Transition metal oxides: Surfaces interfaces and non uniform polarizability

G.A. Sawatzky
Physics and Chemistry departments
University of British Columbia
content

• Very brief introduction to TM oxide electronic structure
• Want happens at surfaces and interfaces
• Surface band gaps, superexchange, orbital ordering
• Polar surfaces
• Non uniform polarizability; Range and sign of Coulomb interactions in ionic compounds
• Strange short range Coulomb interactions in Fe Pnictides
Wide diversity of properties

- Metals: CrO2, Fe3O4 T>120K
- Insulators: Cr2O3, SrTiO3, CoO
- Semiconductors: Cu2O
- Semiconductor – metal: VO2, V2O3, Ti4O7
- Superconductors: La(Sr)2CuO4, LiTiO4, YBCO
- Piezo and Ferroelectric: BaTiO3
- Catalysts: Fe, Co, Ni Oxides
- Ferro and Ferri magnets: CrO2, gammaFe2O3
- Antiferromagnets: alfa Fe2O3, MnO, NiO ---
- Ionic conductors (batteries) LixNi1-xO
- Oxide fuel cells use Manganites and cobaltates

Properties depend in detail on composition and structure
Phase Diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

Uehara, Kim and Cheong

R: Rombohedral

O: Orthorhombic (Jahn-Teller distorted)

O*: Orthorhombic (Octahedron rotated)
Model for Charge, Spin and Orbital Correlations in Manganites

Mn$^{4+}$, d$^3$, S=3/2, No quadrupole; Mn$^{3+}$, S=2, orbital degeneracy
Ordering in strongly correlated systems

Stripes in Nd-LSCO

rivers of Charge—Antiferro/Antiphase

$\Delta Q < 0.5 \text{ e}$

Charge inhomogeneity in Bi2212

$\Delta Q \sim 0.1 \text{ e}$

$\Delta Q_c \sim 1 \text{ e}$

$\Delta Q_0 \sim 0$

Pan, Nature, 413, 282 (2001);
Novel Nanoscale Phenomena in Transition-Metal Oxides

Ionic Oxide Polar Surfaces
Stabilization of polar surfaces by epitaxy

\[
\begin{align*}
\text{Sr} & \quad \text{O} & \quad \text{Sr} & \quad \text{O} & \quad \text{Sr} & \quad \text{O} \\
+1 & \quad -2 & \quad +2 & \quad -2 & \quad +2 & \quad -1 \\
\end{align*}
\]

< 10 ML

Transparent insulator \( \rightarrow \)½ metallic FM

**Applications**: Spintronics; CMR

Correlated Electron System Surfaces
Kinks and steps stabilized by epitaxy

NiO(100) \( \rightarrow \) 1D Metallic steps
Superconducting Copper oxides

**Applications**: Novel SC; QuBits

Strained 2D Layers
Positive and negative pressure

LaMnO\(_3\) \( \quad \text{Mn}^{3+} \text{3d}^4 \)

\( e_g \)

\( t_{2g} \)

**Applications**: CMR; M-I Transition; Orbital Ordering

Electronic Structure of Interfaces
Metal-Insulator interface: gap suppression

**Applications**: Molecular Electronics; Fuel Cells; Thermal Barrier Coatings

Artificial Molecules Embedded into a Material
Ca, Mg, Sr, Ni vacancies or O-N substitution in oxides

**Applications**: Spintronics; Novel Magnets
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 TM Oxides

If $\Delta < \frac{(W+w)}{2}$ → Self doped metal

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

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

If $\Delta < \frac{(W+w)}{2}$ → Self doped metal

Epol depends on surroundings!!!

- ZSA, PRL 55, 418 (1985)

At a surface the charge transfer energy decreases, $U$ increases
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:**

Unit cell of perfect inf. crystal

Supercell with an impurity

Perfectly imperfect inf. crystal
Neutral (110) surfaces of NiO

Slab of 7 NiO layers

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?

Kinks and steps stabilized by epitaxy

NiO(100) 1D Metallic steps
Superconducting Copper oxides

Ni$^{2+}$ goes to Ni$^{1+}$($d^9$) and holes in O 2p for negative charge transfer gap
i.e. self doping --------looks like hole doped cuprates!!!

New High Tc??

Watch out for small particles with lots of surfaces and corners including polar surfaces. To have Magnetism in small particles freshly prepared is actually almost generally expected.
Ionic Materials can exhibit Polar surfaces and interfaces and They HAVE TO reconstruct
Polar (111) Surfaces of MgO

Finite slab of charged planes

$\Delta V = 58 \text{ Volt per double layer!}$
Types of reconstruction

Electronic

- Rearrangement of electrons

<table>
<thead>
<tr>
<th>State</th>
<th>Reaction</th>
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</thead>
<tbody>
<tr>
<td>+Q</td>
<td>+Q → +Q/2</td>
</tr>
<tr>
<td>-Q</td>
<td>-Q → -Q/2</td>
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Ionic

- Rearrangement of ions faceting

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<tbody>
<tr>
<td>+Q</td>
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<td>-Q</td>
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Chemical

- Vacancies or add ions (K+) or OH-

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<td>-Q</td>
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References:

- **K₃C₆₀:**

- **NiO(111):**

- **K-depositon:**
  NiO(111):
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$_2$Cu$_3$O$_{6+δ}$

Perovskites: LaTMO$_3$ (Ti,V,Mn ...)
Spin, charge and orbital ordering

Simple oxides: SrO, NiO, MnO ...

(111) surface
(001) surface in trivalent compounds
(110) surface
Examples of non polar layer structures
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
Octapolar 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-
Fermiology across the Cuprate Phase Diagram

CCOC - $x=0.12$

Overdoped TI2201

Quantitative agreement between single-particle and transport probes

TI2201 - $x=0.26$

YBCO - $x=0.10$

CCOC

High-$T_c$ Superconductor

QO – Doiron-Leyraud (07)

ARPES – Shen (05)

ARPES – Platé (05)

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

AMRO – Hussey (03)
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 ----)

Maanhart et al. MRS bulletin review

**Resp**

Electronic reconstruction – metallic interface
Influence of the La AIO3 thickness on a SrTiO3 substrate on the conductivity

Superconducting interface  SrTiO3/LaAlO3
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
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?

- Coulomb energy: $U = U_0 - \frac{e^2}{2D}$
- Charge transfer energy: $\Delta = \Delta_0 - \frac{e^2}{2D}$
- Band gap: $E_g = E_g^0 - \frac{e^2}{2D}$
Potential of a point charge in the neighbourhood of a dielectric

\[
\begin{align*}
\varepsilon_1 \nabla \cdot E &= 4\pi \cdot l \quad z > 0 \\
\varepsilon_2 \nabla \cdot E &= 0 \quad z < 0 \\
\nabla \times E &= 0
\end{align*}
\]

\[
\phi = \frac{1}{\varepsilon_1} \left( \frac{q}{R_1} + \frac{q'}{R_2} \right) \quad q' = -\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} q
\]

Energy to create a charge \( q \) at \( a \):

\[
E = -\int_0^Q \frac{1}{\varepsilon_1 2a} \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \right) q dq = \frac{Q^2}{4\varepsilon_1 a} \left[ \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right]
\]
Conventional wide band semiconductor – metal interface

\[ E_{\text{gap}} = \text{constant?} \]

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

\[ \Delta E_{\text{gap}} \sim 1 \text{eV} \]

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$_{6}$C$_{60}$") monolayer on Ag(111) and the surface layer of solid K$_{6}$C$_{60}$.


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

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)


Homogeneous Maxwell Equations

\[ \varepsilon(r, r') \rightarrow \varepsilon(r - r') \rightarrow \varepsilon(q) \]

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?
\[ E_{\text{pol}} = \frac{1}{2} \frac{\alpha e^2}{R^4}(Z) \]
\[ H_{\text{int}} = (U - 2zP) \sum_i n_{i\uparrow} n_{i\downarrow} + 2P \sum_{l,i} n_l n_{l+2a_i} \]

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)
FIG. 5. The effective Coulomb interaction on different organic molecules. The carbon polarizability is 0.56 Å³. 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
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

$$\Delta E \text{ (polarizability)} > W ; \quad \Delta E \approx \text{MO energy splitting in molecules, plasma frequency in metals}$$
We are alive because of Solvation

Ions both positive and negative in our bodies regulate most everything
Rough estimate
Atomic or ionic polarizability \( \sim \) volume

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

- For \( Z = 1 \) and 1 electron restoring force =
Reduction of $U$ due to polarizability of O2- (SOLVATION)

$$U = E_I^{TM} - E_A^{TM} - 2E_{pol}$$

$E_I$ ionization energy

$E_A$ electron affinity energy

$$E_I = E_I^0 - \sum \frac{1}{2} \alpha_i F_i^2$$

$$E_A = E_A^0 + \sum \frac{1}{2} \alpha_i F_i^2$$

$E_{pol} = 2 \sum \frac{1}{2} \alpha_i F_i^2$

For 6 nn of O2- ~ 13eV

For 4 nn As3- ~ 17eV

ELECTRONIC POLARON
What about intersite interaction $V$?

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

which reduces to $V = V_0 - 2\alpha E_1 \cdot E_2$, where 2 ref.

Can be repulsive or attractive depending on bond angle

For pnictides the Fe-As-Fe nn bond angle is $\sim 70$ degrees

Therefore the contribution to $V$ is attractive $\sim 4$ eV
Polarization cloud For Two charges on Neighboring Fe "ELECTRONIC BIPOLARON"

Mona Berciu et al PRB 79, 214507 (2009)
The Motion of a single quasi particle
These move like electronic polarons

\[ t_{eff} \]

i.e. the overlap integral of the polarization clouds

Mona Berciu et al PRB 79, 214507 (2009)
The effective polaron mass is simply $t/\text{teff} = 2.2$ this is light compared to conventional lattice polaron masses.

FIG. 3: (a) $t_{\text{eff}}/t$ and (b) $t'_{\text{eff}}/t'$ vs. $\Omega$, for a polarizability $\alpha_p = 7, 10$ and $12 \text{Å}^3$. The dots show the values used here.
Angular resolved photoemission comparison with LDA LaFePO
Lu et. al Nature 455, 81 2008

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

• Ionic CT and MH systems behave very differently at interfaces and surfaces (self doping?)
• Polar surfaces; Chemical, ionic, or electronic reconstruction. Systems that are multivalent may prefer electronic
• Electronic polaron effects for narrow band overlayers on highly polarizable systems
• Non uniform polarizability leads to strong reduction of U and peculiar nearest neighbor interactions which could be either repulsive or attractive
• DESIGN (ARTIFICIAL) STRUCTURES USING HIGHLY POLARIZABLE ATOMS OR SMALL MOLECULES ALTERNATING WITH NARROW BAND METAL FILM FOR HIGHER Tc’s?
collaborators

• Hiroki Wadati  UBC
• Subhra Gupta UBC
• Ilya Elfimov  UBC
• Andrea Damascelli UBC
• Mona Berciu
• David Hawthorn Waterloo
• Hao Tjeng Cologne/Dresden

• Harold Hwang Tokyo
• Peter Abbamonte Urbama
• Jeroen van den Brink Leiden/Dresden
• Jan Zaanen Leiden
• Susanne Stemmer UCSB
Effective interaction plotted vs log $T_c$

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.
Material design and limitations
NiO bulk

- O\textsuperscript{2-}: 2s\textsuperscript{2} 2p\textsuperscript{6}
- Ni\textsuperscript{2+}: 3d\textsuperscript{8}
- Rock salt structure
- AFM insulator (Exp. Gap \(\sim 4\text{eV}\))

**LSDA**

**LSDA+U**

\(U=8\text{eV J}=0.9\text{eV}\)
Electronic Surface Reconstruction in YBa$_2$Cu$_3$O$_{6+x}$
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)
- Electronic reconstruction of polar surfaces in K$_3$C$_{60}$: R. Hesper et al., PRB 62, 16046 (2000)
- High mobility electron gas at LaAlO$_3$ /SrTiO$_3$ interface
Abnormal T-linear susceptibility and Phase diagram of BaFe$_{2-x}$Co$_x$As$_2$ single crystals


FIG. 2: Temperature dependent resistivity for the BaFe$_{2-x}$Co$_x$As$_2$ 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$_x$As$_2$ 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