Computational design of new multifunctional materials

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$$$s:

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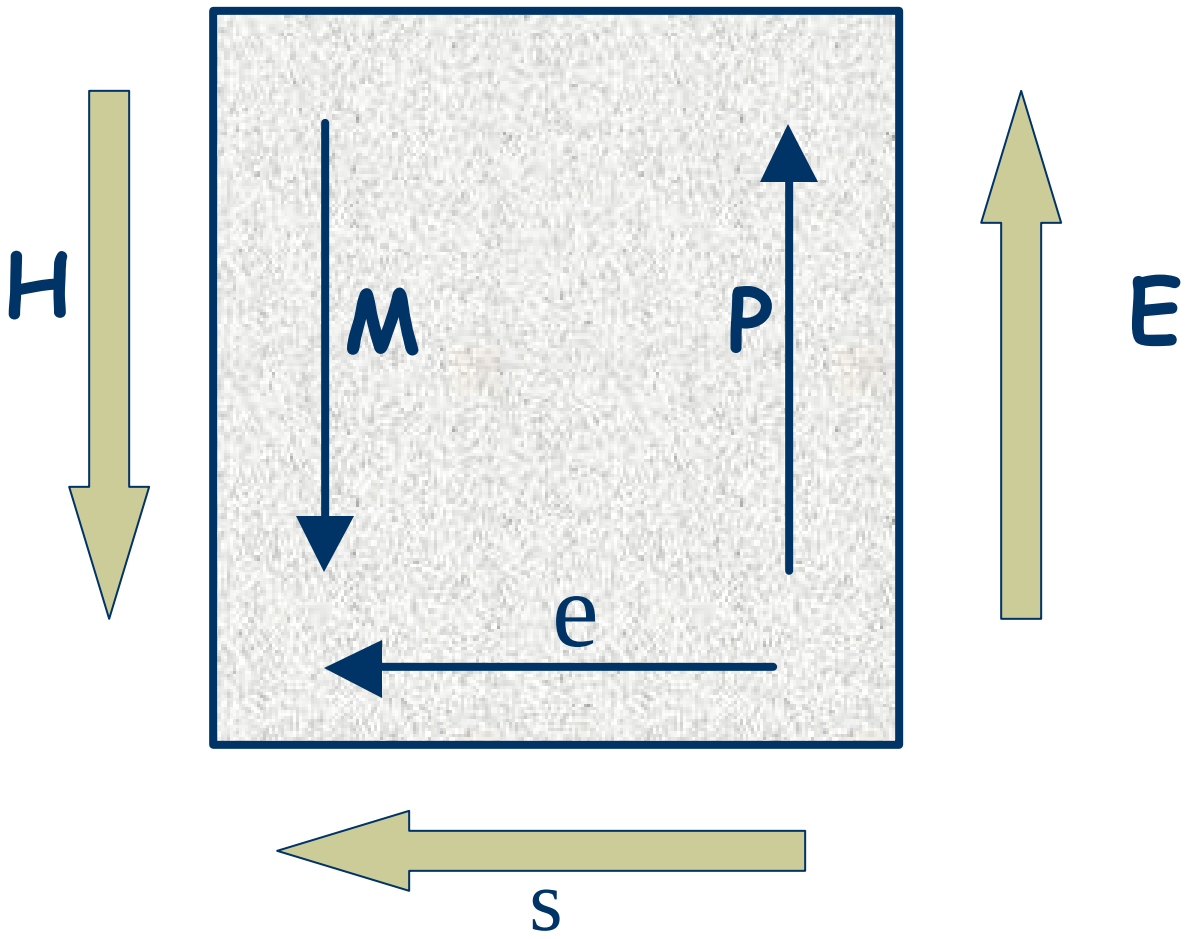
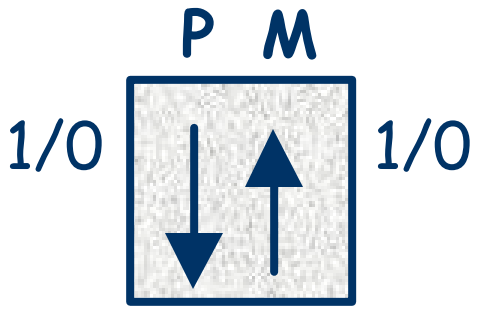
Magnetoelectric multiferroics



Review: N.A. Hill, Ann. Rev. Mat. Res. **32**, 1-37 (2002).

Possible multiferroic applications?

Device applications (long range):



- Multiple state memory elements
- Write to E / read from M
- High μ, high ε materials
- E tunable magnetic properties (and vice versa)

Recent observations:

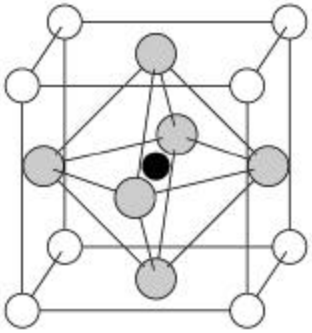
- Giant field-tunable non-linear optical response
- Large magnetocapacitance

Fundamental physics:

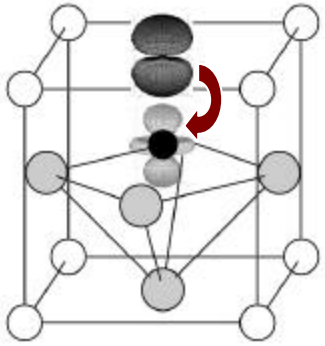
- Nature of coupling between order parameters

Hard to achieve (almost none exist)

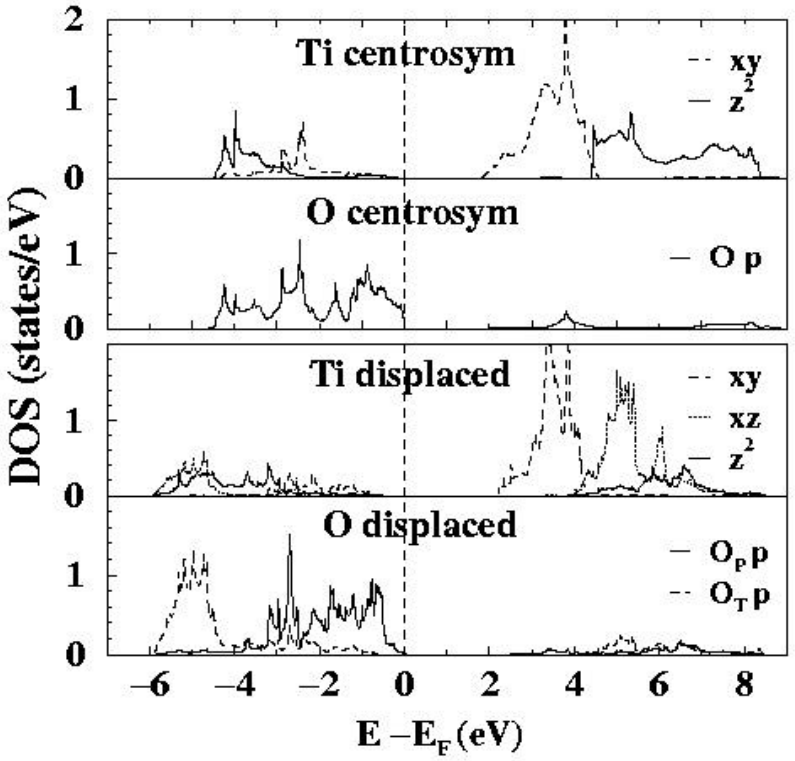
Conventional ferroelectrics have empty cation d orbitals:



paraelectric



ferroelectric



BUT magnetism requires localized electrons!

In perovskite-structure oxides the source of magnetic, localized electrons is usually the transition metal d electrons, e.g. $LaMnO_3$, $SrRuO_3$, etc.

BAD NEWS!

Ferromagnetism requires d electrons

Ferroelectricity requires "d^0-ness"

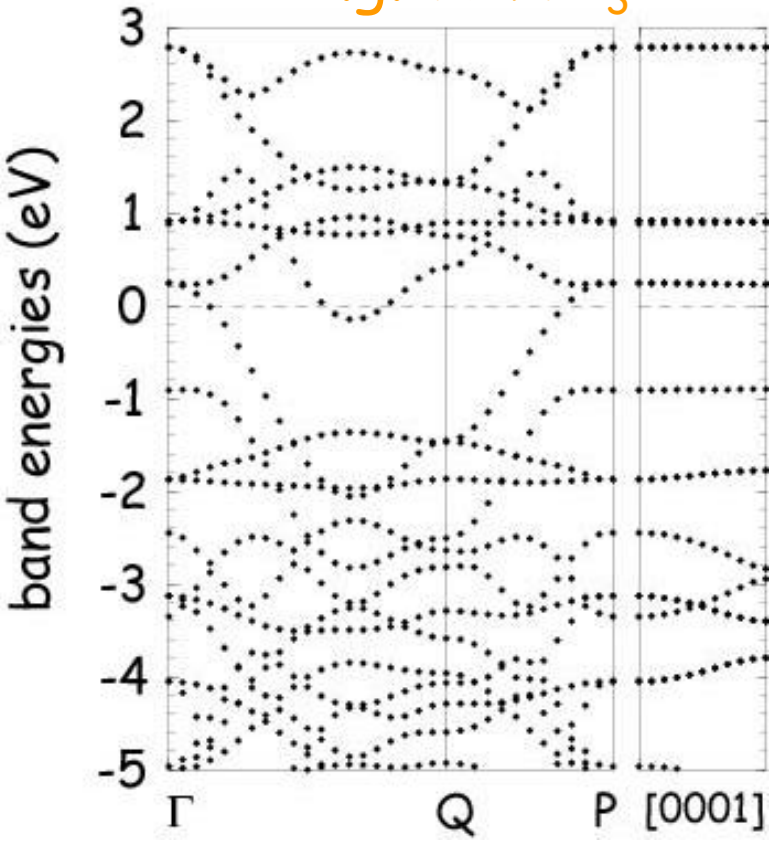
CHEMICALLY INCOMPATIBLE!

Why are there so few magnetic ferroelectrics?
N.A. Hill, J. Phys. Chem. B 104, 6694-6709 (2000)

… and hard to calculate

LSDA? Usually OK for ferroelectrics, but not for MAGNETIC ferroelectrics! Often obtain metallic band structures, prohibiting the calculation of ferroelectric polarization.

e.g. $YMnO_3$



Beyond-LDA methods, LDA+U or Self-Interaction-Corrected (SIC), are needed…

Self-Interaction

The self-interaction is the interaction of an electron's charge with the Coulomb and exchange-correlation potential generated by the same electron.

Consequences:

Underestimated:

- binding energies
- on-site Coulomb energies (Hubbard U)
- exchange splittings of d and f states

Overestimated:

- anion p – cation d hybridizations
- corresponding band widths (W)

Suppression of U and overestimation of W is a problem for materials with partially filled d states where, in real life, U >>W

Our choice: pseudo-SIC method – subtract off the exchange and correlation self-interaction within a pseudopotential formalism

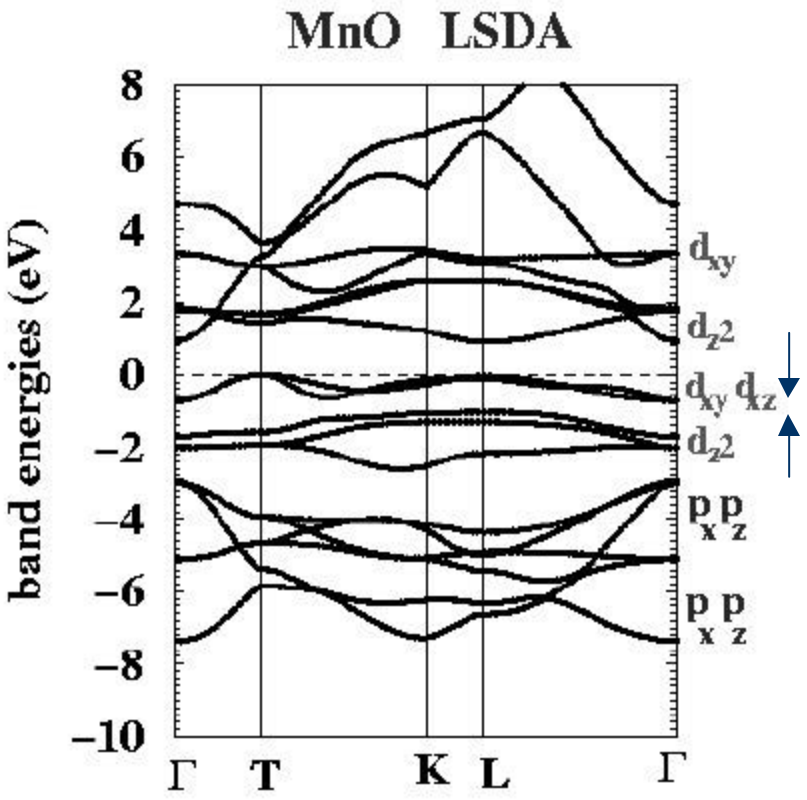
A. Filippetti and N.A. Spaldin, Self-interaction corrected pseudopotential scheme for magnetic and strongly correlated systems, Phys. Rev. B **67**, 125109 (2003).

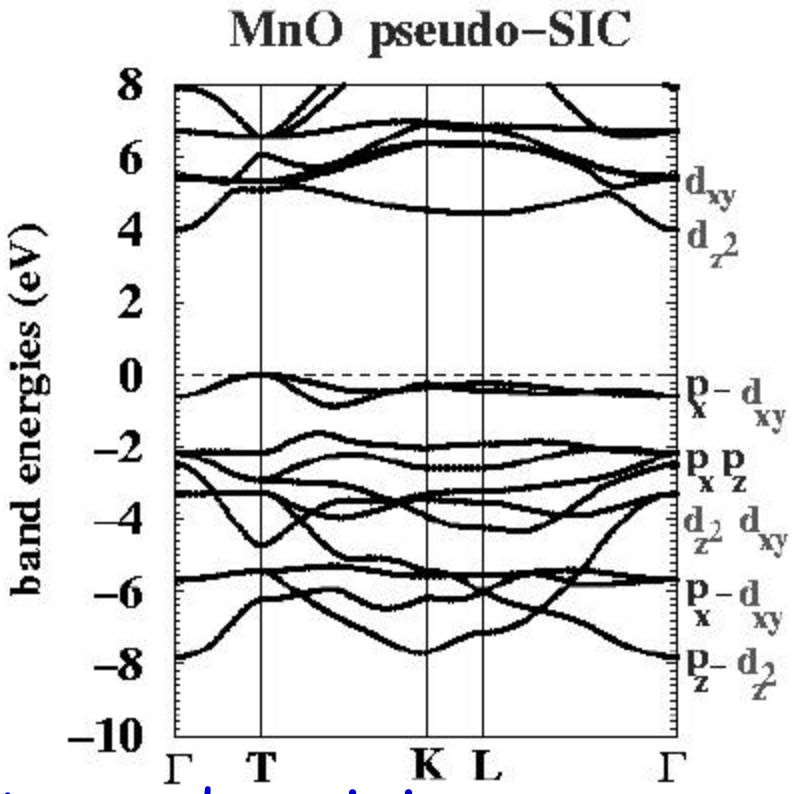
Builds on:

- Perdew and Zunger, PRB **23**, 5048 (1981). Extensive discussion and successful application to atoms and molecules.

- Svane et al., 1994 – present. Application of fully self-consistent SIC to solids. (impressive but expensive! LMTO implementation).

- Vogel et al., 1996-98. SIC pseudopotentials used in regular LDA calculation. Successful and cheap.





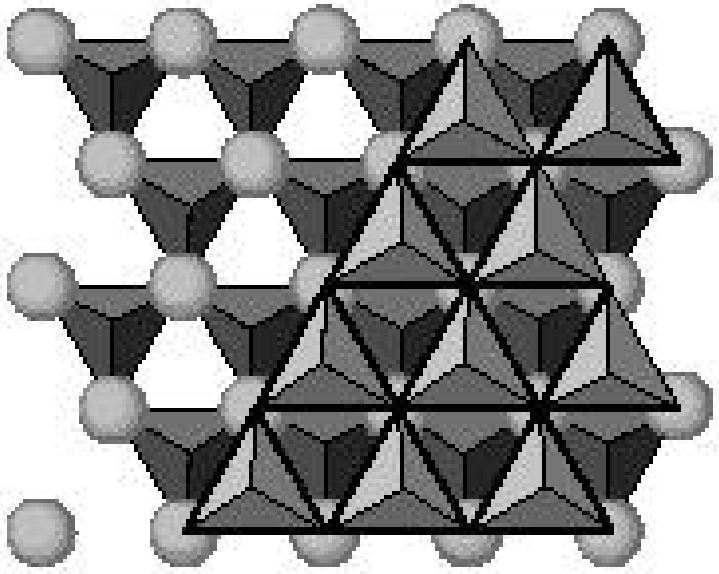
- gap too small and wrong character (Mott-Hubbard)
- incorrect d-p splitting
- magnetic moment too small

✓strong d-p mixing
✓no d-p splitting
✓large gap
✓intermediate charge-transfer/ Mott Hubbard regime
✓correct magnetic moment

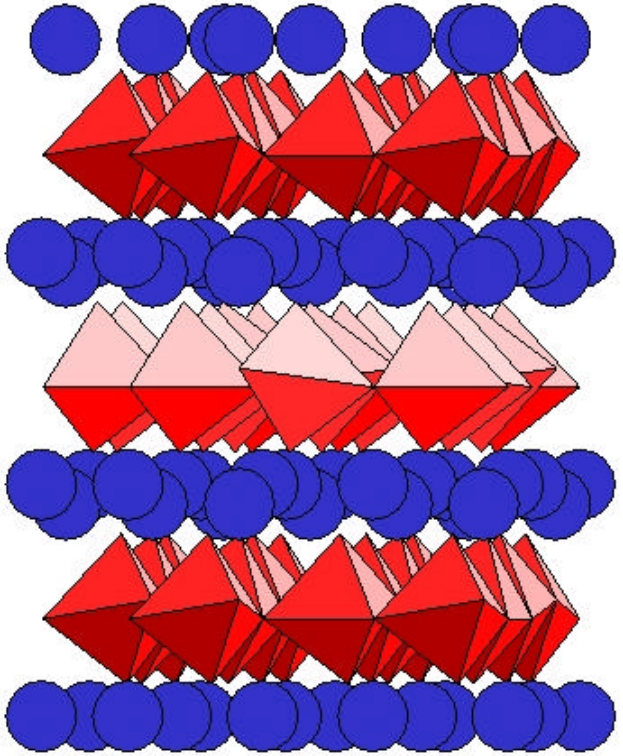
NOTE: pseudo-SIC results are very similar to LDA+U!

An anomalous ferroelectric: $YMnO_3$

View down c, above T_c



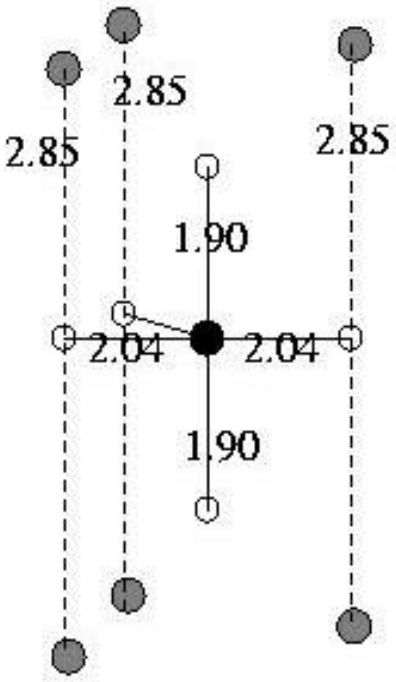
Side view, below T_c



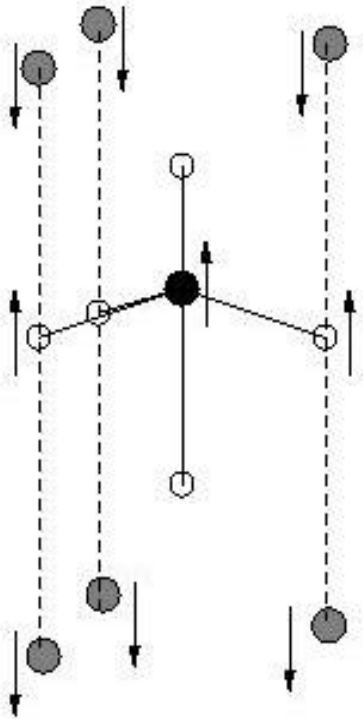
What is the origin of the ferrolectricity?

Explore possible instabilities computationally:

centrosymmetric



unfavorable



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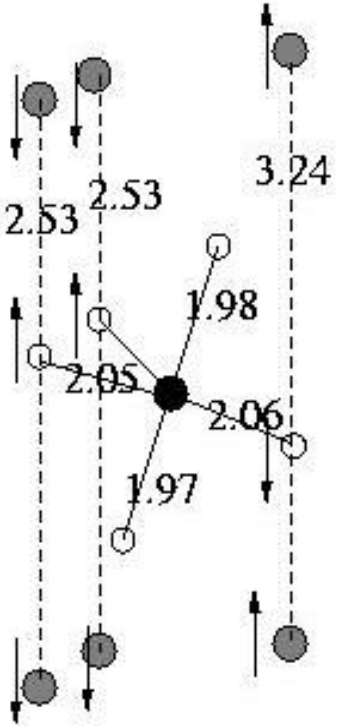
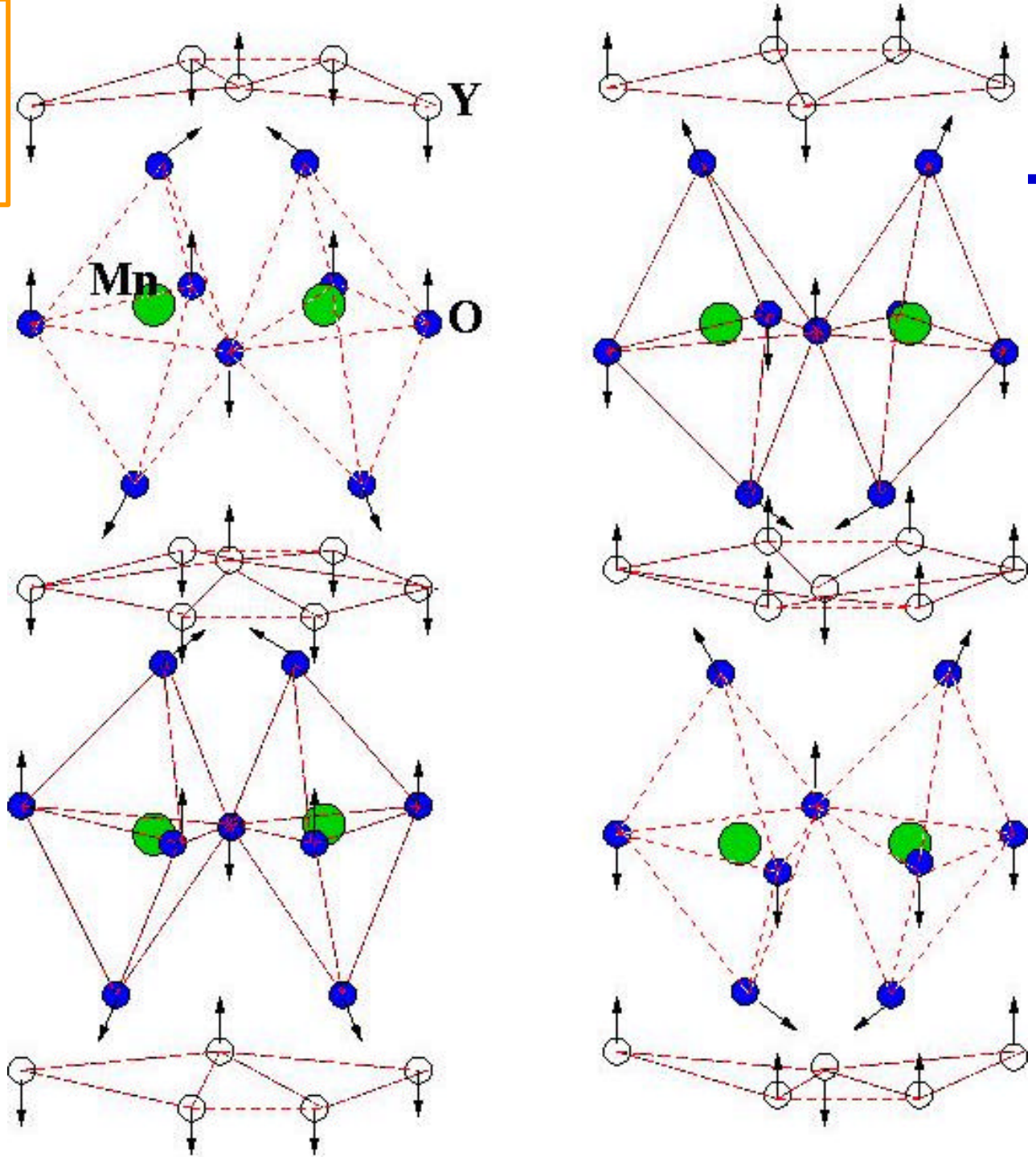
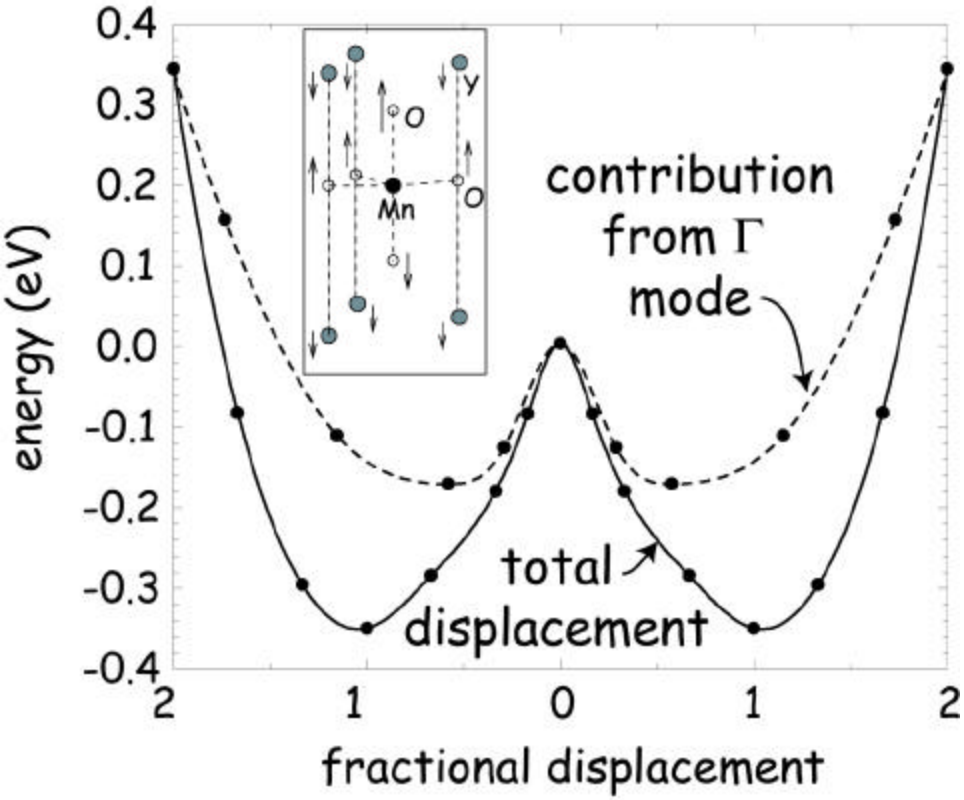


Y
Mn
O

Two stable states:



Geometrically-driven ferroelectricity



1) Buckling of layered MnO5 polyhedra (P63/mmc to P63cm)
2) Relative Y-O motion along c axis (no further symmetry lowering)
3) Driven by electrostatic and size effects
4) PERMITS COEXISTENCE OF FERROELECTRICITY AND MAGNETISM!
5) Two phase transitions since confirmed experimentally

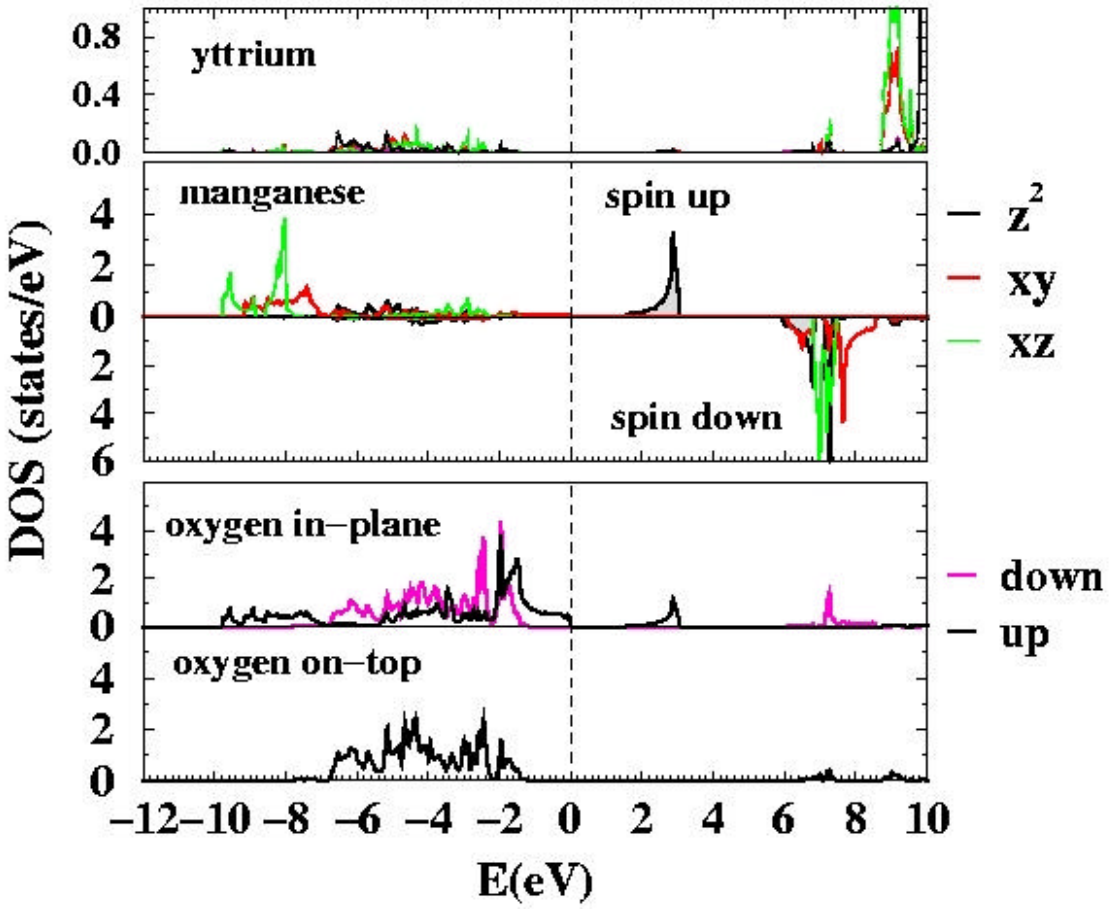
The origin of ferroelectricity in magnetoelectric $YMnO_3$, B.B. van Aken, T.T.M. Palstra, A. Filippetti and N.A. Spaldin, Nature Materials **3**, 164 (2004).

Usual indicators of instability do not hold:

Non-anomalous BECs:

Y	+3.6
Mn	+3.3
O_T	-2.3
O_P	-2.2

DOSs – no re-hybridization

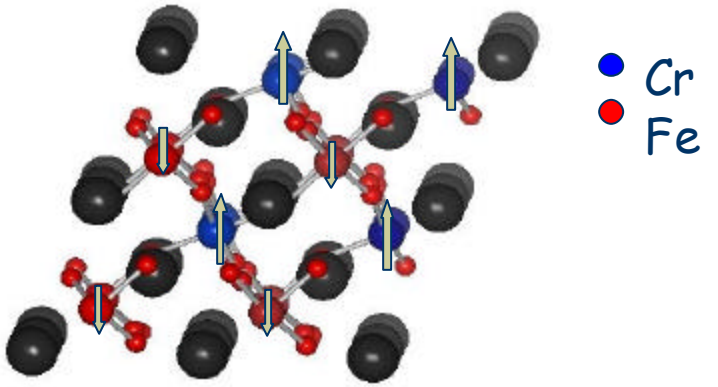


Ongoing work: Better choices for robust magnetic ferroelectrics:

Bi-based ferrimagnets (strongly insulating)

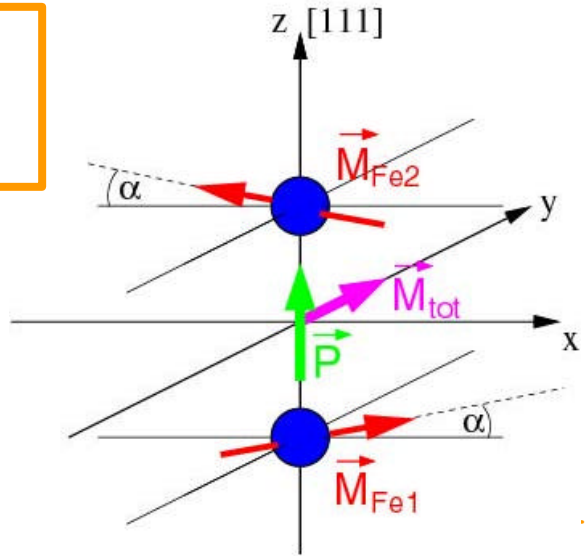
We predict for (111) layered Bi_2FeCrO_6

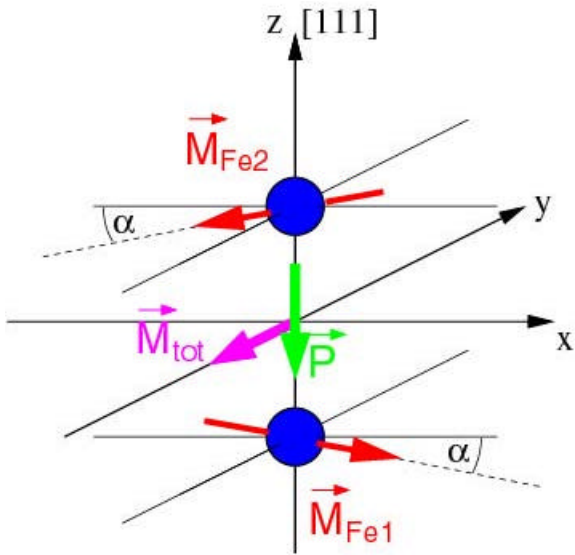
- Magnetic moment = 2 μB/unitcell
- Spontaneous polarization = 70 μC/cm^2



Weak ferromagnets – coupled M and P!

e.g. $BiFeO_3$

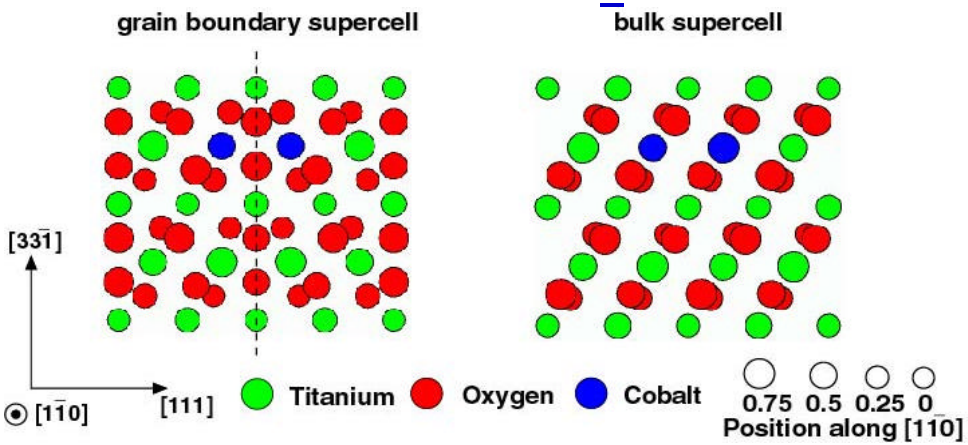




More ongoing Work

Grain boundary effects in $(Co,Ti)O_2$:

We identified a likely grain boundary in anatase TiO_2: $\Sigma 5\ (113)[1\bar{1}0]$



Now we're calculating the influence on magnetic properties.....

Piezoelectric magnetic semiconductors, e.g. (Zn,Mn)O:

✓MnO in wurtzite structure is strongly piezoelectric BUT

XZn,TM)O needs carriers (preferably holes!) for ferromagnetism

→ Possible device architecture

(Zn,Co,Cu)O
ZnO
(Zn,Co,Cu)O
ZnO

Pb-free piezoelectrics, $Bi(Al,Ga)O_3$:

$PbTiO_3$ ← **PZT** → $PbZrO_3$

tetragonal ferroelectric

rhombohedral antiferrodistortive

↓ substitute with ↓

$BiAlO_3$ ← **BGA** → $BiGaO_3$