Electronic structure of correlated electron systems : theory and experiment Lecture 4

G.A.Sawatzky

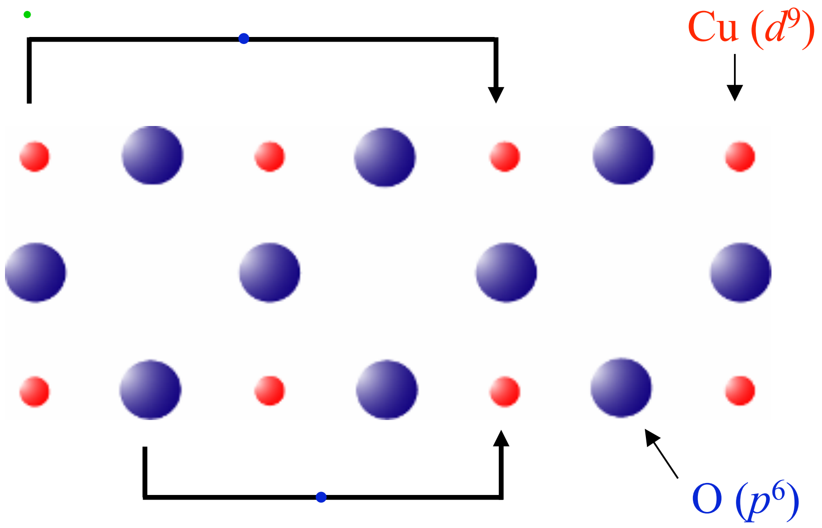
Surfaces and interfaces of ionic solids and pnictides

Important for TM Oxide interfaces

- Charge, spin, orbital, lattice degrees of freedom
- Charge transfer vs Mott Hubbard gaps
- Strongly ionic (Madelung potential effects)
- Polar surfaces/interfaces
- Strongly non uniform polarizabilities
- Electronic polarons and band gap closing at interfaces

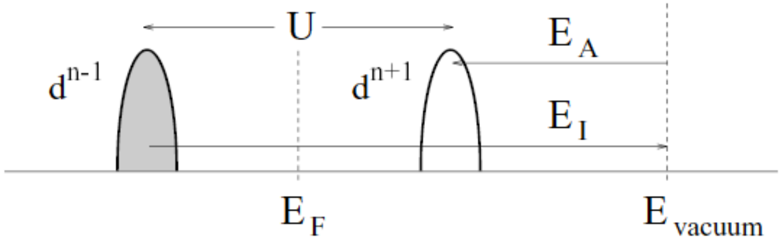
Correlated Electrons in a Solid

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

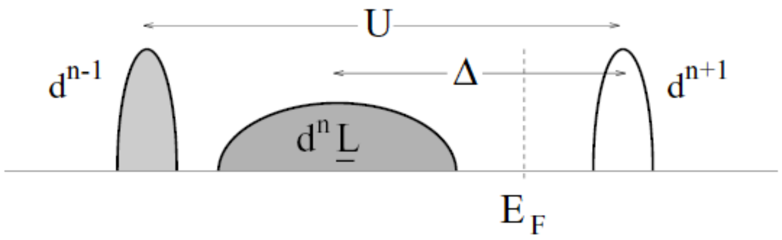


Δ : $p^6 \, d^n \rightarrow p^5 \, d^{n+1}$

(a) Mott-Hubbard insulator



(b) Charge transfer insulator



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

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

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

E_I ionization energy

E_A electron affinity energy

E_M Madelung energy

Epol depends on surroundings!!!

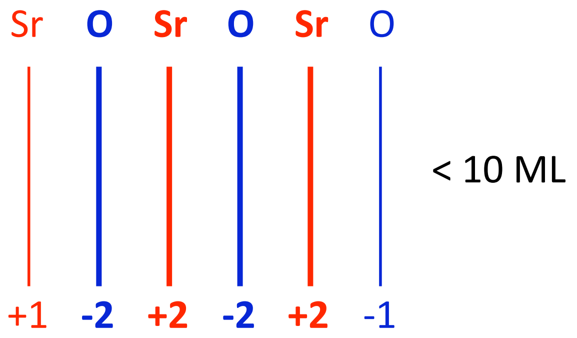
- **J.Hubbard, Proc. Roy. Soc. London A 276, 238 (1963)**
- **ZSA, PRL 55, 418 (1985)**

At a surface the charge transfer energy decreases , U increases

Novel Nanoscale Phenomena in Transition-Metal Oxides

Ionic Oxide Polar Surfaces

Stabilization of polar surfaces by epitaxy

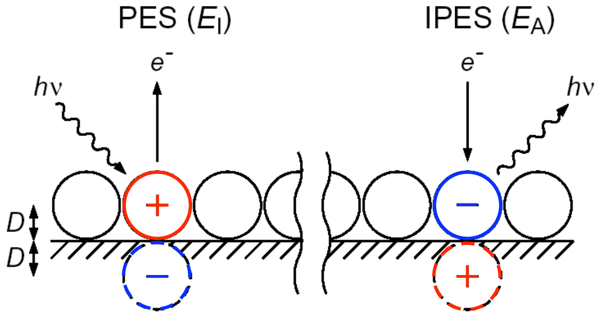


Transparent insulator → ½ metallic FM

Applications: Spintronics; CMR

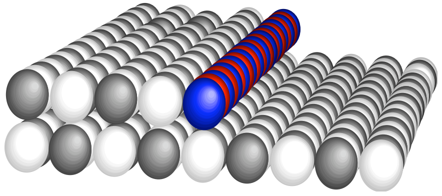
Electronic Structure of Interfaces

Metal-Insulator interface: gap suppression



Applications: Molecular Electronics;
Fuel Cells; Thermal Barrier Coatings

Correlated Electron System Surfaces



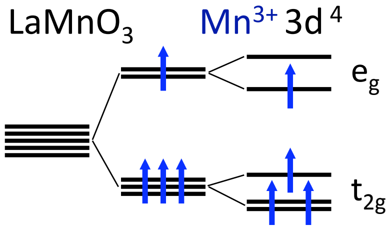
Kinks and steps stabilized by epitaxy

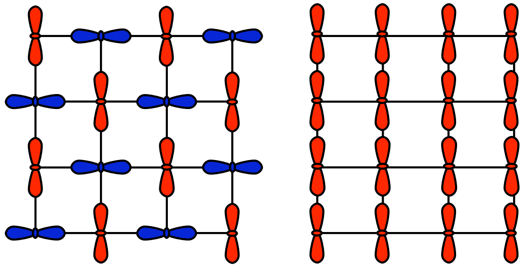
NiO (100) → 1D Metallic steps
Superconducting Copper oxides

Applications: Novel SC; QuBits

Strained 2D Layers

Positive and negative pressure

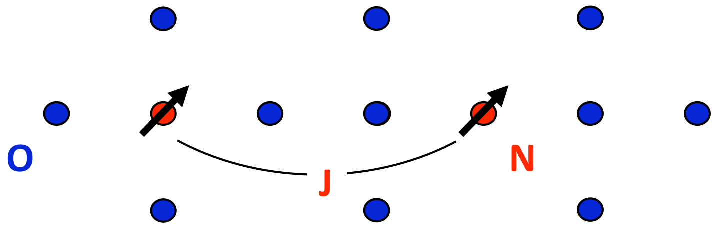




Applications: CMR; M-I Transition; Orbital Ordering

Artificial Molecules Embedded into a Material

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

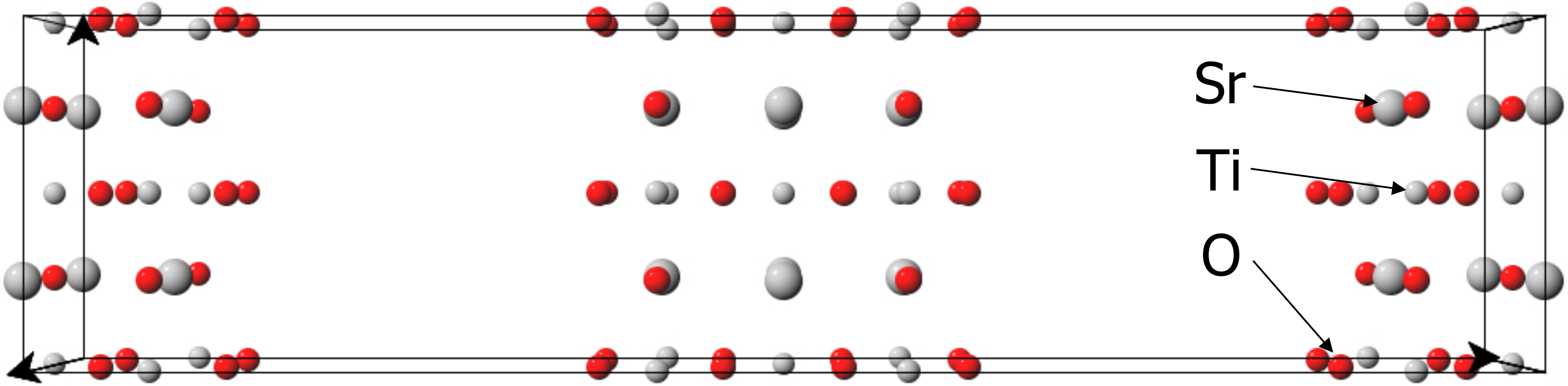


New class of magnetic materials by "low-T" MBE growth
Applications: Spintronics; Novel Magnets

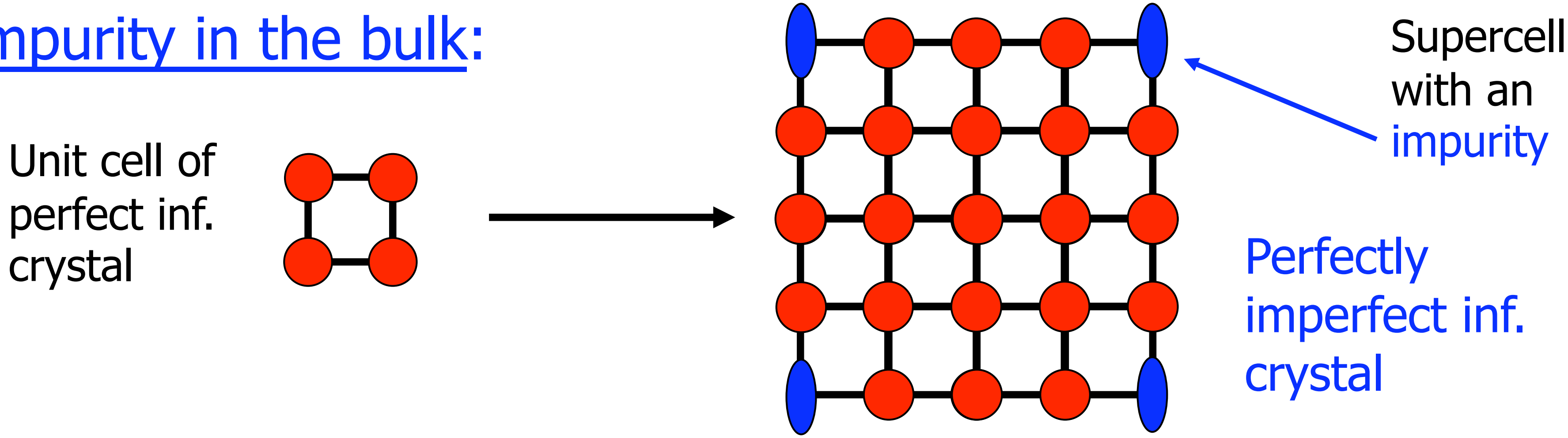
Defects study: Supercell approximation

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

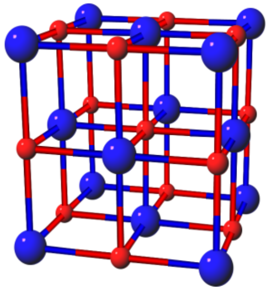
Slab geometry:



Impurity in the bulk:



NiO bulk

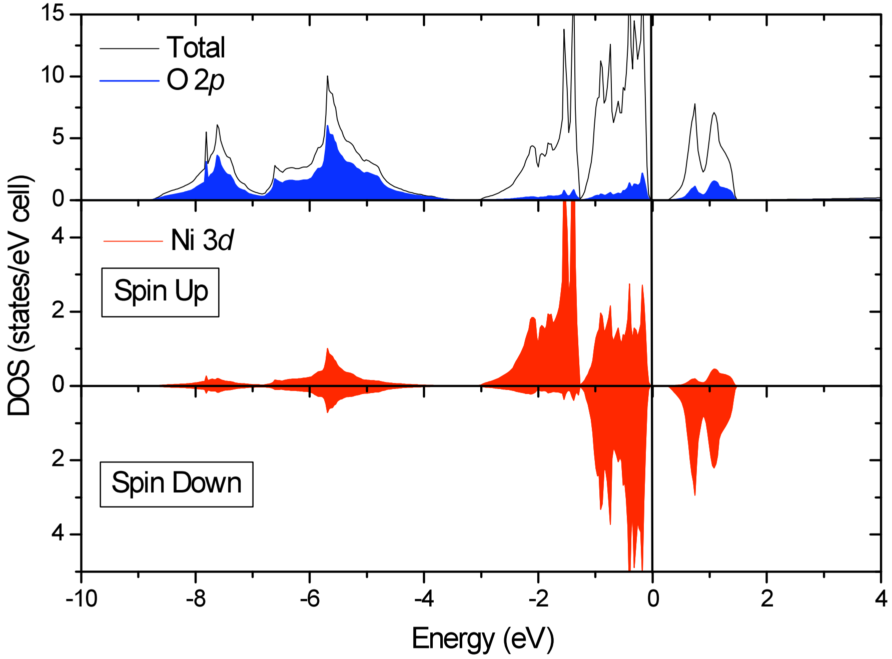


● O^{2-}: $2s^2\ 2p^6$

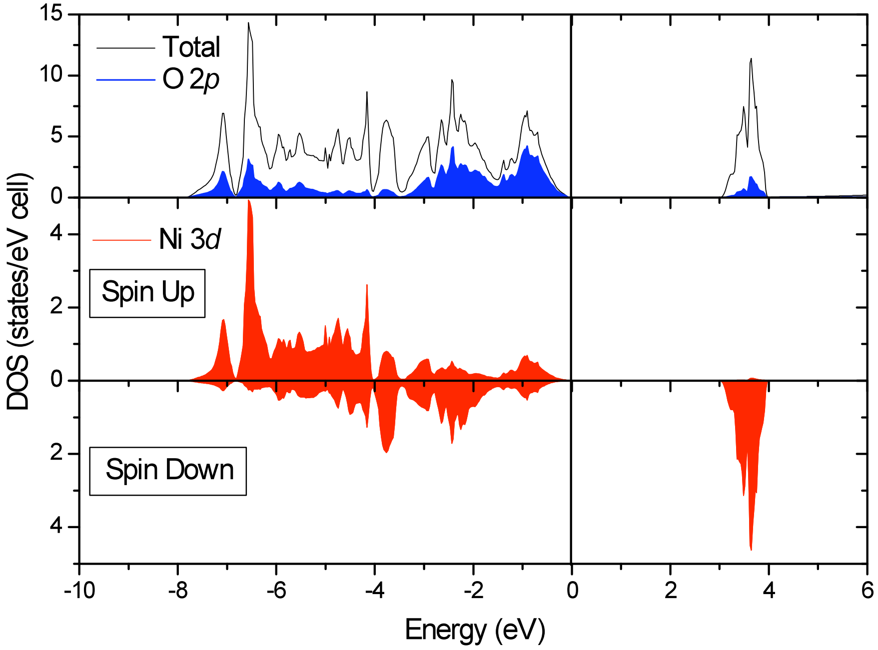
● Ni^{2+}: $3d^8$

- Rock salt structure
- AFM insulator (Exp. Gap ~4eV)

LSDA



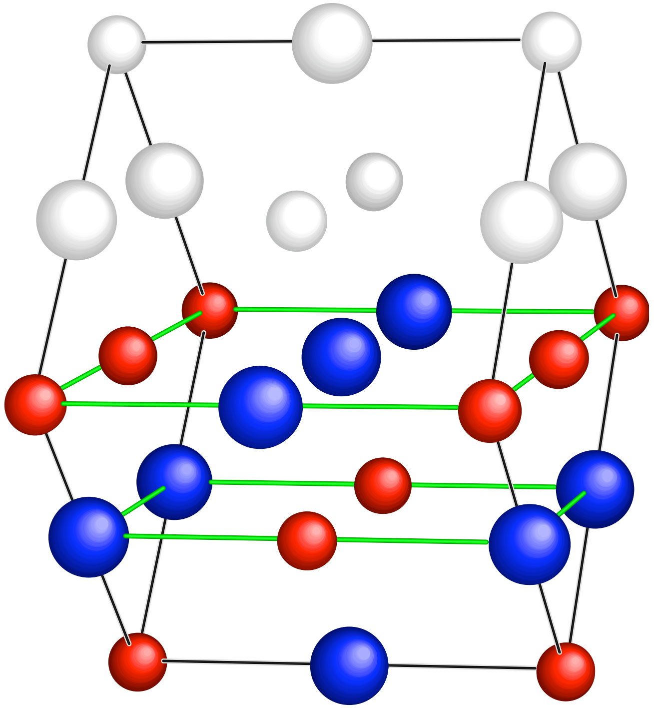
LSDA+U



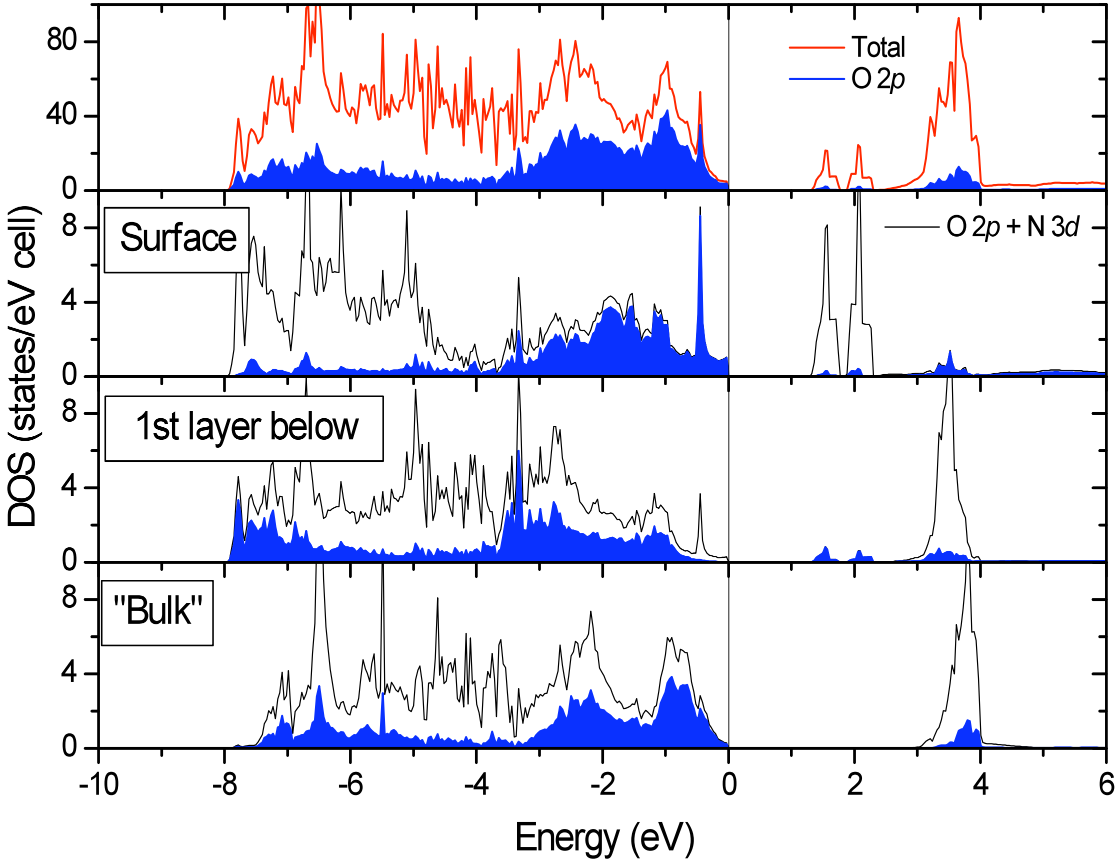
U=8eV J=0.9eV

Neutral (110) surfaces of NiO

Slab of 7 NiO layers



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



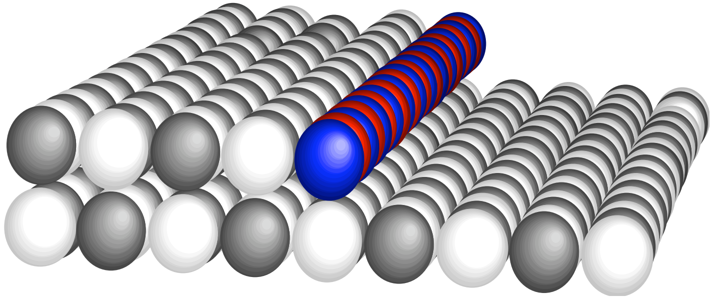
Band gap at the surface decreases from 3 eV to 1.2 eV

Can we get delta to go negative?

Step edges could be 1D strongly correlated metals

Negative CT gap at stepped surfaces?

Correlated Electron System Surfaces



Kinks and steps stabilized by epitaxy

NiO (100) → 1D Metallic steps
Superconducting Copper oxides

Applications: Novel SC; QuBits

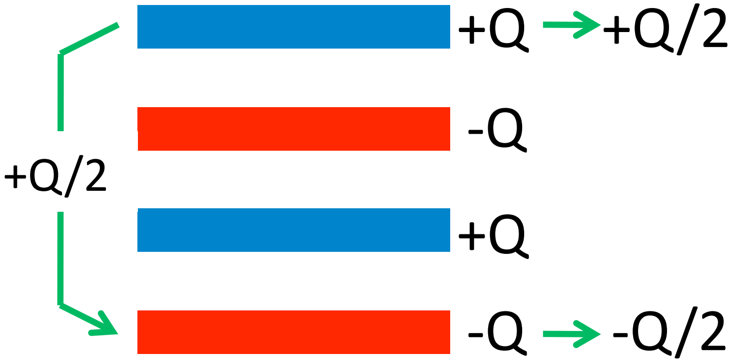
Ni2+ goes to Ni1+(d9) and holes in O 2p for negative charge transfer gap i.e. self doping -------looks like hole doped cuprates!!!

New High Tc??

Ionic Materials can exhibit Polar surfaces and interfaces and can electronically reconstruct

Types of reconstruction

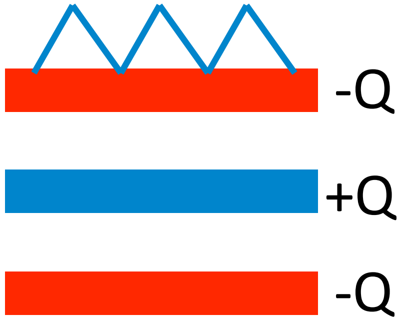
Electronic



Rearrangement of electrons

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

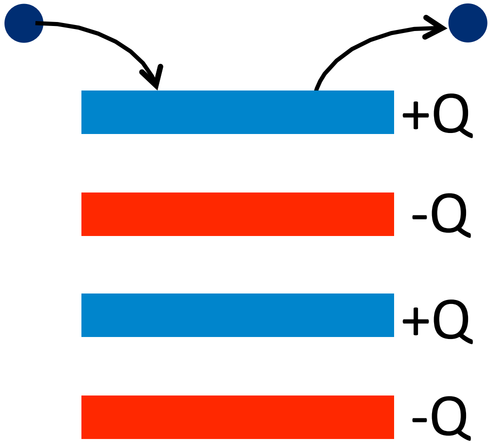
Ionic



Rearrangement of Ions faceting

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

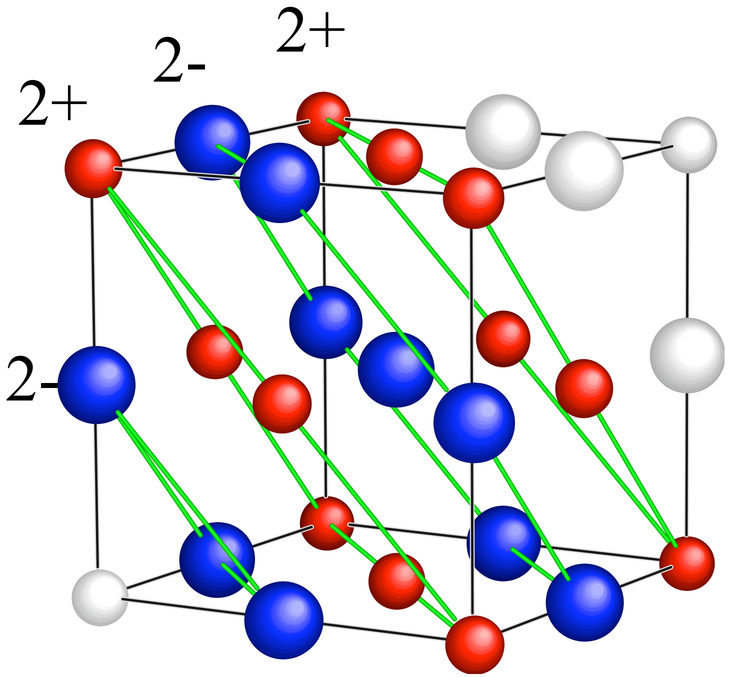
Chemical



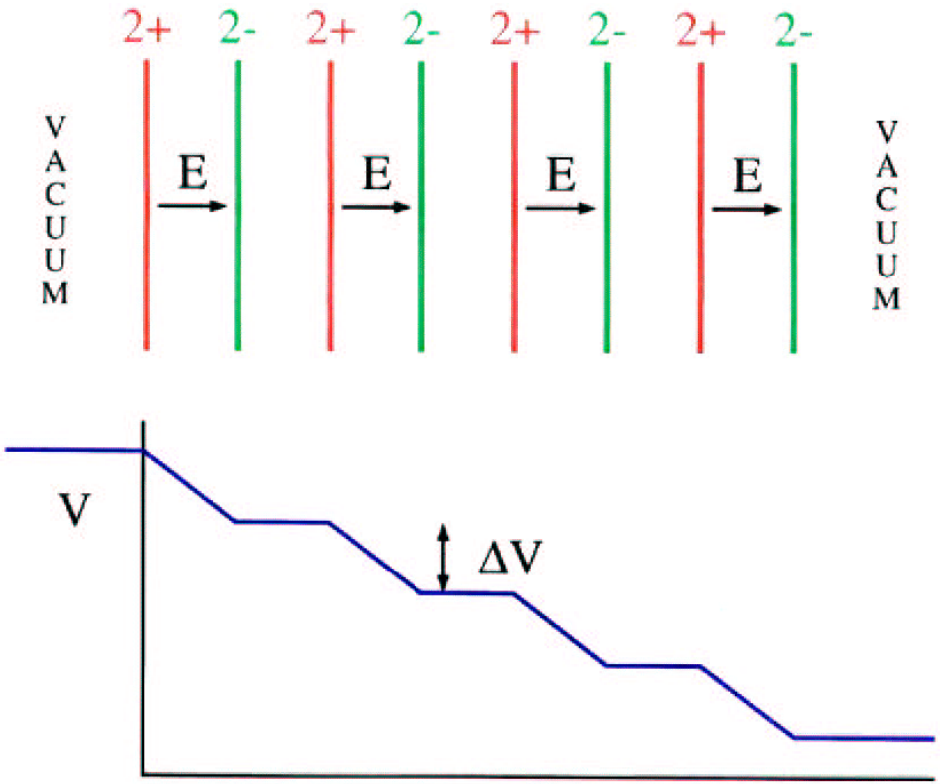
Vacancies or add Ions (K+) or OH-

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

Polar (111) Surfaces of MgO



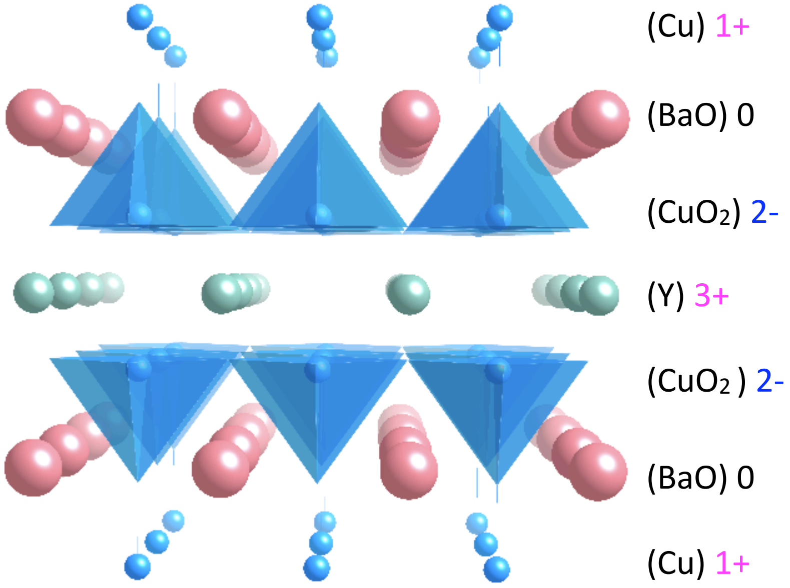
Finite slab of charged planes



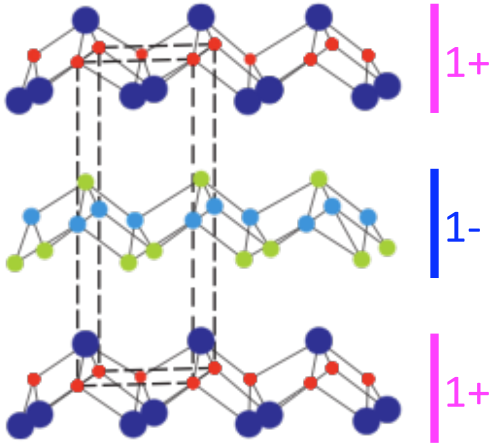
ΔV=58 Volt per double layer!

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.

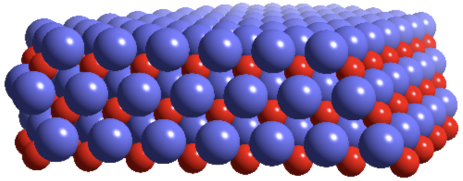
Super Conductors:
$YBa_2Cu_3O_{6+\delta}$



LaOFeAs

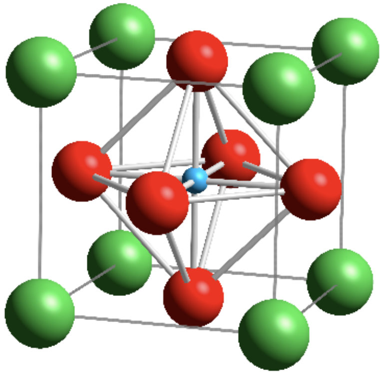


Simple oxides:
SrO, NiO, MnO ...

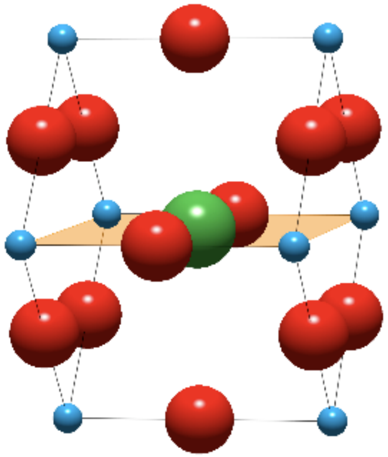


(111) surface

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



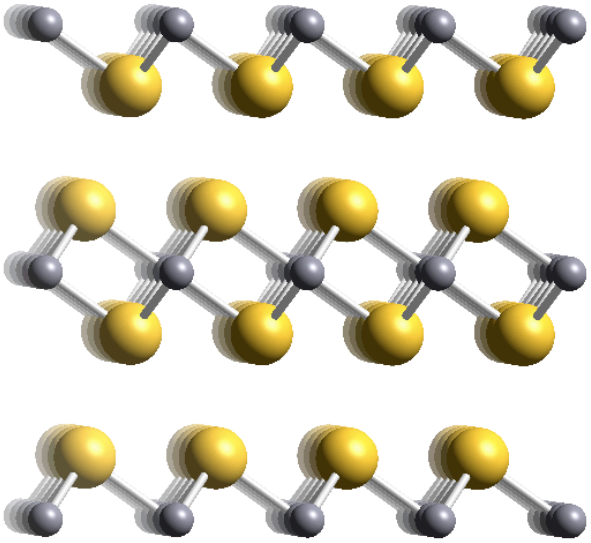
(001) surface in trivalent compounds



(110) surface

Examples of non polar layer structures

TiS_2

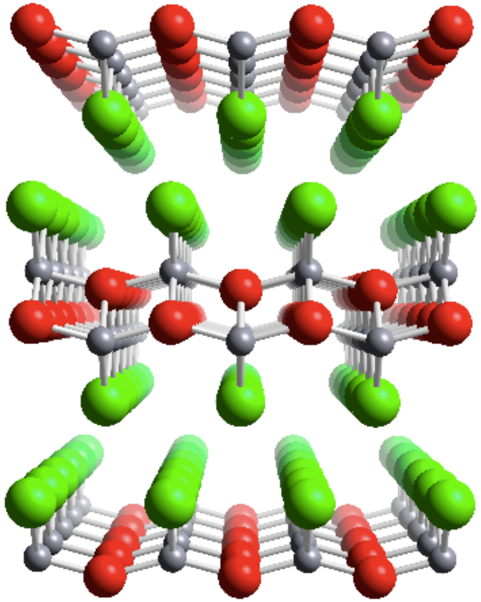


(S) 2-

(Ti) 4+

(S) 2-

TiOCl



(Cl) 1-

$(TiO)_2$ 2+

(Cl) 1-

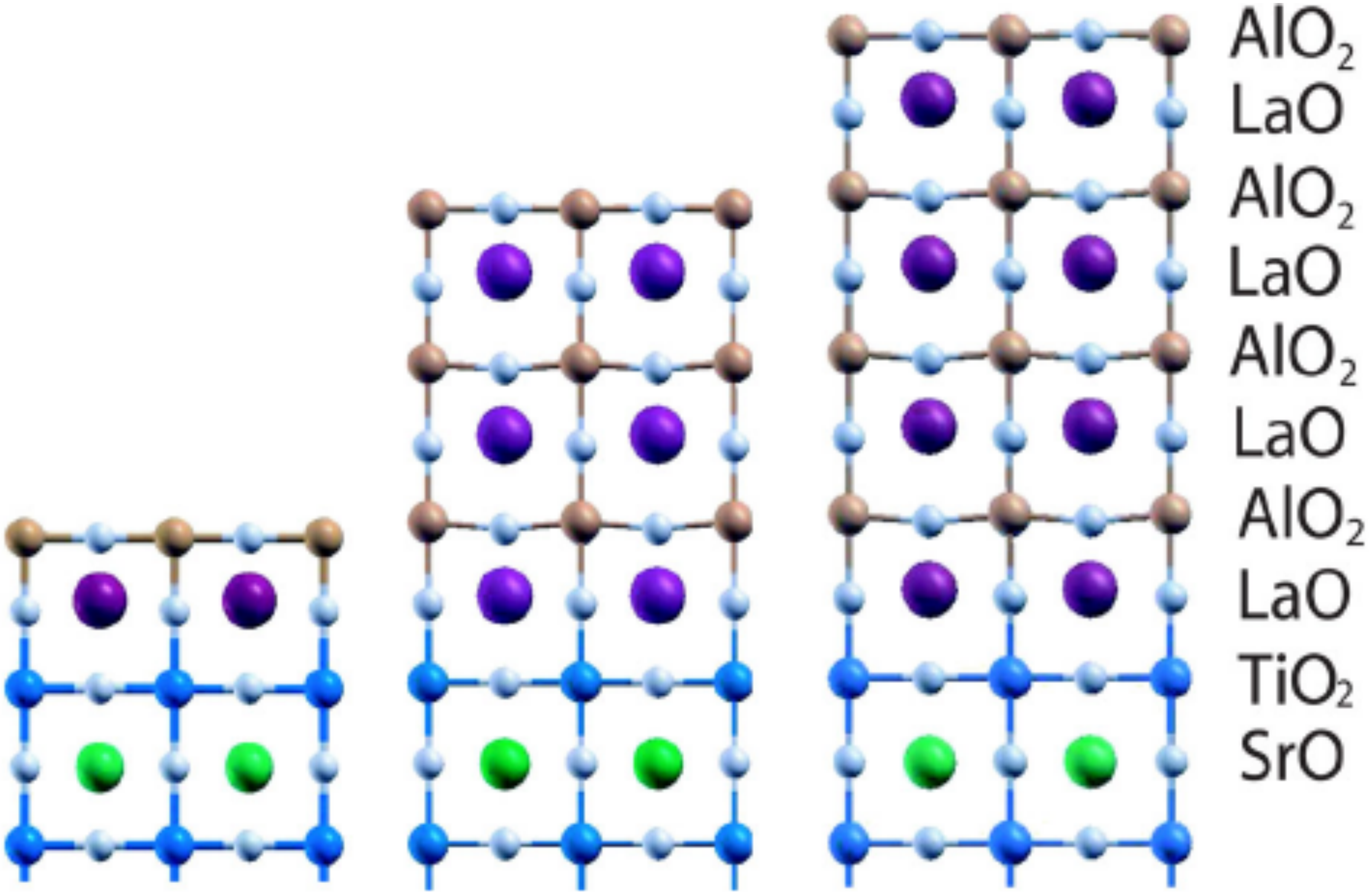
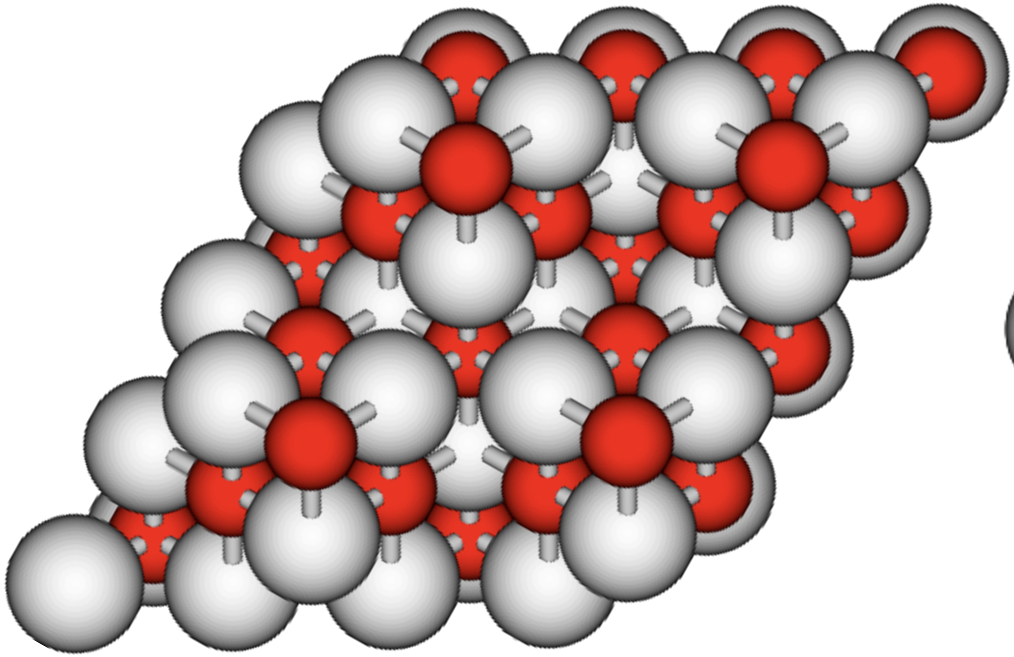


FIG. 1 (color online). Side view of the relaxed structures of 1, 3, and 4 ML LAO on STO(001) showing the polar distortion. The oxygen ions are marked by light grey spheres, while the Sr-, La-, Ti-, and Al-cations are shown by large green (grey), purple (dark grey) and small blue (dark grey) and orange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

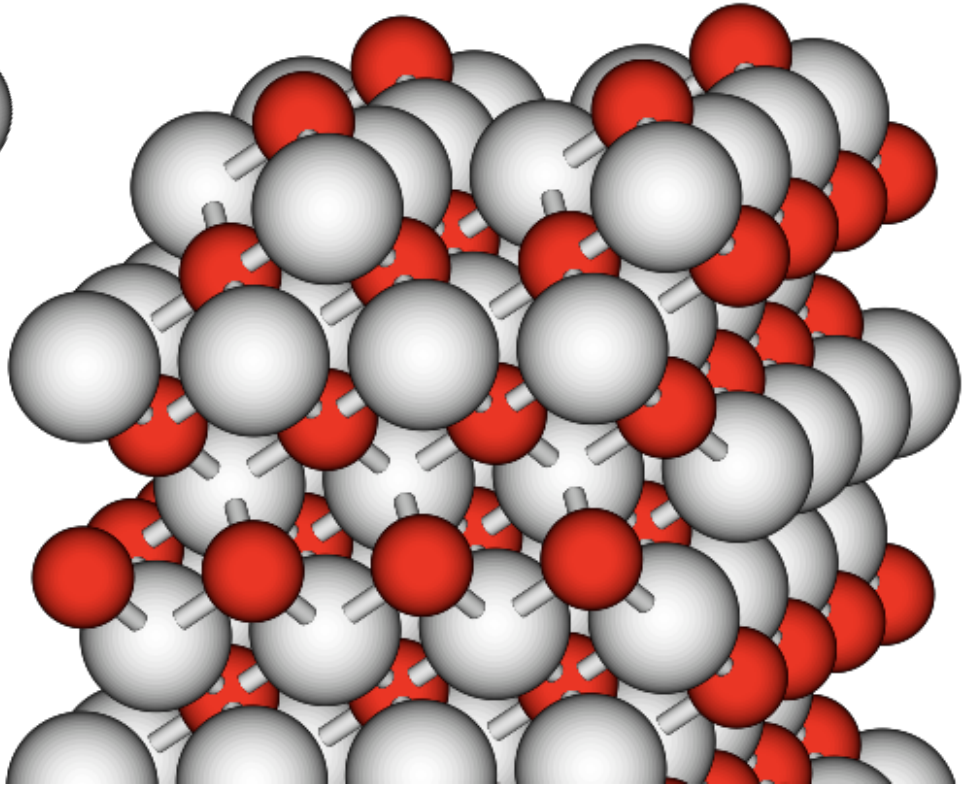
ad atom stabilization of Polar surfaces Important also for growth

- 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 Ba missing on the surface of BaFe2As2
- K+ ad ions on YBCO
- Use add large ions as surfactants during growth of polar surface systems

Octopolar reconstruction of MgO (111) slab



Top view

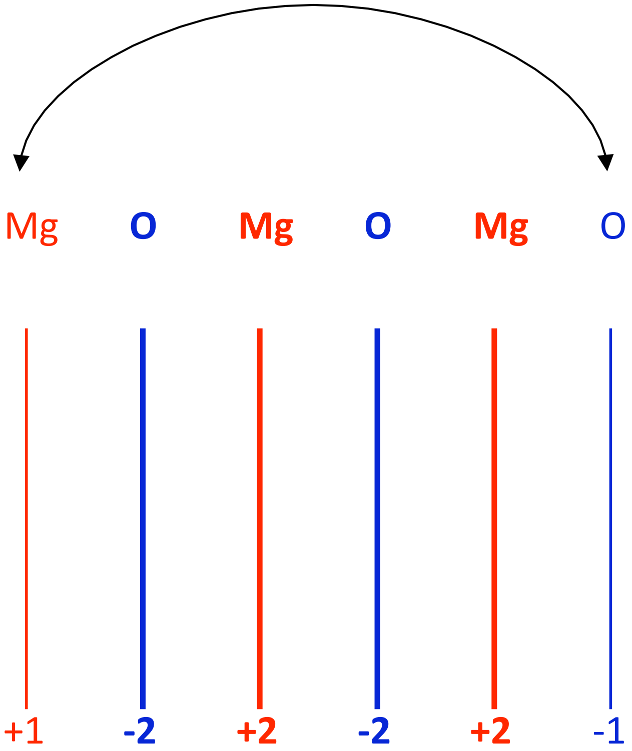


Side view

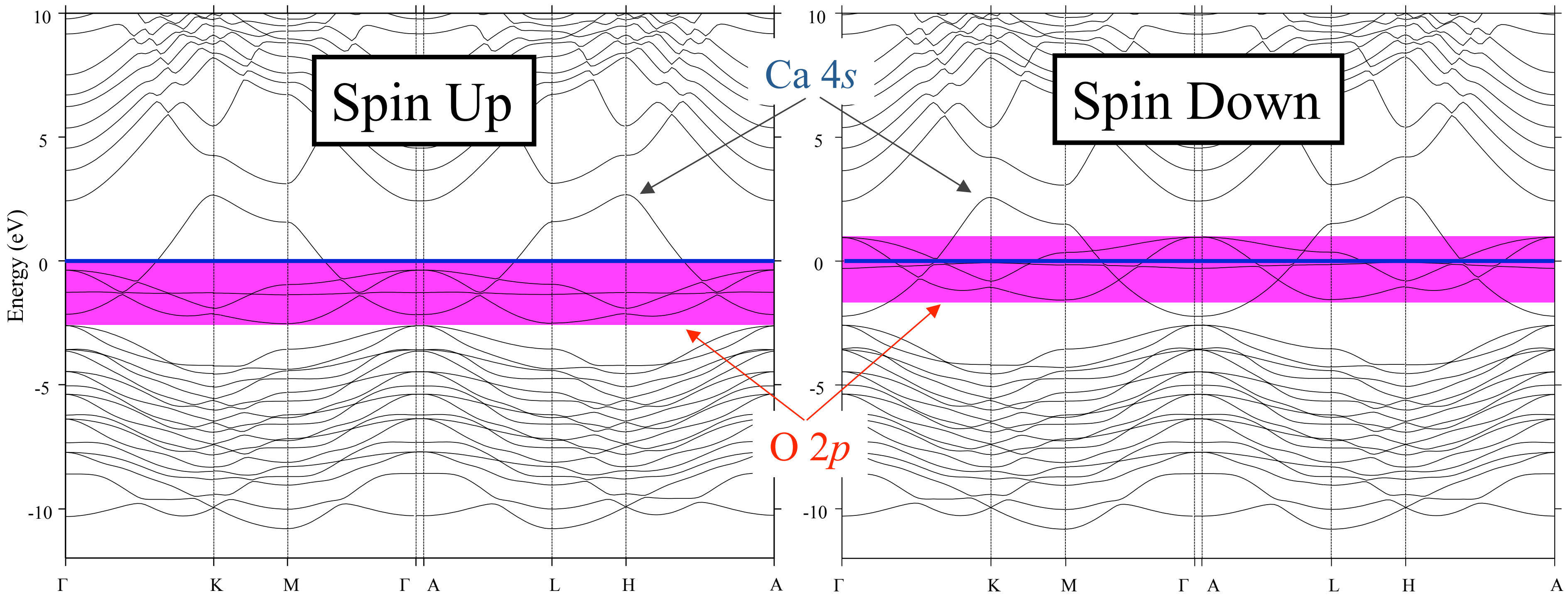
Effective surface layer charge = +2(3/4) -2(1/4) = +1

ELECTRONIC RECONSTRUCTION

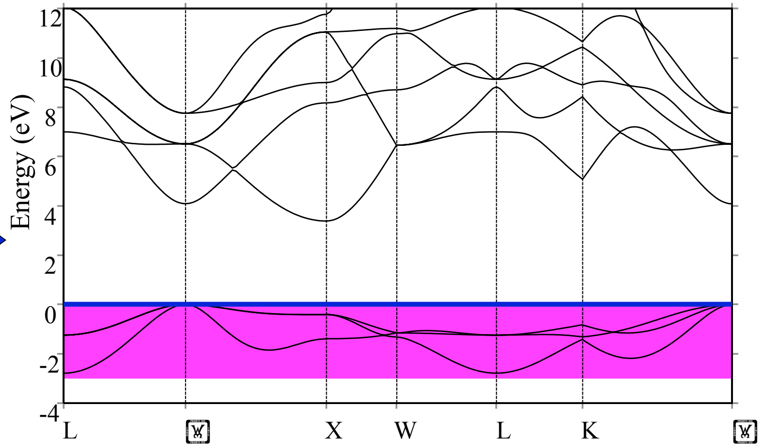
Transfer one electron from O layer to Mg layer



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



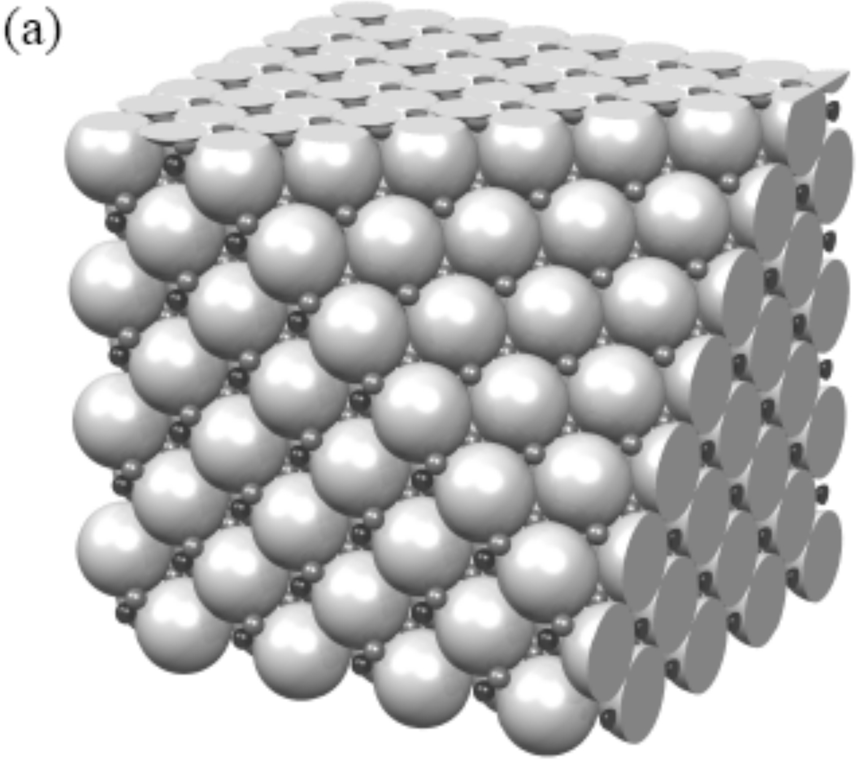
Note:
Bulk material
(no surface)
is an insulator

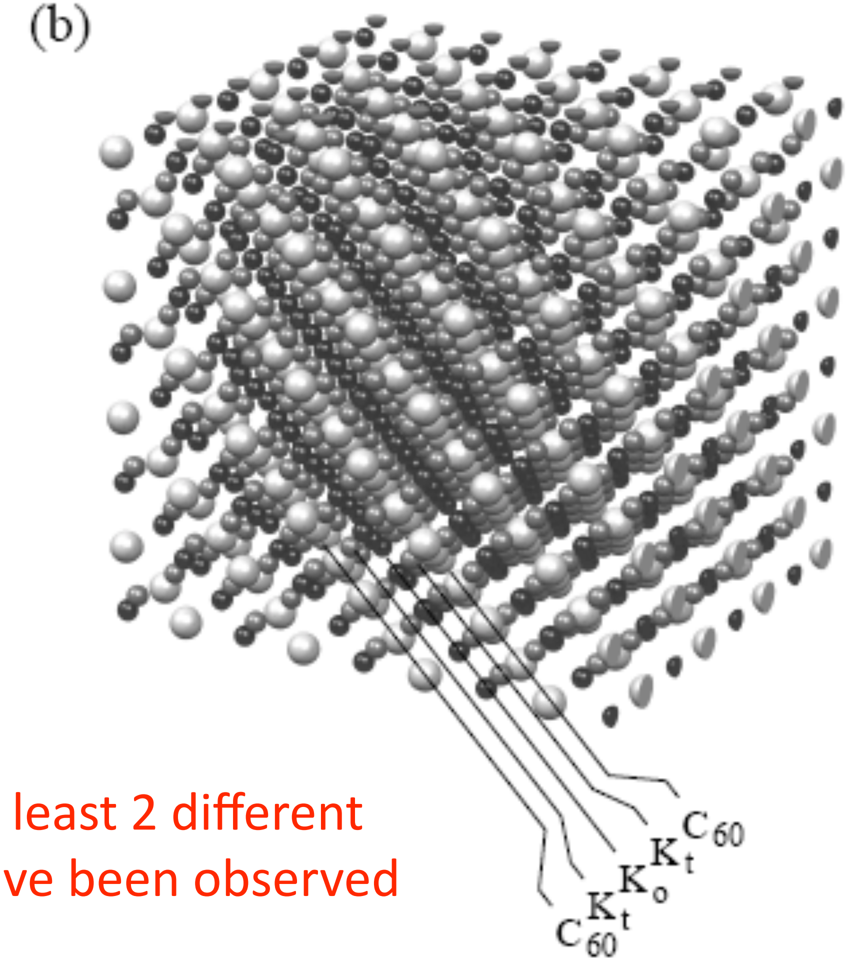


But surface is metallic! And ferromagnetic

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

111 surface of K3C60 and its polar nature.



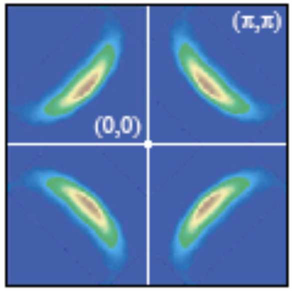


several terminations are possible and at least 2 different Photoemission spectra at the surface have been observed corresponding to C60 1.5-,2.5-

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

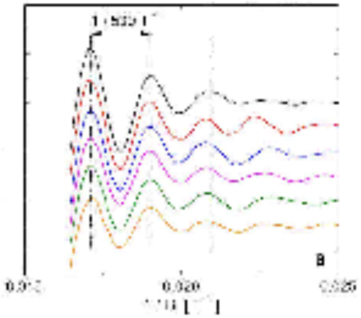
Fermiology across the Cuprate Phase Diagram

CCOC - x=0.12



ARPES – Shen (05)

YBCO - x=0.10

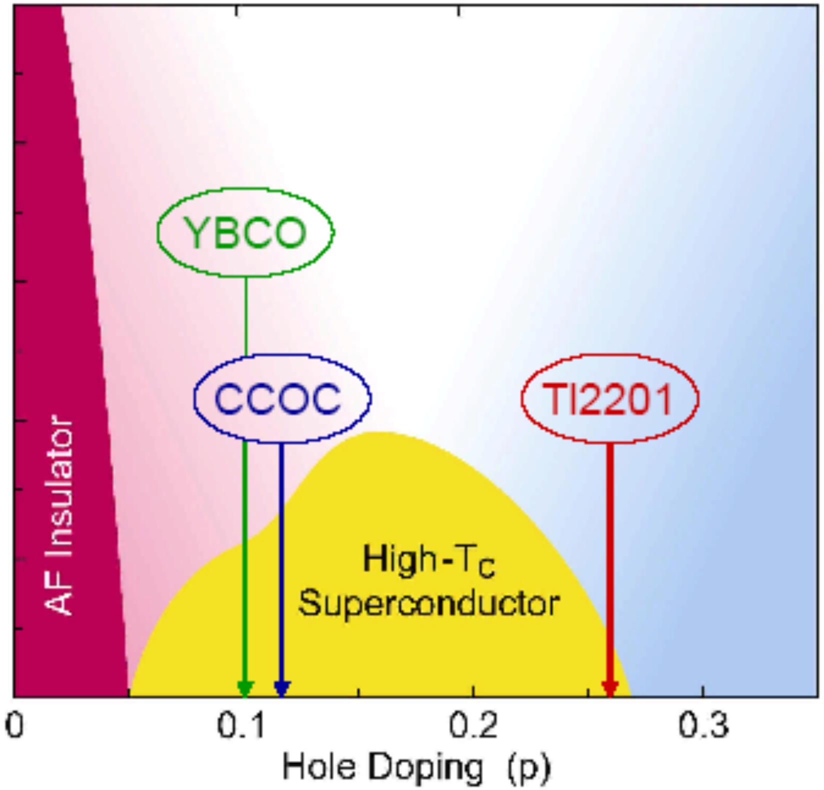


QO – Doiron-Leyraud (07)

ARPES on YBCO6.5

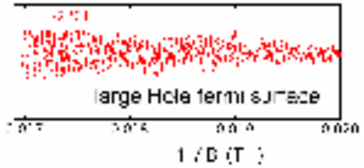
Overdoped Tl2201

Quantitative agreement between single-particle and transport probes

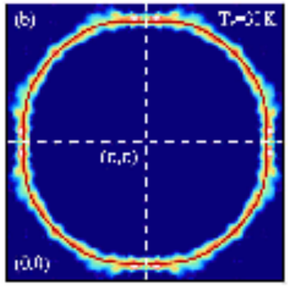


Can this be the gateway to a unified picture for underdoped cuprates?

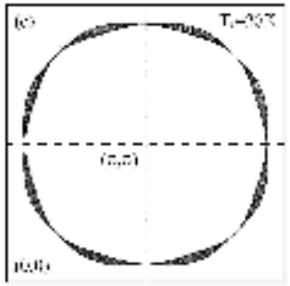
Tl2201 - x=0.26



dHvA – Vignolle (08)

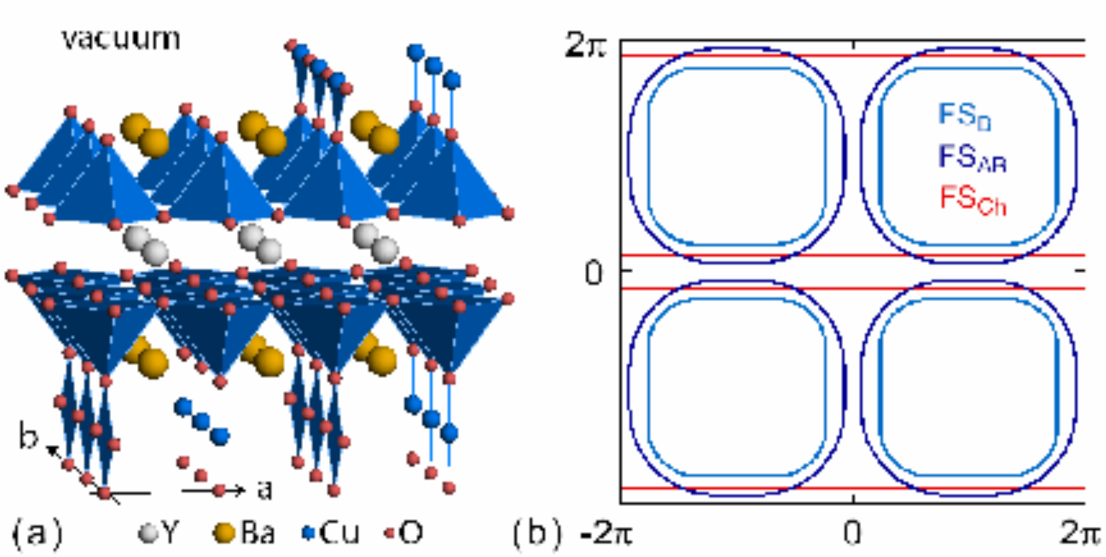


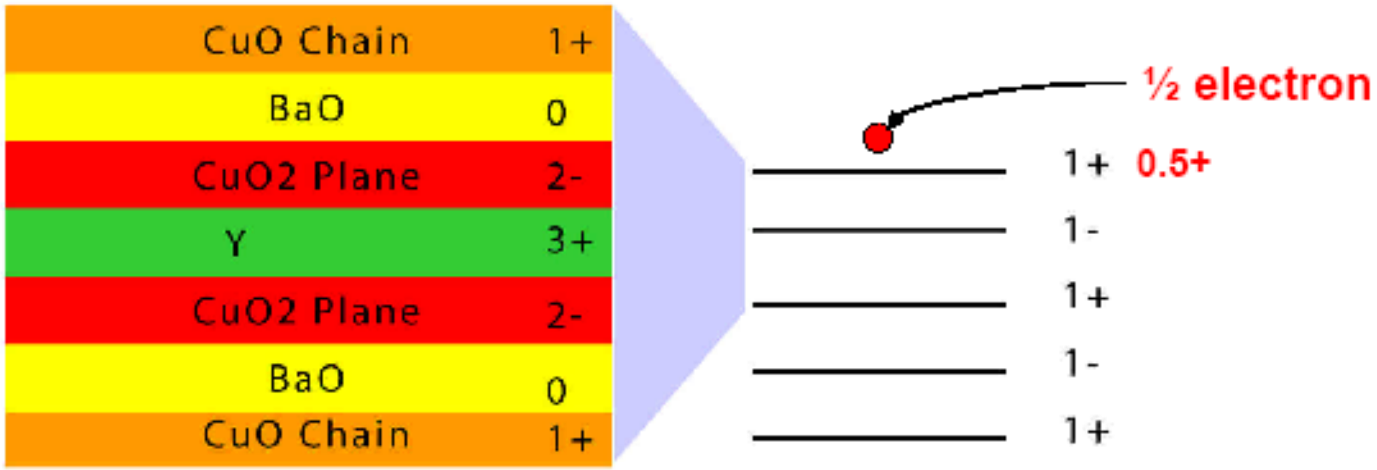
ARPES – Platé (05)



AMRO – Hussey (03)

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





CuO Chain	1+	
BaO	0	
CuO2 Plane	2-	
Y	3+	
CuO2 Plane	2-	
BaO	0	
CuO Chain	1+	

½ electron

1+ **0.5+**
1-
1+
1-
1+

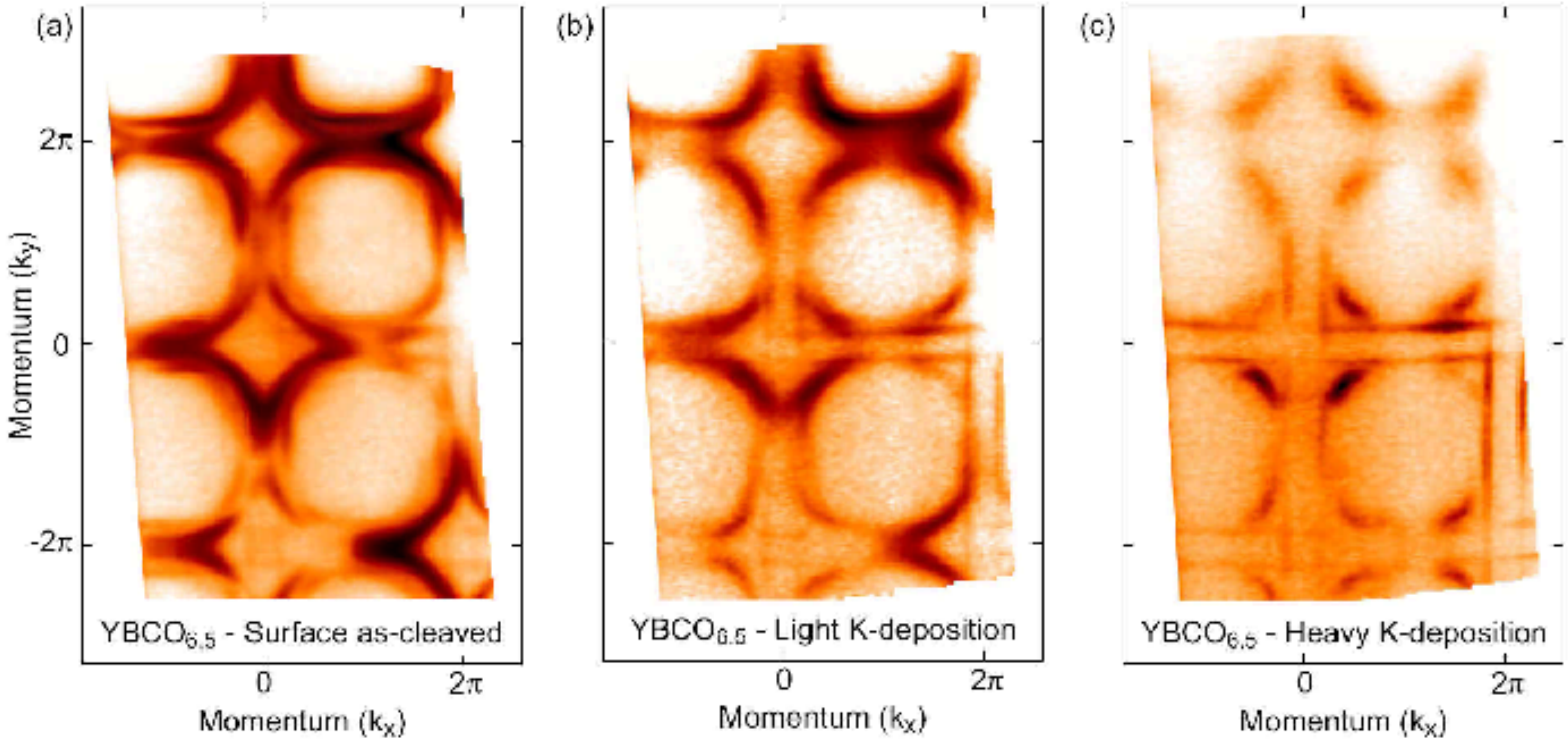
Hossain et al., Nature Physics 4, 527 (2008)

Our ARPES studies of Ortho-II YBCO6.5

Fresh

Surface Treatment 1

Surface Treatment 2



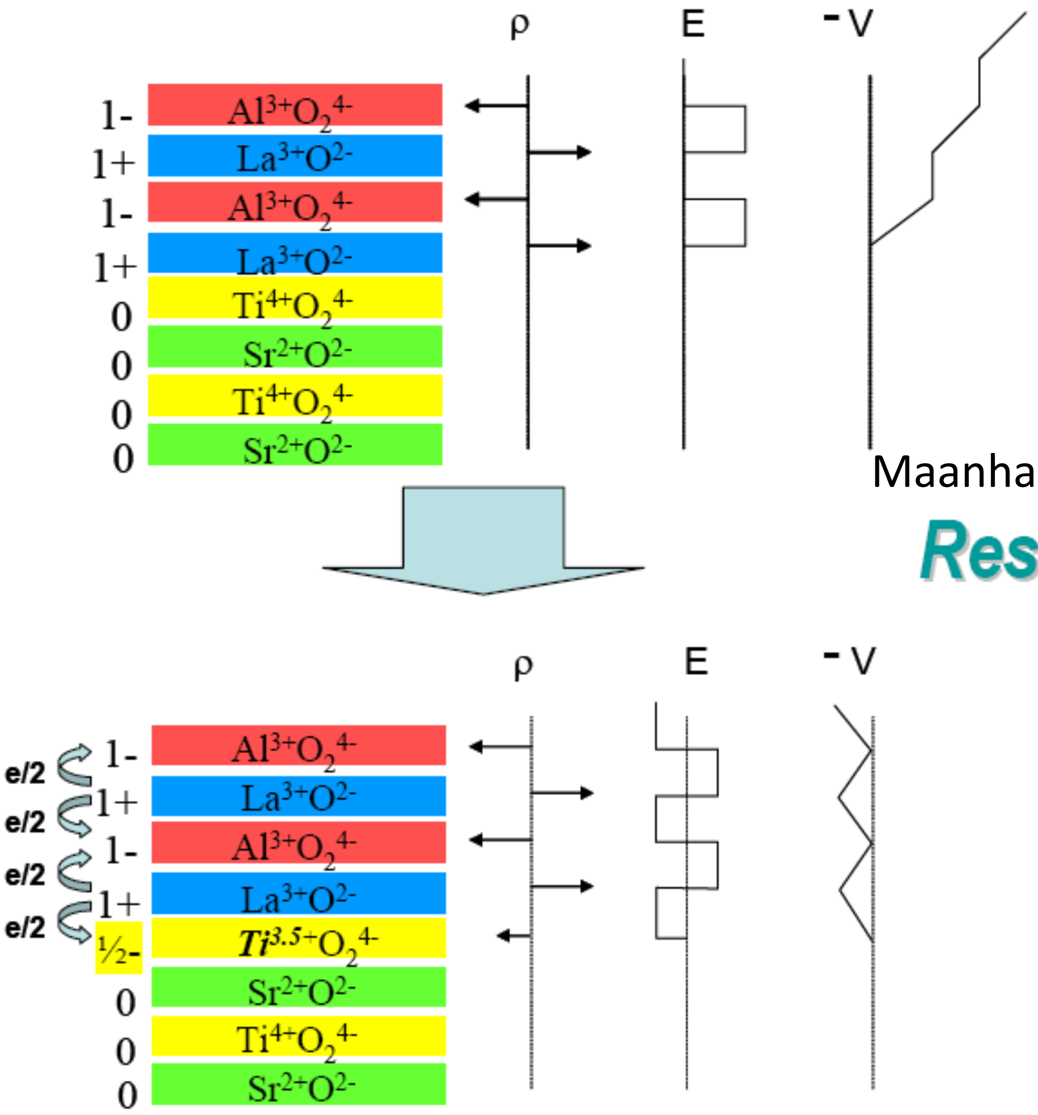
Electron doping

LDA → **Fermi arcs**

Electronic Reconstruction

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

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



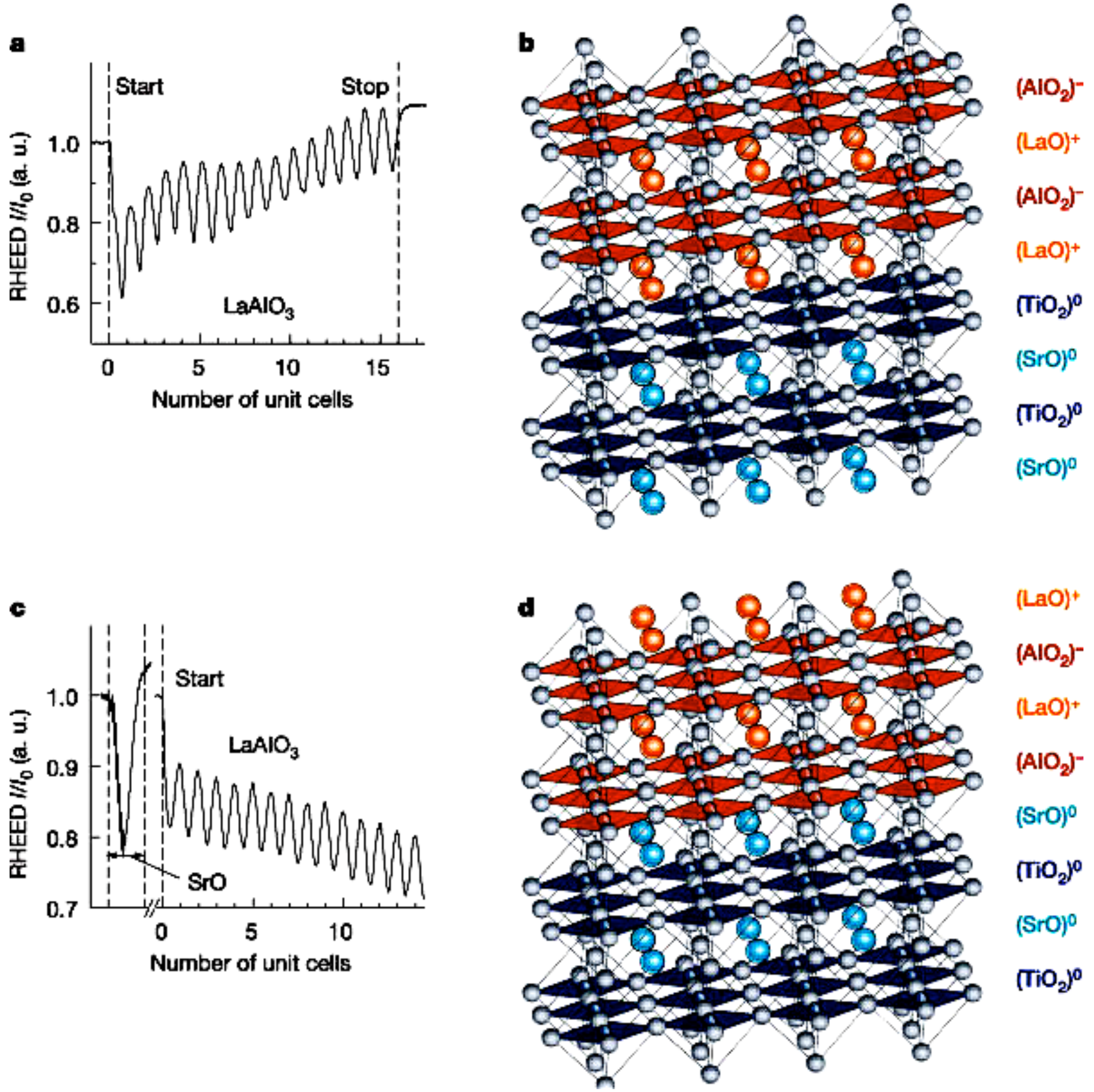
Maanhart et al MRS buletin review

Resp

electronic reconstruction –
metallic interface

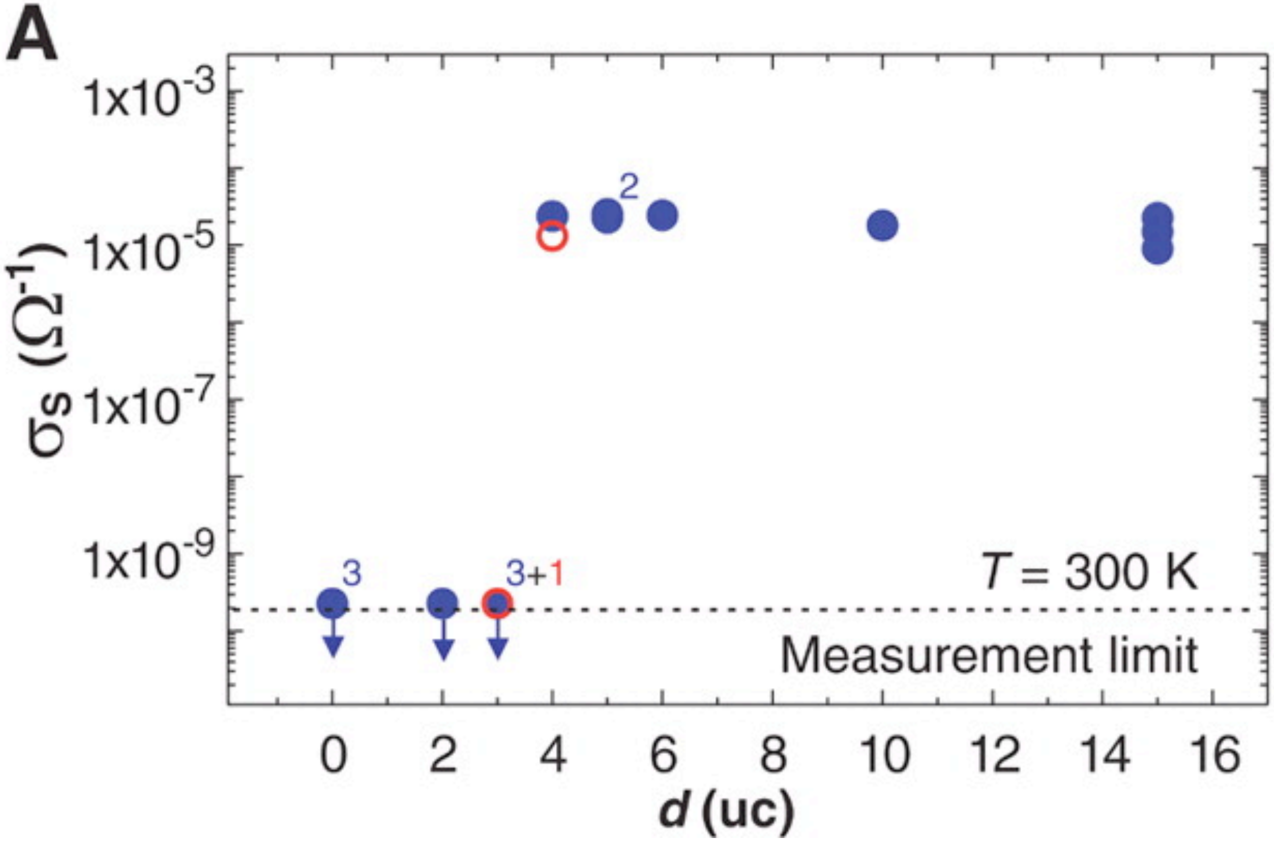
Ohtomo and Hwang Nature 427, 423, 2004

Metallic interface due to electronic reconstruction



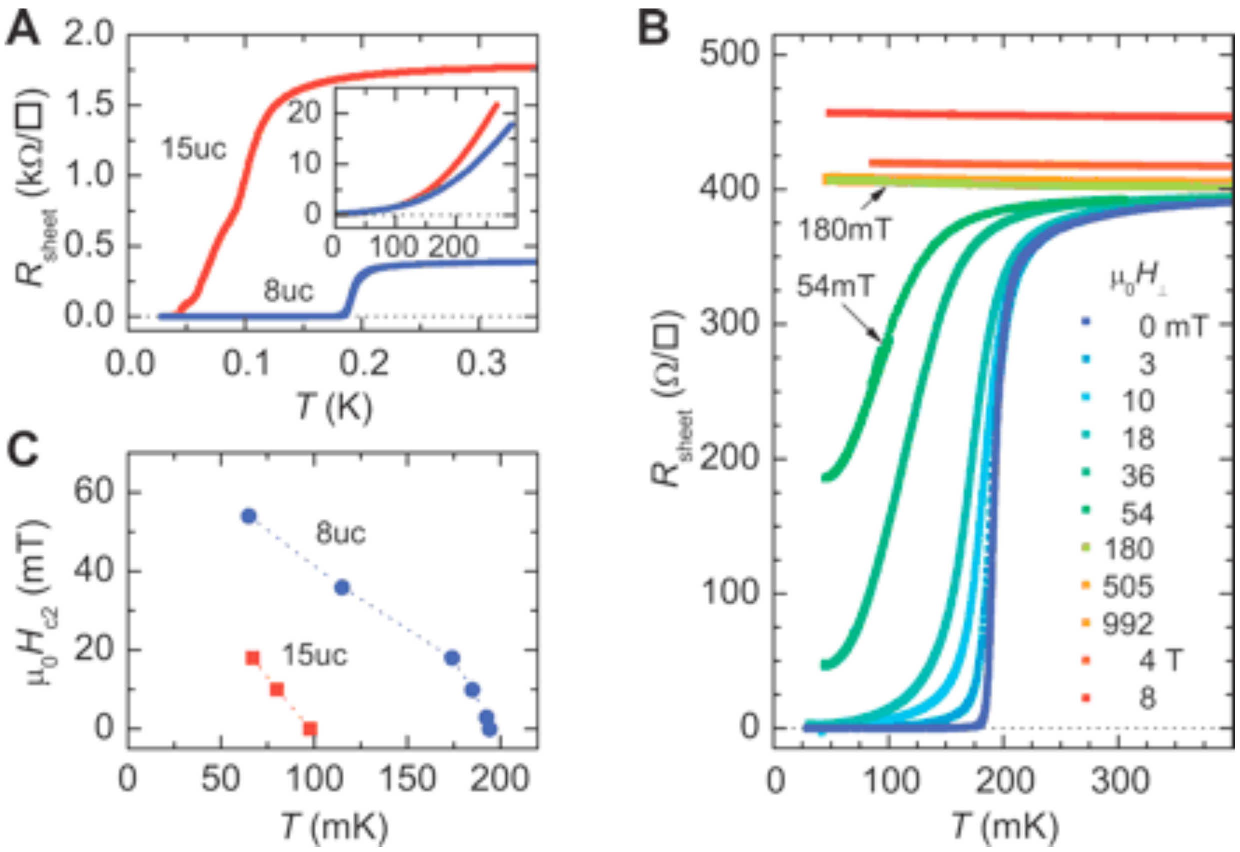
S.Thiel et al   Science 313, 1942 (2006)

Influence of the La AlO3 thickness on a SrTiO3 substrate on the conductivity



N.Reyren et al Science express 317, 1196 207

Superconducting interface SrTiO3/LaAlO3



Some key papers on polar surfaces and interfaces

- R. Lacman, Colloq. Int. CNRS 152, 195 (1965)
- The stability of ionic crystal surfaces
  P.W. Tasker, J. Phys. C 12, 4977 (1979)
- Reconstruction of NaCl surfaces
  D. Wolf, PRL 68, 3315 (1992)
- Adsorption on Ordered Surfaces of Ionic solids ed. H. J. Freund and E. Umbach, Springer Series in Surface Science, Springer, Berlin, 1993, vol. 33.
- Electronic reconstruction of polar surfaces in K_3C_{60}:
  R. Hesper et al., PRB 62, 16046 (2000)
- High mobility electron gas at $LaAlO_3$ /$SrTiO_3$ interface
  A. Ohtomo and H.Y. Hwang, Nature 427, 423 (2004)

Interfaces between narrow band semiconductors and metals may be very different from broad band semiconductors like Si or GaAs

Narrow band width ultra thin layers on Polarizable media

- correlated electron systems mostly have band widths of only 1-2 eV
- Molecular solids have very small band widths of 1eV or less

- Si,GaAs have band widths of 20-30 eV and behave very differently at interfaces

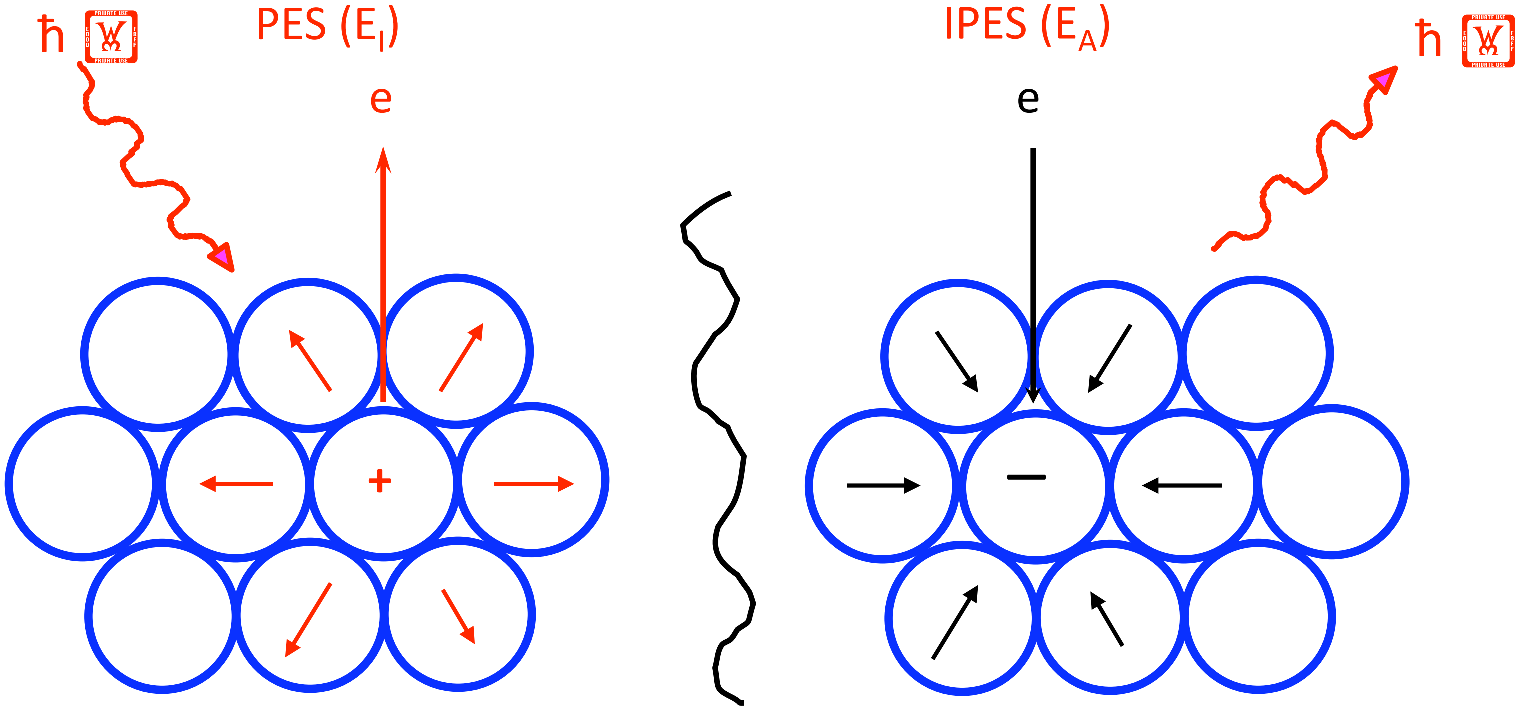
Definition of Conductivity Gap

$$E_{gap} = (E_{gr}^{N-1} - E_{gr}^{N}) + (E_{gr}^{N+1} - E_{gr}^{N})$$

$$= E_{gr}^{N-1} + E_{gr}^{N+1} - 2\,E_{gr}^{N}$$

E_{gr} > Ground state

A Picture of Solvation of ions in a polarizable medium



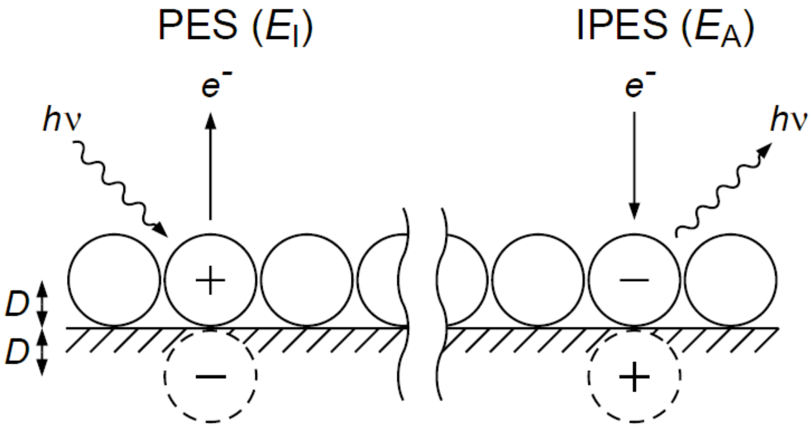
Full polarization can develop provided that Dynamic Response Time of the polarizable medium is faster than hopping time of the charge

□E (polarizability) > W ; □E □ MO energy splitting in molecules, plasma frequency in metals-----

Manipulating Material Properties

- magnetic : (super) exchange, T_C, T_N
- electrical : (super) conductivity, T_C, M-I-T
- optical : band gaps

How about using Image Charge Screening ?



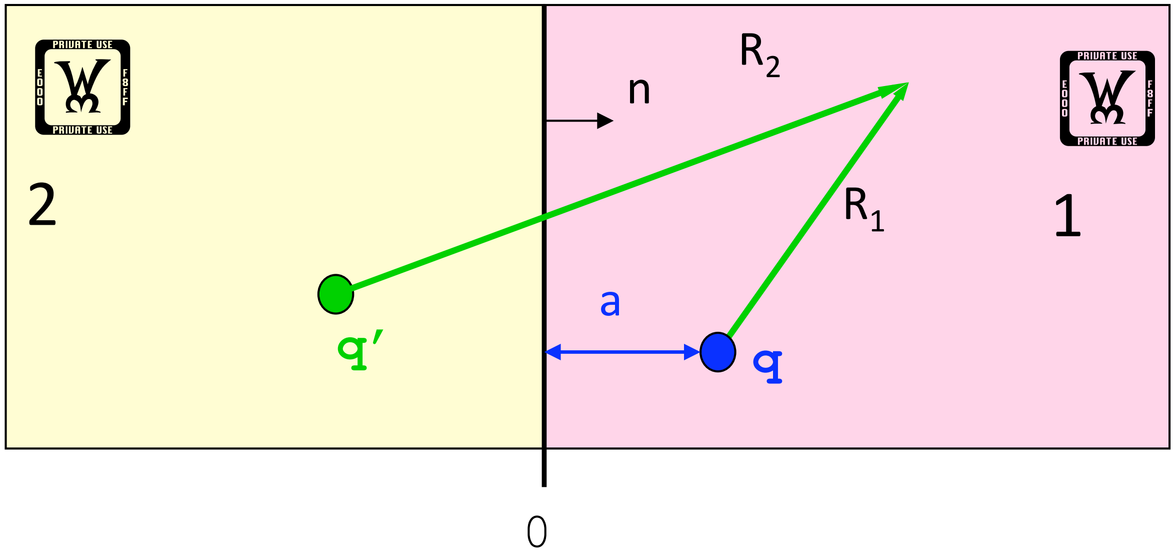
$$E_I = E_I^0 - \frac{1}{2}\frac{e^2}{2D}$$

$$E_A = E_A^0 + \frac{1}{2}\frac{e^2}{2D}$$

- Coulomb energy : $U = U_0 - \frac{e^2}{2D}$ $\quad J \propto \frac{t^2}{U}$
- Charge transfer energy : $\Delta = \Delta_0 - \frac{e^2}{2D}$ $\quad J \propto \frac{t^4}{\Delta^2 U}$
- Band gap : $E_g = E_g^0 - \frac{e^2}{2D}$

Potential of a point charge in the neighbourhood of a dielectric

Macroscopic continuum - uniform



$$(D_1 - D_2)\bullet n = 4\pi\sigma$$
$$(E_1 - E_2)\times n = 0$$

- *surface charge*

$$\varepsilon_1 \nabla \bullet E = 4\pi \cdot l \quad z > 0$$
$$\varepsilon_2 \nabla \bullet E = 0 \quad z < 0$$
$$\nabla \times E = 0$$

$$\phi = \frac{1}{\varepsilon_1}\left(\frac{q}{R_1} + \frac{q'}{R_2}\right) \qquad q' = -\frac{(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_2 + \varepsilon_1)} q$$

Energy to create a charge q at a :

$$E = -\int_o^Q \frac{1}{\varepsilon_1 2a}\left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1}\right) q\,dq = \frac{Q^2}{4\varepsilon_1 a}\left[\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right]$$

Note that image charge screening goes as Q squared!!!

Cannot be treated as a change in single particle potential   ELECTRONIC POLARONS

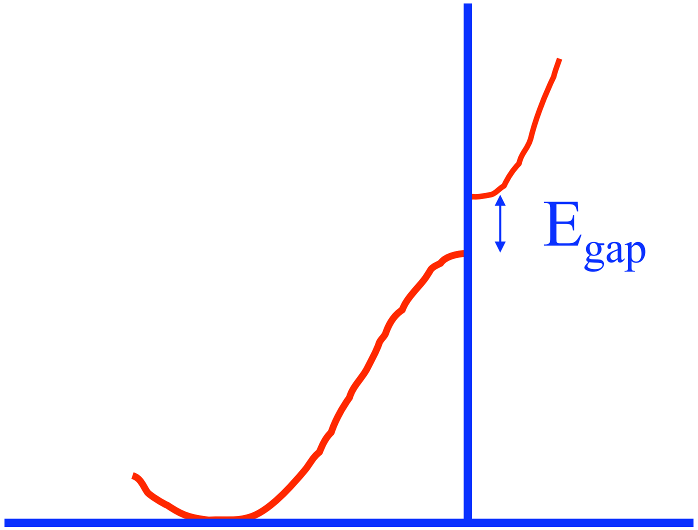
The energies of electrons (cond. Band) and holes (valence band) are both lowered

Therefore conductivity gap is lowered

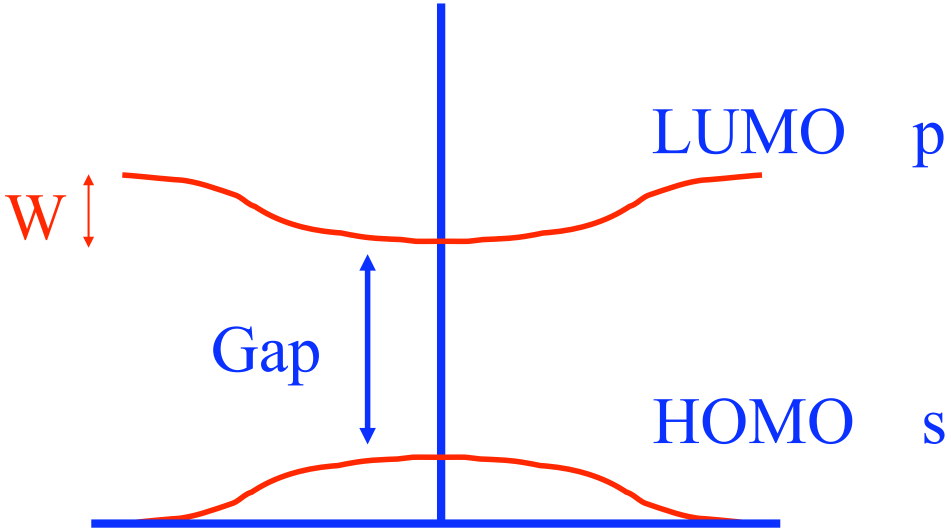
Both electrons and holes will want to move to the interface

Frenkel like exciton states are not affected to lowest order

Si, Ge

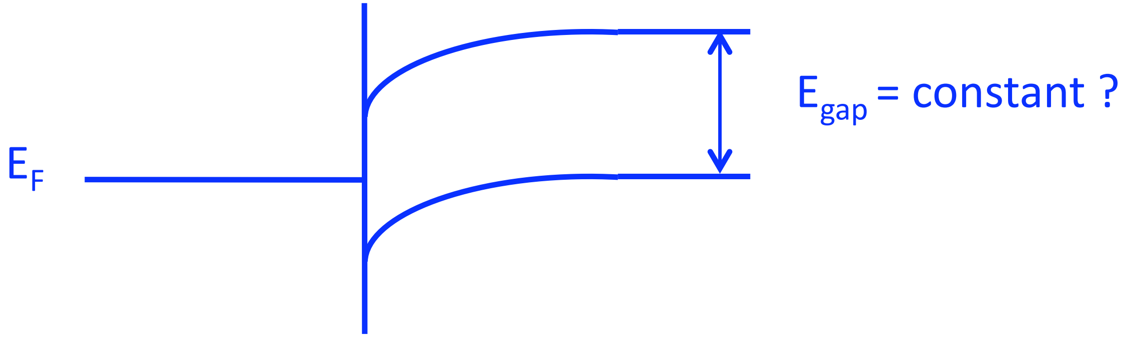


Molecular

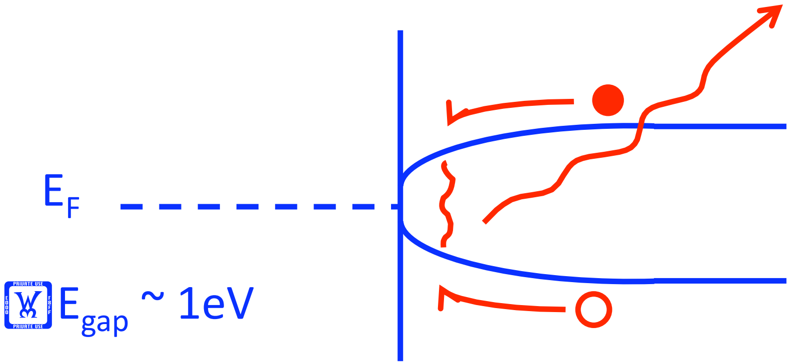


	Molecules	Si, Ge, GaAs
Band width	~ 0.5 eV	>10 eV
Exciton B.E.	~ 1 eV	~20 meV
Polarons	ħ □$_0$ ~ W (□ ~ >1)	—
Electr. – Electr.	U□W	U<<W
Magnetism	Yes (T-S~0.5eV)	No
Cond. Gap	E_{gap} □ W	E_{gap} << W

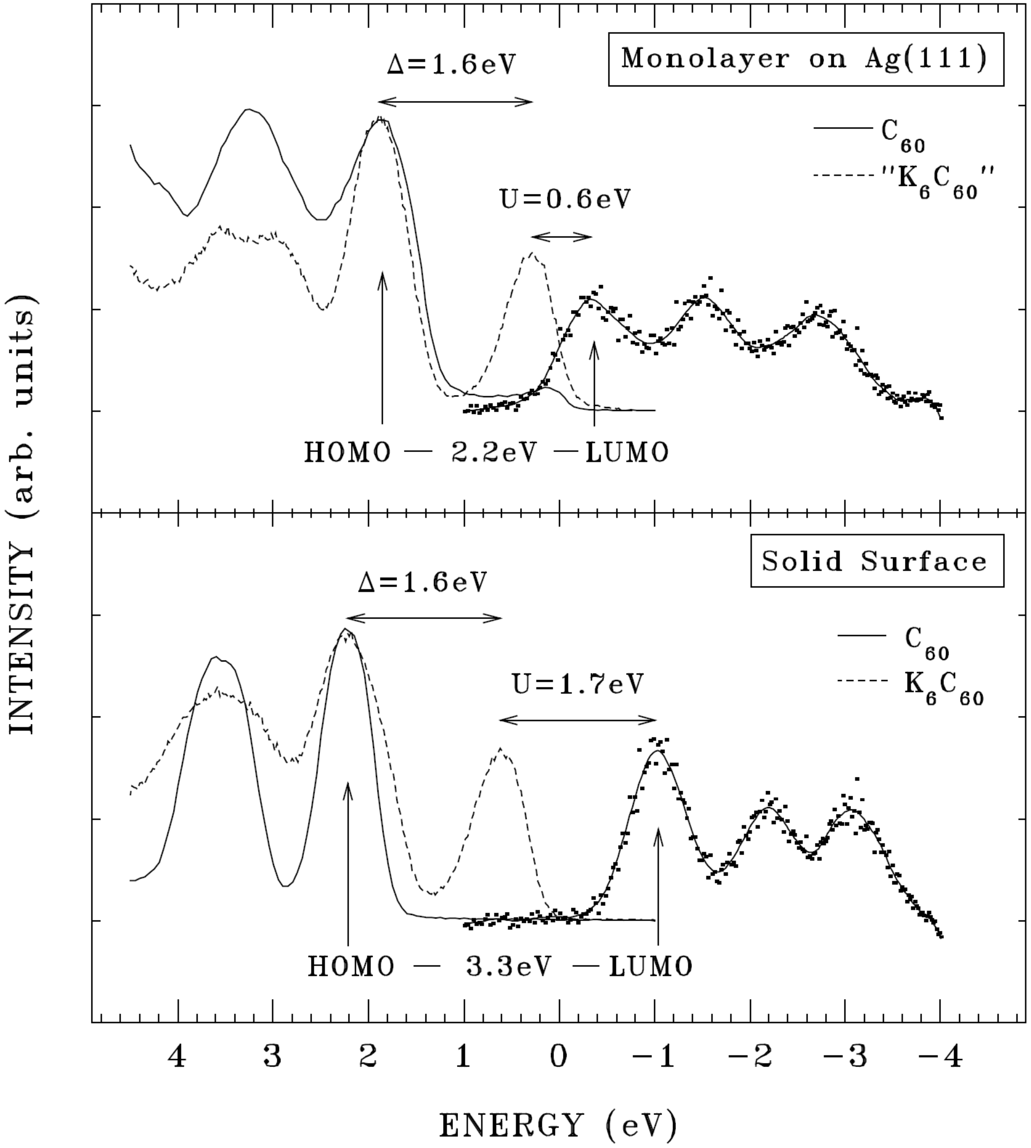
Conventional wide band semiconductor –metal interface



Narrow band semiconductor –metal interface in which
The polarization cloud can follow the electron yielding
“ELECTRONIC POLARON’’



Examples are molecular solids , strongly correlated systems , TM, RE-----



Combined photoemission (solid lines) and inverse photoemission (dots with solid lines as guide to the eye) spectra of the C_{60} monolayer on Ag(111) (upper panel) and the surface layer of solid C_{60} (lower panel). Also included are the photoemission spectra (dashed lines) of the fully doped C_{60} ("K_6C_{60}") monolayer on Ag(111) and the surface layer of solid K_6C_{60}.

**R. Hesper, et al Strongly reduced band gap in a correlated insulator in close proximity to a metal
Europhysics Letters 40, (1997) 177-182.**

- Band gap is reduced !
- Molecular Orbital Structure is conserved !

S. Altieri, et al. Reduction of Coulomb and charge transfer energies in oxide films on metals Phys. Rev. B59 (1999) R2517-2520.

polarizability in TM compounds is very non uniform

The dielectric constant is a function of r,r’,w and not only r-r’,w and so Is a function of q,q’,w

Strong local field corrections for short range interactions

Meinders et al PRB 52, 2484 (1995)
Van den Brink et al PRL 75, 4658 (1995)

arXiv:0808.1390 Heavy anion solvation of polarity fluctuations in Pnictides
G.A. Sawatzky, I.S. Elfimov, J. van den Brink, J. Zaanen

arXiv:08110214v Electronic polarons and bipolarons in Fe-based superconductors
Mona Berciu, Ilya Elfimov and George A. Sawatzky

Homogeneous Maxwell Equations

□(r,r') —> □(r – r') —> □(q)

Ok if polarizability is uniform

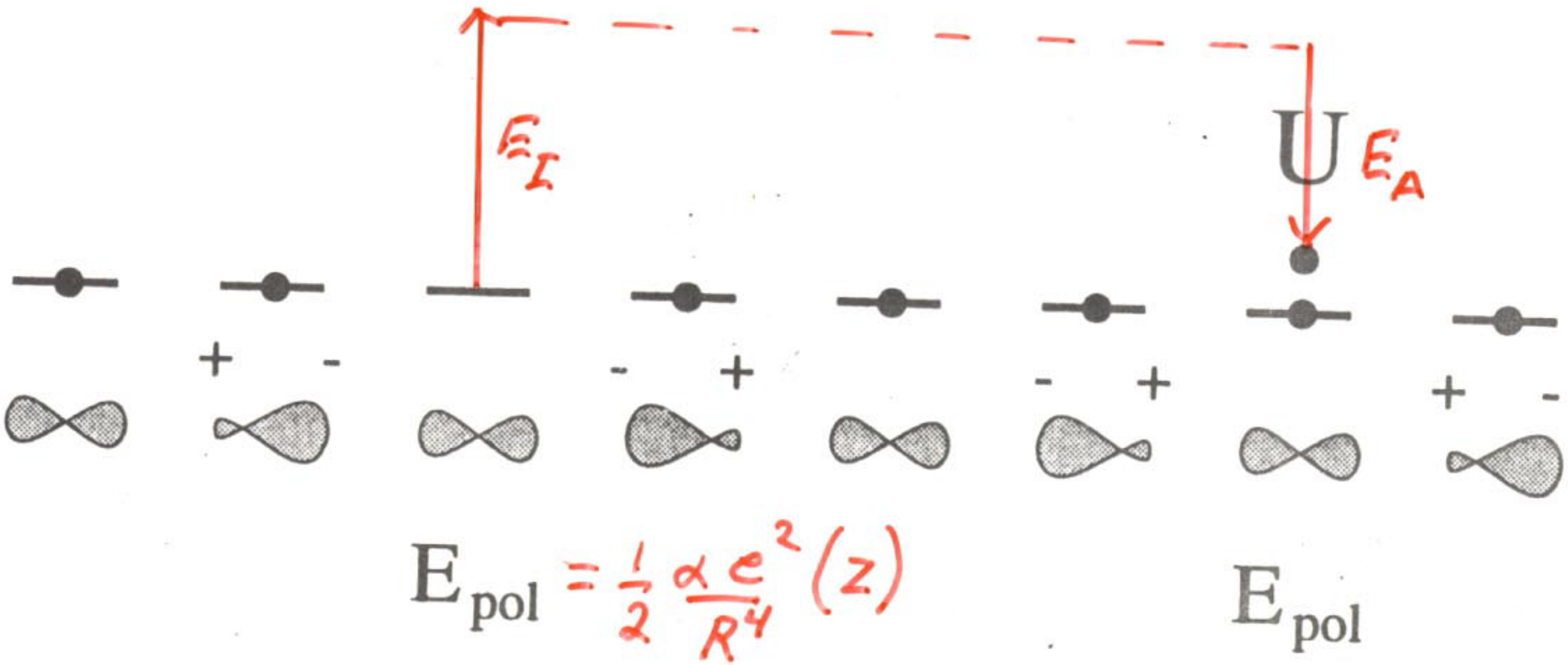
$$V(q) = \frac{V^0(q)}{\varepsilon(q)}$$

In most correlated electron systems and molecular solids the polarizability is actually Very NONUNIFORM

Effective Hamiltonians can be misleading

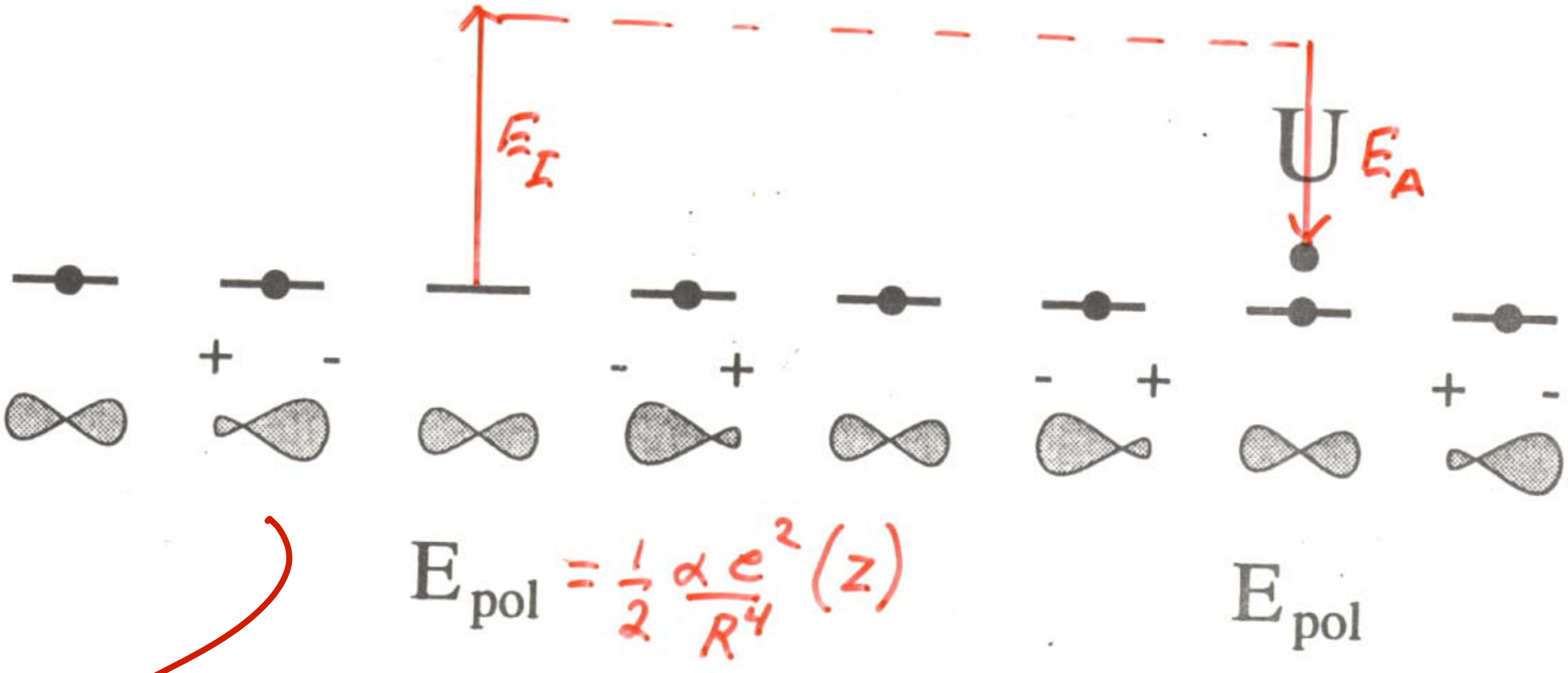
- Hubbard like models are based on the assumption that longer range coulomb interactions are screened and the short range on site interactions remain
- However U for the atom is about 20 eV but U as measured in the solid is only of order 5 eV and for the pnictides even less than this
- HOW IS THIS POSSIBLE?

Reduction of onsite interactions and changing the nearest neighbor interactions with polarizable ions in a lattice



We assume that the hole and electron move slowly compared to the response time of the polarizability of the atoms.

Note the oppositely polarized atoms next to the hole and extra electron



$$\vec{P}_i = \sum_{\sigma} (n_{\sigma i+1} - n_{\sigma i-1}) \alpha \frac{e}{R^2}$$

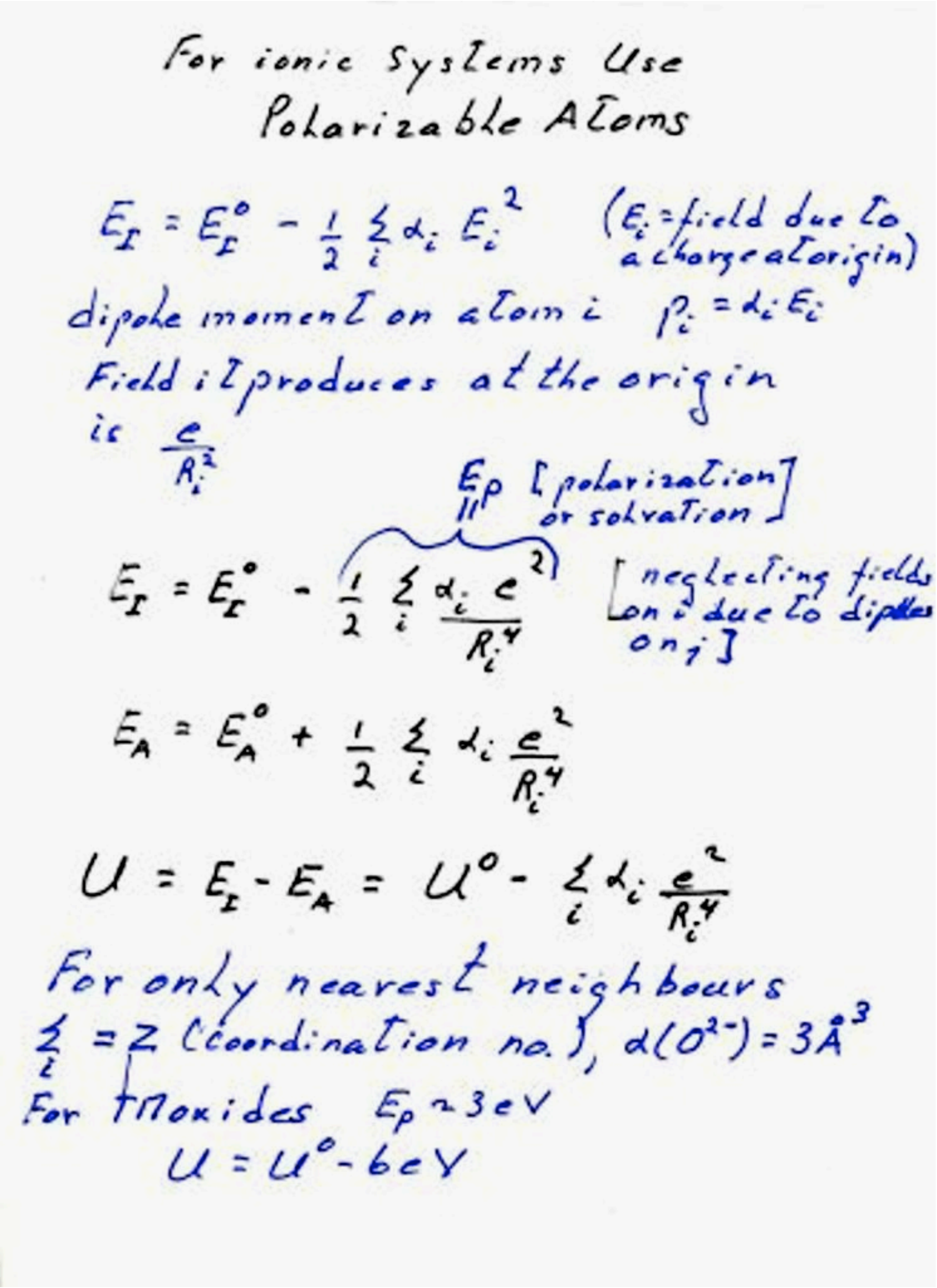
$$E_{pol}(i) = -(\vec{P}_{i-1} + \vec{P}_{i+1}) \frac{e}{R^2}$$

Will be a net repulsion between n_i and $n_{i\pm2}$ so the field on $i\pm1 \neq 0$

$$H_{\text{int}} = (U - 2zP)\sum_{i} n_{i\uparrow} n_{i\downarrow} + 2P \sum_{l,i} n_l n_{l+2a_i}$$

So the reduction of the Hubbard U in a polarizable medium like this introduces a strong
Next nn repulsive interaction. This changes our model!!

For a different geometry actually the intersite
interaction can also be strongly reduced perhaps even
Attractive (Fe Pnictides)



For ionic Systems Use
Polarizable Atoms

$$E_I = E_I^0 - \frac{1}{2}\sum_i \alpha_i E_i^2$$ (E_i = field due to a charge at origin)

dipole moment on atom i $p_i = \alpha_i E_i$

Field it produces at the origin is $\frac{e}{R_i^2}$

$$E_I = E_I^0 - \overbrace{\frac{1}{2}\sum_i \alpha_i \frac{e^2}{R_i^4}}^{E_p \text{ [polarization or solvation]}}$$ [neglecting fields on i due to dipoles on j]

$$E_A = E_A^0 + \frac{1}{2}\sum_i \alpha_i \frac{e^2}{R_i^4}$$

$$U = E_I - E_A = U^0 - \sum_i \alpha_i \frac{e^2}{R_i^4}$$

For only nearest neighbours

$\sum_i = Z$ (coordination no.), $\alpha(O^{2-}) = 3\,Å^3$

For TM oxides $E_p \approx 3\,\mathrm{eV}$

$U = U^0 - 6\,\mathrm{eV}$

Rest comes from bond
Polarization involving
O 2p and TM 4s states

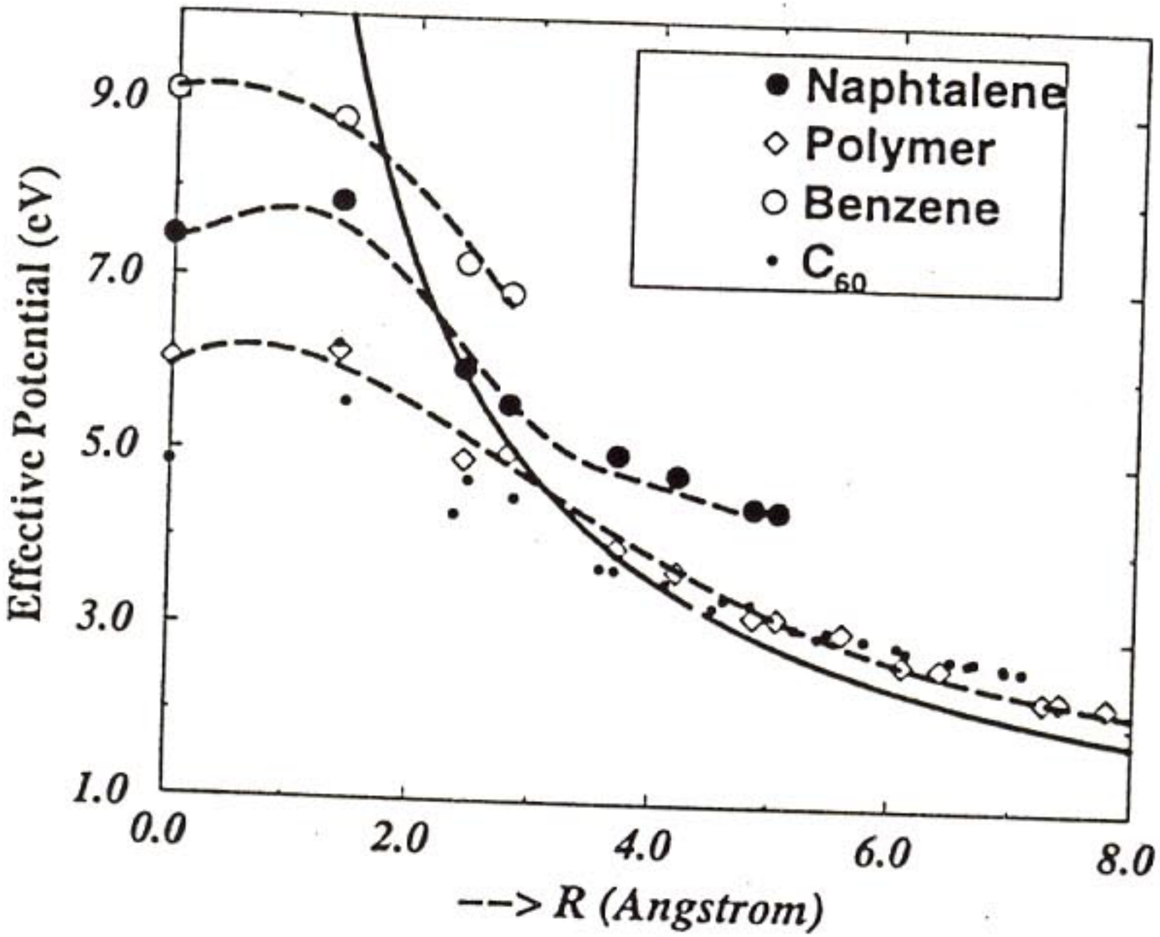


FIG. 5. The effective Coulomb interaction on different organic molecules. The carbon polarizability is 0.56 Å^3. The full line represents the bare Coulomb repulsion. The dashed lines are guides for the eye.

Note short range interactions are reduced “ screened ” and intermediate range interactions are enhanced or antiscreened-quite opposite to conventional wisdom in solid state physics

Jeroen van den Brink Thesis U of Groningen 1997

Using non uniform polarizability in artificially engineered structures?

Use an FeAs layer as in LaFeAsO as an example

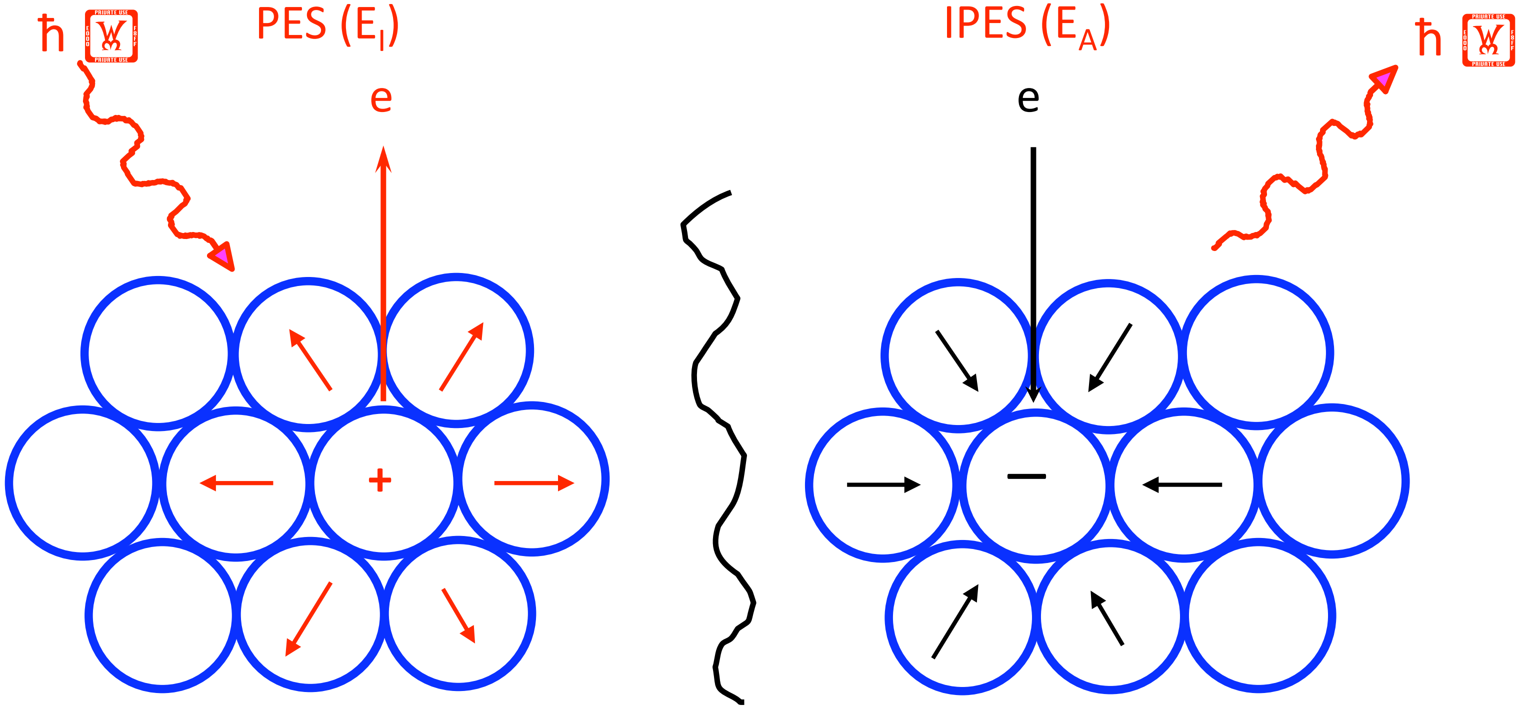
Now to compounds

- In TM compounds the TM is weakly polarizable while the anions are strongly polarizable
- The charge motion is usually on the cation i.e TM ion.
- So the polarizable entities are not the ones on which the mobile charge resides.
- As for ions in polar solvents

I will show that

- The polarizability of anions results in a strong reduction of the Hubbard on site U
- The charged carriers living on transition metal ions are dressed by virtual electron hole excitations on the anions resulting in electronic polarons
- The nearest neighbor coulomb interactions can be either screened or antiscreened depending on the details of the structure

A Picture of Solvation of ions in a polarizable medium



Full polarization can develop provided that Dynamic Response Time of the polarizable medium is faster than hopping time of the charge

□E (polarizability) > W ; □E □ MO energy splitting in molecules, plasma frequency in metals-----

We are alive because of Solvation

Ions both positive and negative in our bodies regulate most everything

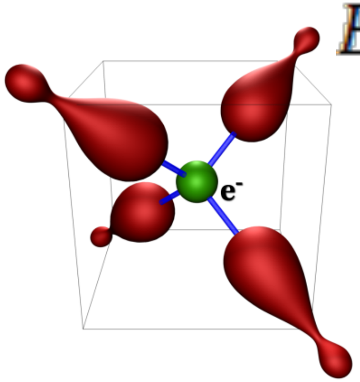
Reduction of U due to polarizability of O2- (SOLVATION)

$$U = E_I^{TM} - E_A^{TM} \;\; -2Epol$$

E_I	ionization energy
E_A	electron affinity energy

$Epol=\frac{1}{2}\sum_i \sum$

$$E_I = E_I^0 - \sum_i \frac{1}{2}\alpha_i F_i^2 \qquad E_A = E_A^0 + \sum_i \frac{1}{2}\alpha_i F_i^2$$



ELECTONIC POLARON

$$Epol = 2\sum_i \frac{1}{2}\alpha_i F_i^2$$

For 6 nn of O2- ~ 13eV

For 4 nn As3- ~17eV

What about intersite interaction V?

$$V = V_0 - \frac{1}{2} \sum_{common} \alpha[(\mathbf{E}_1 + \mathbf{E}_2)^2 - E_1^2 - E_2^2],$$

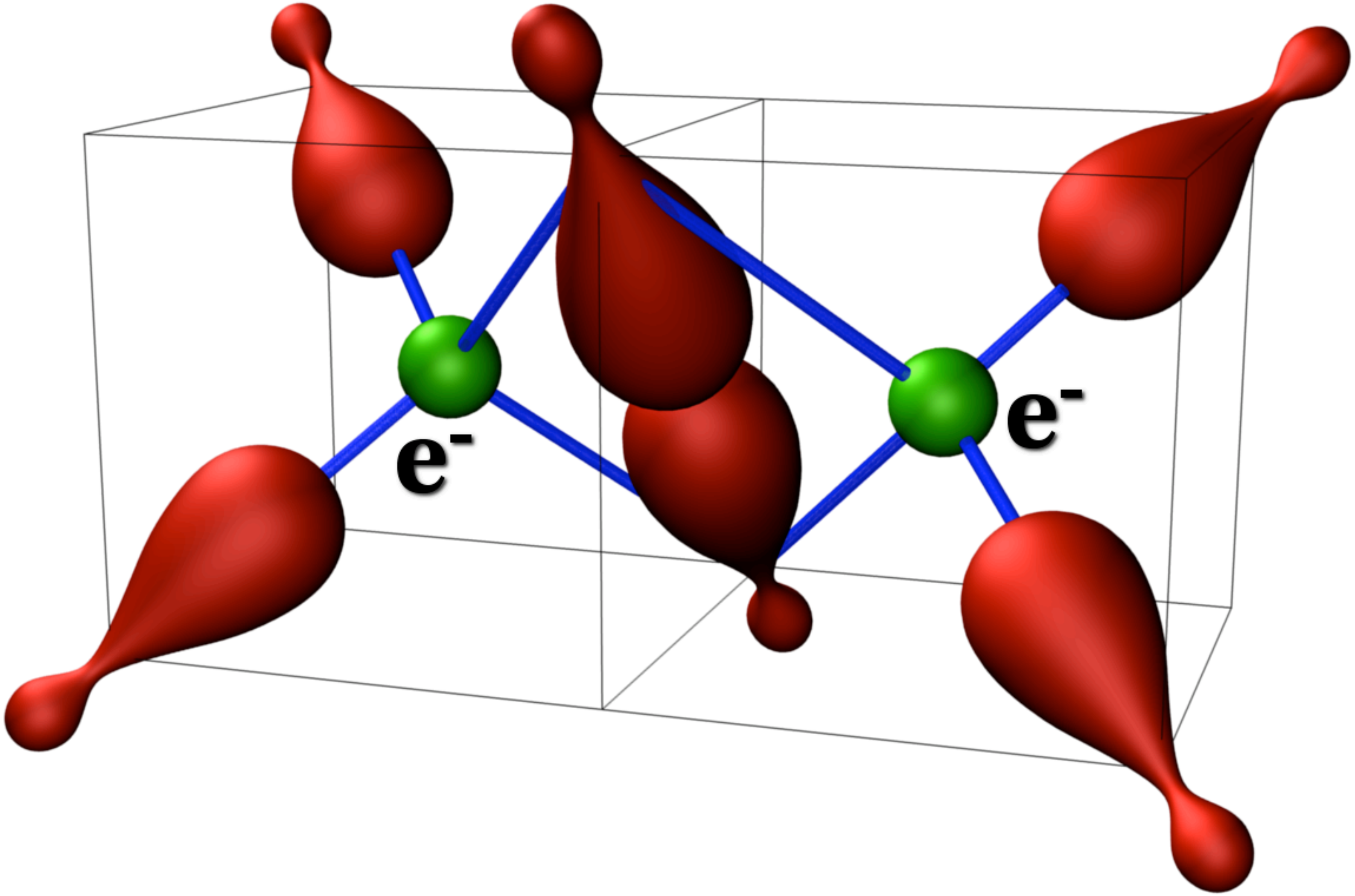
vhich reduces to $V = V_0 - \boxed{2\alpha \mathbf{E}_1 \cdot \mathbf{E}_2}$, where 2 ref

Can be repulsive or attractive depending on bond angle

For pnictides the Fe-As-Fe nn bond angle is ~70 degrees

Therefore the contribution to V is attractive ~4 eV

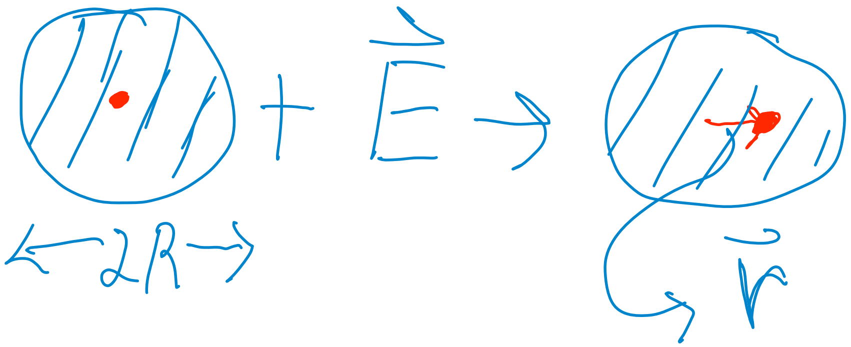
Polarization cloud For Two charges on Neighboring Fe “ELECTRONIC BIPOLARON



Rough estimate

Atomic or ionic polarizability ~volume

- Consider atom = nucleus at the center of a uniformly charge sphere of electrons
- In a field E a dipole moment is induced P=αE



$e\vec{E} = \vec{F}$ at eq.

$$F = e^2\left(\frac{r^3}{R^3}\right)\left(\frac{\vec{r}}{r^3}\right)$$

- For Z = 1 and 1 electron restoring force = $(e^2/R^3)\,\vec{r}$

$$= f$$

$$\vec{p} = -e\vec{r} = \frac{e^2}{f}E = \alpha E \qquad \alpha = R^3$$

$$r = \frac{eE}{f}$$

Whats the importance of As or P?

- Very large anions
- Electronic polarizabilities roughly equal to volume

$\alpha(P^{3-}) \simeq 6-8\ \text{Å}^3 \quad \alpha(As^{3-}) \simeq 10-12\ \text{Å}^3$

$\alpha(O^{2-}) \simeq 1-3\ \text{Å}^3$

- 4p orbitals have 2 radial nodes –very diffuse
- Weak hybridization with highly directed local Fe 3d orbitals (from band theory)
- Large polarizability strongly reduces U on Fe and the nearest neighbor interaction V between Fe 3d

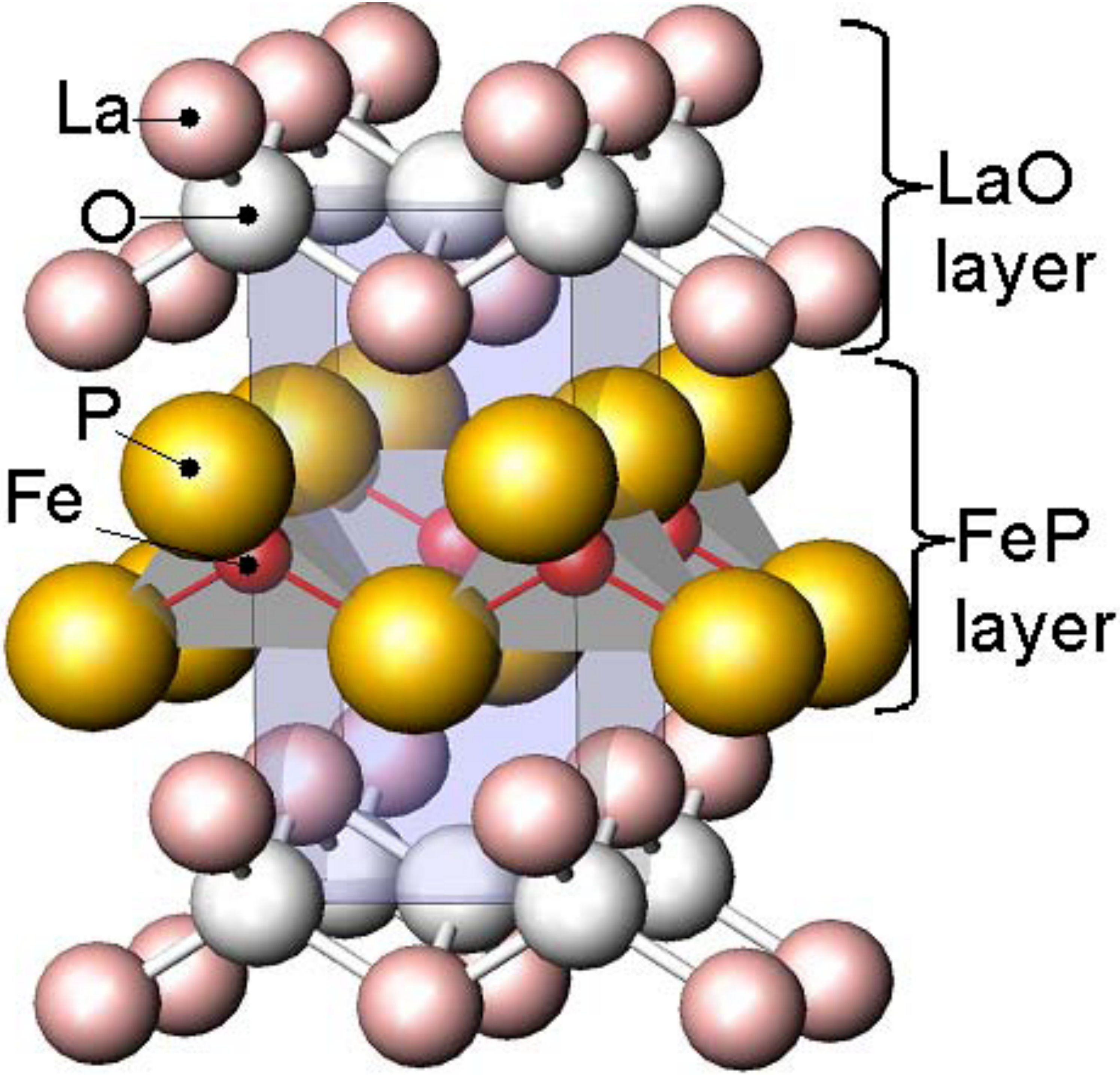
Comparison of Cuprates and Pnictides
The role of polarizable heavy anions

George Sawatzky
Physics and astronomy dept.
UBC Vancouver BC Canada

Some earlier papers on polarizabiiity
Meinders et al PRB 52, 2484 (1995)
Van den Brink et al PRL 75, 4658 (1995)
J. van den Brink et al Europhysics Letters 50, 447 (2000)

Are Cuprates and Pnictides really similar?

Cuprates	**Fe Pnictides**
Local moments S=1/2	Small variable amplitude SDW
Large crystal field > d band dispersion	Small crystal fields < Fe d band dispersion
Large superexchange Antiferromagnetic	Some evidence of large spin wave dispersion
Charge transfer gaps not Mott Hubbard	Reports support small Mott Hubbard gap if any
Charge carriers mostly of anion p character	Charge carriers Fe d electrons and holes
Strong Cu 3d-O 2p hybridization	Relatively weak Fe 3d-As 4p hybrid.
2 Dimensional	Weak anisotropy (pen.depth)
No orbital degrees of freedom	Possible orbital ordering


La
O
P
Fe
LaO layer
FeP layer

What would the Fe 3d states look like if we started in the same way as in the Cuprates?

Not layered like TiS2!! the surface as drawn is POLAR!!

Ba 122 Mark Golden B 455,
and 218 surface Ba ordering

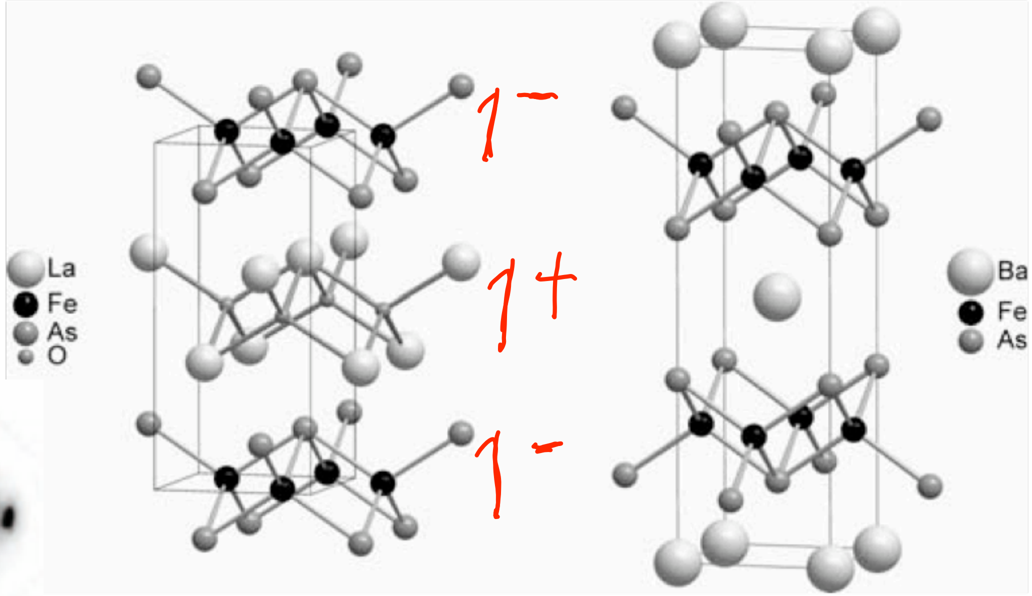
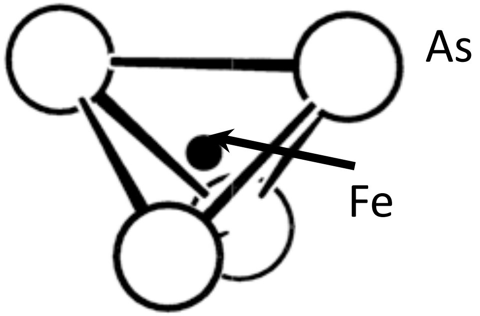
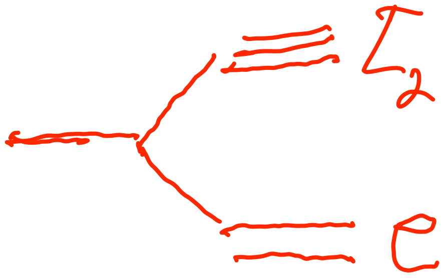


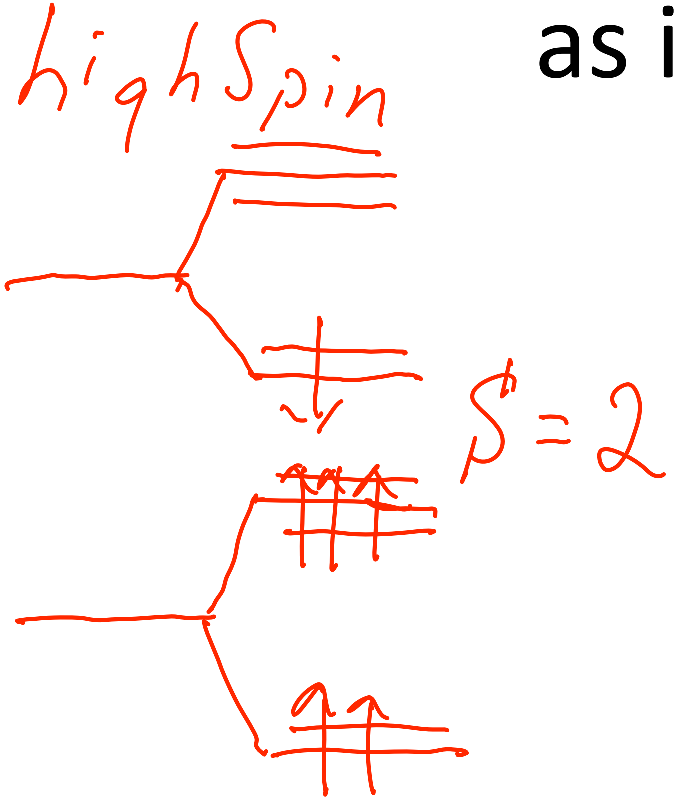
Figure 1. Crystal structures of LaFeAsO (left) and $BaFe_2As_2$ (right)

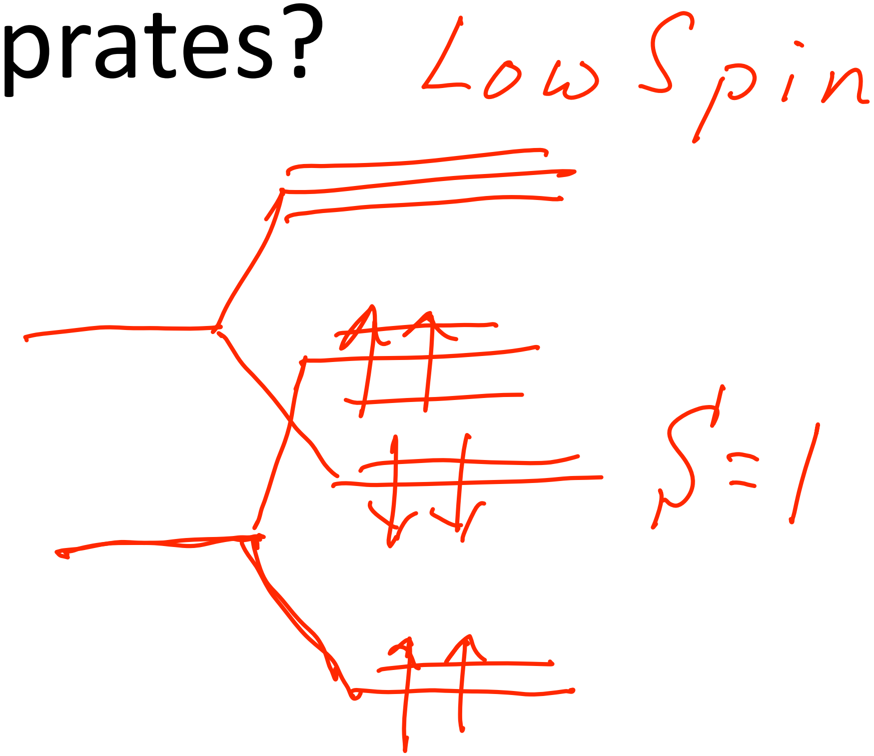


~ Tetrahedral coordination
Crystal field splitting
Is inverted as compared to Octahedral



Local crystal/ ligand field picture as in Cuprates?

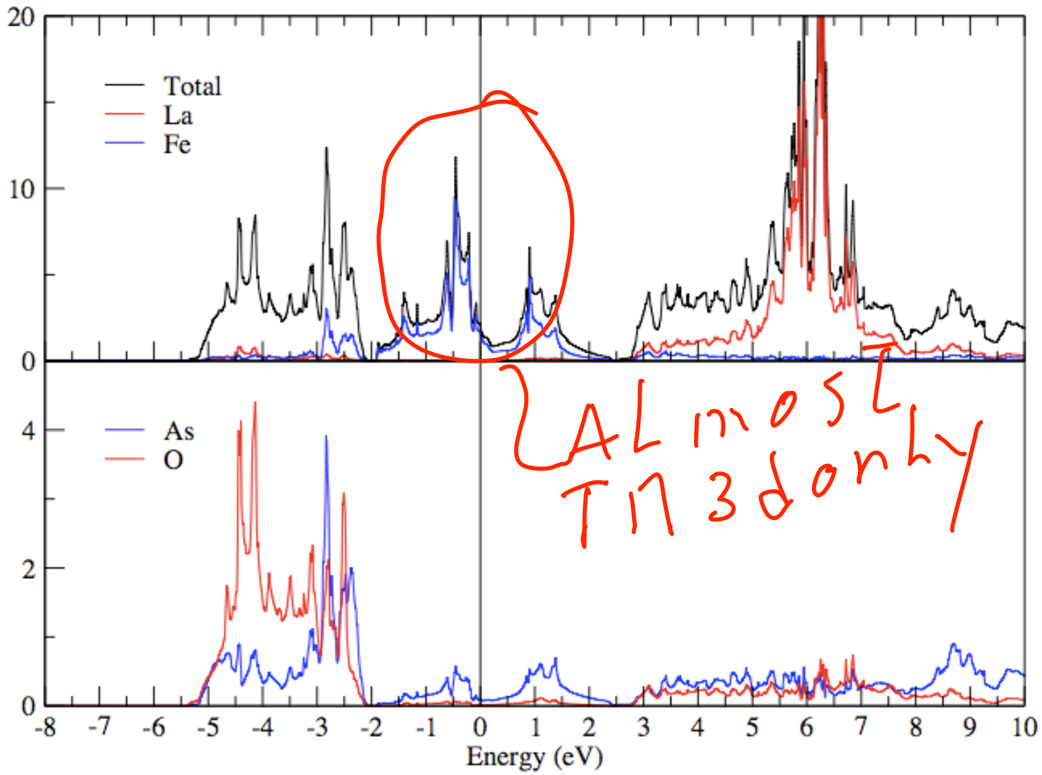




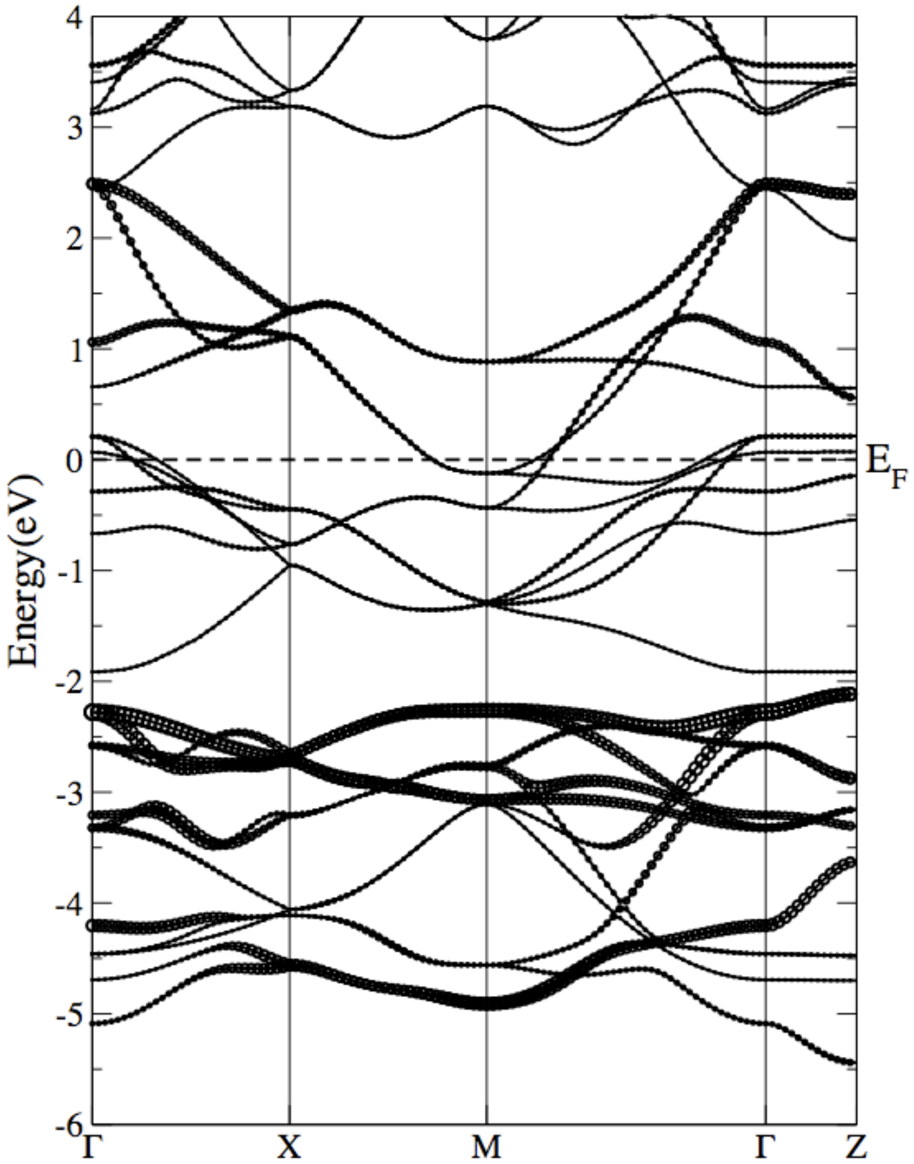
Band theory - Cystal/ligand field splitting is not very large
And less important than the 3d band structure.

Very different from the cuprates!!

Electronic Structure of LaOFeAs band theory (Elfimov)



Almost TM 3d only



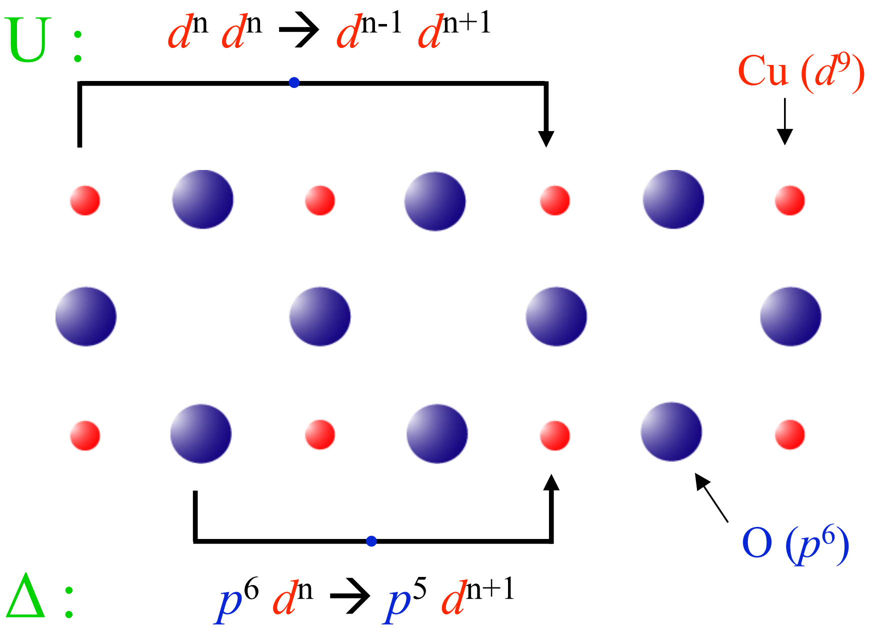
GGA; non magnetic

Fat bands show As 4p character

MT Radii (A) :

La	1.22
Fe	1.01
As	1.38
O	1.11

Correlated Electrons in a Solid



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

Cu (d^9)

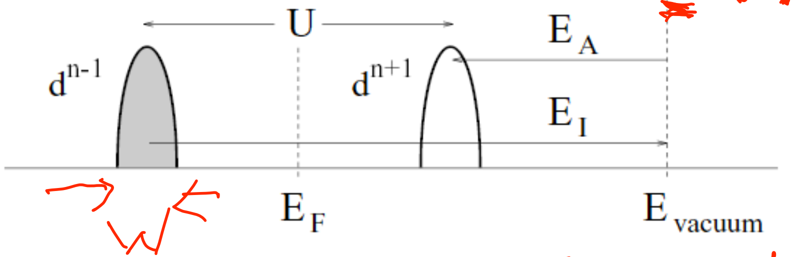
O (p^6)

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

Pnictides

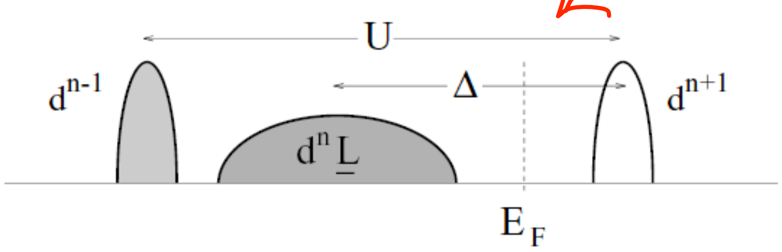
$\leftarrow U \lesssim W$

(a) Mott-Hubbard insulator



cuprates

(b) Charge transfer insulator



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

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

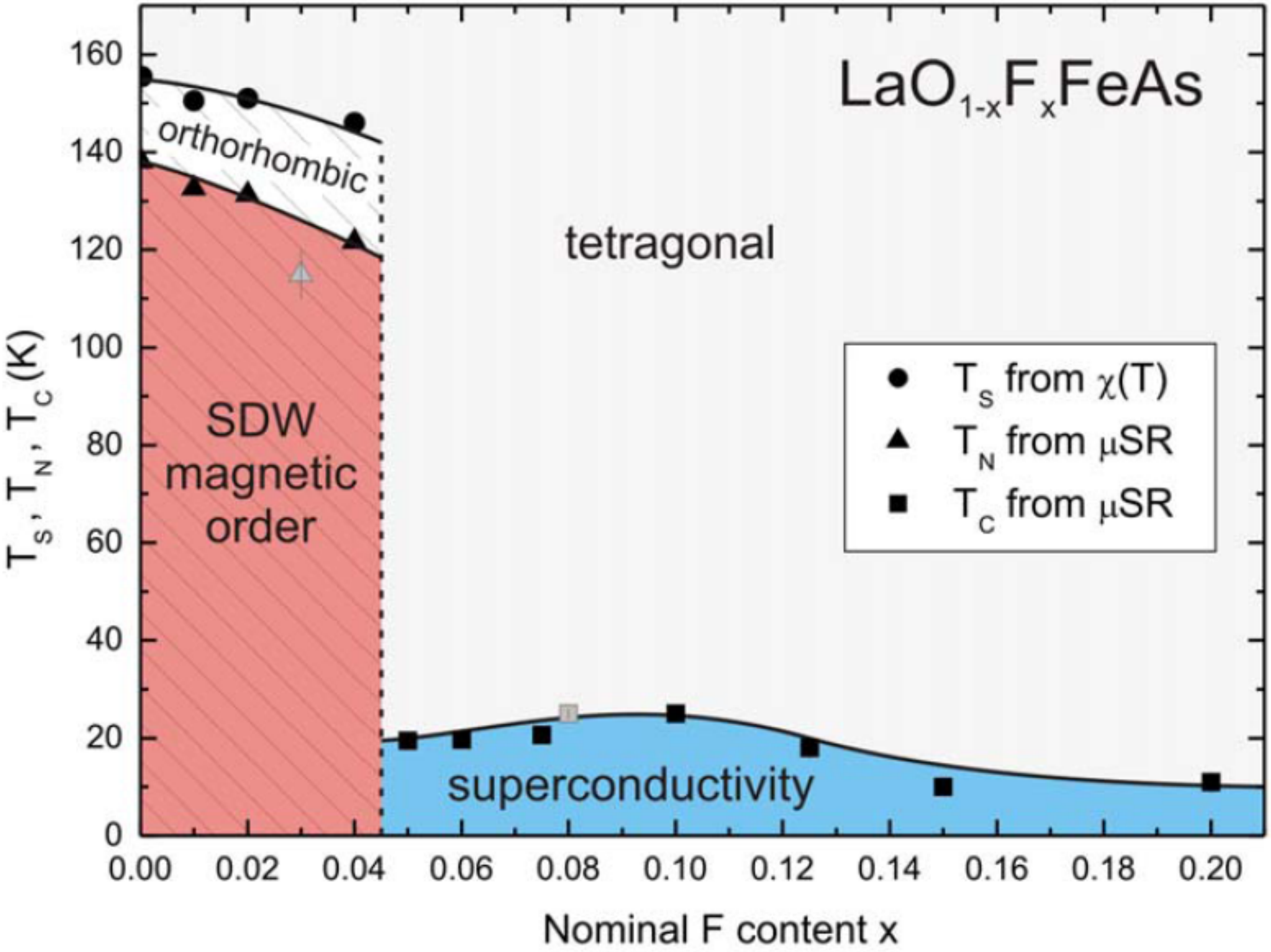
E_I	ionization energy
E_A	electron affinity energy
E_M	Madelung energy

Epol depends on surroundings!!! $E_p = \dfrac{ze^2\alpha}{R^4}$

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

Since the pure pnictides like LaFeAsO, BaFe2As2, etc are (bad) metals we would have to conclude that U<the 3d band width

However the T dependent conductivity and magnetic susceptibilities are strange


LaO$_{1-x}$F$_x$FeAs
orthorhombic
tetragonal
SDW magnetic order
superconductivity
T$_S$ from χ(T)
T$_N$ from μSR
T$_C$ from μSR
T$_S$, T$_N$, T$_C$ (K)
Nominal F content x
0
20
40
60
80
100
120
140
160
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20

arXiv:0808.0708 LaFeAsO$_{1-x} F_x$ R. Klingeler et al IFW Dresden)

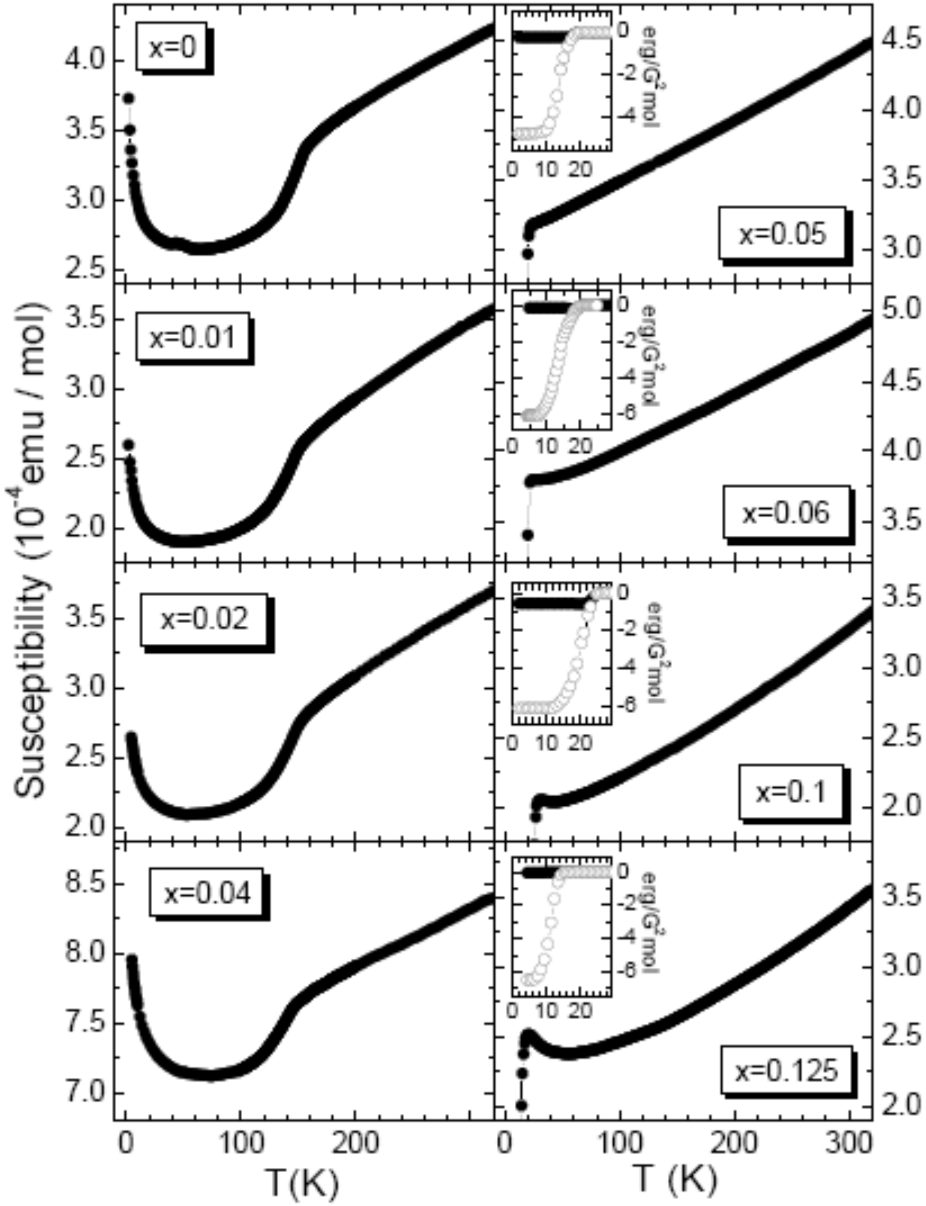
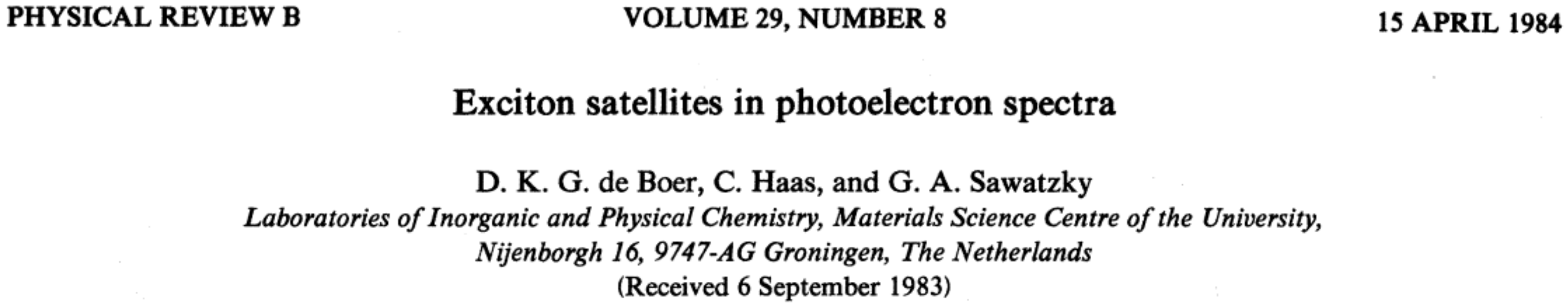


FIG. 3: Static susceptibility $\chi = M/B$ of LaFeAsO$_{1-x}$F$_x$, for different doping level between $0 \leq x \leq 0.125$ at $B = 1$ T. Note, that for all graphs the ordinate covers the range $\Delta\chi = 2$ emu/mol. Insets: M vs T for $B = 2$ mT.

How can we explain the low strongly varying magnetic moment?

- Low Hubbard U i.e. U< 3d band width - strong polarity fluctuations –reduce the effect of JH
- Band width is about 2-3 eV so U~2-3eV?
- How do we reduce an on site interaction from about 20eV in the free ion to less than 2 eV?
- A large contribution is the Polarizability of the anion!!!

2 level model for the dynamic high frequency polarizability and motion of the polaron/bipolaron



PHYSICAL REVIEW B VOLUME 29, NUMBER 8 15 APRIL 1984

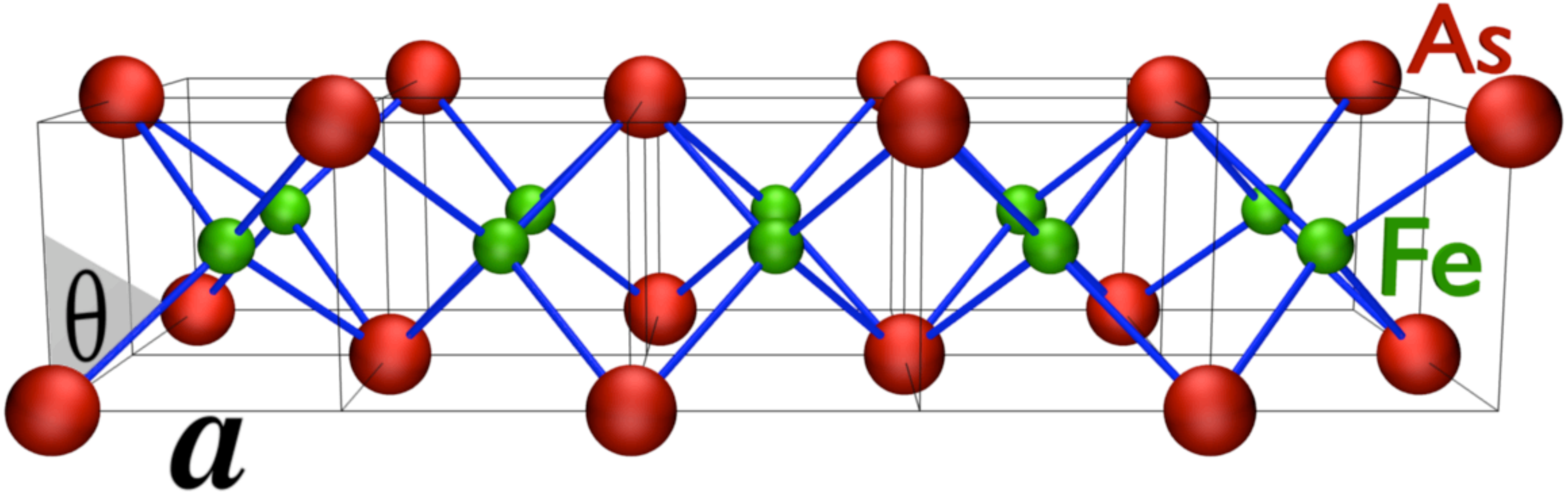
Exciton satellites in photoelectron spectra

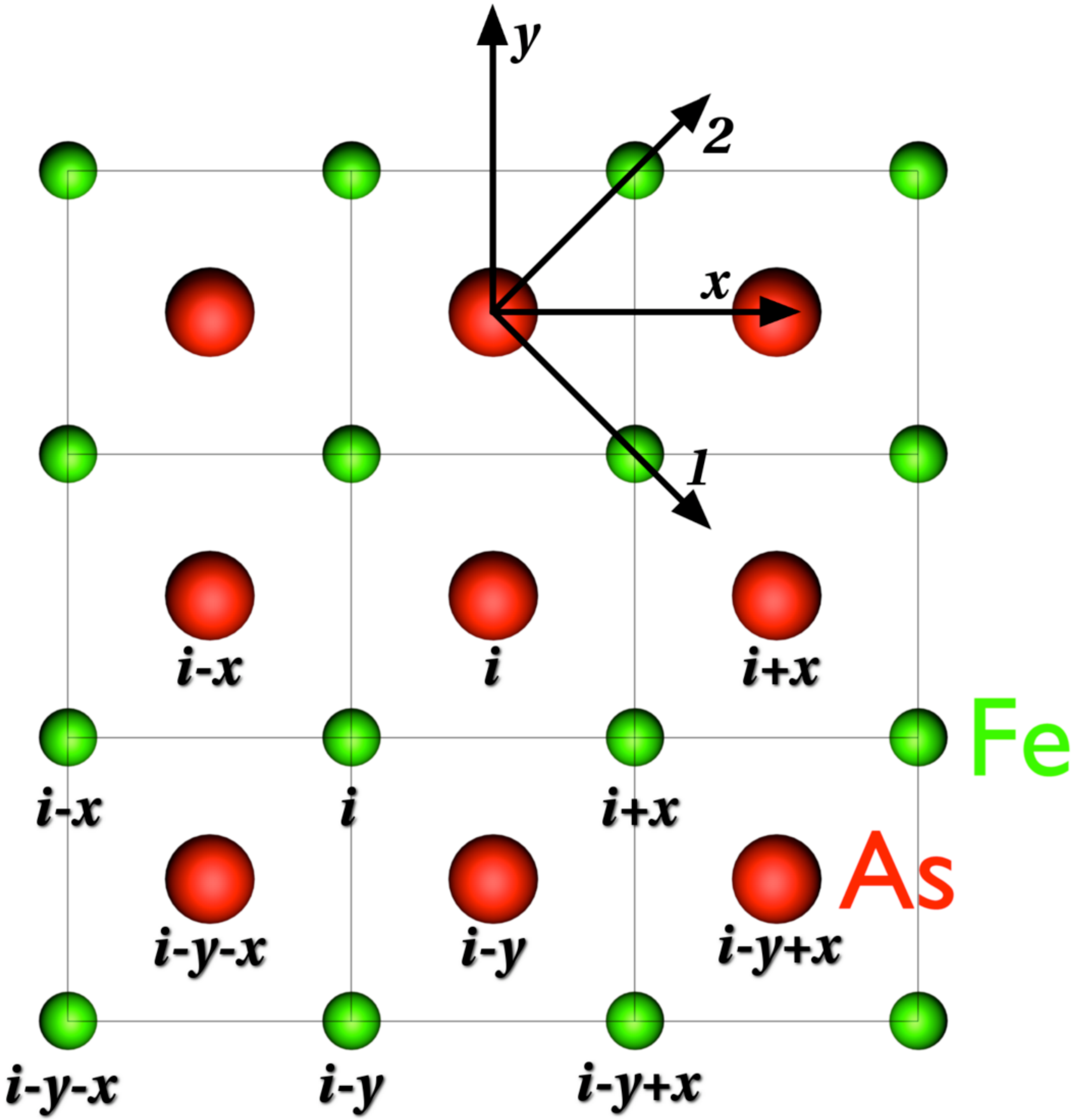
D. K. G. de Boer, C. Haas, and G. A. Sawatzky
Laboratories of Inorganic and Physical Chemistry, Materials Science Centre of the University,
Nijenborgh 16, 9747-AG Groningen, The Netherlands

(Received 6 September 1983)

Use a two level model of As i.e. 4p occupied and 5s empty.
In an electric field due to the point charge they mix yielding
The pictures we draw of the polarization cloud.

Mona Berciu et al PRB in press


As
Fe
θ
a


y
2
x
1
i-x
i
i+x
Fe
i-x
i
i+x
As
i-y-x
i-y
i-y+x
i-y-x
i-y
i-y+x

$$\mathcal{H}_{\mathrm{Fe}} = -\sum_{i,j,\sigma} \left(t_{ij} c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c. \right) + U_H \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

$$\mathcal{H}_{\mathrm{As}} = \Omega \sum_{i,\lambda,\sigma} p^{\dagger}_{i,\lambda,\sigma} p_{i,\lambda,\sigma} ,$$

= 4p-5s excitation energy

$$\begin{aligned}
\mathcal{H}_{\mathrm{int}} \quad &= g \sum_{i,\sigma} \hat{n}_i \Big[s^{\dagger}_{i,\sigma} \left(-\sin\theta p_{i,2,\sigma} + \cos\theta p_{i,3,\sigma} \right) \\
&+ s^{\dagger}_{i-y,\sigma} \left(-\sin\theta p_{i-y,1,\sigma} + \cos\theta p_{i-y,3,\sigma} \right) \\
&+ s^{\dagger}_{i-x-y,\sigma} \left(\sin\theta p_{i-x-y,2,\sigma} + \cos\theta p_{i-x-y,3,\sigma} \right) \\
&+ s^{\dagger}_{i-x,\sigma} \left(\sin\theta p_{i-x,1,\sigma} + \cos\theta p_{i-x,3,\sigma} \right) + h.c. \Big] (3)
\end{aligned}$$

Because Omega is a high energy we
can use perturbation theory
in t as the smallest
We assume only one particle so that U
is not active

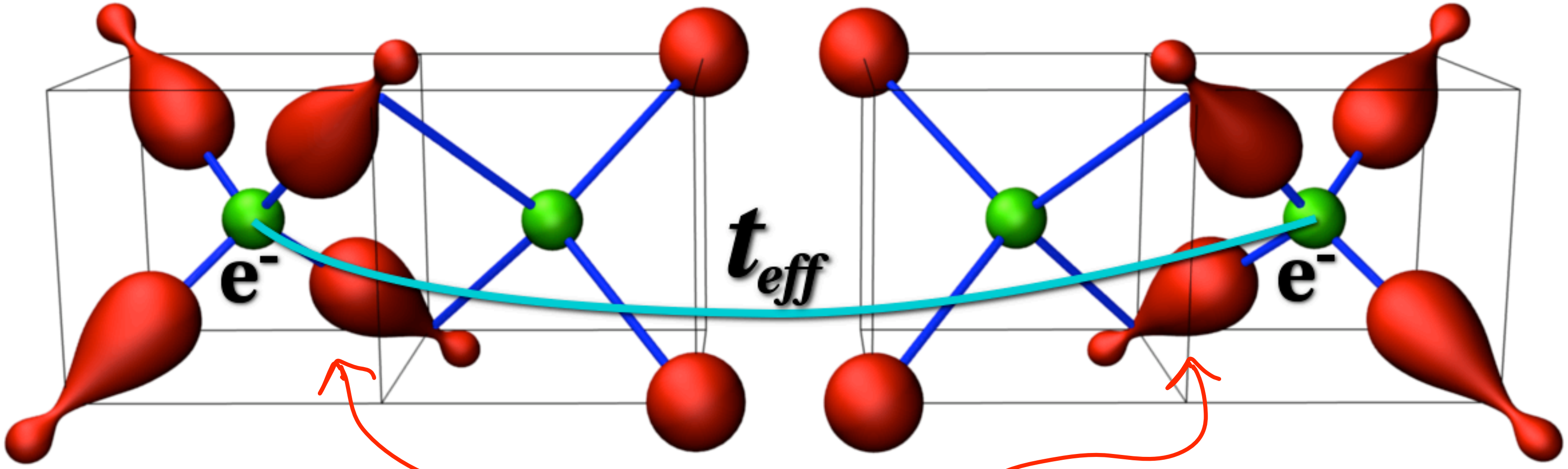
The electronic Polaron eigen energies are given by

$$E_P(\vec{k}) = 4(\Omega - \sqrt{\Omega^2 + 4g^2}) + \epsilon_{\mathrm{eff}}(\vec{k}).$$

$$\epsilon_{\mathrm{eff}}(\vec{k}) = -2t_{\mathrm{eff}}\left[\cos(k_x a) + \cos(k_y a)\right] - 4t'_{\mathrm{eff}}\cos(k_x a)\cos(k_y a)$$

We use the know electronic polarizability of As to determine g
For small g i.e. in the linear regime. g=2.5 eV for α= 10 cubic A

The Motion of a single quasi particle These move like electronic polarons



$$t_{eff} \sim t\,|\langle \phi_1 | \phi_2 \rangle|^2$$

i.e. the overlap integral of the polarization clouds

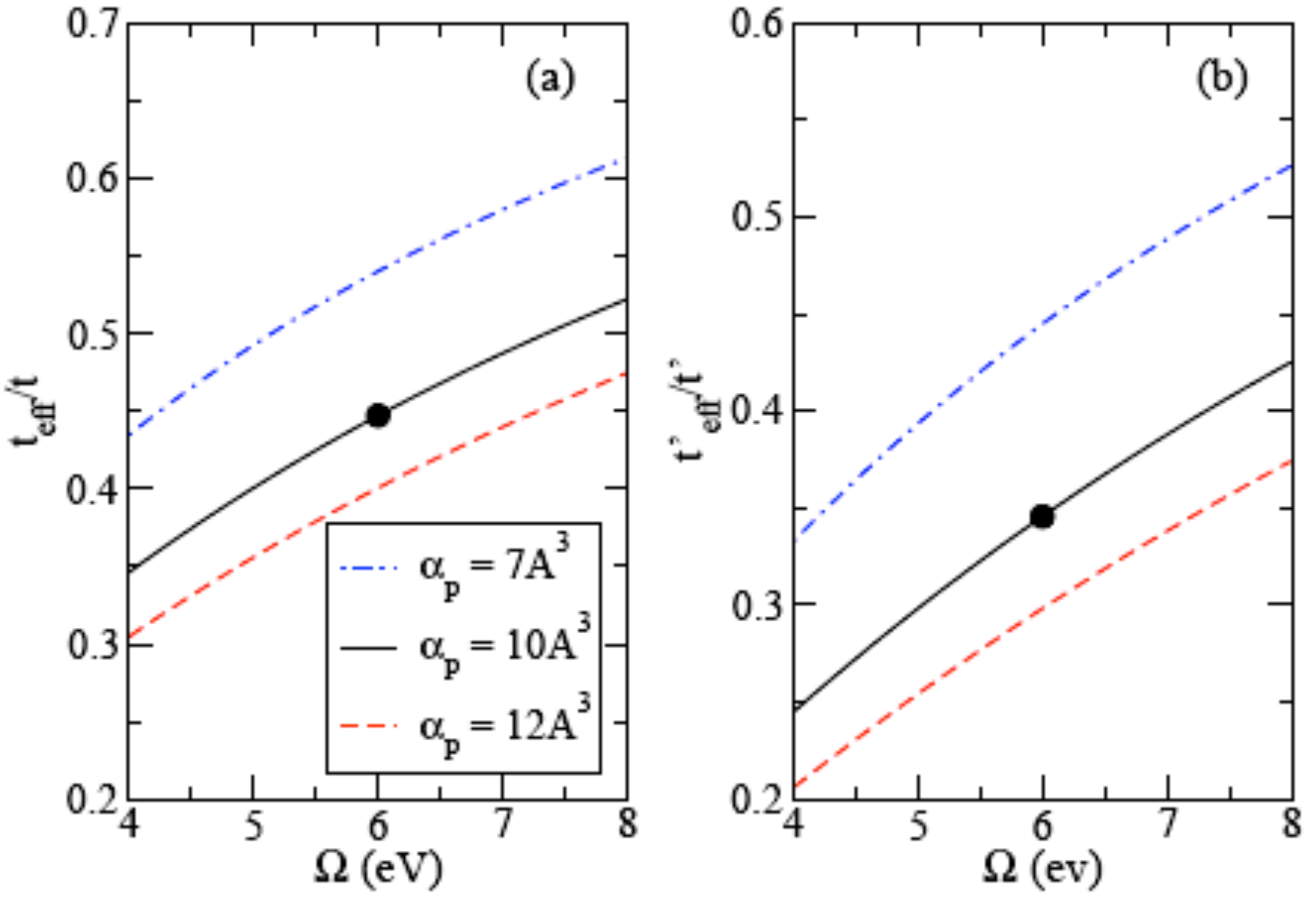


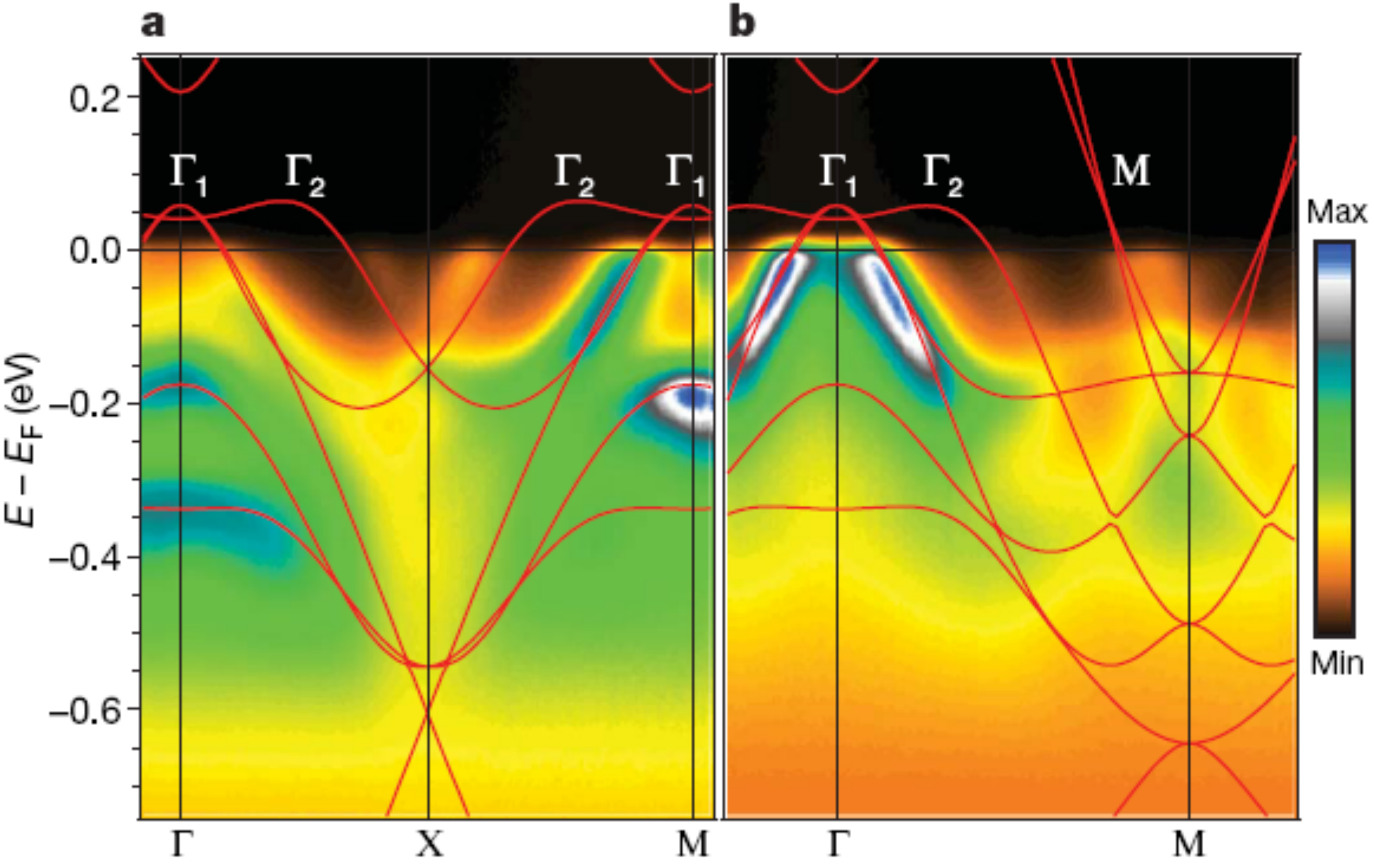
FIG. 3: (a) $t_{\rm eff}/t$ and (b) $t'_{\rm eff}/t'$ vs. Ω, for a polarizability $\alpha_p = 7, 10$ and $12 \mathring{A}^3$. The dots show the values used here.

The effective polaron mass is simply t/teff =2.2 this is light compared to conventional lattice polaron masses

Angular resolved phtoemission comparison with LDA LaFePO
Lu et. al Nature 455, 81 2008

→ close to our $1/z \sim 2$

NOTE The band theory result has been shifted up by 0.11 eV and scaled down by a factor of 2.2



How about the reduction of the coulomb interactions between two electrons on Fe sites?

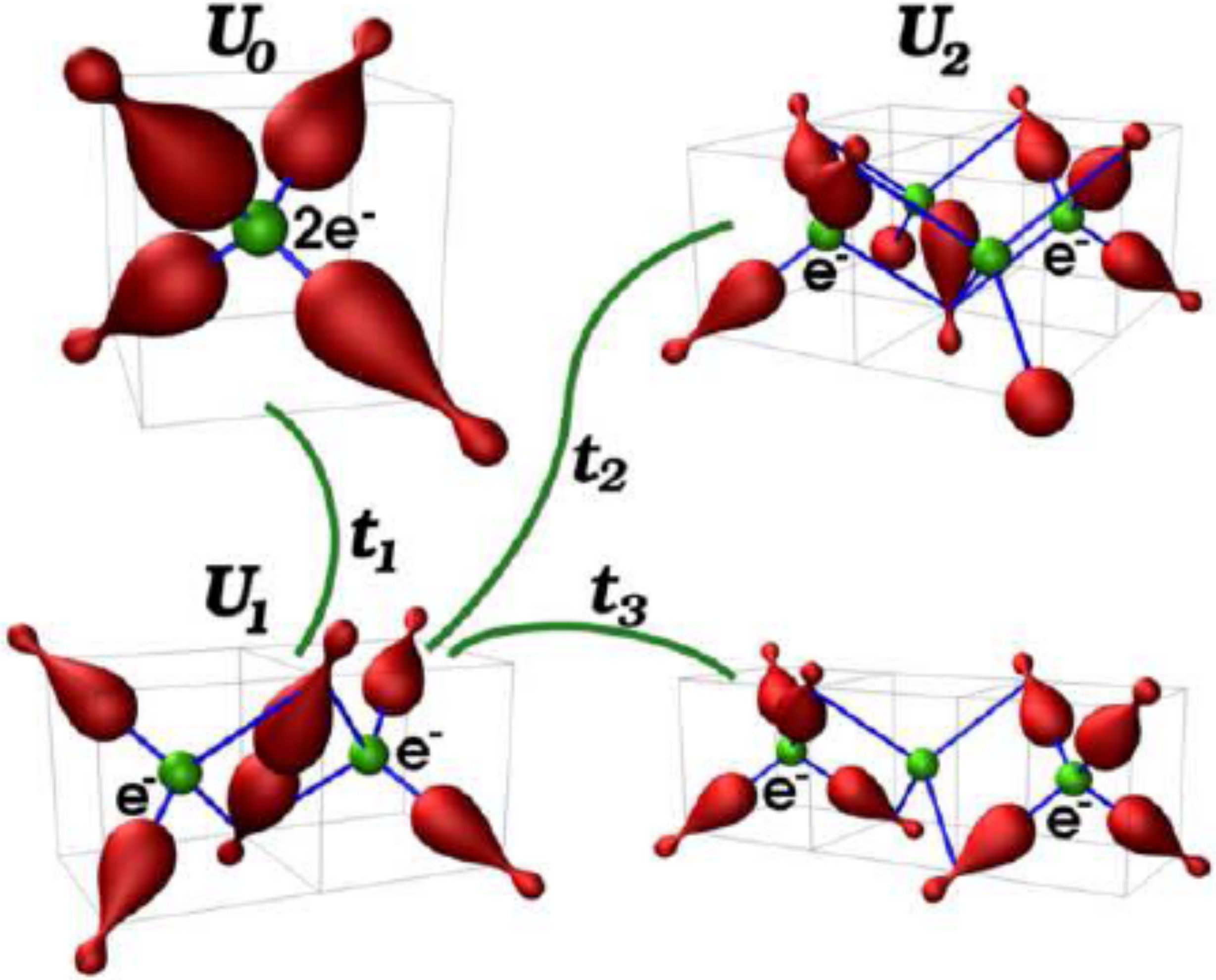


FIG. 4: Sketches of on-site, 1^{st}, 2^{nd} and 3^{rd} nn bipolarons. The first three configurations have interaction energies U_0, U_1 and U_2, respectively. Several of the special effective hopping integrals are also indicated.

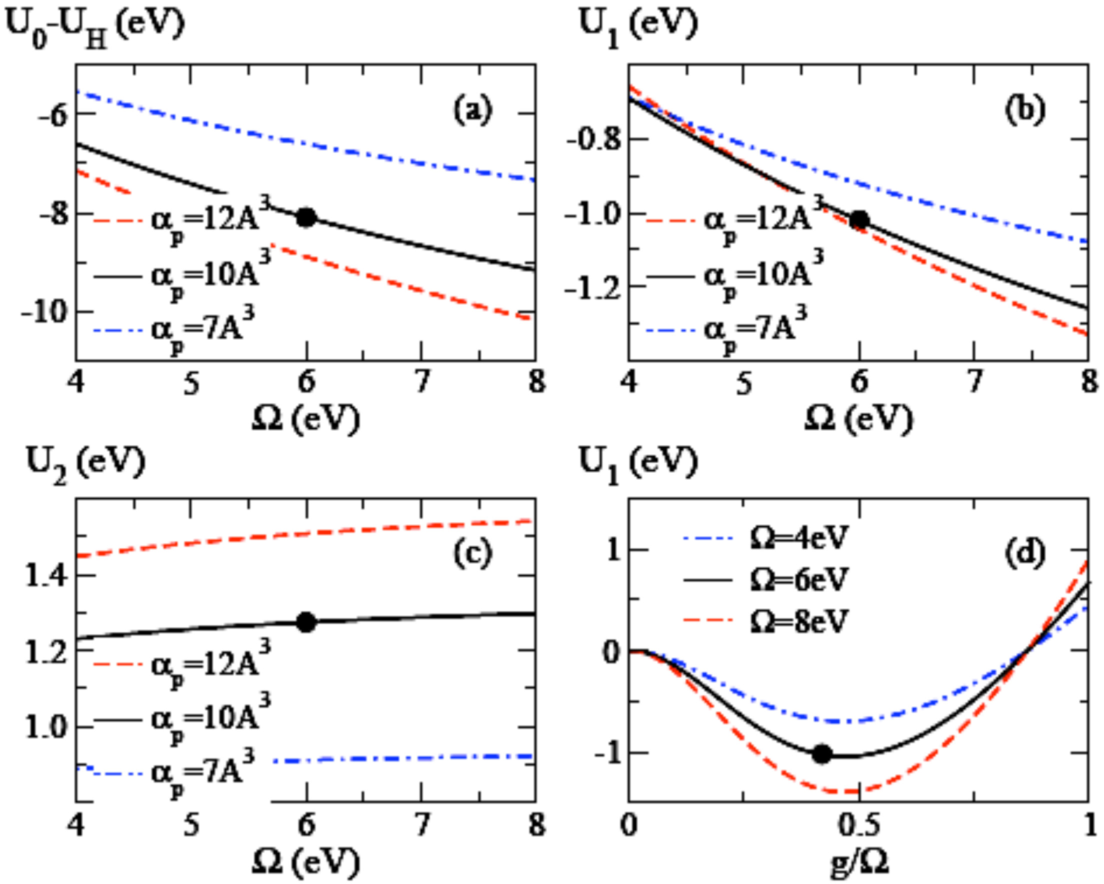


FIG. 5: (a) Renormalization of on-site interaction, $U_0 - U_H$; (b) nn energy U_1 and (c) 2^{nd} nn energy U_2 vs. Ω for various polarizabilities. (d) U_1 vs. g/Ω when $\Omega = 4, 6, 8$eV. The dots show our typical values.

Can this lead to bipolaronic bound states? And if so what is their mass

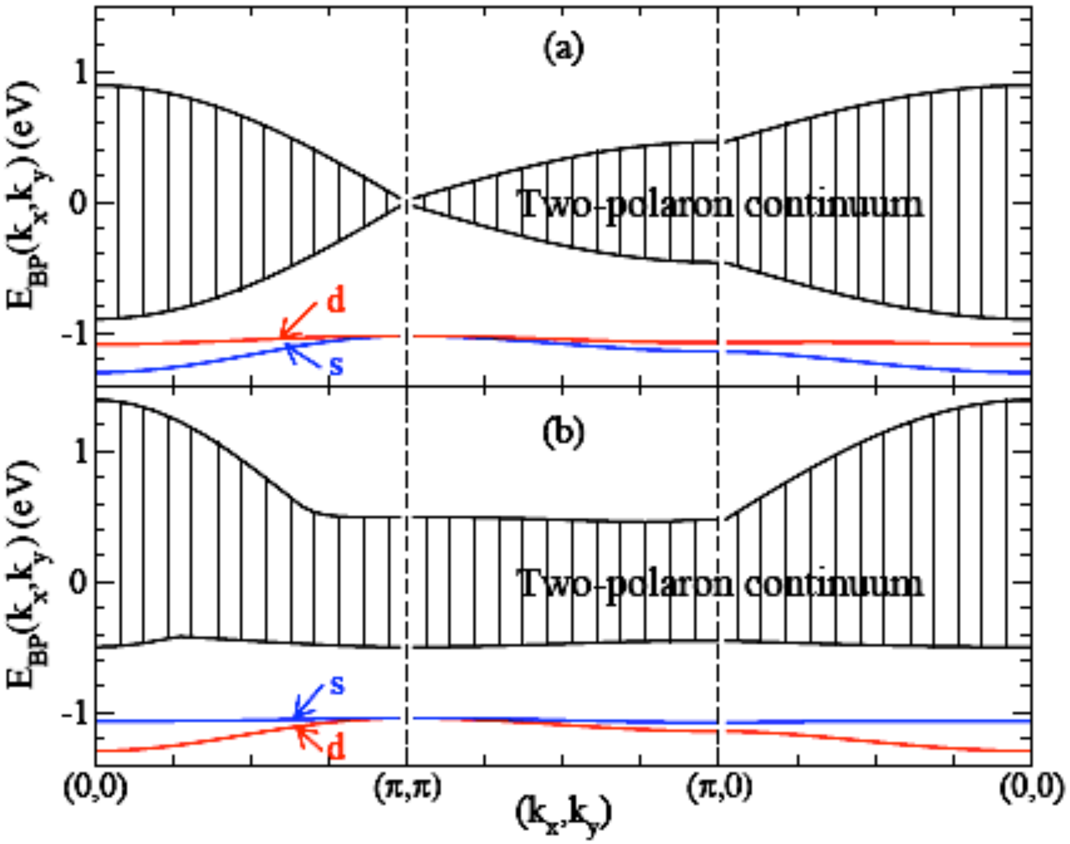


FIG. 7: Dispersion of the two bound bipolaron states along high-symmetry axes in the Brillouin zone, for (a) $t' = 0$ and (b) $t' = -t/2$. The two-polaron continuum is also shown. Parameters are $U_H = 10$ eV, $\alpha_p = 10\mathring{A}^3, \Omega = 6$ eV (similar results are found for all $\alpha_p = 7 - 12\mathring{A}^3, \Omega = 4 - 8$ eV). The symmetry of the ground state changes from s to d if $t' \neq 0$.

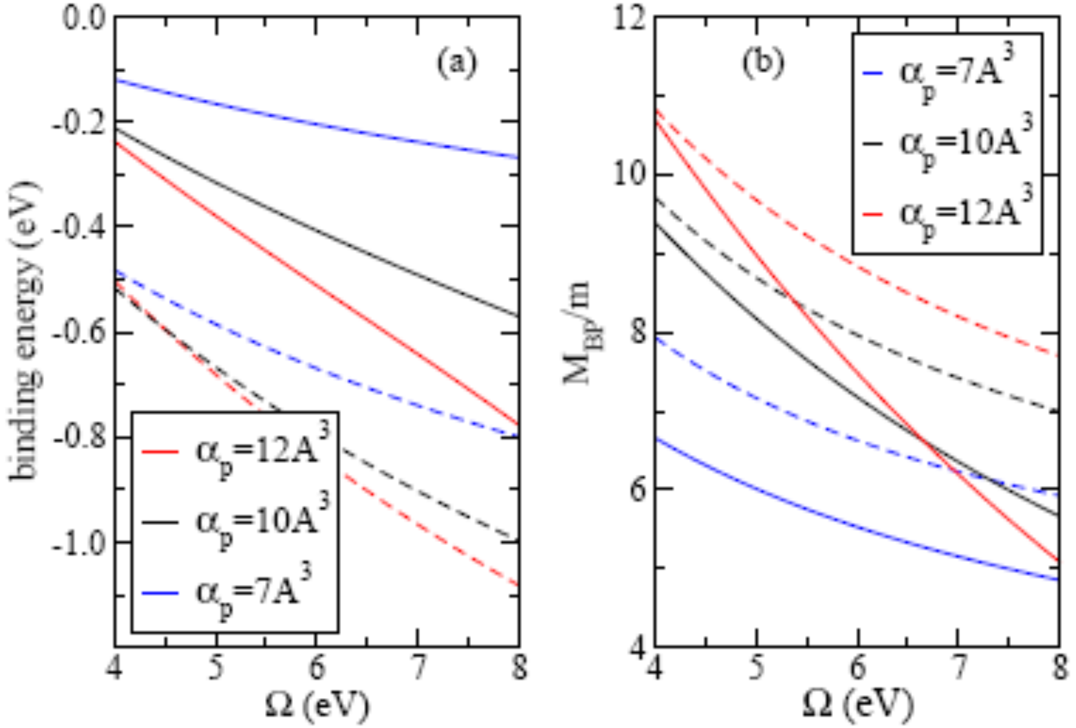


FIG. 8: Ground-state bipolaron (a) binding energy, and (b) effective mass in units of the free carrier mass vs. Ω, for various polarizabilities. The full lines correspond to $t' = 0$, dashed lines to $t' = -t/2$. Here $U_H = 10$eV.

Note that the bipolaron mass is only 8 times the free particle mass this Is again much lighter than for lattice bipolarons allowing for an eventual high Bose Einstein condensation T.

Systematics of Tc

- Tc variation with bond angles bond lengths and polarizabilities
- Note that often the As-Fe-As bond angle is used or the orthorhombic distortion in the plane or the Fe-As-Fe diagonal bond angle is used for systematics.
- Our model suggests rather using bond lengths and the Fe-As-Fe nearest neighbor bond angle

Effective interaction plotted vs log Tc

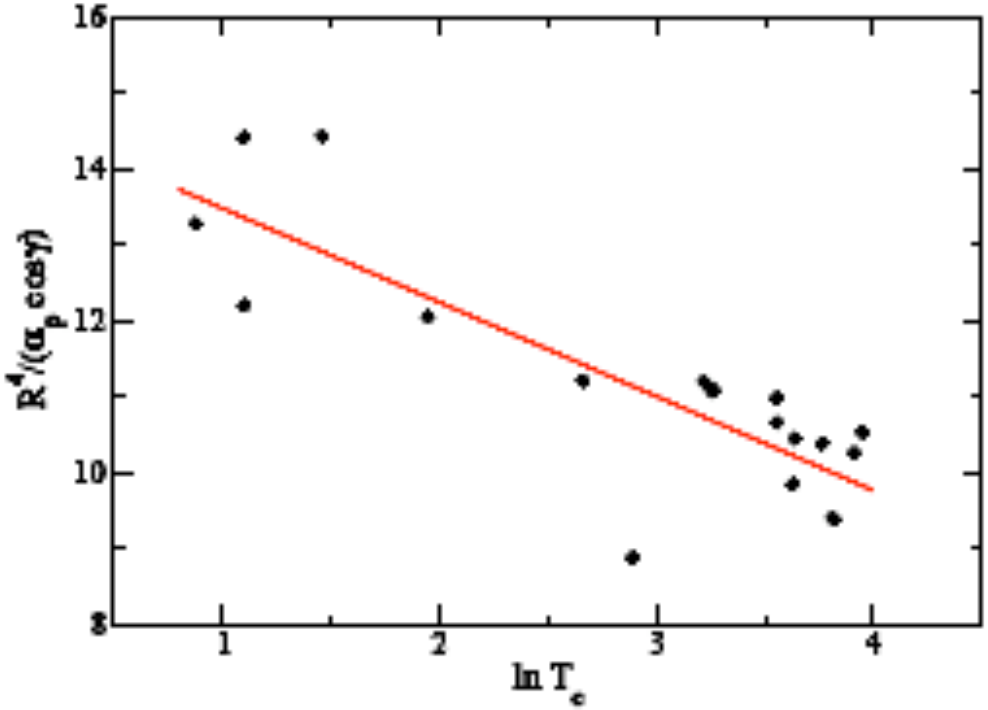


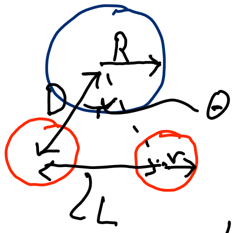
FIG. 13: Linear fit of $\ln T_c$ vs. $\frac{R^4}{\alpha_p \cos\gamma}$. The data points are taken from Refs. 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16.

Conclusions

- The Fe pnictides and heavy anion chalcogenides are very different from the cuprates with regard to low energy scale properties: spin, charge, orbital, and lattice degrees of freedom
- Hybridization covalency involving Fe 3d is weak crystal and ligand fields are small, electronic structure given by band structure with weak correlation
- We suggest that the As 4p – Fe 4s and 4p hybridization and especially the Arsenic ELECTRONIC polarizability set the scene for a band structure approach.
- The quasi particles are electronic polarons with a modest mass of about 2-3 with possibly an attractive nn interaction resulting in bipolarons with s,or d wave superconductivity and also a modest mass

- DESIGN (ARTIFICIAL) STRUCTURES USING HIGHLY POLARIZABLE ATOMS OR SMALL MOLECULES ALTERNATING WITH NARROW BAND METAL FILM FOR HIGHER Tc's?

Material design and limitations



$D_{min} = R + r$ $\quad$ $Z = n$ common polarizable neighbors

Interaction $= Z\alpha\left(\frac{1}{R+r}\right)^4\cos(\theta) > \frac{1}{L}$ (bare repulsion)

$L = 2(R+r)\sin\theta$ $\quad$ $2Z\alpha\left(\frac{1}{R+r}\right)^3\cos\theta\sin\theta > 1$

$\alpha = CR^3$ $\quad$ $\simeq 2ZC\frac{1}{(1+\frac{r}{R})^3}\cos\theta\sin\theta > 1$

For $r = 0.5\,\text{Å}$ $\quad$ $R = 2\,\text{Å}$ $\quad$ $\simeq 2ZC\frac{1}{2}\cos\theta\sin\theta > 1$

Can be attractive for $Z \geq 2$

need to maximize Z and minimize θ

Z is limited by R i.e Anion-Anion $> 2R$

Fe pnictides do a good job of this

Abnormal T-linear susceptibility and Phase diagram of $BaFe_{2-x}Co_xAs_2$ single crystals

X. F. Wang, T. Wu, G. Wu, R. H. Liu, H. Chen, Y. L. Xie and X. H. Chen*

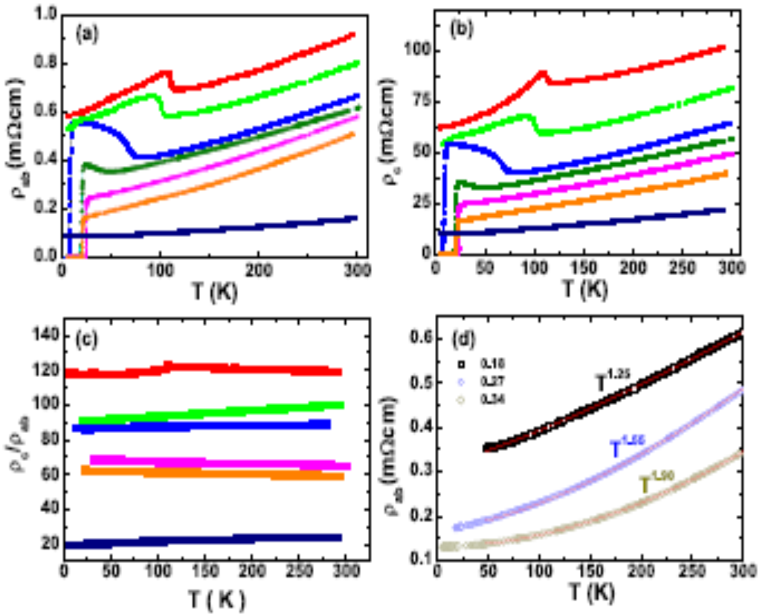


FIG. 2: Temperature dependent resistivity for the $BaFe_{2-x}Co_xAs_2$ single crystals. (a): In-plane resistivity (0.08-red , 0.12-green , 0.17-blue , 0.18-cyan , 0.20-magenta , 0.25-yellow , 0.60-pink, respectively; (b): out-of-plane resistivity; (c): Temperature-dependent anisotropy; (d): power law fitting for x=0.18, 0.27 and 0.34. The red solid line is the fitting line.

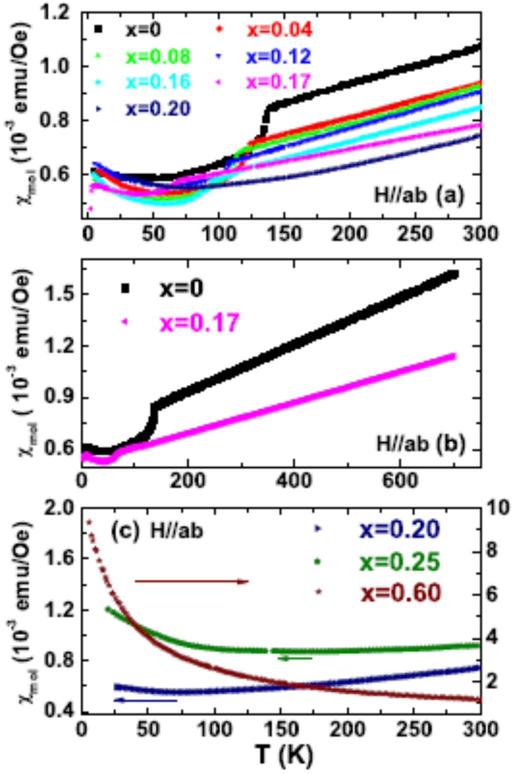


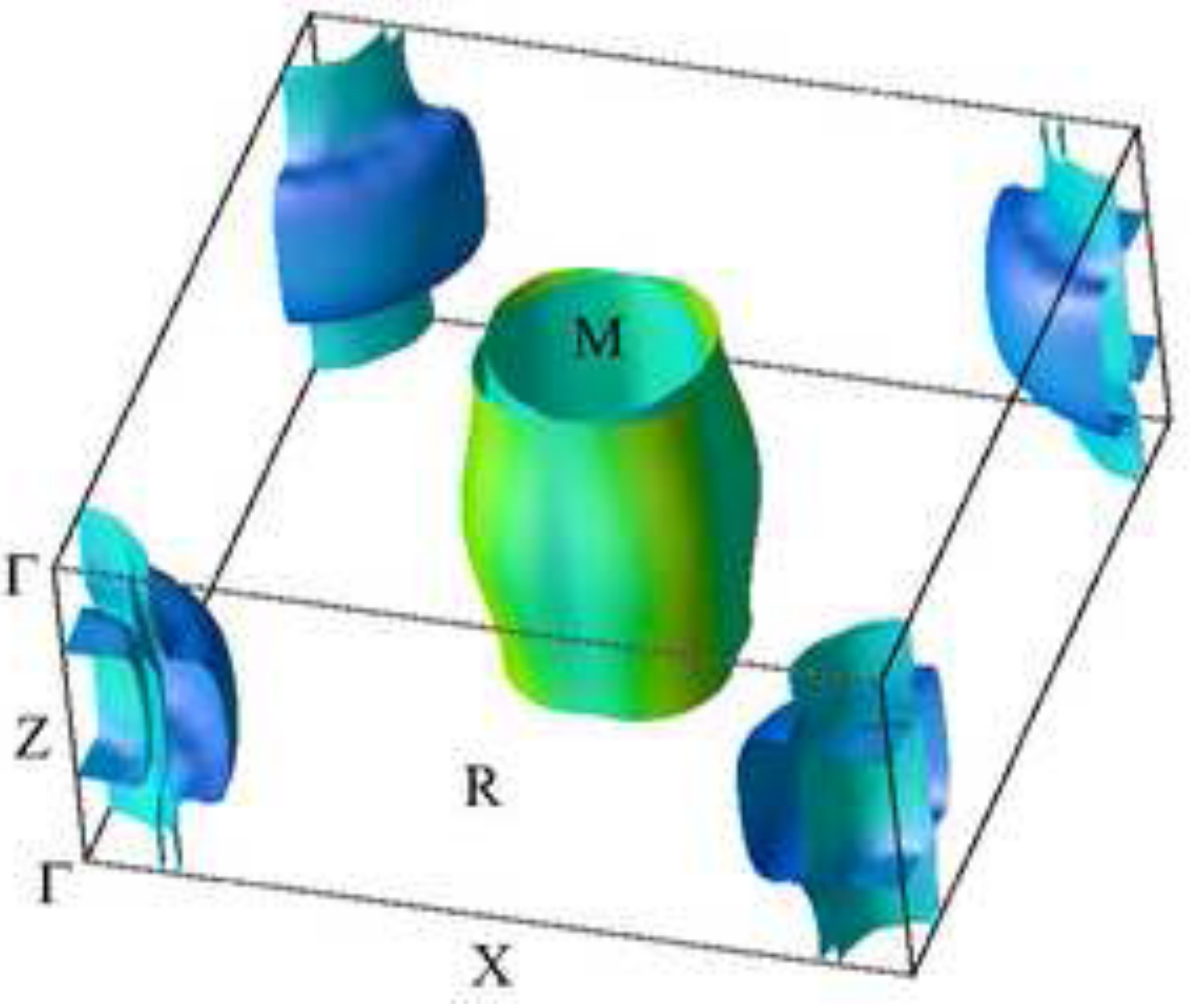
FIG. 4: Temperature dependent in-plane susceptibility for $BaFe_{2-x}Co_xAs_2$ single crystals under H =6.5T. (a): in the temperature range from 2 K to 300 K for x≤0.2; (b): in the temperature range from 2 K to 700 K for x=0 and 0.17; (c): in the temperature range from 2 K to 300 K for x=0.20,0.25 and 0.60.

What does Co do? Dope???

Some other experimental results

- Neutron scattering yields ordered moments ranging from very small to 0.9 μ B
- Magnetic ordering is antiferromagnetic SDW like 1D ferromagnetic chains coupled antiferromagnetically
- Neutron inelastic scattering yields a large spin wave velocity i.e. large J but also a large spin wave gap of 10 meV and the spin waves are heavily damped above about 30 meV. " Stoner Continuum?"

Singh et al Fermi surface LaFeAsO LDA



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