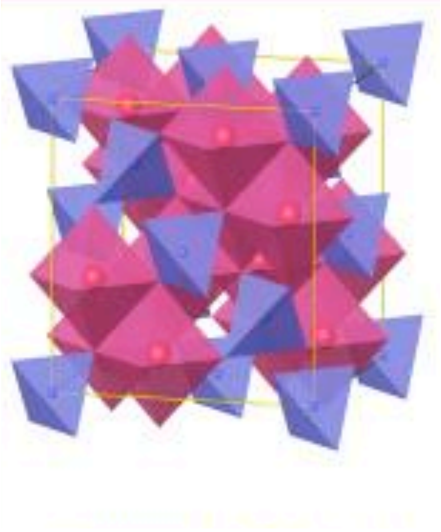
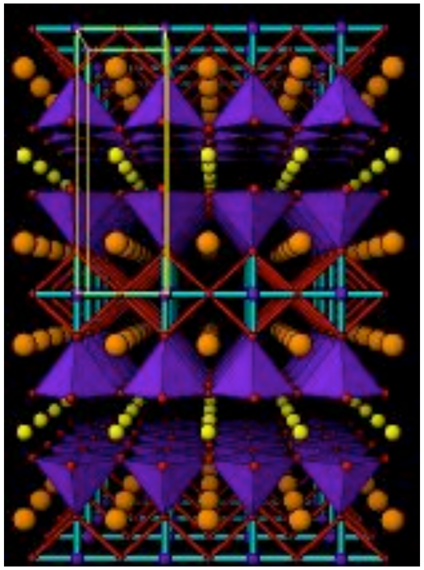
Grand Challenges in Oxides Research



Nicola Spaldin
Materials Department
UC Santa Barbara

nicola@mrl.ucsb.edu
805 893-7920



with valuable input from:

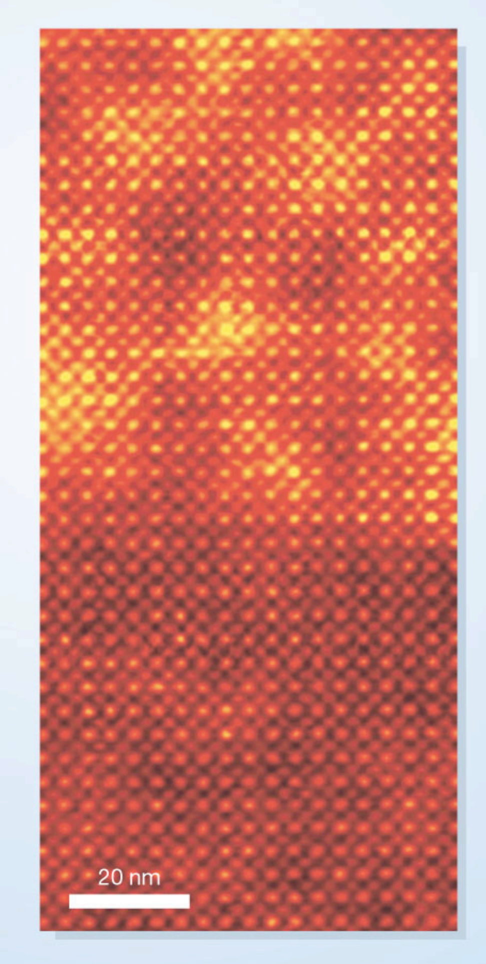
Leon Balents (UCSB), Jeroen van den Brink (U Leiden), Jaques Chakalian (U Arkansas), Matthew Fisher (UCSB), Michael Fisher (U Maryland), Supratik Guha (IBM), Werner Hanke (U Wurzburg), Daniel Khomskii (U Koln), R. Ramesh (UC Berkeley), Art Ramirez (Bell Labs.), Richard Scalletar (UC Davis), Darrell Schlom (Penn State), Jim Speck (UCSB), Susanne Stemmer (UCSB), Chris van de Walle (UCSB)

the CMMP 2010 and BESAC Grand Challenges reports

The simplest complex oxide: $SrTiO_3$

with
oxygen
vacancies

without
oxygen
vacancies



Semiconductor physics: The value of seeing nothing, J. Mannhart and D. G. Schlom, Nature 430, **620** (2004)

Atomic-scale imaging of nano-engineered oxygen vacancy profiles in $SrTiO_3$,
D. Muller et al., Nature 430, **657** (2004)

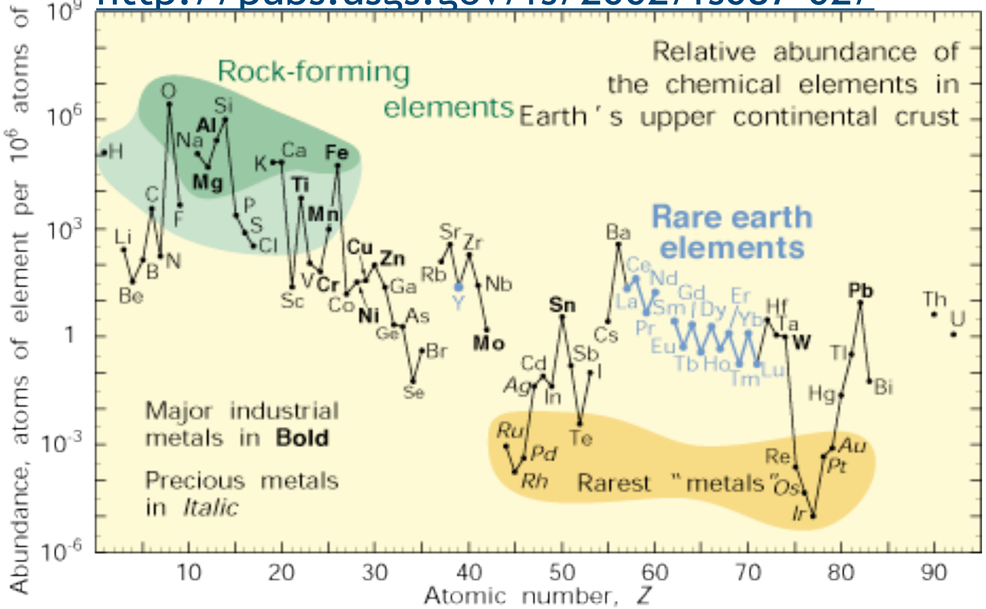
Grand challenge

To achieve the same level of synthetic control and fundamental understanding as is currently attained in semiconductors and simple metals

Why oxides?

abundance!

http://pubs.usgs.gov/fs/2002/fs087-02/



non-toxic

polarizability *just right*

- nitrides too covalent
- fluorides too ionic

diverse chemistries, structures and dimensionalities

strong correlations! behavior of one electron explicitly influences the others

Strong correlations

a wide range of couplings:	potential technological relevance:
electron-lattice	high-k dielectrics ferroelectricity high-T_c superconductivity large thermopower
electron-spin(-lattice)	multiferroism magnetoelectricity magnetoresistance spintronics
spin-orbital	piezomagnetism magnetic frustration

Spin/orbital/lattice couplings have similar energy scales

small energy changes (surfaces, interfaces, defects, external perturbations) can shift balance between competing large energy interactions and vastly alter ground state

⟶ TUNABILITY!

Strong correlations

<u>Spin/orbital/lattice couplings with similar energy scales</u>

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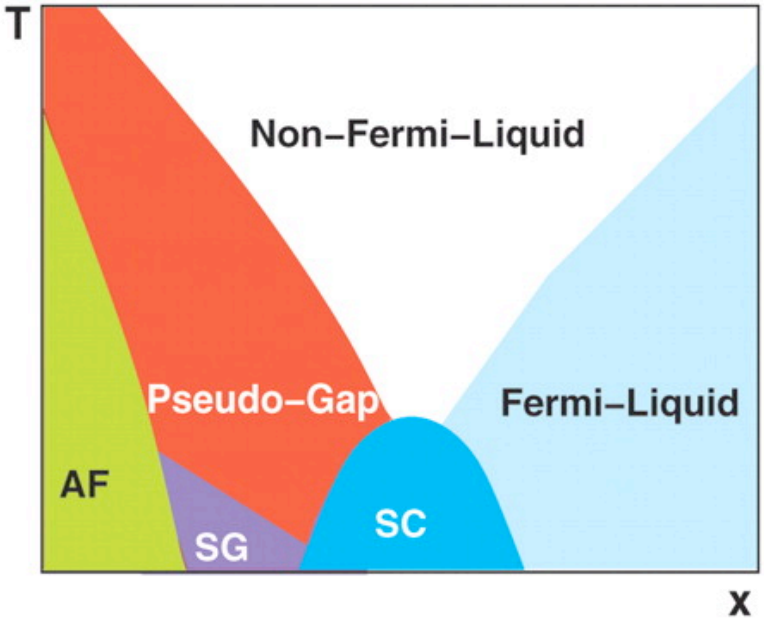
→ TUNABILITY!



Complexity in strongly correlated electronic systems, E. Dagotto, Science **309**, 257 (2005)

Comparison with conventional semiconductors

<u>Conventional semiconductors</u>

Physics:

- large overlap of s/p orbitals gives extended wavefunctions
- no intrinsic magnetism or other correlations

Technology:

- <u>Quality</u>: high! can be fabricated into complex structures
- <u>Understanding</u>: Semiconductor modeling is straightforward
- <u>Tunability:</u> control charge with modest doping/ E fields

MATERIALS
UC Santa Barbara

Comparison with conventional semiconductors

UCSB

Conventional semiconductors	Complex oxides
Physics:	Physics:
– large overlap of s/p orbitals gives extended wavefunctions	– localization of 3d/2p orbitals gives strong Coulomb interactions
– no intrinsic magnetism or other correlations	– diverse magnetic and other strong correlations
Technology:	Technology:
– Quality: high! can be fabricated into complex structures	– Quality: materials chemistry challenging; fabrication less developed
– Understanding: Semiconductor modeling is straightforward	– Understanding: strong correlations challenging to theoretical tools
– Tunability: control charge with modest doping/ E fields	– Tunability: high! due to competing ordered states

Comparison with conventional semiconductors

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Complex oxides

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- diverse magnetic and other correlations

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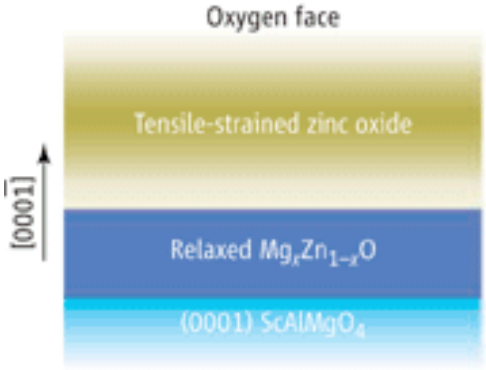
vastly richer physics suggests entirely new functionalities provided *Oxides Grand Challenge* can be met:

To achieve the same level of synthetic control and fundamental understanding as is currently attained in semiconductors and simple metals

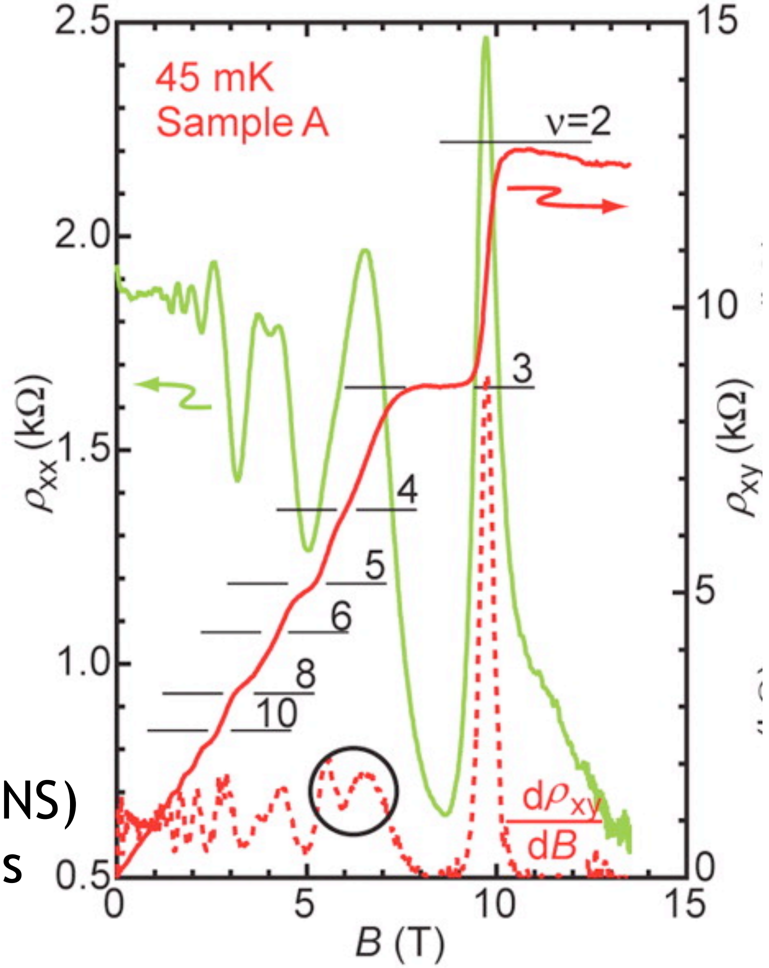
Why now?

Growth/synthesis:

Quantum Hall Effect at ZnO/(Zn,Mg)O interface ⟶ high quality samples



A. Tsukazaki et al. *Quantum Hall Effect in Polar Oxide Heterostructures*, Science **315**, 1388 (2007)



Understanding:

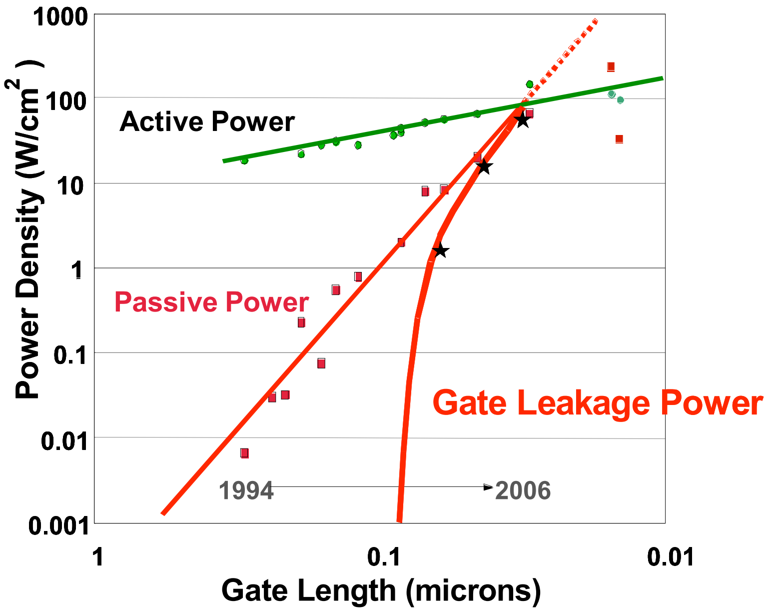
improved experimental probes (ARPES, STM, SNS)

theory/computation able to address intricacies numerically

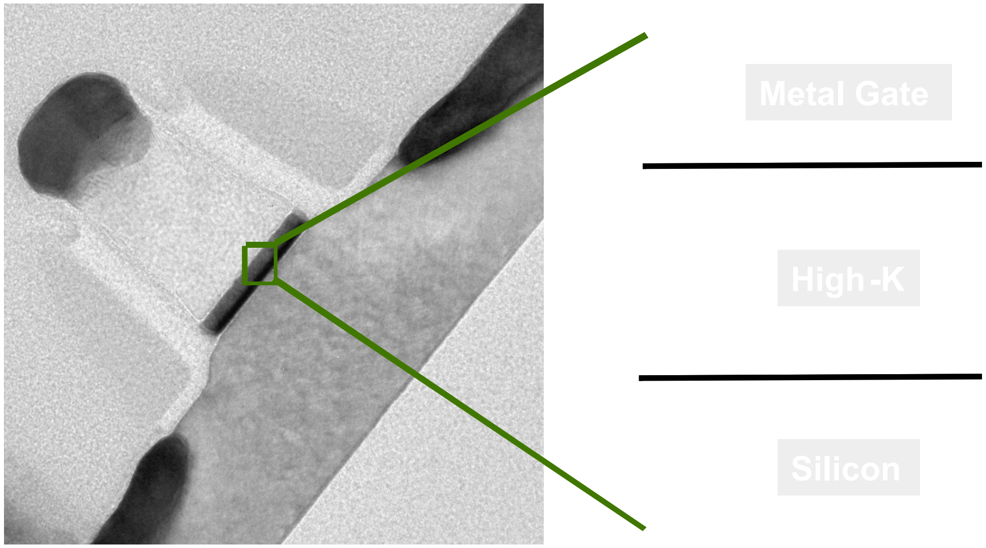
Existing technology need: High-k oxide-based CMOS technology:

Gate leakage power growing exponentially as gate length is reduced

C = k/d; Need a high-k replacement for SiO_2 to continue CMOS scaling



Fully processed transistor with high-k/metal gate:



IBM high-k product : Expected 2008

This is the first major technology application for nanoscale metal oxides in electronics

Outline

To achieve the same level of synthetic control and fundamental understanding as is currently attained in semiconductors and simple metals

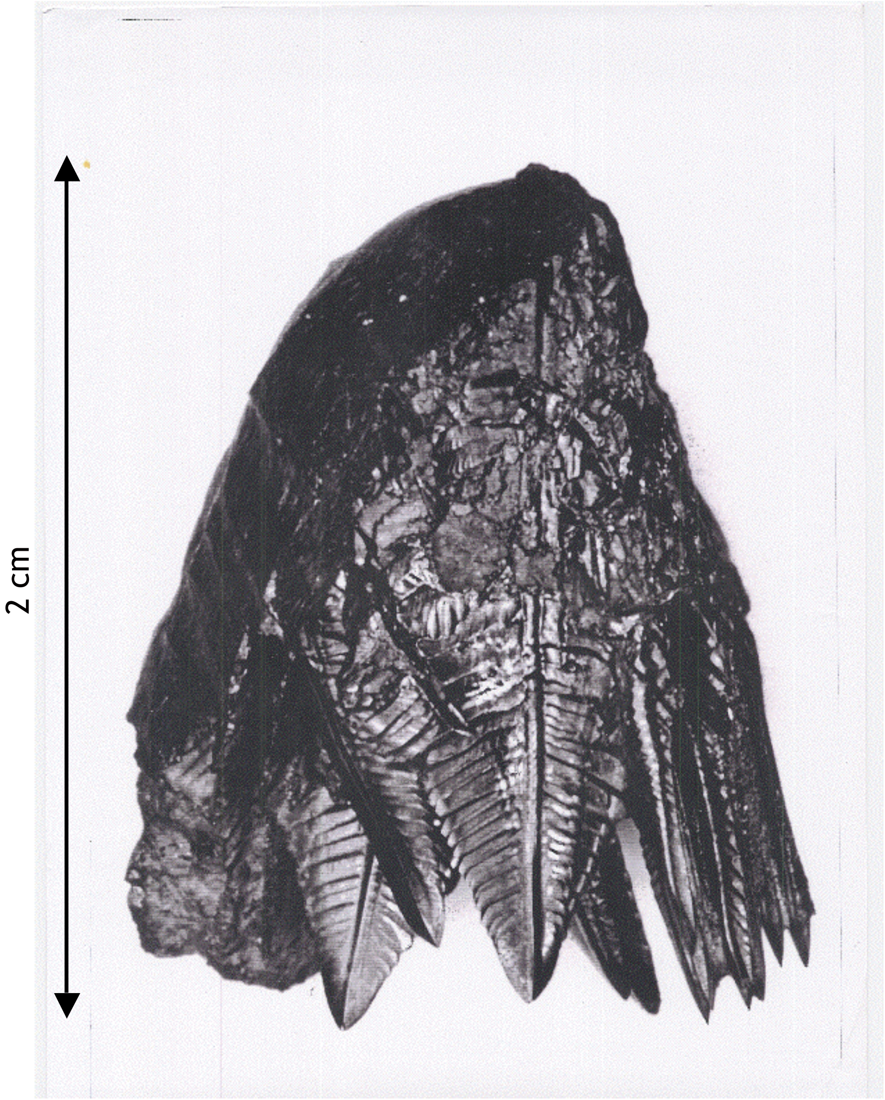
Sub-challenges:

- growth/synthesis
- theory/computation

Two most exciting current/developing areas:

- oxide-oxide interfaces
- multi-functional oxides
- A “mini seminar” on theory/experiment interplay in multiferroics

Challenge: Synthesis



BiFeO$_3$

grown from B$_2$O$_3$/Bi$_2$O$_3$/Fe$_2$O$_3$ flux

Bi$_2$Fe$_4$O$_9$ more stable
Fe$_3$O$_4$ decomposition product!

Single crystal growth

<u>need for bulk single crystal growth</u>

- best (sometimes essential) for accurate characterization (dielectric measurements, neutrons, x-rays)
- required as substrates for homoepitaxy
- new materials: ternaries and quaternaries

<u>dedicated equipment and operators</u>

- many oxides melt at high temperatures (> 1500°C)
- some require toxic fluxes (e.g. Bi)
- some require high pressure (many Bi-based multiferroics)

New materials synthesis and crystal growth study
Paul Peercy and Art Ramirez, tomorrow am

cubic anvil press at Kyoto University

typical operation: 6GPa and 1000°C

Thin film growth

Films offer additional capabilities

stabilizing phases which are not the bulk thermodynamic ground state

chemical control through layer-by-layer deposition

multilayers with precisely engineered interfaces

modifying properties with strain

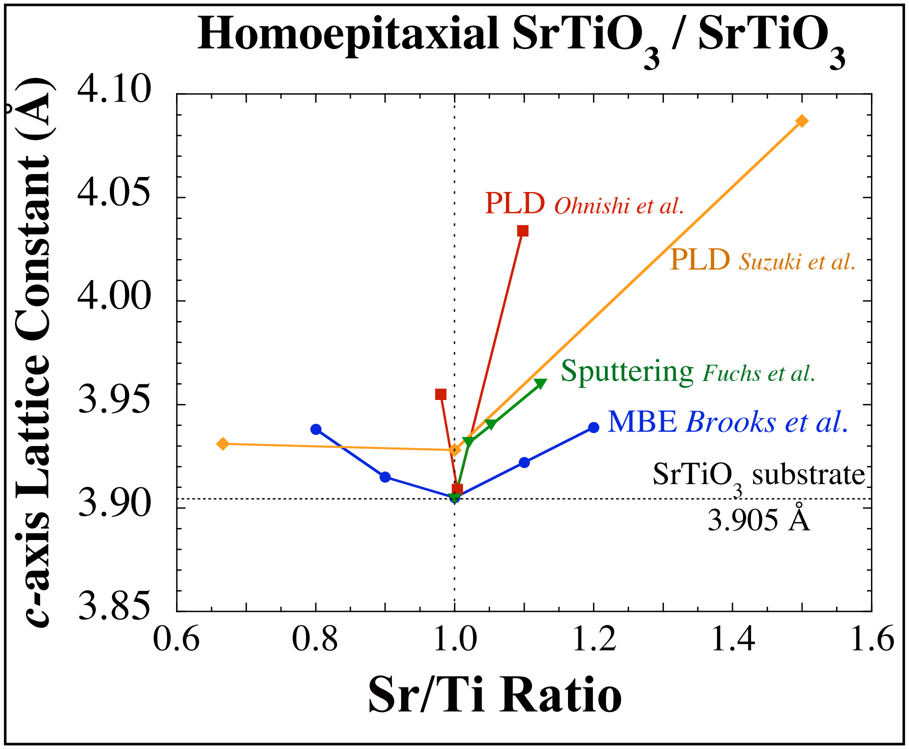
required for devices

Need for improved film quality

complex oxide films are often far from stoichiometry

current composition control limits around 1%

oxide MBE (molecular beam epitaxy) versus PLD (pulsed laser deposition)



Challenges in theoretical description of complex oxides

strong correlations lead to many-body effects

- traditionally (successfully) described with model Hamiltonians

Steven White
tomorrow am

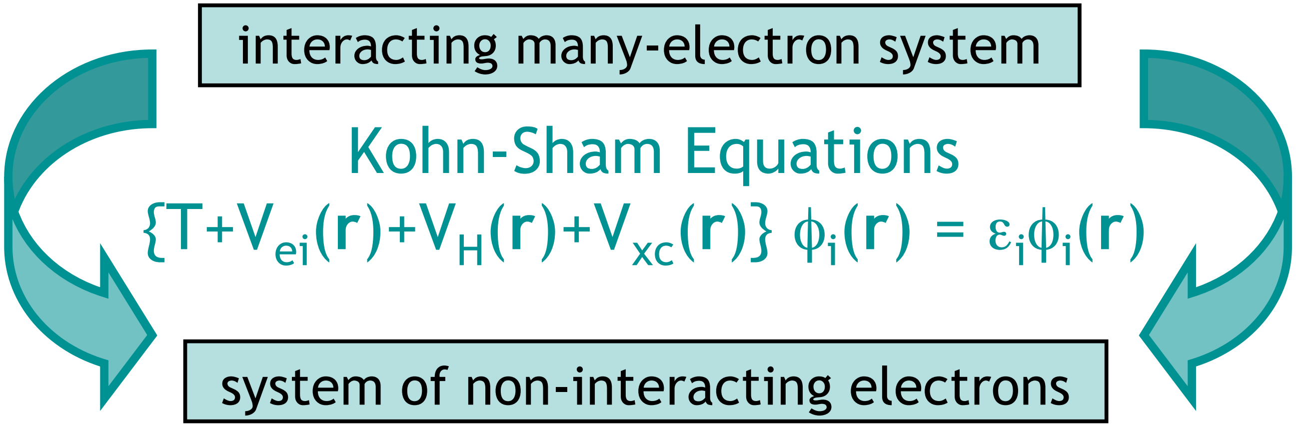
complete description of structure and chemistry essential

- traditionally (successfully) performed within a mean-field treatment

need techniques that include chemistry, structure and many-body interactions on an equal footing

Incorporating many-body effects in "structure and chemistry" methods

Density Functional Theory



interacting many-electron system

Kohn-Sham Equations

$$\{T+V_{ei}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\}\ \phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

system of non-interacting electrons

Allows us in principle to calculate ground state properties:

charge densities and energies, **crystal structures**, electronic band structures, **magnetic ordering**, phonon frequencies, **ferroelectric polarizations**, dielectric response, piezoelectric coefficients…

Incorporating many-body effects in "structure and chemistry" methods

$\{T+V_{ei}(r)+V_H(r)+ V_{xc}(r) \}\ \phi_i(r) = \varepsilon_i\phi_i(r)$

BUT…

$V_{xc}(r)$ is approximated

"Standard" local density approximation (LDA) treats as a homogeneous electron gas

Beyond-LDA methods:

- LDA+U attempts to incorporate Coulomb repulsions (U)
- Self-interaction corrections (SIC) attempt to account for spurious self-XC
- LDA+DMFT (dynamical mean field theory)

Downfolding:

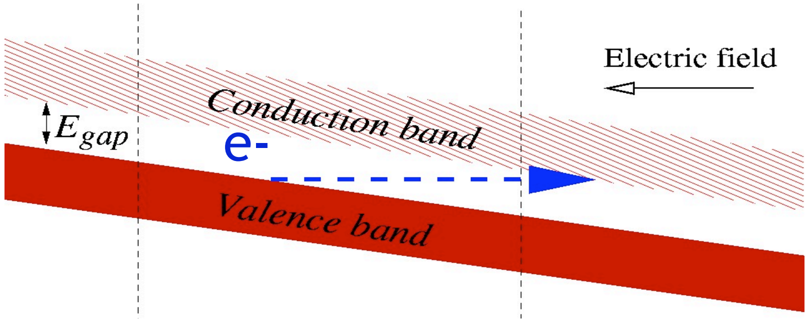
- Extract essential interaction parameters from LDA and construct a model

Needs:

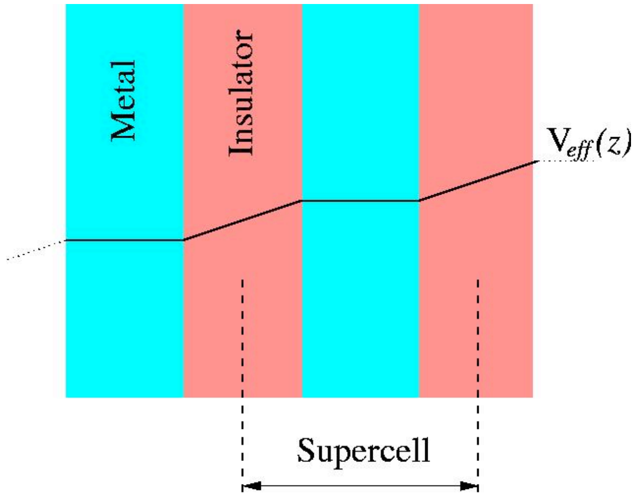
- Greater supercomputing capacity in central facilities
- A system for supporting the maintenance of public codes

Other challenges in DFT-based theory: Finite Electric Fields

Two difficulties:



1) Infinite crystal in uniform external field <u>does not have a ground state:</u>



2) Potential with electric field is <u>non-periodic</u>

Solved (very recently) using tricks:

I. Souza, J. Iniguez and D. Vanderbilt, *First-principles approach to insulators in finite electric fields*, Phys. Rev. Lett. **89**, 117602 (2002)

M. Stengel and N.A. Spaldin, *Ab-initio theory of metal-insulator interfaces in finite electric field*, PRB **75**, 205121 (2007).

Outline

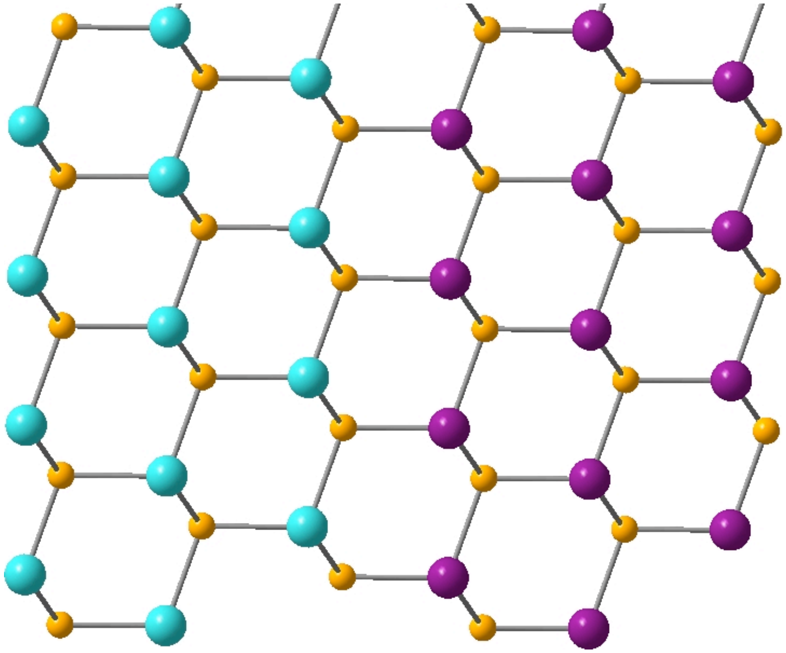
Sub-challenges:

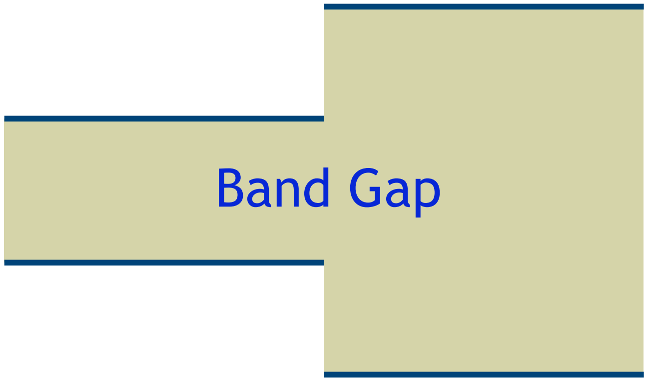
- growth/synthesis
- theory/computation

Two most exciting current/developing areas:

- oxide-oxide interfaces
- multi-functional oxides
- A “mini seminar” on theory/experiment interplay in multiferroics

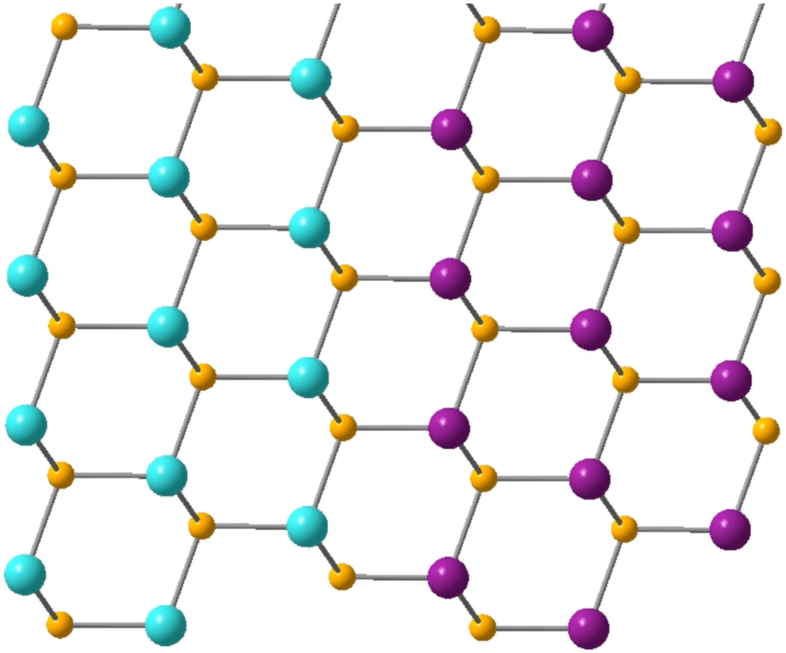
Oxide-oxide interfaces

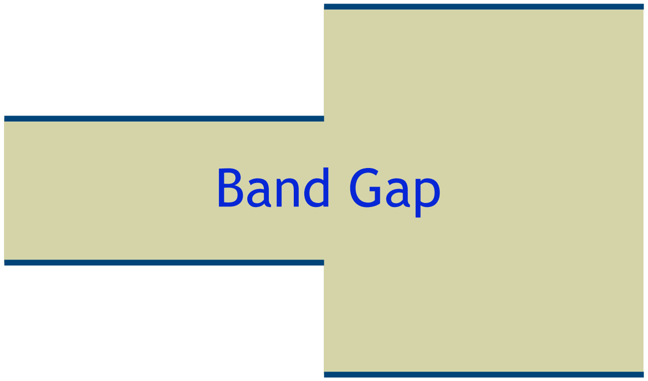


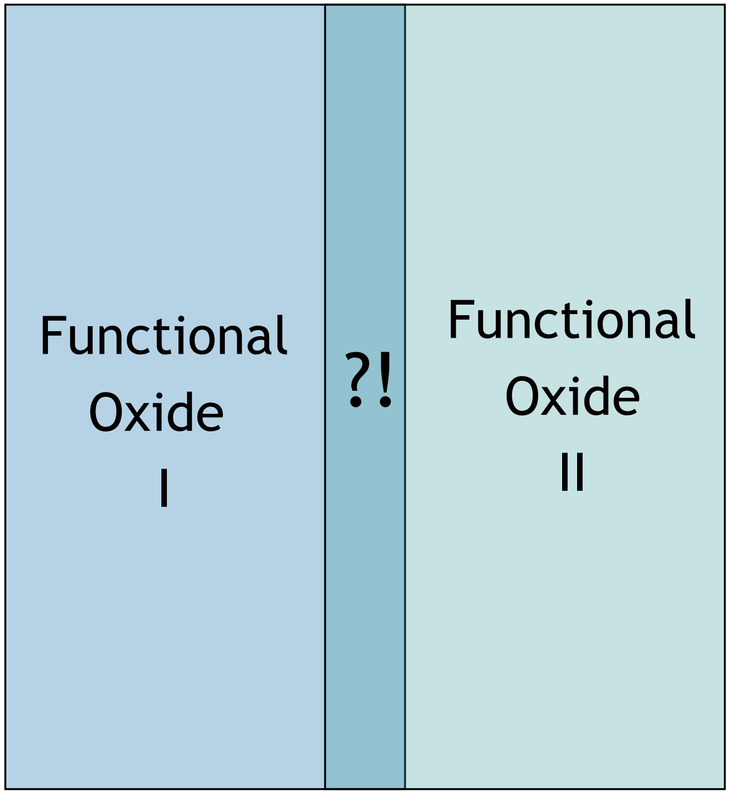


“The interface is the device”
Herbert Kroemer,
Nobel lecture, Dec 8 2000

Oxide-oxide interfaces







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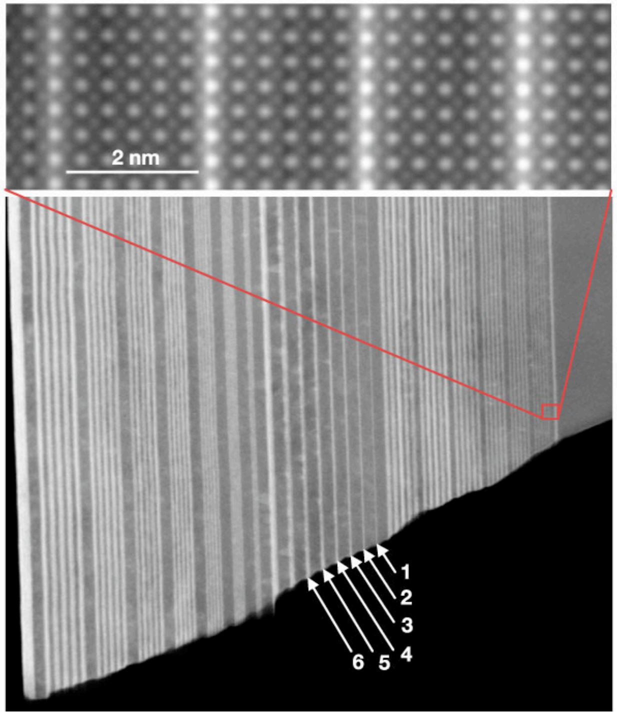
Example of new functionality at oxide-oxide interfaces

Electron microscopy image of $LaTiO_3$ layers (bright) spaced by $SrTiO_3$ layers



Artificial charge modulation in atomic scale perovskite titantate superlattices, A. Ohtomo et al., Nature **419**, 378 (2002)

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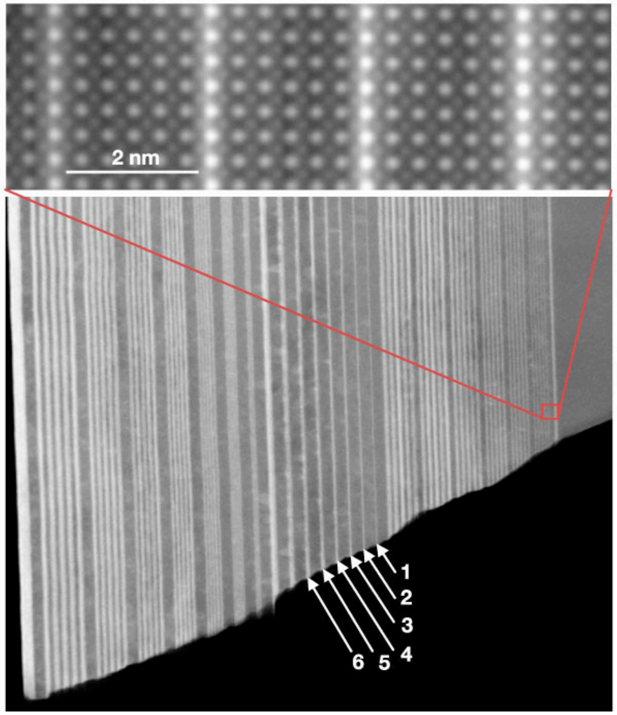

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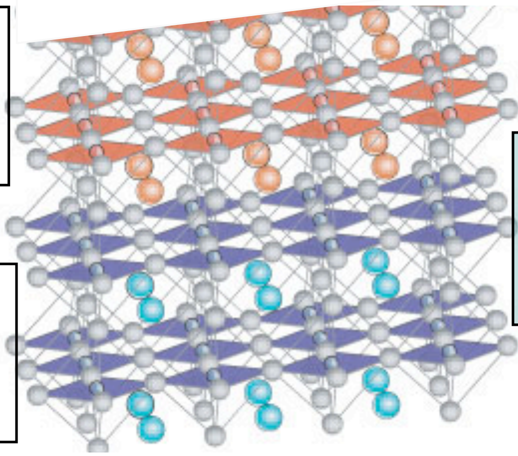

$LaTiO_3$
Ti^{3+} $(3d)^1$
Mott insulator

$SrTiO_3$
Ti^{4+} $(3d)^0$
Band insulator

LaO
TiO_2 (Ti^{3+}) ($3d^1$)

LaO
TiO_2 (Ti??)
SrO

TiO_2 (Ti^{4+}) ($3d^0$)
SrO

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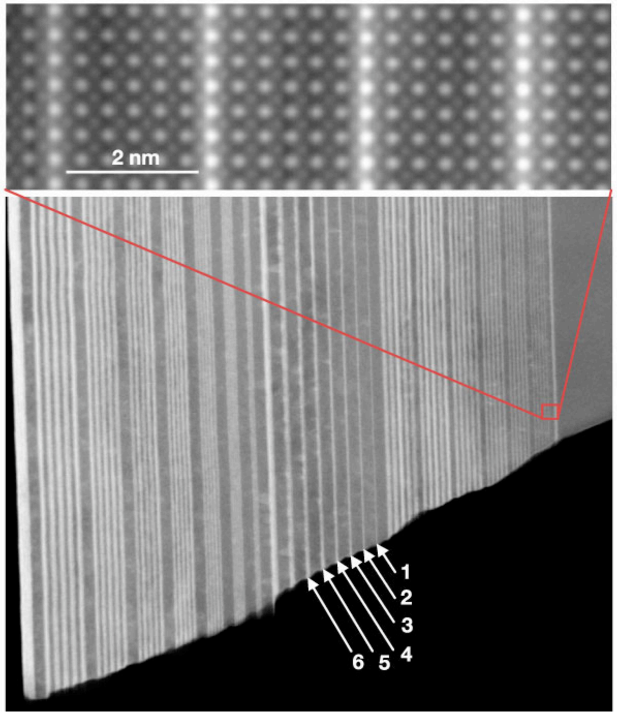

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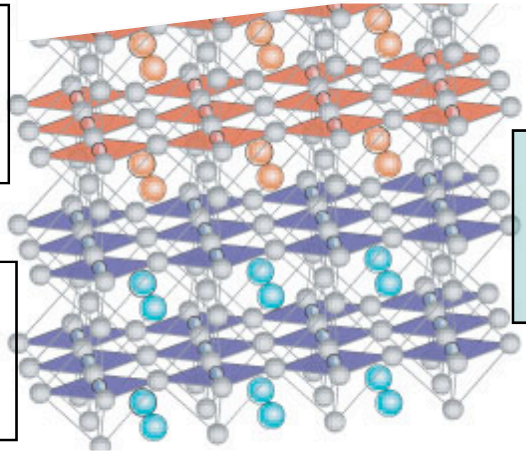
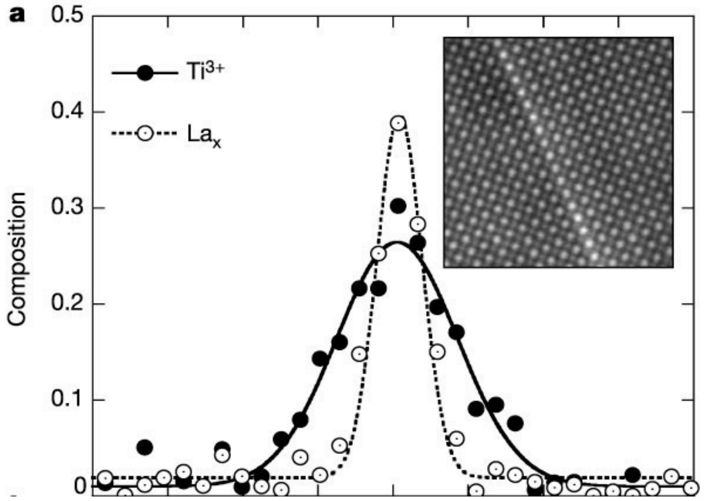


LaO
TiO_2 (Ti^{3+}) ($3d^1$)

LaO
TiO_2 (Ti??)
SrO

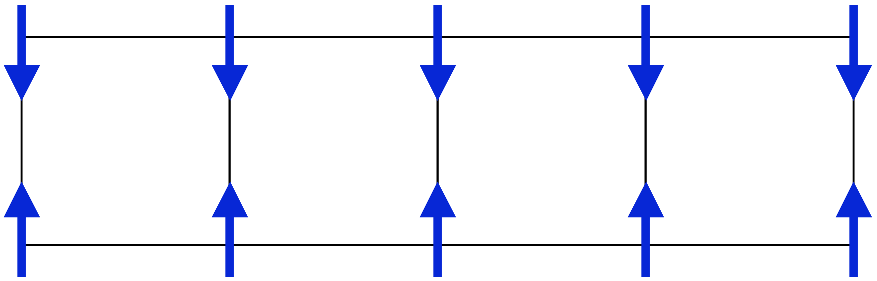
TiO_2 (Ti^{4+}) ($3d^0$)
SrO

The conflicted d electron spreads out…

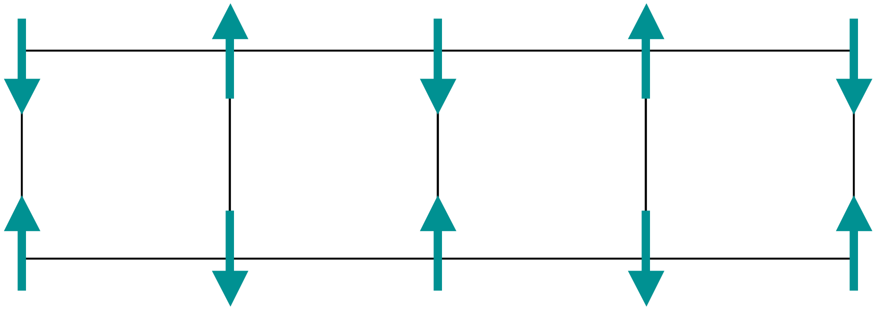


→ (magnetic) metal at the interface!

Incompatible magnetism at oxide-oxide interfaces

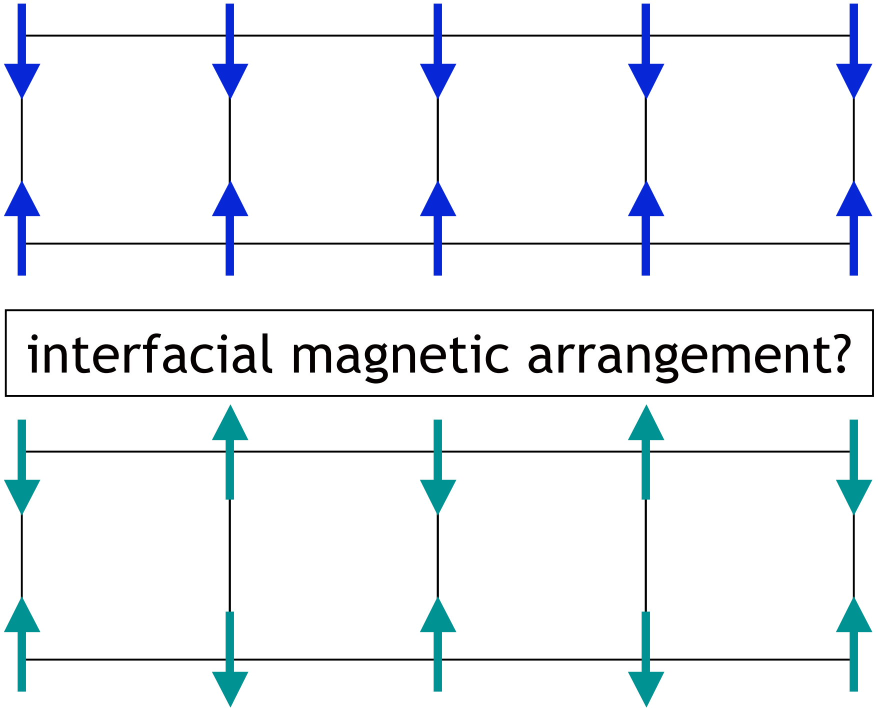


"A-type" antiferromagnet
e.g. $LaMnO_3$



"G-type" antiferromagnet
e.g. $LaFeO_3$

Frustrated magnetism at oxide-oxide interfaces



interfacial magnetic arrangement?

“A-type” antiferromagnet
e.g. $LaMnO_3$

“G-type” antiferromagnet
e.g. $LaFeO_3$

Possibilities: frustrated magnetism, change in orbital ordering at interface (propagation into bulk?), charge transfer/change in oxidation states, ???

HUGE POTENTIAL!

Outline

Sub-challenges:

- growth/synthesis
- theory/computation

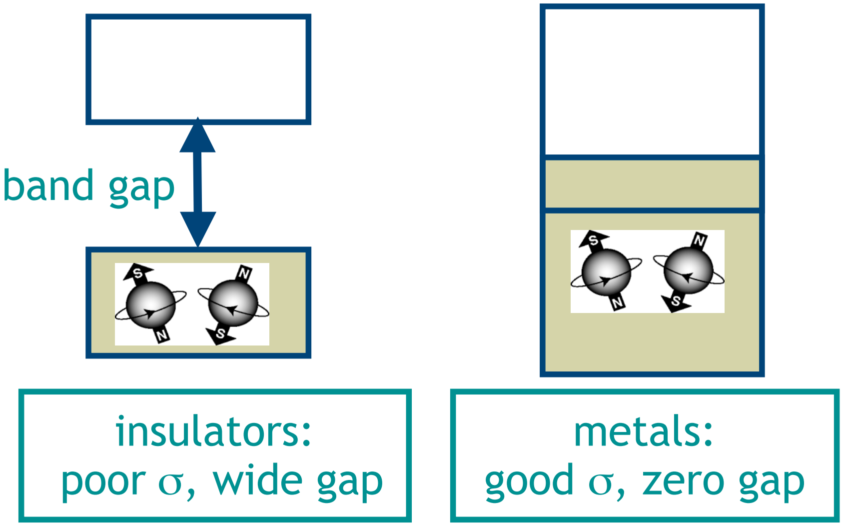
Two most exciting current/developing areas:

- oxide-oxide interfaces
- multi-functional oxides
- A “mini seminar” on theory/experiment interplay in multiferroics

Combine multiple functionalities in a single phase oxide

Often chemically or physically *contra-indicated*

high conductivity and wide band gap (transparent conductors)



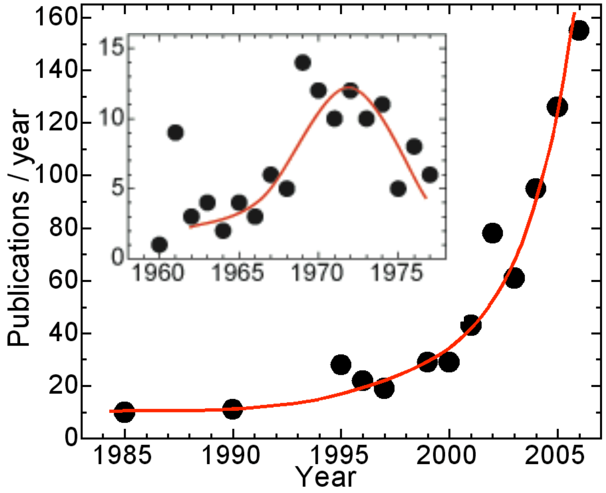
insulators:
poor σ, wide gap

metals:
good σ, zero gap

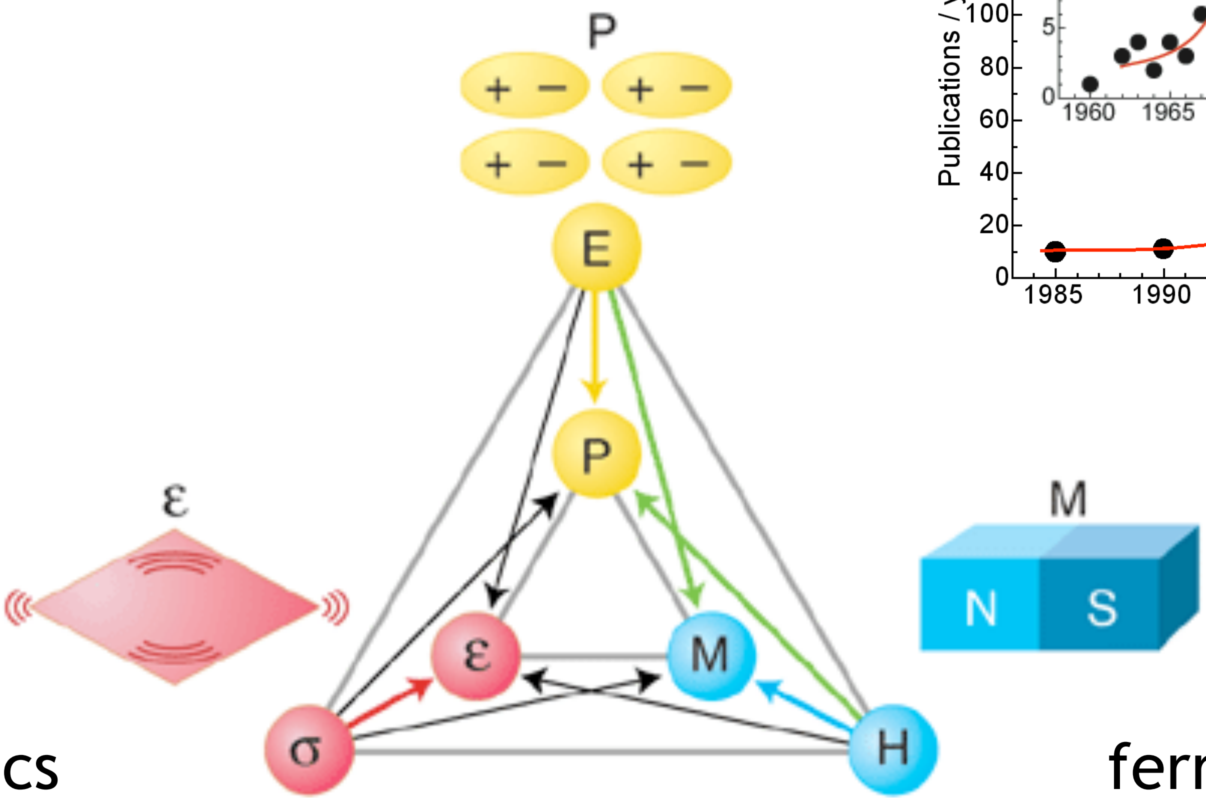
high electrical conductivity, high Seebeck coefficient, low thermal conductivity (thermoelectrics)

ferromagnetism and ferroelectricity (magnetoelectric multiferroics)

Multifunctional oxides: Magnetoelectric Multiferroics



ferroelectrics



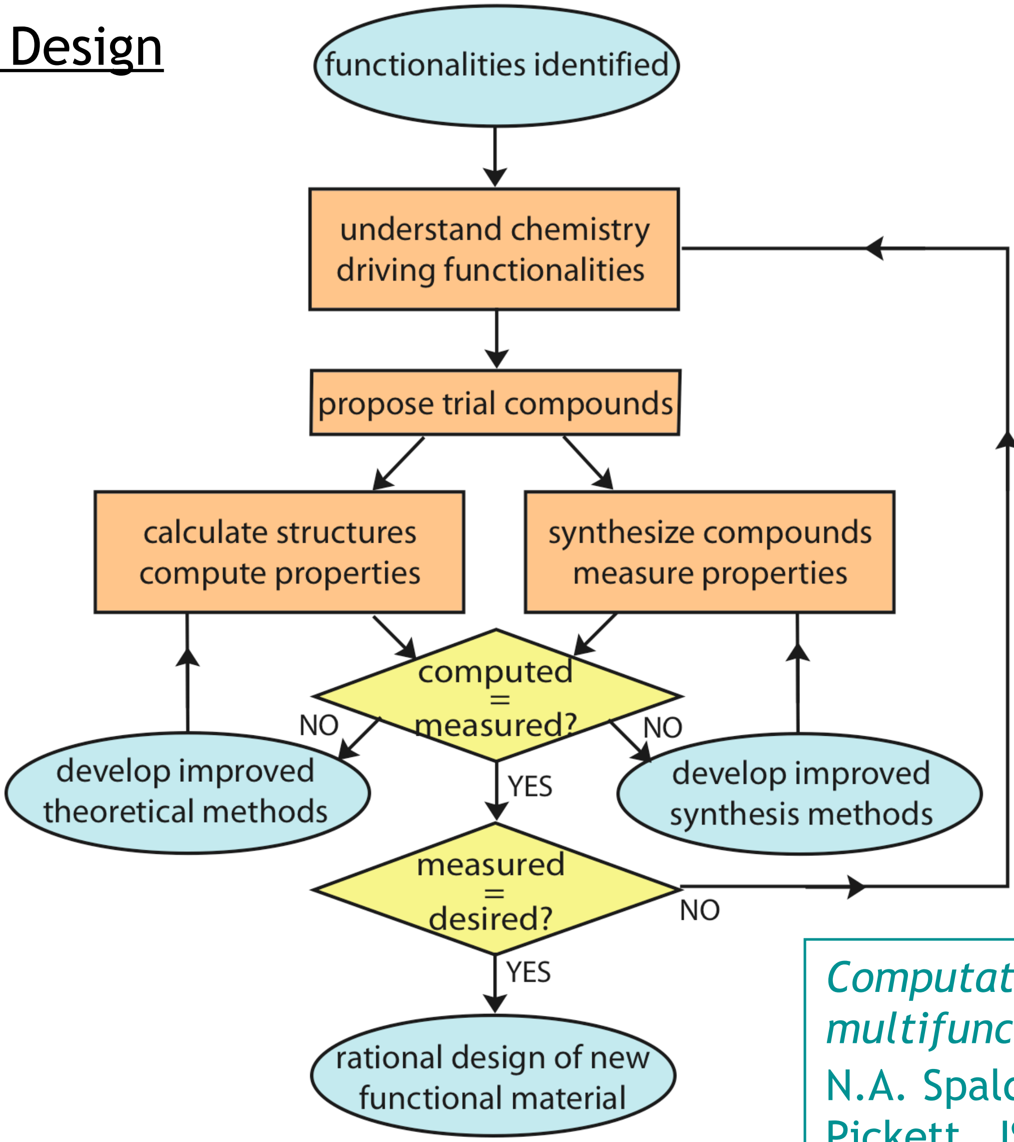
ferroelastics

ferromagnets

The renaissance of magnetoelectric multiferroics, N. A. Spaldin and M. Fiebig, Science **15**, 5733 (2005)

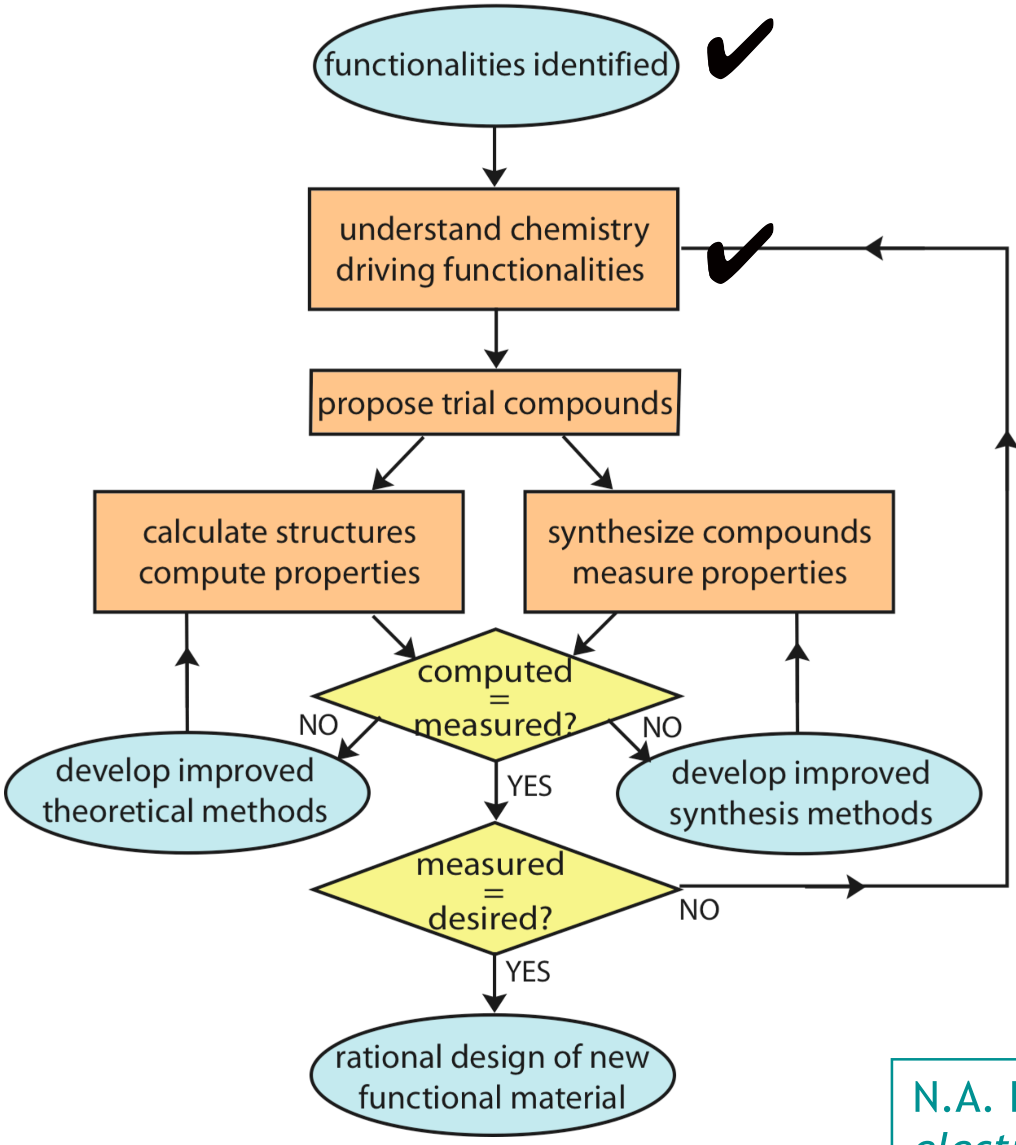
Interplay between theory and experiment

Goal: Materials by Design



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

“Designer” multiferroics



✔ functionalities identified

✔ understand chemistry driving functionalities

propose trial compounds

calculate structures compute properties

synthesize compounds measure properties

computed = measured?

NO

develop improved theoretical methods

NO

develop improved synthesis methods

YES

measured = desired?

NO

YES

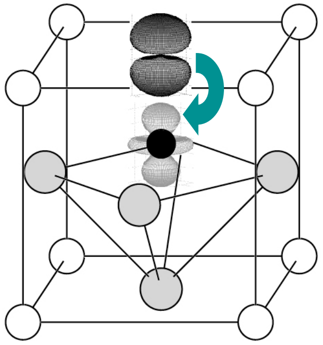
rational design of new functional material

Ferromagnetism and ferroelectricity

Theory (DFT):

conventional FM requires d electrons

conventional FE requires “d^0-ness”



FM and FE are

CHEMICALLY CONTRA-INDICATED

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

Propose trial compounds

either

1) use an alternative mechanism for P

or

2) use an alternative mechanism for M

Propose trial compounds

either

1) use an alternative mechanism for P

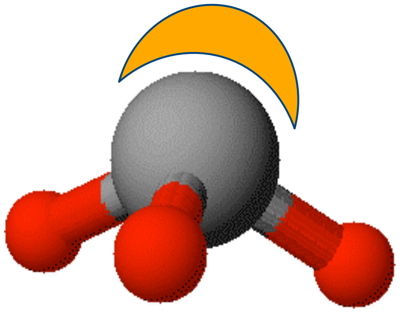
or

2) use an alternative mechanism for M

Propose trial compounds: New mechanisms for ferroelectricity

Theory: lone pair active

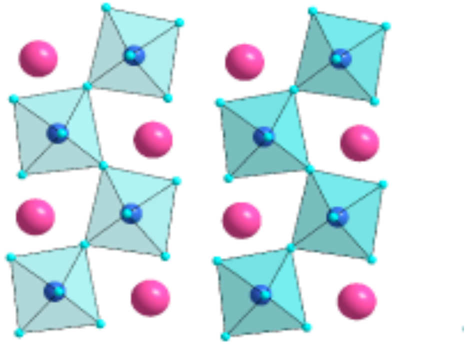
e.g. $BiMnO_3$, $BiFeO_3$



Theory: geometric ferroelectricty

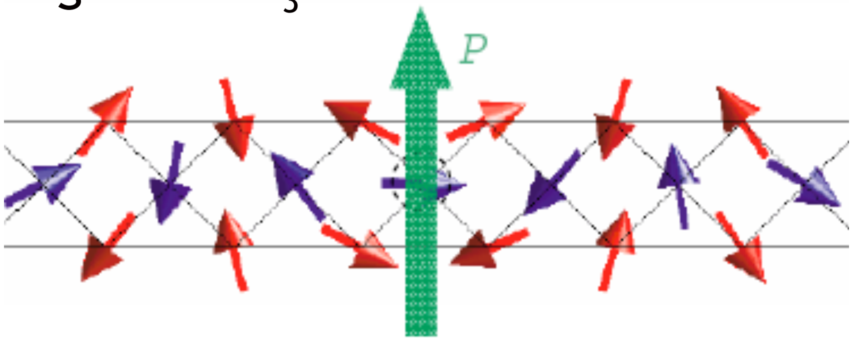
e.g. $BaNiF_4$

C. Ederer and N.A. Spaldin, Electric-field switchable magnets: The case of $BaNiF_4$, PRB **74**, 020401(R) (2006)



Experiment: magnetically driven

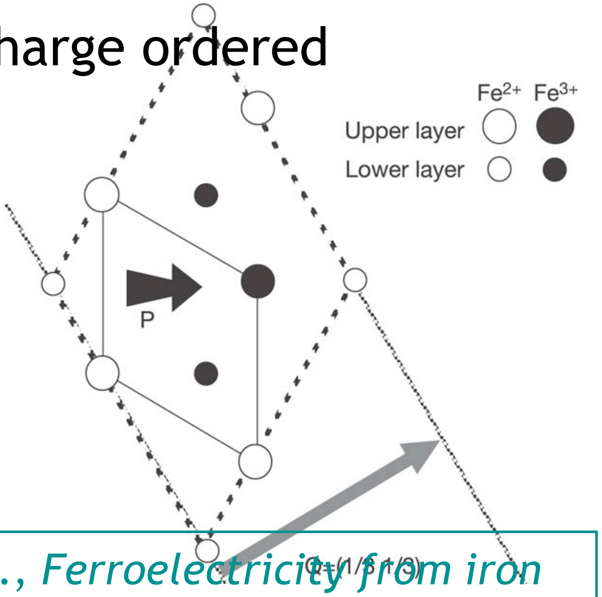
e.g. $TbMnO_3$



T. Kimura et al., *Magnetic control of ferro-electric polarization*, Nature **426**, 55 (2004)

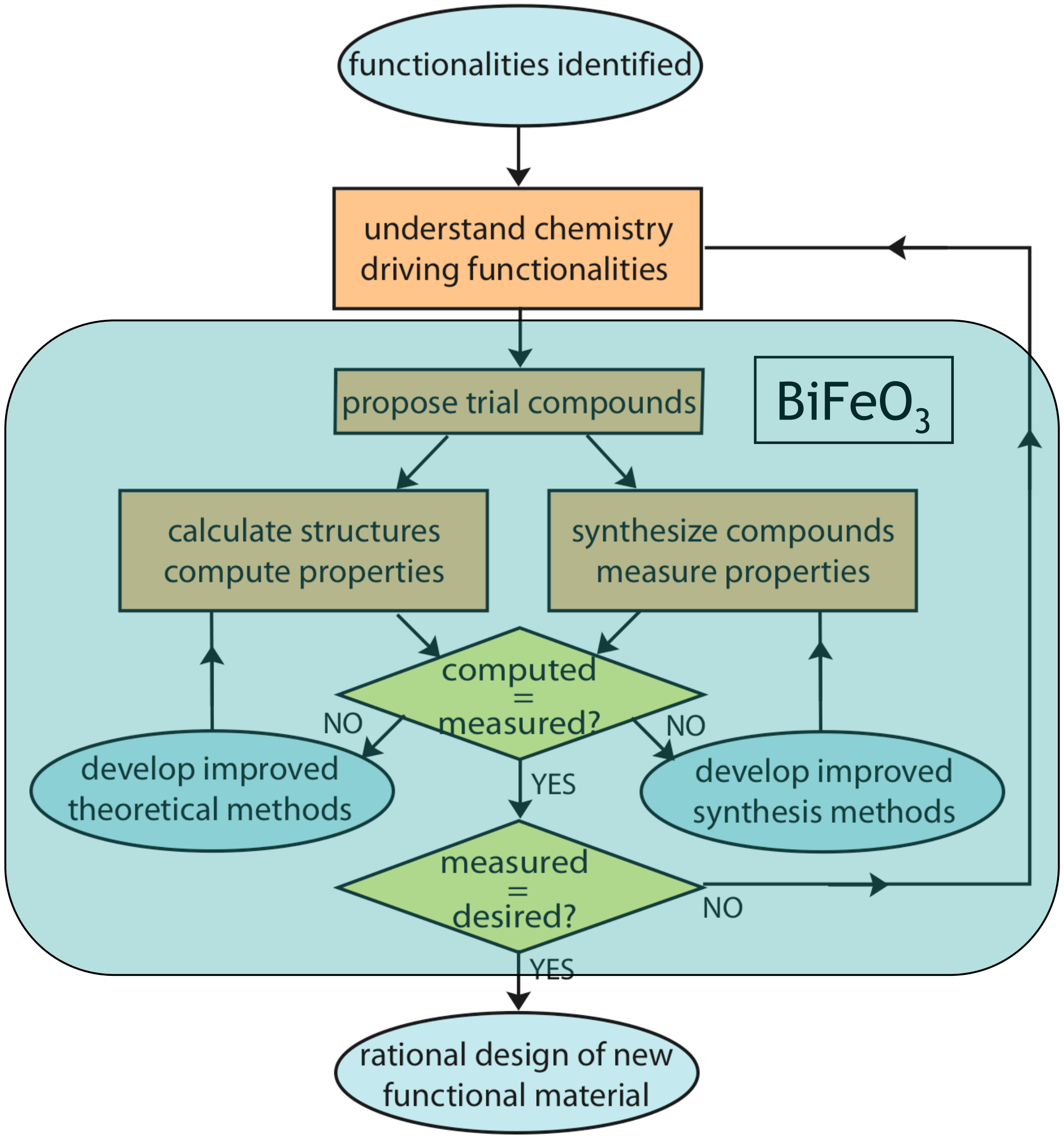
Experiment: charge ordered

e.g. $LuFe_2O_4$



N. Ikeda et al., *Ferroelectricity from iron valence ordering in the charge-frustrated system $LuFe_2O_4$*, Nature 436, 1136 (2005)

“Designer” multiferroics: $BiFeO_3$



functionalities identified

understand chemistry driving functionalities

propose trial compounds

$BiFeO_3$

calculate structures compute properties

synthesize compounds measure properties

computed = measured?

NO

develop improved theoretical methods

NO

develop improved synthesis methods

YES

measured = desired?

NO

YES

rational design of new functional material

Old literature on $BiFeO_3$

rhombohedrally-distorted perovskite (R3c)

ferroelectric,

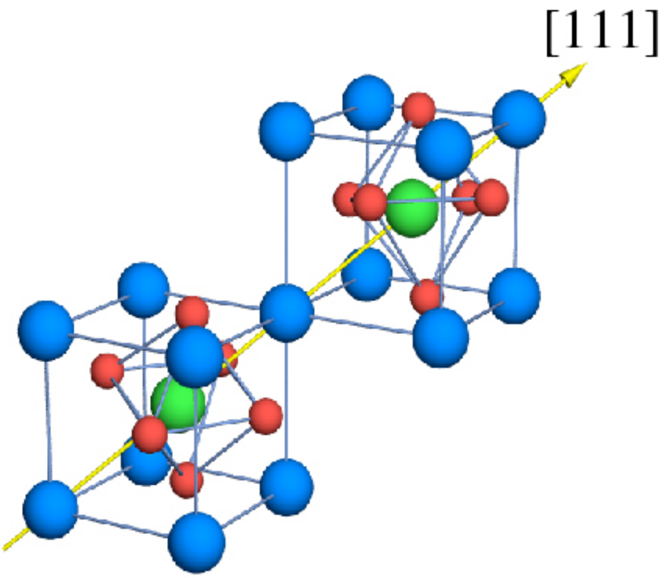
$T_c = 1103K$

$P = 6\ \mu C/cm^2$

antiferromagnetic (G-type), $T_N = 643K$

possible weak ferromagnetism?

incommensurate long-wavelength spin spiral



J.R. Teague, R. Gerson and W.J. James, Sol. Stat. Comm. **8**, 1073 (1970)

G.A. Smolenskii and I. Chupis, Sov. Phys. Usp. **25**, 475 (1982)

Questions

Why is the polarization so small?

Is there a weak ferromagnetism?

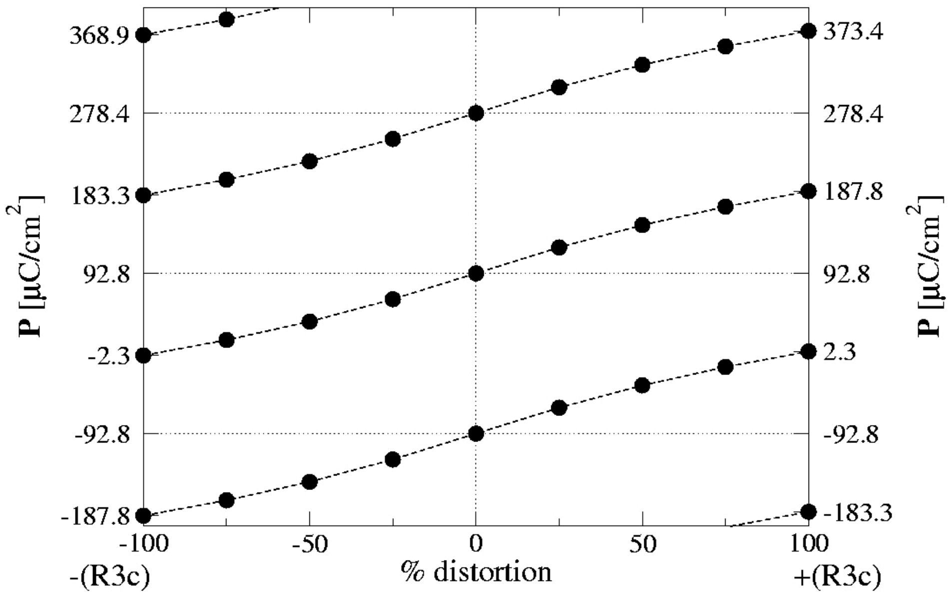
If so, does the magnetism couple to the ferroelectricity?

Desirable:

Developments in theory

Beyond LDA methods: Centrosymmetric reference structure metallic in LSDA

Modern theory of polarization: Non-zero P in centrosymmetric structure

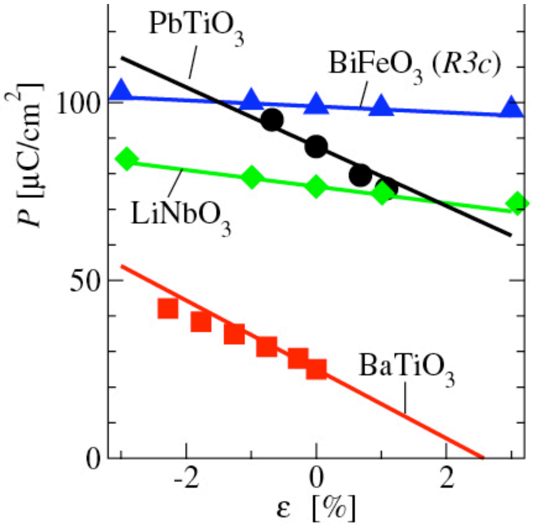


Calculate P = 95 μC/cm^2 along [111]

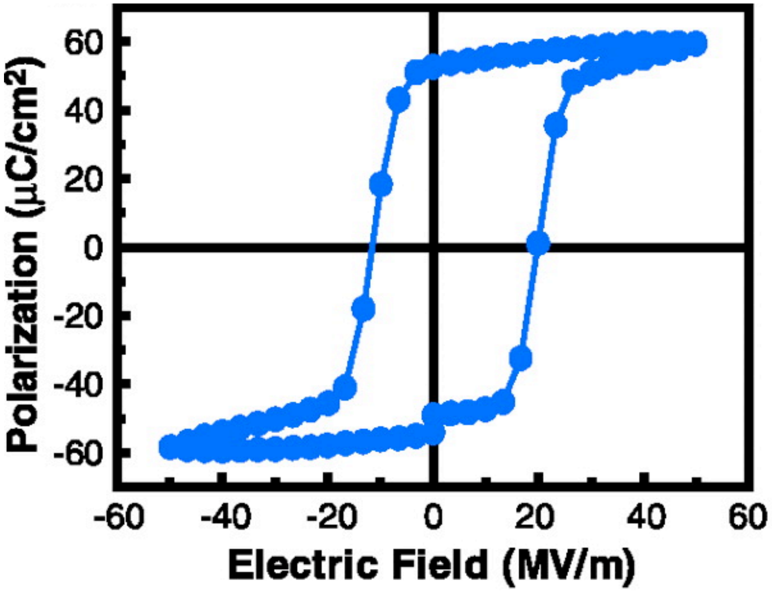
J.B. Neaton, U.V. Waghmare, C. Ederer, N.A. Spaldin and K.M. Rabe, *First-principles study of spontaneous polarization in multiferroic BiFeO$_3$*, PRB **71**, 014113 (2005)

Absence of strain dependence:

Effect of epitaxial strain on the spontaneous polarization of thin film ferroelectrics, C. Ederer and N.A. Spaldin, Phys. Rev. Lett. **95**, 257601 (2005)



Experiment: Thin films



Polarization = 60 μC/cm^2 along [111]. Consistent with theory.

Old bulk samples showed incomplete switching

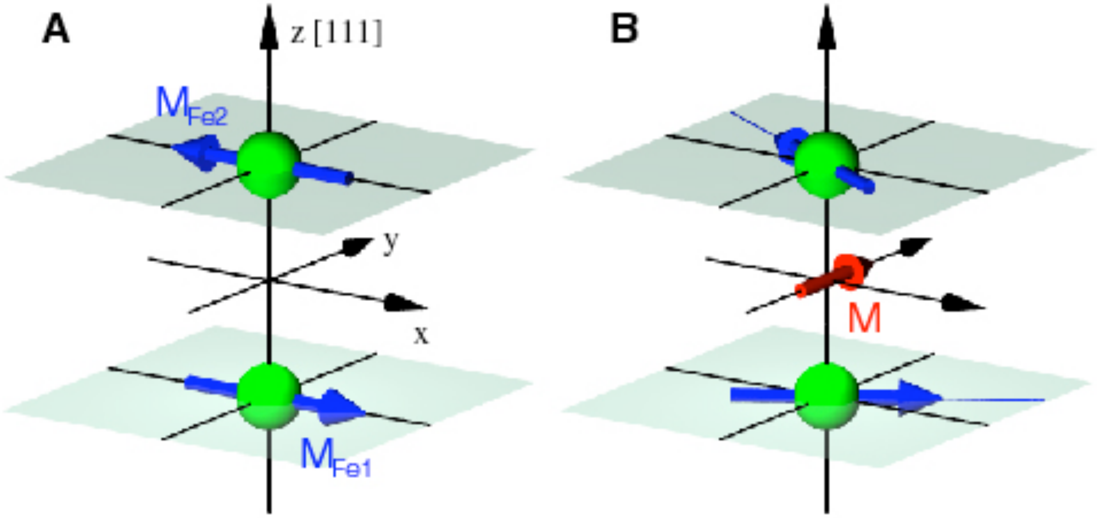
Small magnetization measured. Origin?

Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, Wang, Spaldin, Ramesh et al., Science 299, 1719 (2003)

Theory: Magnetoelectric coupling in $BiFeO_3$

Calculated magnetic anisotropy → magnetic moments lie in (111) plane (allows weak FM)

6 equivalent easy axes within (111) plane



Canting of 1^o results in net magnetization of 0.05 μ_B per Fe atom (consistent with recent measurements)

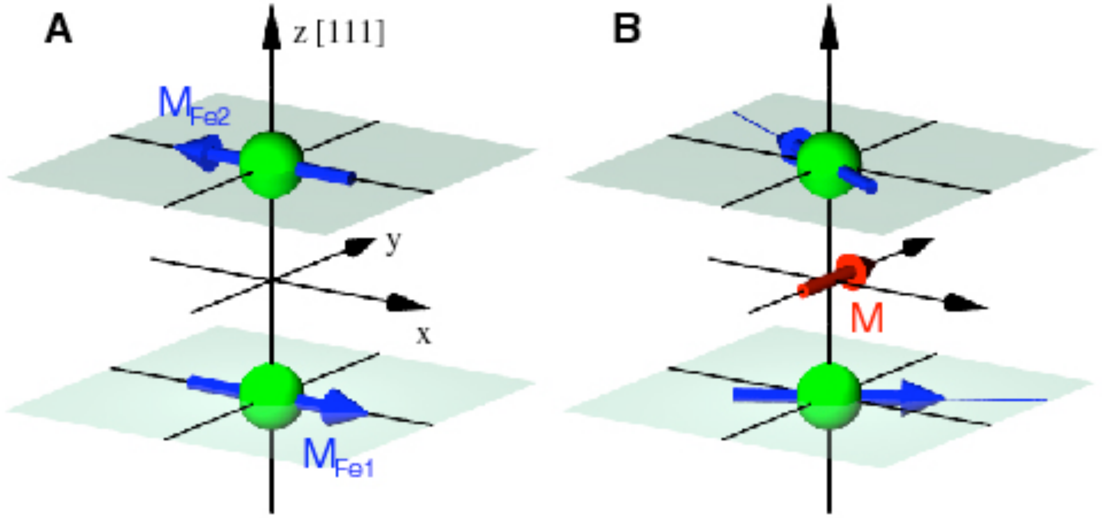
C. Ederer and N.A. Spaldin, *Weak ferromagnetism and magnetoelectric coupling in bismuth ferrite*, PRB **71**, 060401(R) (2005)

Theory: Magnetoelectric coupling in $BiFeO_3$

Calculated magnetic anisotropy → magnetic moments lie in (111) plane (allows weak FM)

6 equivalent easy axes within (111) plane

caused by polarization



Canting of 1° results in net magnetization of 0.05 μ_B per Fe atom (consistent with recent measurements)

caused by oxygen rotations

C. Ederer and N.A. Spaldin, *Weak ferromagnetism and magnetoelectric coupling in bismuth ferrite*, PRB **71**, 060401(R) (2005)

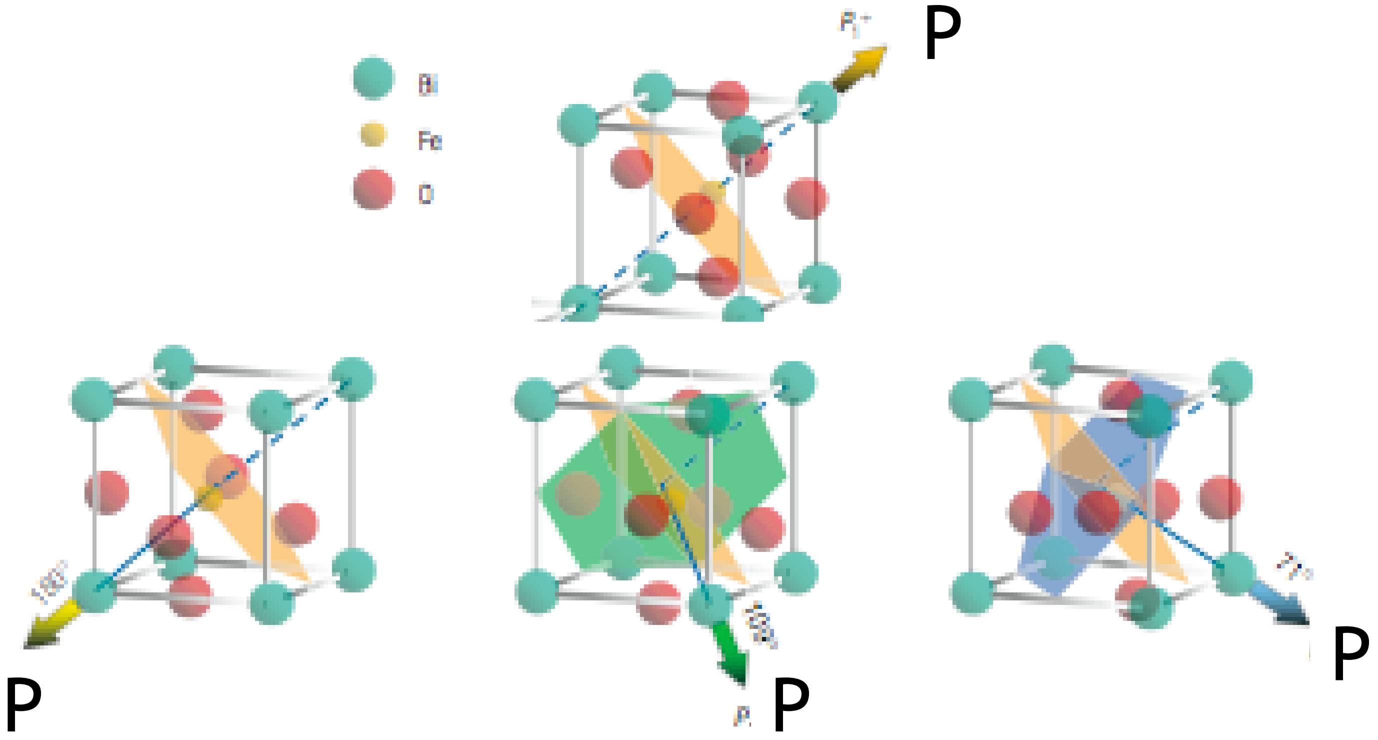
Theory: Effect of switching on magnetic easy plane

Easy magnetic plane determined by ferro**elastic** domain state!

180° switching does not change easy plane

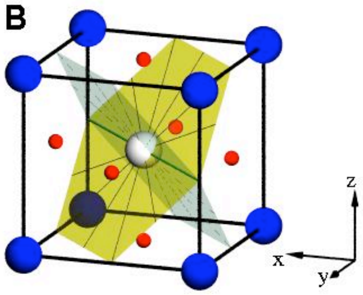
71°, 109° switching DO change easy plane

6 equivalent easy axes in easy plane ⟶ easy axis changes 5/6 of the time!

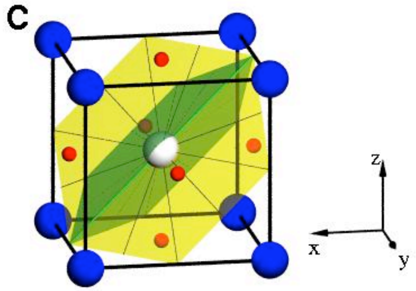


Electric-field-switching of AFM domains

Theory: Small monoclinic strain favors $[1\bar{1}0]$ direction!

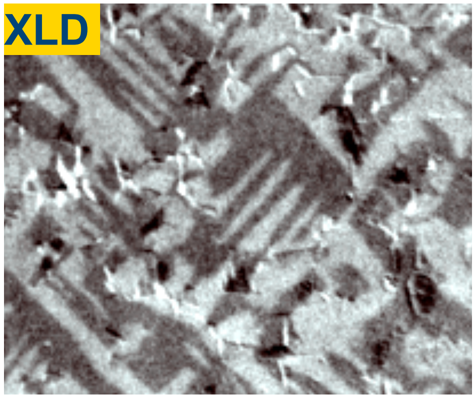


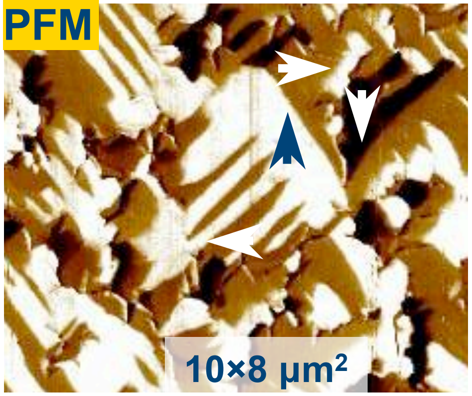
71° switching
→ AFM axis preserved



109° switching
→ AFM axis changed

Experiment: confirms change in AFM axis with 109° switching, no change with 71° switching





T. Zhao, N.A. Spaldin, R. Ramesh et al., *Electrical control of antiferromagnetic domains in multiferroic BiFeO$_3$ at room temperature*, Nature Materials **5**, 823 (2006)

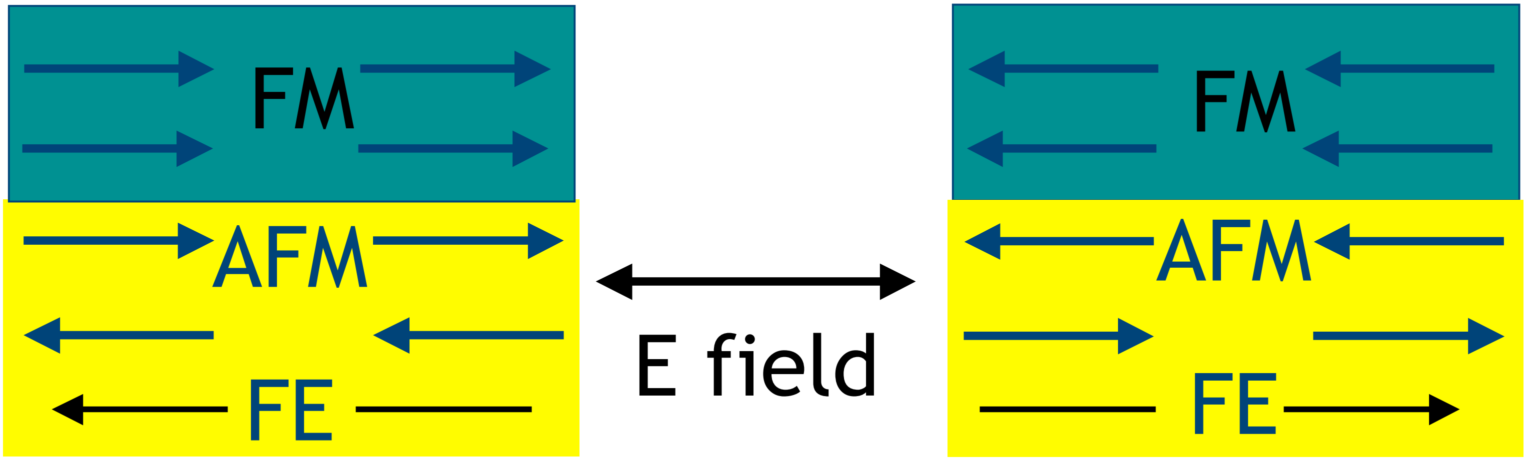
E-field switchable ferromagnetism through exchange bias coupling?

Plan:

Control AFM vector using an E-field

Couple FM to AFM using exchange bias

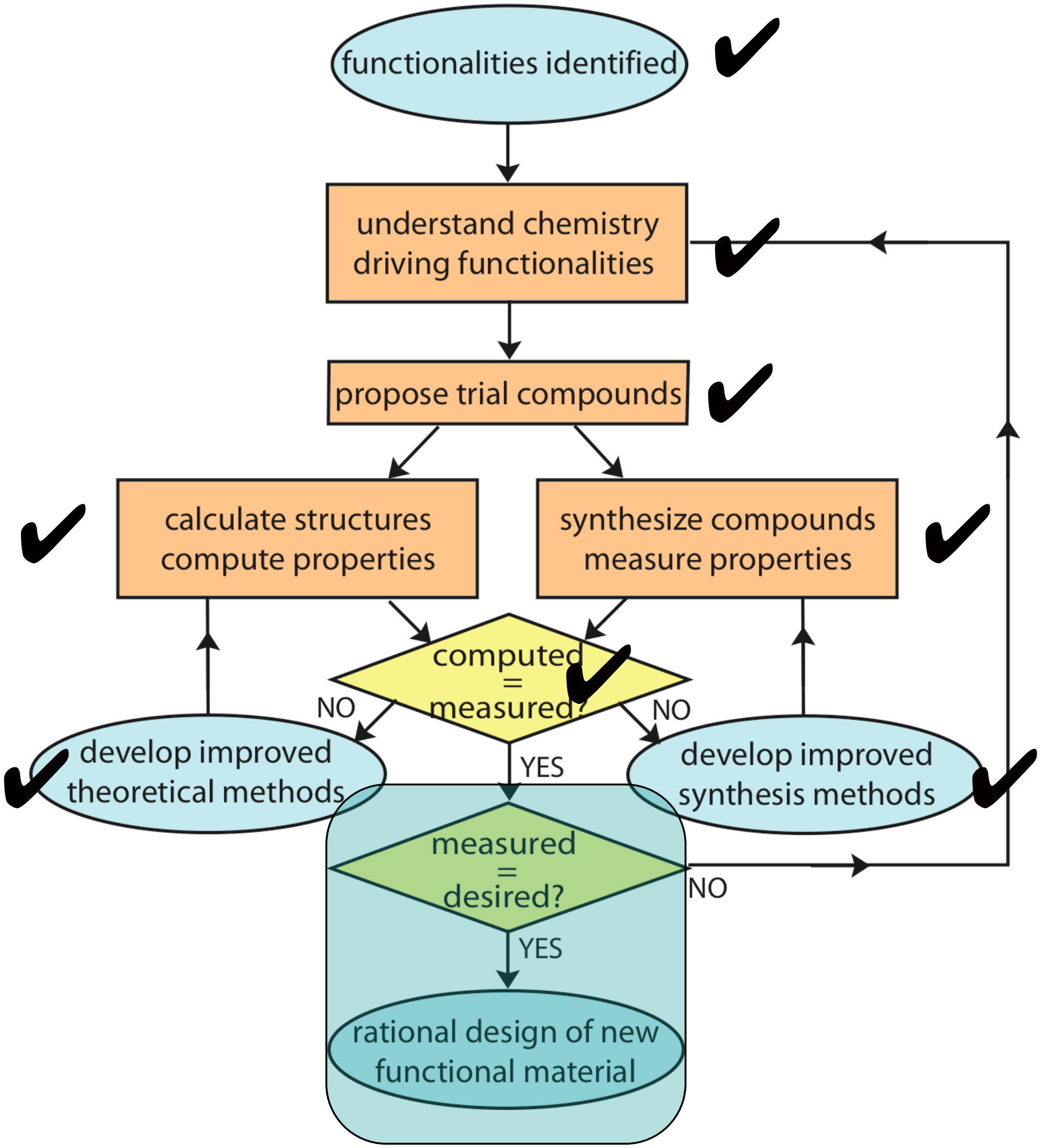
Control FM using an E field



Experimental studies underway

Theory: Nature of exchange bias in a ferroelectric antiferromagnet?

Status of “rational design” for multiferroics?



functionalities identified ✔

understand chemistry driving functionalities ✔

propose trial compounds ✔

✔ calculate structures compute properties

synthesize compounds measure properties ✔

computed = measured? ✔

NO

NO

✔ develop improved theoretical methods

develop improved synthesis methods ✔

YES

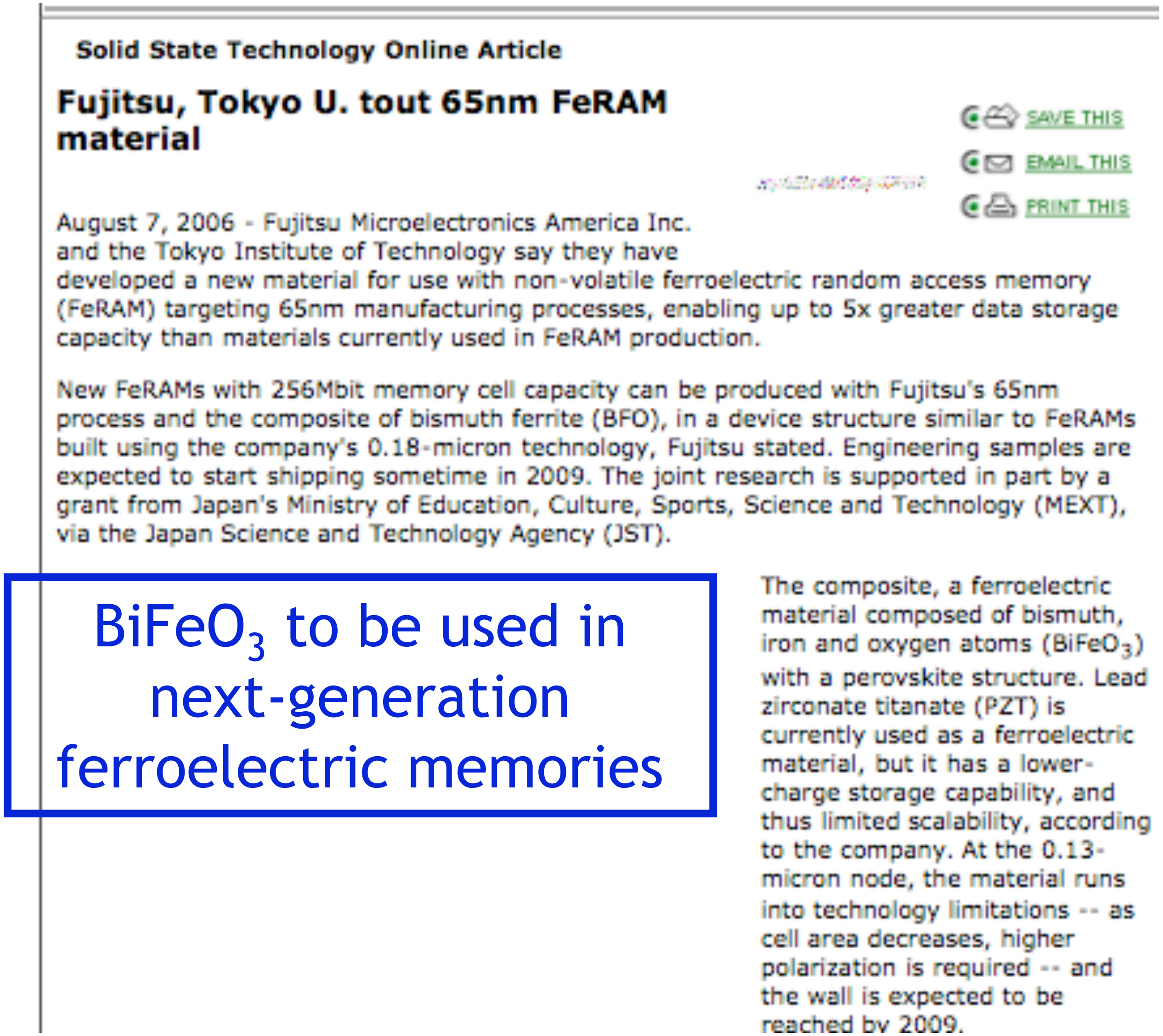
measured = desired?

NO

YES

rational design of new functional material

An aside: Pb-free ferroelectrics with large polarization



Solid State Technology Online Article

Fujitsu, Tokyo U. tout 65nm FeRAM material

August 7, 2006 - Fujitsu Microelectronics America Inc. and the Tokyo Institute of Technology say they have developed a new material for use with non-volatile ferroelectric random access memory (FeRAM) targeting 65nm manufacturing processes, enabling up to 5x greater data storage capacity than materials currently used in FeRAM production.

New FeRAMs with 256Mbit memory cell capacity can be produced with Fujitsu's 65nm process and the composite of bismuth ferrite (BFO), in a device structure similar to FeRAMs built using the company's 0.18-micron technology, Fujitsu stated. Engineering samples are expected to start shipping sometime in 2009. The joint research is supported in part by a grant from Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT), via the Japan Science and Technology Agency (JST).

The composite, a ferroelectric material composed of bismuth, iron and oxygen atoms ($BiFeO_3$) with a perovskite structure. Lead zirconate titanate (PZT) is currently used as a ferroelectric material, but it has a lower-charge storage capability, and thus limited scalability, according to the company. At the 0.13-micron node, the material runs into technology limitations -- as cell area decreases, higher polarization is required -- and the wall is expected to be reached by 2009.

$BiFeO_3$ to be used in next-generation ferroelectric memories

Summary

Tremendous progress in synthesis, characterization and understanding of novel complex oxides

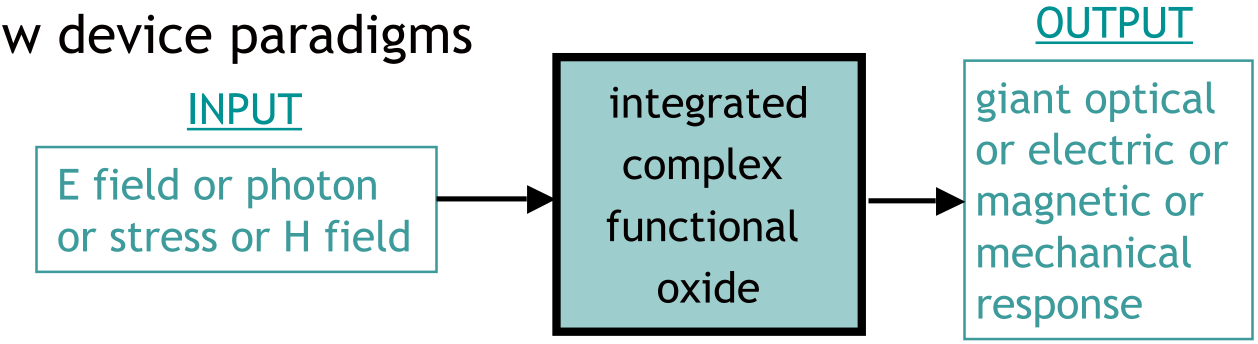
Many new (unanticipated) physical phenomena emerging in single phases and at interfaces

Demand for oxides in existing technological applications

- high-k dielectrics
- oxides as semiconductors
- dissipationless wires from high (room) temperature superconductors

Possibility for entirely new device paradigms

- strong correlations
- multifunctionality



INPUT

E field or photon or stress or H field

integrated complex functional oxide

OUTPUT

giant optical or electric or magnetic or mechanical response

Plan for coordinating fundamental discoveries with new technologies?

SPARE SLIDES FOLLOW

Practical approach to electric fields in DFT for periodic insulators

I. Souza, J. Iniguez and D. Vanderbilt, *First-principles approach to insulators in finite electric fields*, Phys. Rev. Lett. **89**, 117602 (2002)

Minimize electric enthalpy F (instead of Kohn-Sham energy E_{KS})

$$F = E_{KS} - \Omega\, P . \mathcal{E}$$

Express E_{KS} and P in terms of field-polarized Bloch functions: allows periodic boundary conditions

Discretize k-space: ensures F has minima and prevents Zener charge leakage

How to Obtain P? (next)

Calculation of P

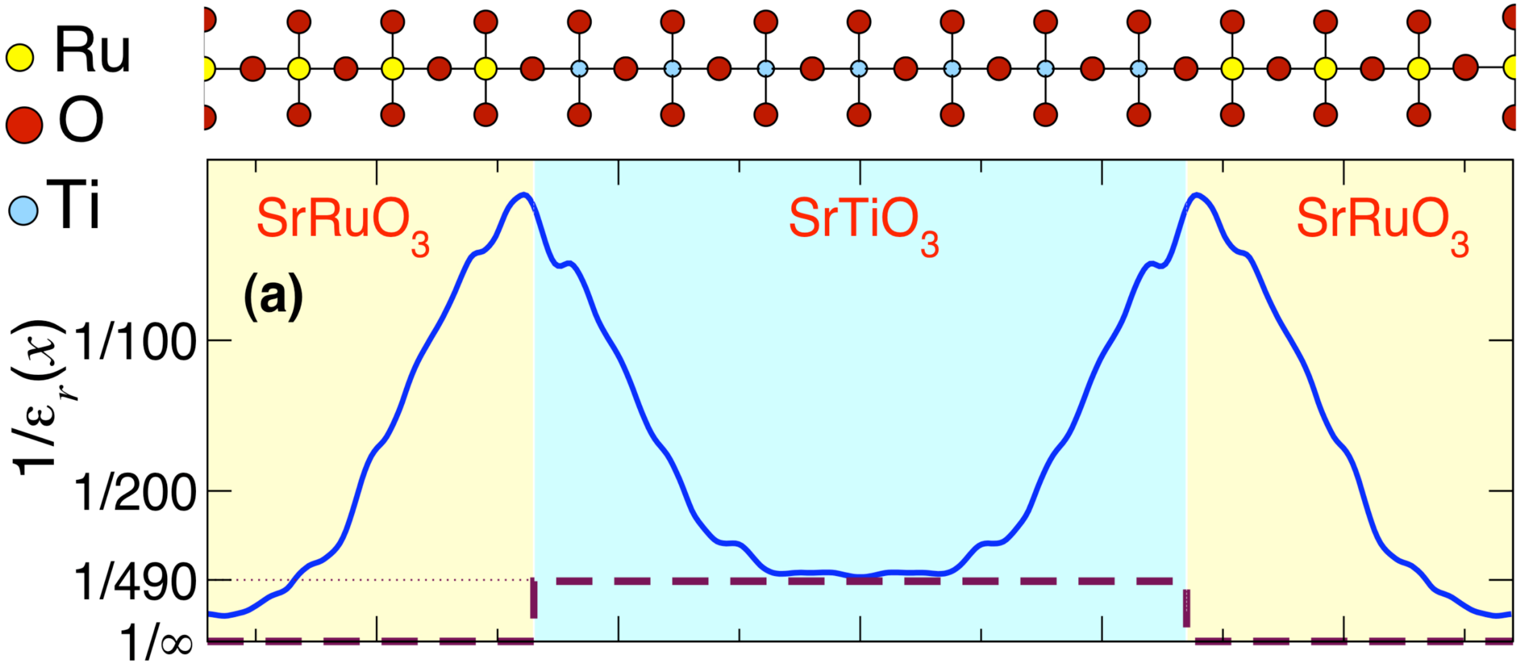
Polarization in a **pure insulator** can be written as a gradient in ***k*-space** (Berry phase) integrated over filled bands

R. D. King-Smith and D. Vanderbilt, *Theory of polarization of crystalline solids*, PRB **47**, 1651 (1993)

For metallic capacitors, we use hermaphrodite Wannier functions (localized in 1D) to obtain polarization

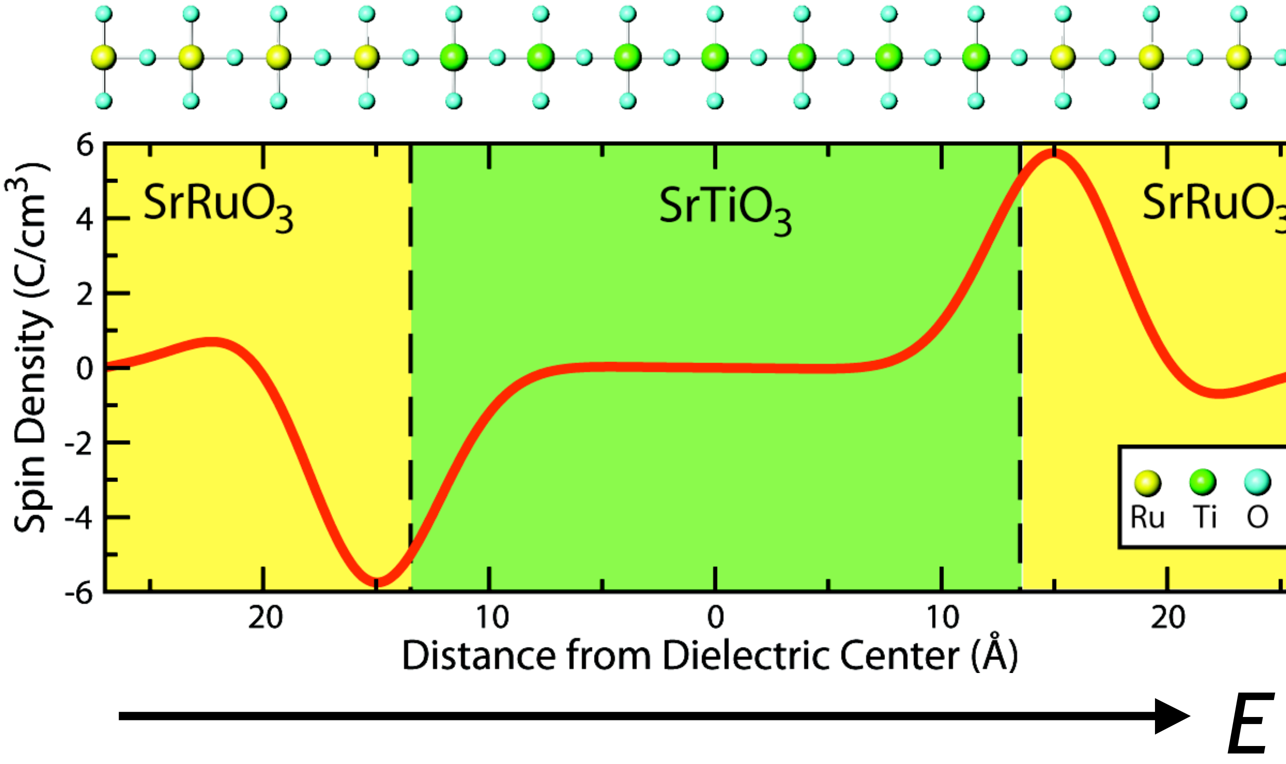
M. Stengel and N. Spaldin, *Ab-initio theory of metal-insulator interfaces in finite electric field*, PRB **75**, 205121 (2007).

Dielectric response



M. Stengel and N.A. Spaldin, *Origin of the dielectric dead layer in nanoscale capacitors*, Nature **443**, 679 (2006)

Magnetoelectric response of interface

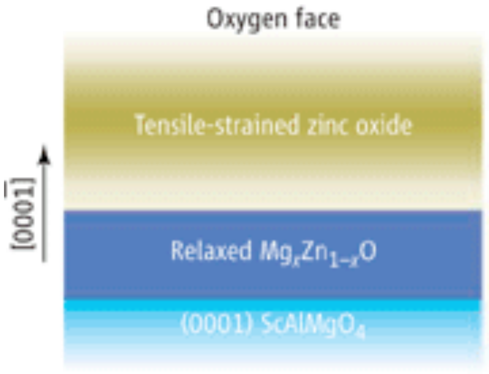


J.M. Rondinelli, M. Stengel and N.A. Spaldin, *Carrier-mediated magnetoelectricity in complex oxide heterostructures*, cond-mat 0706.2199

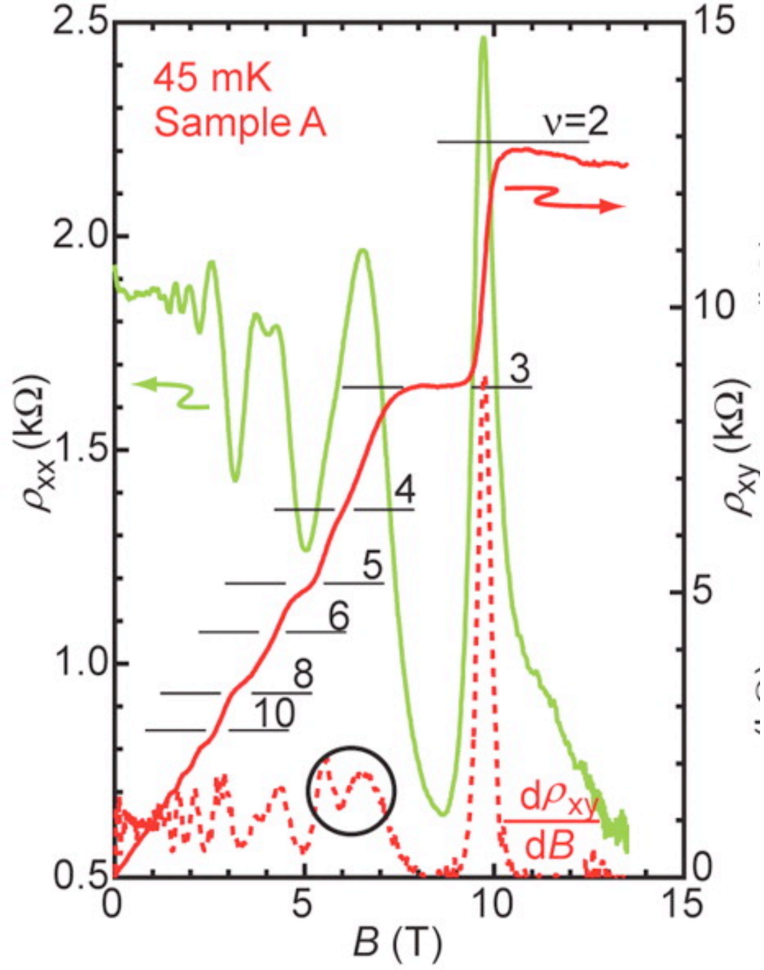
Potential in future technologies: Oxides as semiconductors

Quantum Hall Effect at ZnO/(Zn,Mg)O interface

→ high quality samples



A. Tsukazaki et al. *Quantum Hall Effect in Polar Oxide Heterostructures*, Science **315**, 1388 (2007)



Challenges:

- need for *p*-type material
- understanding and control of defect structure
- good mobilities at room temperature

Challenges in Theory:
Beyond DFT

GW:

QMC:

good wavefunctions; poor scaling wrt Z - complex oxides have large Z

expenisve 2p and 3d are tightly bound (no 1p or 2d to orthogonalize to!) therefore require large basis sets

problems with core/valence exchange if core is treated with LDA (need entire shell in valence which gets expensive)

“Designer” multiferroics

<u>Theory (DFT):</u>

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

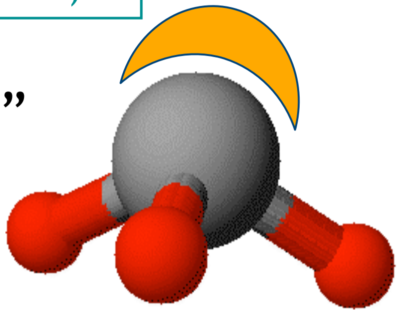
Magnetism and ferroelectricity are *chemically contra-indicated*:

- Magnetism requires localized transition metal d electrons
- Atoms with localized d electrons don’t off-center to form polar ferroelectric states

<u>Idea:</u>

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

- Ferroelectricity from a “stereochemically active lone pair”
- Magnetism from a 3d transition metal (Mn^{3+})



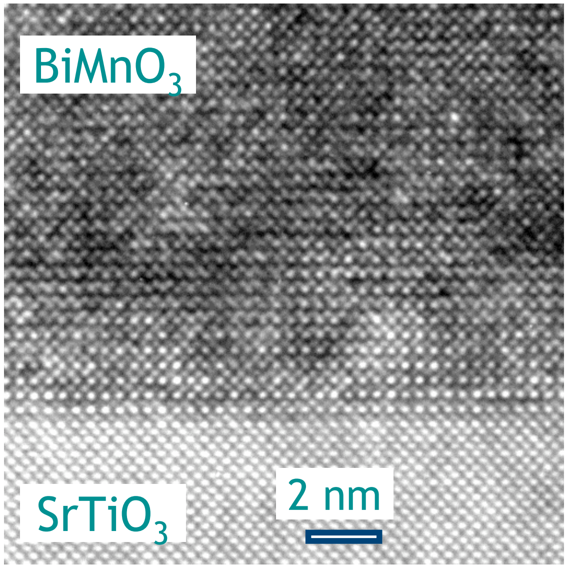
<u>Motivated Experiments:</u> synthesis and x-ray determination of atomic positions

<u>Motivated Theoretical Developments:</u> beyond-LDA methods

Subsequent Experiments

Synthesis (thin film):

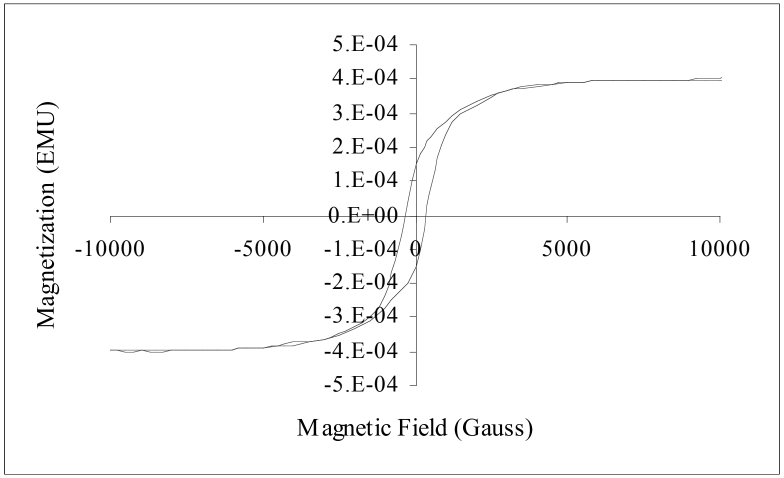
A. Moreira dos Santos et al., *Epitaxial growth and properties of metastable $BiMnO_3$ thin films*, Appl. Phys. Lett. **84**, 91-93, 2004



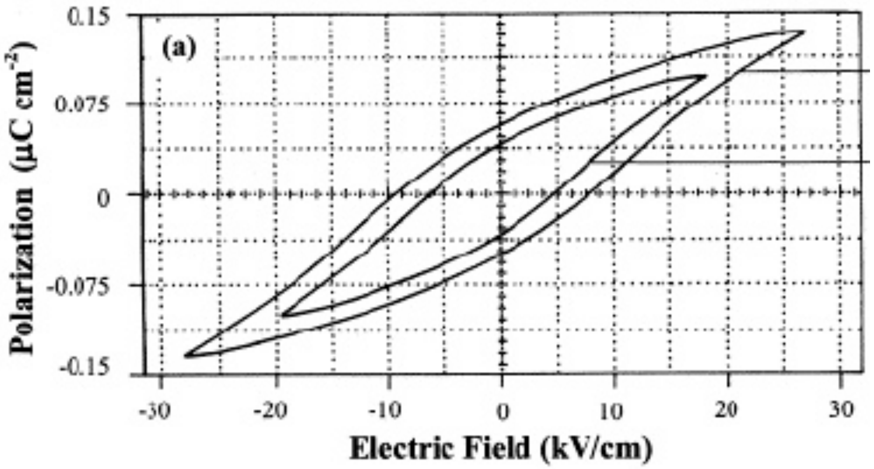
Characterization:

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).

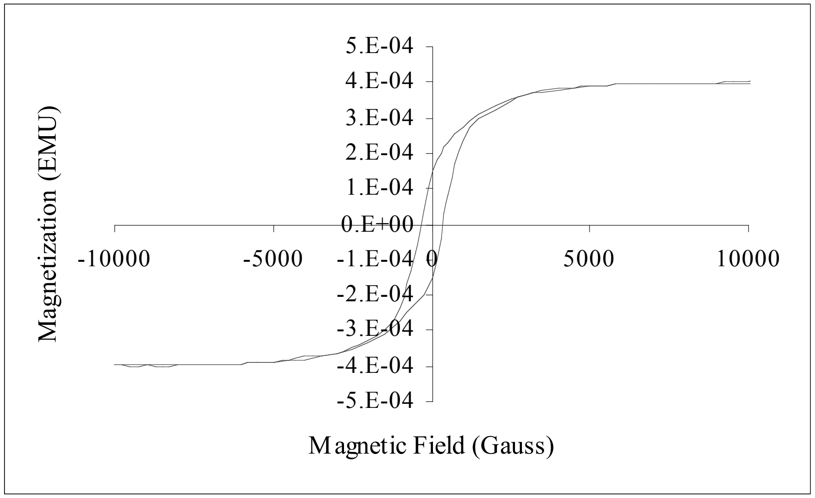
M-H hysteresis **ferromagnetism**



P-E hysteresis **ferroelectricity**



Experimental Characterization: Ferromagnetism and Ferroelectricity

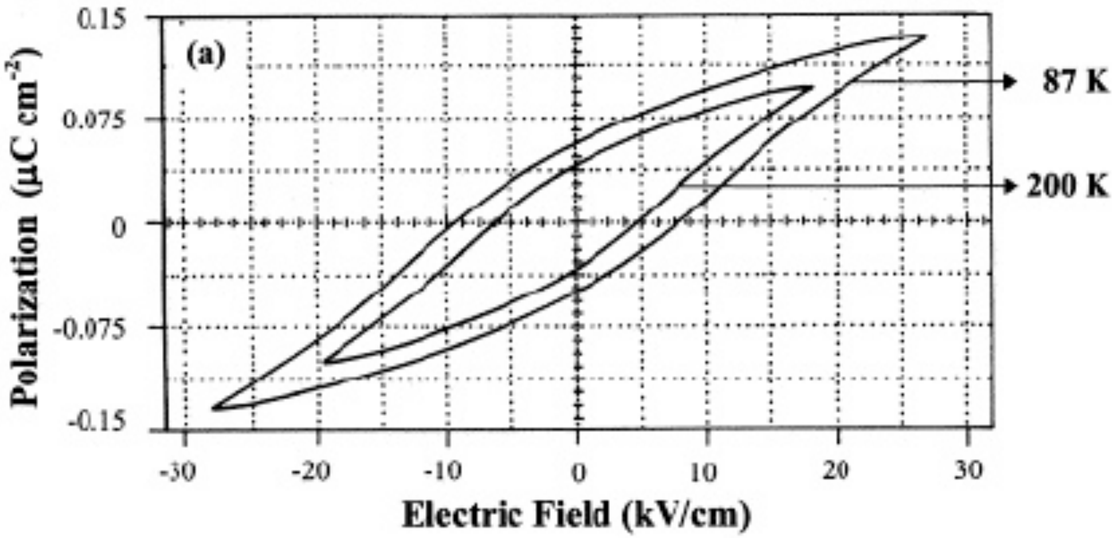


Hysteresis in magnetization versus magnetic field **indicates ferromagnetism**

T_c = 100K

Hysteresis in polarization versus electric field **indicates ferroelectricity**

small polarization

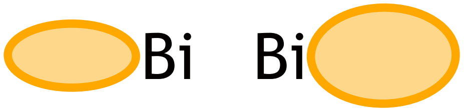


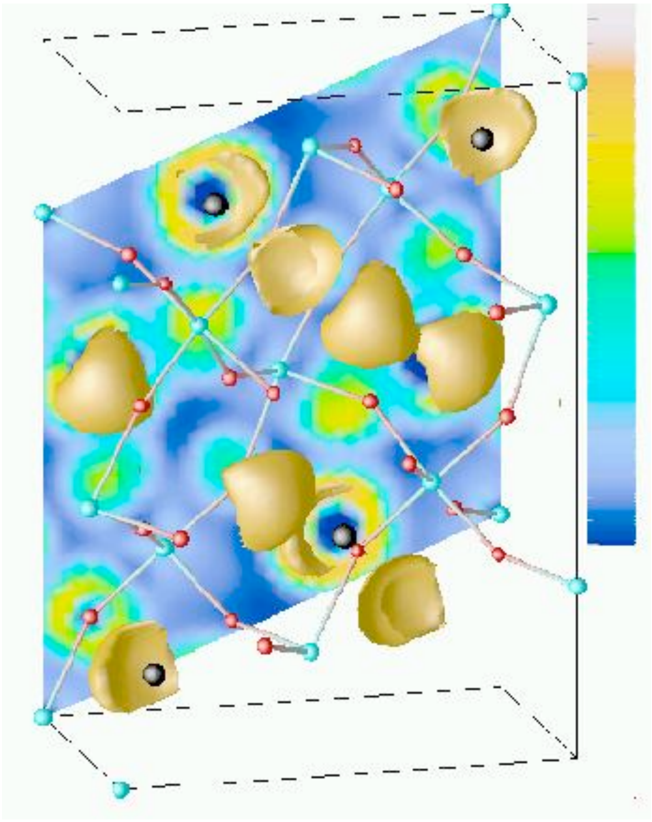
A.M. Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham and C.N.R. Rao, *Evidence for the likely occurrence of magnetoferroelectricity in* $BiMnO_3$, Sol. Stat. Comm. 122, **49** (2002).

Calculation of polarization I

DFT Calculations at reported atomic positions find:

Ferromagnetic ground state
Almost *anti*-ferroelectric (ferr *i* -electric!)
with small polarization



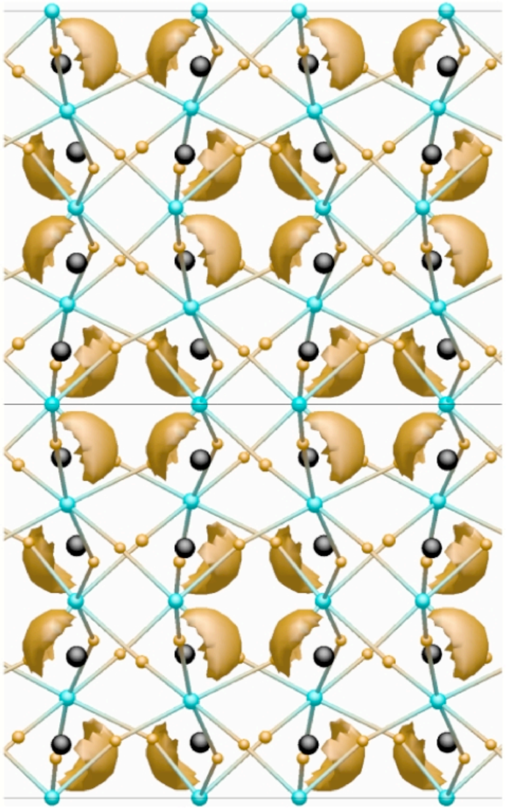


R. Seshadri and N.A. Hill, *Visualizing the role of Bi 6s “lone pairs” in the off-center distortion in ferromagnetic* $BiMnO_3$, Chemistry of Materials **13**, 2892 (2001).

T. Shishidou et al., *First-principle study on the electronic structure of bismuth transition metal oxides*, J. Phys. Condens. Matter **16**, S5677 (2004).

Calculation of polarization II

Reported positions
ferr*i*electric arrangement
small polarization

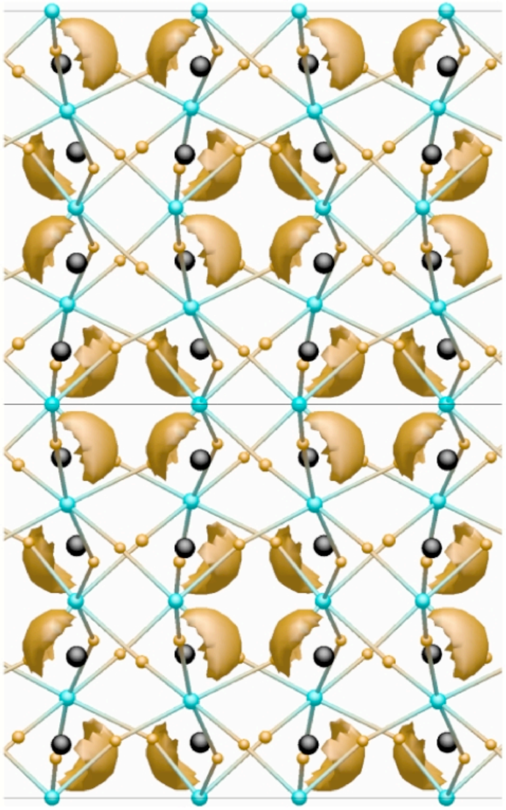


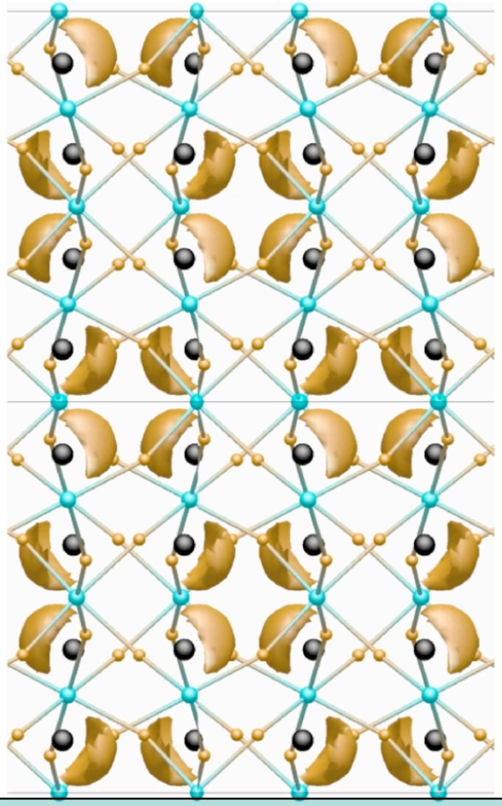
P. Baettig, R. Seshadri and N. A. Spaldin, *Anti-polarity in ideal BiMnO*$_3$, JACS, 129, 9854 (2007).

Calculation of polarization II

Reported positions
ferr*i*electric arrangement
small polarization

Full structural optimization
anti-polar arrangement
zero polarization





P. Baettig, R. Seshadri and N. A. Spaldin, *Anti-polarity in ideal BiMnO$_3$*, JACS, 129, 9854 (2007).

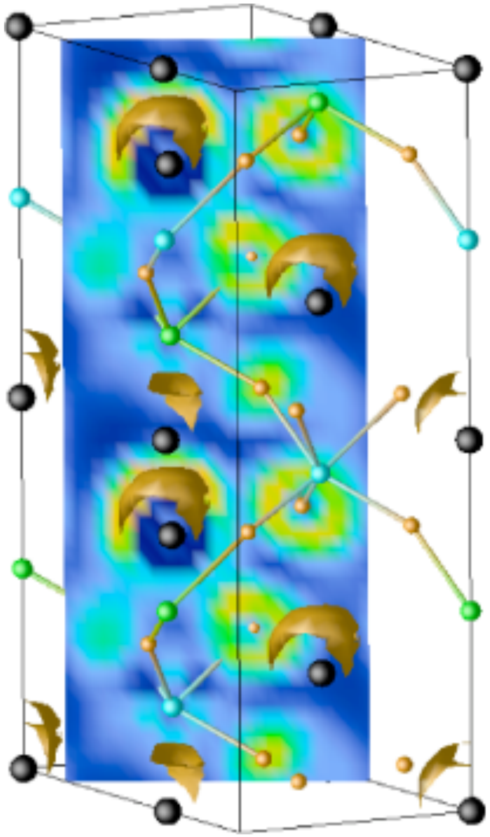
Motivated neutron determination of atomic positions ⟶ C2/c!

Open questions

Reconciling measured polar behavior with centrosymmetric calculated structure and neutron refinement in $BiMnO_3$

Do epitaxial strain or defects cause polarization?

Can ferroelectric alignment of the lone pairs be achieved, while retaining ferromagnetism?

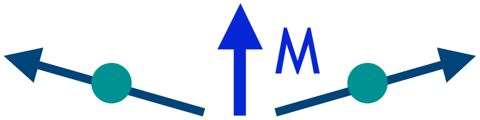


A 2nd attempt:

$\underline{BiFeO_3}$: Calculate and measure P = 90 $\mu C/cm^2$ (huge!)

Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, Wang, Spaldin, Ramesh et al., Science 299, 1719 (2003)

Anti-ferromagnetic alignment of Fe^{3+} ions but with *weak ferromagnetism*



Weak ferromagnetism and magnetoelectric coupling in $BiFeO_3$, C. Ederer and N.A. Spaldin, PRB **71**, 06041R (2005)

Grand challenges to enable future information technologies

Understanding high-T_c

developing a room temperature superconductor

A room temperature multiferroic

large and coupled polarization and magnetization

control/coupling of charge/spin/orbital/lattice degrees of freedom

} strongly correlated "complex" oxides

p-type semiconducting behavior

oxide electronics

high-ε, large band gap, Si compatible material

further miniaturization of Si devices

} weakly correlated "simple" oxides

Challenges for high k materials for CMOS over next ~10 years:

- A clear understanding of the materials science of semiconductor-ionic metal oxide-metal electrode heterostructures with nanoscale thicknesses.
- Dielectric layer thicknesses that are electrically equivalent to less than 0.6 nm of SiO_2 for 32 nm technologies and beyond.
- Epitaxial oxides and silicon-oxide-silicon epitaxy for 3-D stacking and silicon on insulators.

poly-Si/HfO_2/SiOxNy/Si