# Surfaces and Interfaces: Correlated Electron ~~Sys~~ Materials

© A J Millis
July 2002

- How do the characteristic behaviors of correlated electron materials change ~~at the~~ near an interface or surface (= material/vacuum int)

— Many questions: device engineering → basic physics

— Ability to find answers — now within reach

— Still: more questions than answers
more areas where the good question needs to be formulated

Here: present questions + a few basic concepts

— These lectures: mainly transition metal oxides

~~(I) Motivating Questions + Foundational Expts~~
~~(II) The polarization catastrophe~~
~~(III) The $LaTiO_3/SrTiO_3$ heterostructure~~
~~(IV) Colossal Magnetoresistance~~
~~(V) Prospects~~

(I) The Questions
(II) Some motivating experiments
(III) ~~Theory~~ polarization catastrophe
(IV) Theory
(V) The $LaTiO_3/SrTiO_3$ heterostructure
(VI) CMR heterostructures
(VII) Prospects

## The Questions

- Correlated electron materials: (TMO)
  - $La_{2-x}Sr_xCuO_4$ - high $T_c$
  - $La_{1-x}Sr_xMnO_3$ - "half metal" (pol. cond. band)
    - charge, orbital, mag. order
    - "colossal" MR + other enhanced respons
  - $V_2O_3$ - metal insulator transition

General: "exotic" electronic phases
enhanced response

~~Qn. how does this change near an interface~~
~~Both "academic" and practical relevance~~

Physics: d-orbital. Starts 5 x degen.
⇒ can hold 10 el.

~~occupancy~~ +physics strongly affected by
- ~~Carrier density~~
- Interaction effects: - $U_{dd} = E(N+1) + E(N-1) - 2E(N)$
  - Hund coupling (max spin state)
  -
- Ligand Field [split d-levels] ⇔ lattice
- Hybridization (electron itinerancy)
- Carrier density

In many materials, different states close by in energy are finely balanced
⇒ even small changes ⇒ big difference

- What is different about surface/interface
  - Surface: lower coordination (1 direction electrons can't go)
  - Different interaction.
    [U dep. on environment] - Sawatzky
  - Different crystal symmetry (typically lower)

Rules of thumb:
- lower coordination: less KE ⇒ more Us
- vacuum: less screening ⇒ larger U
- lower sym: less fluct., easier to localize.

⇒ CVO prl.
⇒ moore PRL

- Question not just academic
  $3(1-x) + 2(x) - 6 + [V_{Mn}] = 0 \Rightarrow V_{Mn} = 3+x$
  $\Rightarrow n_d = 4-x$

$La_{1-x}Sr_xMnO_3$: Mn: ≈ cubic environment
= $e_g$ $x^2-y^2$ $3z^2-r^2$
⇒ 5 Mn d: ≡ $t_{2g}$ ($d_{xy}, d_{xz}, d_{yz}$)

Interactions such that $4-x$ d $e^-$/Mn
3 in $t_{2g}$, max spin state,
$(1-x)$ in $e_g$. Spin "slaved" to $t_{2g}$ "core" spin.

Sawatzky: MgO $\quad$ Mg: $1s^2 2s^2 2p^6 3s^2$

Mg in MgO: $1s^2 2s^2 2p^6$ $\quad O^{2-}$

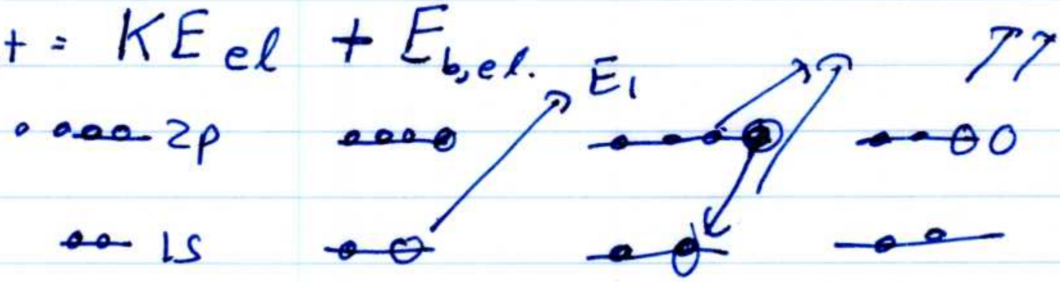
Would like to compare energy of $2p^6$, $2p^5$, $2p^4$: "U for holes": $E_{p^4} + E_{p^6} - 2E_{p^5}$

Abs ~ – Note: 2 holes: singlet: S, D
E not same: multiplet

· XPS: Blow 1 $e^-$ out of core.

$$E_{phot} = KE_{el} + E_{b,el.}$$

· Auger




⇒ 2 E out from 2p. in singlet state

$$E_{phot} = KE_1 + KE_2 + (2E_{2p} + U) - E_{1s}$$

$\Rightarrow H_{eg} = - t_{ij}^{ab} d^{+}_{ai} d_{bj} + H_{int} \mp J [\vec{S}_{ci} \cdot d^{+}_{i} \vec{\sigma} d_{i}]$

~~⇒ FM~~ .

in FM state: spin dep. chemical potential "$2JS_c$"


⇒ "half metal" (fully spin pol. cond. band)

⇒ material should be very effective "spin valve" for $T < T_c \approx 350 - 400K$

↳ (Sun)

⇒ something happens at interface different from bulk

~~etc~~
~~Electron XMCD~~
~~Surface physics of manganites~~

• Ex 2: orbital order:

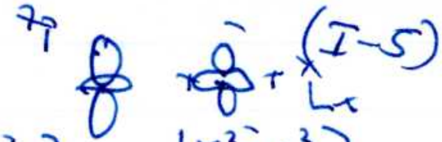
while $La_{1-x}Sr_xMnO_3$ is FM. met w bul

Planar $(La_{0.5}Sr_{1.5})MnO_4$ is insulating + orbitally ordered

Count: $.5 \times 3^+ + 1.5 \times 2^+ - 4 \cdot (2) = 3.5 = .5$ eg h

This eg goes into 1 of the 2 eg orbitals

insulator ⇒ definite pattern of orb occ




Basis for $e_g$: $|3z^2-r^2\rangle$ $|x^2-y^2\rangle$

$\Rightarrow$ approp. ln. comb. $|3x^2-r^2\rangle$ $|3y^2-r^2\rangle$

Bulk $La_{0.5}Sr_{1.5}MnO_4$ : plane

| | | | | |
|---|---|---|---|---|
| — | o | \| | o | — |
| o | — | o | \| | o |
| \| | o | — | o | \| |
| o | \| | o | — | o |
| — | o | \| | o | — |

$\Rightarrow$ period 4 in x, y

<u>What happens at surface:</u>

Recall Bragg scatt: bulk

$\infty$ periodic crystal

Suppose ~~...~~ perfectly ordered, $3d_\infty$ lattice cst a, b, c

~~Scattering amplitude:~~ $\Phi(x,y,z) = \sum_{n_x = -\infty}^{n_y, n_z} f(x-n_x a, y-n_y b, z-n_z c)$

$$\Phi_k = \int dx\,dy\,dz\, e^{i\vec{k}\cdot\vec{r}} f$$

$$= \sum_{n_x n_y n_z} e^{ik_x a n_x} e^{ik_y b n_y} e^{ik_z c n_z} f_{k_x k_y k_z}$$

only nonzero when Bragg condition obeyed

Suppose semi-infinite:

$$\sum_{n_z=0}^{\infty} \left( \sum_{n_x n_y = -\infty, \infty} e^{ik_x a n_x} e^{ik_y b n_y} f_{k_x k_y k_z} \right) e^{ik_z c}$$

$$\sum_{n_z=0}^{\infty} \left(e^{ik_z c\, n_z - \varepsilon n_z}\right) f_{k_\parallel, k_z} = \frac{f_{k_\parallel, k_z}}{1 - e^{ik_z c} e^{-\varepsilon}}$$

(↙ regularization)

⇒ away from Bragg peak: $\frac{f_{k_\parallel, k_z}}{1-e^{ik_z c}} \sim \frac{1}{i(k_z - G)c}$

Prob: $|\text{ampl}|^2 \sim \frac{1}{|\Delta k_z|^2}$ "Bragg Rod"

Now suppose top layer is different: $f^{n_z=0} \neq f^{n_z>0}$

$$Q_k = \frac{f_{k_\parallel, k_z}}{1-e^{ik_z c}} + \frac{f^{n=0} - f}{~~1~~} = \frac{f_{k_\parallel, k_z} e^{ik_z c}}{1-e^{ik_z c}} + f^{n=0}$$

If top layer is phase incoherent with lower layer

Scat prop: $\frac{|f_{k_\parallel, k_z}|^2}{4\sin^2\frac{k_z c}{2}} + |f^{n=0}|^2$

↳ decaying rpy ↳ not (or more slowly) decaying rpy

This picture oversimplified, but general idea seems to work

→ Hill

~~New~~ So far: different manifestations of old physics

Most intriguing possibility: some new physics

ex) proposal: Khalliulin. PRL 07

Recall high-$T_c$
— $x^2-y^2$: $1e^-$ (IX) ⇒ high $T_c$
— $3z^2-r^2$ filled $2e$
≡ $t_{2g}$: filled $6e^-$

Inference: 1 carrier in $x^2-y^2$ band is good for HTSC

Qn: How else might you get this

He says: Take $LaNiO_3$ ⇒ 3 holes in d-shell
Mott insulator, 2 holes in d-shell. Bad

=

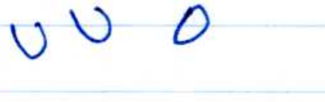
≡ $t_{2g}$ — Put in appropriate environment - split $3z^2-r^2$ d-level far enough away that $e^-$ only in $x^2-y^2$

Qn can this work?

Discussion so far: - surfaces (ill controlled)
QN: How "passivate" a TMO surface
- speculation

Rest of lectures: superlattice. Apparently better controlled system

Ohtomo, Muller Grazul Hwang. Nature 419 378 (2002)
"Oxide epitaxy" = "careful pulsed laser deposition"

Idea



Shoot calibrated "puffs" of ions at substrate, under appropriate oxygen pressure. Monitor result by high class scattering

- Can grow many "materials by design"

So far: mainly studied variants on "$ABO_3$" perovskite. structure.
- B site: simple cubic lattice. Latt. par ≈ 4Å
- O : in between each pair of B's
- A : body center of B cube

Typically: B site: electronically active
A site: controls carrier conc. on B

Simplest superlattice: change only A