Computational design of new multifunctional materials

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Collaborators:

Alessio Filippetti, Chuck Schelle, Ram Seshadri, Umesh Waghmare, Richard LeSar, Karin Rabe, Warren Pickett, Claude Ederer, Pio Baettig, Antonio dos Santos, Tony Cheetham,

ABINIT workshop, Paris 2004

$$$s:

NSF DMR, MRSEC and IGERT, DOE, ONR, ACS PRF.

Plan for designing for multifunctionality

- Understand origin of each function separately (DFT)
- Design a trial compound with required properties (intuition/experience)
- Check that the trial compound indeed behaves as required (DFT)
- Persuade an experimentalist to make and characterize it!

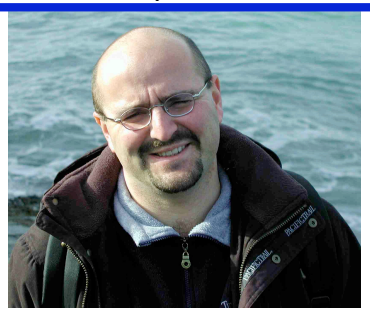
Computational design of multifunctional materials,
N.A. Spaldin and W.E. Pickett, JSSC, 176, 615 (2003)

Interesting multifunctional materials:

- Magnetoelectric multiferroics
  - Magnetic insulators (beyond LDA)
  - Visualization of lone pairs
  - Polarization, dielectric response
  - Spin-orbit coupling and non-collinearity
- Diluted magnetic semiconductors
  - Defects and impurities (large supercells)
  - Band gaps important (beyond LDA)
  - Grain boundary effects (large supercells)

My group and their codes….

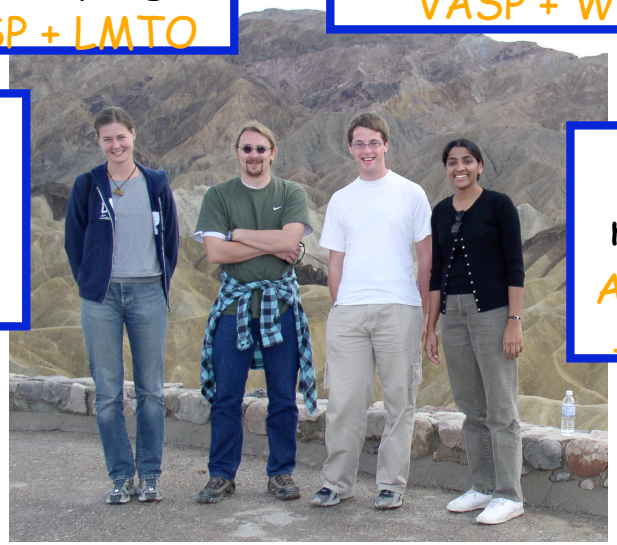
Stefano Sanvito (TCD) DMSs; SIESTA



Claude Ederer, ME coupling; VASP + LMTO

Pio Battig, FM FEs; VASP + Wien

Rebecca Janisch, grain boundaries; ABINIT

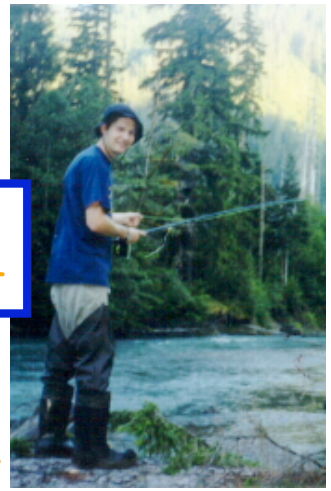


Priya Gopal, magnetic PEs; ABINIT, VASP + Pseudo-SIC

Alessio Filippetti (U. Cagliari), FMFEs; PSEUDO-SIC

Kim Goto, FM metal/ Nanotubes; SIESTA

Chuck Schelle, Pb-free Piezoelectrics; ABINIT



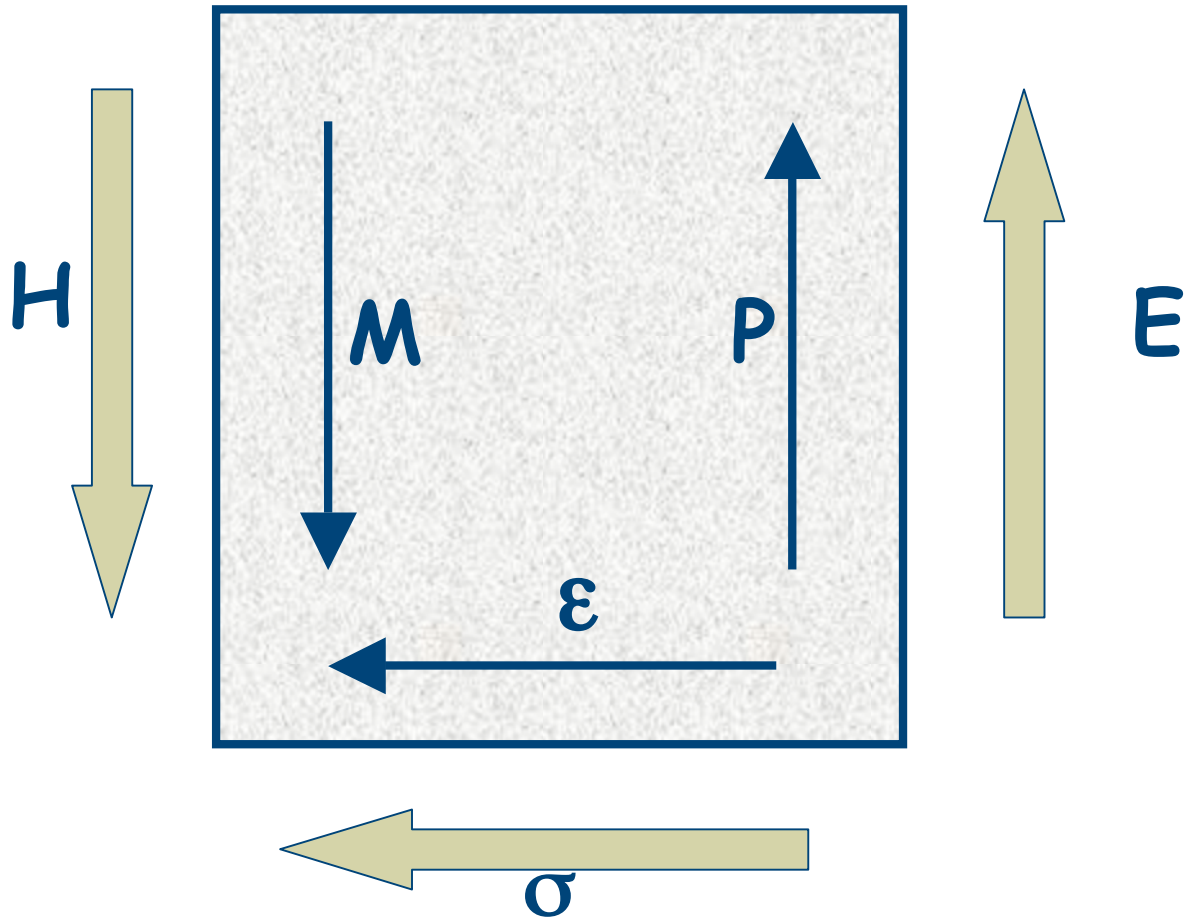
ABINIT workshop,

Is there a better way?

Can we use just ONE code for a specific material design project?

Let's look at an example.....

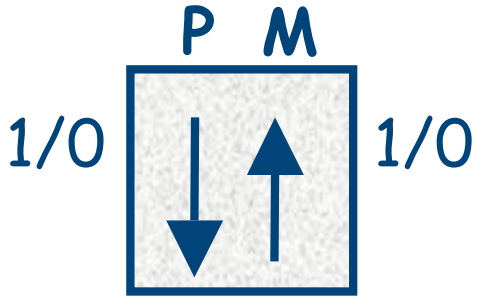
Multiferroic magnetoelectrics



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:

Problem:

Almost none exist.

1st question: *Why are there so few magnetic ferroelectrics?*

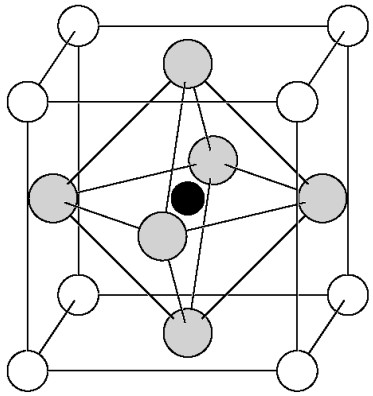
N.A. Hill, J. Phys. Chem. B 104, 6694-6709 (2000)

Requirements for magnetoelectric multiferroicity

-
- Symmetry

1, 2, 2', m, m', 3, 3m', 4, 4m'm', m'm2', m'm'2', 6, 6m'm'

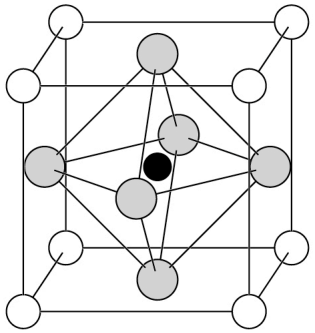
- Electrical Properties
- Chemistry – "d^0-ness"



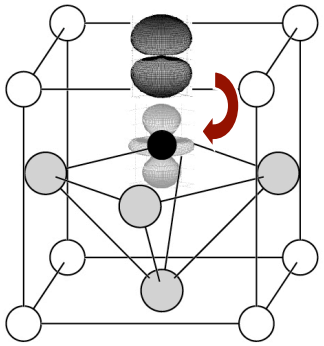
ION	Ti^{4+} d^0	Nb^{5+} d^0	Zr^{4+} d^0	Mn^{3+} d^4	Ti^{3+} d^1	V^{4+} d^1
SIZE (pm)	74.5	78.0	86.0	78.5	81.0	72.0

Conventional mechanism for ferroelectricity:

Ligand field stabilization of *empty* cation d orbitals by oxygen p electrons:

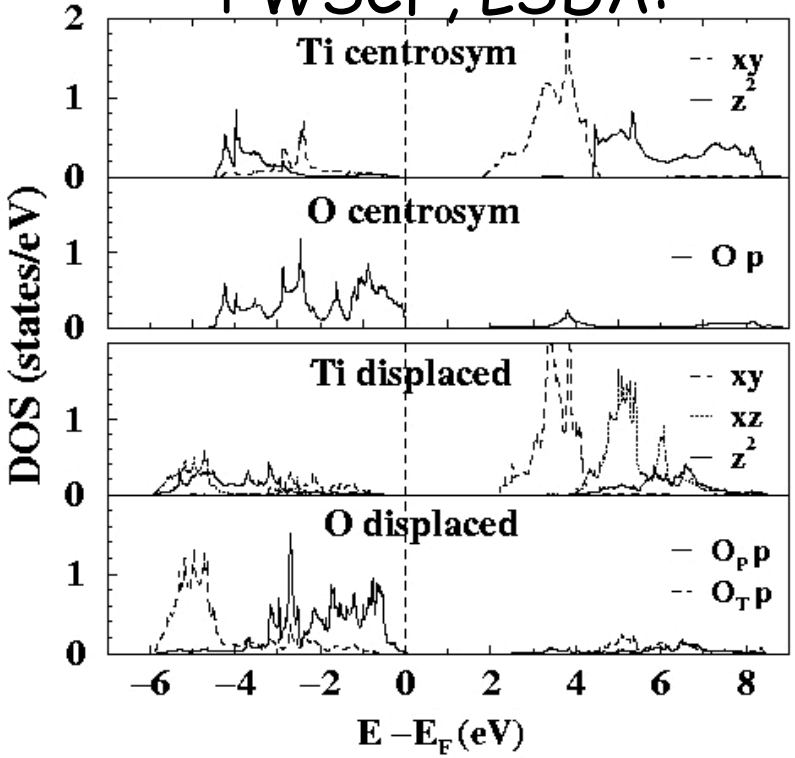


paraelectric



ferroelectric

PWSCF, LSDA:



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!

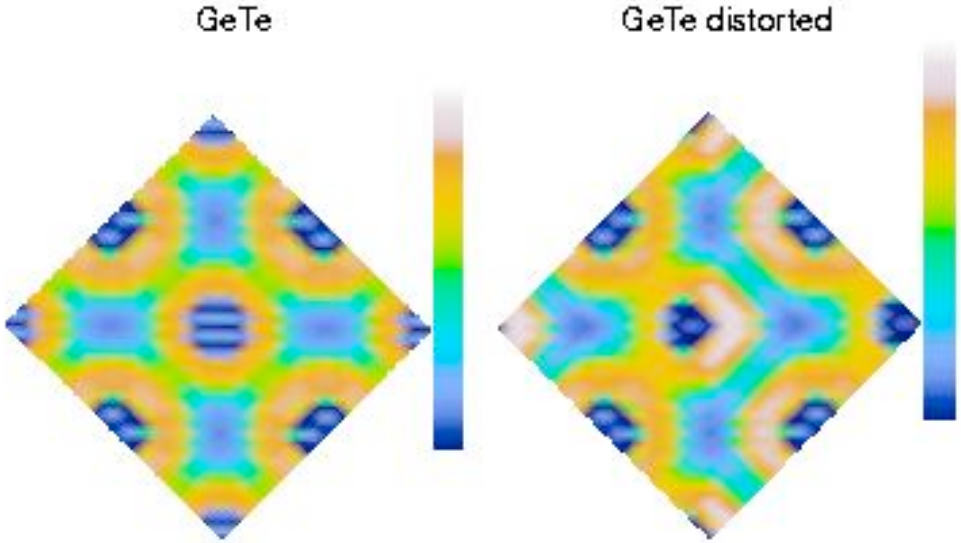
But……

Alternative mechanism for ferroelectricity:

Cation lone pair localization

e.g. IV-VI compounds, $PbTiO_3$, etc.

U.V. Waghmare, N.A. Spaldin, H.C. Kandpal and R. Seshadri, *First principles indicators of metallicity and cation off-centricity in the IV-VI rock-salt chalcogenides of divalent Ge, Sn and Pb*, PRB **67**, 125111 (2003).



(Stuttgart LMTO code)

needs an $(ns)^2$ pair of electrons

Perovskite design:

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- Transition metal cation with *d* electrons for magnetism
- Ferro- (or ferri-) magnetic ordering of the above
- Large cation with $(ns)^2$ electron configuration

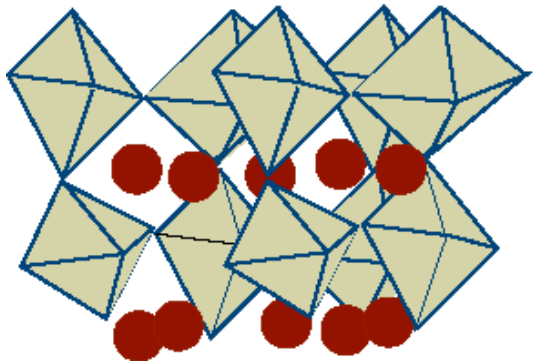
$(6s)^2$: Tl^+, Pb^{2+}, Bi^{3+}
$(5s)^2$: In^+, Sn^{2+}, Sb^{3+}
$(4s)^2$: Ga^+, Ge^{2+}, As^{3+}

Candidate multiferroic: $BiMnO_3$?

What was known:

- Distorted cubic perovskite structure
- Ferromagnetic! (Tc = 100K)

Structure Determination:
Monoclinic, C2
T.Atou et al., J. Sol. State. Chem.
145, 639 (1999).



Use DFT to check:

- Ferroelectric (and why)?
- *Intrinsically* ferromagnetic?

What kind of DFT should we use?

LSDA? Usually OK for ferroelectrics, but not for MAGNETIC ferroelectrics! Tiny gap for the distorted structure; metal for the high symmetry phase.

Beyond-LDA methods, LDA+U or Self-interaction-corrected (SIC), are needed to calculate the polarization

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

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

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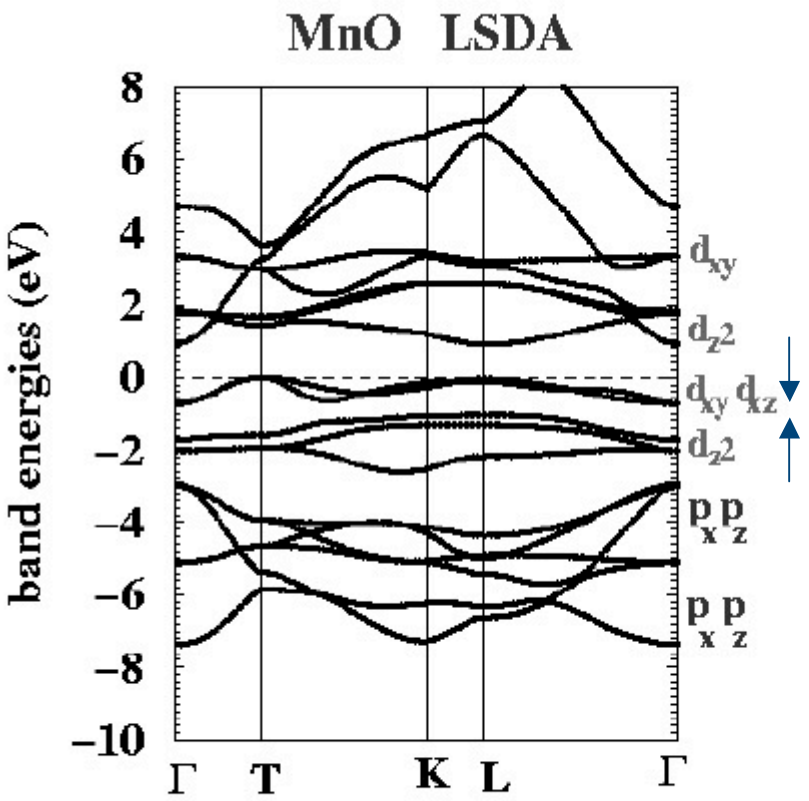
A. Filippetti and N.A. Spaldin, *Self-interaction corrected pseudopotential scheme for magnetic and strongly correlated systems*, Phys. Rev. B **67**, 125109 (2003).

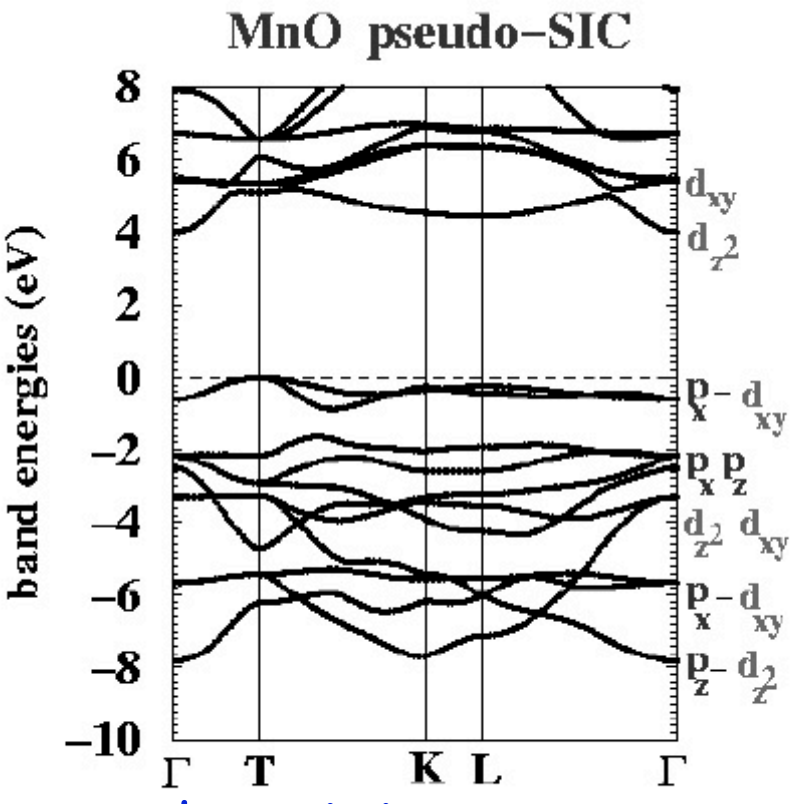
Builds on:

- 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

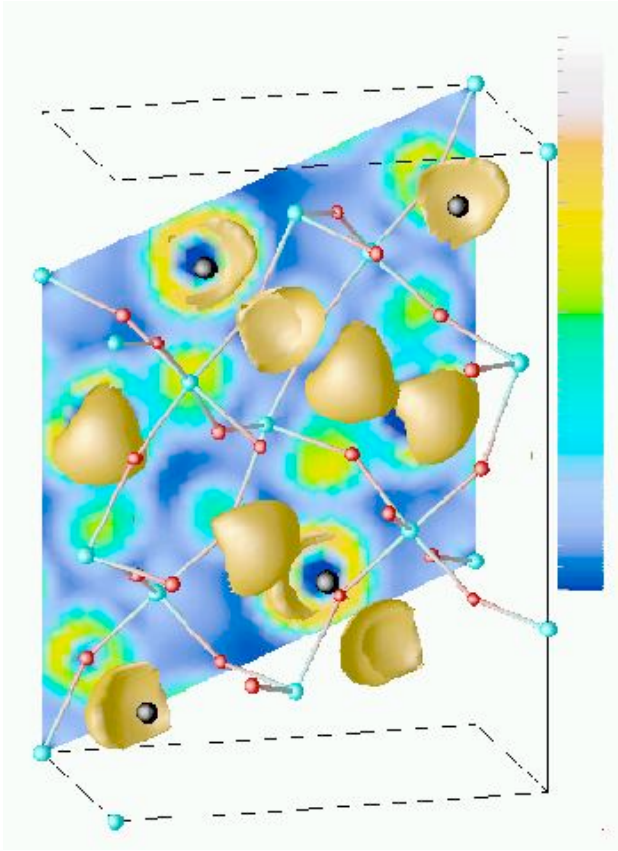
⟩ strong d-p mixing
⟩ no d-p splitting
⟩ large gap
⟩ intermediate charge-transfer/ Mott Hubbard regime
⟩ correct magnetic moment

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

Is $BiMnO_3$ ferroelectric and intrinsically ferromagnetic?

YES!

N.A. Hill and K.M. Rabe, *First-principles investigation of ferromagnetism and ferroelectricity in bismuth manganite*, Phys. Rev. B **59**, 8759 (1999).



DFT Calculations predict:

- Ferromagnetic ground state
- Strong ferroelectric instability in FM $BiMnO_3$ (calculated polarization of ~70$\mu C/cm^2$)
- Ferroelectricity results from – O displacement!

R. Seshadri and N.A. Hill, *Visualizing the role of Bi 6s "lone pairs" in the off-center distortion in ferromagnetic $BiMnO_3$*, Chemistry of Materials **13**, 2892 (2001).

Plan for designing for multifunctionality

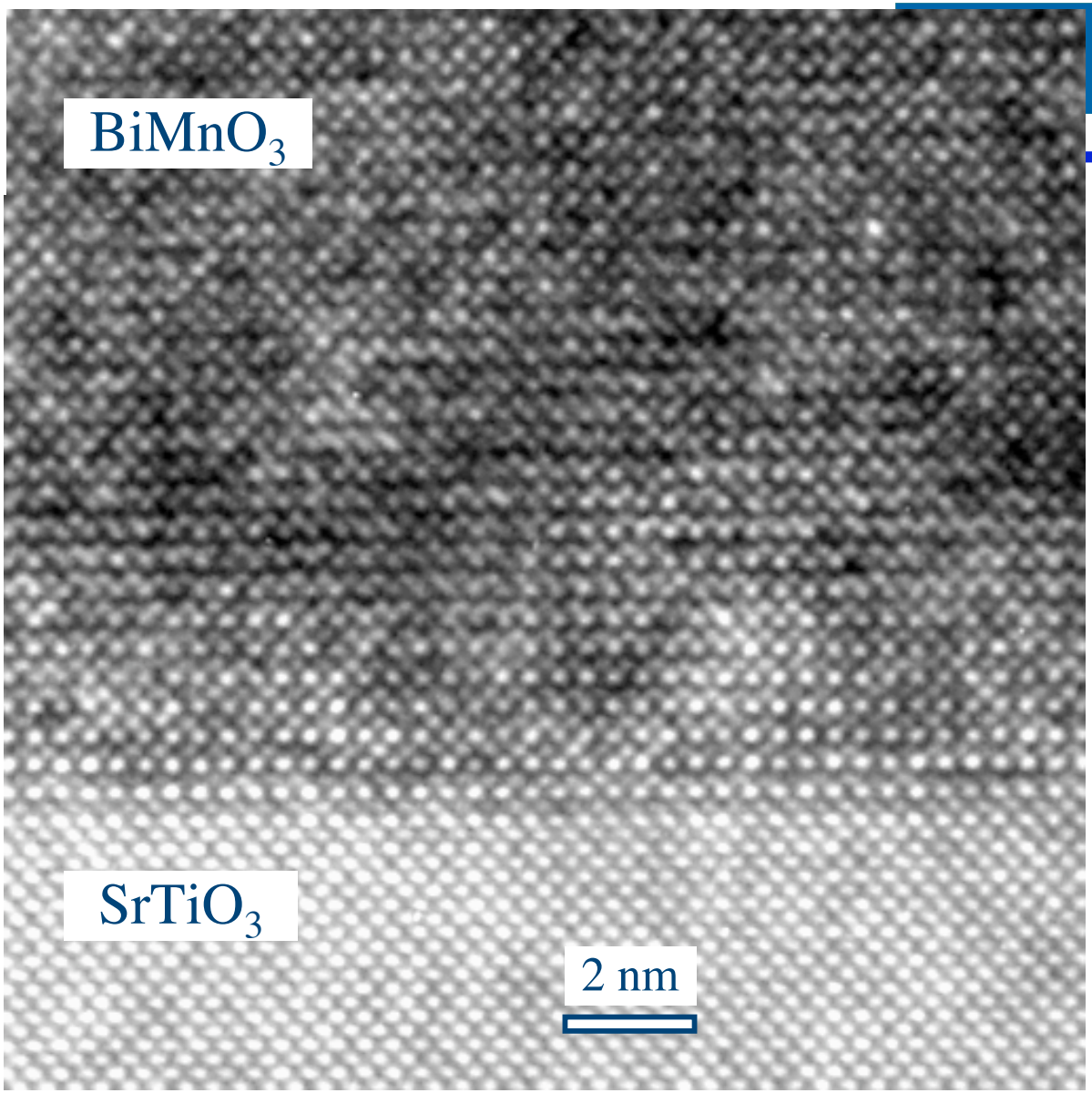
Understand origin of each function separately (DFT)

Design a trial compound with required properties (intuition/experience)

Check that the trial compound indeed behaves as required (DFT)

- Persuade an experimentalist to make and

From Darrell Schlom:

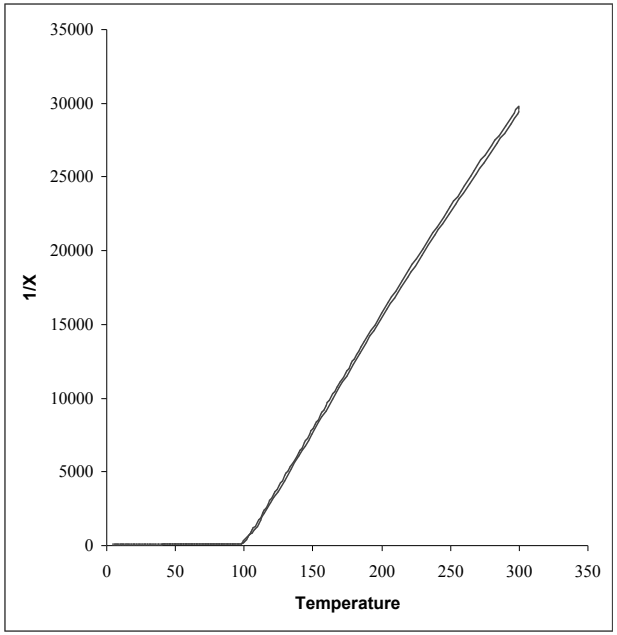


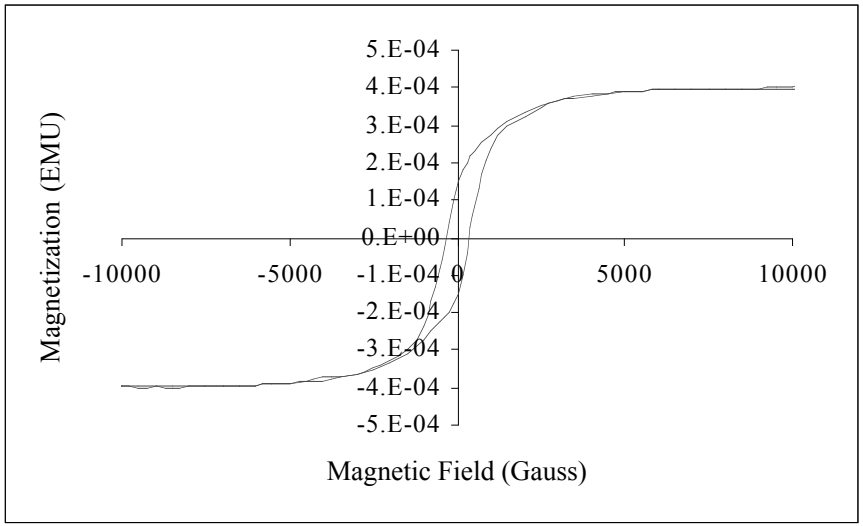
Interface between $SrTiO_3$ and $BiMnO_3$

ABINIT workshop, Paris 2004

Magnetic properties

Magnetic characterization of the bulk $BiMnO_3$ sample: inverse susceptibility vs. temperature, indicating a ferromagnetic material with T_C=105 K.

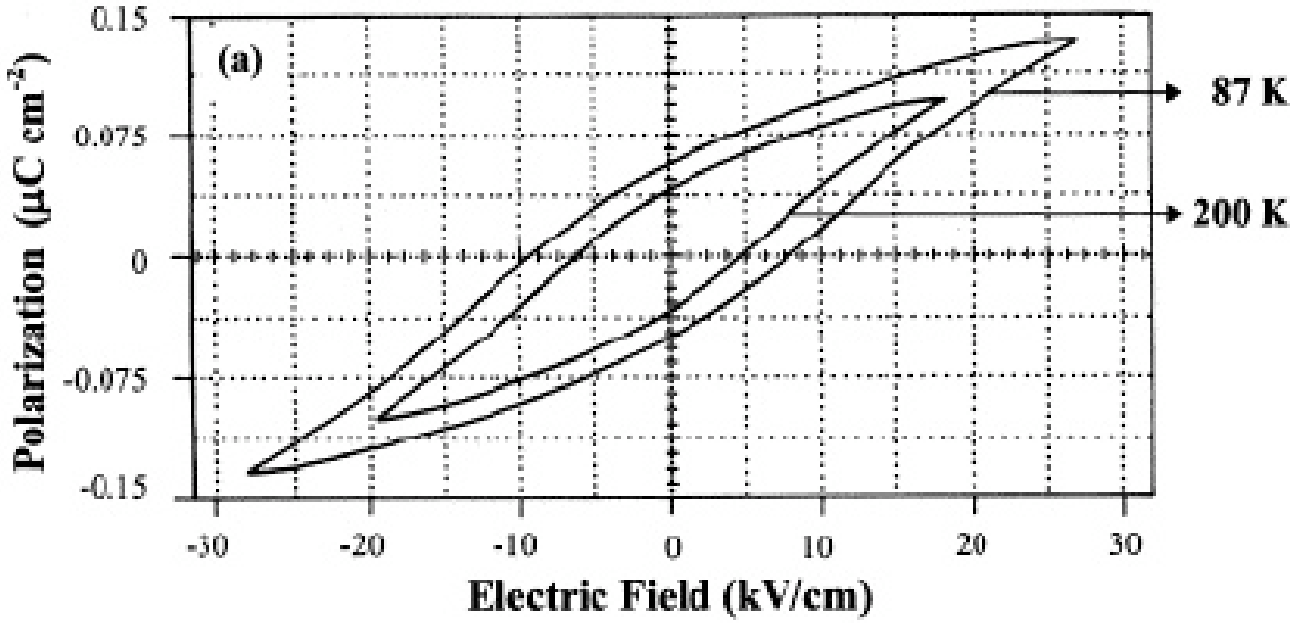




Magnetic hysteresis loop, measured at 10 K, of PLD grown $BiMnO_3$ on $SrTiO_3$.

A.M. Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham and C.N.R. Rao, *Evidence for the likely occurrence of magnetoferroelectricity in $BiMnO_3$*, Sol. Stat. Comm. 122, **49** (2002).

Experimental Data: Ferroelectric hysteresis in $BiMnO_3$



A.M. Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham and C.N.R. Rao, *Evidence for the likely occurrence of magnetoferroelectricity in $BiMnO_3$*, Sol. Stat. Comm. 122, **49** (2002).

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Issues:

Physics:

- Ferromagnetic Curie temperature of 100K (and why is it ferromagnetic anyway)
- Leaky! (Measured P lower than predicted; polarization lost just above room temperature)
- Need to understand origin of ferromagnetism, and to choose materials that are easier to grow

Computational:

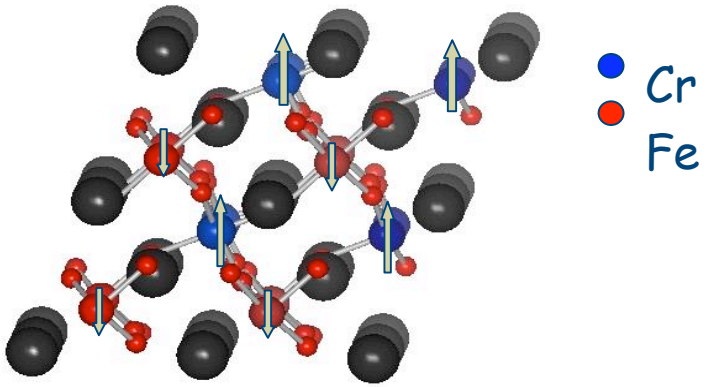
- Relationship between magnetization direction

Better choices for robust magnetic ferroelectrics:

Ferrimagnets (more strongly insulating)

We predict (VASP, LDA+U) for (111) layered Bi_2FeCrO_6

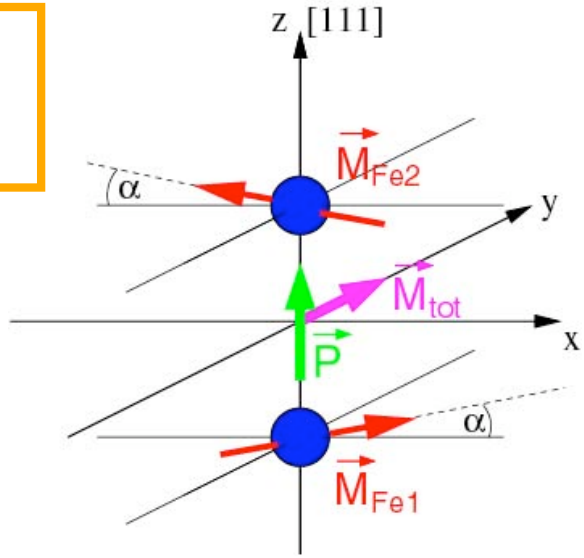
- Magnetic moment = 2 μB/unitcell
- Spontaneous polarization = 70 μC/cm²

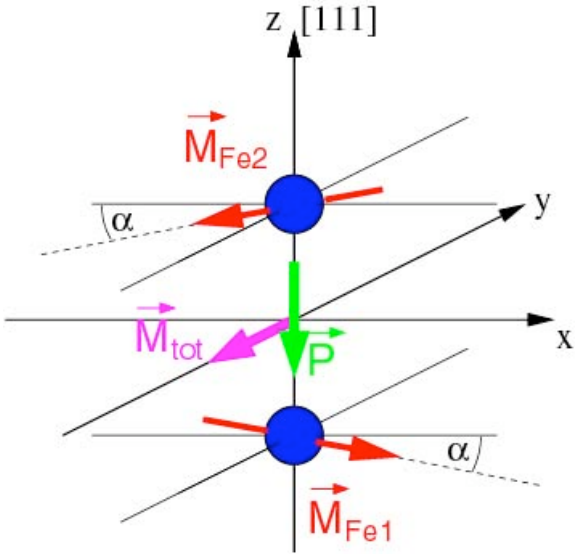


Weak ferromagnets – coupled M and P!

e.g. $BiFeO_3$

(LDA+U, SO coupling; VASP/LMTO)





Conclusions/Discussion points

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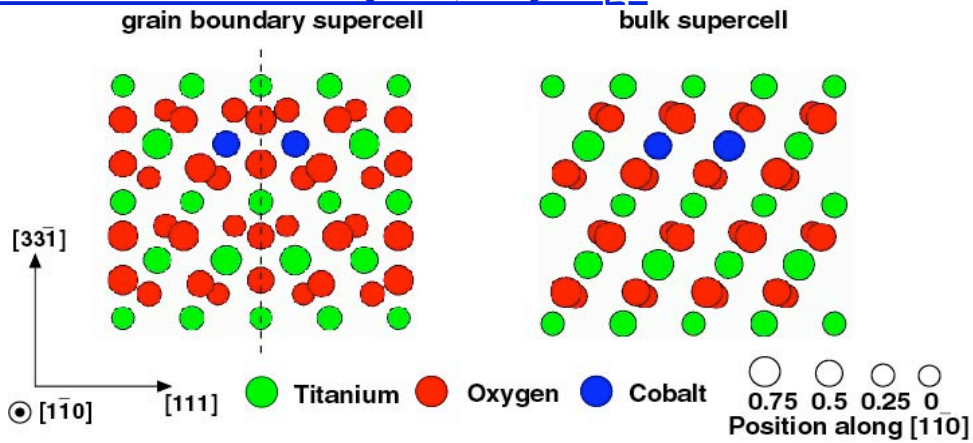
- DFT-based methods are invaluable in the design of new materials
- Complex, multifunctional materials require a range of techniques (different physics AND different algorithms)
- Can we (should we) try to incorporate them all into one code?

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
- X(Zn,TM)O needs carriers (preferably holes!) for ferromagnetism

→ Possible device architecture

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

P

$PbTiO_3$ ← **PZT** → $PbZrO_3$

tetragonal ferroelectric — rhombohedral antiferrodistortive

substitute with