Electronic structure of correlated electron systems

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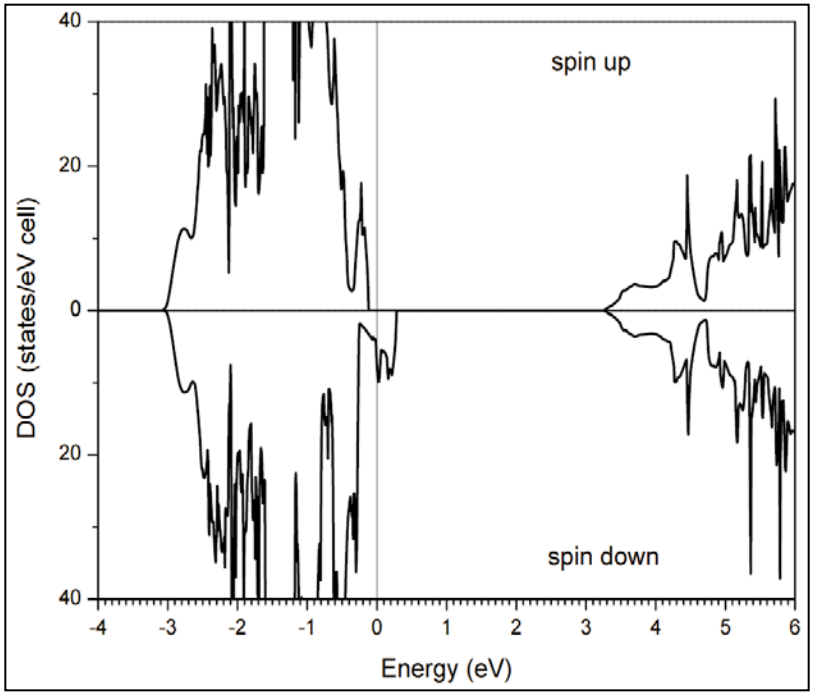
Before we gone into surfaces and interfaces just a brief glance at defects in oxides as an example of one of the home work assignments

Defects in ionic insulators leading to Effective imbedded magnetic molecules

Cation vacancies in simple Oxides

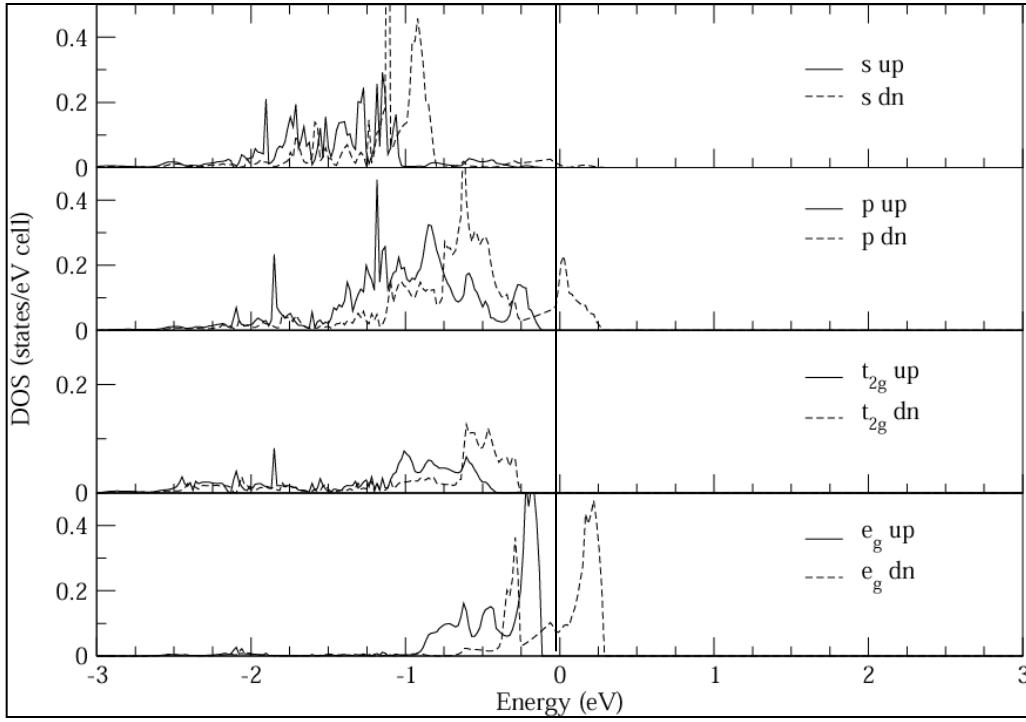
Elfimov et al;Phys. Rev. Lett. **89**, 216403 (2002)

Cation Vacancy

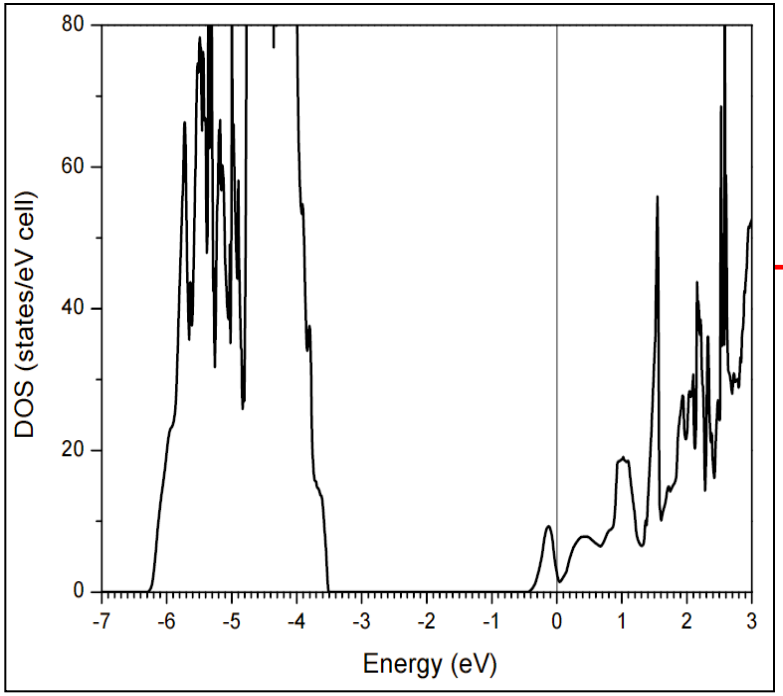


Total Density of States this is a half metallic ferromagnet

Partial Density of States projected on Ca-vacancy site

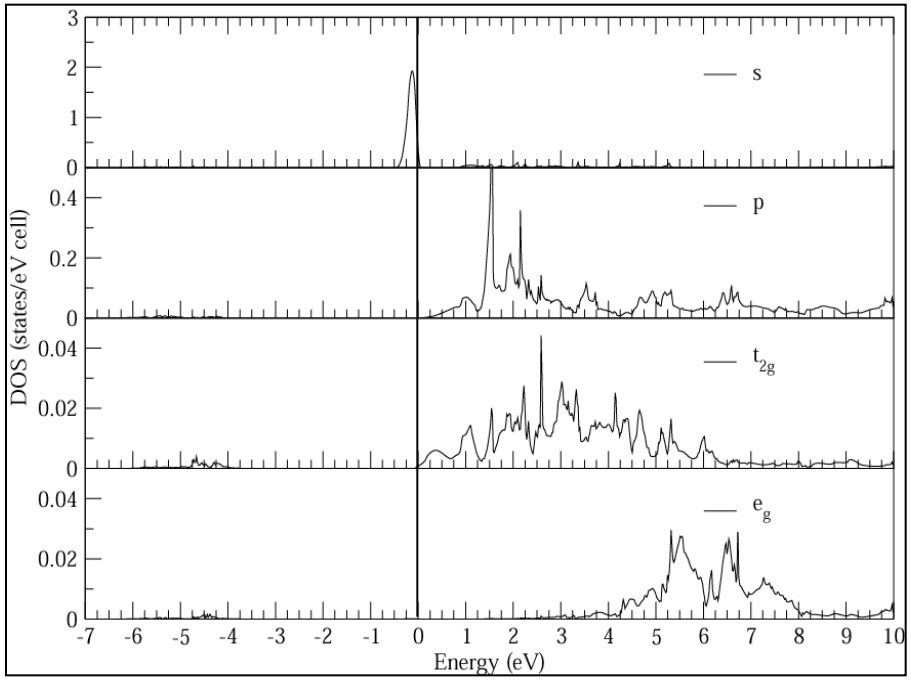


Anion Vacancy



Total Density of States this is non magnetic. Why the difference between cation and anion vacancies?

Partial Density of States projected on O-vacancy site



Summary of DFT calculations

- **Pure CaO**
  - ✓ Insulator
  - ✓ None-magnetic

- **3% Anion Vacancies**
  - ✓ Metal
  - ✓ Number of compensating charges in the cation orbitals around impurity: ~1.7 e
  - ✓ None-magnetic

- **3% Cation Vacancies**
  - ✓ Half-metal
  - ✓ Number of compensating charges in the anion orbitals around impurity : ~1.8 h
  - ✓ Ferromagnet
  - ✓ Magnetic moment per super cell : 2 μ_B

Cluster model

Definition of hopping parameters

$t_{pp}=1/2(t_{pp\sigma}-t_{pp\pi})$

$t'_{pp}=1/2(t_{pp\sigma}+t_{pp\pi})$

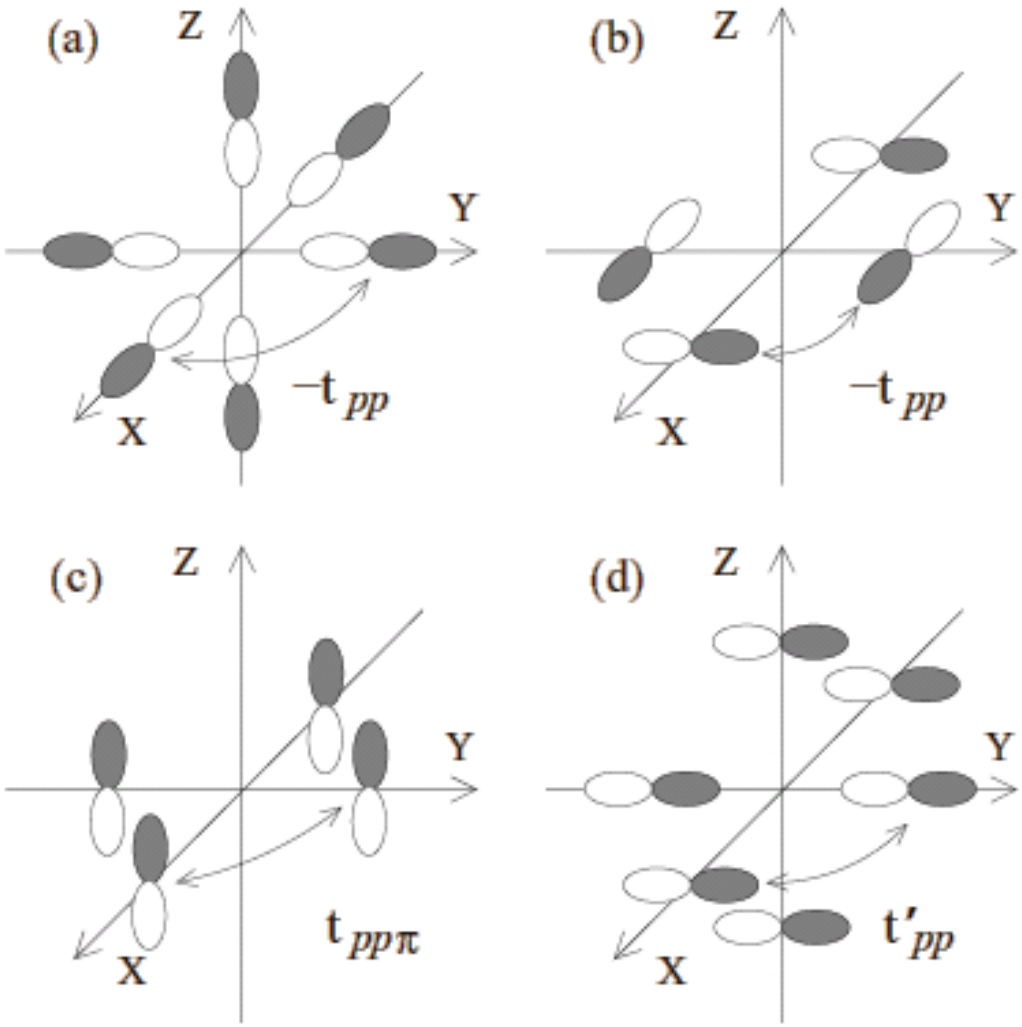
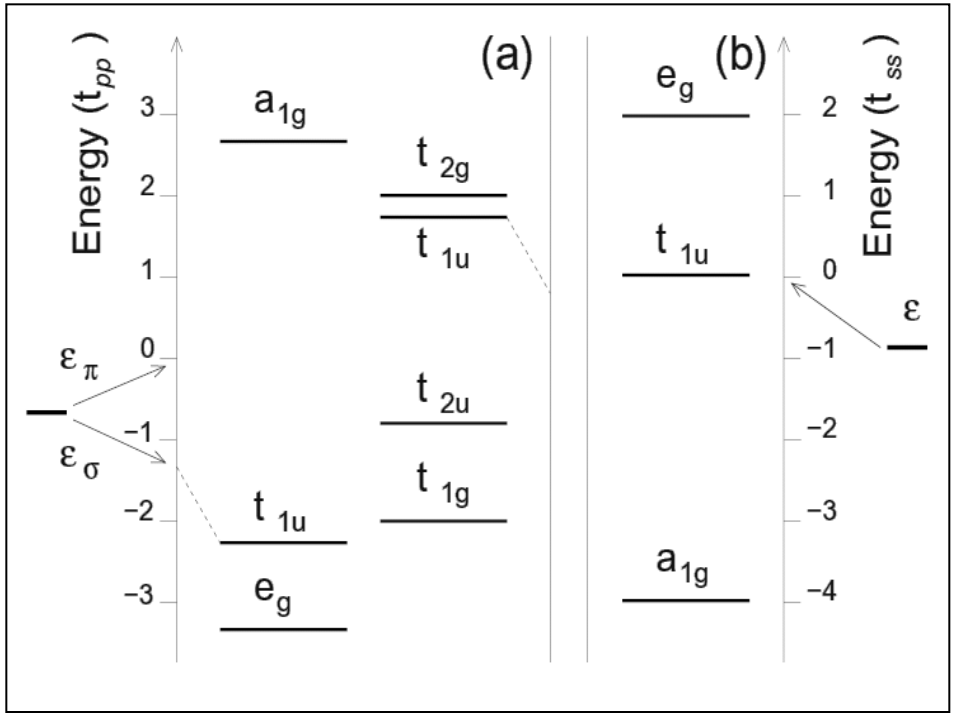


FIG. 1: An artists concept of the oxygen σ (a) and π (b,c) bonding orbitals relative to the O-vacancy bond direction surrounding a Ca vacancy. Also shown are the definitions of the hopping integrals (b) t_{pp}, (c) $t_{pp\pi}$, and (d) t'_{pp} given in terms of electrons.

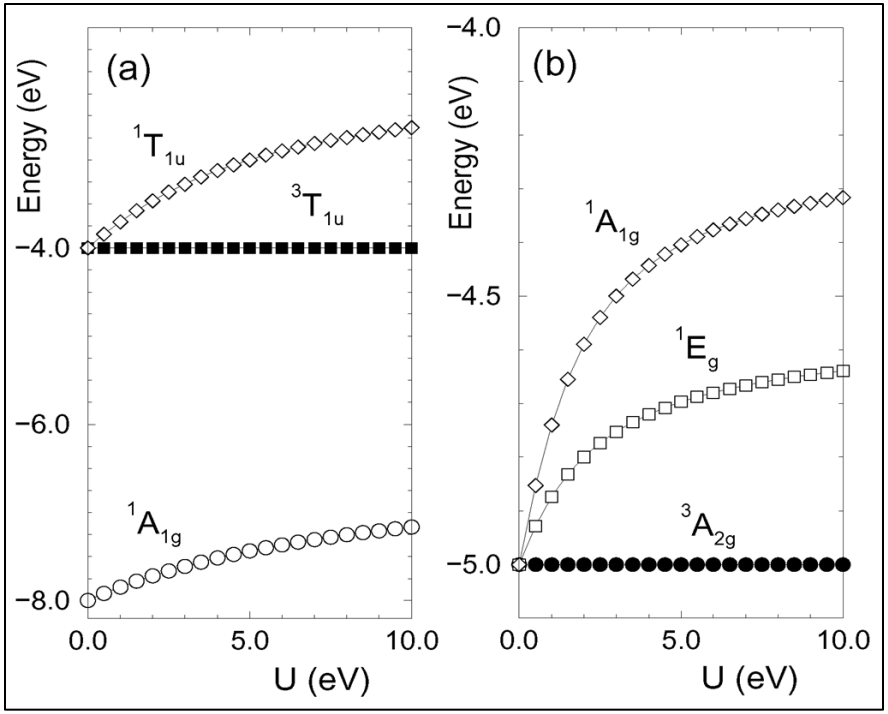
Exact diagonalization results

Single-particle picture



(a) HOLES in anion orbitals and
(b) ELECTRONS in cation orbitals.

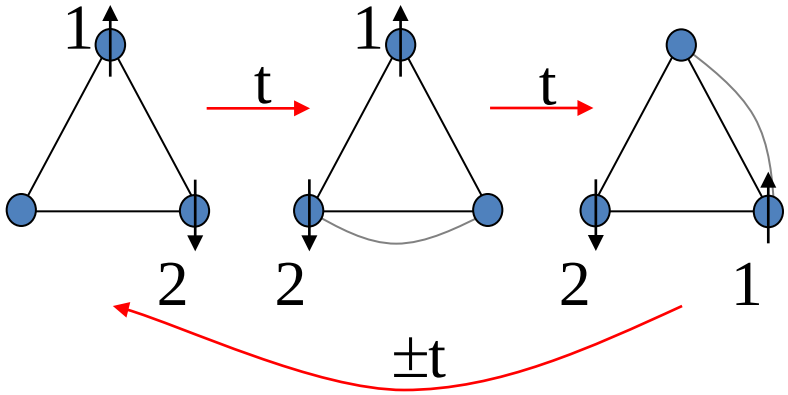
Three lowest states for two particle



(a) ELECTRONS in cation orbitals and
(b) HOLES in anion orbitals.

Solid symbols are for triplet state

This is related to our Example of two particles in U=∞ limit



$$\Psi = \phi(x_1, x_2) \cdot \chi(m_{s1}, m_{s2})$$

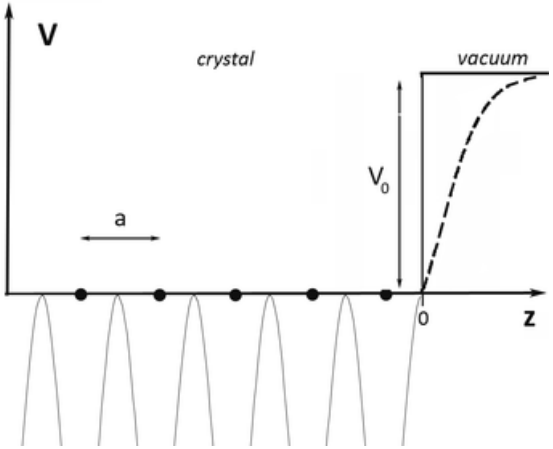
$$\chi(m_{s1}, m_{s2}) = \begin{cases} \frac{1}{\sqrt{2}}(\chi_{+-} + \chi_{-+}) & \text{Triplet} \\ \frac{1}{\sqrt{2}}(\chi_{+-} - \chi_{-+}) & \text{Singlet} \end{cases}$$

$$H = \begin{pmatrix} 0 & t & \pm t \\ t & 0 & t \\ \pm t & t & 0 \end{pmatrix}$$

"+" for singlet; "-" for triplet

Energy level diagram for holes (t>0)

Surfaces,interfaces and heterostructures



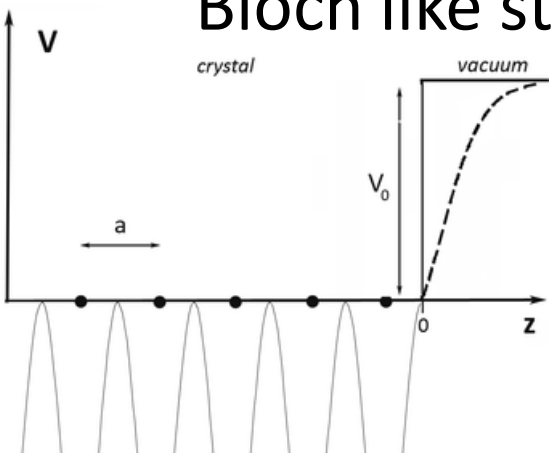
Model for the potential change at the termination of a one dimensional chain of atoms. The dashed line shows the gradual increase of the potential an electron would feel outside of the surface taking into account an image like potential form up to the vacuum level

Two kinds of surface states Shockley states generally referring to materials in which a nearly free electron model is applicable i.e. where the interatomic distances are comparable to the radial extend of the valence orbitals and Tamm surface states generally referred to in tight binding like band materials which are closer to the correlated systems we have been talking about. However there is no clear distinction between these formally.

Surface states exist as distinct states if their energies occur either in the gap of a semiconductor or in a gap of the bulk band structure when projected onto the surface. This projected density of states may have gaps in certain crystalogaphically oriented surfaces and in certain ranges of k space.

One also identifies surfaces resonances which result from surface states not in a bulk projected gap . These surface states will be broadened because of their hybridization with the bulk band states giving them a finite “lifetime”.

One dimensional periodic potential terminated at the surface where it rises up to the vacuum level and the corresponding bulk Bloch like states and the surface state

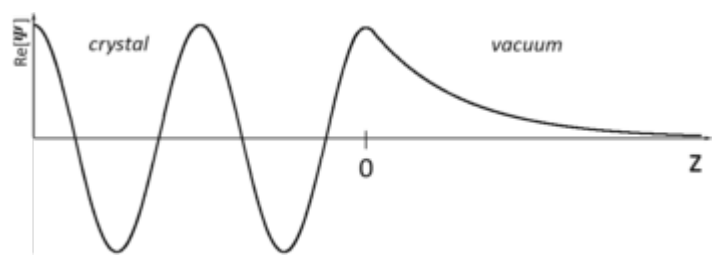


$$V(z) = V\left[\exp\left(i\frac{2\pi z}{a}\right) + \exp\left(-i\frac{2\pi z}{a}\right)\right]$$

$$= 2V\cos\left(\frac{2\pi z}{a}\right),$$

And V0 FOR Z>0

Bulk states decaying into the vacuum



Surface states decaying in both directions

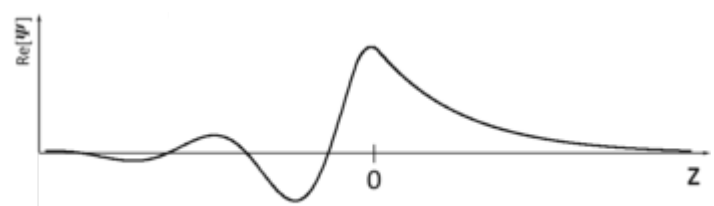
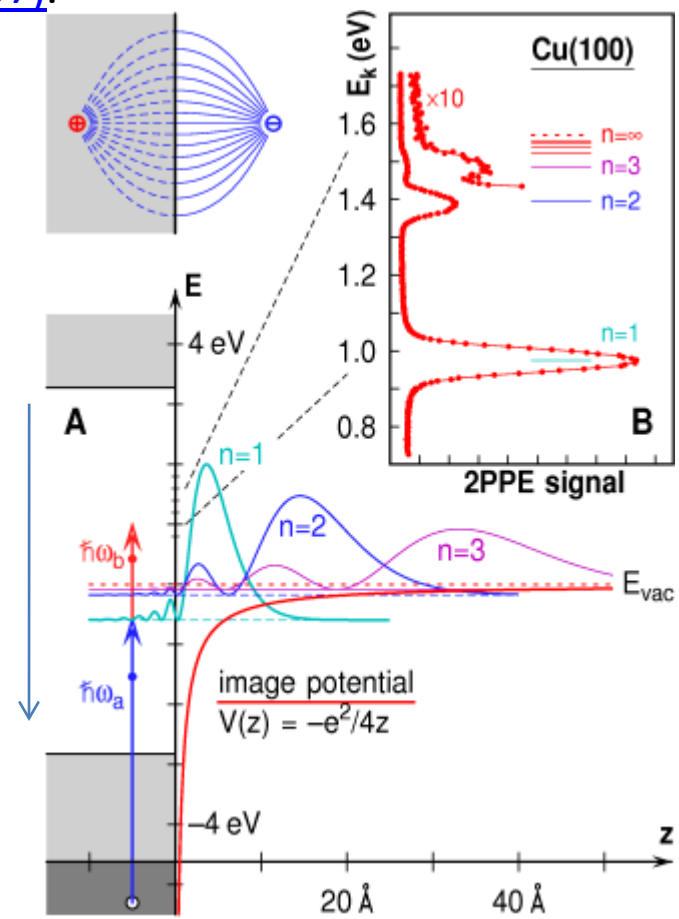


Image potential states. Electron bound to its own image potential forming hydrogenic like Rydberg series of state

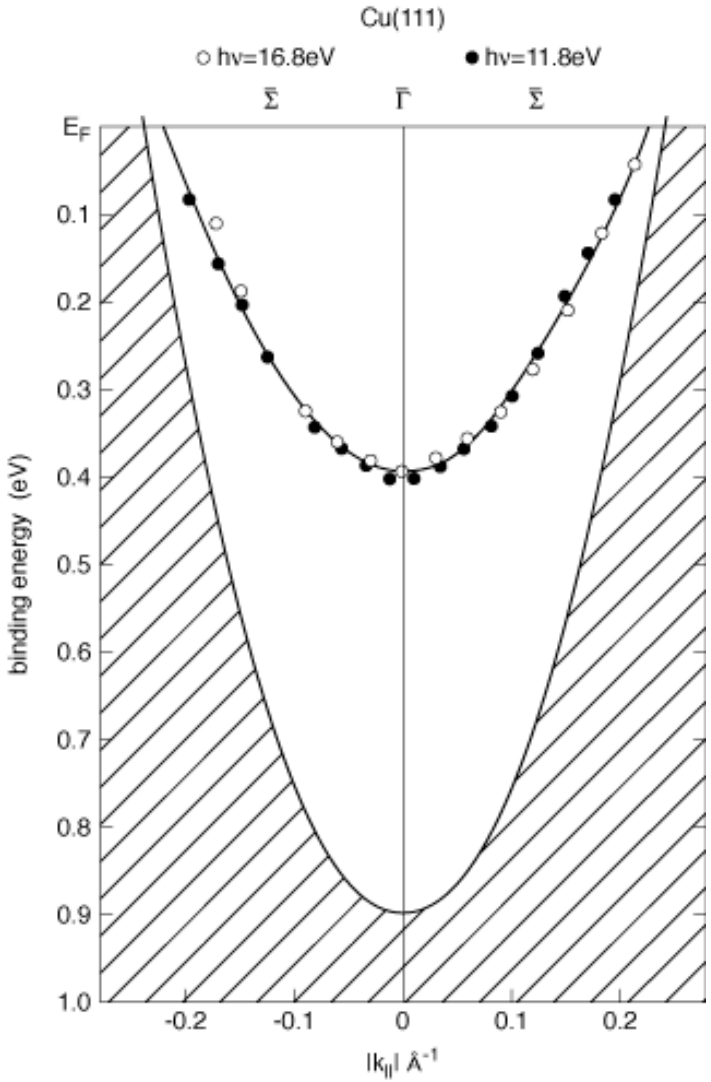
U. Höfer et al., Science **277**, 1480-82 (1997).

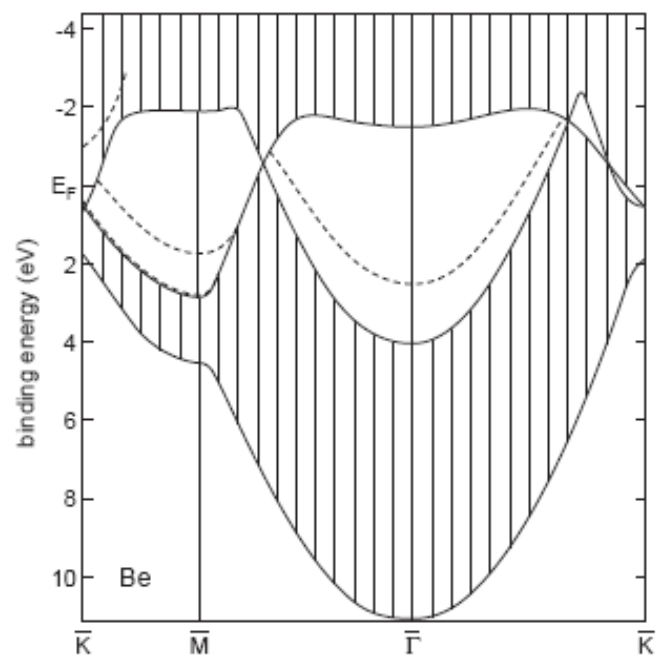
These are image potential surface states living outside the surface and bound by the image potential itself. The experiments using 2 photon photoemission to study these by first excited an electron to an image potential state and then photoemitting it with a second photon

Large gap in the bulk
Surface projected band structure



Arpes measurement of the surface state dispersion at a Cu 111 surface. These are occupied surface states i.e. below the Fermi level and so accessible with ARPES . The hatched region corresponds to bulk states projected onto the 111 surface demonstrating the gap at Gamma i.e. K (parallel) =0. The bulk projection involves a summation or integral over all K perpendicular wave vectors for a given K parallel.

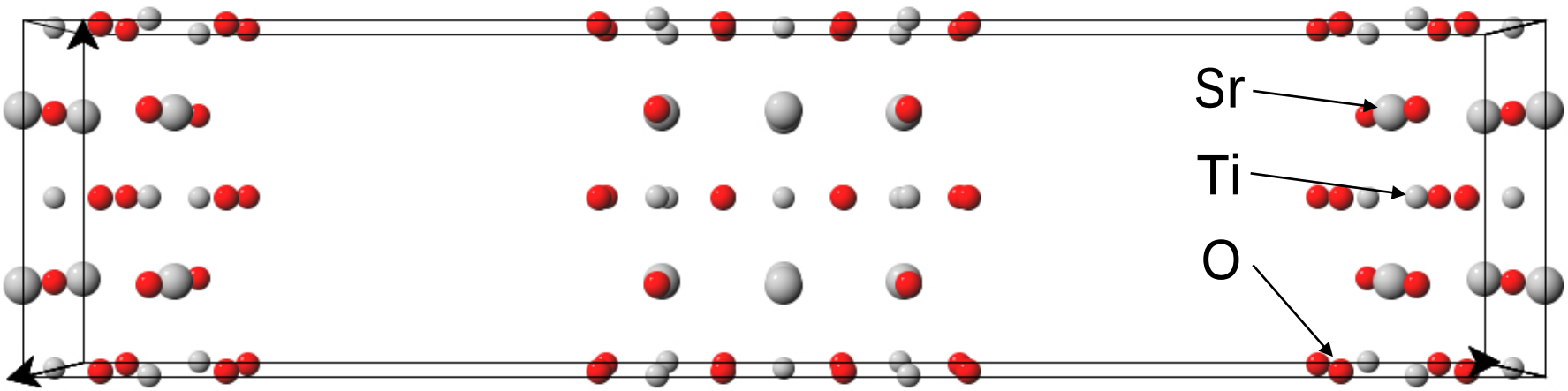




Defects study with DFT: Supercell approximation

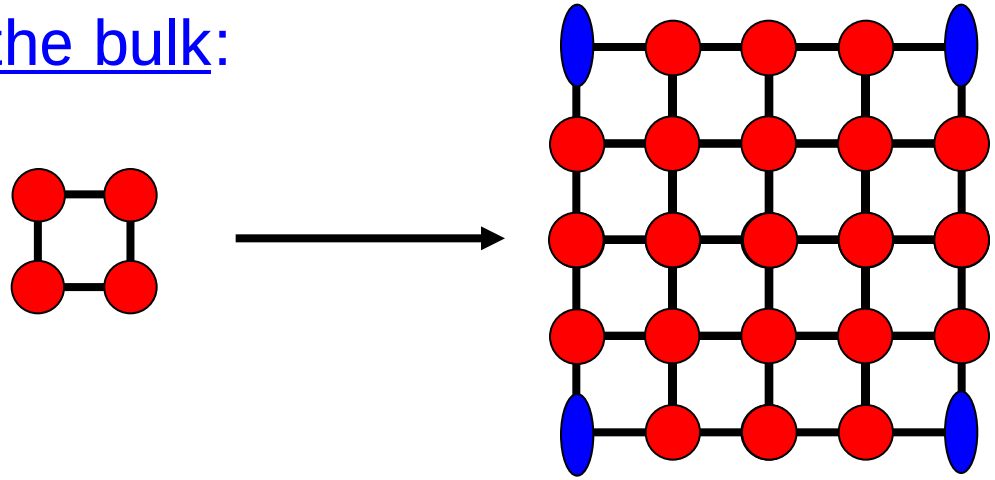
To study defects we want to “break” periodicity in one (surface), two (wires) or three (single impurity) dimensions.

Slab geometry:



Impurity in the bulk:

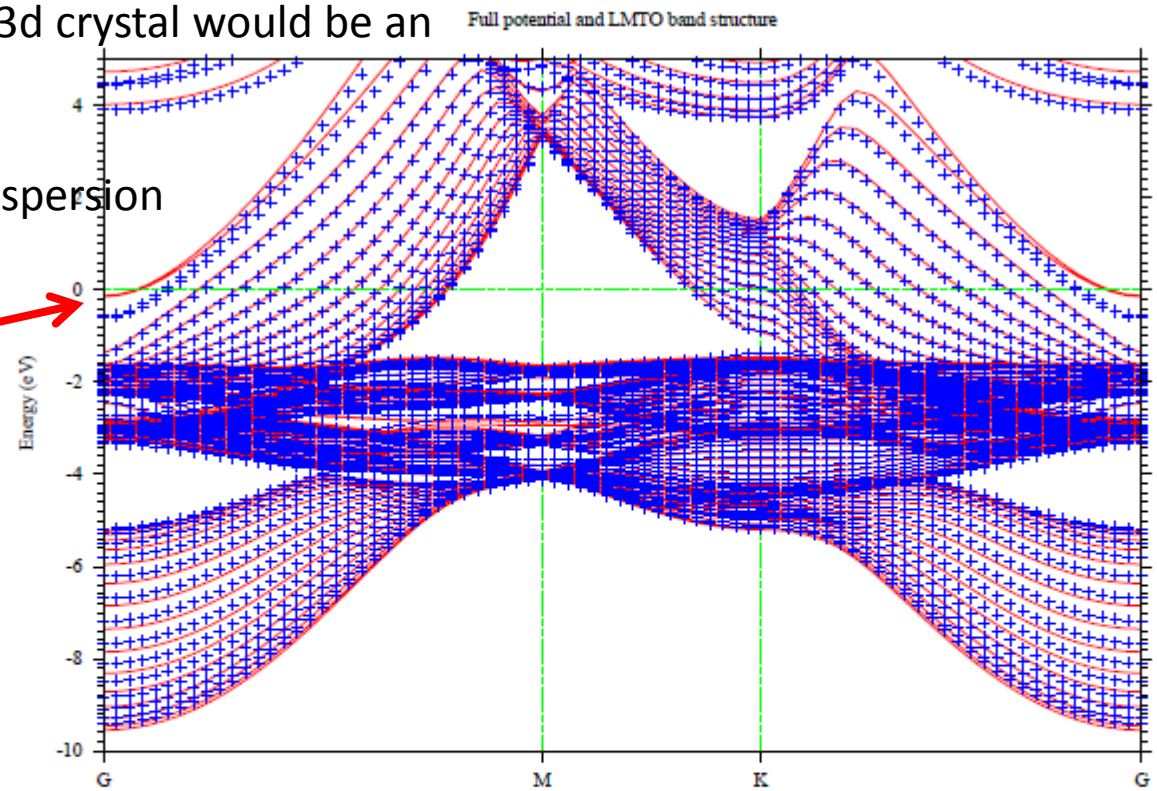
Unit cell of perfect inf. crystal



Band structure of a slab of 15 Cu 111 layers

You should be able to count 15 Cu 4s,p Bands which in a 3d crystal would be an infitie number Corresponding to Kperpendicular dispersion

Surface band



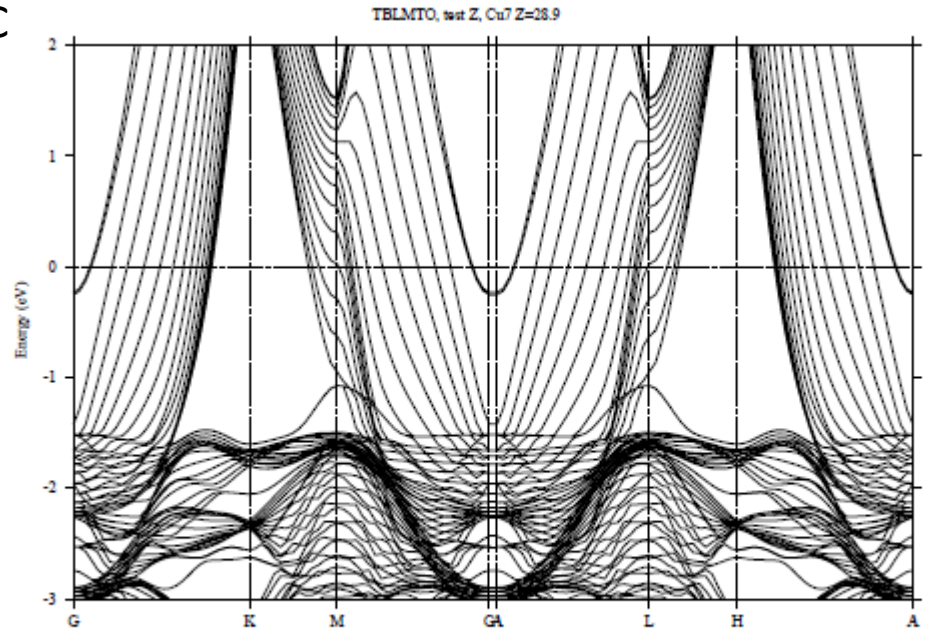
Cu 3d bands

Cu 4s,p bands

Figure 3.8: Band structures of 15 Cu(111) plane by Full potential and LMTO method where lines represents LMTO bands and points represents full potential bands. Both the band structures are almost similar accept the surface states at Γ point which are found to be at 0.6 eV and 0.13 eV below Fermi energy respectively in full potential and LMTO method.

DFT slab calculation of Cu(111) surface state

Arefa Hossain
Masters thesis UBC



: LMTO band structure of 15 Cu(111) planes with 28.9e charge on the outer most Cu plane.

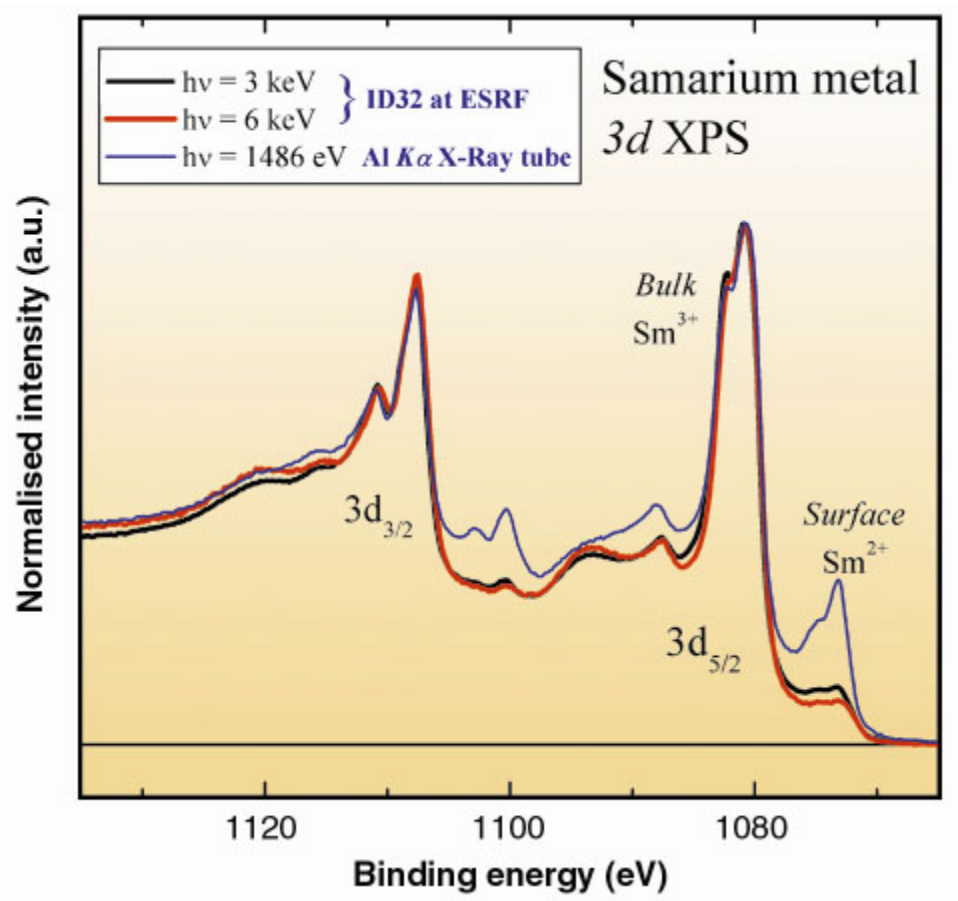
The Cu 111 surface was used to study magnetic impurities on the surface in the quantum corral studies and in Co on the surface exhibiting what is thought To be a Konod resonance in Scanning Tunneling spectroscopy

H.C. Manoharan, C.P. Lutz, and D.M. Eigler, Nature 403, 512

In some cases more drastic surface effects can occur

- In Rare earth metals the effective valence (counts the number of 4f electrons) can be different at the surface than in the bulk. For example SmSe has Sm 2+(4f6 S=3,L=3,J=0) at the surface and Sm3+(4f5 S=5/2, L=5,J=5/2)
- Also at the surface of transition metal compounds the charge transfer gap could be smaller because of the Madelung potential, the Hubbard U could be larger because of less “screening” and the band widths would be smaller

C. Dallera , L. Duò , G. Panaccione , G. Paolicelli L. Braicovich and A. Palenzona .



Increasing photon energy in photoelectron spectroscopy probes deeper into the bulk i.e. less surfgace sensitive. Damascelie's lecture.

The change in valence at the surface is a very important part of correlated electron physics of quantum dots, thin films interfaces and add atoms on surfaces. For the rare earths this change is due to mainly the change in the spd conduction band structure and width .

Photoemission spectra of 3d levels in pure metallic samarium. Spectra at 3 and 6 keV were measured at ID32 while the spectrum excited at 1486 eV was taken with an X-ray tube. A relevant decrease of the divalent surface component with increasing energy is seen.

Electronic Structure of oxide surfaces and interfaces

A path to new materials and devices?

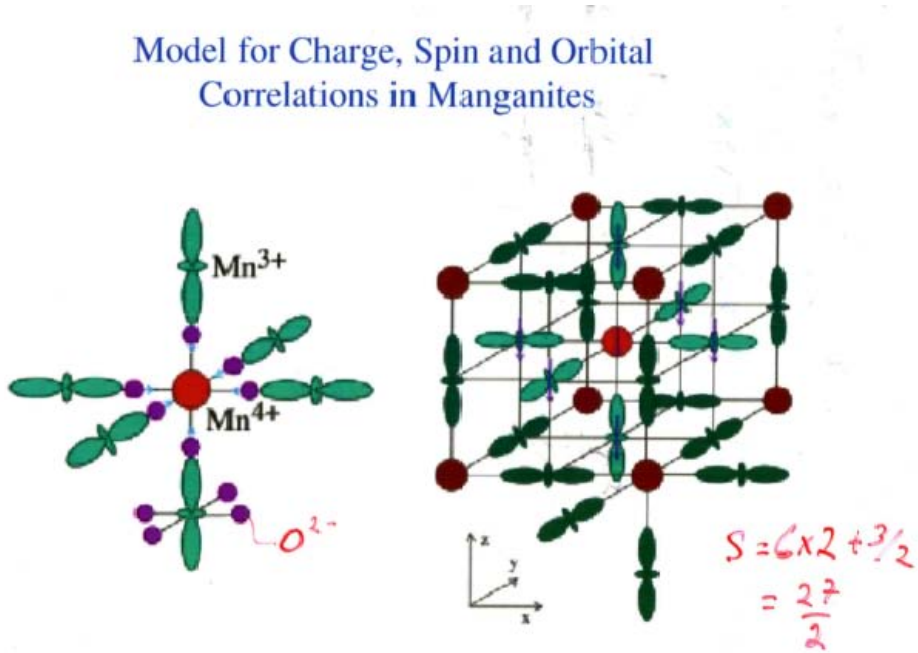
Summary

- **Surface electronic structure of Oxides**
- **Reconstruction at Polar surfaces and interfaces; electronic, ionic, chemical**

There still is a lot of uncertainty/controversy concerning the electronic structure changes at oxide surfaces and interfaces. We need improved materials and improved methods to study buried interfaces.

New quantum materials Based on Oxides

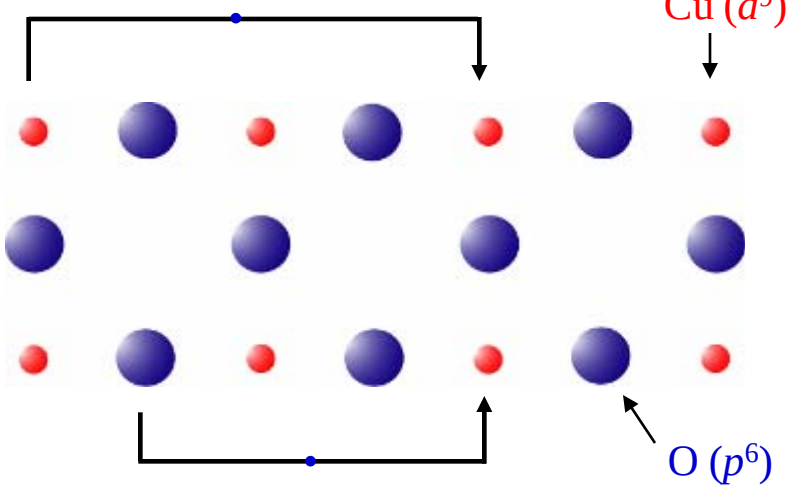
- Interplay charge, spin, orbital and lattice



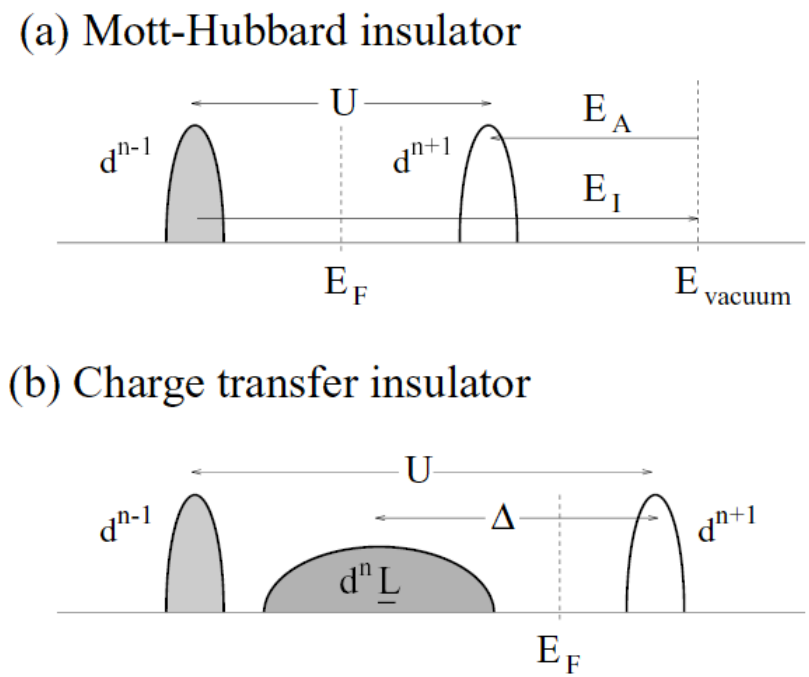
- Interface control : strain- pressure, internal electric fields, local symmetry changes which change crystal fields and superexchange interactions

Correlated Electrons in transition metal compounds

U : $d^n\, d^n \rightarrow d^{n-1}\, d^{n+1}$



Δ : $p^6\, d^n \rightarrow p^5\, d^{n+1}$



$$U = E_I^{TM} - E_A^{TM} - Epol$$

$$\Delta = E_I^{O} - E_A^{TM} - Epol + \delta E_M$$

If $\Delta < (W+w)/2 \rightarrow$ Self doped metal

E_I ionization energy
E_A electron affinity energy
E_M Madelung energy

Epol depends on surroundings!!!

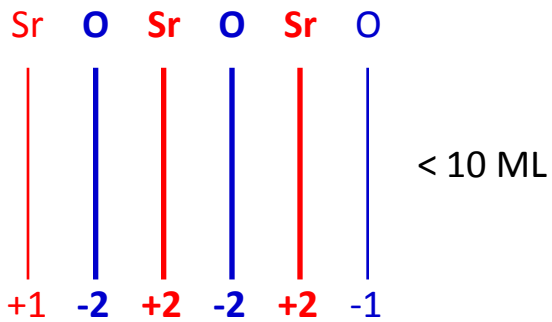
- **J.Hubbard, Proc. Roy. Soc. London A 276, 238 (1963)**
- **ZSA, PRL 55, 418 (1985)**

At a surface the charge transfer energy decreases ,
And U also increases and the band widths also decrease

Novel Nanoscale Phenomena in Transition-Metal Oxides

Ionic Oxide Polar Surfaces

Stabilization of polar surfaces by epitaxy

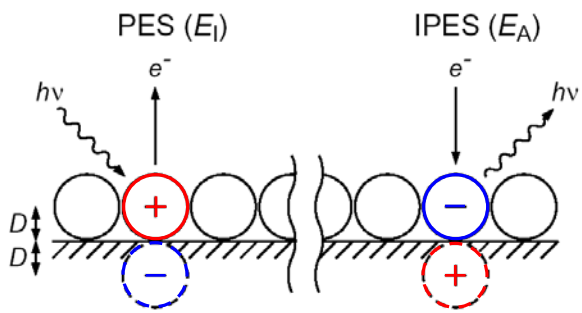


Transparent insulator → ½ metallic FM

Applications: Spintronics; CMR

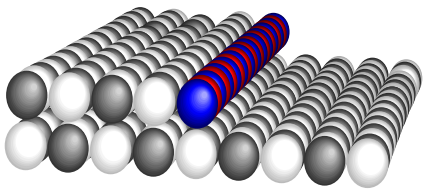
Electronic Structure of Interfaces

Metal-Insulator interface: gap suppression



Applications: Molecular Electronics; Fuel Cells; Thermal Barrier Coatings

Correlated Electron System Surfaces



Kinks and steps stabilized by epitaxy

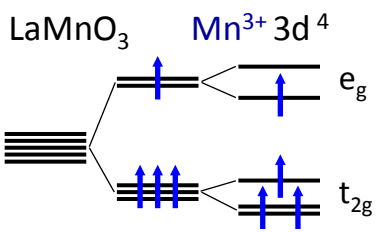
NiO(100) → 1D Metallic steps

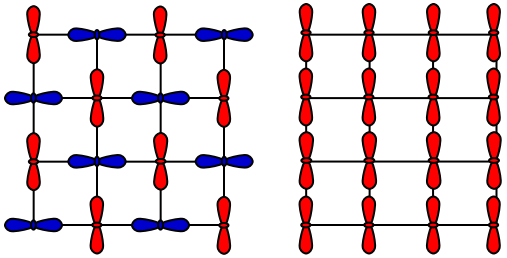
Superconducting Copper oxides

Applications: Novel SC; QuBits

Strained 2D Layers

Positive and negative pressure

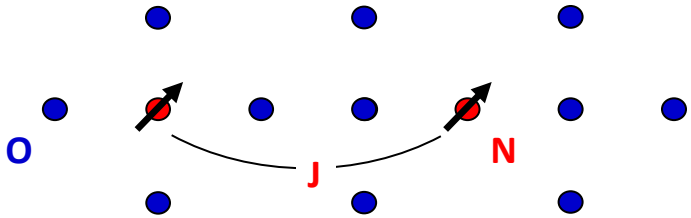




Applications: CMR; M-I Transition; Orbital Ordering

Artificial Molecules Embedded into a Material

Ca, Mg, Sr, Ni vacancies or O-N substitution in oxides



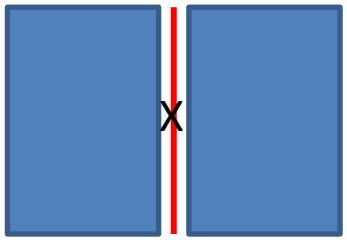
New class of magnetic materials by ‘‘low-T’’ MBE growth

Applications: Spintronics; Novel Magnets

Surface Madelung potential

- Divide the solid into two halves plus a single layer in between . The single layer plus one of the two halves would form a half infinite solid with the single layer as the surface.
- An ion marked X in the single layer would feel a MP due to the half infinite plus that produced by the single layer.
- The bulk MP at the same ion X would be twice that of the half infinite solid plus that from the single layer.
- MP(bulk)=MP(left half)+MP (right half)+MP(single layer)= 2MP(half infinite)+MP(single Layer)
- MP(half infinite)=1/2 MP(Bulk) –MP(single layer)
- MP(surface)=MP(half infinite)+ MP(single layer)

  =1/2(MP(bulk)+MP(single layer))



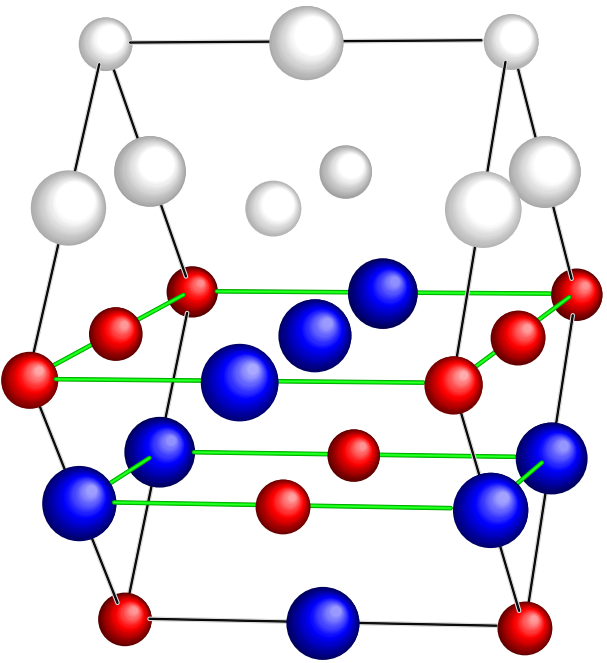
Madelung potentials for rock salt structure TM monoxides

- Two extreme cases are considered ,fully ionic i.e. 2+ and 2- charges and 1+,1- charges

		$2E_{\mathrm{mad}}(\mathrm{TM}^{1+}\mathrm{O}^{1-})$			$2E_{\mathrm{mad}}(\mathrm{TM}^{2+}\mathrm{O}^{2-})$		
	a(Å)	bulk	(100)	(110)	bulk	(100)	(110)
MnO	4.44	22.64	21.79	19.95	45.28	43.58	39.89
FeO	4.31	23.36	22.48	20.58	46.72	44.96	41.15
CoO	4.26	23.62	22.73	20.81	47.25	45.40	41.62
NiO	4.18	24.08	23.17	21.21	48.16	46.34	42.42

.1: *Surface Madelung potentials in eV for the late transition metal oxides.*

Madelung potential depends on coordination number



Drawn is a 110 surface where TM has 2 missing O2- Neighbors.

The front face is 100 and in it each TM ha one O2- nearest neighbor missing

Basically this describes the systematics of the surface Madelung potential

Remember that for the charge transfer gap materials the band gaps are determined by the charge transfer energy which changes by twice the change in the Madelung potential or by 2.6 eV for the monovalent case and twice this for the divalent case

Things are more dramatic at step edges

These changes could lead to
Negative charge transfer energies

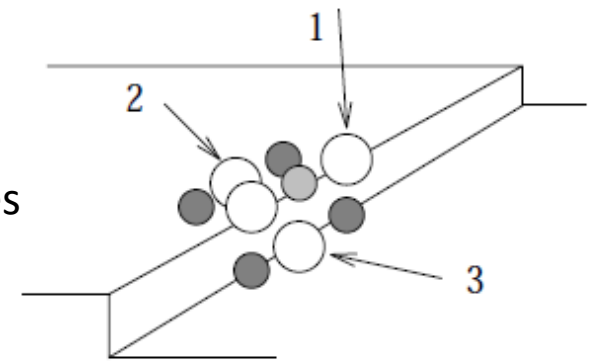


Figure VI.1: *The different Madelung potential contributions involved in the possible charge transfer excitations at a step defect on a rock-salt (100) surface. The small spheres represent the TM ions, the larger unfilled spheres the O ions.*

	ΔE_{mad}(average)					
	bulk	(100)	step.1-1	step.1-2	step.1-3	(110)
MnO	33.96	32.69	30.47	31.61	31.90	29.93
FeO	35.04	33.72	31.43	32.62	32.90	30.87
CoO	35.43	34.10	31.79	32.99	33.28	31.22
NiO	36.12	34.76	32.40	33.62	33.92	31.82

Table VI.2: *Calculated average Madelung potential differences at a step on a (100) surface.*

Metallic states for negative charge transfer gap energies as could happen at step edges.

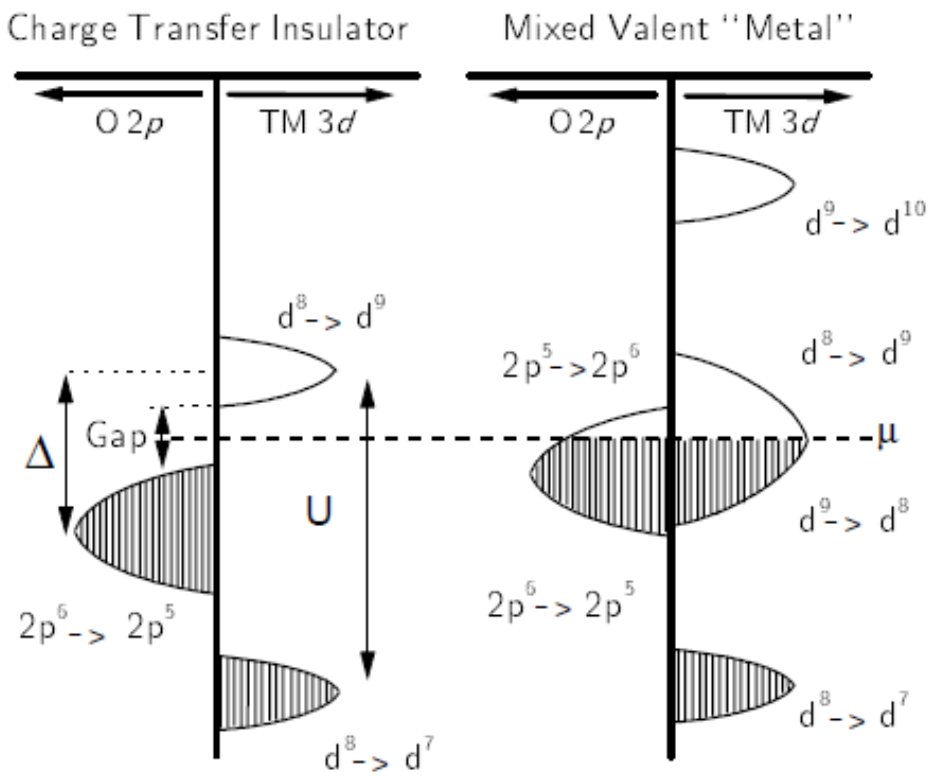


Figure VI.5: *Possible mixed valency on NiO(110). The mixed valent situation in the right panel is compared to the ionic bulk NiO charge transfer situation, shown in the left panel. The left side of each panel corresponds to the O 2p states, the right side to the TM 3d states.*

The theory of systems with negative charge transfer gap energies

- This is really complicated since we now cannot use our simple non metallic ansatz. We then have a problem of a high density of local spins in dn states with strong hybridization and exchange with the holes on O.
- The case I alluded to of LaNiO3 is perhaps such an example.
- We might be able make interesting new materials using vicinal or Stepped surfaces to generate negative chanrge transfer gaps.

Systemtics of conductivity gaps gaps

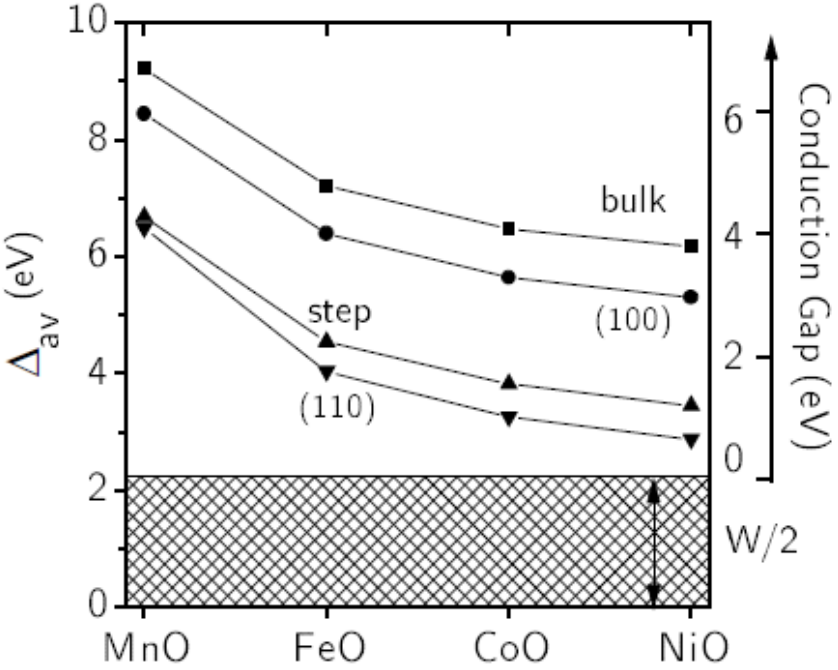


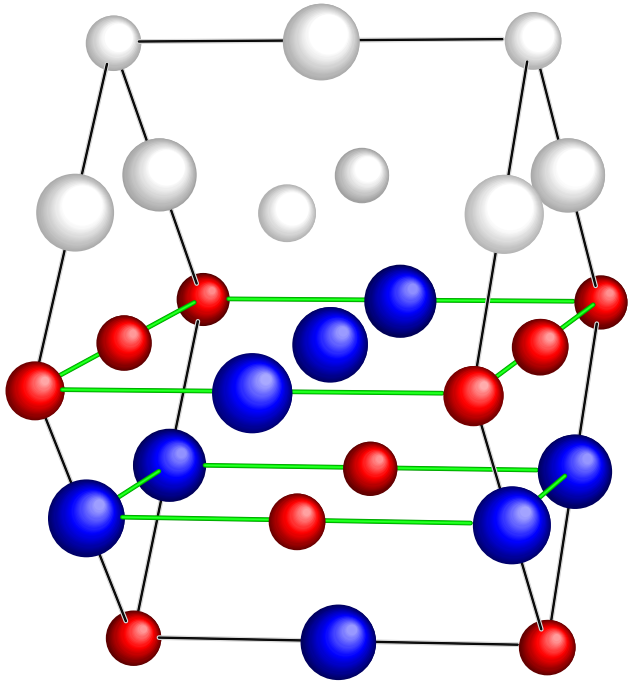
Figure VI.3: *Calculated charge transfer energies and half the oxygen band width values of the late transition metal monoxides for different surface terminations. Along the right axis the corresponding conduction gap values can be read.*

We can do a bit better than the above model with LDA+U calculations

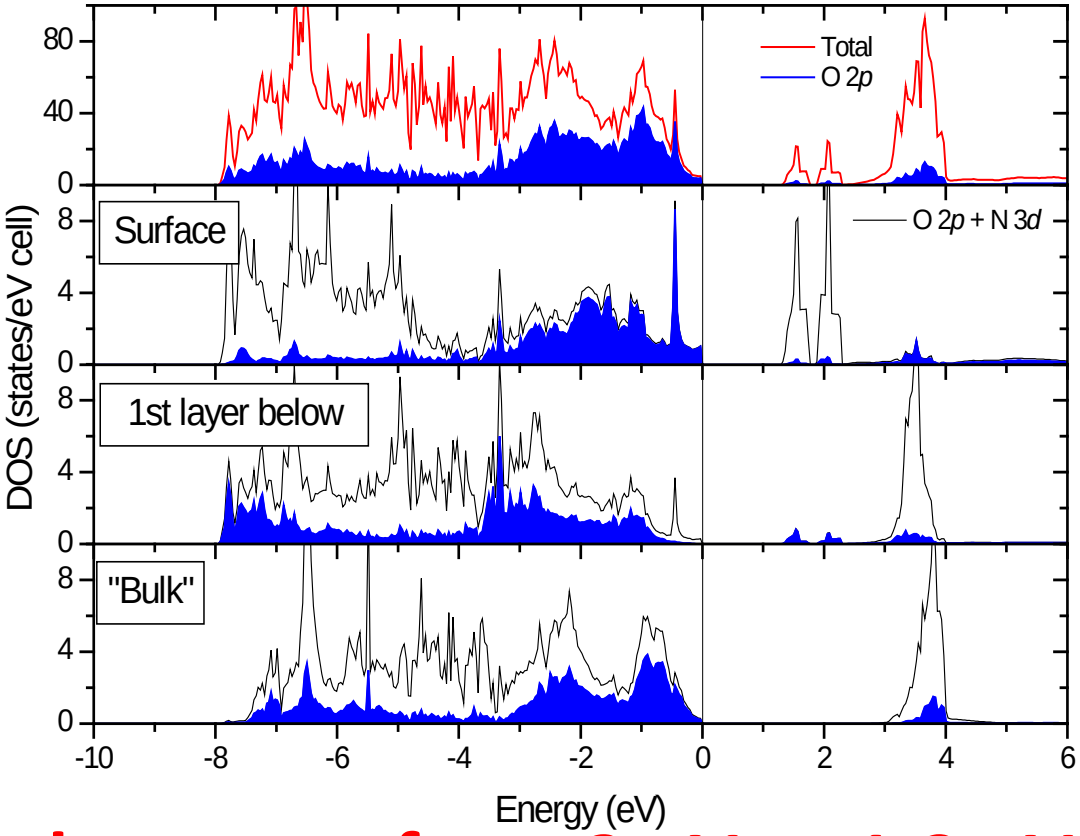
- Of course we recall the problems also with LDA+U Hoever LDA gives us accurate Madelung potentials, charges and crystal field splittings since it can handle the change in symmetry at surfaces

Neutral (110) surfaces of NiO

Slab of 7 NiO layers



LSDA+U: U=8eV J=0.9eV



Band gap at surface decreases from 3 eV to 1.2 eV

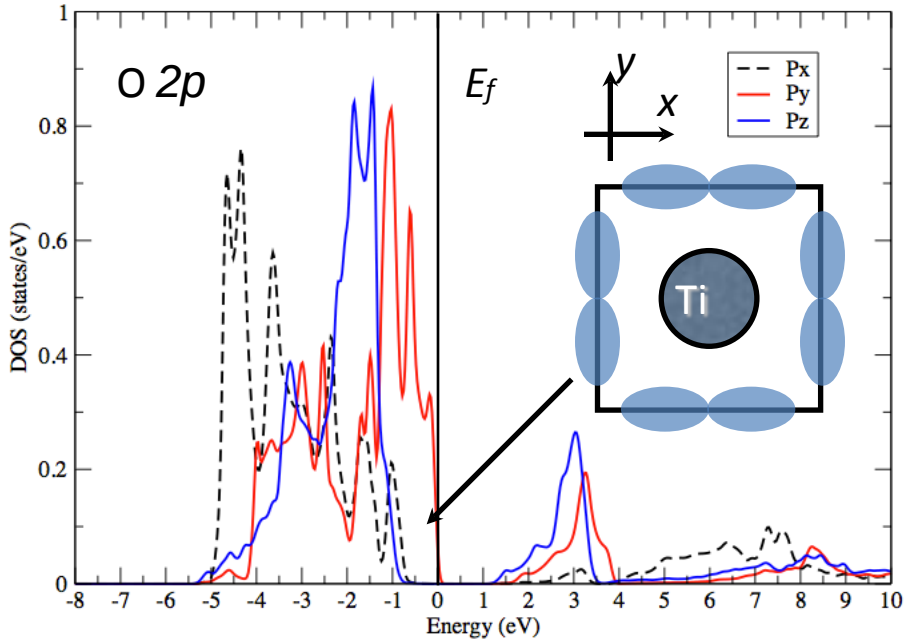
Step edges could be 1D strongly correlated metals

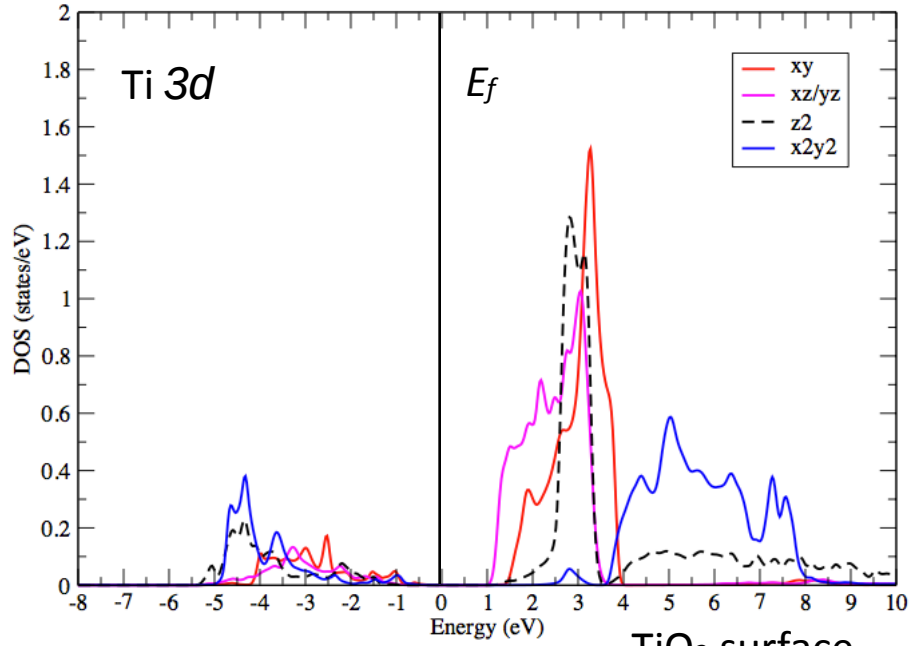
Note the splitting of the eg unoccupied bands due To the symmetry lowering at the surface

Can you identify the two split of low energy unoccupied states?Whats your guess as to the identity of these two states?

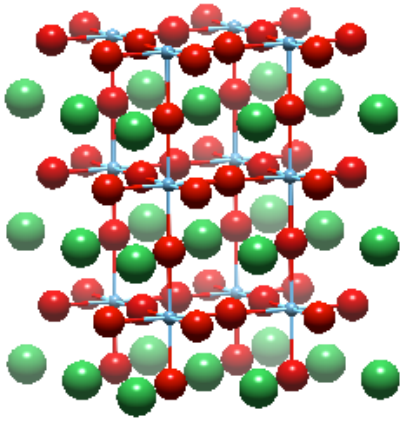
SrTiO3 (001) surface

TiO_2 terminated surface PDOS





TiO_2 surface



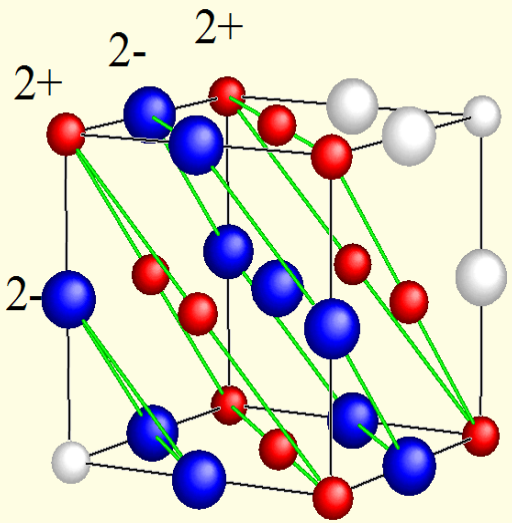
- The degeneracy of states at the surface is lifted due to reduced symmetry.
- Surface band gap is reduced by 0.8eV from 1.9eV in the bulk.

Reduction of Madelung potential and hybridization at the surface of ionic material.

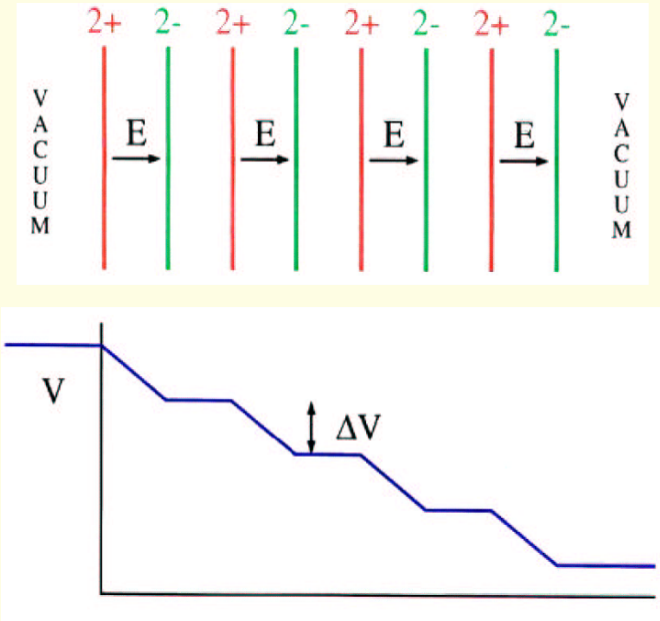
What happens for surfaces with a net charge and a +,-,+,- alternation of layers?

- These are so called polar surfaces and they have an infinite energy and cannot exist as the termination of a bulk materials.
- SO WHAT HAPPENS?
- These are the examples that yield a metallic and also superconducting interface between two insulating materials of which one is polar.

Polar (111) Surfaces of MgO



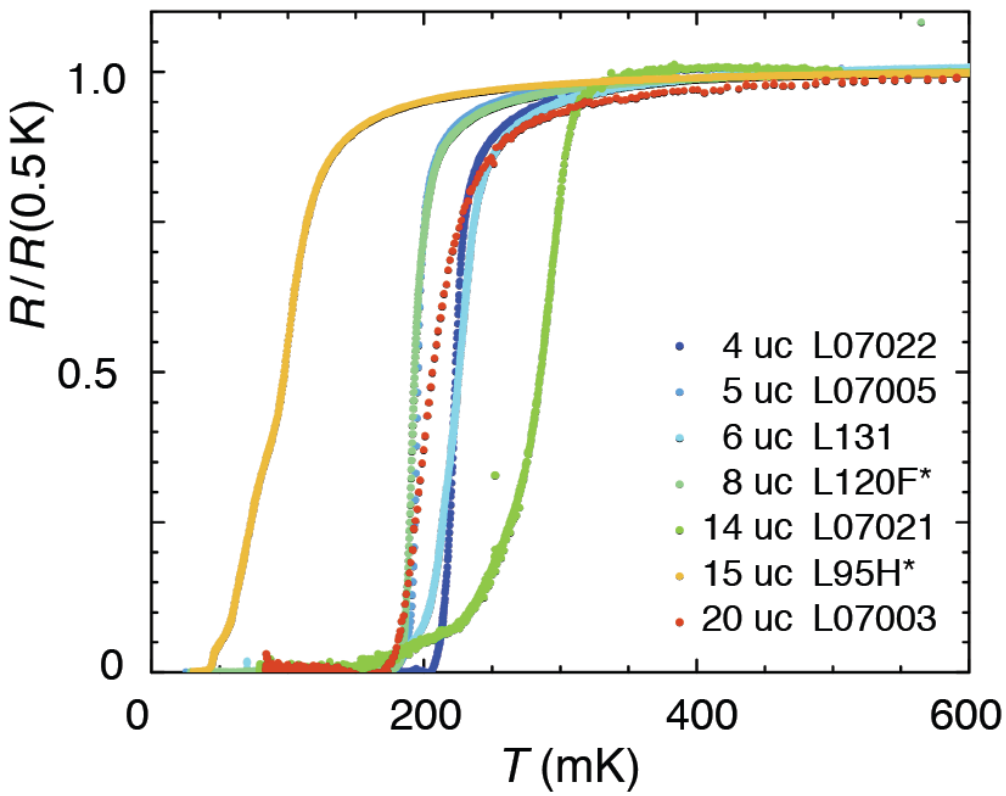
Finite slab of charged planes



ΔV=58 Volt per double layer!

POLAR SURFACES

The basic physics involved in the new discoveries of Spectacular properties of some oxide interfaces?



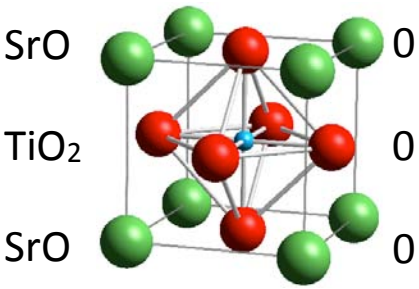
LaAlO3/SrTiO3
Interface of two insulators = superconductor

Hwang, Mannhart, Trisconne, Blanck, -------

Classification of Ionic Crystals Surfaces

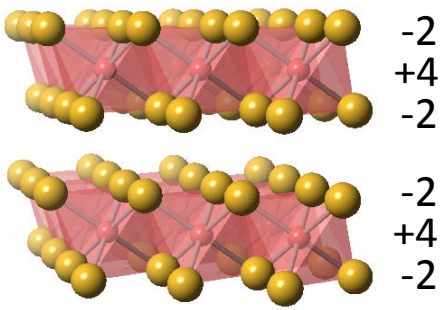
Type 1 : all planes are charge neutral

(001) surface of tetravalent perovskites $SrTiO_3$ ...

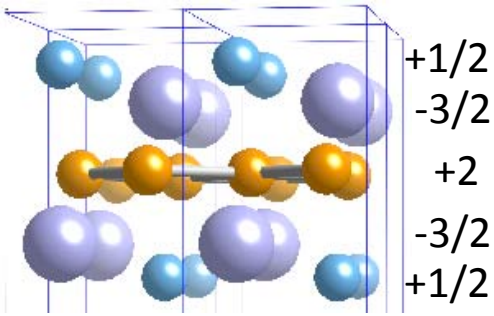


Type 2 : planes are charged but there is no dipole in repeat unit

TiS_2

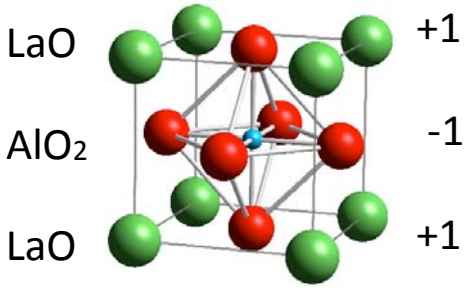


LiFeAs



(001) surface of trivalent perovskites $LaAlO_3$, $LaMnO_3$ ...

Type 3 : planes are charged and there is dipole in repeat unit

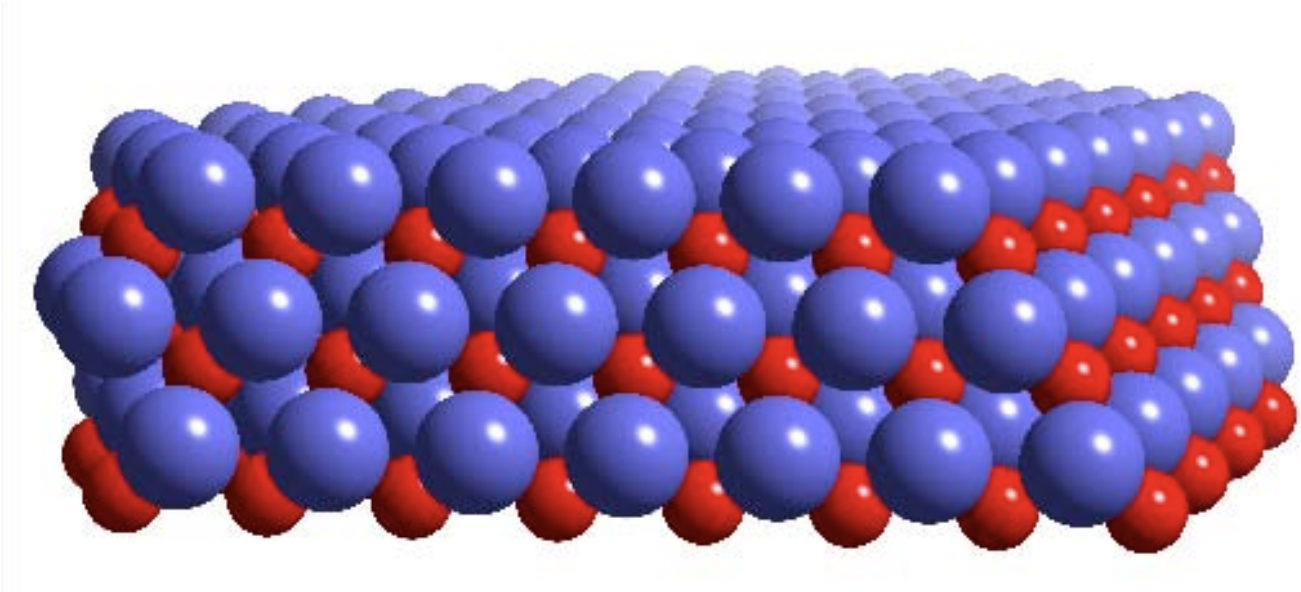


P.W. Tasker, J. Phys. C **12**, 4977 (1979)

Thanks to Ilya Elfimov

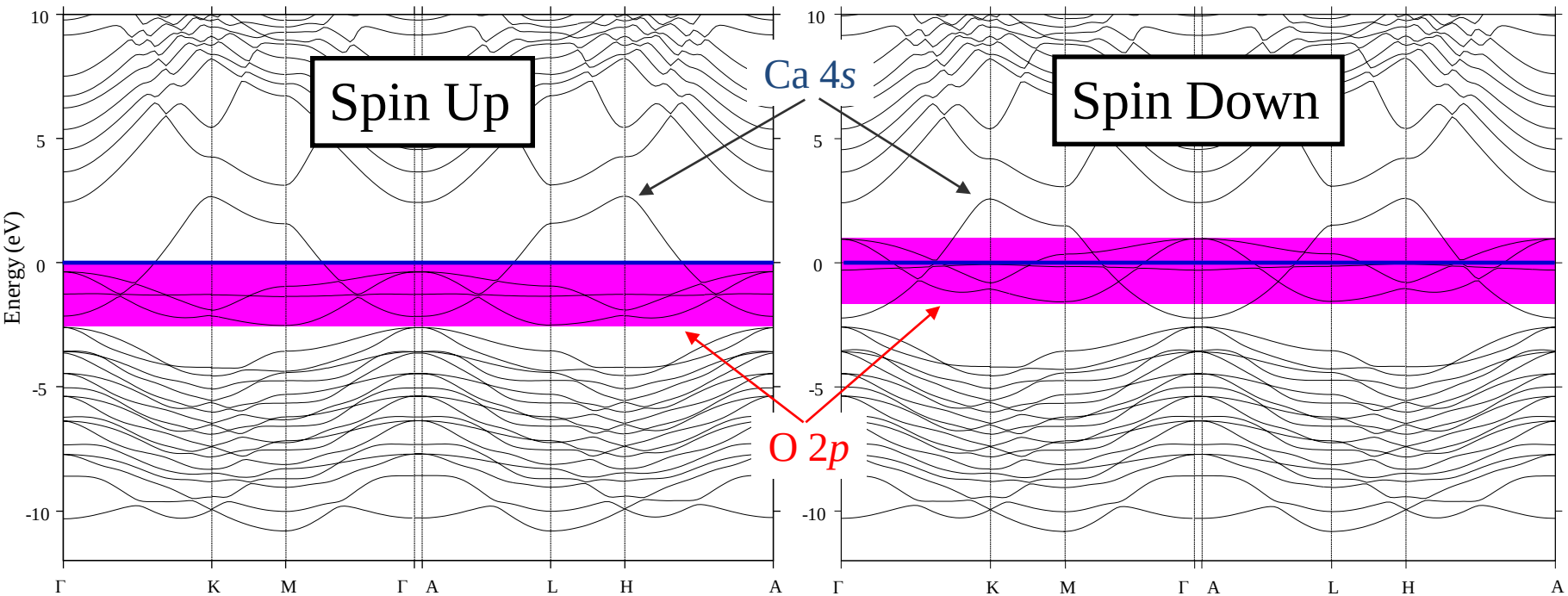
What happesn if we have a polar surface?

- Take the NaCl Rock salt structure as in NiO, CaO, MgO, MnO etc

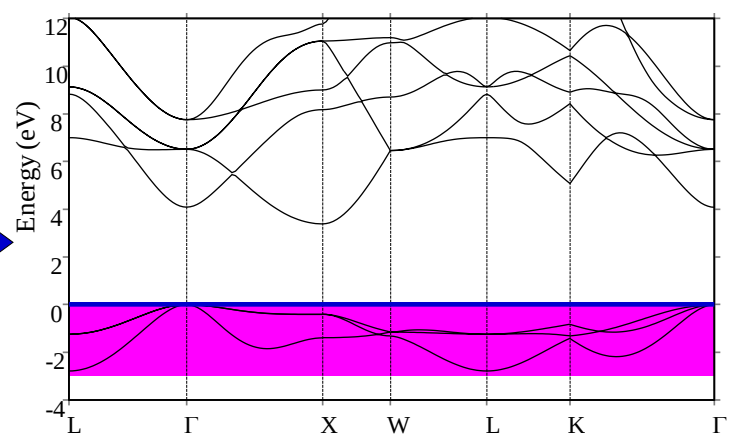


Alternating layers of +2 ,-2 charges in the ionic limit.

LSDA Band Structure of CaO (111) Slab terminated with Ca and O



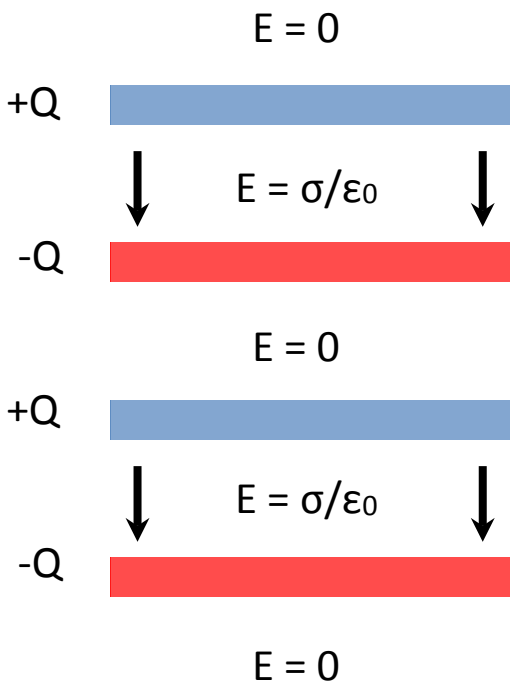
Note:
Bulk material
(no surface)
is an insulator

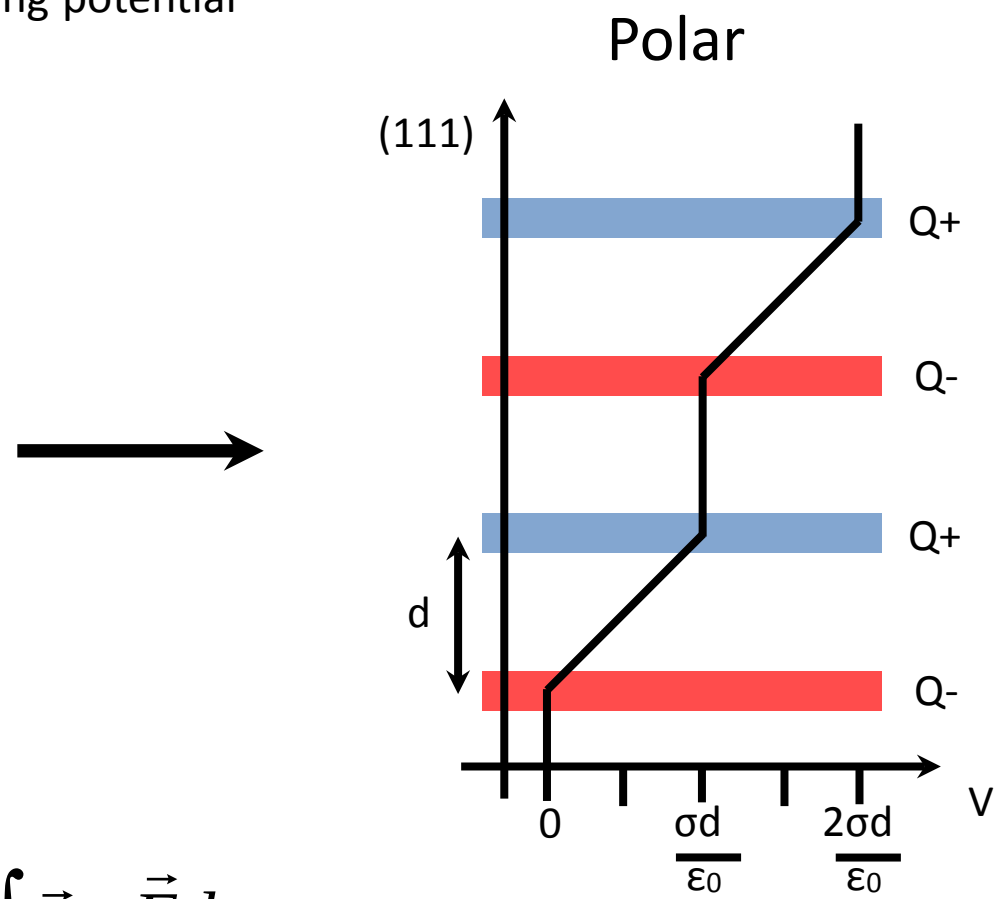


But surface is metallic! And ferromagnetic! half metallic ferromagnet

Why are polar surfaces i.e. type 3 different?

Asymmetric boundary condition: Diverging potential





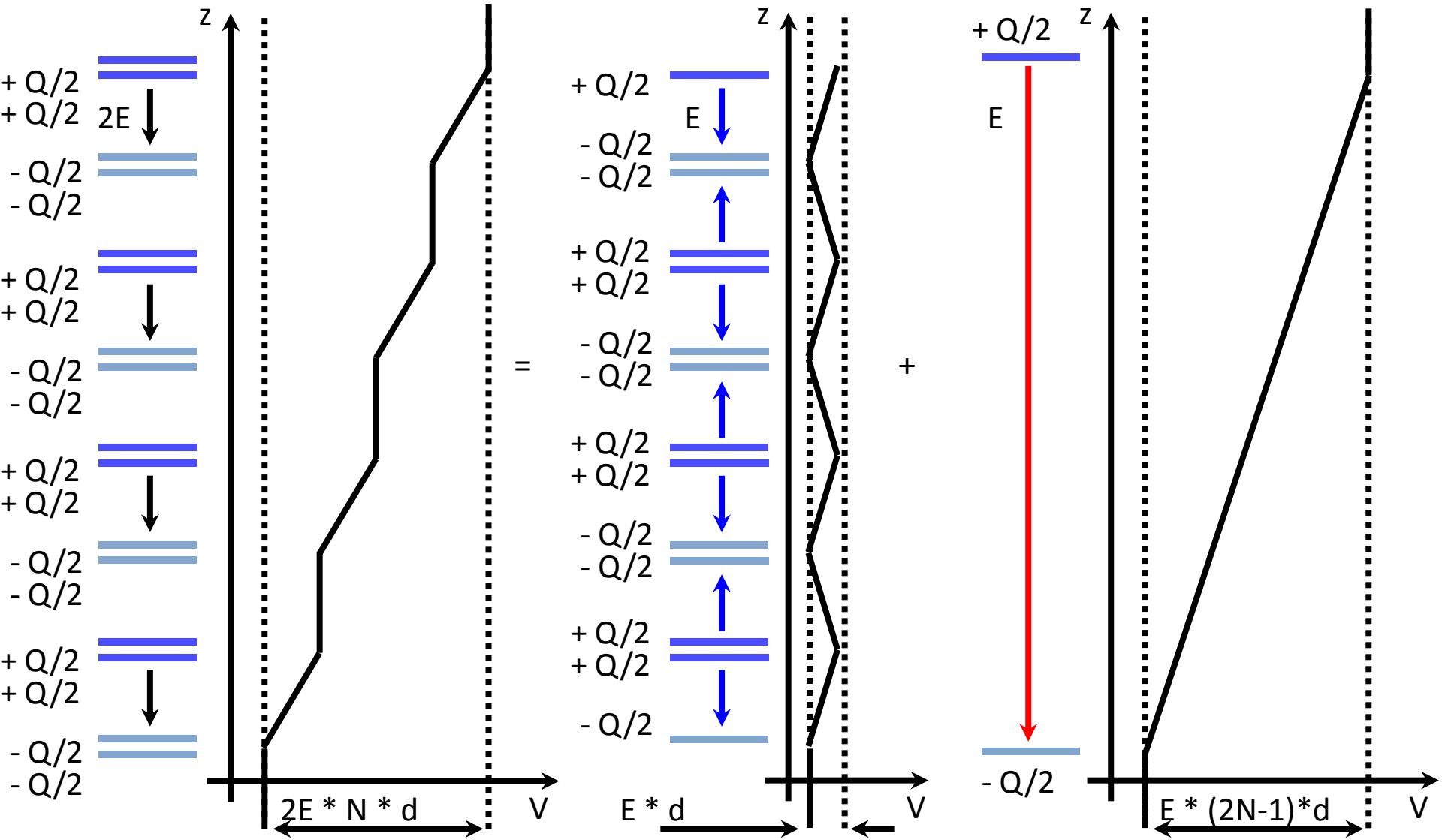
Remember Gauss's Law?

$$Q = \int \vec{n} \bullet \vec{E} ds$$

The field outside an infinite charged plane of small thickness is given by

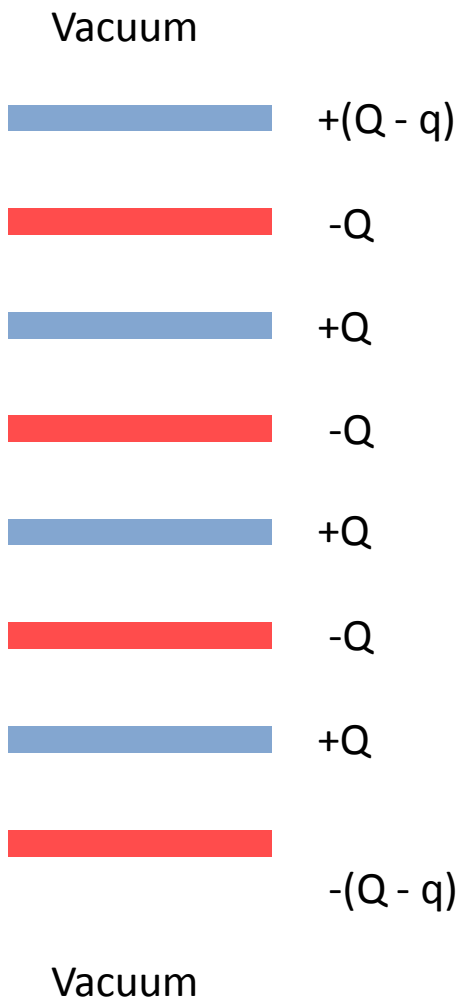
$$\vec{E} = \vec{n} \frac{Q}{\varepsilon_0 A}$$

Simple explanation : big capacitor



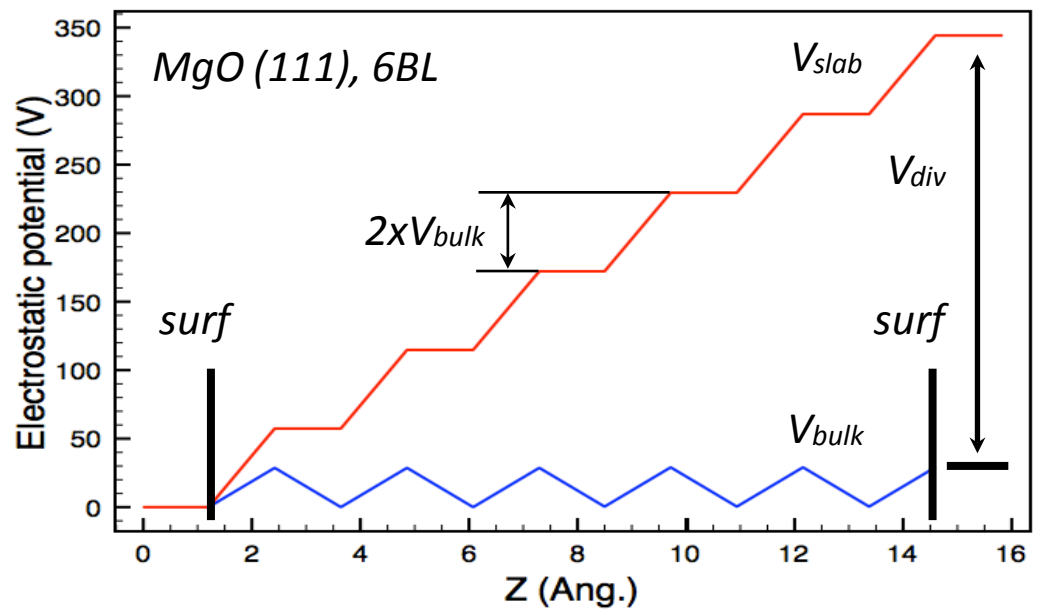
Solution to polar catastrophe problem is to get rid of big capacitor.

Potential difference between two surfaces of the slab



$$\Delta V = \underbrace{\frac{(Q-2q)(2N-1)d}{2\epsilon_0 A}}_{V_{div}} + \underbrace{\frac{Qd}{2\epsilon_0 A}}_{V_{bulk}}$$

N - number of bilayers
d - distance between planes
A - unit area



For 18 bilayer thick films the Potential difference is in eV)

	V_{div}
MgO (111)	1002eV
$LaAlO_3$ (001)	418eV

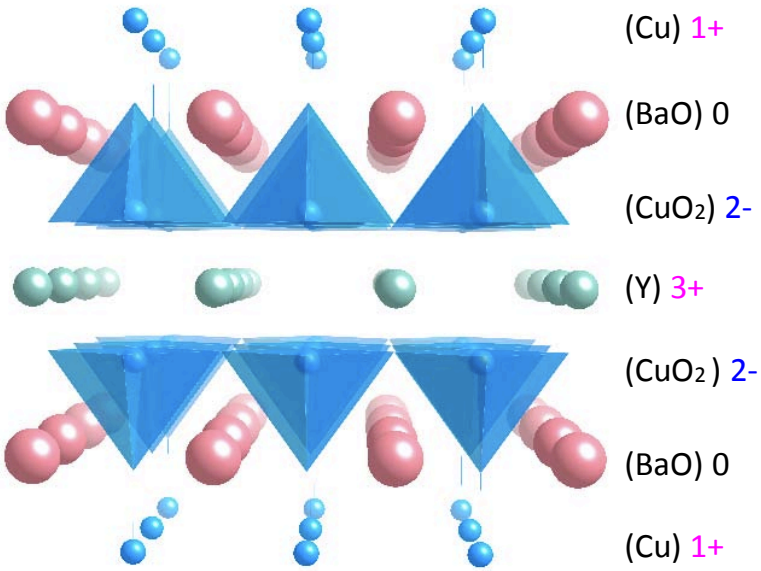
Far above the Zener breakdown Limit =Egap

Polar surfaces and interfaces

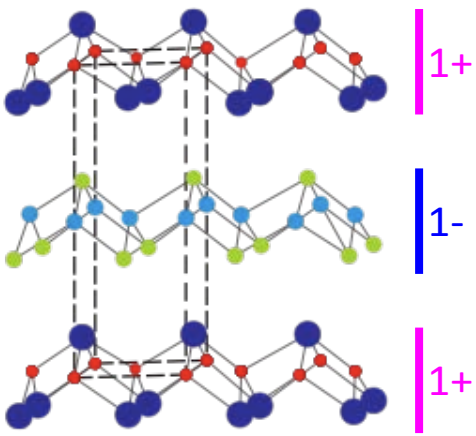
- Cannot be compensated by simply moving things across the interface as in intermixing
- Cannot be compensated by moving around charges outside of the polar material as for example compensating for LAO at the LAO/STO interface by moving electrons around O vacancies in STO to the interface!
- We need to add charge of order 1 per unit cell to the region around the interface and an equal an opposite charge at the surface or other interface. The materials remains charge neutral

Interesting materials in which electronic reconstruction can strongly alter properties and which can be used for interface engineering to develop new devices with exotic properties.

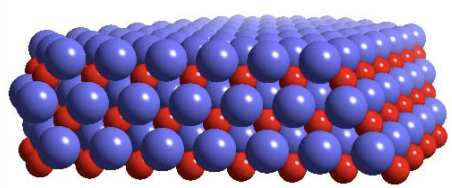
Super Conductors:
$YBa_2Cu_3O_{6+\delta}$



LaOFeAs

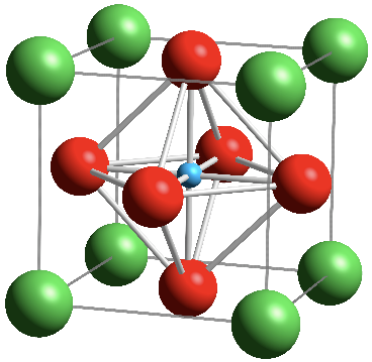


Simple oxides:
SrO, NiO, MnO ...

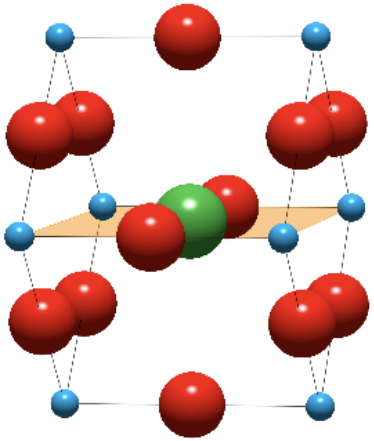


(111) surface

Perovskites: $LaTMO_3$ (Ti,V,Mn ...)
Spin, charge and orbital ordering



(001) surface in trivalent compounds



(110) surface

Some key papers on polar surfaces and interfaces

R. Lacman, Colloq. Int. C.N.R.S. 152 (1965) 195

D. Wolf, Phys. Rev. Lett. 68 (1992) 3315.

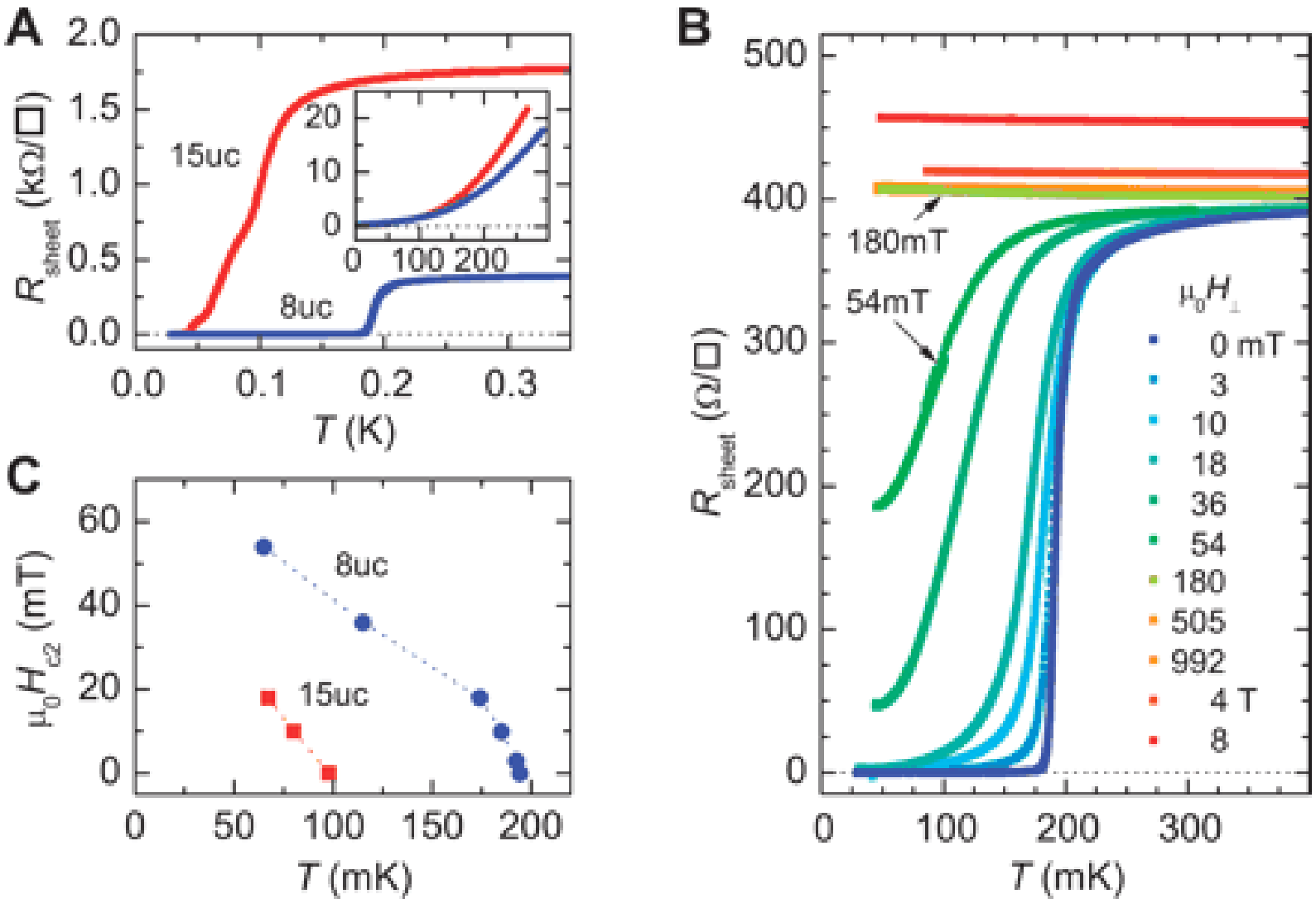
H.-J. Freund and E. Umbach, Eds., Adsorption on Ordered Surfaces of Ionic Solids and Thin Films, Vol. 33 of Springer Series in Surface Science (Springer, Berlin, 1993).

Hesper et al PRB 62, 16046 2000 coined the phrase Electronic Reconstruction for K3C60 surfaces

A. Ohtomo and H. Y. Hwang Nature **427**, 423 (2004) Insulating Oxide heterostructures

N.Reyren et al Science express 317, 1196 2007

Superconducting interface SrTiO3/LaAlO3

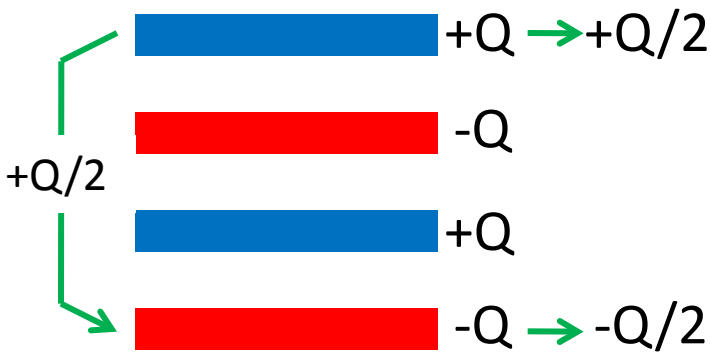


There are several ways to stabilize a polar surface

- Oxygen vacancies at the surface (remove O2- i.e. charge or it won't work!)
- Facetting i.e. piramids with 100 faces (again result has to be removing charge!!)
- Adsorbed molecules i.e. OH- on outermost Mg surface (again OH- replaces O2- as outer layer)
- Terminating monovalent ions
- Electronic reconstruction (move charge from one surface to the other)

Types of reconstruction

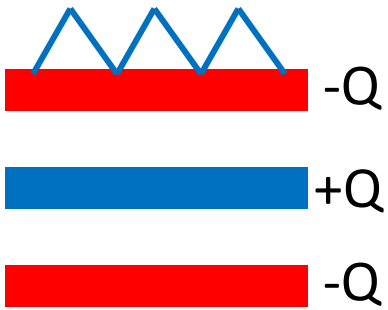
Electronic



Rearrangement of electrons

K_3C_{60}:
R. Hesper *et al.*, Phys. Rev. B **62**, 16046 (2000).

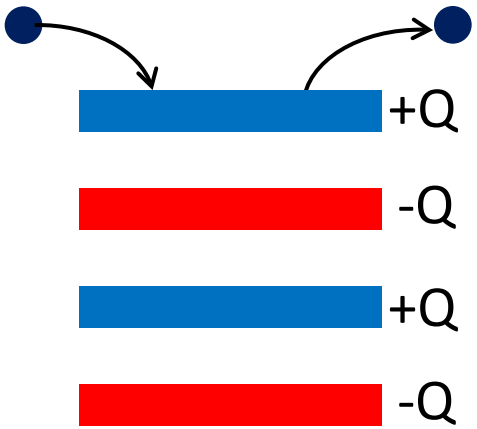
Ionic



Rearrangement of Ions faceting plus charging

NiO(111):
D. Cappus *et al.*, Surf. Sci. **337**, 268 (1995).

Chemical



Vacancies or add Ions (K+) or OH- adds charge

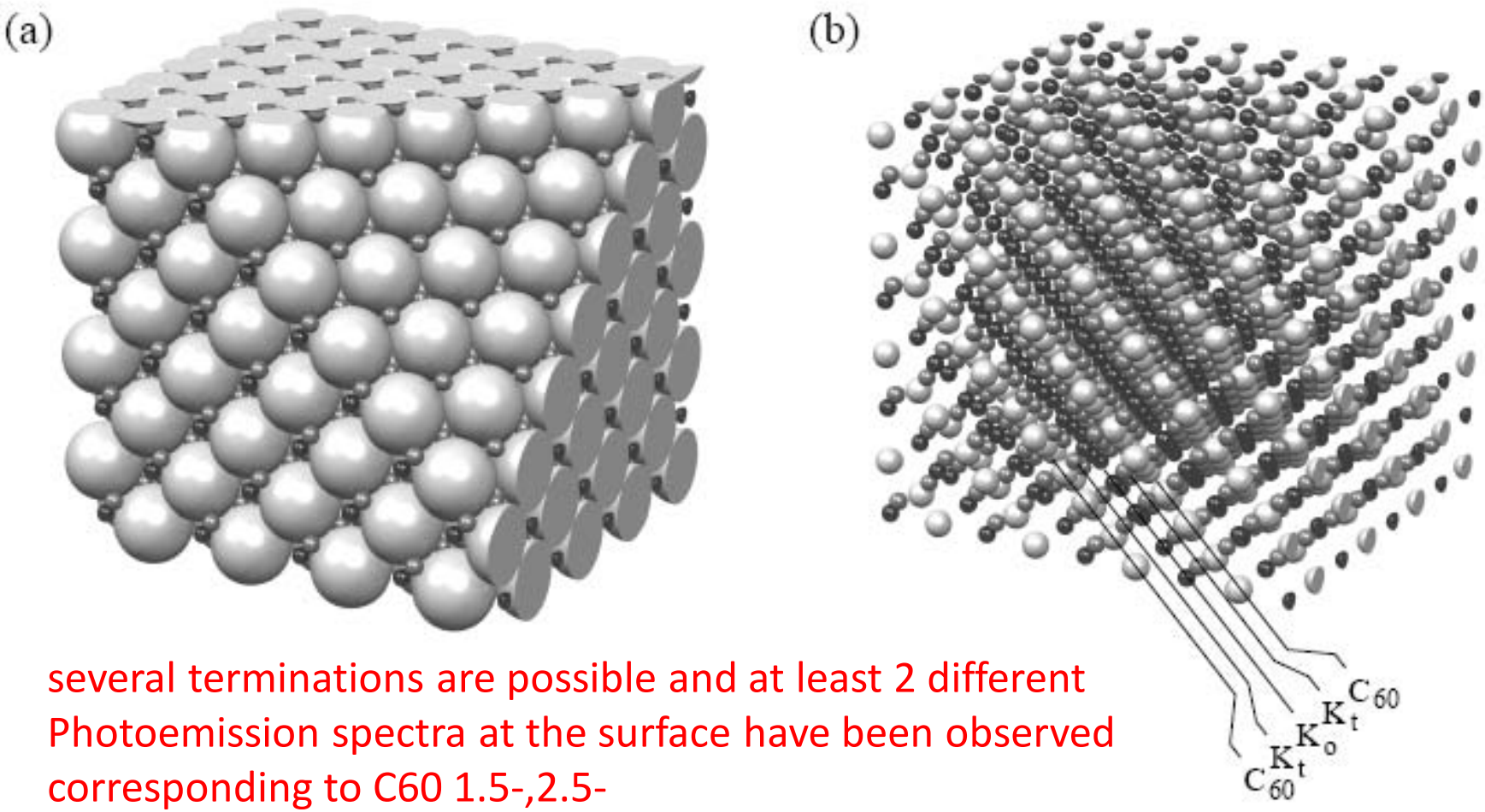
K-depositon:
M.A. Hossain *et al.*, Nat. Phys. **4**, 527 (2008).
NiO(111):
D. Cappus *et al.*, Surf. Sci. **337**, 268 (1995).

Electronic Reconstruction

- Energetically favourable in ionic systems with small band gaps and in systems with multivalent components (Ti,V,C60,Ce,Eu ----)

Hesper et al PRB 62, 16046 2000 coined the phrase electronic Reconstruction for K3C60 surfaces

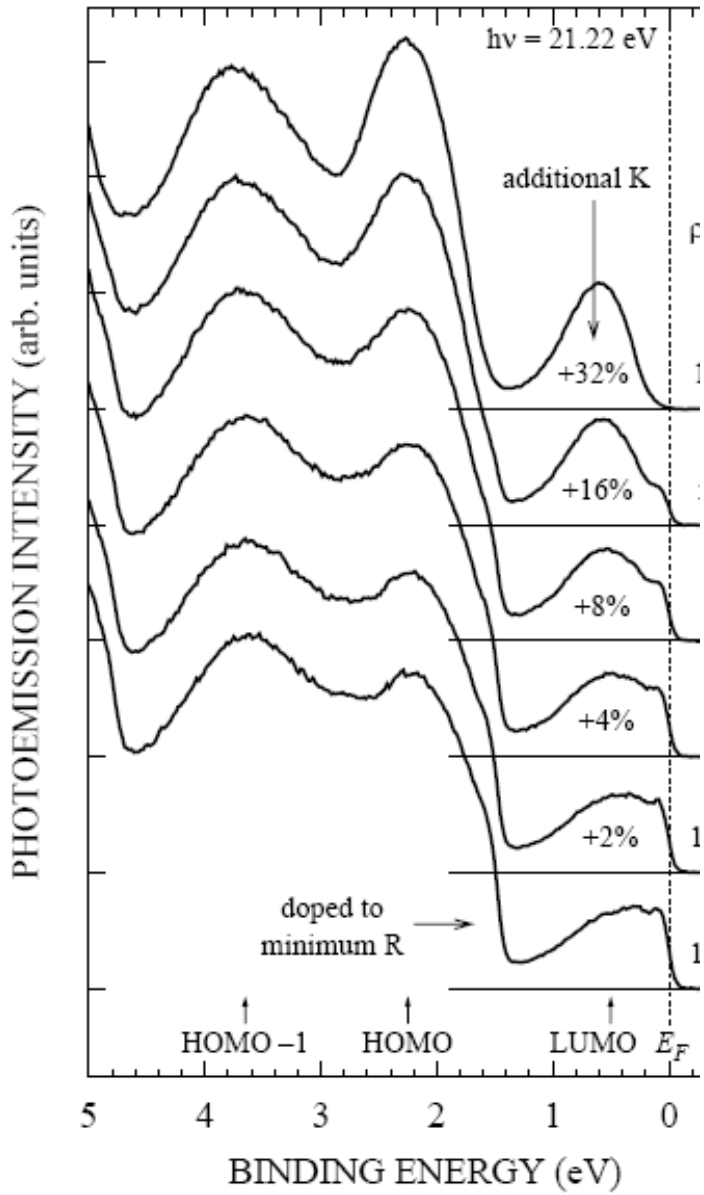
111 surface of K3C60 and its polar nature.



several terminations are possible and at least 2 different Photoemission spectra at the surface have been observed corresponding to C60 1.5-,2.5-

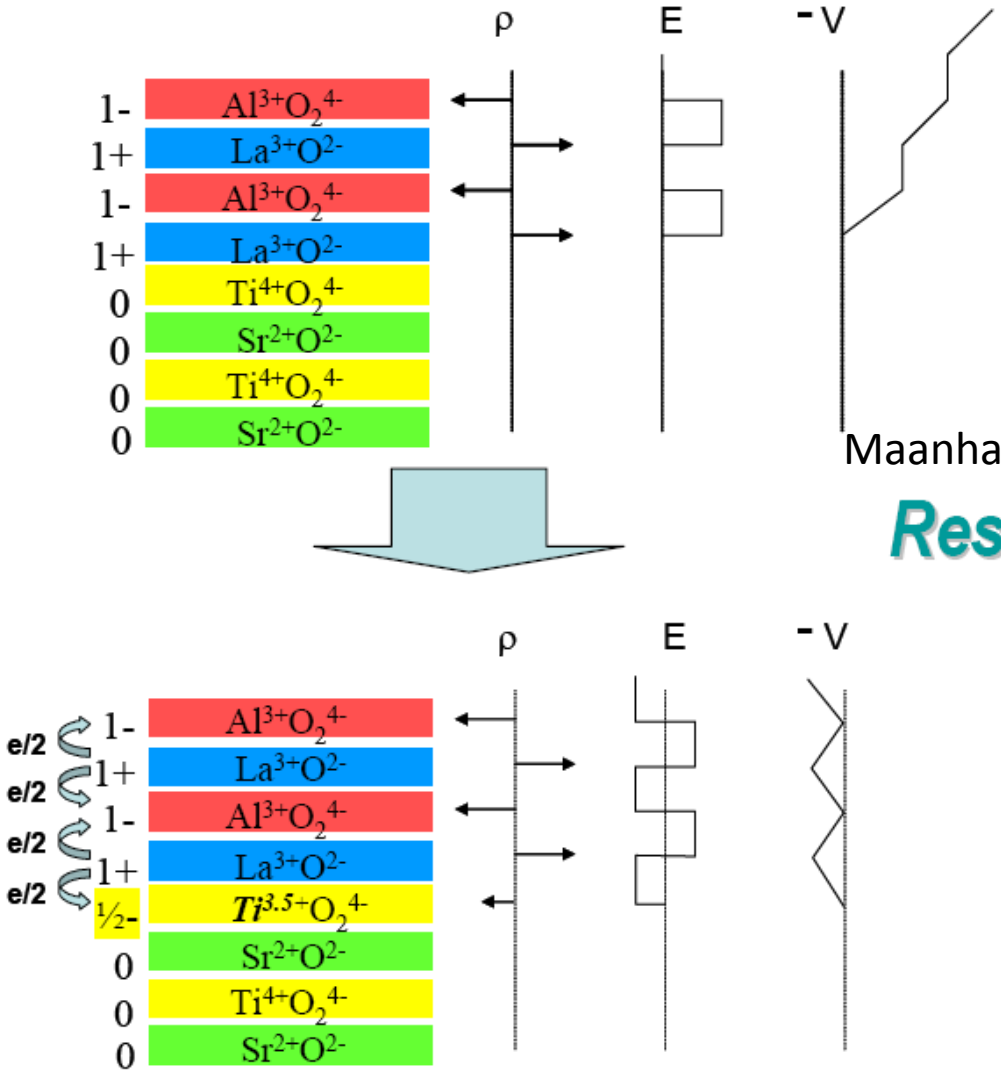
Hesper et al PRB 62, 16046 2000

Electronic reconstruction of K3C60 surfaces



A collection of published Phoptoelectron spectra of K3C60. The spectra vary From 0.5,1.5,2.5 negative Charge on C60 depending On the termination

A. Ohtomo, and H.Y. Hwang, *Nature* **427**, 423 (2004).



Maanhart et al MRS buletin review

Resp

electronic reconstruction – metallic interface

Interfaces involving polar surfaces

Interfaces between polar and non polar srufaces as In $SrTiO_3$ and $LaAlO_3$ for example can be magnetic And Metallic . They will be “self doped” perhaps even superconducting

The best candidates for electronic reconstruction at surfaces and interfaces is if one component does not mind changing its valence !

So use systems exhibiting multi valence or mixed valence behaviour Ti,V, are good examples

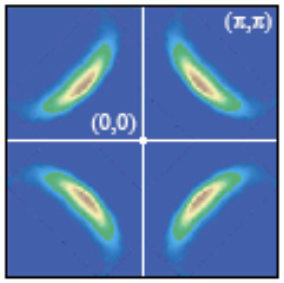
Examples of ad atom stabilization of Polar surfaces

- NiO grown by MBE is covered by a monolayer of OH - =1/2 the charge of the Ni2+ layer underneath and therefore stable
- MnS single crystals grown with vapor transport methods yield large crystals with 111 facets???? Covered by a single layer of I- and the crystal grows underneath. Like a surfactant
- ½ Ba2+ missing on the surface of BaFe2As2
- Elfimov has DFT calculations of O vacancies , and various forms of add atoms
- K+ ad ions on YBCO

Hossain et al., Nature Physics 4, 527 (2008)

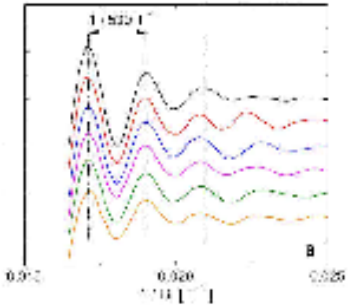
Fermiology across the Cuprate Phase Diagram

CCOC - x=0.12



ARPES – Shen (05)

YBCO - x=0.10

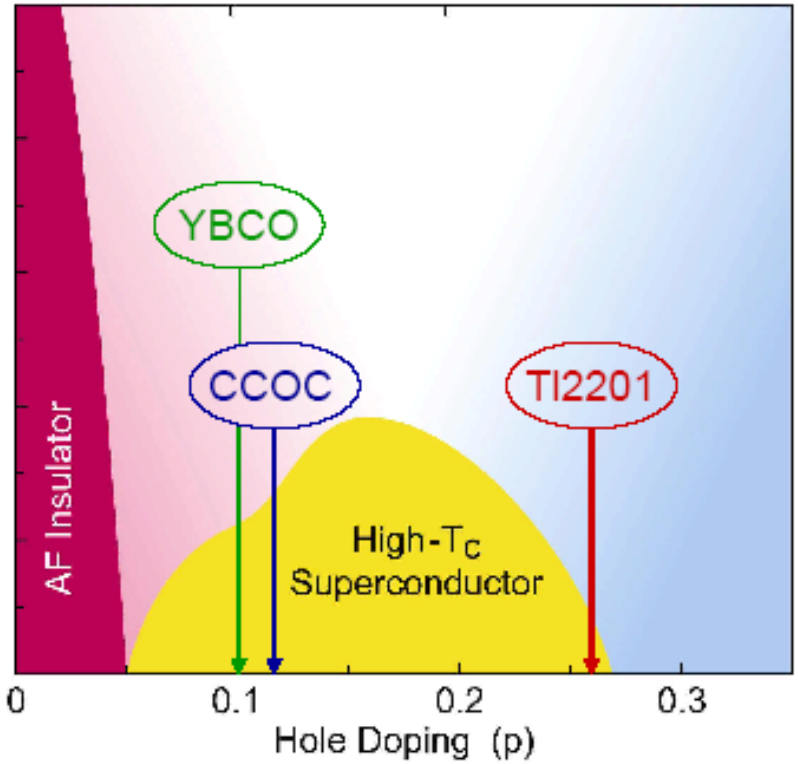


QO – Doiron-Leyraud (07)

ARPES on YBCO6.5

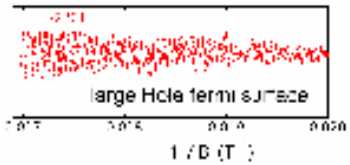
Overdoped Tl2201

Quantitative agreement between single-particle and transport probes

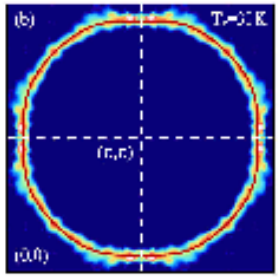


Can this be the gateway to a unified picture for underdoped cuprates?

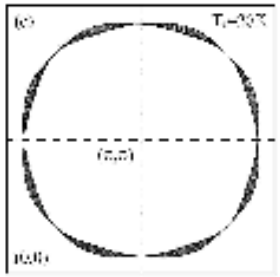
Tl2201 - x=0.26



dHvA – Vignolle (08)

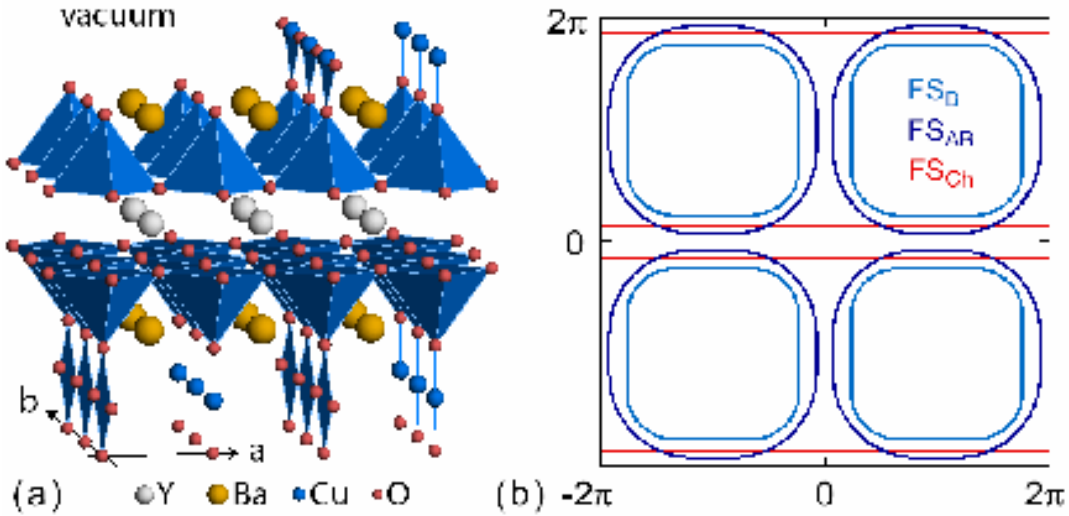


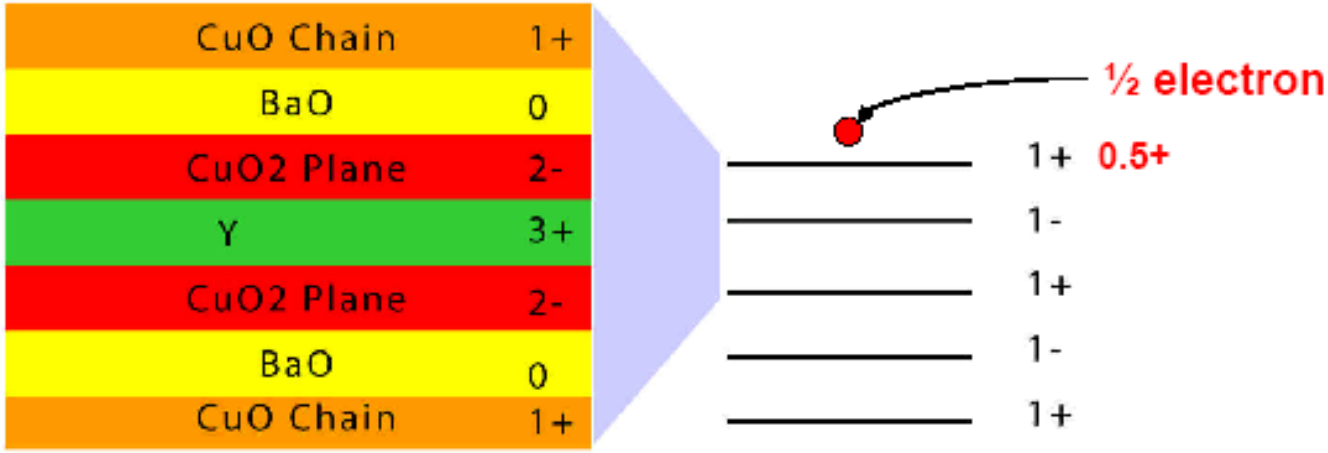
ARPES – Platé (05)



AMRO – Hussey (03)

Electronic Surface Reconstruction in $YBa_2Cu_3O_{6+x}$

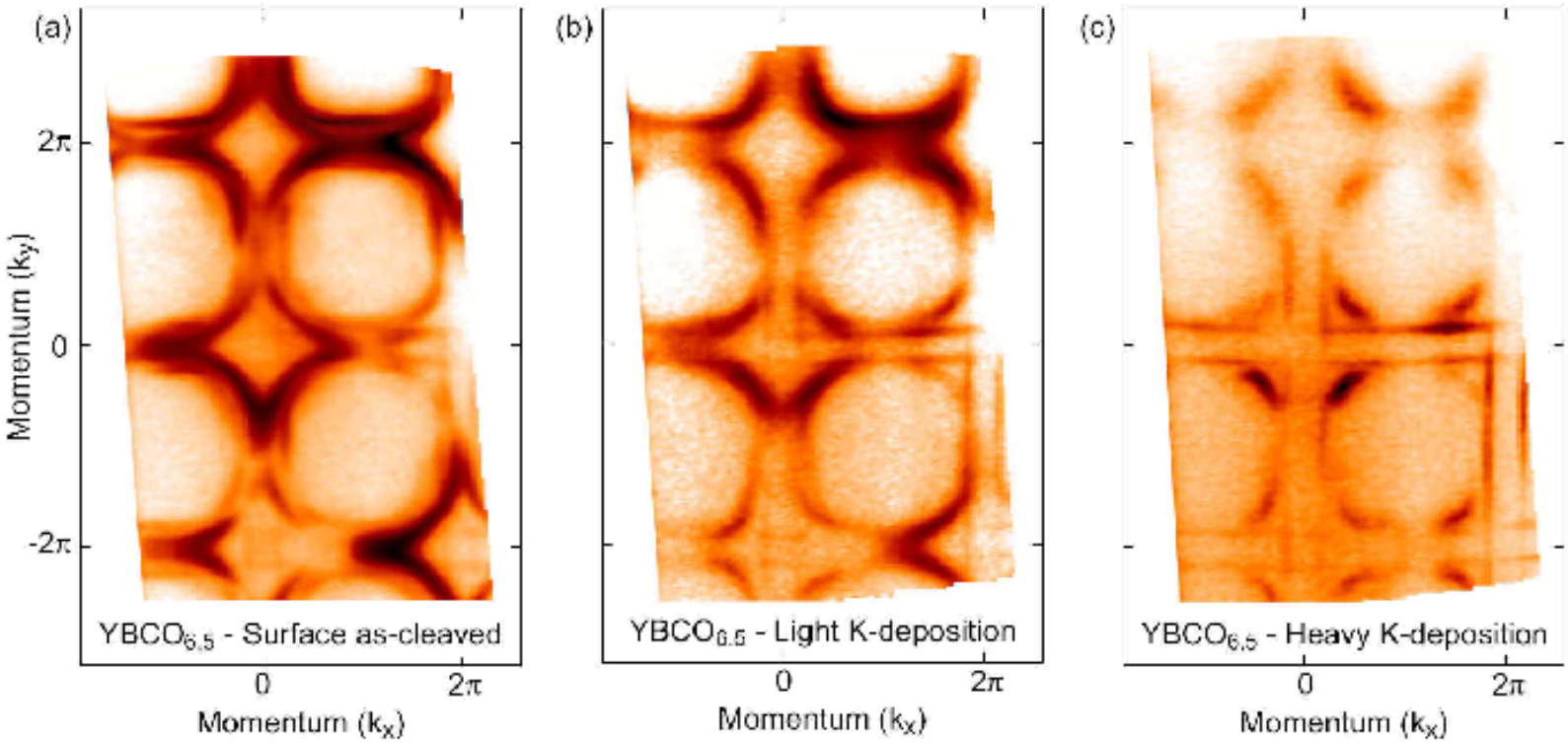




Hossain et al., Nature Physics 4, 527 (2008)

Our ARPES studies of Ortho-II YBCO6.5

Fresh | **Surface Treatment 1** | **Surface Treatment 2**



Electron doping

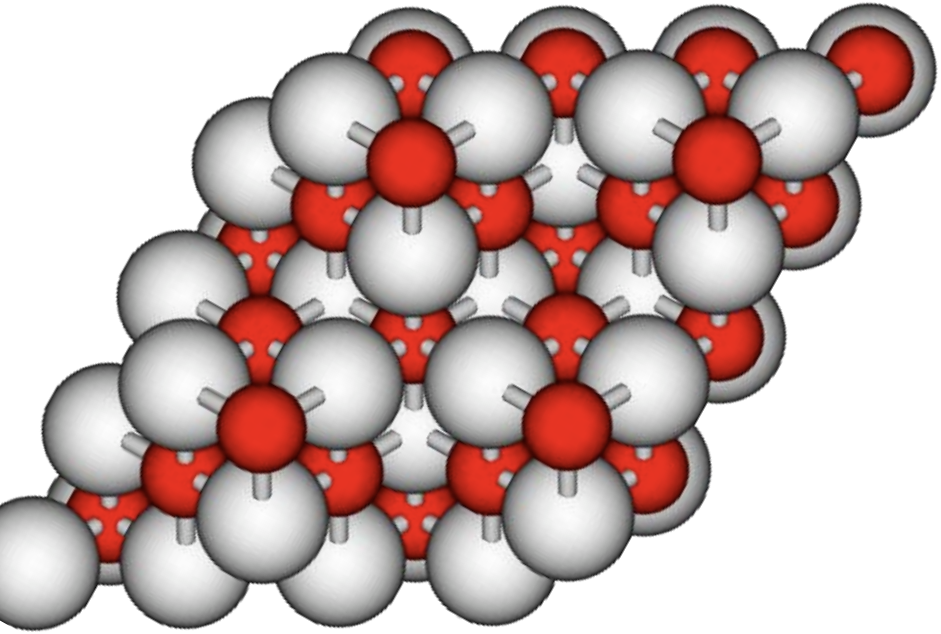
LDA → **Fermi arcs**

Atomic reconstruction

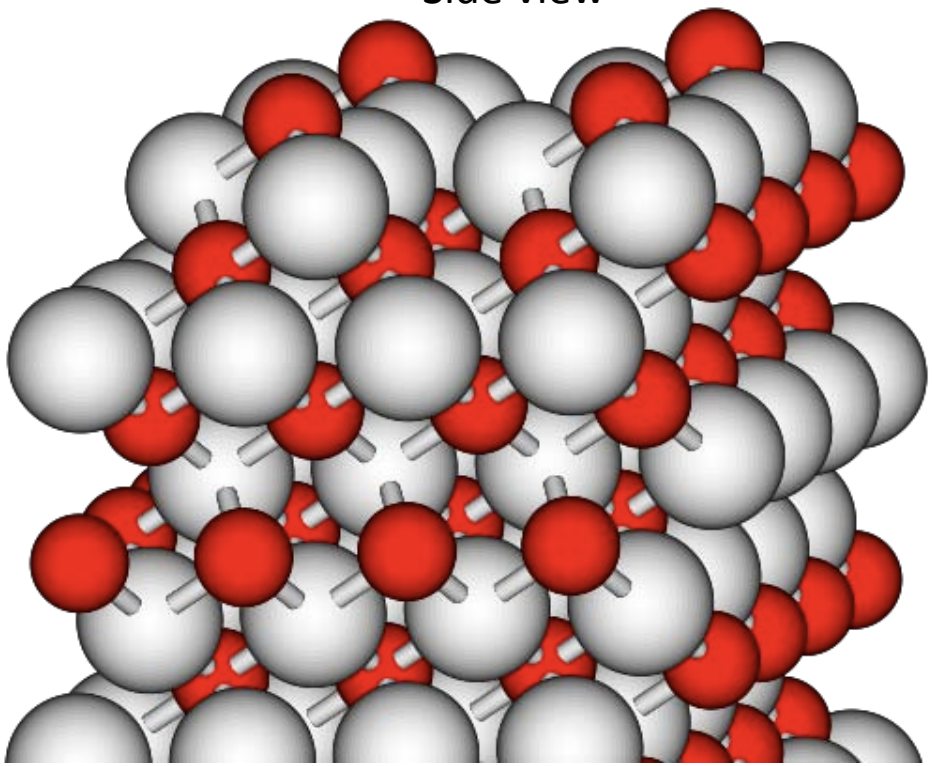
Facetting or ion displacements forming dipole moments to compensate for the electric field.

Octopolar reconstruction of MgO (111) slab

Top view



Side view



Effective surface layer charge = +2(3/4) -2(1/4) = +1
Note that in or to be totally charge neutral other surfaces must change their charge accordingly by one of 3 methods described. If the other surface is an interface the charge could be in the substrate as proposed for the system LAO/STO

PRL 102, 107602 (2009) PHYSICAL REVIEW LETTERS week ending 13 MARCH 2009

Avoiding the Polarization Catastrophe in $LaAlO_3$ Overlayers on $SrTiO_3$(001) through Polar Distortion

Rossitza Pentcheva[1] and Warren E. Pickett[2]

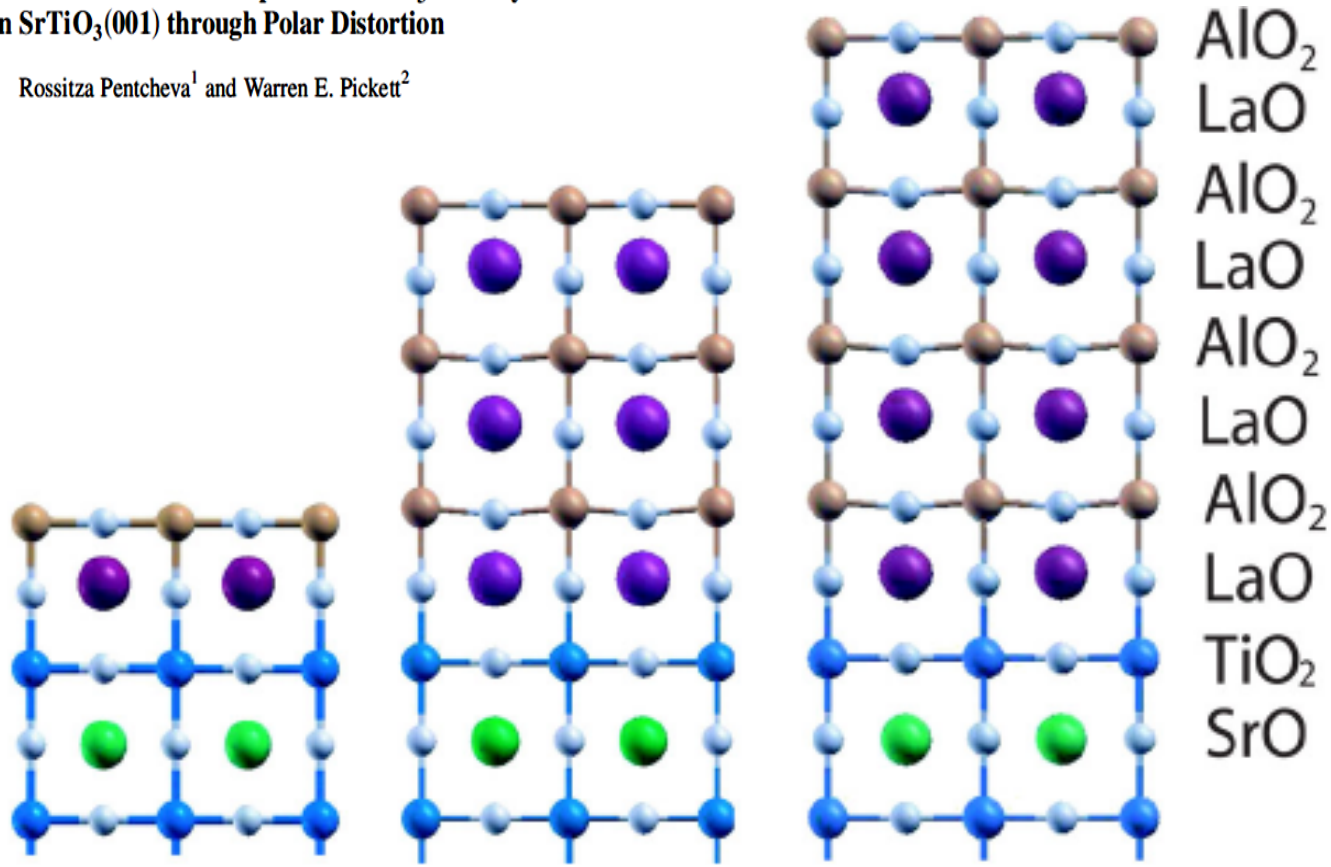


FIG. 1 (color online). Side view of the relaxed structures of 1, 3, and 4 ML LAO on STO(001) showing the polar distortion. The oxygen ions are marked by light grey spheres, while the Sr-, La-, Ti-, and Al-cations are shown by large green (grey), purple (dark grey) and small blue (dark grey) and orange (grey) spheres.

Avoiding the Polarization Catastrophe in $LaAlO_3$ Overlayers on $SrTiO_3(001)$ through Polar Distortion

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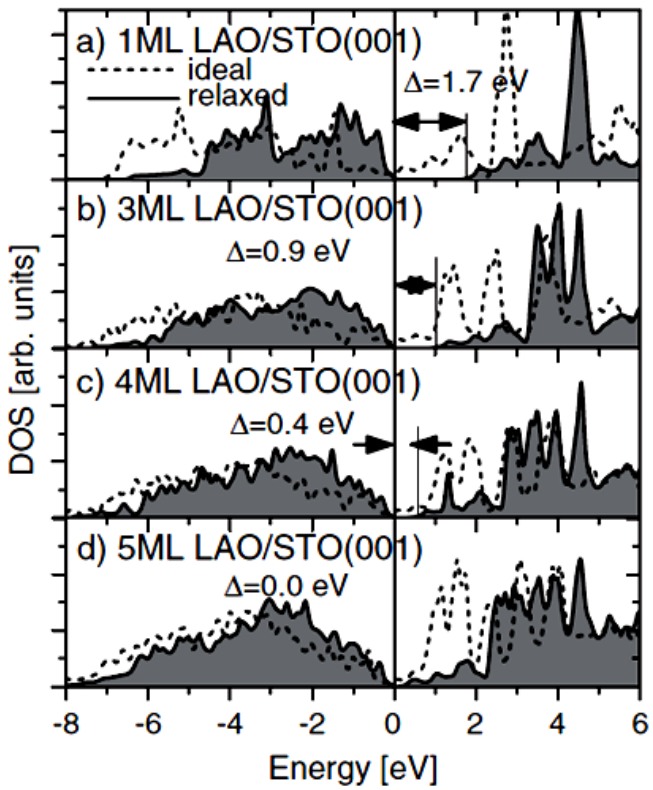

FIG. 3. Density of states for the ideal (dashed line) and relaxed (solid line, grey filling) structure of 1–5 ML LAO on STO(001). Relaxation opens a band gap, but its size decreases with each added LAO layer.

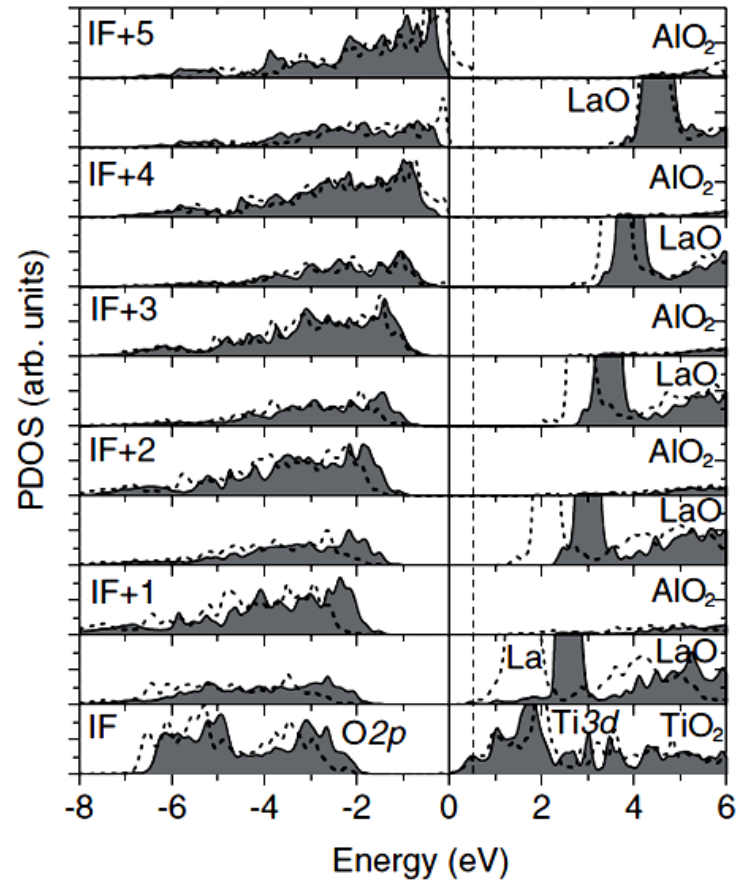

FIG. 4. Layer-resolved density of states of 5 ML LAO on STO (001) with ideal (dashed line) and relaxed (grey shaded area) coordinates. The DOS for the ideal positions was shifted by 0.5 eV to align with the conduction band of the system with the relaxed atomic positions. Its Fermi level is marked with a dashed line.

$\epsilon = 24$, this becomes approximately $\Delta V = 4\pi e \frac{\mathcal{D}_{\text{bare}}}{\epsilon(3.9\ \text{Å})^2} \sim$ 3.5 eV, which can be sustained by the 5.6 eV gap of LAO.

The dipole shift due to the polar distortion can be

Summary

- Reduced dimensionality enforces correlations and could result in self doping= dramatic change in the properties of materials
- Thin films of Oxides on highly polarizable substrates can lead to band gap narrowing and changes in exchange interactions
- Polar surfaces/ interfaces-electronically reconstruct = Metals,ferromagnets, even superconductors
- Point defects like Cation vaqcancies may result in local magnetic moments being formed due to a **molecular** Hund's rule coupling involving O 2p holes leading to ferromagnets.