LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN

Materials by Design,
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Manipulating electronic states at oxide surfaces and interfaces

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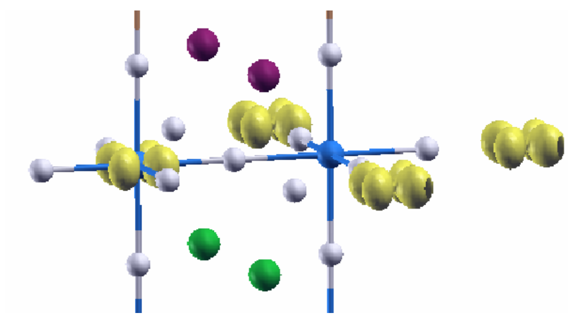

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DFG

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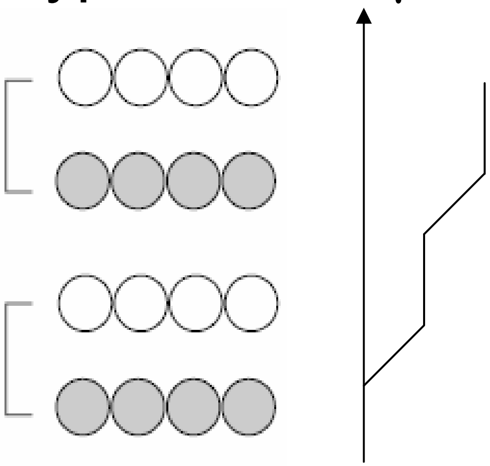
Polar Oxide Surfaces

Type 3: Q≠0, $\mu \neq 0$



Stabilization mechanisms:

- ionic model *(Tasker, 1979) – diverging surface energy – polarization catastrophe*
- autocompensation rule *(LaFemina,1994)*
- strong changes in surface stoichiometry
  surface (atomic) reconstruction/facetting
- structural and electronic relaxations
- strong modification of electronic structure: electronic relaxations, surface states, metallization: electronic reconstruction

  (Noguera, JPCM. 12, 2000, Okamoto and Millis, Nature 2004)
- TM oxides: further mechanisms, *e.g.* correlation driven *e.g.* charge ordering
- finite size effects

Outline

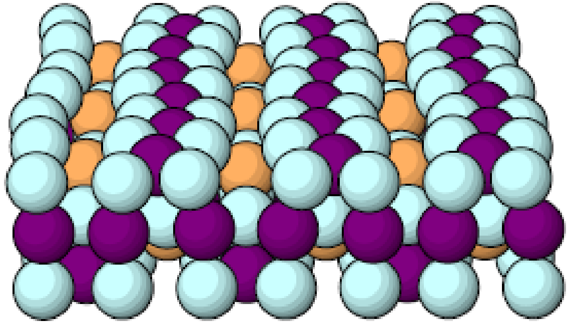
1. Introduction
2. Stabilisation Mechanisms at a Polar Oxide Surface:

   H_2O on Fe_3O_4(001)
3. Perovskite superlattices (SL) and thin films

   - $LaAlO_3$/$SrTiO_3$ SL: the n-type interface

   - finite size effects in $LaAlO_3$ films on $SrTiO_3$(001)
4. Summary

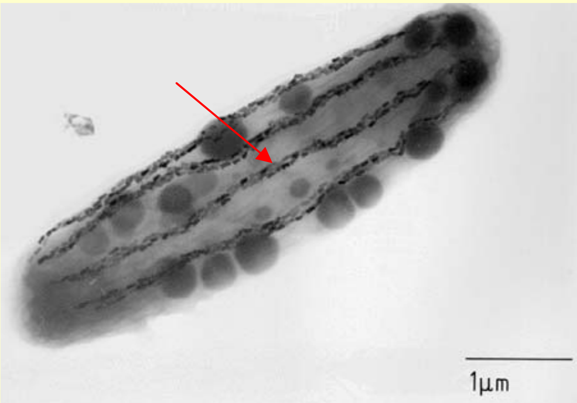
2. Stabilisation Mechanism at a polar Oxide Surface: Fe_3O_4(001)



Magnetite Fe_3O_4: Applications

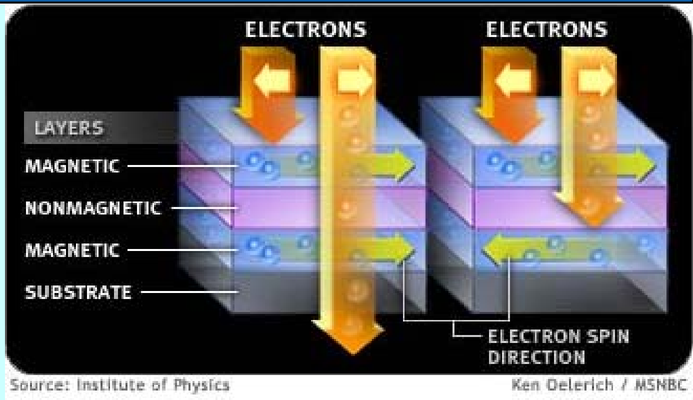
paleomagnetism

Biomineralisation
(magnetotactic Bacterium)

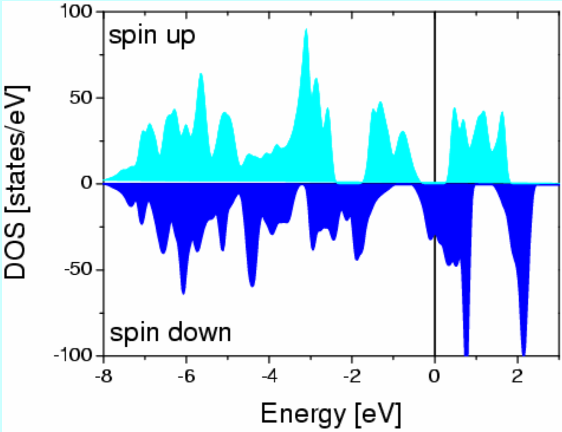


Hanzlik, Winklhofer, Petersen, JMMM, 248, 258-67 (2002)

Spintronics



Fe_3O_4 :



- halfmetal behavior

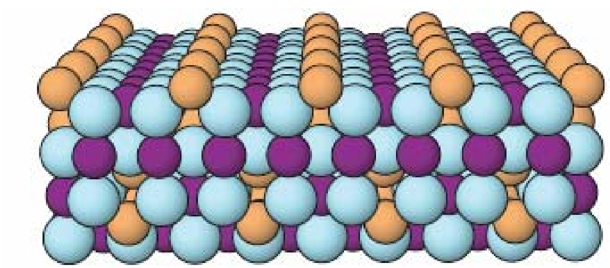
(Zhang&Satpathy,PRB44,'91)

- high Curie Temperature: 858K

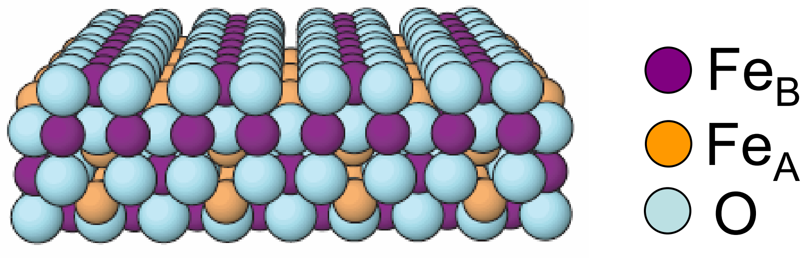
⇒ potential material for spintronics-devices *(Eerenstein et al., PRL88 ,2002)*

$Fe_3O_4(001)$: bulk truncations

A-Termination



B-Termination

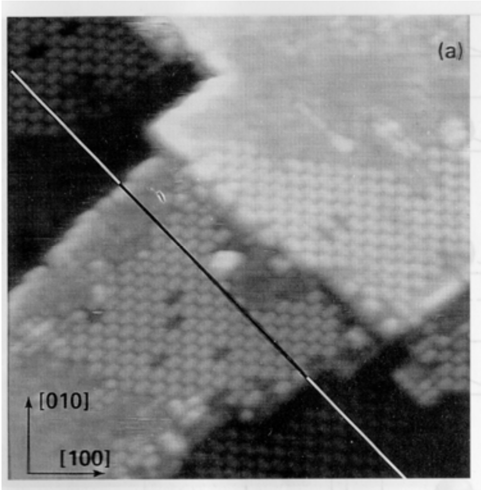


Both bulk terminations – polar Type 3 *(Tasker,1979)*

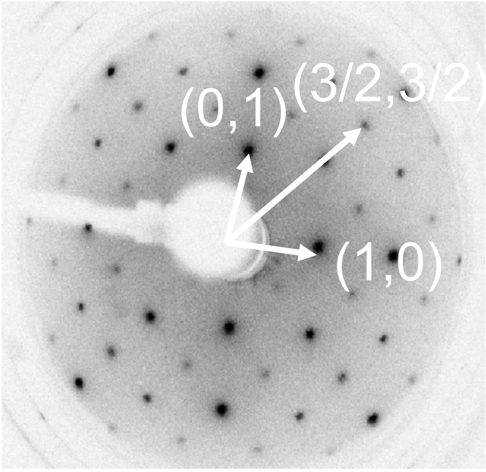
⇨ discarded based on electrostatic considerations

Experimental results:

$\left(\sqrt{2}\times\sqrt{2}\right)R45^{\circ}$ – reconstruction

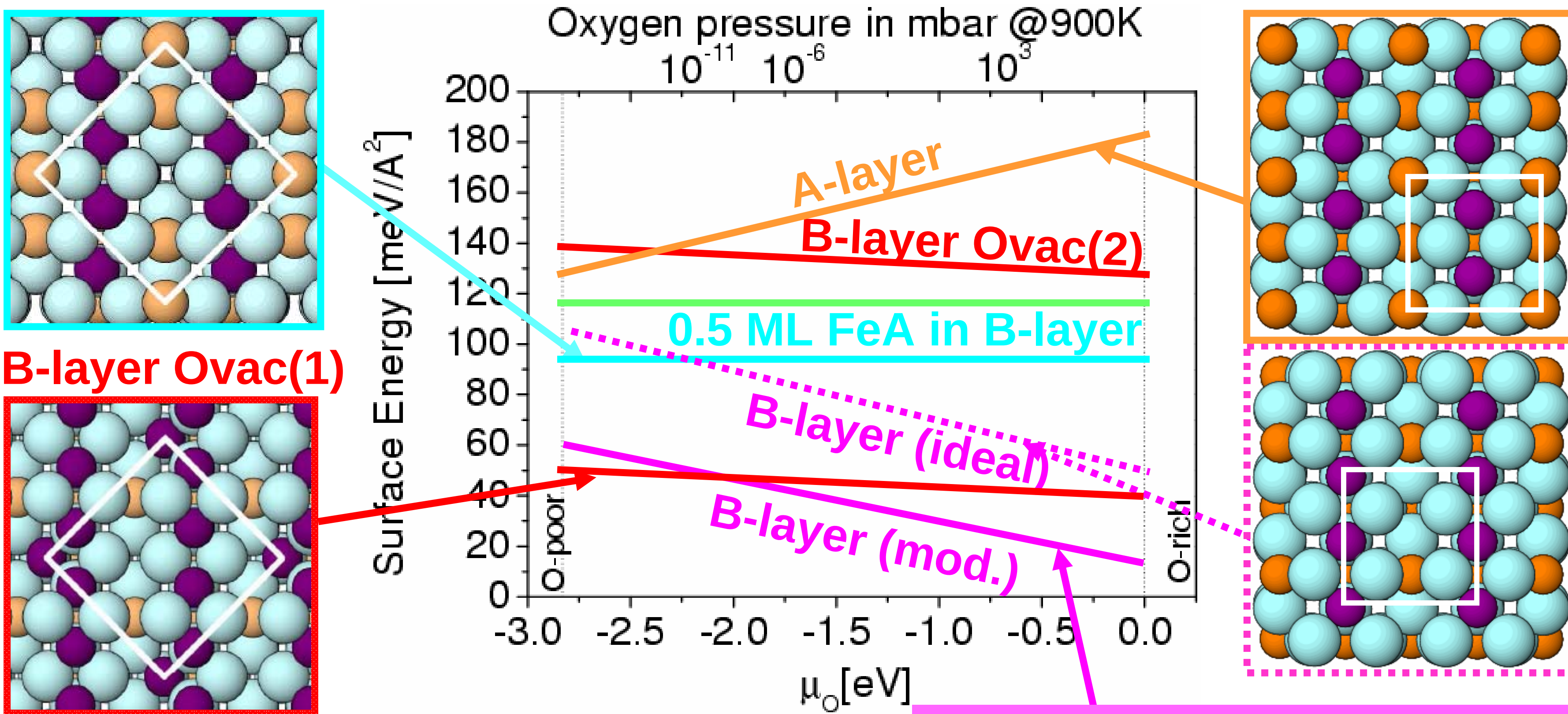


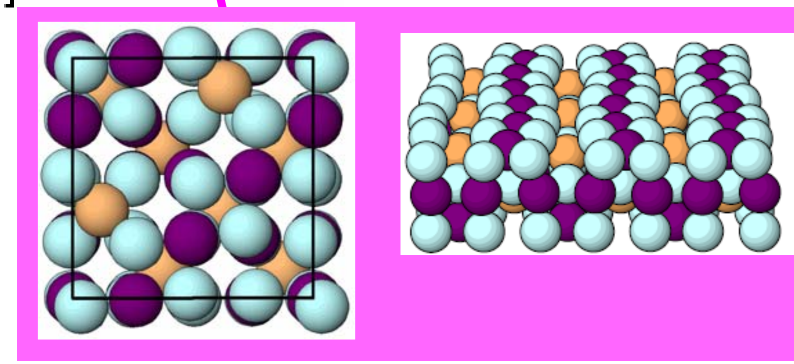
Gaines et al., Surf. Sci. 373 (1997)



LEED pattern of $Fe_3O_4(001)$ annealed in UHV at 900 K

Surface Phase Diagramm of $Fe_3O_4(001)$:



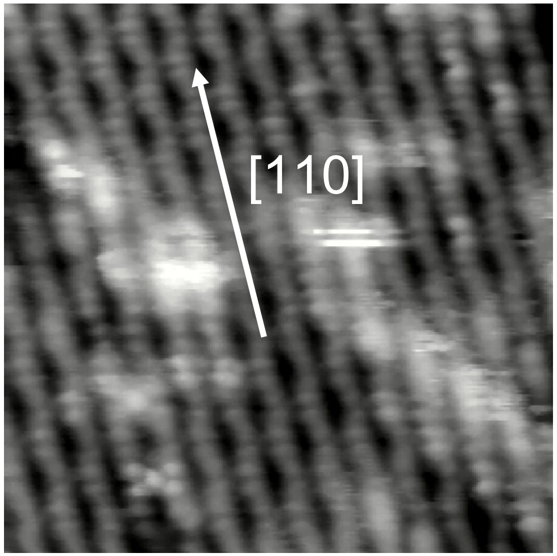


symmetry reduction through lateral and vertical distortions!

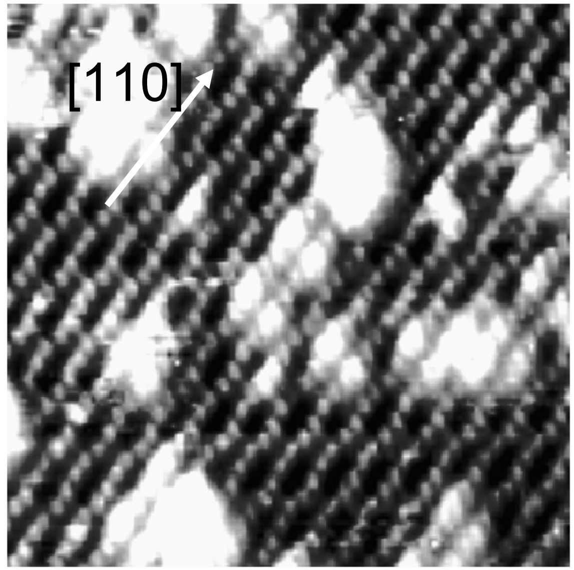
Pentcheva, et al. , PRL94,126101,2005

Modified B-layer: STM measurements and simulations

Experiment

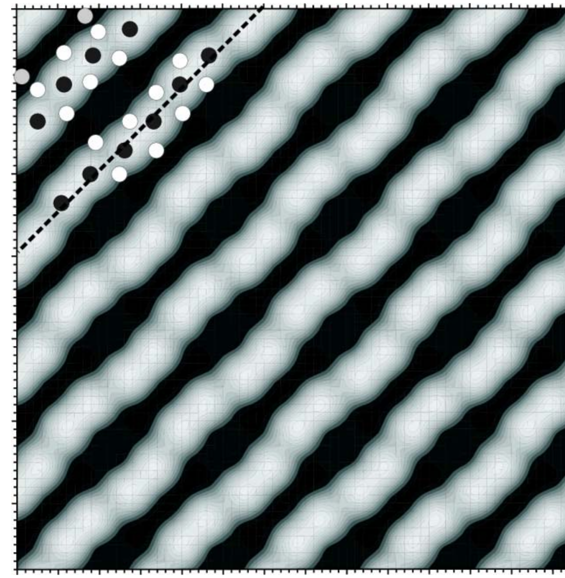


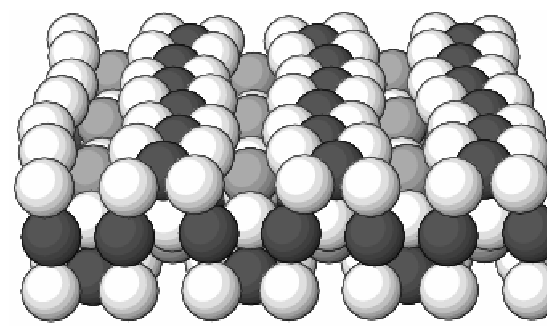
100Ax100 A, 0.6V, 0.3nA
Stanka et al., SS 448, 2000



100Åx100 Å, 1.1V, 1.2 nA

Theorie

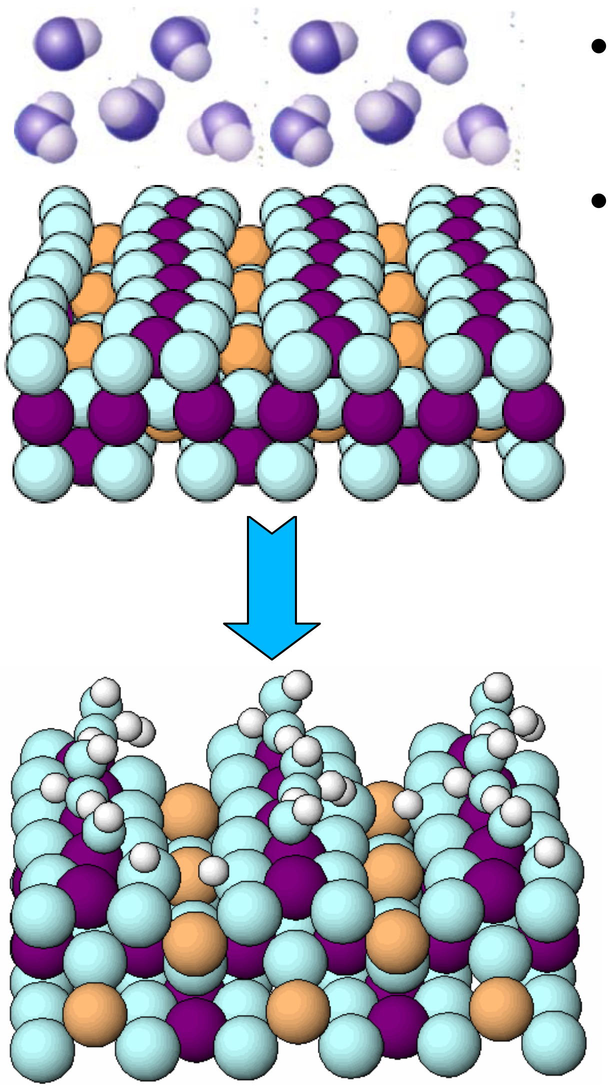




Fonin, RP et al.,
PRB72, 104436 (2005).

- *wave-like* structure along [110]-direction

Adsorption of H_2O on $Fe_3O_4(001)$



Applications:

- Adsorption and reduction of heavy metals like As(V), Cd(IV) in aqueous environments
- Water gas phase shift reaction at high temperatures

Questions

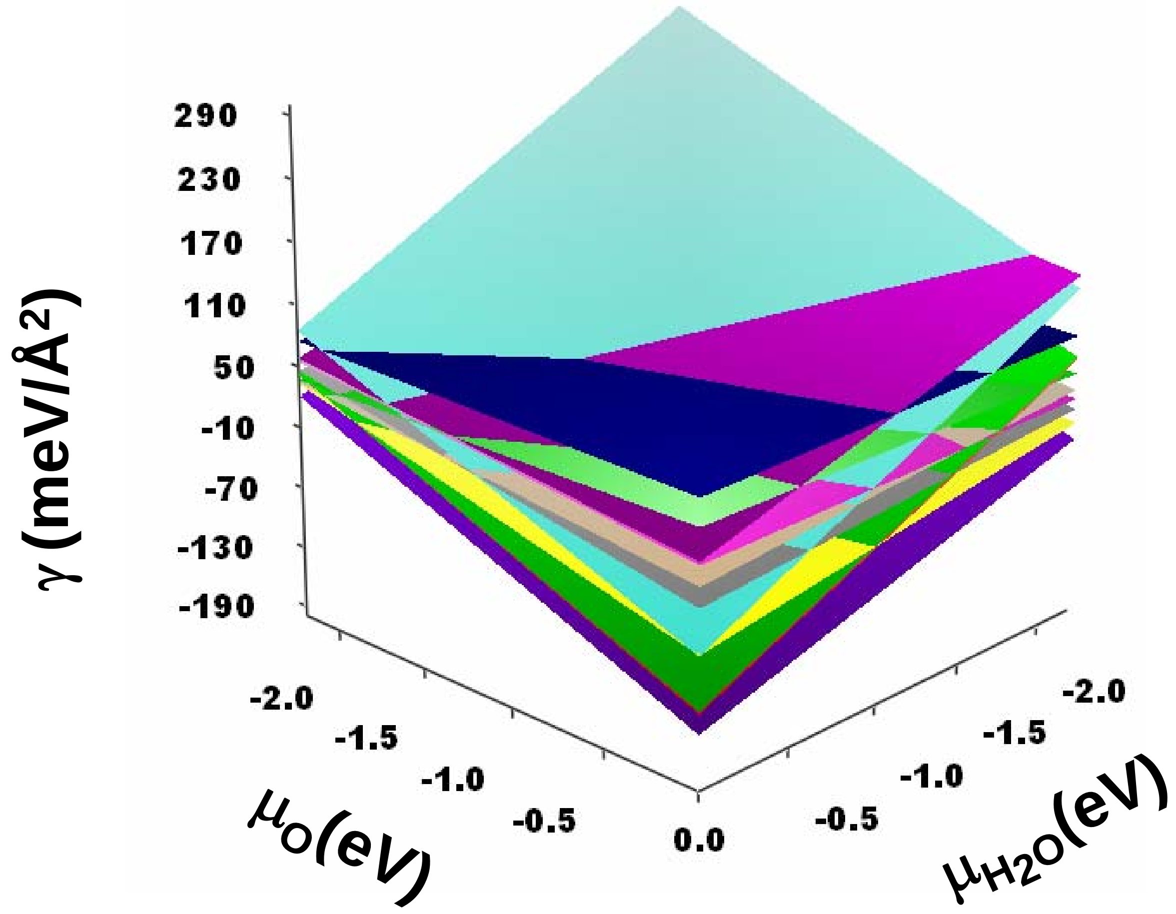
- What is the mode of water adsorption on the magnetite surface?

  Molecular vs. Dissociative

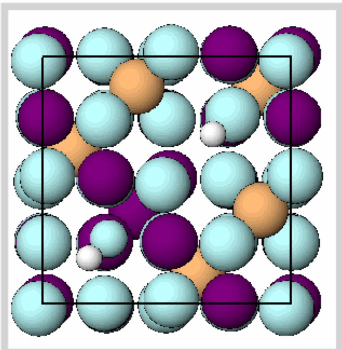
- How does the adsorption affect
  - the surface reconstruction?
  - electronic properties

Surface Phase Diagram

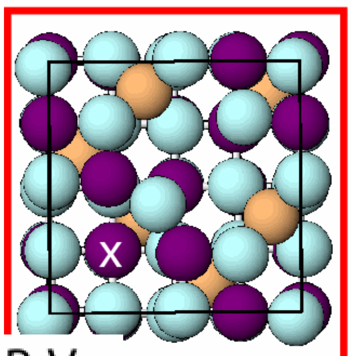
$$\gamma_{Surface} = \gamma(T,P) = \frac{1}{2A}\left(E_{total} - N_{Fe}\mu_{Fe} - N_O\mu_O - N_H\mu_H\right)$$



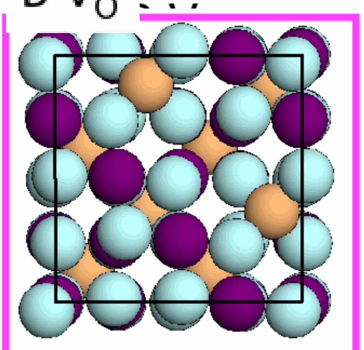
Surface Phase Diagram
Bottom View



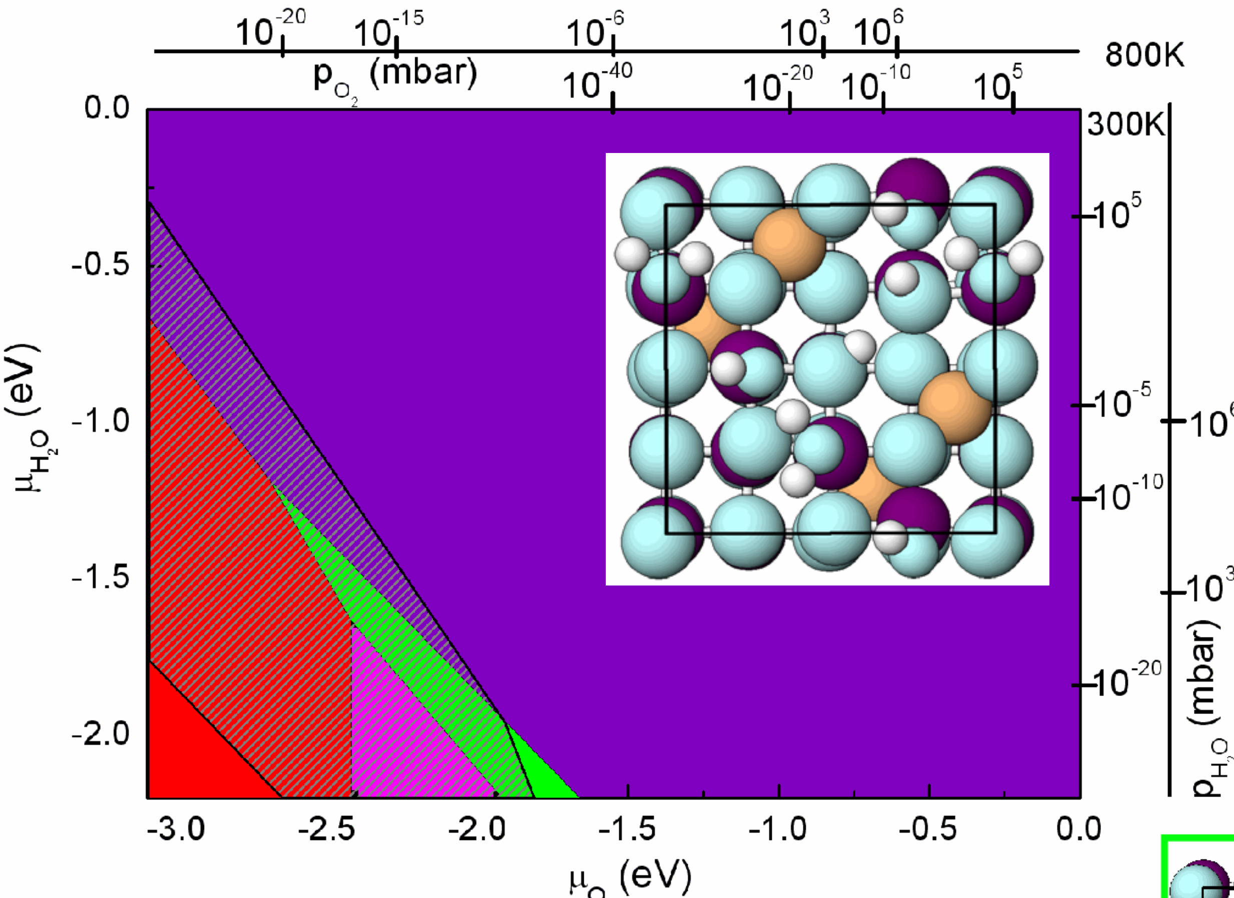
B-V_O+1H_2O(D)



B-V_O

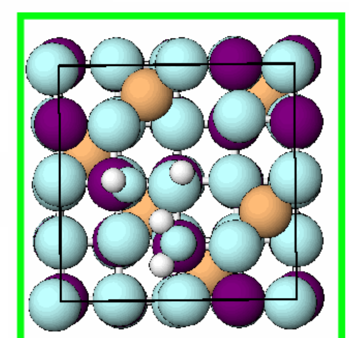


B-layer



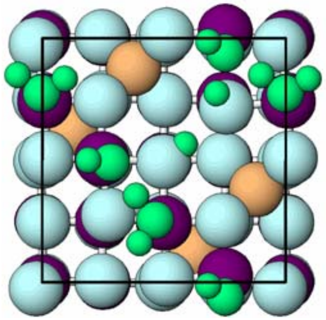
Fe_A
Fe_B
O
O^w
H

B-2H_2O(M)



N. Mulakaluri, RP, et al, PRL 103, 176102 (2009)

DFT &Quantitative LEED analysis

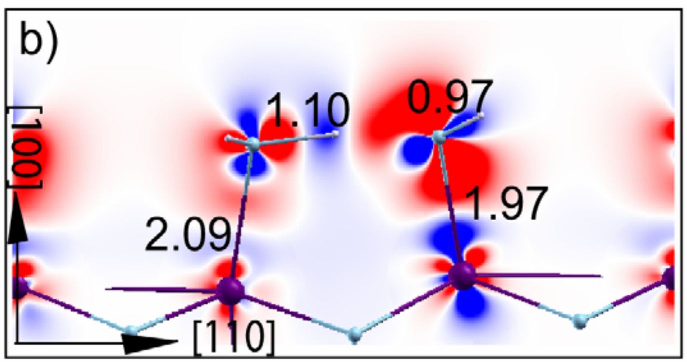


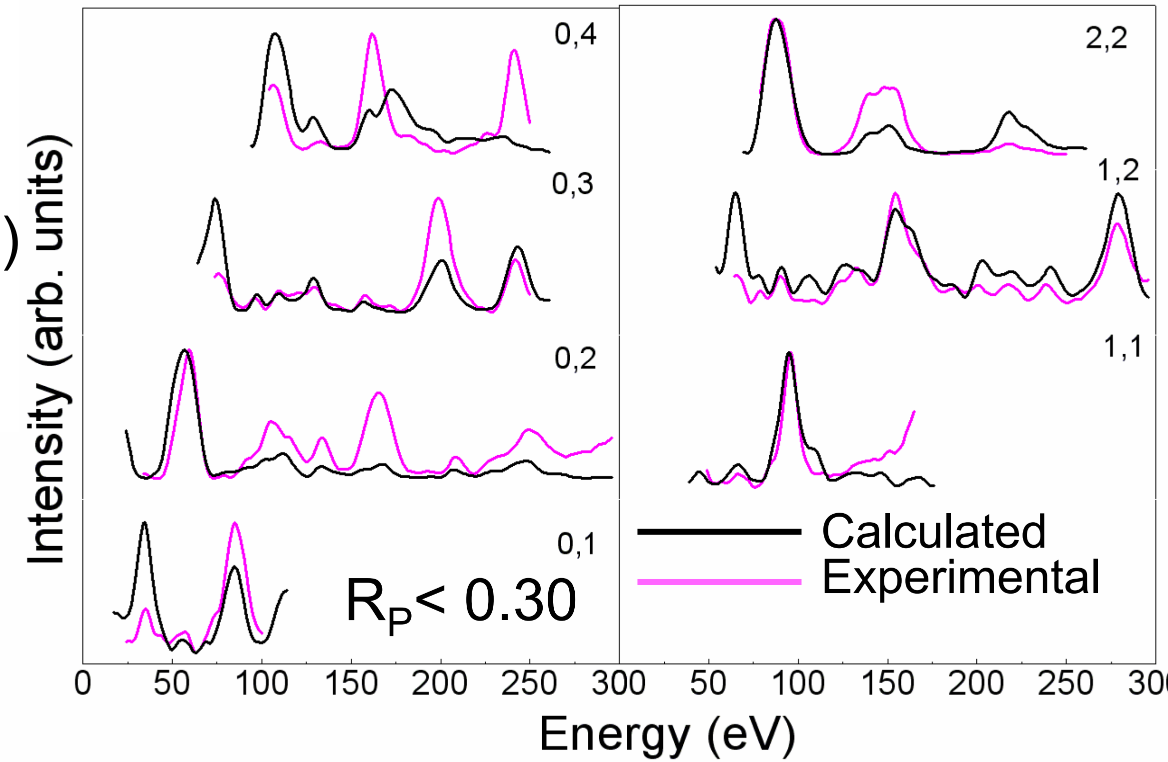
DFT (LEED)

2.09 (2.12)

1.97 (1.87)

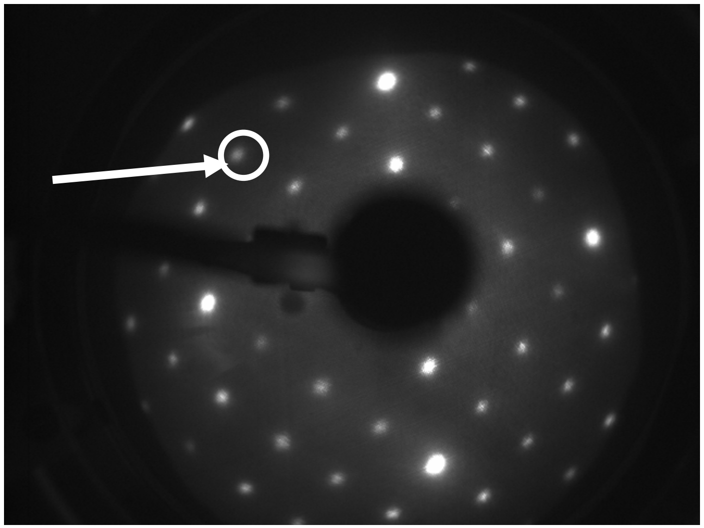
∡HOH 104.9°



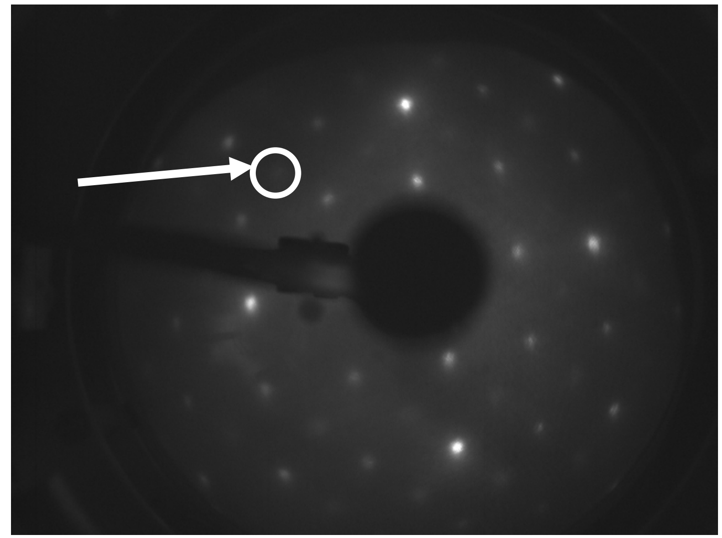


- Two different bond lengths found for Fe_B-O(H_2O/OH)
- Experimental evidence for partial dissociation on the surface
- Partial occupation numbers are found in LEED analysis

LEED Measurements



Before Water Adsorption



After Water Adsorption

Energy of the electron beam is 100.8 eV

Exposure pressure = 1.5×10^{-5} mbar time= 5 mins

Superstructure spots nearly suppressed

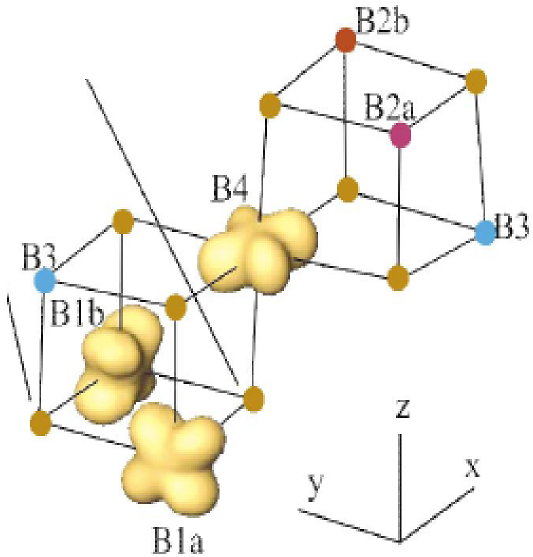
Charge and orbital order in Fe_3O_4 bulk

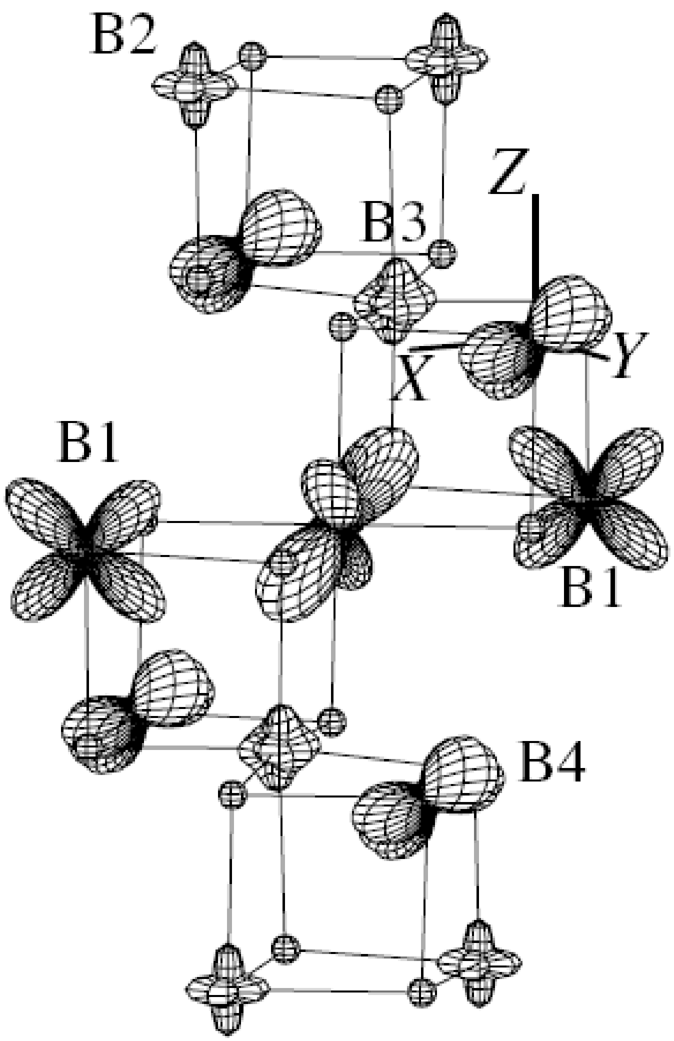
@121-126K Verwey transition
Fd3m →P2/c *(Wright et al.PRL 2001)*
a/√2x a/√2x2a

Change in conductivity:
MIT or semiconductor-to-semiconductor

LDA+U: CO/OO does not fulfill Anderson's criterion

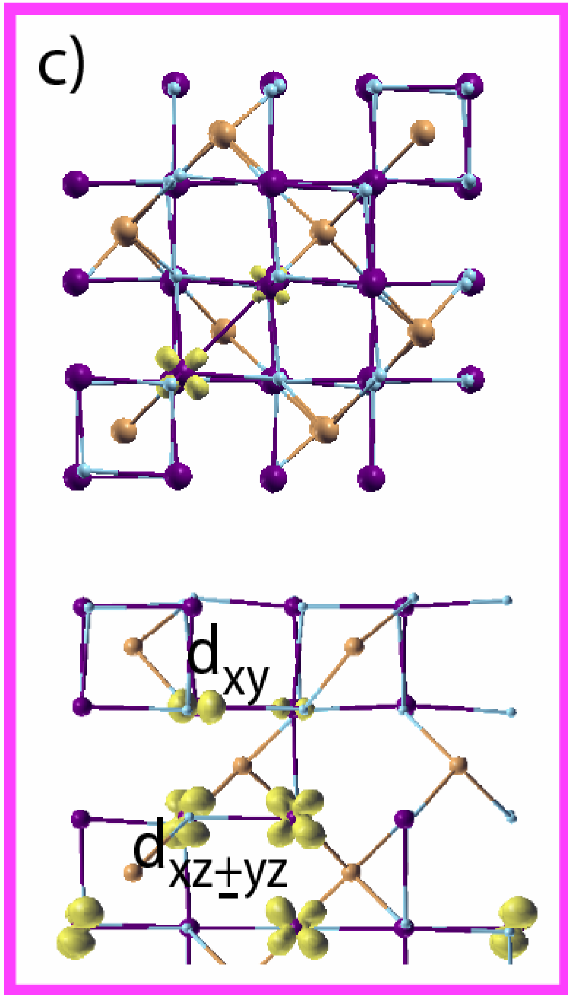
Antiferroorbital ordering

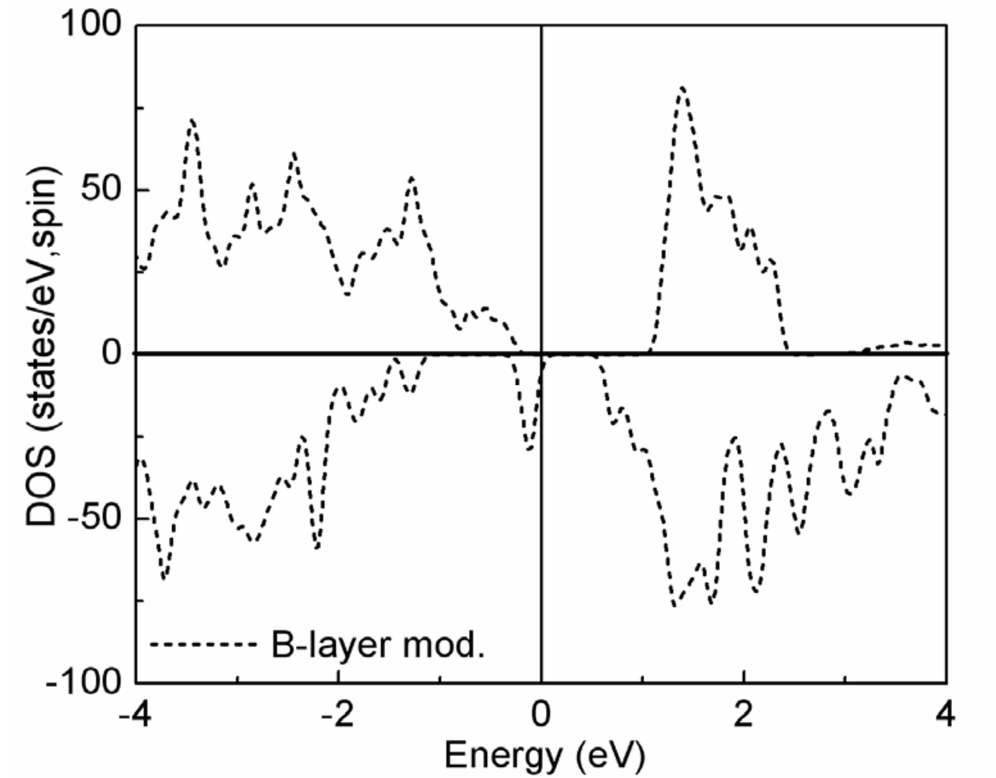




Leonov et al, PRL 2004
Guo et al, PRL 2004

Electronic Properties@Fe_3O_4(001)

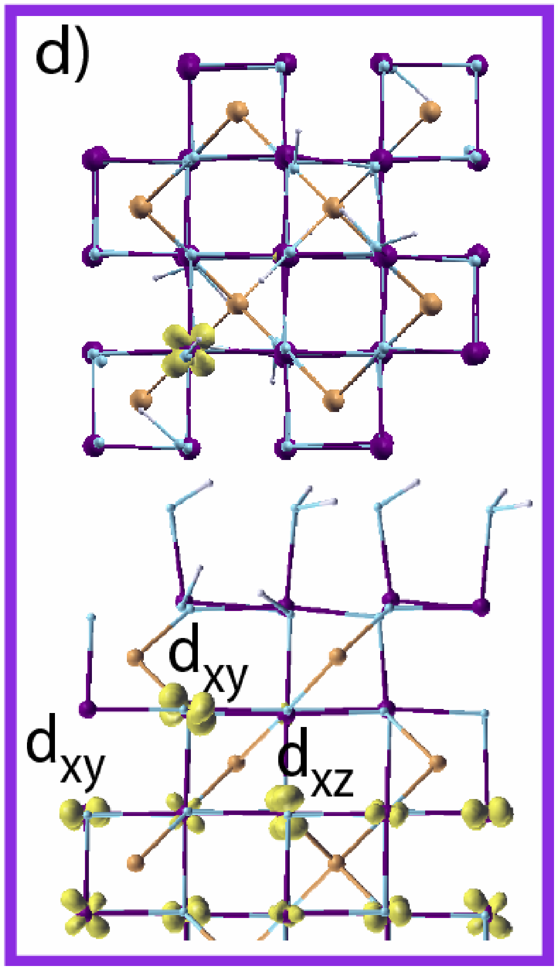


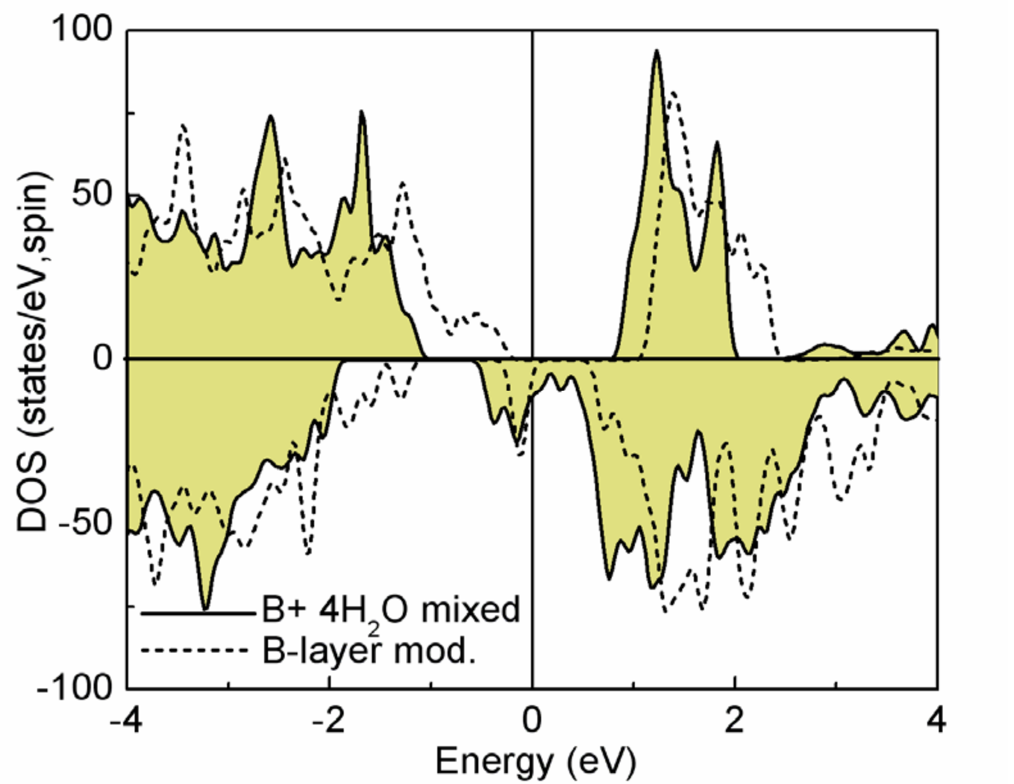


- Clean Fe_3O_4(001)-insulating: surface STS: Δ=0.2 eV

(*Jordan et al. PRB 74, 085416 (2006); also Lodziana, PRL 99 206402 (2007)*

Electronic Properties@Fe_3O_4(001)

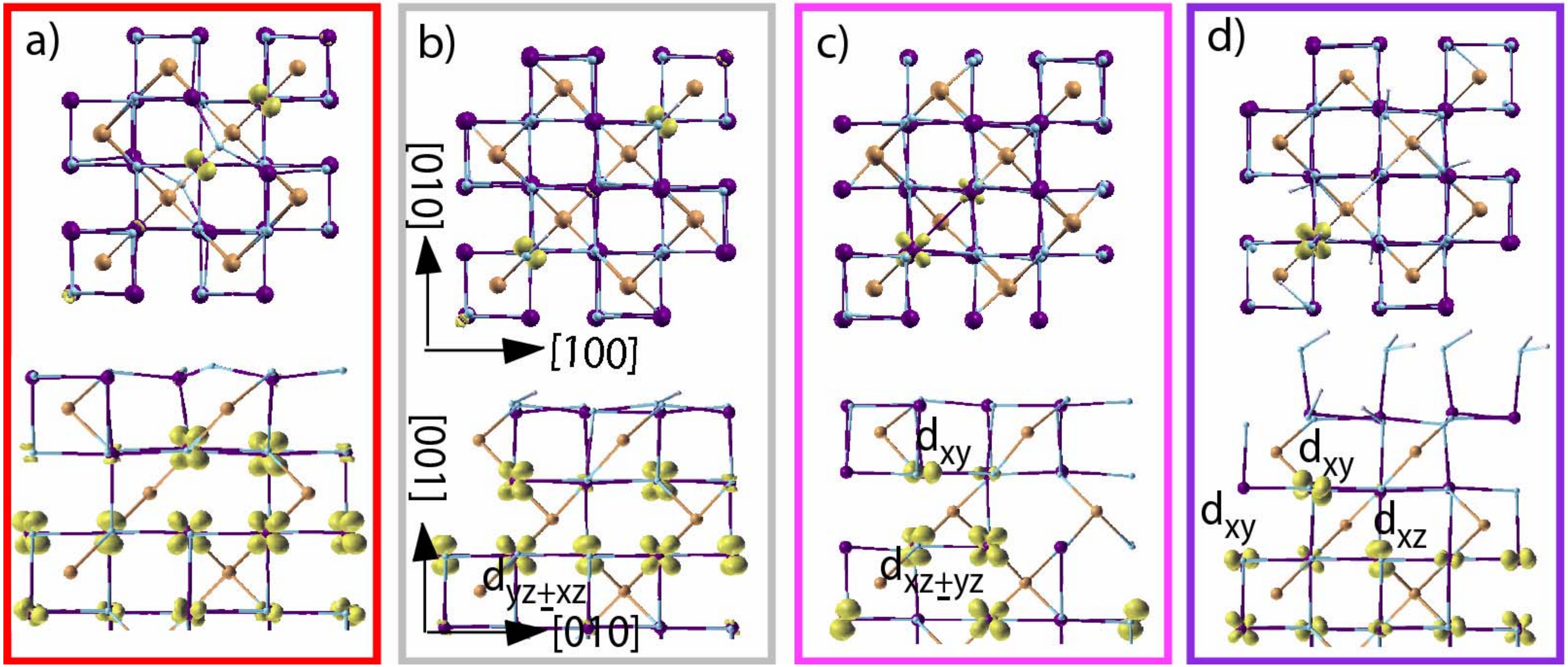




- Insulator to halfmetal transition

(N. Mulakaluri, RP, et al, PRL 103, 176102 2009)

Charge and orbital order@Fe_3O_4(001)



- Surface layer Fe^{3+}
- charge and orbital order in the subsurface layer

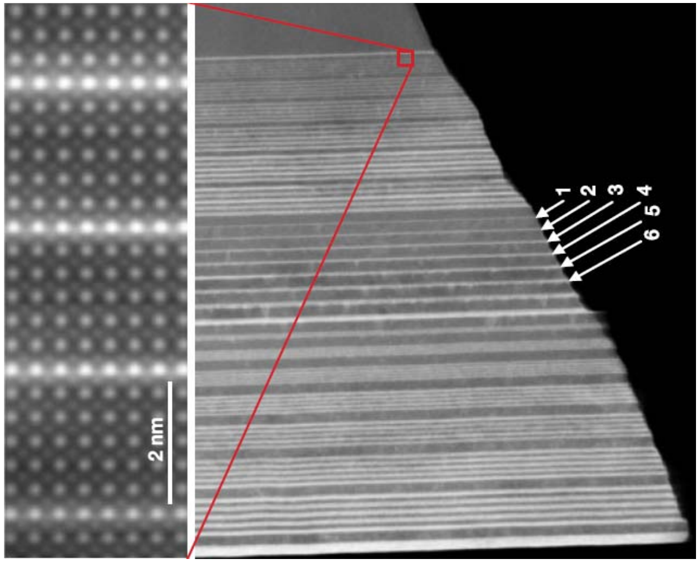
N. Mulakaluri, RP, et al, PRL 103, 176102 (2009)

Summary I

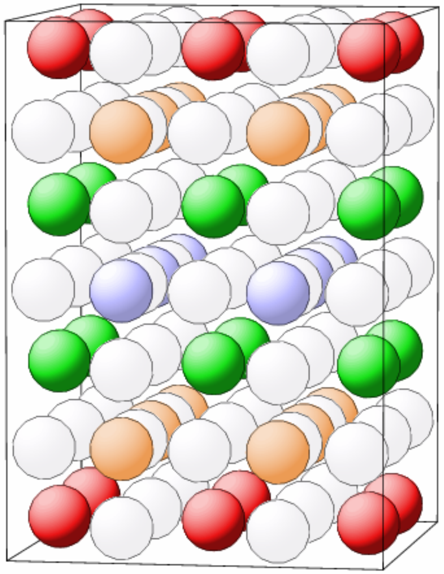
- Isolated molecule: dissociation on defect-free surface and at surface defects
- Higher coverages: crossover to mixed mode of adsorption
- DFT and LEED: suppression of $(\sqrt{2}x \sqrt{2})R45°$ reconstruction upon water adsorption
- Surfaces and adsorbates (H, H_2O) induce unique CO/OO states

N. Mulakaluri, RP, et al, PRL 103, 176102 (2009), Parkinson, Mulakaluri et al, submitted

3. Electronic phases at digital perovskite heterostructures: $LaAlO_3/SrTiO_3$

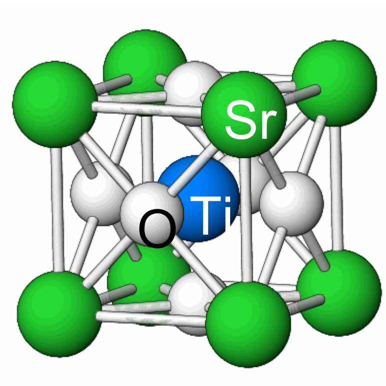


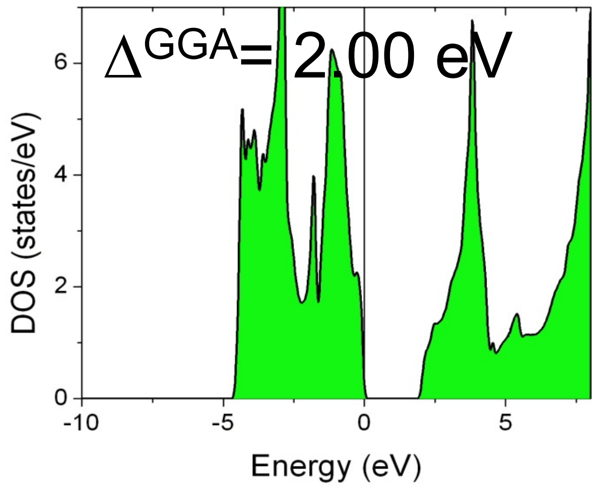
Ohtomo et al., Nature 419, 378 2002



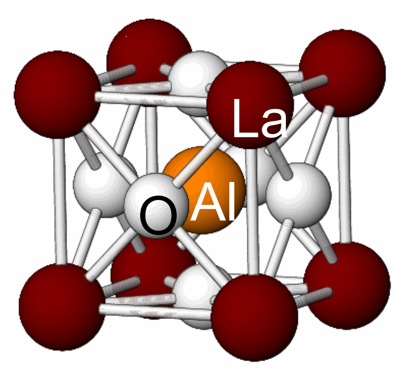
$LaAlO_3/SrTiO_3$ superlattices

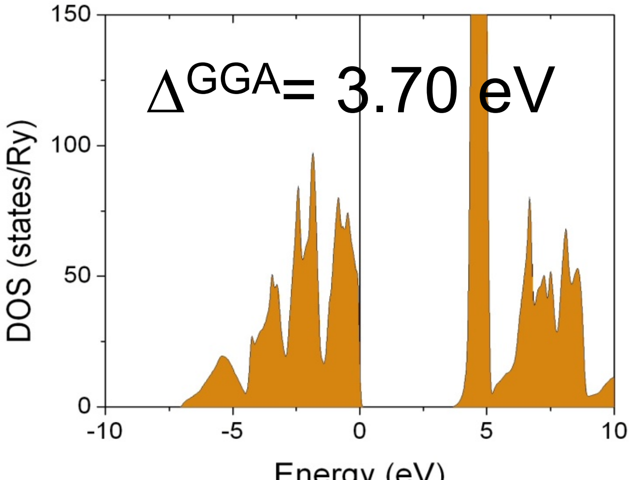
$Sr^{2+}Ti^{4+}O_3$



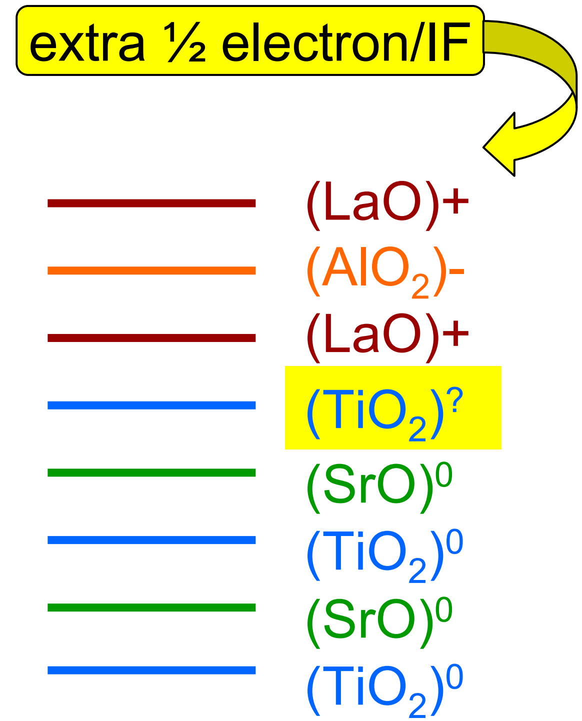


$La^{3+}Al^{3+}O_3$



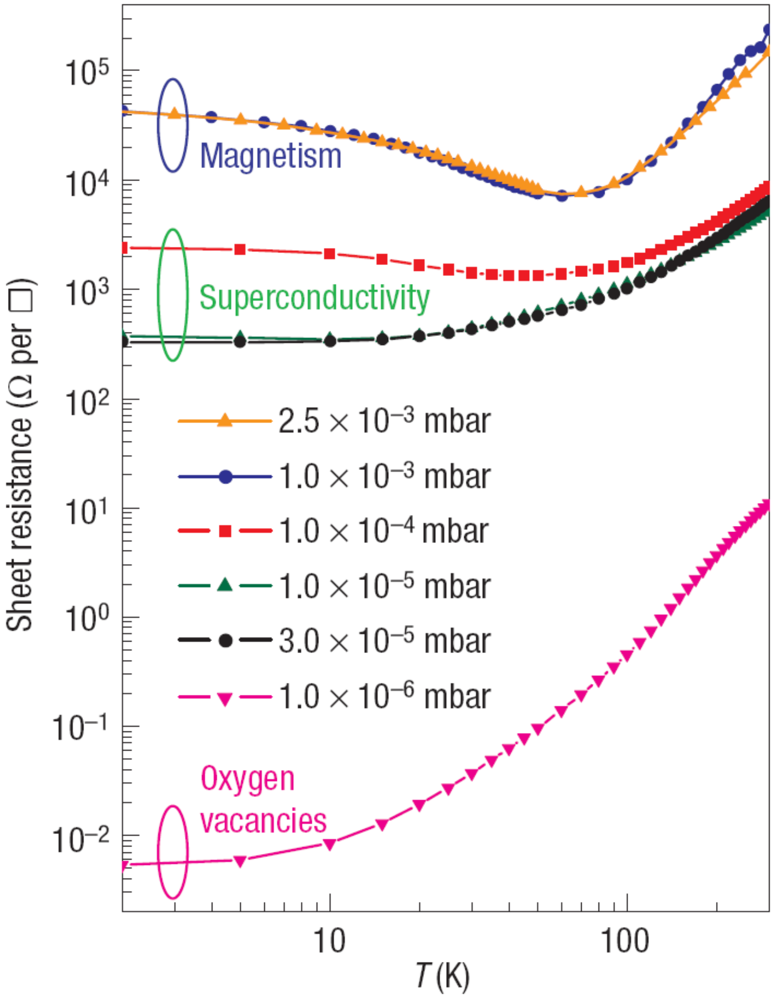


n-type interface



- What is the compensation mechanism?
- novel electronic phases?

n-type $LaAlO_3/SrTiO_3$ IF: Experiments



(Rijnders&Blank, Nat. Mat. 2008)

- magnetism

(Brinkman et al, Nat. Mat. 2007)

- superconductivity

(Reyren et al, Science 2008)

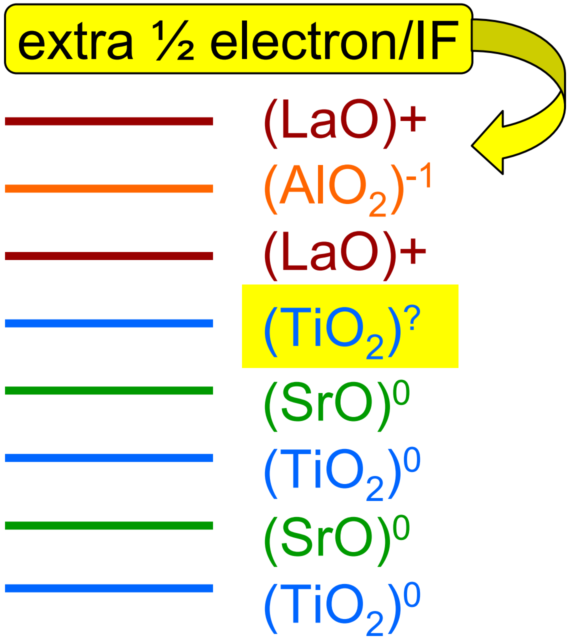
- conductivity

(Ohtomo&Hwang, Nature 2004)

Role of p_{O2}:

(Nakagawa, Hwang&Muller, Nat. Mat. (2006),
Herranz et al., PRL 2007,
Siemons et al., PRL 2007,
Kalabukhov et al., PRB R, 2007,
Basletic et al., Nat. Mat. 2008)

The *n*-type LAO/STO interface



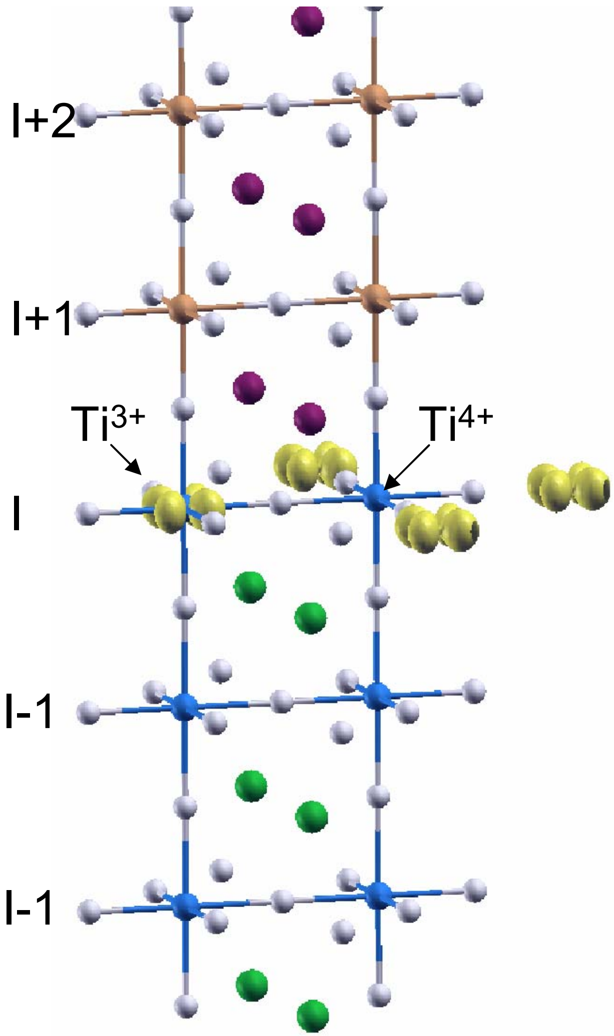
- Mechanisms of charge accommodation
- Influence of electronic correlations
- Influence of lattice relaxations

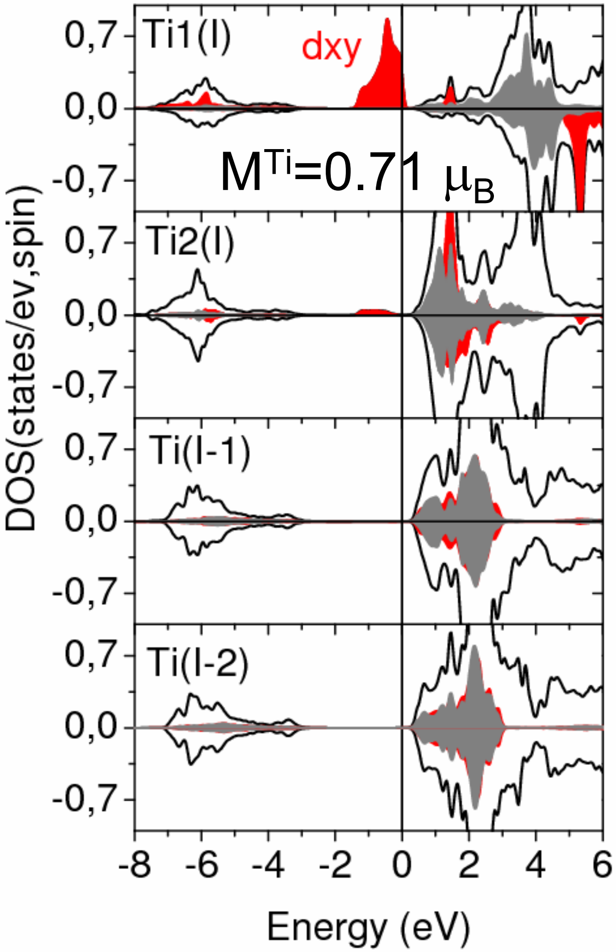
Hubbard modeling
of LTO/STO
by Okamoto and Millis
(*e.g. Nature 428, 630, 2004)*

(n,m) LTO(or LAO)/STO,
($1 \leq n,m \leq 9$):
- WIEN2k code,
- GGA+U
- *c(2x2)* or *p*(2x2)-unit cells

n-type $(LaAlO_3)_5/(SrTiO_3)_5$-IF: GGA+U results

Ideal coordinates



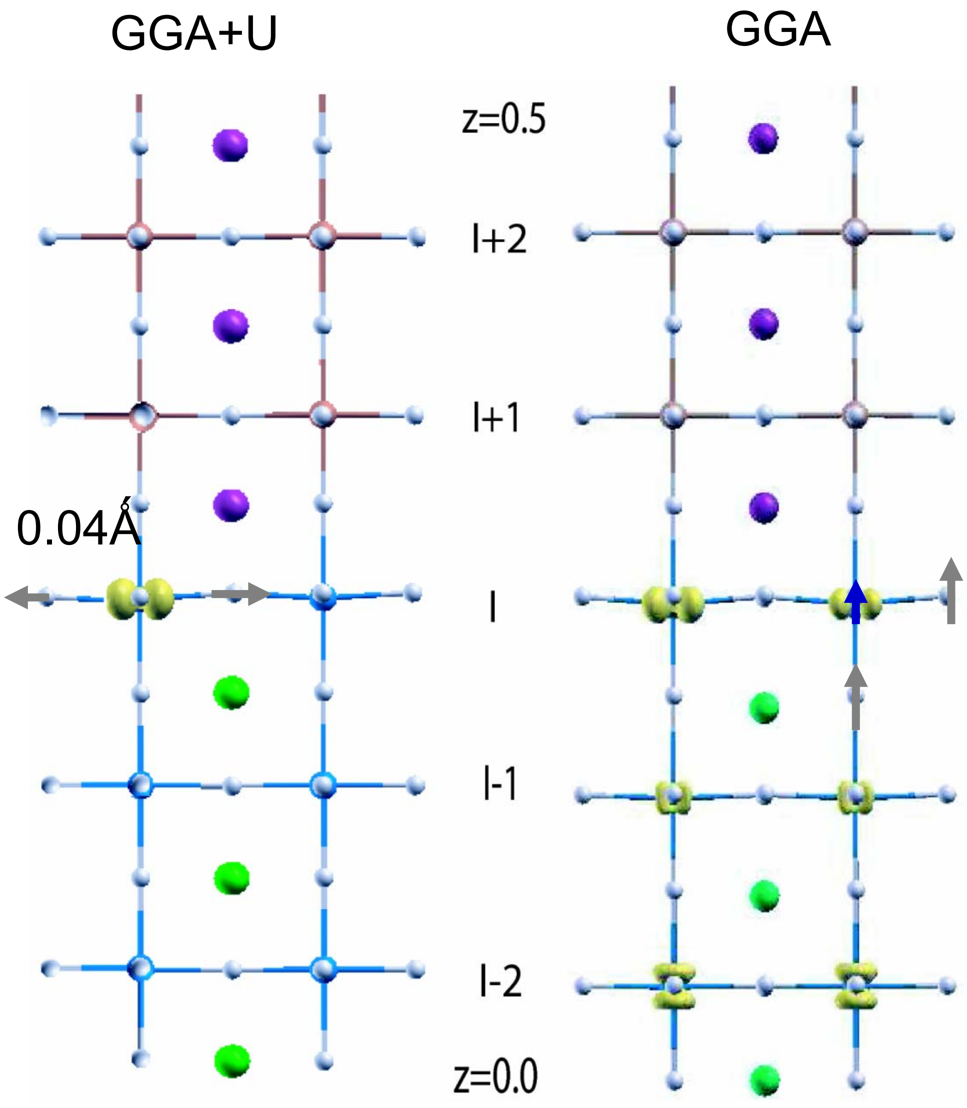


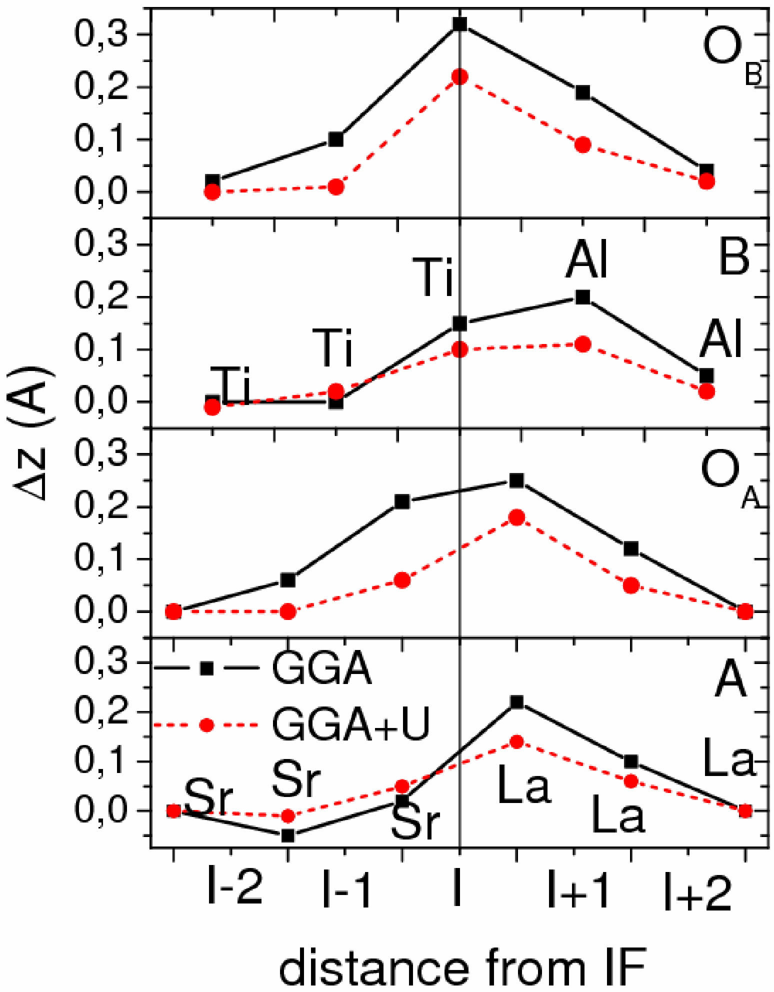
- Ti@IF
  charge ordered: Ti^{3+} and Ti^{4+}
- d_{xy} orbital order

Magnetism@IF of nonmagnetic materials

RP&Pickett, PRB 74, 035112, 2006: ibid 78 (2008)

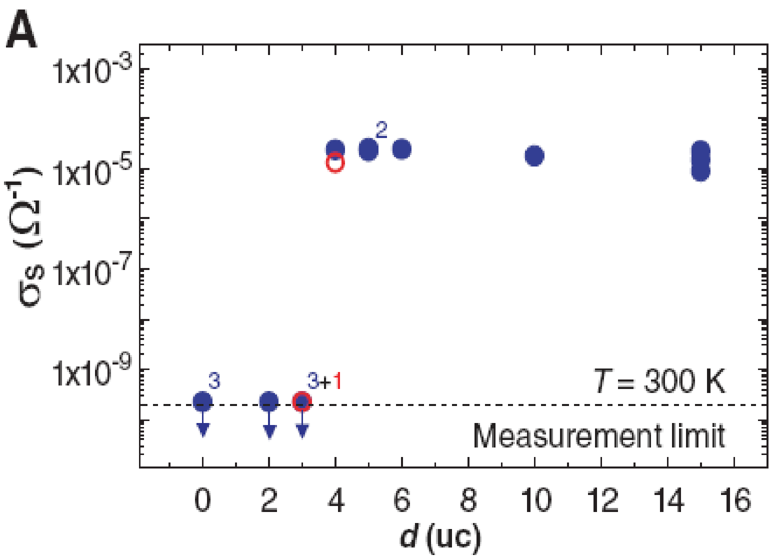
Relaxations in LAO_5/STO_5 : GGA vs GGA+U

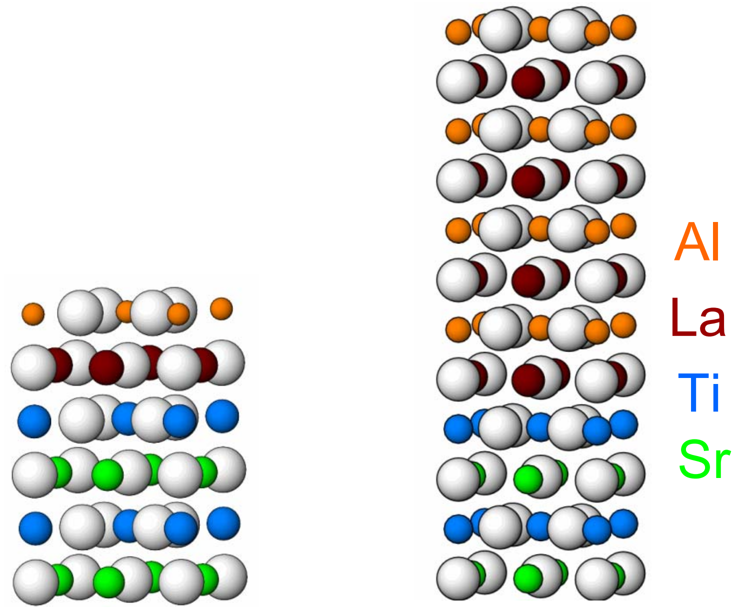




RP&Pickett, PRB 78 2008,
Popovich et al, PRL 2008
Zhong&Kelly, EPL 2008

n-type LAO/STO(001) surfaces: Experimental results



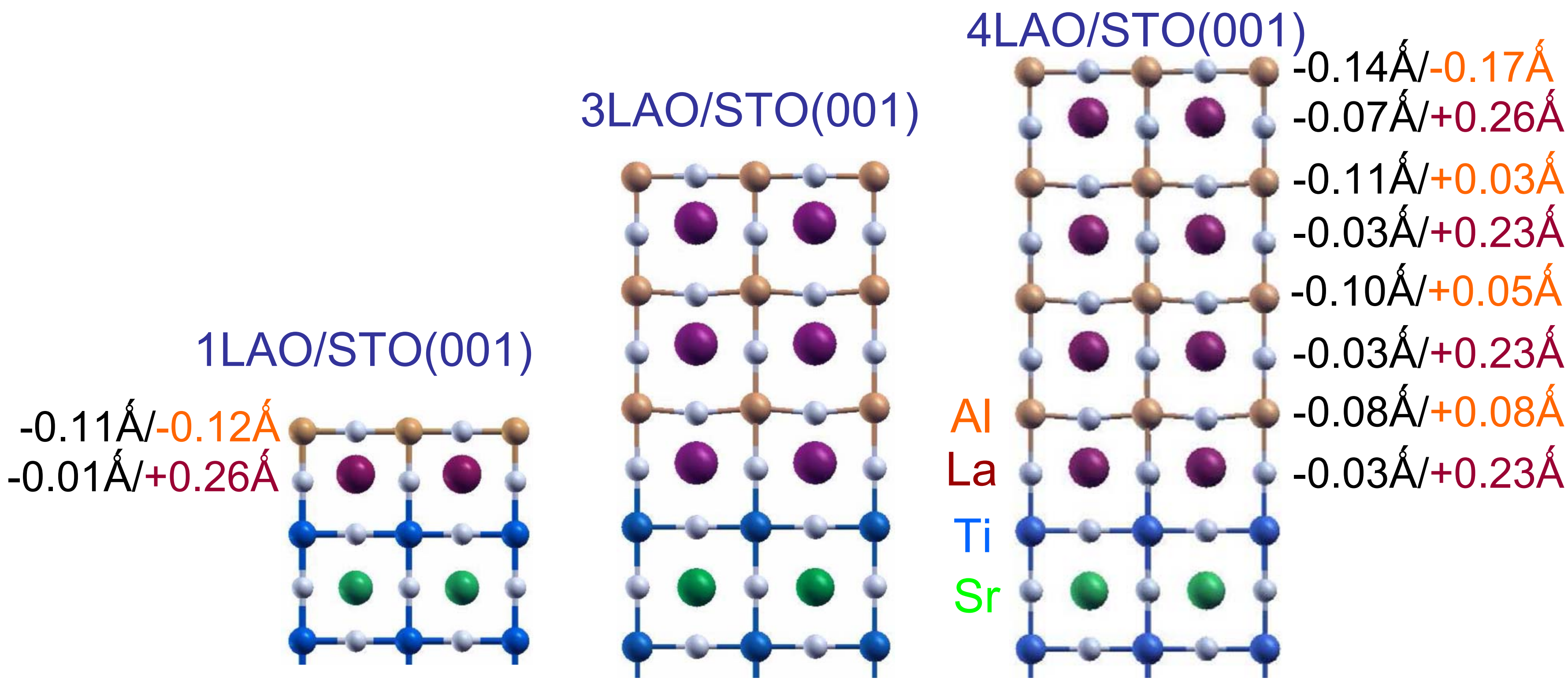


1LAO/STO(001)   4LAO/STO(001)

d_{crit}=4 ML LAO
$d< d_{crit}$ insulating
$d \geq d_{crit}$ conducting
Thiel, Hammerl, Schmehl, Schneider&Mannhart, Science 313 (2006)

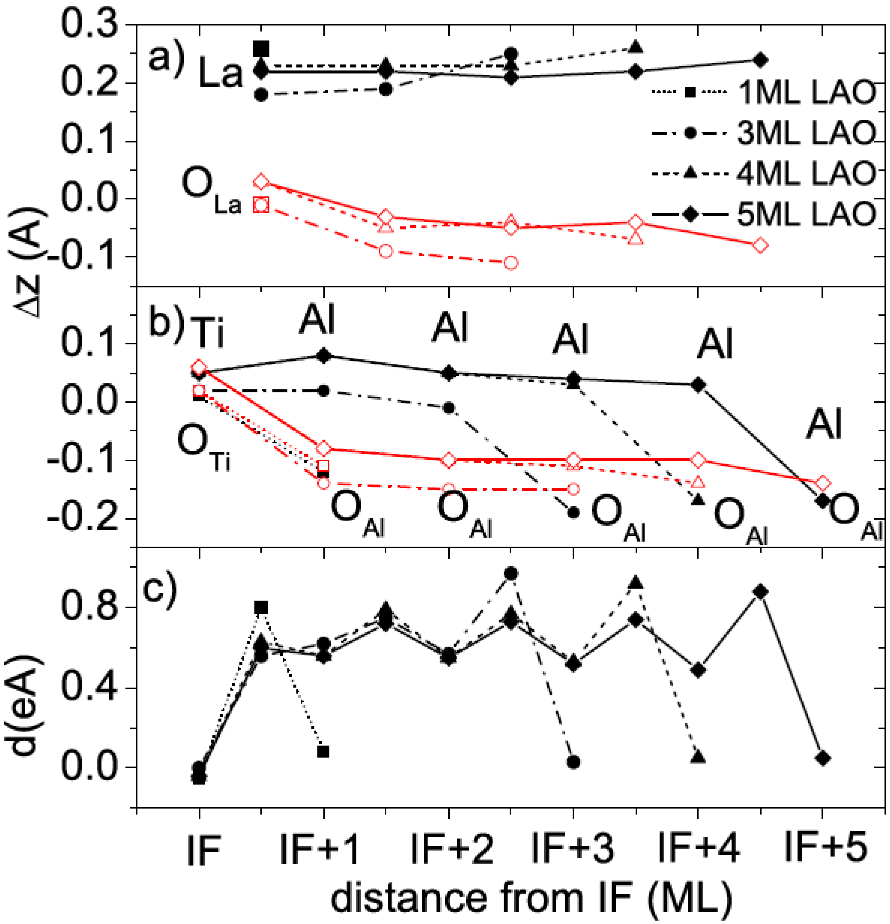
Polar discontinuity **both** at IF and surface → how does the proximity to the surface influence the electronic properties of the IF:

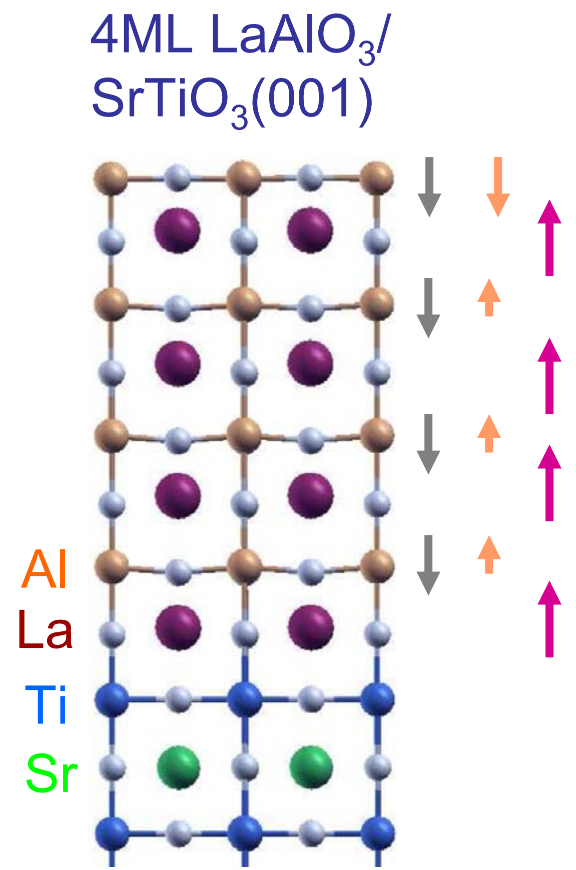
n-type LAO/STO(001) surfaces: structural changes



- uniform polar distortion
  - outward shift of La^{3+} of 0.20-0.26 Å
- response to electric dipole?

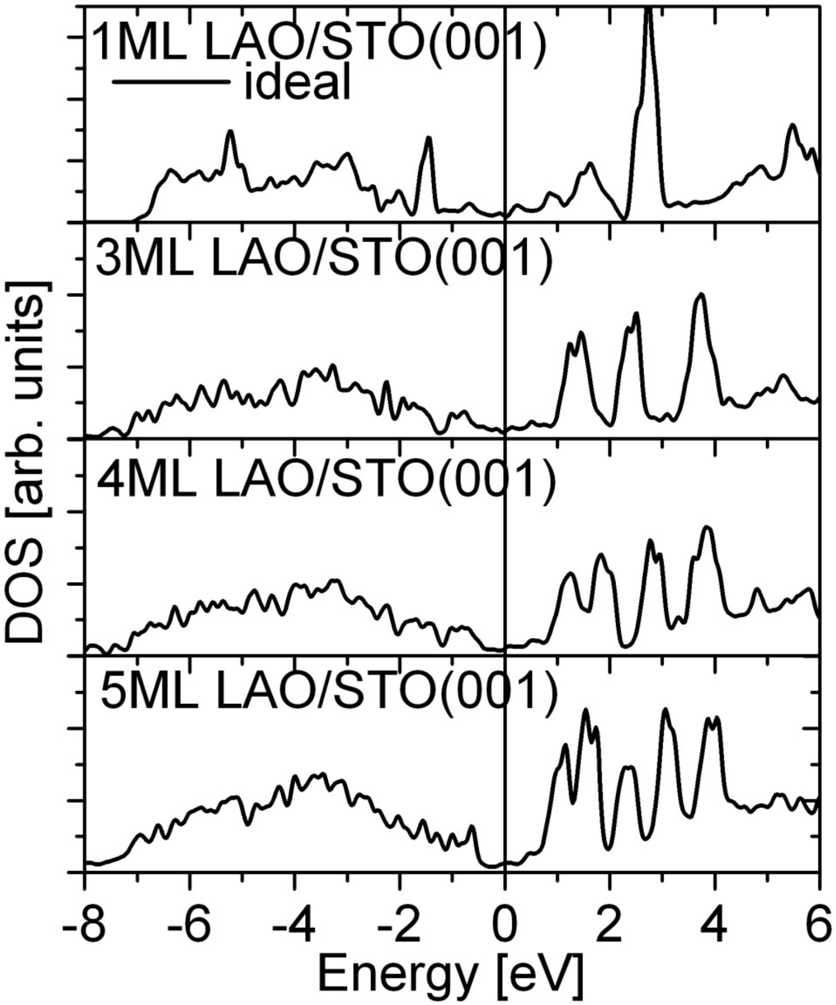
n-type LAO/STO(001) surfaces: structural changes





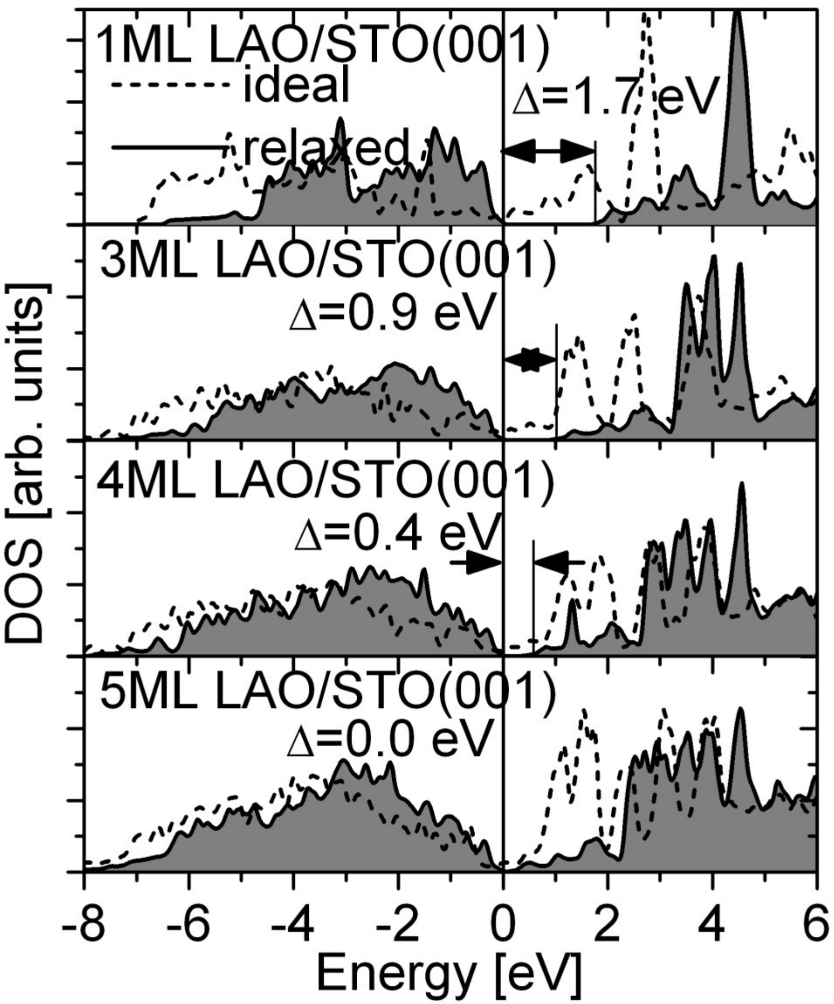
- Dipole shift D_{bare}≈-0.5ex3.9x4=-7.8eÅ
- dipole shift due to FE distortion $D_{FE}=\sum Z_i x \Delta z_i$ = 4.8eÅ=60%x D_{bare}

n-type $LaAlO_3/SrTiO_3(001)$: electronic properties



- without relaxation – all systems *metallic*

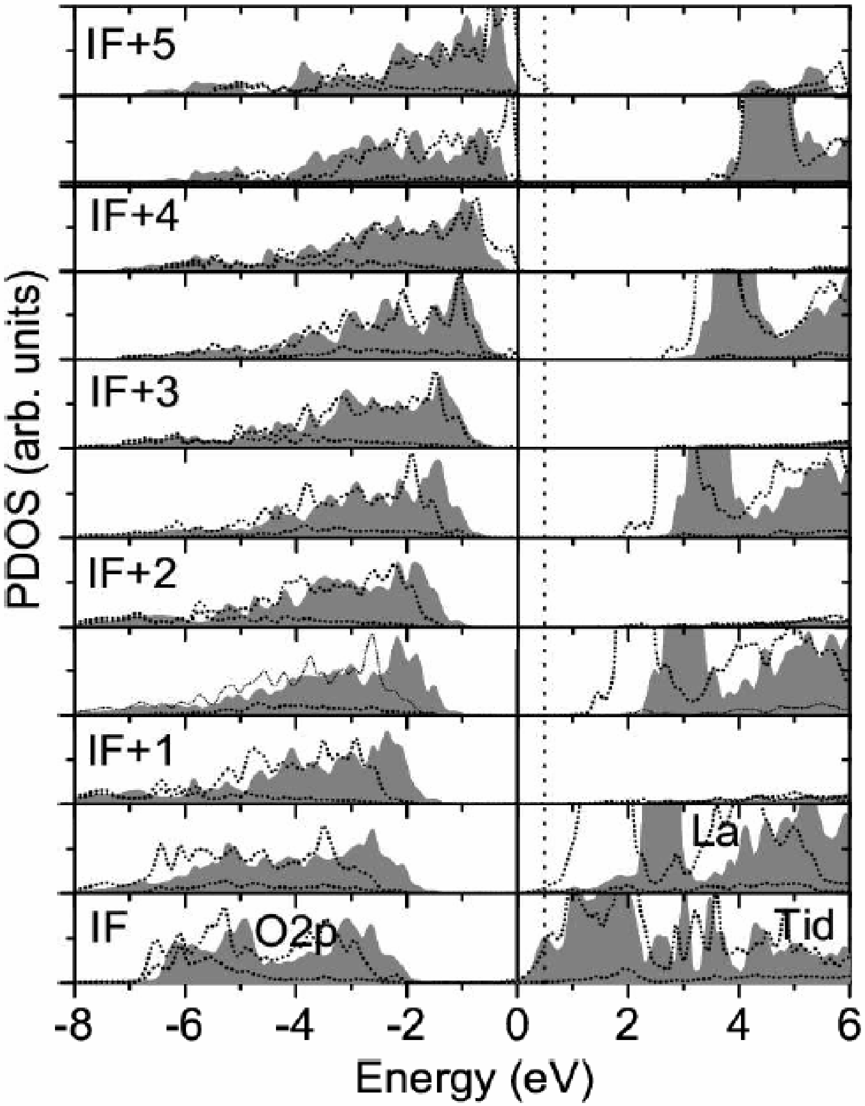
n-type LAO/STO(001) surfaces: electronic properties



- without relaxation – all systems *metallic*
- *insulating* behavior due to FE distortion
- reduction of the band gap with increasing number of LAO-layers (~0.4eV/ML)
- closing of the gap at 5ML LAO

RP&W.E. Pickett, PRL 102, 107602 (2009)
See also Chen et al., Nat Mat. 2008

5ML LAO/STO(001) surfaces: band alignment



Rigid upward shift of O2p bands

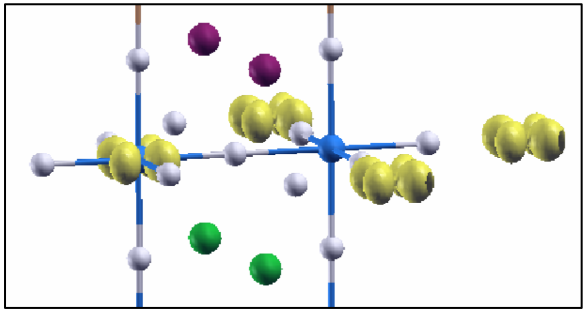
Ideal positions: metallic behavior with partial occupation of Ti 3d states@IF

Relaxed structure:
VBM determined by O*2p*@surface
CBM by Ti *3d* states,
Ti remains in 4+

Summary II

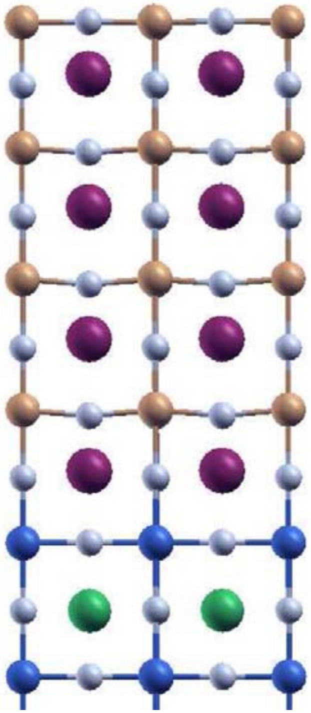
Isolated *n*-type LAO/STO IF

- CO,OO (Ti^{3+} and Ti^{4+})@ IF
- magnetism: (A)FM
- Relaxations -two competing states:
  - GGA: polar distortion - delocalization
  - GGA+U: CO/OO, stronger localization



LAO/STO(001) –surfaces:

- Proximity to the surface matters!
- finite size effects: strong polar distortions in LAO → insulating
- thickness dependent insulator-to-metal transition
- crossover to electronic reconstrution n≥5ML
- STO capping layer can trigger IMT@2ML LAO



*RP&Pickett, PRB**74**, 035112 (2006); PRB 78 2008;*
PRL 99, 016802 (2007), PRL 102, 107602 (2009),
JPCM 22, 043001 (2010); RP et al, condmat/0912.4671

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