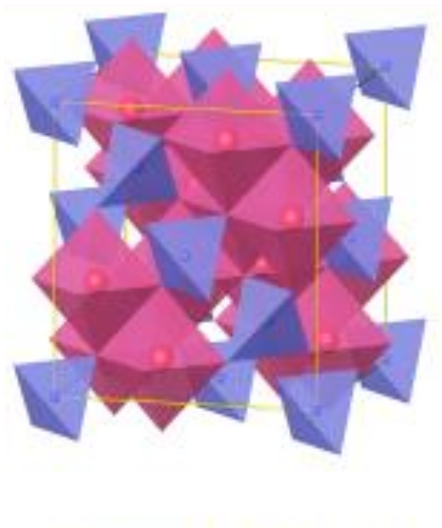
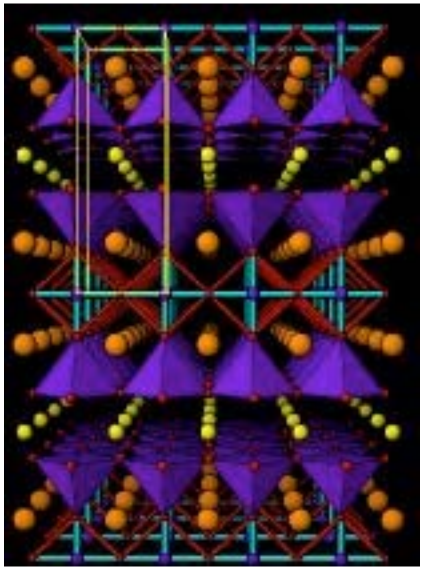
Grand Challenges in Oxides Research



Nicola Spaldin
Materials Department
UC Santa Barbara

nicola@mrl.ucsb.edu
805 893-7920



with valuable input from:

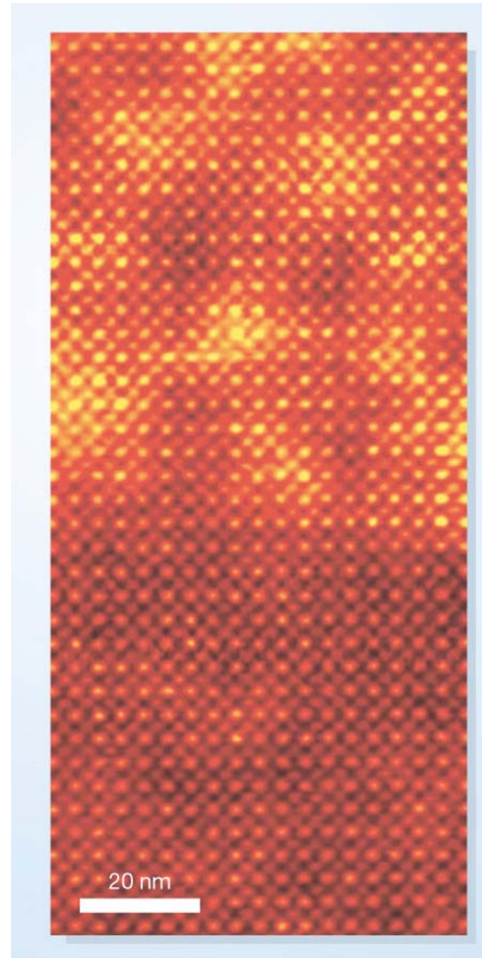
Leon Balents (UCSB), Jeroen van den Brink (U Leiden), Jaques Chakalian (U Arkansas), Matthew Fisher (UCSB), Michael Fisher (U Maryland), Supratik Guha (IBM), Werner Hanke (U Wurzburg), Daniel Khomskii (U Koln), R. Ramesh (UC Berkeley), Art Ramirez (Bell Labs.), Richard Scalettar (UC Davis), Darrell Schlom (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

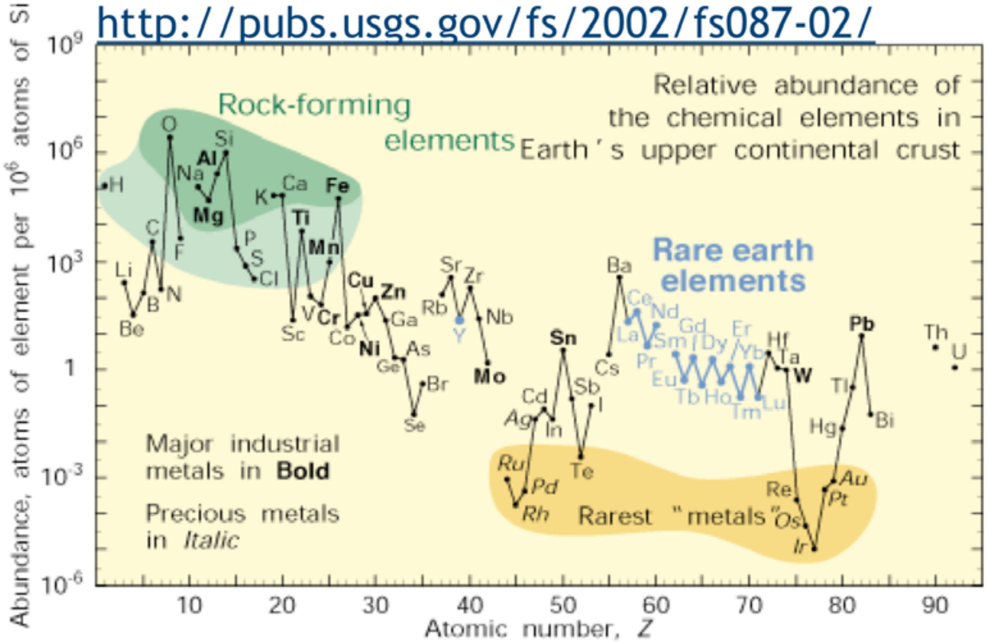
Why oxides?

abundance!

non-toxic

polarizability *just right*
- nitrides too covalent
- fluorides too ionic

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



diverse chemistries, structures and dimensionalities

strong correlations! behavior of one electron explicitly influences the others

Strong correlations

a wide range of couplings:

electron-lattice
- high-k dielectrics
- ferroelectricity
- high-T_c superconductivity
- large thermopower

electron-spin(-lattice)
- multiferroism
- magnetoelectricity
- magnetoresistance
- spintronics

spin-orbital
- piezomagnetism
- magnetic frustration

potential technological relevance:

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

$\longrightarrow$ TUNABILITY!

Strong correlations

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

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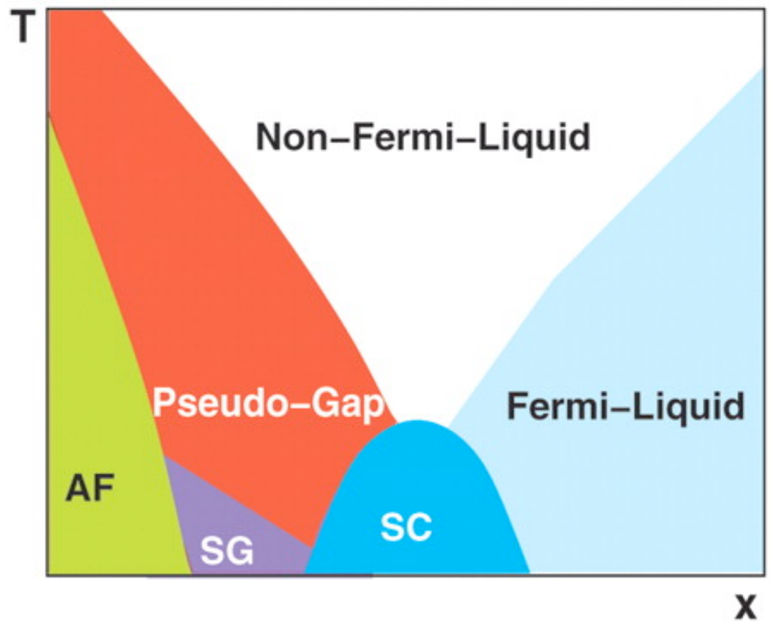
→ TUNABILITY!



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

Comparison with conventional semiconductors

Conventional semiconductors

Physics:

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

Technology:

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

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Complex oxides

Physics:

- localization of 3d/2p orbitals gives strong Coulomb interactions
- diverse magnetic and other strong correlations

Technology:

- Quality: materials chemistry challenging; fabrication less developed
- Understanding: strong correlations challenging to theoretical tools
- Tunability: high! due to competing ordered states

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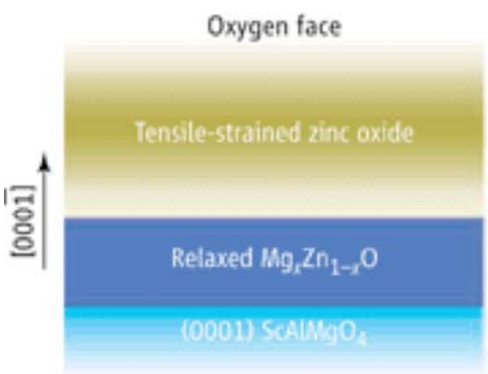
vastly richer physics suggests entirely new functionalities provided *Oxides Grand Challenge* can be met:

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

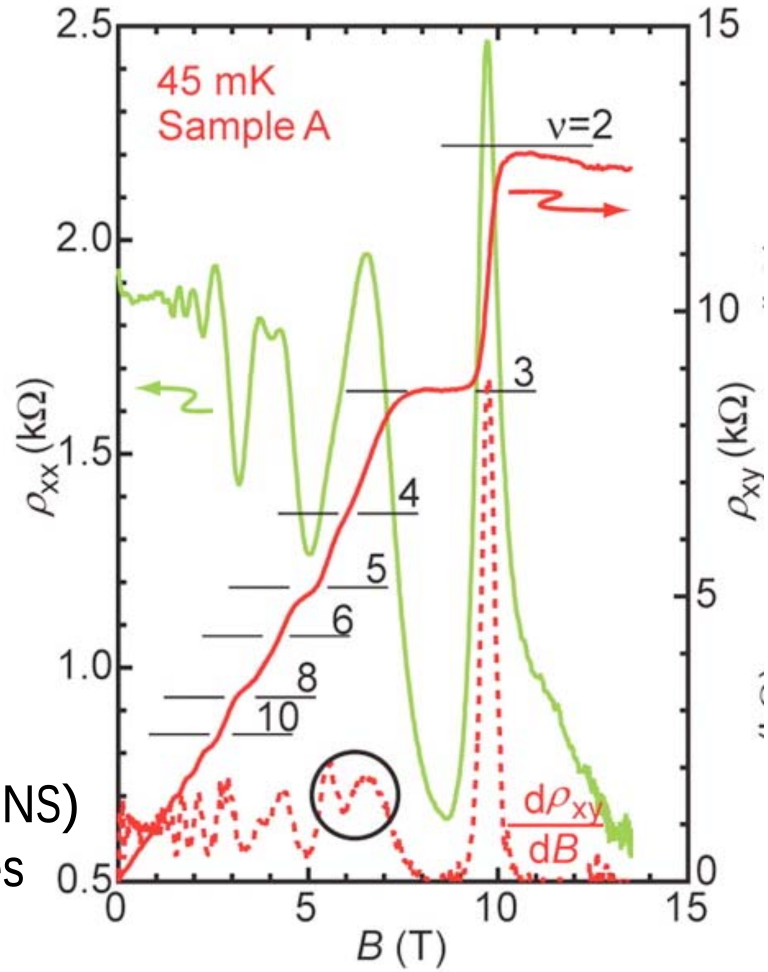
Why now?

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:

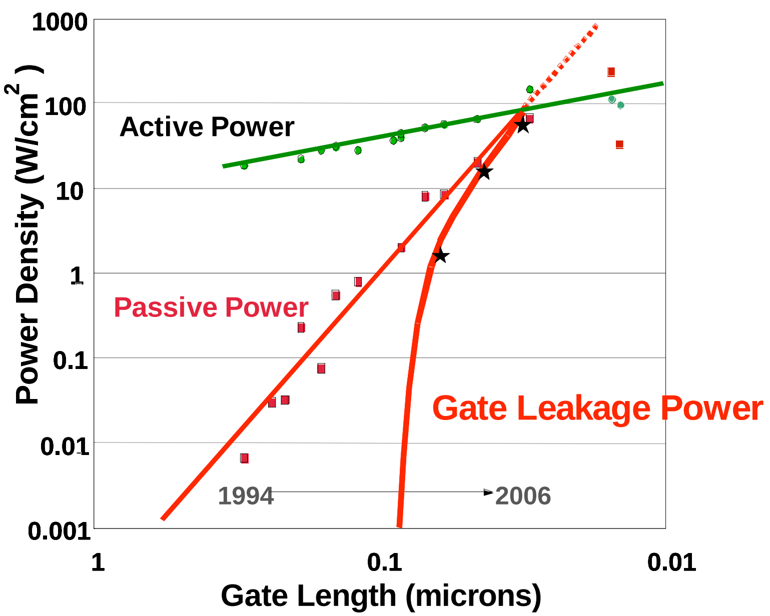
improved experimental probes (ARPES, STM, SNS)

theory/computation able to address intricacies numerically

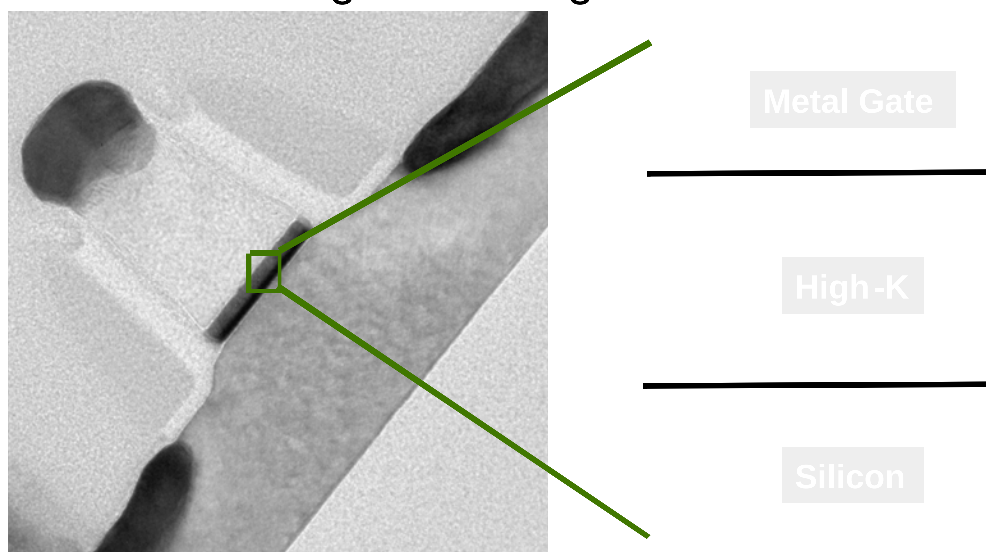
Existing technology need: High-k oxide-based CMOS technology:

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

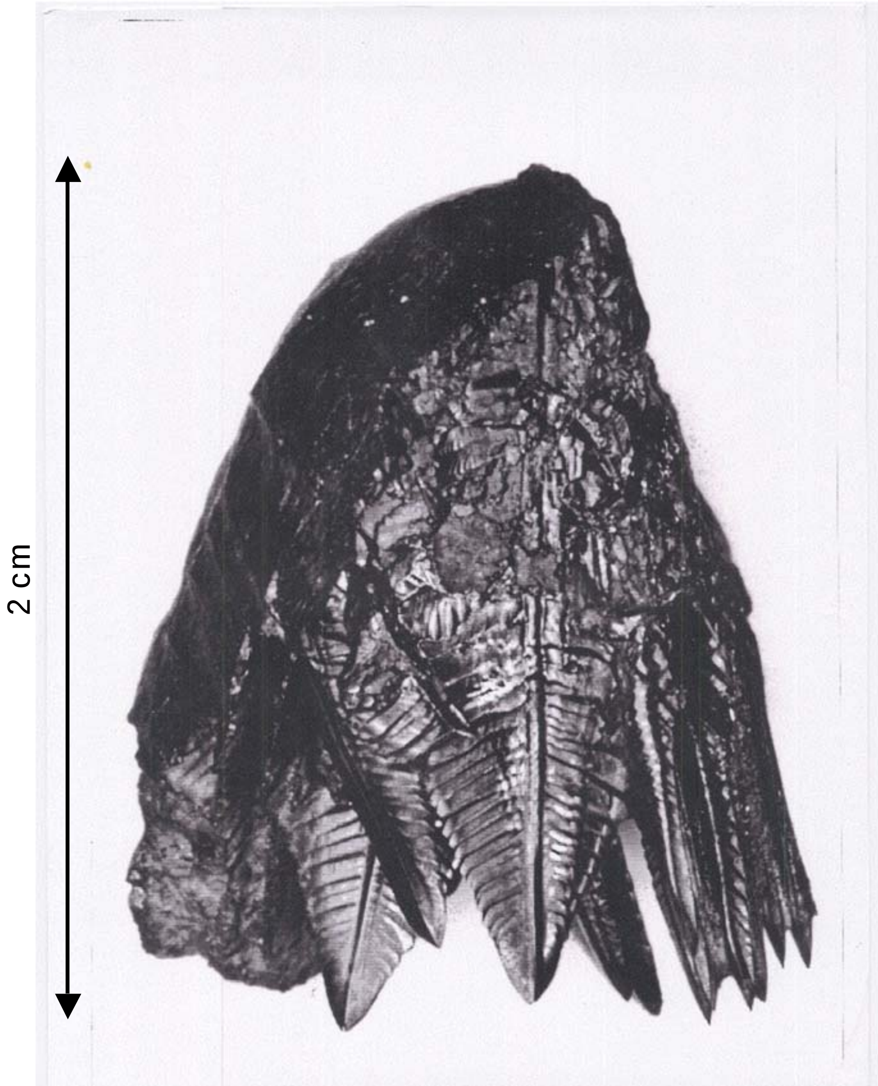
Sub-challenges:

- 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 $B_2O_3/Bi_2O_3/Fe_2O_3$ flux

$Bi_2Fe_4O_9$ more stable

Fe_3O_4 decomposition product!

Single crystal growth

need for bulk single crystal growth

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

dedicated equipment and operators

- 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

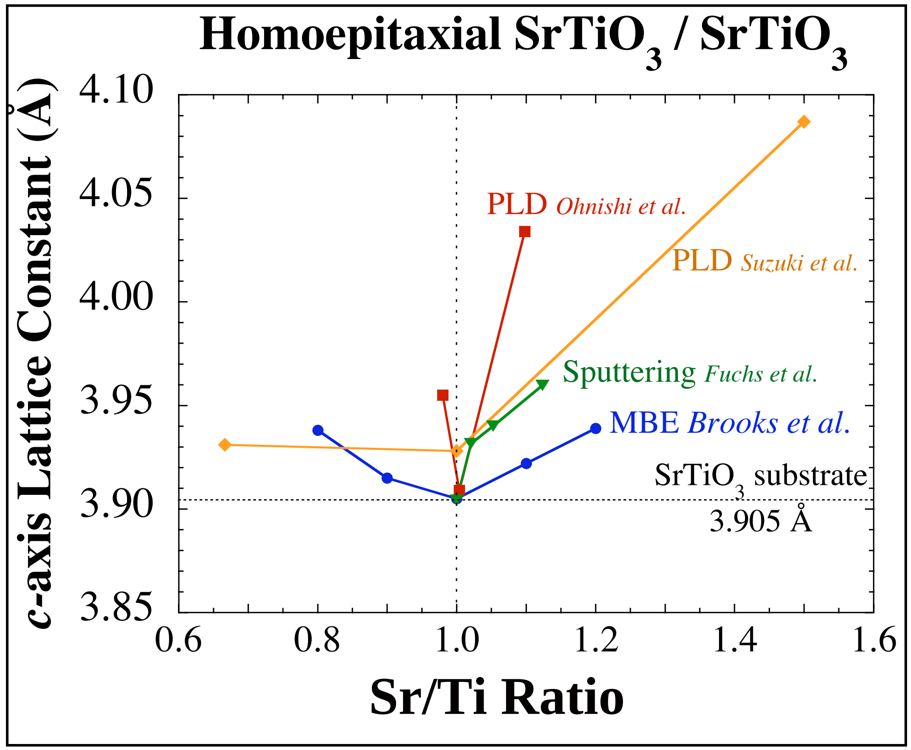
Thin film growth

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

<u>Density Functional Theory</u>

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

BUT…

$V_{xc}(r)$ is approximated

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

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

<u>Beyond-LDA methods:</u>

- 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)

<u>Downfolding:</u>

- Extract essential interaction parameters from LDA and construct a model

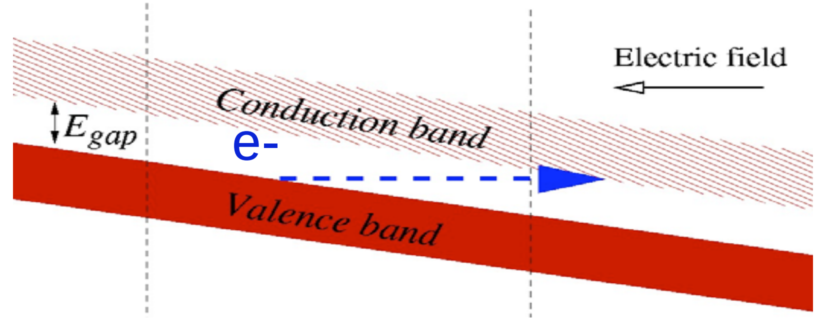
<u>Needs</u>:

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

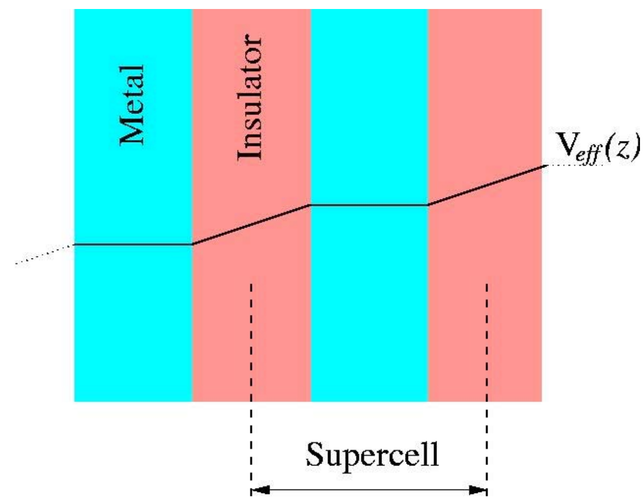
Other challenges in DFT-based theory: Finite Electric Fields

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

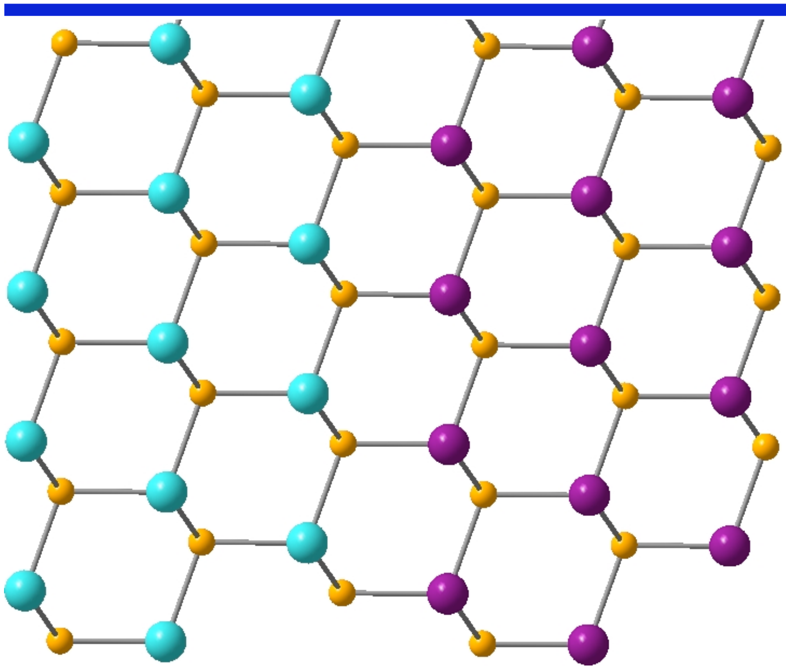
Two most exciting current/developing areas:

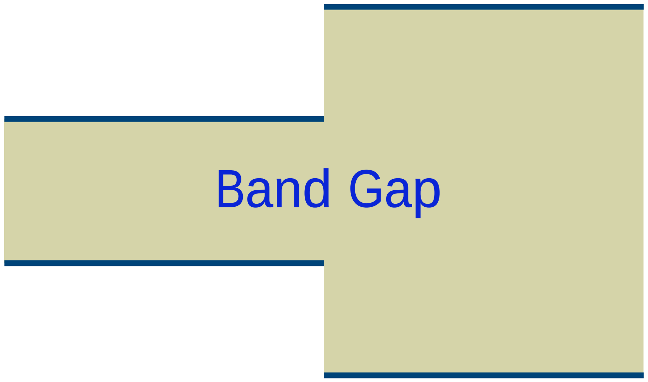
oxide-oxide interfaces

multi-functional oxides

A “mini seminar” on theory/experiment interplay in multiferroics

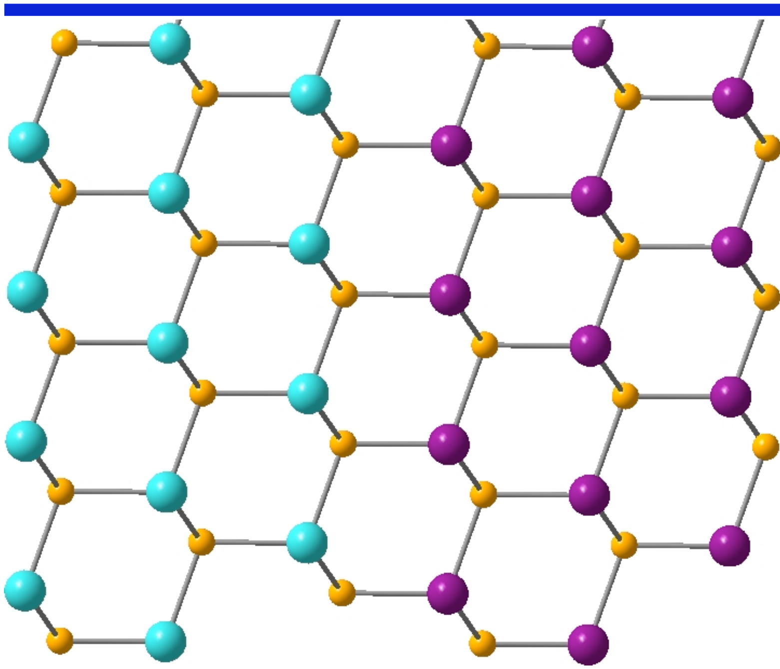
Oxide-oxide interfaces

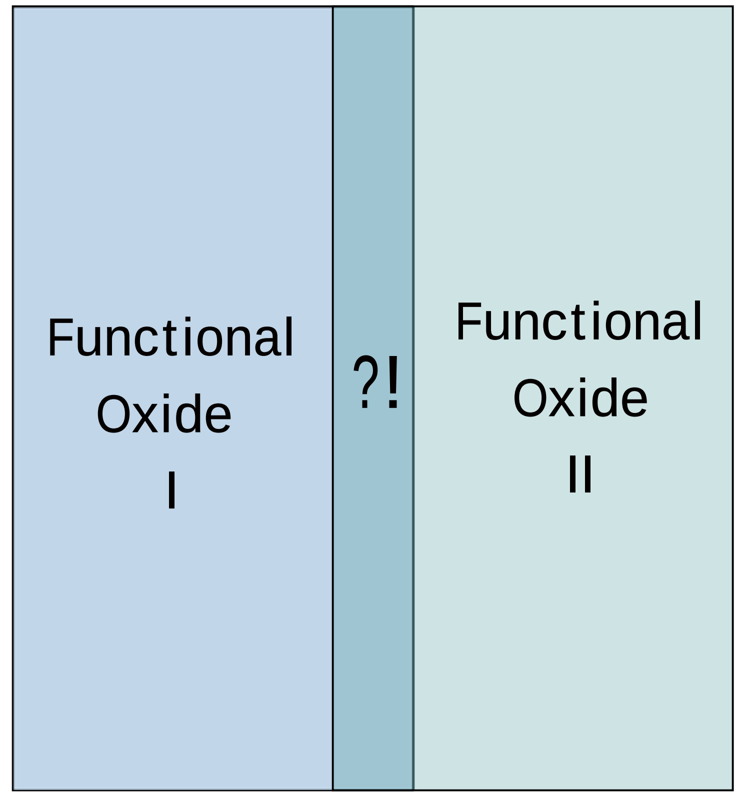


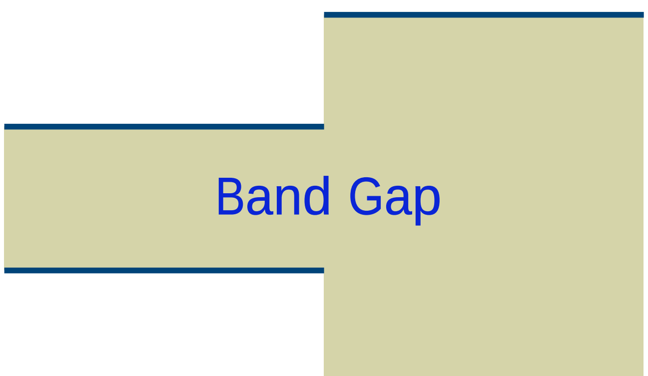


"The interface is the device"
Herbert Kroemer,
Nobel lecture, Dec 8 2000

Oxide-oxide interfaces







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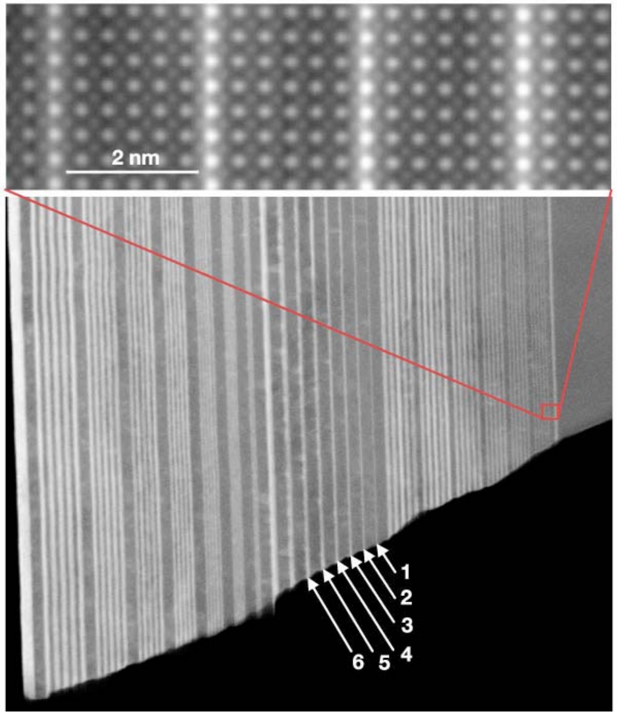
Example of new functionality at oxide-oxide interfaces

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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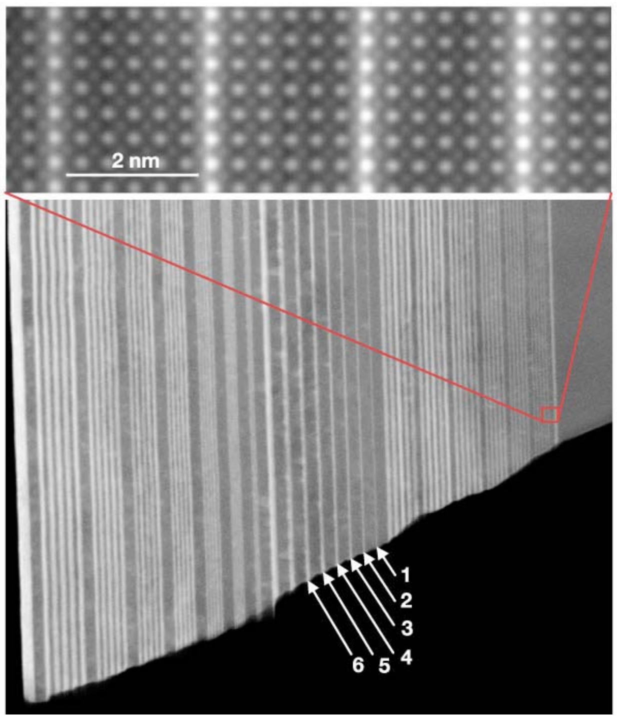

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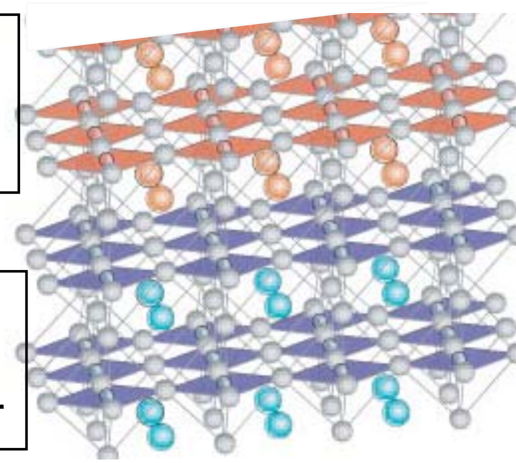
$LaTiO_3$
Ti^{3+} $(3d)^1$
Mott insulator

$SrTiO_3$
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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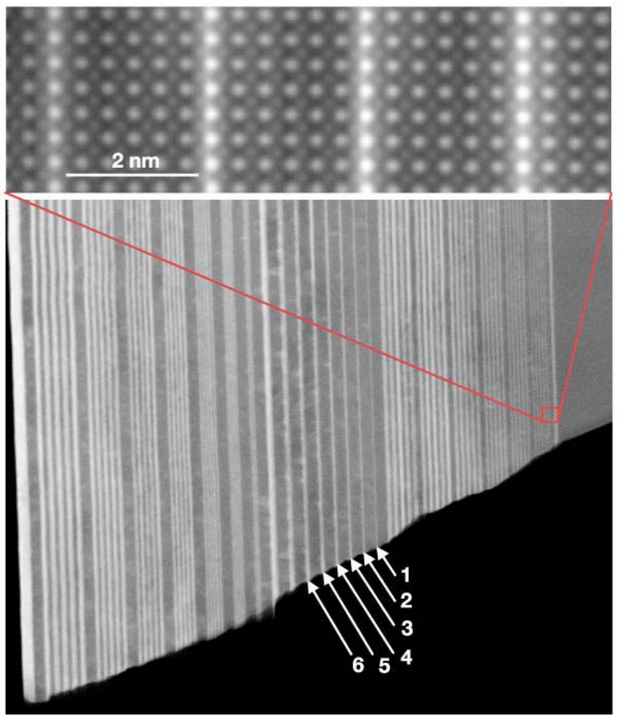

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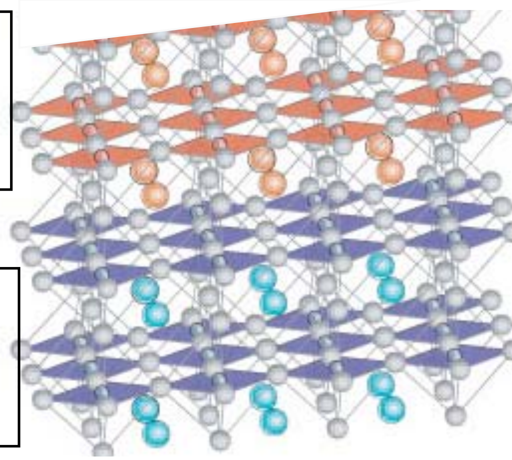

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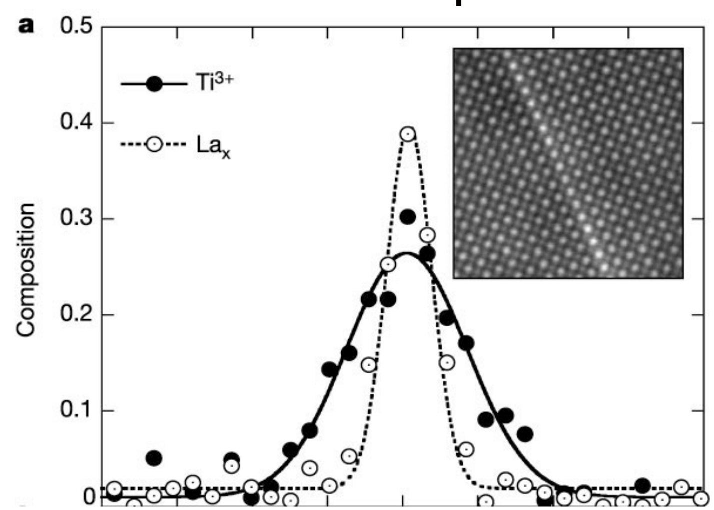
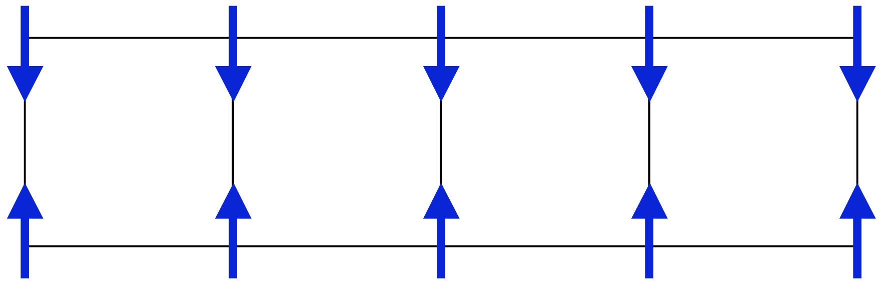
The conflicted d electron spreads out…

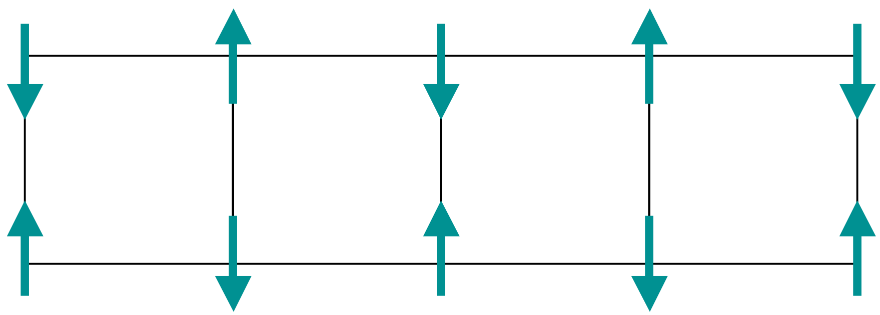


→ (magnetic) metal at the interface!

Incompatible magnetism at oxide-oxide interfaces

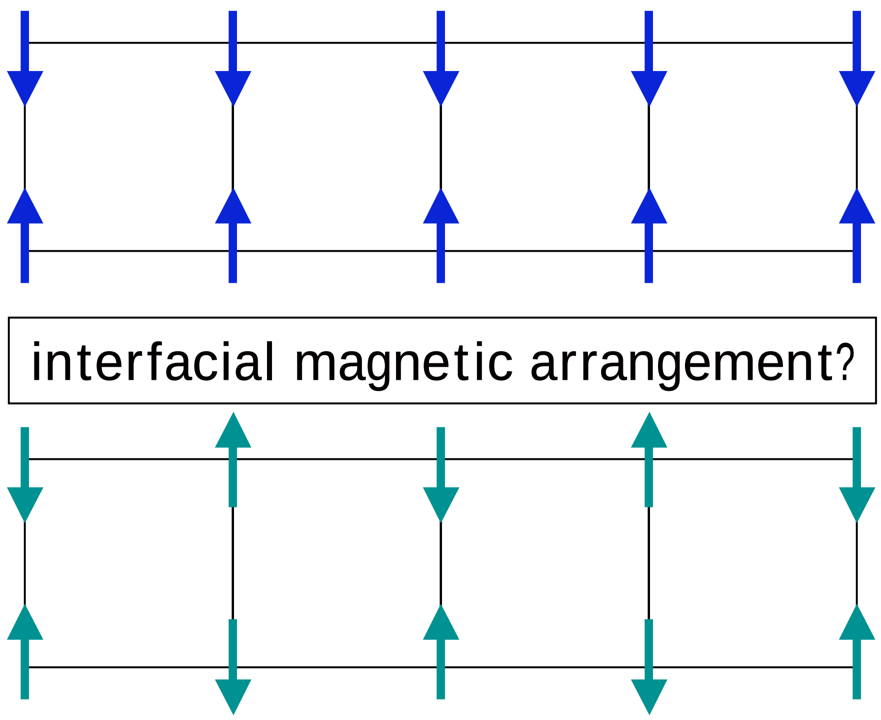


“A-type” antiferromagnet
e.g. $LaMnO_3$



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

Frustrated magnetism at oxide-oxide interfaces



"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!

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?