Application of density functional theory to real materials problems

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From Harry Suhl's lecture notes:

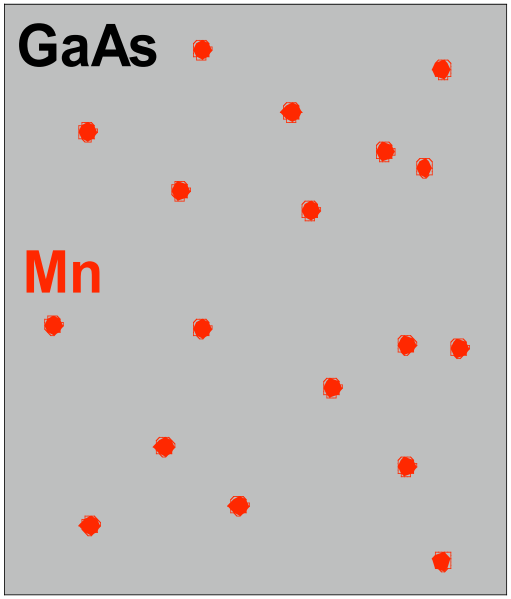
> *In theoretical physics, one obective is to explain what has been seen in past experiments; the other is to predict what will be seen in future experiments.*

Here we'll use DFT to:

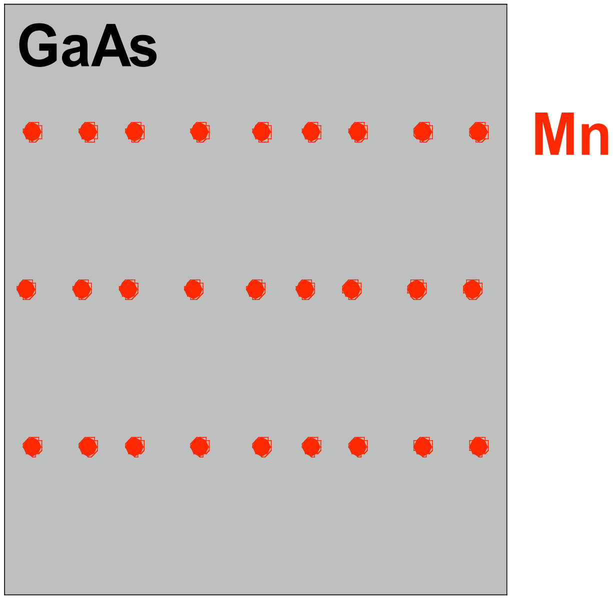
1) Explain experimentally observed behavior in (Ga,Mn)As
2) Design new magnetic ferroelectrics

Improved diluted magnetic semiconductors

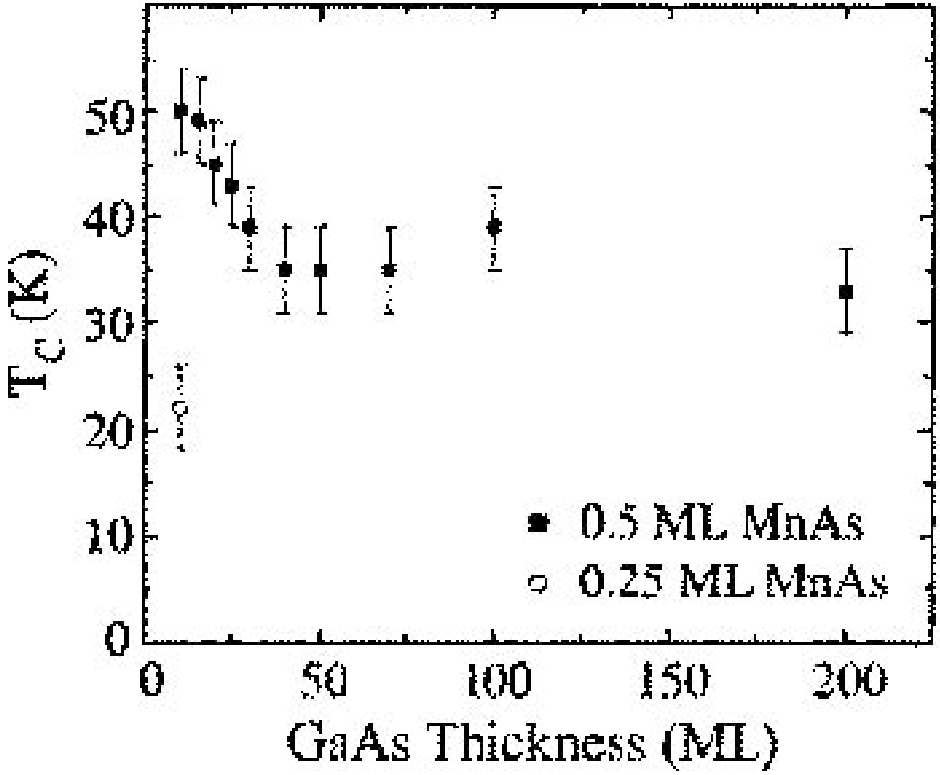
Random Alloy



"DFH"



Unusual magnetic behavior in DFHs:



R.K. Kawakami et al., Appl. Phys. Lett. 77, 2379 (2000).

Questions we'd like to answer:

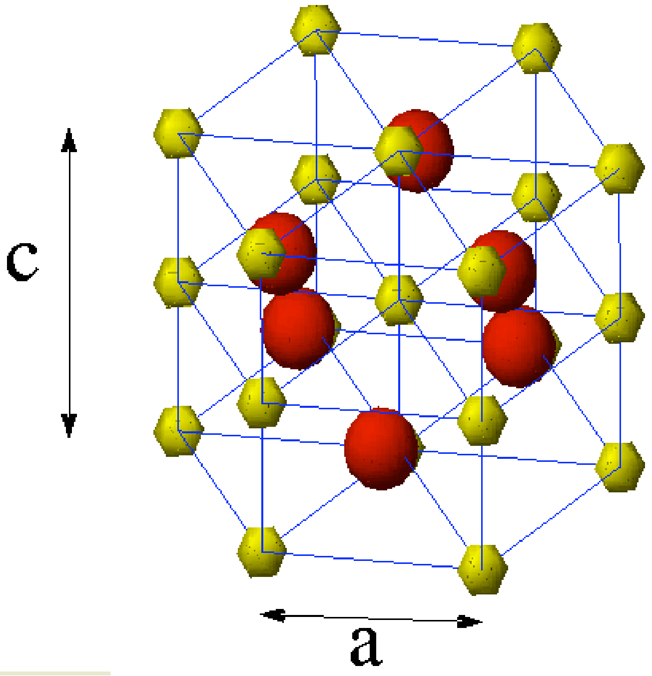
- Can we grow thicker layers of MnAs, and would the properties be desirable if we could?
- What causes ferromagnetism in (Ga,Mn)As, and how can we strengthen it?
- What is the effect of defects on the magnetic properties?
- How does the arrangement of Mn ions affect magnetism and transport?

↓

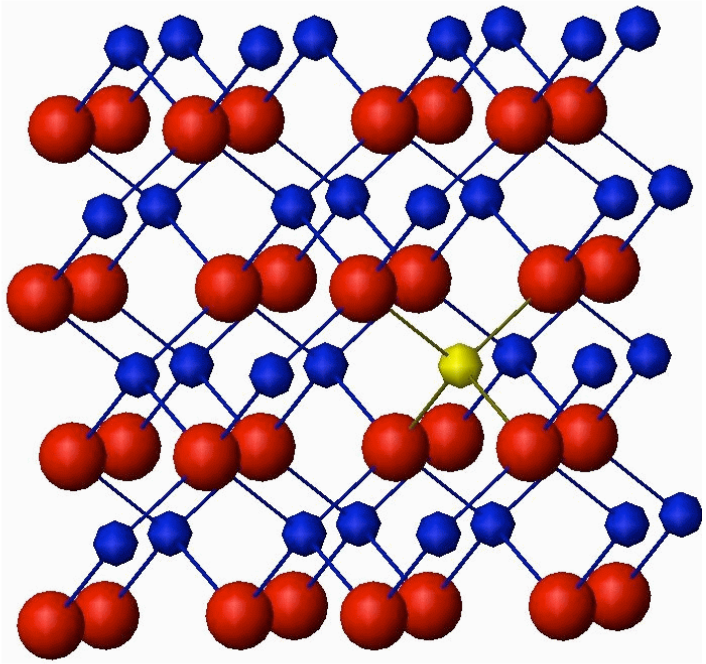
Design of new (and better!) spintronic materials

MnAs: two crystalline phases

NiAs-type structure of bulk MnAs:



Zincblende structure of (Ga,Mn)As:



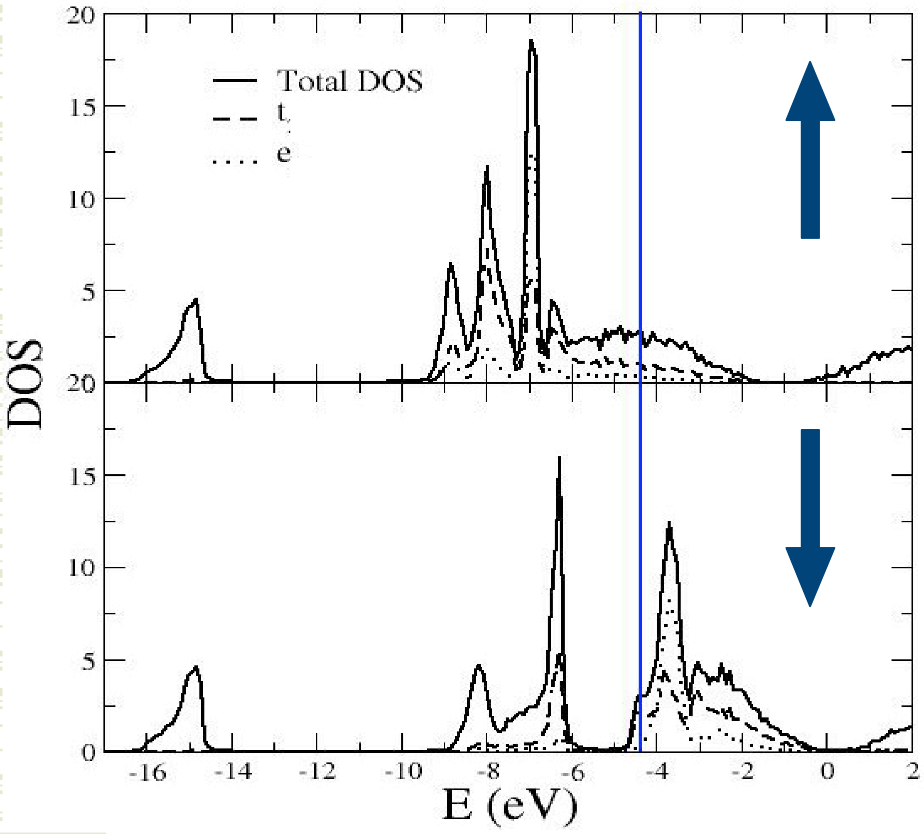
● Ga

● As

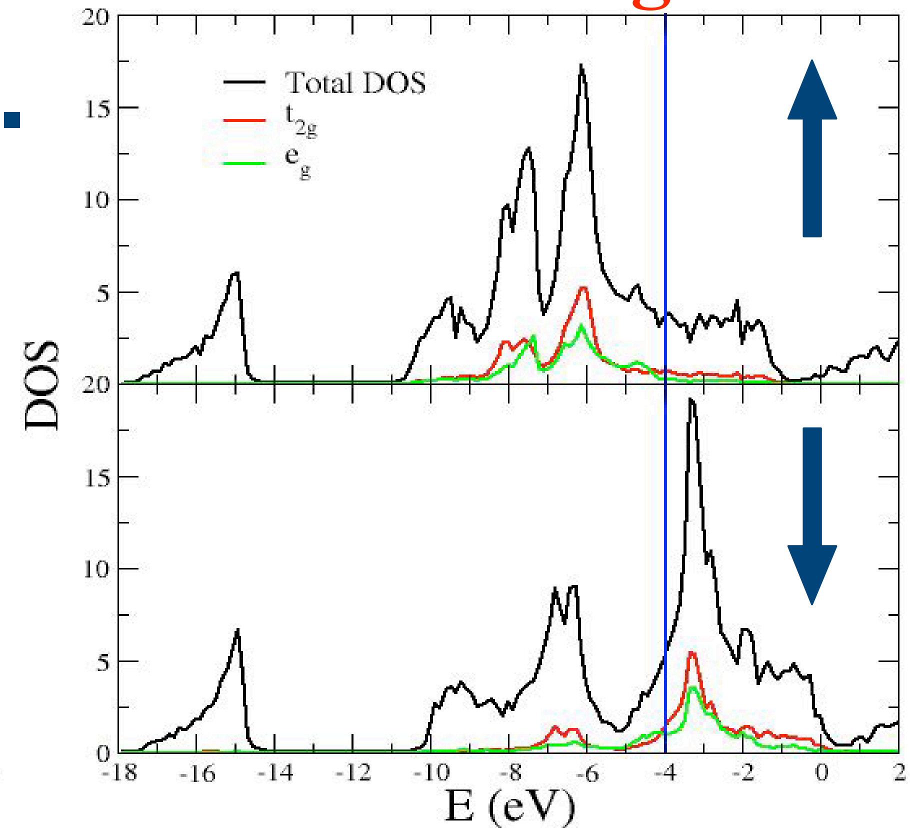
● Mn

MnAs: ZB vs Hexagonal

LDOS Zincblende

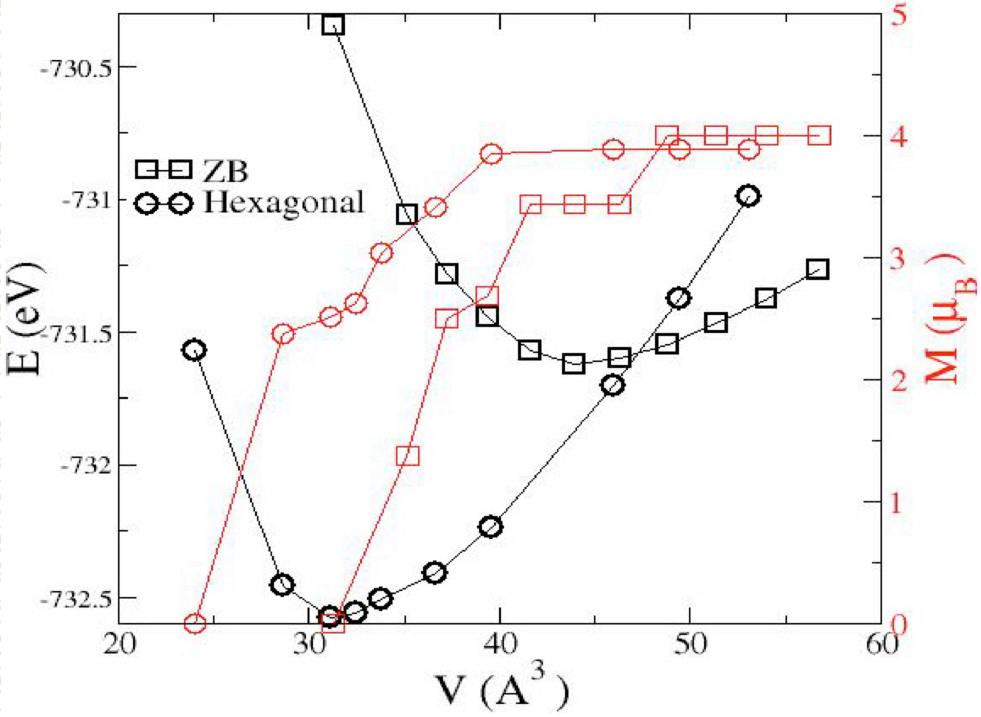


LDOS Hexagonal

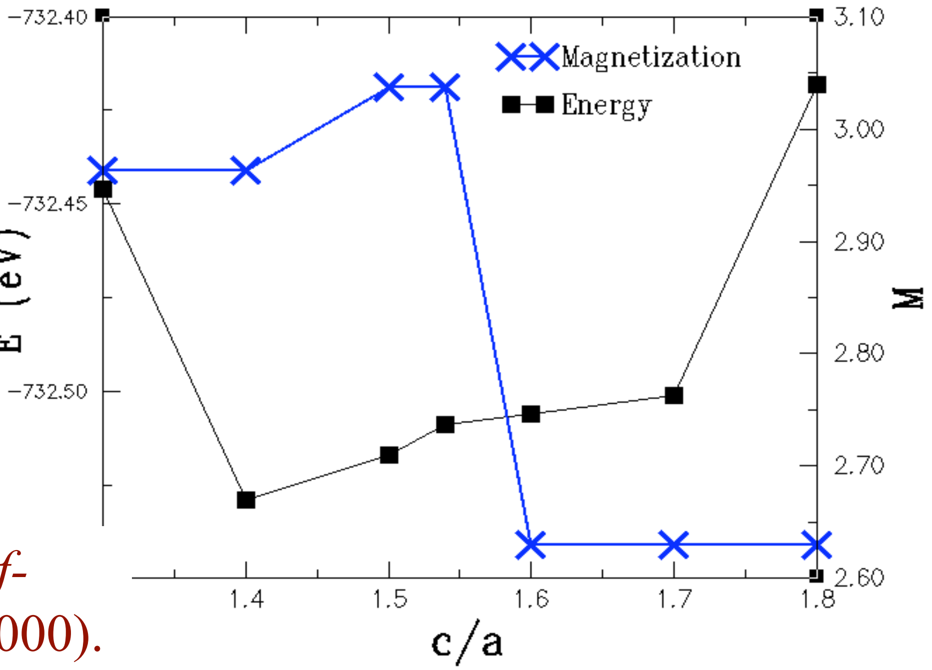


- In the minority band of ZB MnAs the Fermi Energy cuts through a dispersionless d-band. For large lattice spacing it is **Half Metallic**

MnAs: ZB vs Hexagonal



- NiAs-type is more stable with smaller unit cell volume
- Crossover volume for large stress



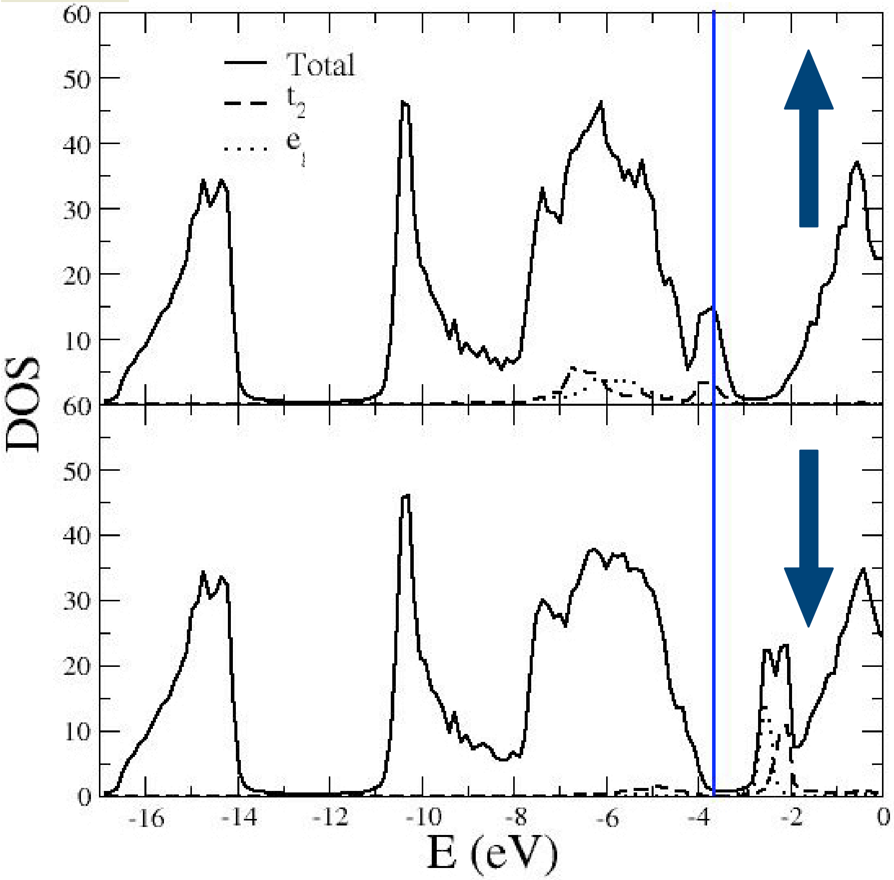
- BUT NiAs-type MnAs can accommodate large distortions therefore **ZB MnAs is hard to stabilize**

S. Sanvito and N.A. Hill, *Ground state of half-metallic zincblende MnAs*, PRB **62,** 15553 (2000).

Questions we'd like to answer:

- ✓ Can we grow thicker layers of MnAs, and would the properties be desirable if we could?
- What causes ferromagnetism in (Ga,Mn)As, and how can we strengthen it?
- What is the effect of defects on the magnetic properties?
- How does the arrangement of Mn ions affect magnetism and transport?

GaAs:Mn Local DOS



32 atom unit cell with 1 Mn impurity

- Large spin-splitting of Mn-d orbitals
- The Fermi energy cuts through the Mn-d impurity band in the majority spin band
- Almost no-occupation of the Mn-d orbitals in the minority band – half-metallic!
- Mn impurity band strongly hybridized with the As-p orbitals of the nearest neighbors

S. Sanvito, P. Ordejon and N.A. Hill, *First principles study of the origin and nature of ferromagnetism in (Ga,Mn)As,* PRB **63,** 165206 (2000).

GaAs:Mn Mn configuration

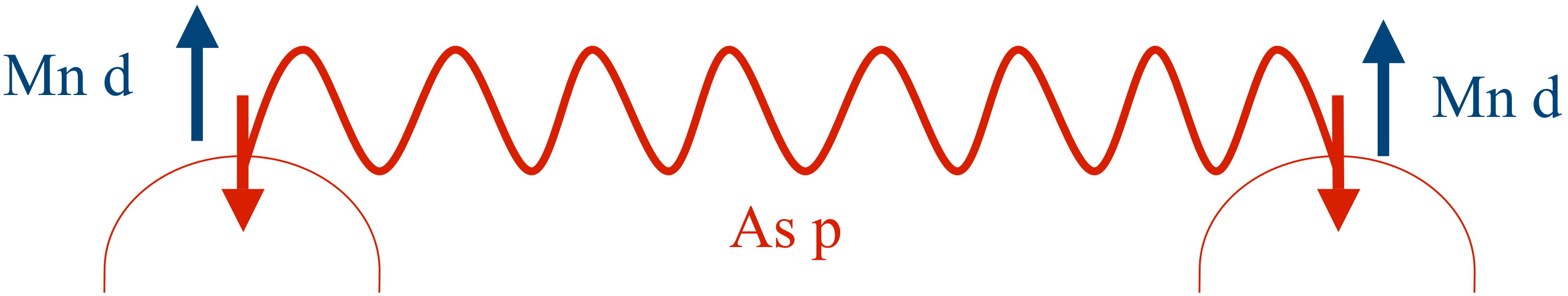
Mülliken Population analysis shows:

- Polarization per unit cell

$$n(\mathrm{Mn}-\mathrm{d}\uparrow)-n(\mathrm{Mn}-\mathrm{d}\downarrow)=3.904$$

$$n(\mathrm{As}-\mathrm{p}\uparrow)-n(\mathrm{As}-\mathrm{p}\downarrow)=-0.432$$

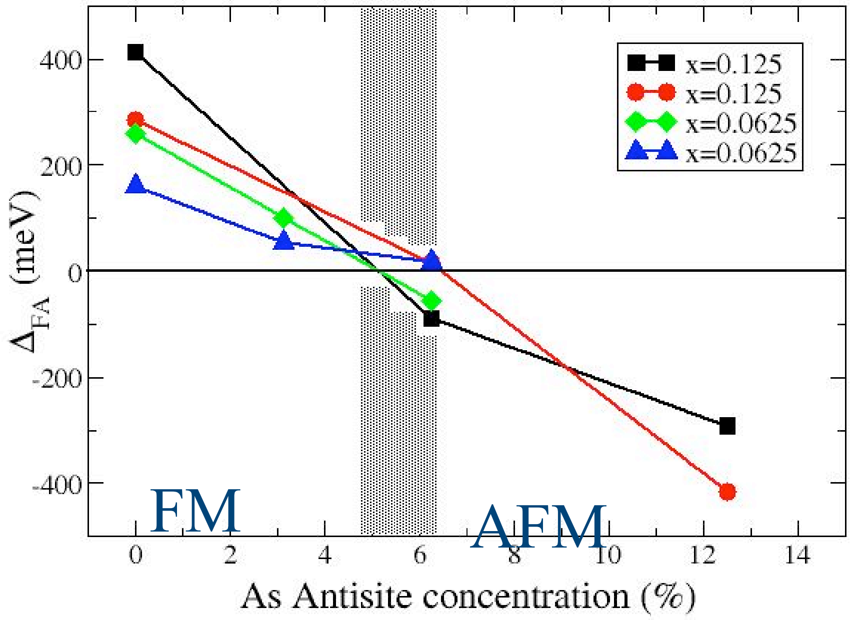
p-d antiferromagnetic exchange and the presence of holes drive the ferromagnetic coupling



(Ga,Mn)As and As antisites

Do As antisites weaken the ferromagnetism in (Ga,Mn)As? Look at energy difference between the ferromagnetic and antiferromagnetic alignment of Mn ions in a large GaAs cell

$$\Delta_{FA} = E_{FM} - E_{AF}$$



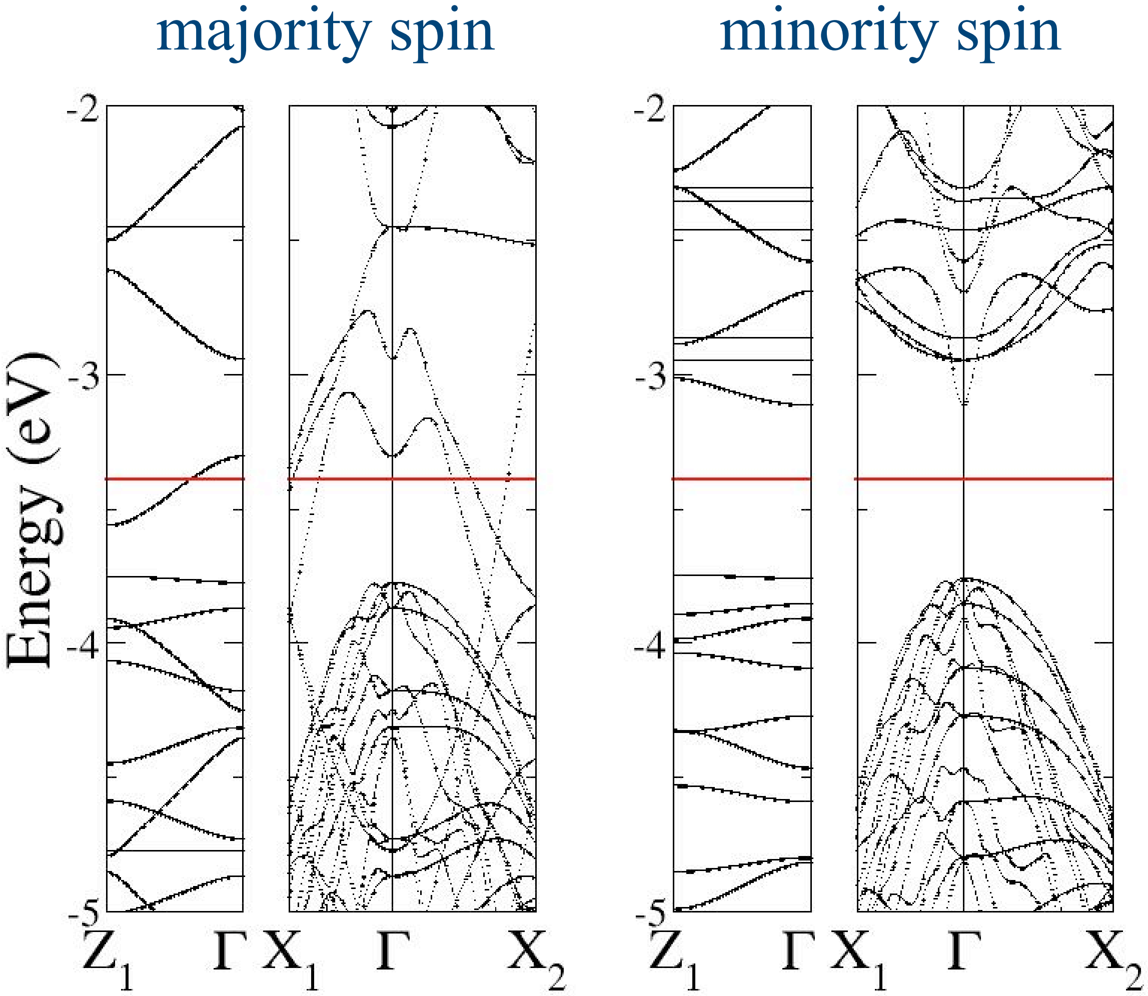
- No As antisites = strong FM order
- Presence of As antisites weakens FM alignment
- Picture of hole-mediated exchange not strictly valid since ferromagnetic order persists at compensation

S. Sanvito and N.A. Hill, *Influence of the local As antisite distribution on ferromagnetism in (Ga,Mn)As,* Appl. Phys. Lett. **78**, 1 (2001).

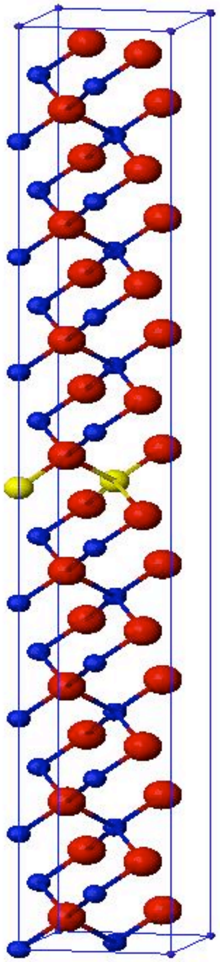
Questions we'd like to answer:

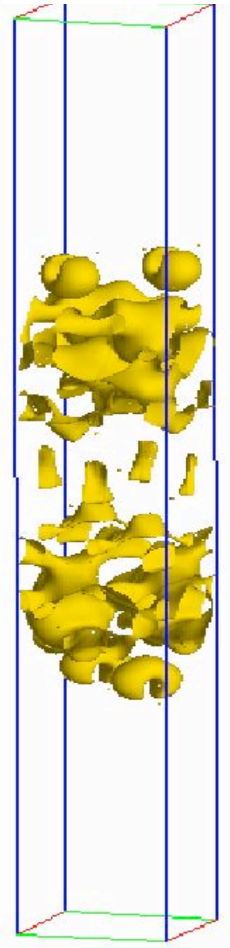
- ✓ Can we grow thicker layers of MnAs, and would the properties be desirable if we could?
- ✓ What causes ferromagnetism in (Ga,Mn)As, and how can we strengthen it?
- ✓ What is the effect of defects on the magnetic properties?
- How does the arrangement of Mn ions affect magnetism and transport?

Band structure of a DFH

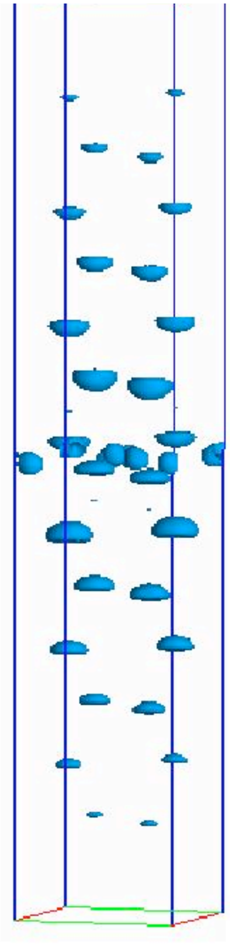


Transport through a DFH





Current in-plane



Current out of plane

- Calculate transport using Landauer-Buttiker fomalsim
- Strongly anisotropic
- Not strictly 2-dimensional
- Confinement to planes explains high T_cs

S. Sanvito and N.A. Hill, *Ab-initio transport theory for digital ferromagnetic heterostructures*, Phys. Rev. Lett. **87**, 267202 (2001).

(Ga,Mn)As Conclusions

- The Mn-d band is antiferromagnetically coupled with the As-p band; holes in the As p band mediate ferromagnetism
- As antisites weaken the ferromagnetism and a transition to an antiferromagnetic alignment is possible
- DFHs are two-dimensional half-metals, with carriers confined to the MnAs plane
- Thicker layers of MnAs would have desirable properties but will be hard to grow

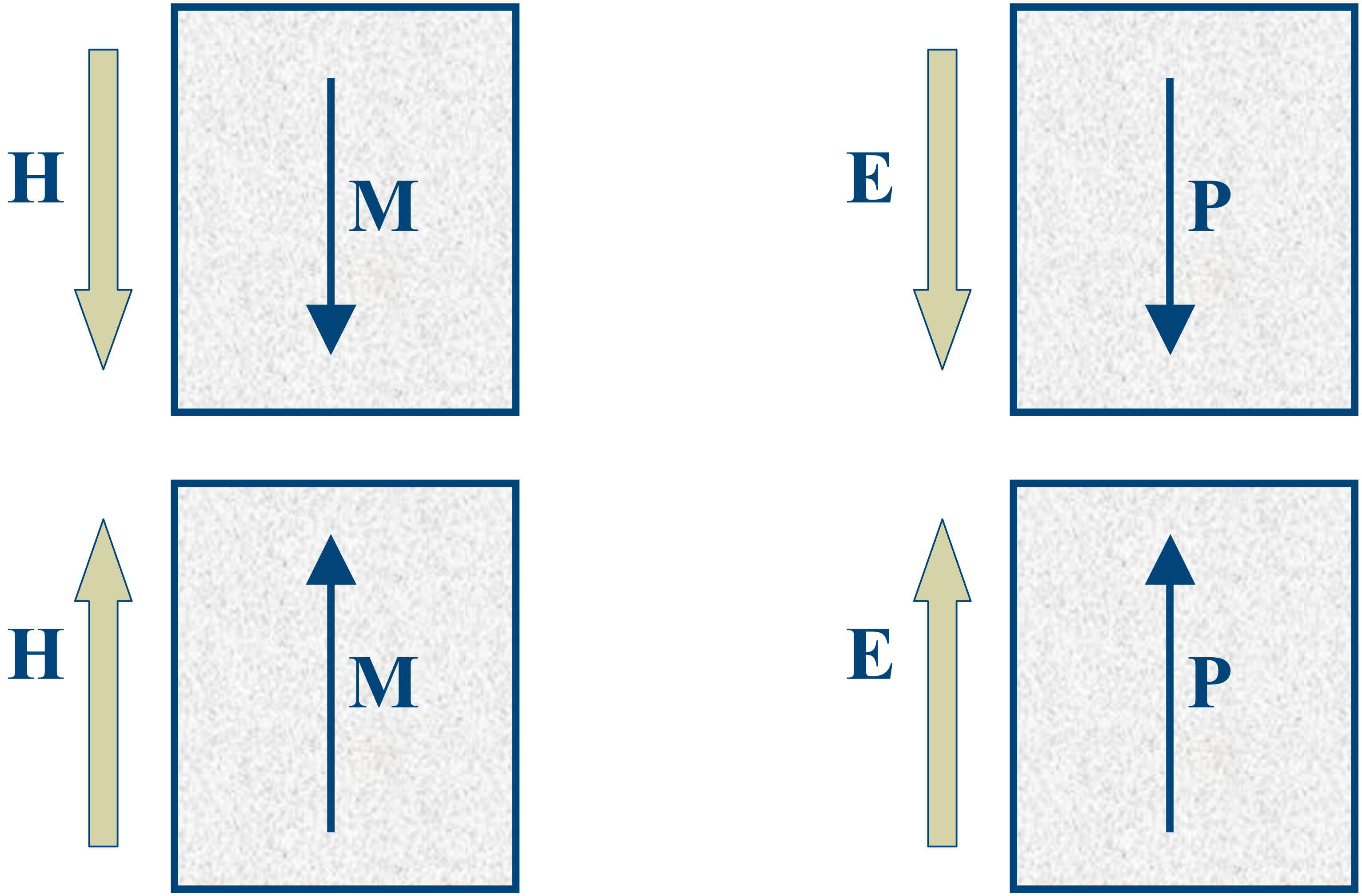
Computational design of new multiferroics

Plan for designing for multifunctionality:

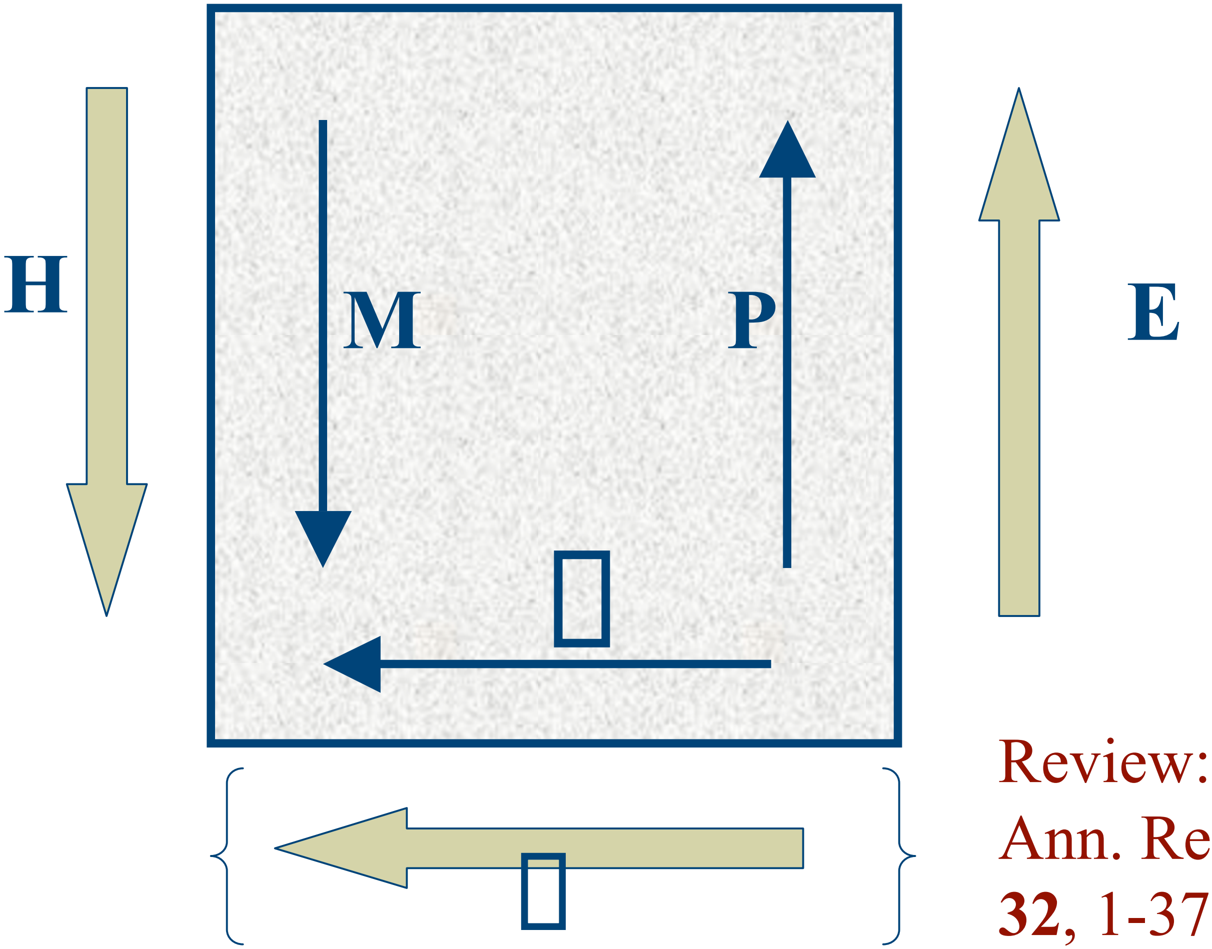
- Understand origin of each function separately (DFT)
- Design a trial compound with required properties (intuition/experience)
- Check that the trial compound indeed behaves as requirec (DFT)
- Persuade an experimentalist to make and characterize it!

Computational design of multifunctional materials,
N.A. Spaldin and W.E. Pickett, JSSC, in press

Ferromagnetism and Ferroelectricity

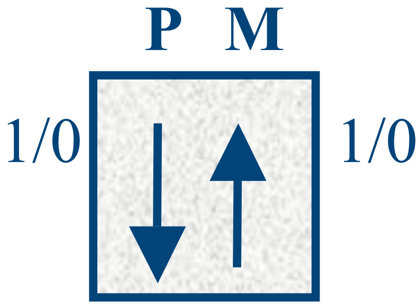


Multiferroic magnetoelectrics



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

Why Do We Care?



Device applications:

- Multiple state memory elements
- Write to E / read from M
- Extra degree of freedom

Fundamental physics:

- Nature of coupling between order parameters

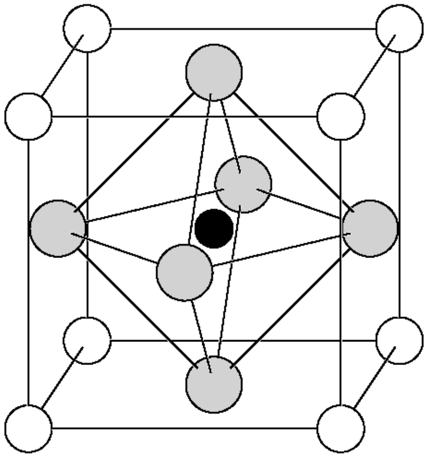
Known ferromagnetic ferroelectrics:

1) Nickel Iodine Boracite, **$Ni_3B_7O_{13}I$**

- Ferroelectric, weak ferromagnet
- 24 atoms per formula unit and 8 fla units per unit cell!

2) Mixed Perovskites

- e.g. B-site ordered $Pb_2(CoW)O_6$
- Ferroelectric from diamagnetic W^{6+}
- Ferromagnetic from d^6 Co^{2+}
- Dilution ⟶ low Curie temp.



3) Simple Perovskites

- $BiFeO_3$
- $YMnO_3$

Why Are There So Few Magnetic Ferroelectrics?

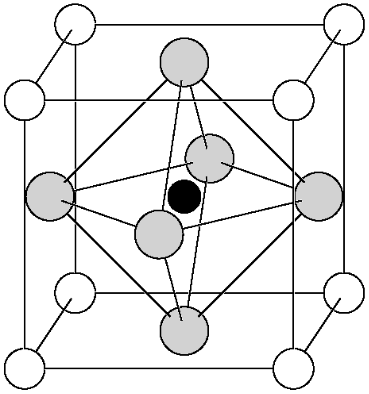
N.A. Hill, *Why are there so few magnetic ferroelectrics?*, J. Phys. Chem. B **104**, 6694-6709 (2000).

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"



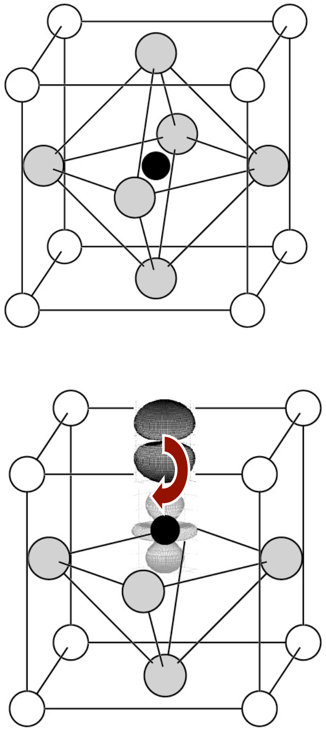
ION	Ti^{4+} d^0	Nb^{5+} d^0	Zr^{4+} d^0	Mn^{3+} d^4	Ti^{3+} d^1	V^{4+} d^1
SIZE (pm)	74.5	78.0	86.0	78.5	81.0	72.0

Outline – remainder….

- What causes ferroelectricity?
- (What causes ferromagnetism?)
- How can we incorporate both?
- A success story – $BiMnO_3$

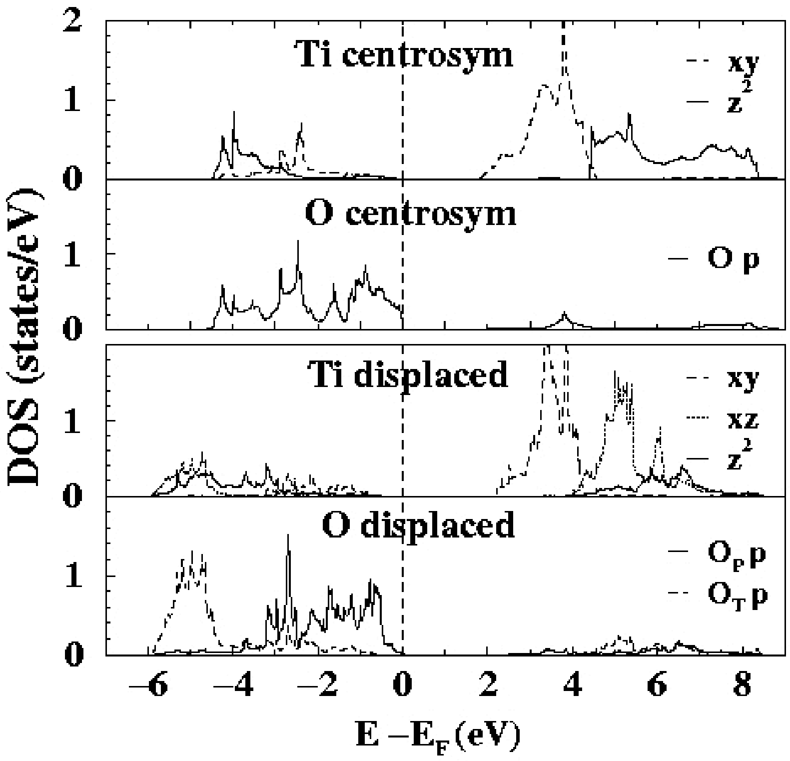
Conventional mechanism for ferroelectricity:

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



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”

INCOMPATIBLE!

Why Are There ANY magnetic ferroelectrics?

N.A. Hill and A. Filippetti, *Why are there any magnetic ferroelectrics?*, J. Mag. Mag. Mat. **242**, 976 (2002).

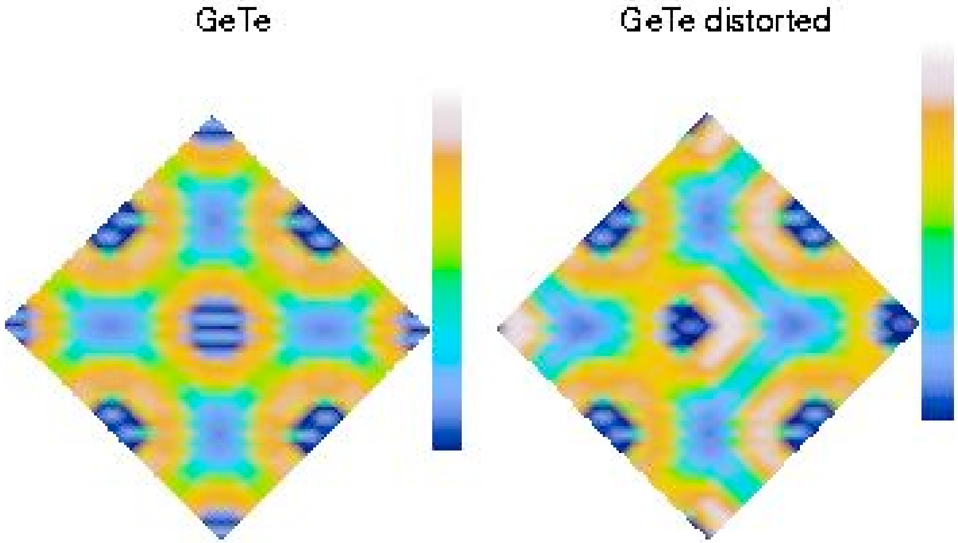
But……..

Alternative mechanism for ferroelectricity:

Cation lone pair localization

e.g. IV-VI compounds

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).



$PbTiO_3$, etc.

needs an *ns*^{2} pair of electrons

Perovskite design:

- Transition metal cation with *d* electrons for magnetism

- Ferro- (or ferri-) magnetic ordering of the above

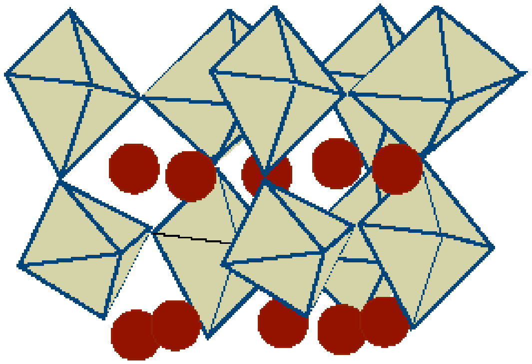
- Large cation with $(ns)^2$ electron configuration

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

A 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).

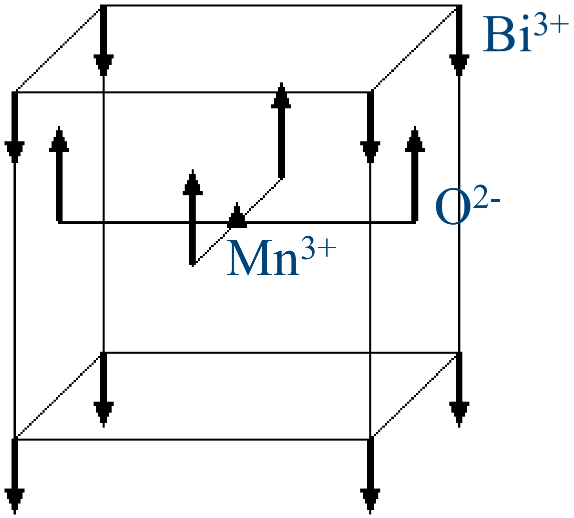
Use DFT to check:

- Ferroelectric?

Is $BiMnO_3$ ferroelectric and intrinsically ferromagnetic?

DFT Calculations predict:

- Ferromagnetic ground state
- Strong ferroelectric instability in FM $BiMnO_3$
- Ferroelectricity results from Bi – O displacement!



N.A. Hill and K.M. Rabe, PRB **59**, 8759 (1999).

Plan for designing for multifunctionality

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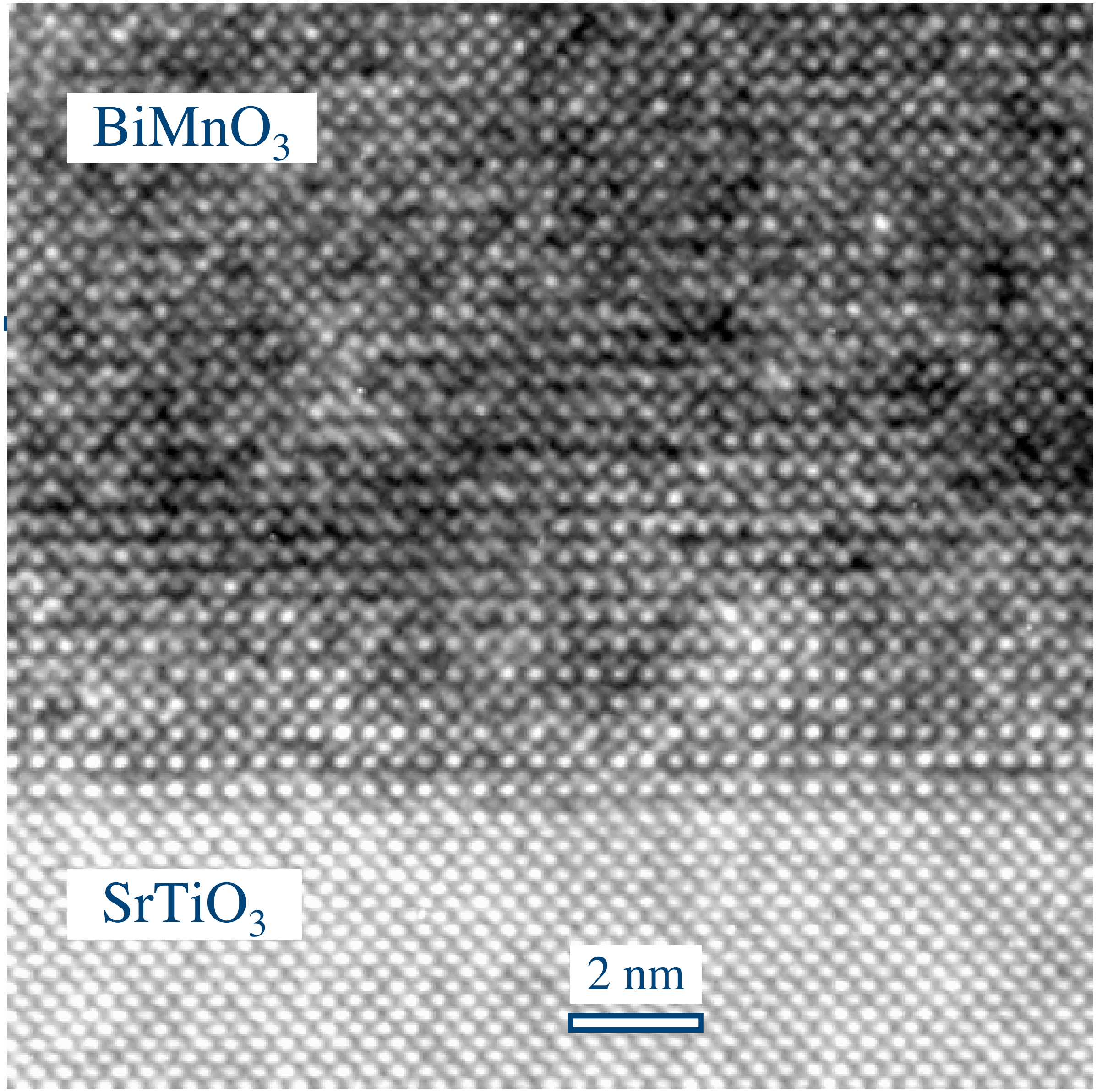
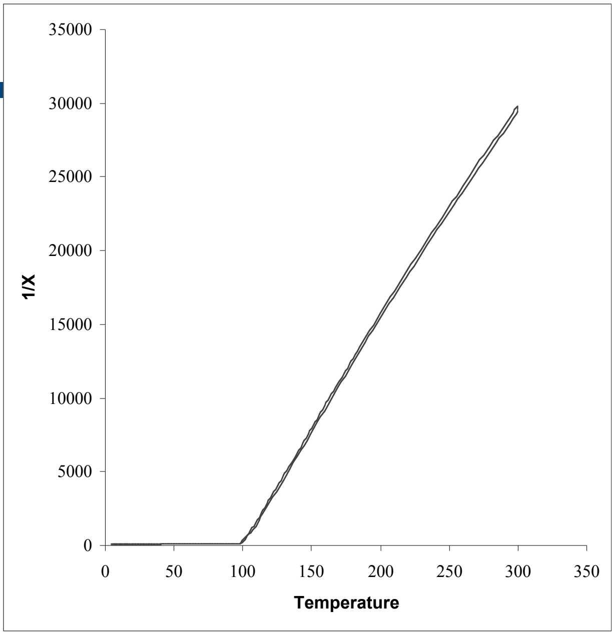
- Persuade an experimentalist to make and characterize it!

From Darrell Schlom:

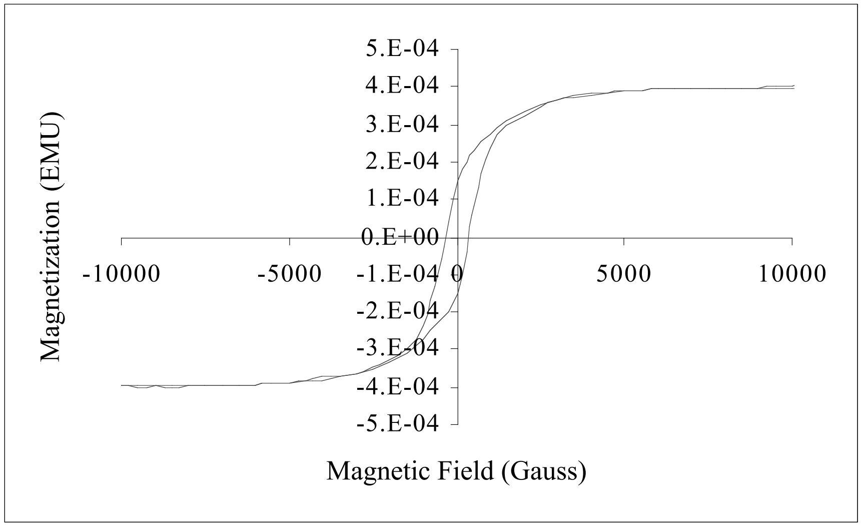


Interface between $SrTiO_3$ and $BiMnO_3$

Magnetic properties



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

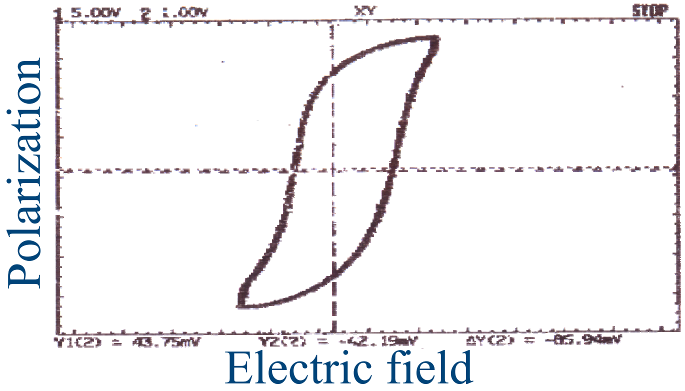


Magnetic hysteresis loop, measured at 10 K, of PLD grown $BiMnO_3$ on $SrTiO_3$.

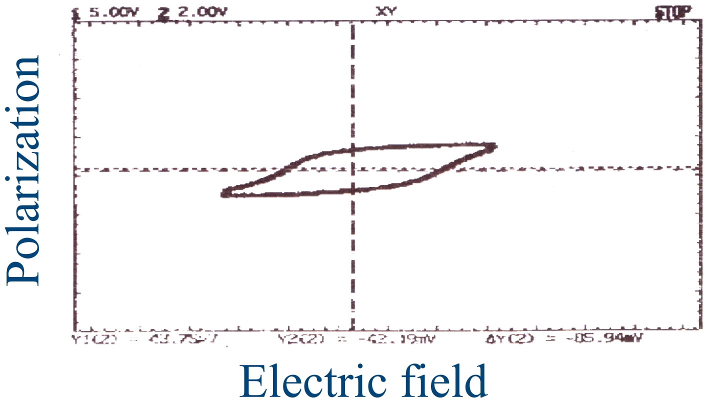
A.M. Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham and C.N.R. Rao, *Evidence for the likely occurrence of magnetoferroelectricity in* $BiMnO_3$, Sol. Stat. Comm. 122, **49** (2002).

Experimental Data: Ferroelectric hysteresis in $BiMnO_3$

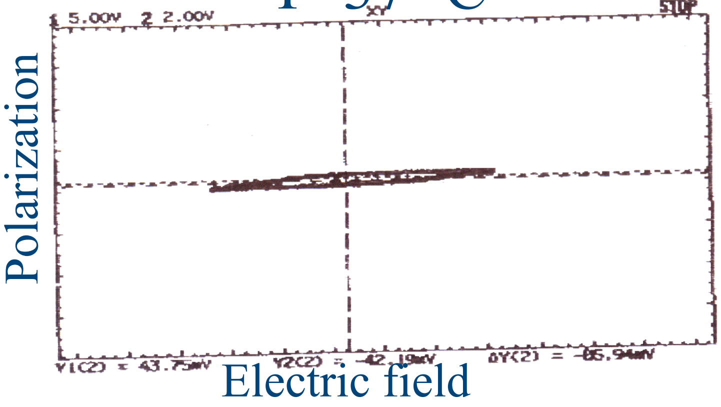
T=25 °C



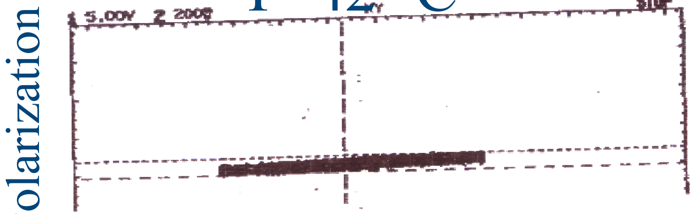
T=35 °C



T=37 °C



T=42 °C



(Measurement at 5.00 V)

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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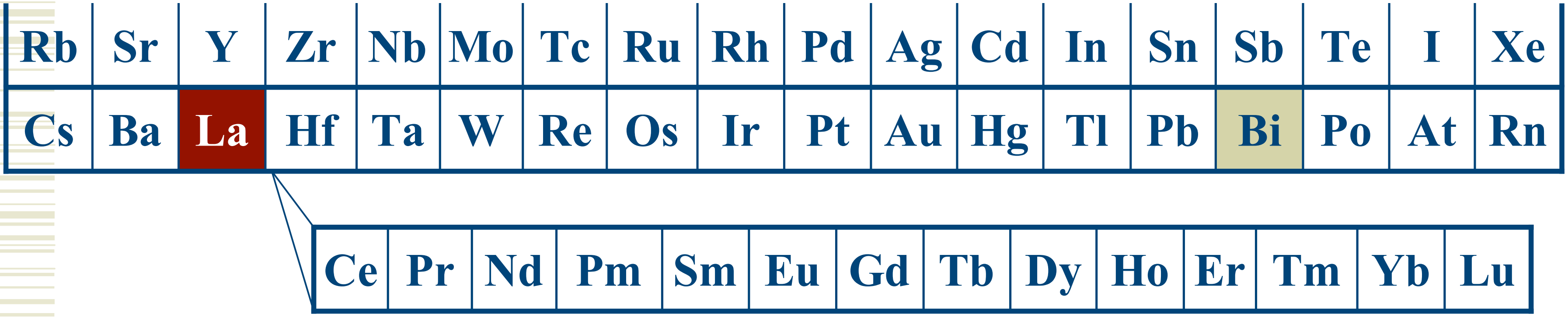
Remaining questions:

- Is the Bi lone pair causing the ferroelectricity?
- What is causing the ferromagnetism?

(cf. $LaMnO_3$ – antiferromagnetic and not ferroelectric)

Compare with $LaMnO_3$

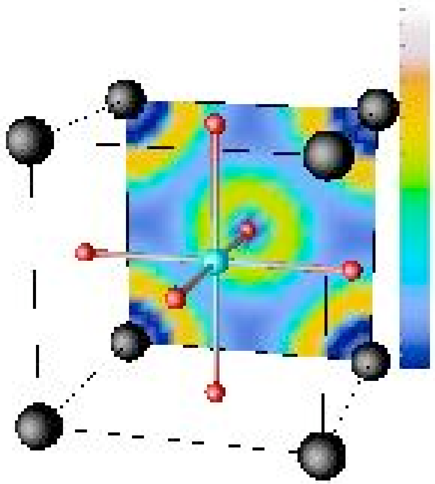


Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

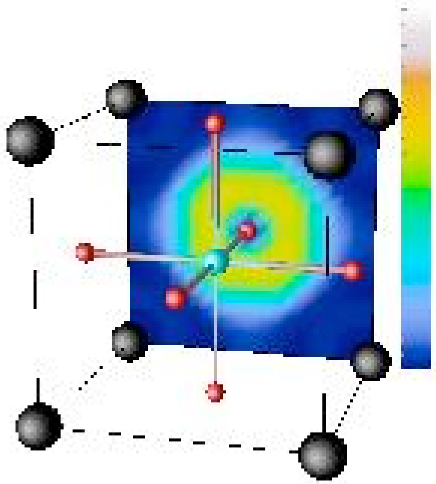
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

- La^{3+} has no valence electrons
- cf $BaTiO_3$ ↔ $PbTiO_3$ system

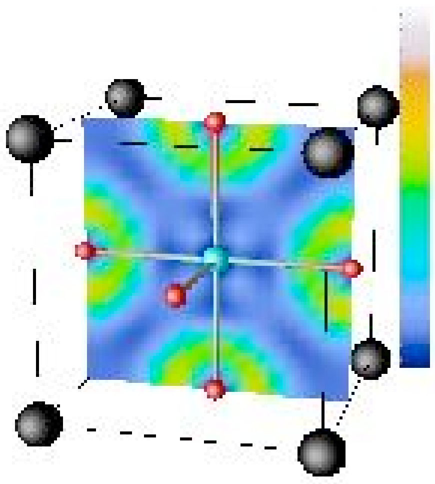
Role of the Bi lone pair (I)



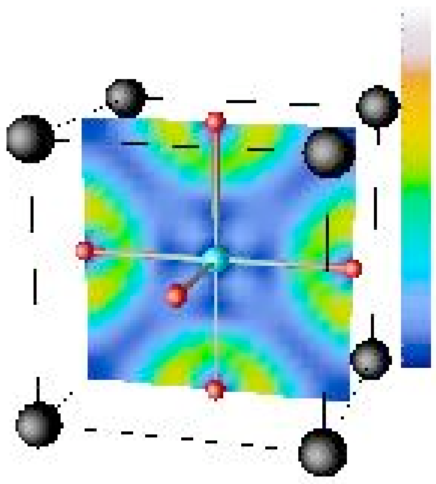
Cubic BiMnO$_3$, Bi-O plane



Cubic LaMnO$_3$, La-O plane

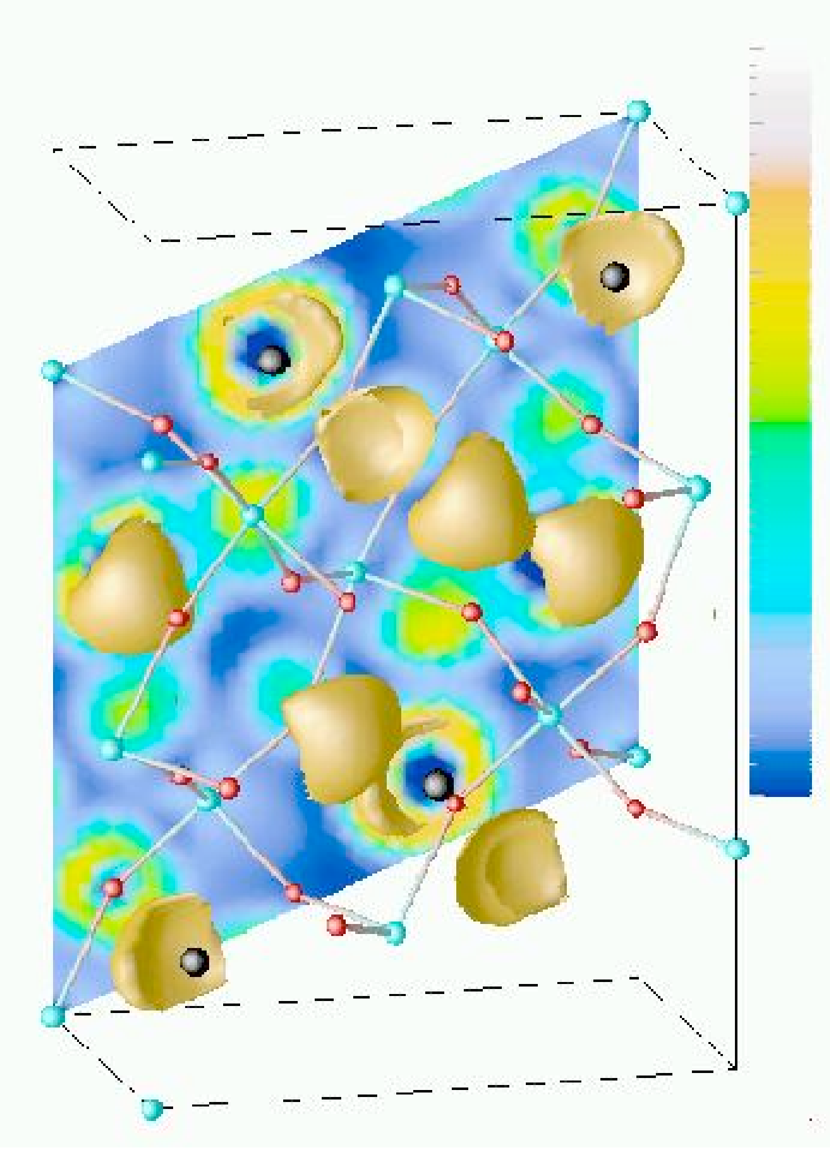


Cubic BiMnO$_3$, Mn-O plane



Cubic LaMnO$_3$, Mn-O plane

Role of the Bi lone pair (II)



- Lone pair is stereochemically active and causes the ferroelectricity

- Asymmetry results from mixing of Bi 6s with *both* Bi 6p and O 2p

- Next: the lone pair distortion *also* drives the ferromagnetism!

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).

Theory of the Role of Covalence in the Perovskite-Type Manganites $[\mathrm{La},M(\mathrm{II})]\mathrm{MnO}_3$†

JOHN B. GOODENOUGH
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts

(Received May 16, 1955)

The theory of semicovalent exchange is reviewed and applied to the perovskite-type manganites $[\mathrm{La},M(\mathrm{II})]\mathrm{MnO}_3$. With the hypothesis of covalent and semicovalent bonding between the oxygen and manganese ions plus the mechanism of double exchange, detailed qualitative predictions are made about the magnetic lattice, the crystallographic lattice, the electrical resistivity, and the Curie temperature as functions of the fraction of Mn^{4+} present. These predictions are found to be in accord with recent findings from neutron-diffraction and x-ray data as well as with the earlier experiments on this system by Jonker and van Santen.

I. INTRODUCTION

IN a recent paper[1] on the influence of covalent effects in spinel-type structures, it was shown how covalent bonding influences lattice distortions and indirect magnetic-exchange interactions between two magnetic cations separated by an anion. The magnetic interaction was termed semicovalent exchange since it depends upon the concept of semicovalent bonding, a concept which was also introduced in that same paper. Although there are certain similarities between this exchange mechanism and the superexchange mechanism which was first proposed by Kramers[2] in 1934, the two have fundamental differences: in some oxides the two lead to identical predictions, but in others they lead to opposite predictions. The perovskite-type manganites represent a system in which the magnetic moments of the manganese ions are coupled by indirect exchange mechanisms; it is a system for which semicovalent exchange and superexchange give opposite predictions. It is, therefore, a particularly appropriate system for evaluating the merits of the semicovalent-exchange hypothesis, especially as Wollan and Koehler,[3] with the support of x-ray

II. SEMICOVALENCE

There are three principal contributions to the internal energy of a solid, the electrostatic, electronic, and elastic contributions. In an ideal ionic lattice the electronic contribution is negligible, the principal binding energy coming from the electrostatic term. In a homopolar or metallic lattice the electrostatic term is negligible, the principal binding energy coming from the electronic term.

Previous workers have assumed that the transition-element cations in oxide lattices are ionically bound. Although the superexchange mechanism depends upon the nonionic component of the cation-oxygen bonds, in this model it is presumed that the atomic electron orbitals provide a fairly accurate description for the electrons in the lattice, or that a tight-binding approximation is valid. Whereas various authors[4] have considered the perturbations of the cation d orbitals caused by internal electric fields, there has been no serious consideration of the perturbations of the empty cation orbitals. The empty cation orbitals are assumed to have so much higher an energy than either the cation

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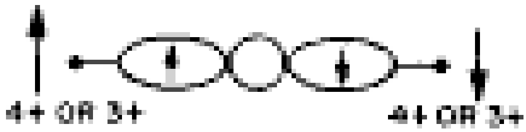
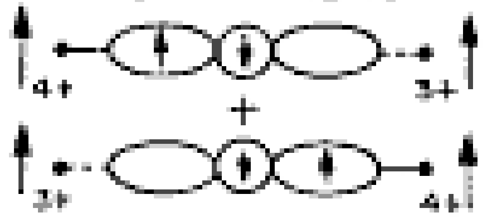
SCHEMATIC ELECTRON-SPIN CONFIGURATIONS	Mn-Mn SEPARATION	TRANSITION TEMPS.	RESISTIVITY	CASE
ORDERED LATTICES				
ANTIFERROMAGNETIC 	SMALLEST	$T_0 > T_c$	HIGH	1
FERROMAGNETIC 	LARGE	$T_0 > T_c$	HIGH	2
PARAMAGNETIC 	LARGEST	$T_c \approx 0$	HIGH	3
DISORDERED LATTICES				
FERROMAGNETIC 	SMALL	$T_0 = T_c$	LOW	4

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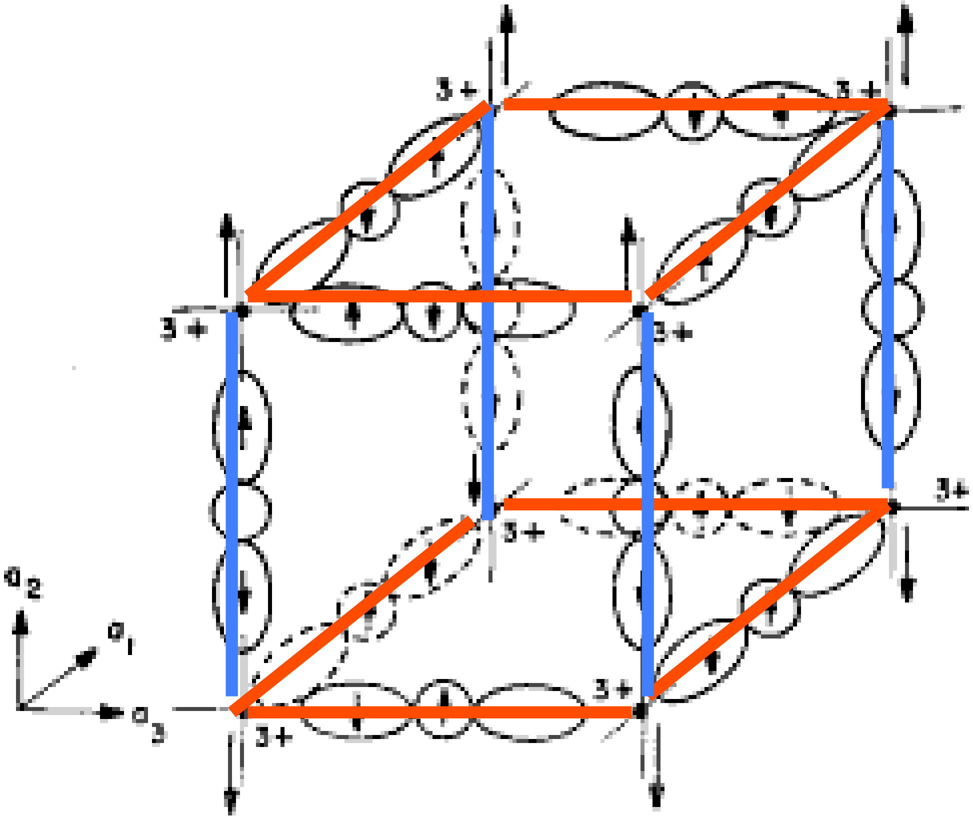


FIG. 2. Magnetic lattice for $x=0$; type A.

single Mn^{3+} ion cannot be said to be ordered, it couples

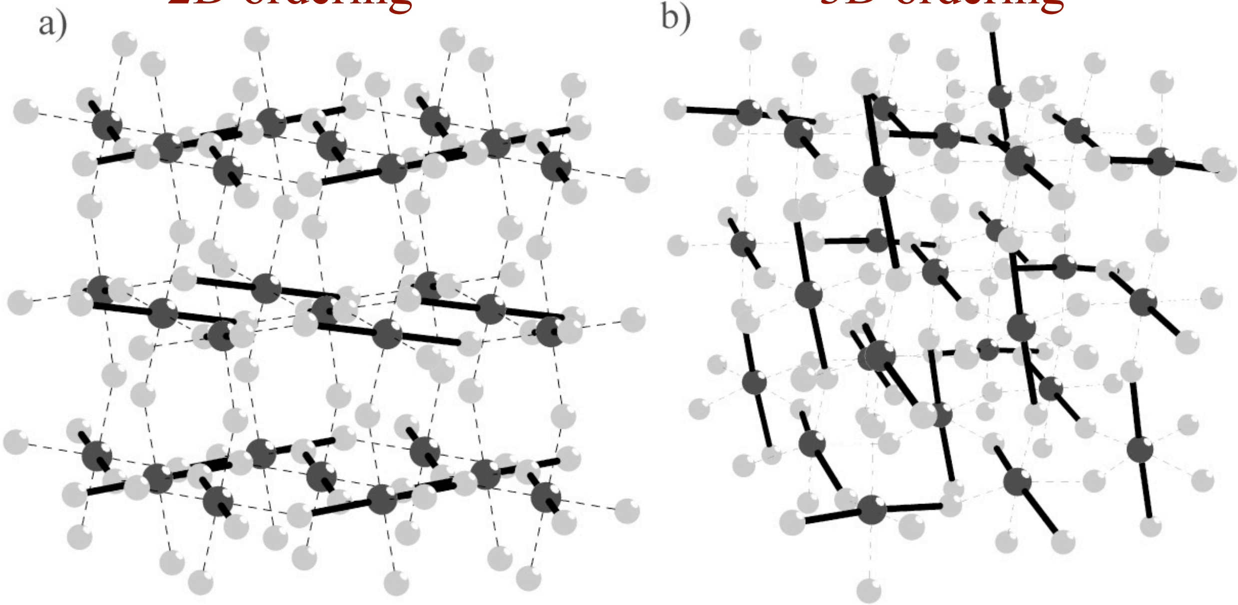
Orbital Ordering

$LaMnO_3$ – AFM

2D ordering

$BiMnO_3$ - FM

3D ordering



(The bonds in bold are the d_Z^2 orbitals)

Orbital ordering as the determinant for ferromagnetism in biferroic $BiMnO_3$, A.M dos Santos et al., Phys. Rev. B 66, 064425 (2002).

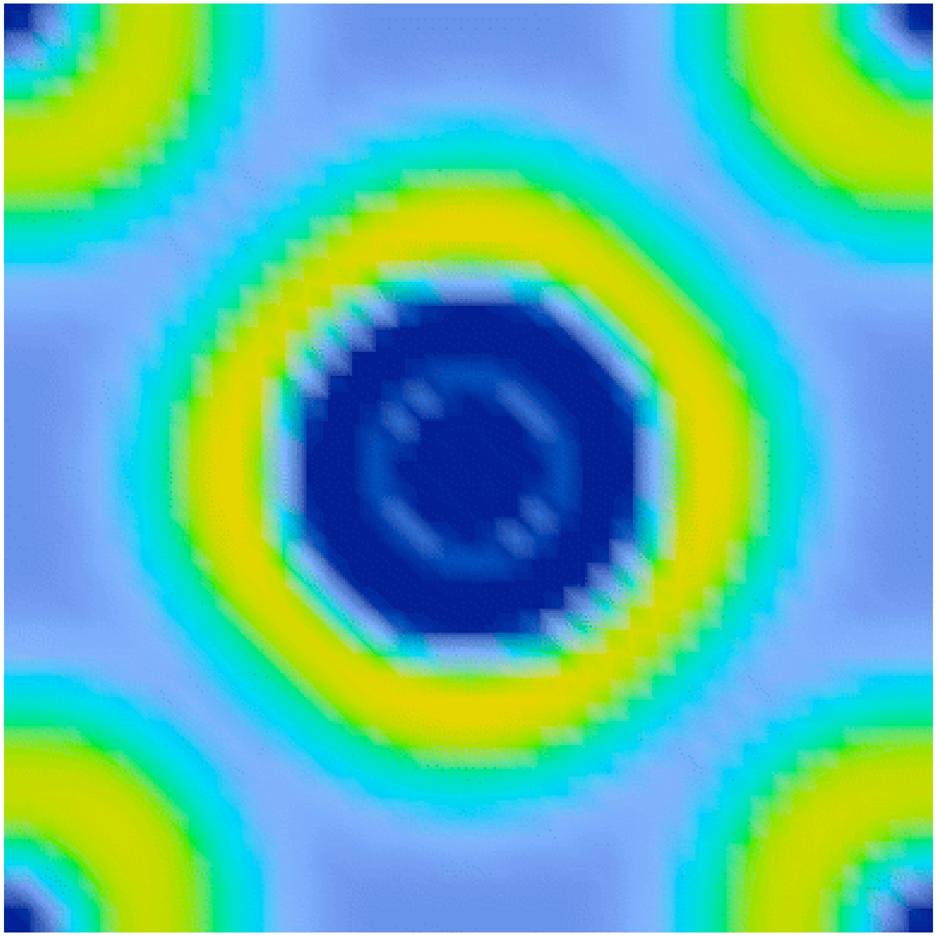
Conclusions

- In $BiMnO_3$ the stereochemically active Bi lone pair causes a structural distortion which gives rise to

  1. Ferroelectricity
  2. Orbital ordering and ferromagnetism

- Computational materials is a useful tool in the design of new multiferroics
- Lone pair activity can be exploited to create "designer" ferroelectrics…….

Stereochemical activity of the Bi lone pair in $BiAlO_3$



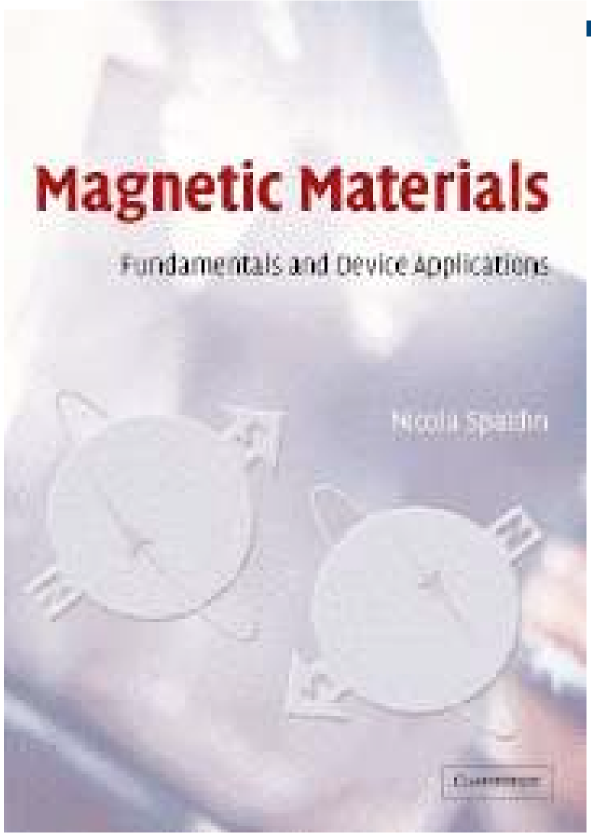
BECs	(formal charges)
Bi +6.2	(+3.0)
O_P –3.4	(–2.0)
O_T –2.4	(–2.0)
Al +2.9	(+3.0)

Ongoing work on magnetic materials in my group

- Hexagonal perovskites, e.g. $YMnO_3$
- Design of a magnetic piezoelectric semiconductor, e.g. (Zn,Mn)O
- Grain boundary effects in $(Ti,Co)O_2$
- Design of single phase high □ AND high □materials
- Molecular spintronic devices

Blatant self-promotion

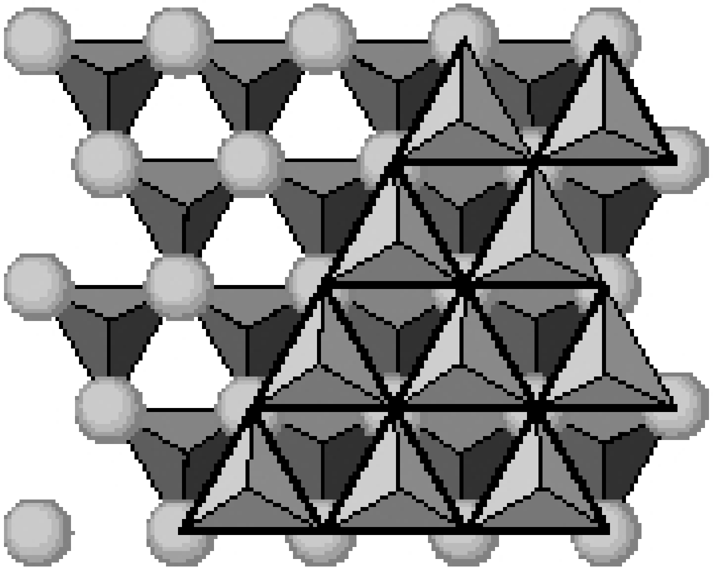
You can buy my book….



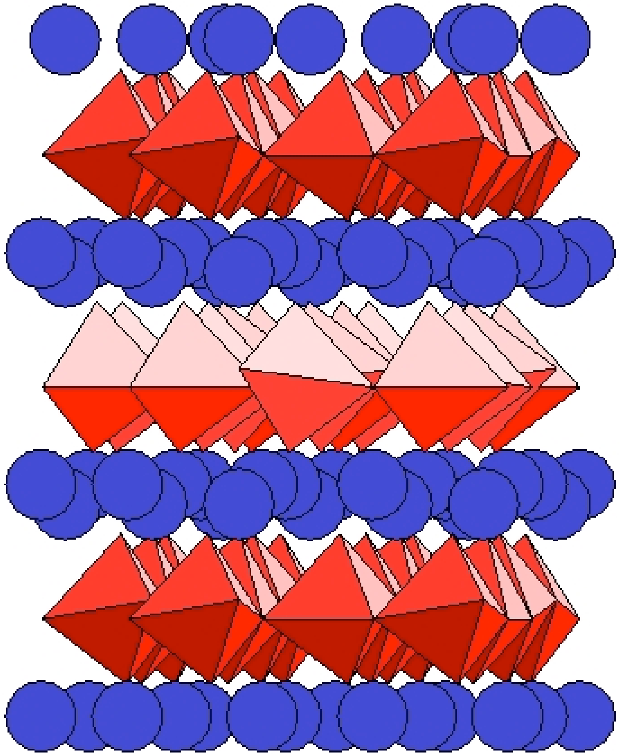
……. from the Cambridge University Press web-site:
http://books.cambridge.org/0521016584.htm

An anomalous ferroelectric: $YMnO_3$

View down c, above T_c

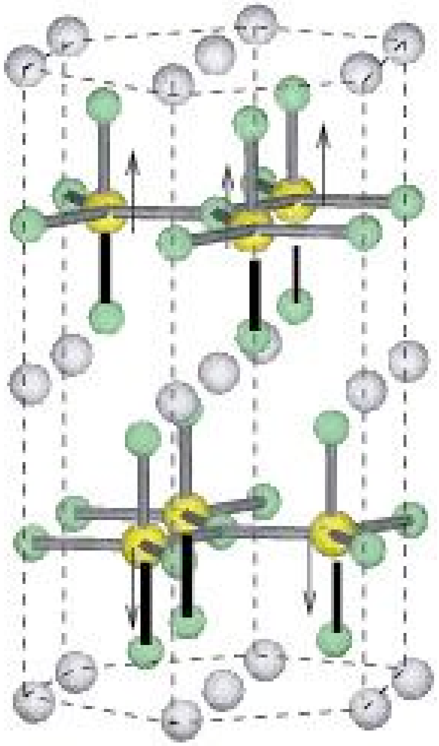


Side view, below T_c

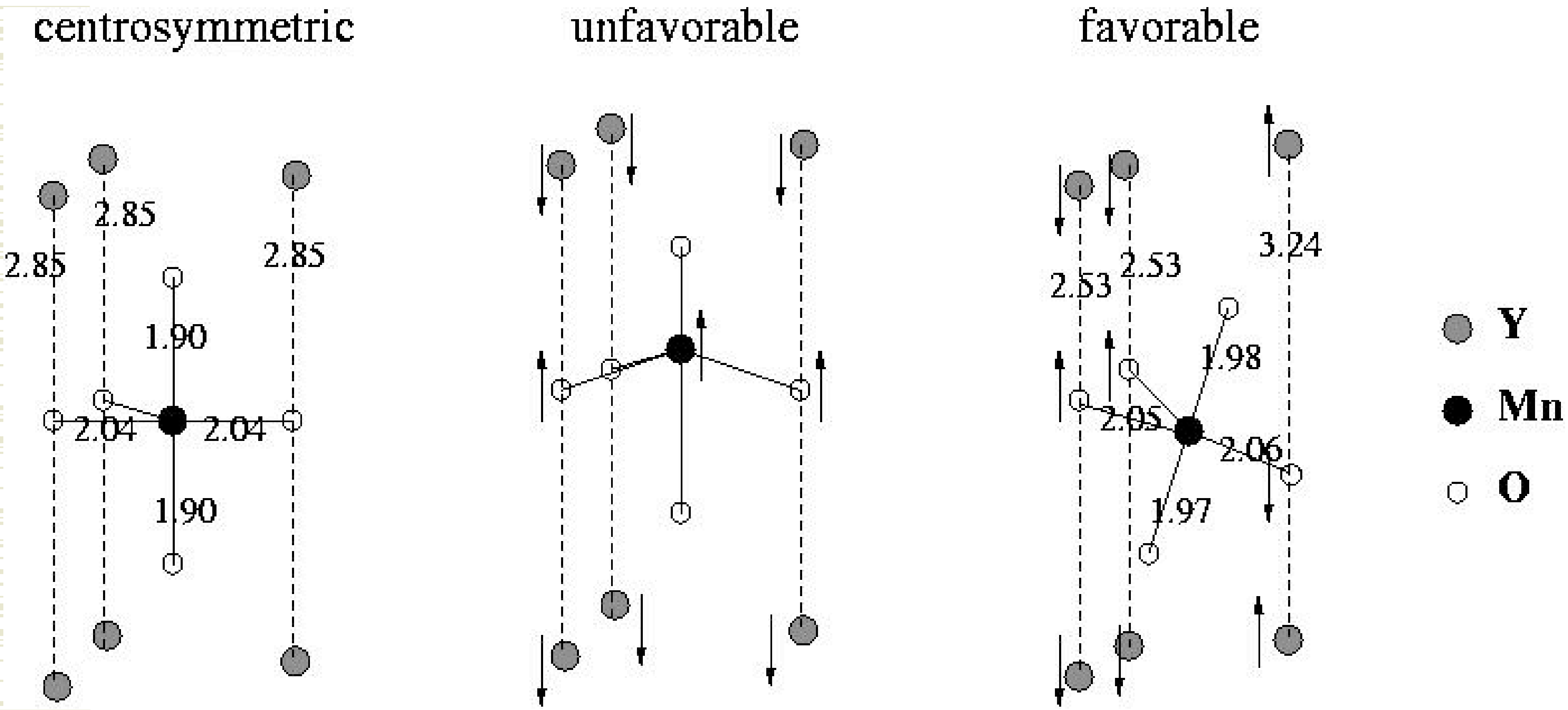


What's known about $YMnO_3$?

- Hexagonal perovskite structure, $P6_3cm$
- ABCACB stacking of oxygen layers
- Mn^{3+} ions 5-fold coordinated
- Y^{3+} in 7-fold coordinated interstices
- Antiferromagnetic, T_N=80K
- Ferroelectric along *c*, T_c=900K, **P**=5.5μC/cm^2
- $HoMnO_3$ – $LuMnO_3$ are analogous
- Also exists in non-FE cubic structure

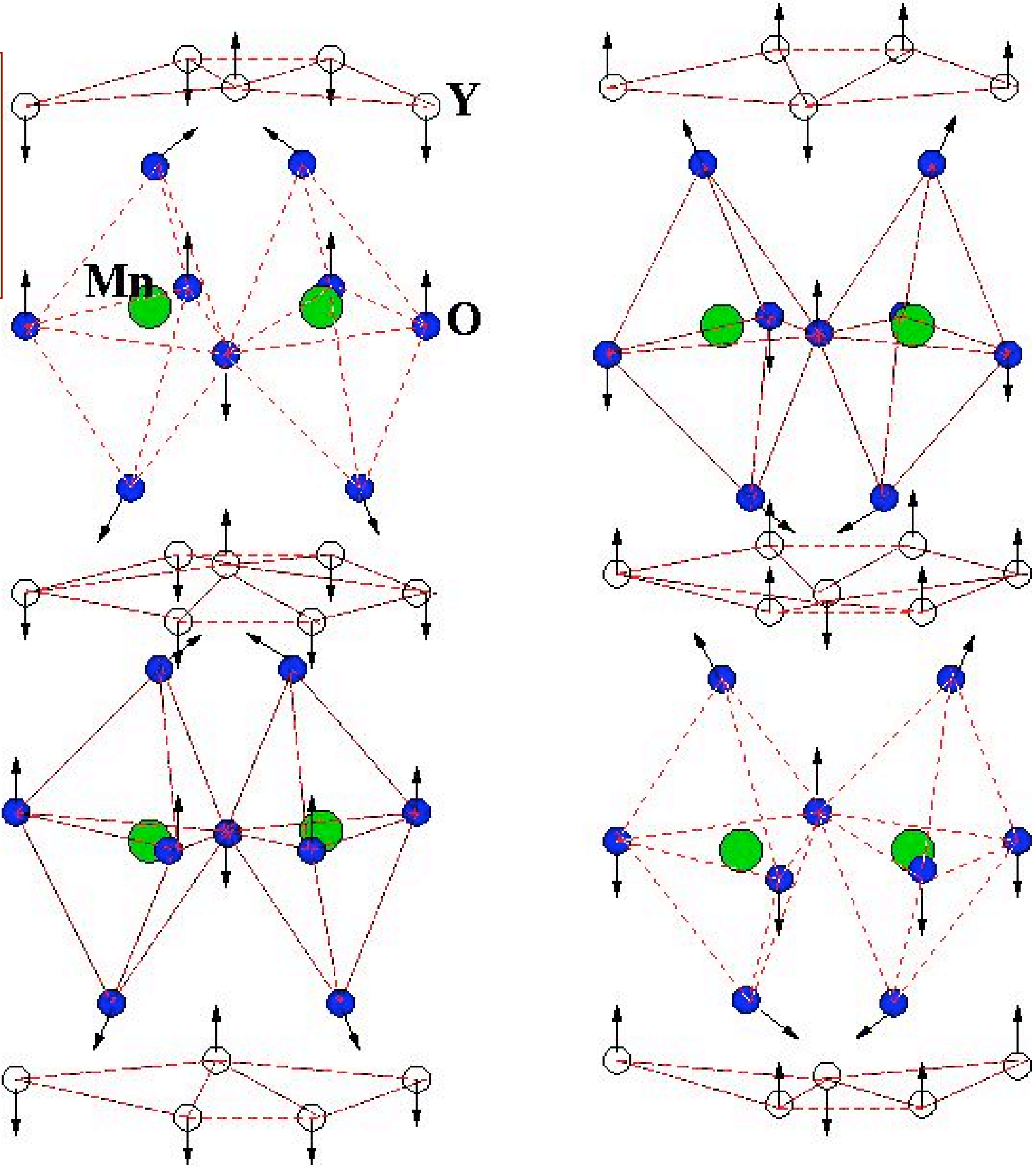


Possible instabilities



A. Filippetti and N.A. Hill, *Coexistence of magnetism and ferroelectricity in perovskites*, Phys. Rev. B **65**, 195120 (2002).

Two stable states:

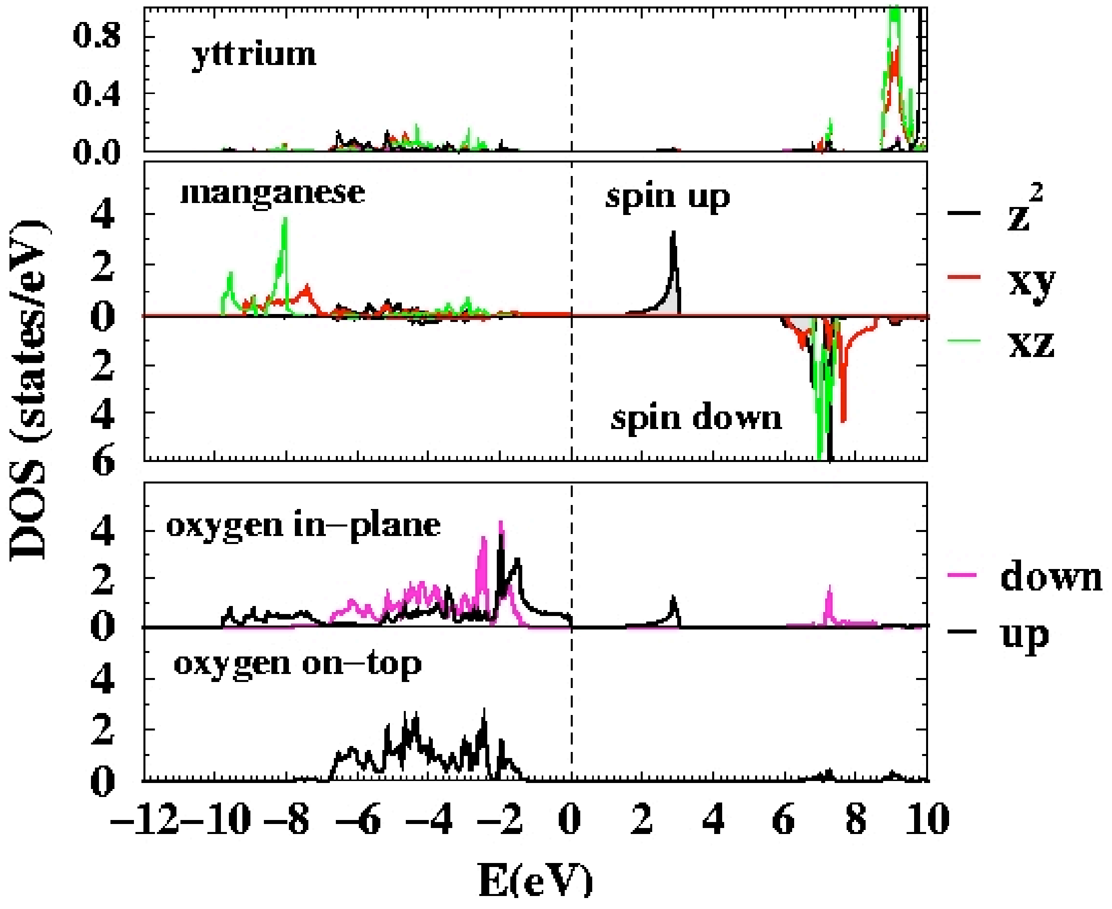


Usual indicators of instability do not hold

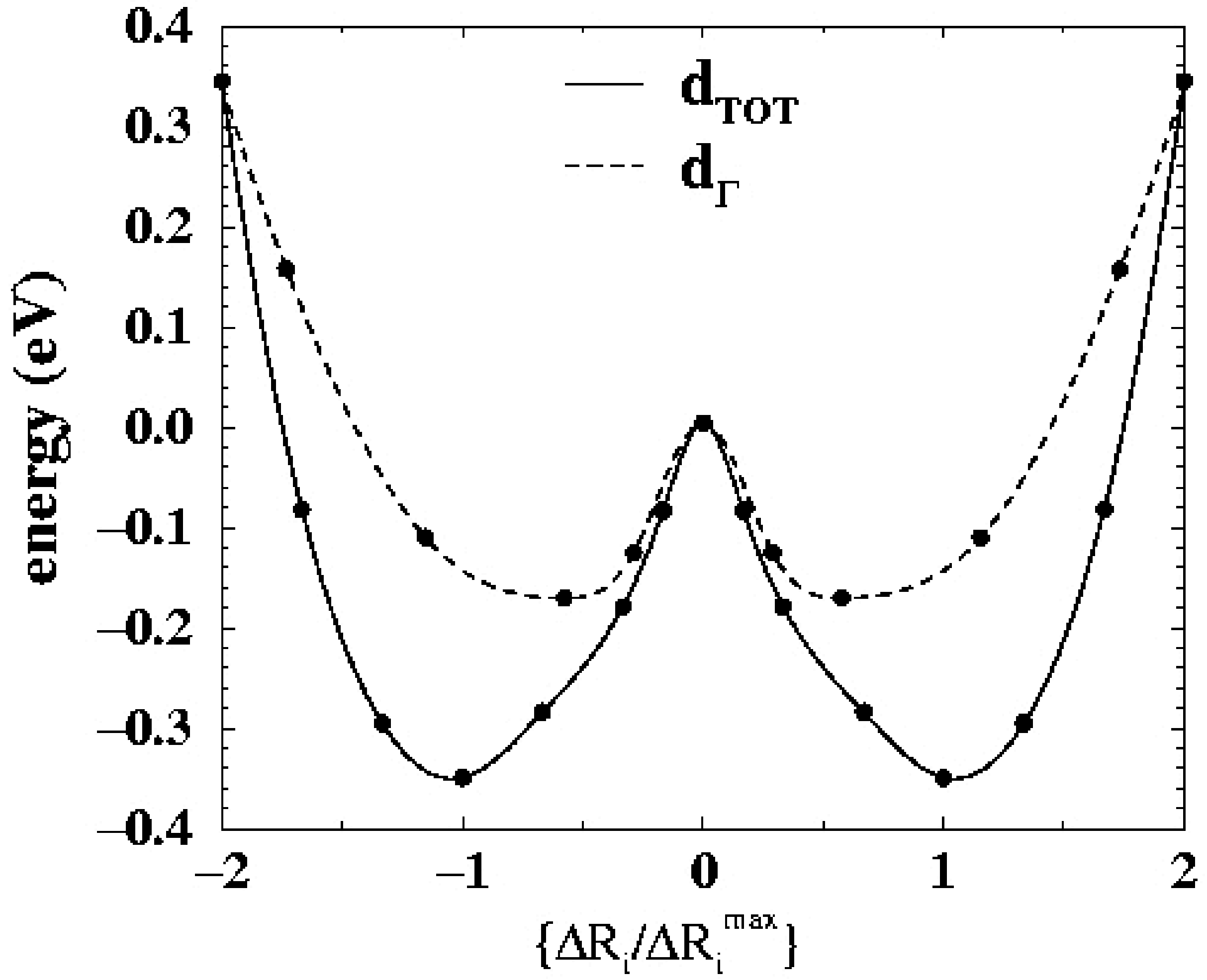
BECs:

Y	+3.6
Mn	+3.3
O_T	–2.3
O_P	–2.2

DOSs – no re-hybridization



Ferroelectricity results from the Γ point part of a primarily *rotational* instability!



Gamma point motion:

Y	↓	0.008
O1	↑	0.025
O2	↑	0.016
O3	↓	0.013

B.B. van Aken, T.T.M. Palstra, A. Filippetti and N.A. Spaldin, *Geometrically-driven ferroelectricity in hexagonal manganites*, in preparation.