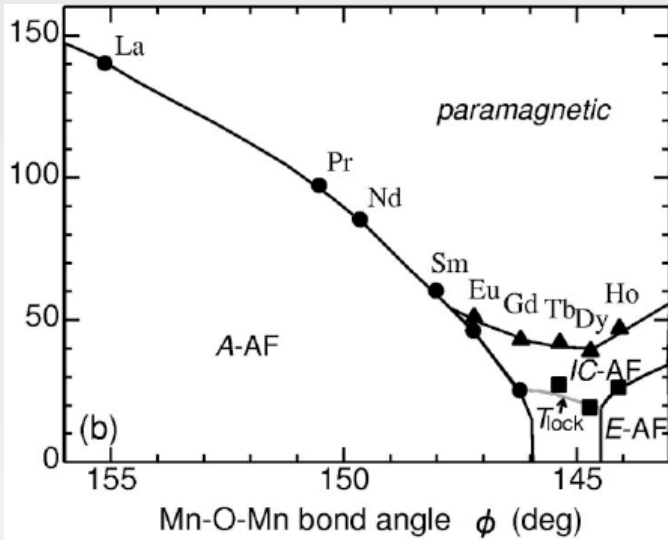
Work in progress: what happens for other rare-earth manganites ?



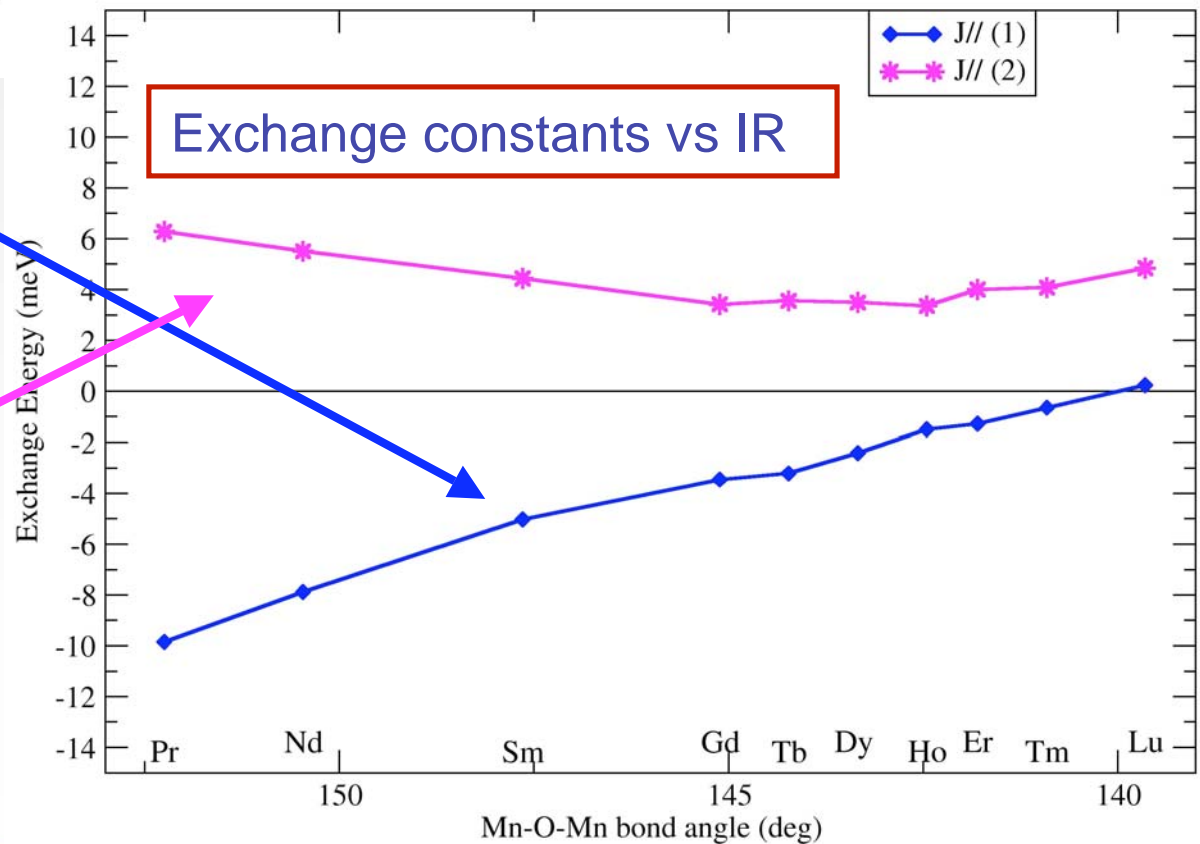
- In-plane 1st nearest neighbour $J_{||}^{(1)}$ decreases with IR: “less FM”



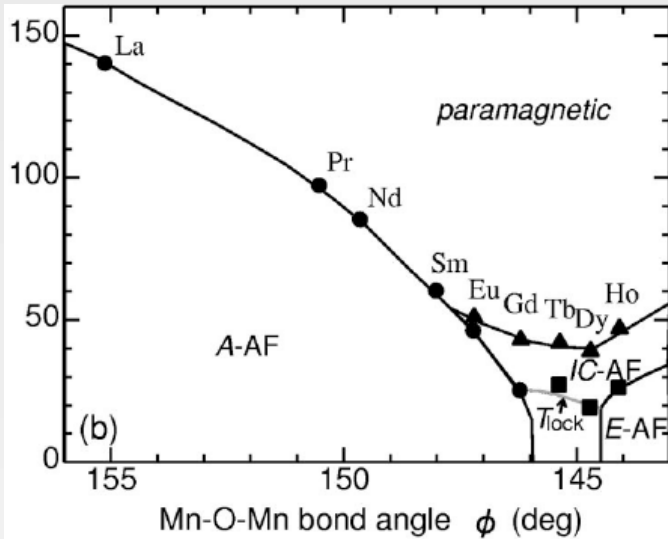
Work in progress: what happens for other rare-earth manganites ?



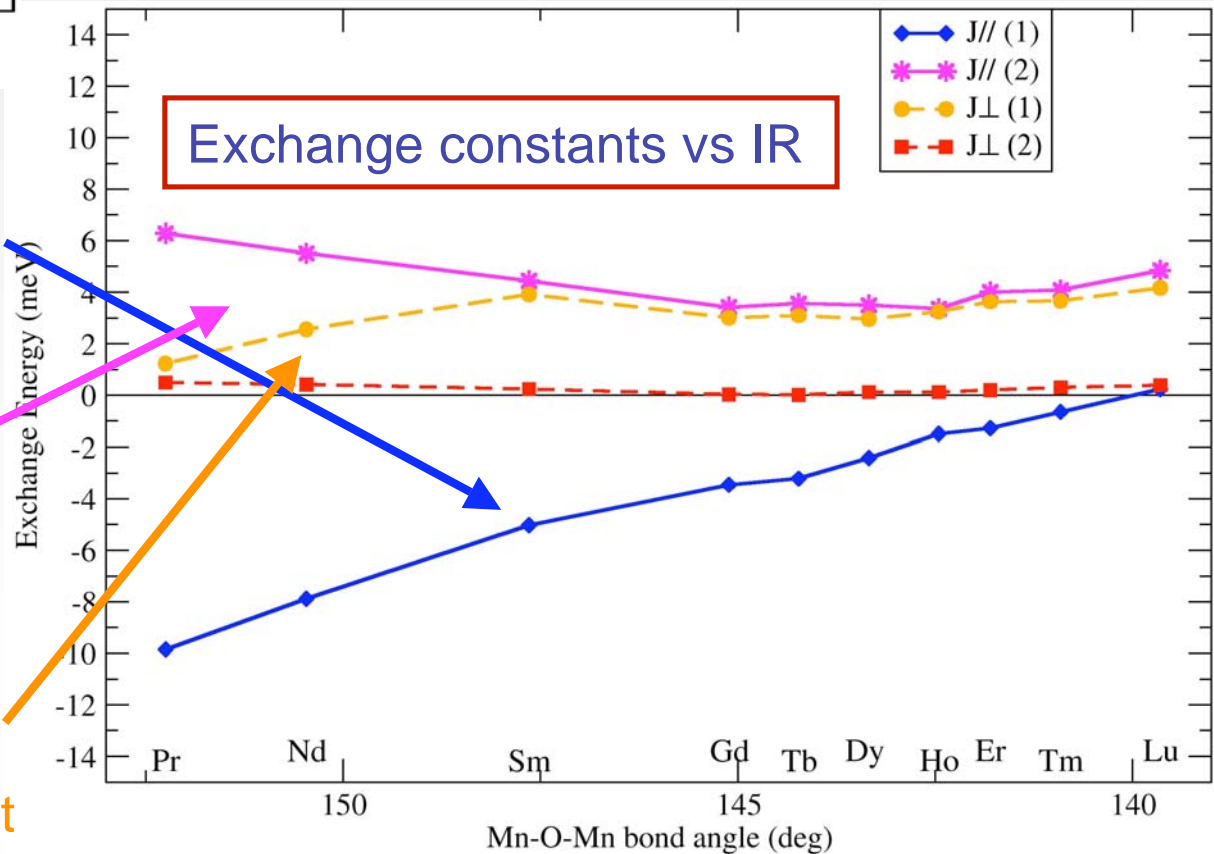
- In-plane 1st nearest neighbour $J_{||}^{(1)}$ decreases with IR: “less FM”
- In-plane 2nd nearest neighbour $J_{||}^{(2)}$ (AFM) becomes important



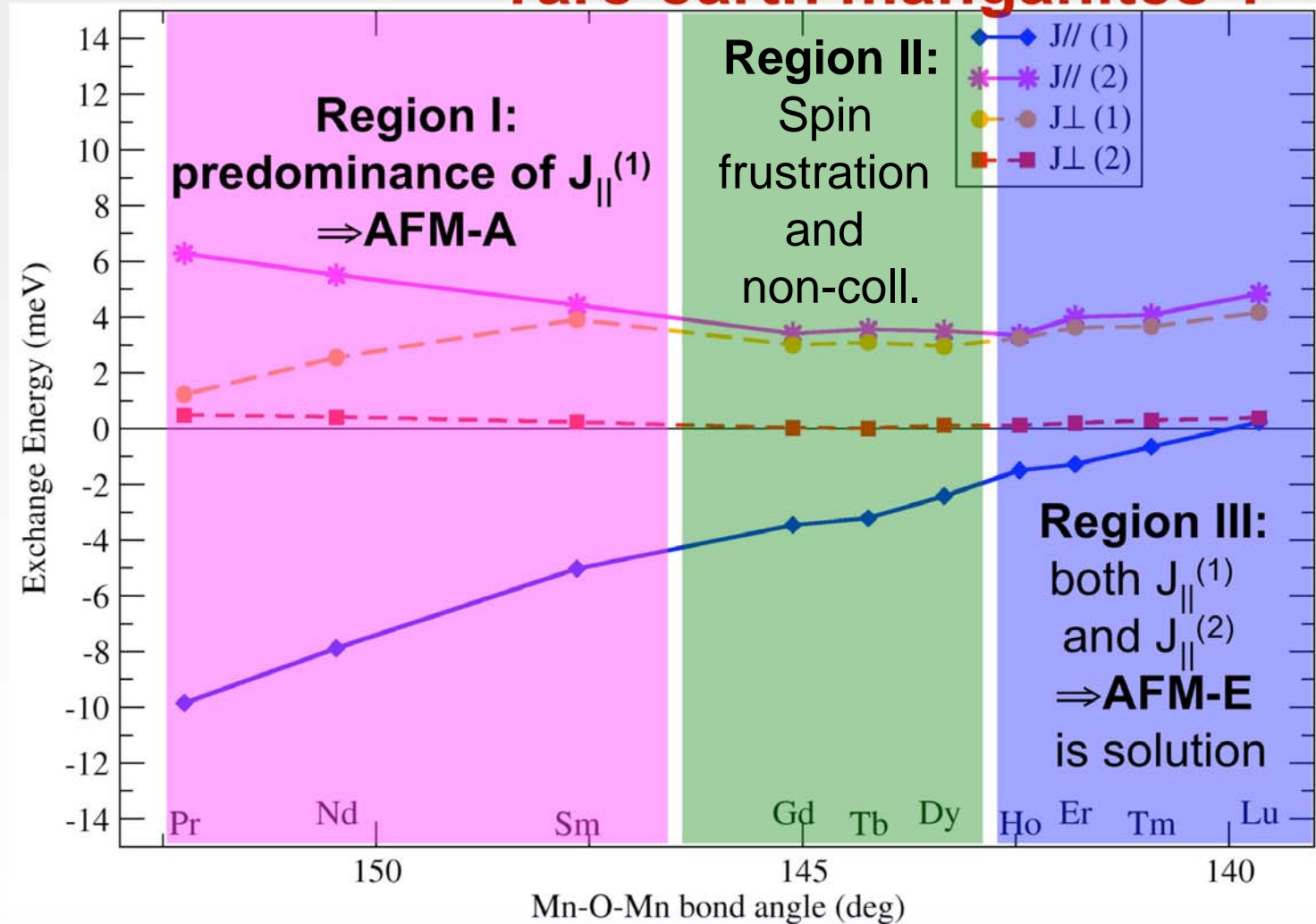
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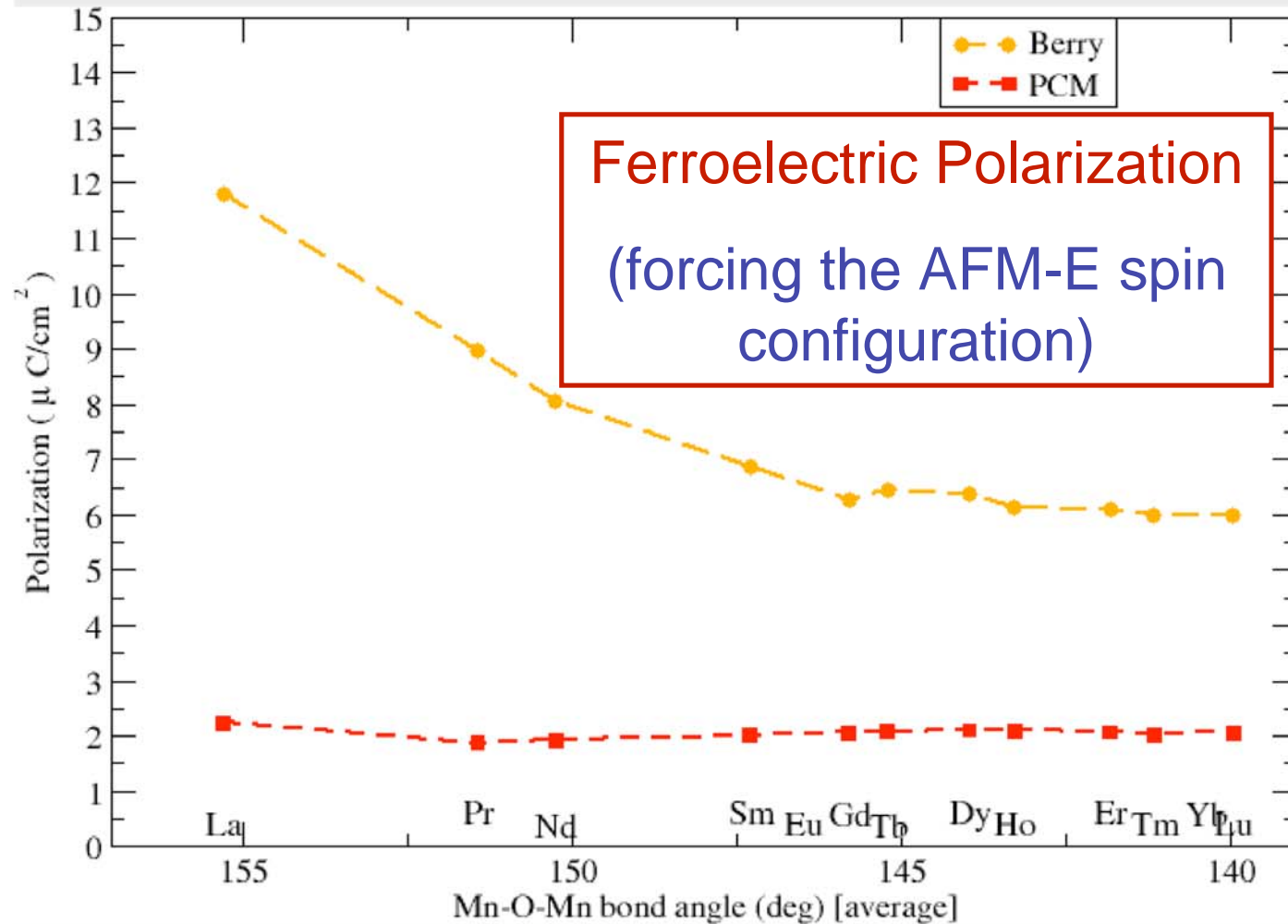
- In-plane 1st nearest neighbour $J_{||}^{(1)}$ decreases with IR: “less FM”
- In-plane 2nd nearest neighbour $J_{||}^{(2)}$ (AFM) becomes important
- Out-of-plane 1st nearest neighbour $J_{\perp}^{(1)}$ (AFM) increases for large IR but then stays almost constant



Work in progress: what happens for other rare-earth manganites ?



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- P goes up to 12 $\mu\text{C}/\text{cm}^2$, but on the “wrong” side (AFM-E is stable for small Mn-O-Mn angles)!
- Very large electronic effects in LaMnO_3 : orbital ordering involved? Hopping terms ?



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



Take-home message:

“Dual nature” of P in real compounds:

- displacements of ions and
- electronic/magnetic moments can both contribute to P

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For ferroelectricity we need to break inversion symmetry.
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1. spin degree of freedom
2. orbital degree of freedom
3. charge degree of freedom



Any good candidates?



Magnetic ordering: Auxiliary “artificial” structures

	YMnO ₃	TbMnO ₃ (7↑,1↓)	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


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

Change
Tb 4f core
polarizat.:
4↑,4↓



	TbMnO ₃ (4↑,4↓)
FM	0
AFM-E	-45
AFM-E*	-30
AFM-A	-21
AFM-C	9
AFM-G	-17

Legenda:

-  = Ground state

- (7↑,1↓): Tb 4f frozen “open core”
(7↑,1↓)

