Surfaces and Interfaces: Correlated Electron \& Materials © A.J. Mills
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- How do the characteristic behaviors of correlated electron materials change near an interface or surface (e.g. material/vacuum)?
- Many questions: device engineering vs. basic physics
- Ability to find answers—now within reach
- Still: more questions than answers, more areas where the good questions need to be formulated
- Here: present questions + a few basic concepts
- These lectures: mainly transition metal oxides

1. Motivating Questions + Foundational Expts
   - The polarization catastrophe
   - The LaTiO$_3$/SrTiO$_3$ heterostructure
   - Colossal Magneto-resistance
   - Prospects

1. The Questions
   - Some motivating experiments
   - Theory: polarization catastrophe
   - CMR heterostructures
   - Prospects
The Questions

- Correlated electron materials: CTMO
  \[ \text{La}_{2-x} \text{Sr}_x \text{Cu}_0 \text{O}_y \] - high Tc
  \[ \text{La}_{1-x} \text{Sr}_x \text{Mn}_0 \text{O}_3 \] - "half metal" (pol. cond. 5d)
  - charge, orbital, mag. order
  - "colossal" M\(\kappa\) + other enhanced response

\[ \text{V}_2\text{O}_3 \] - metal insulator transition

General: "exotic" electronic phases enhanced response

Qn. how does this change need a interfer

Both "academic" and practical relevance

Physics: d-orbital. Starts S x d degener.
3 can hold 10 el.

- physics
  - occupancy strongly affected by e
  - Interaction effects: \( U_{dd} = E(N+N) + E(N-1)-2E(N) \)
  - Hund coupling (max spin

- Ligand Field [split d-levels] \& lattice
- Hybridization (electron itinerant)
- Carrier density
In many materials, different states close by in energy are finely balanced; even small changes ⇒ big differences.

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

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

⇒ CVO pr.
⇒ moore pr.

- Question not just academic:

\[ 3(1-x) + 2x - 6 + \left[ 2(1-x) \right] = 0 \]
\[ \Rightarrow V_{\text{m}} = \frac{3+1}{3} \]
\[ \Rightarrow \text{nd} = 3+4-1 \]

La_{1-x}Sr_xMnO_3:
- Mn: 8 cubic environm
  \[ \text{eg} \quad x,y,z,\cdot \cdot \cdot \]
  \[ \Rightarrow S \text{ Mn d: } \quad \text{t}_{2g} \quad (\text{dx}_y,\text{dx}_z,\text{dy}_x) \]

Interactions such that: \[ 4-x \quad d^+e^-/Mn \]
- 3 in \text{t}_{2g}, max spn state
- \( (1-x) \) in \text{eg} spn "slabbed" to \text{t}_{2g} "core" spn.
Sawatzky: MgO  \[ \text{Mg: } 1s^2 2s^2 2p^6 3s^2 \]

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

Would like to compare energy of  \[ 2p^6, 2p^5, 2p^4 \]: "U for holes": \[ E_p + E_p - 2E_p \]
\[ \text{Abs} \text{ ~ Note: } 2 \text{ holes: } s, p \]
\[ \text{XPS: Blow 1 } e^- \text{ out of core}. \]

\[ E_{\text{phot}} = KE_{\text{el}} + E_{b, \text{el}} \]
\[ \text{Auger} \]
\[ \text{=} 2E_{\text{out}} \text{ from } 2p \text{ in } s, p \text{ sub.} \]

\[ E_{\text{phot}} = KE_1 + KE_2 + (2E_{2p} + U) - E_{1s} \]


\[ \text{Hag} = - t_{ij} \delta^+_i \delta^+_j + H_{\text{int}} + J \sum_{\sigma} \left( \delta^+_i \delta^+_j \delta^+_\sigma \delta^+_\sigma \right) \]

- In FM state: spin dep. chemical potential \( 2JS_c \)
- \( 2JS \) \( \Rightarrow \) "half metal" (fully spin pol. cond. band)

- Material should be very effective "spin value" for \( T < T_c \approx 350 \text{ to } 400 \text{ K} \)

\( \Rightarrow \) Sun

- Something happens at interface different from bulk

- Neel\( \rightleftharpoons \) Néel CD
- Neél\( \rightleftharpoons \) Neél phenomenon

- Ex 2: orbital order: met

  while \( \text{La}_{1-x} \text{Sr}_x \text{MnO}_3 \) is FM, \( x \neq 1 \)

  Plan \( \text{La}_{0.5} \text{Sr}_{1.5} \text{MnO}_3 \) is insulating + orbitally ordered

  Count: \( 5 \times 3^+ + 1.5 \times 2^+ - 4 \times 1^+ = 3.5 = 0.5 \text{eg} \text{ in Mn} \)

  This \( \text{eg} \) goes into 1 of the 2 \( \text{eg} \) orbitals

  Insulator \( \Rightarrow \) definite pattern of orbitals
Basis for eg: \( 13x^2 - r^2 \) \( 1x^2 - y^2 \)
\( \Rightarrow \) approx. In. carb. \( 3x^2 - r^2 \) \( 3y^2 - r^2 \)

Bulk \( La_{0.5}Sr_{0.5}MnO_4 \): planar

\[ \begin{array}{cccc}
 0 & 1 & 0 & 0 \\
 0 & 0 & 1 & 0 \\
 1 & 0 & 0 & 1 \\
 0 & 1 & 0 & 0 \\
 0 & 0 & 1 & 0 \\
\end{array} \]
period 4 mnx

What happens at surface:

Recall Bragg scatt: bulk

\( \infty \) periodic crystal

Suppose perfectly ordered, 3d\( \infty \)

\( \Phi(x, y, z) = \frac{\infty}{n_x \infty} f(x-nx, y-ny, z) \)

\( q_{nx} = \int dx dy dz e^{i\frac{2\pi x}{a}} f(x, y, z) \)

\( = \sum_{n_x, n_y} e^{i\frac{2\pi (x+nx)}{a}} e^{i\frac{2\pi (y+ny)}{b}} f_{nx, ny} \)

only non-zero w/ Bragg condition obeyed

Suppose semi-infinite:

\[ \sum_{n_x, n_y = 0} ^\infty \left( E \right) e^{i\frac{2\pi x}{a}} e^{i\frac{2\pi y}{b}} f_{nx, ny} \]
\[ \sum_{n_z=0}^{\infty} \left( e^{i h z c n_z - \varepsilon n_z} \right) f_{k11, k2} = \frac{f_{k11, h2}}{1 - e^{i h z c - \varepsilon}} \]

Away from Bragg peak:

\[ \frac{f_{k11, h2}}{1 - e^{i h z c}} \sim \frac{1}{i(kz - \varepsilon)c} \]

Prob: \( |\text{amp}|^2 \sim \left| \Delta k_z \right|^2 \) "Bragg Rod"

Now suppose top layer is different: \( f_{n=0} \neq f_{n=0} \)

\[ \Delta k = \frac{f_{k11, h2}}{1 - e^{i h z c}} + \frac{f_{n=0} - f_{n=0}}{i(kz - \varepsilon)c} = \frac{f_{k11, h2} e^{i h z c}}{1 - e^{i h z c}} + f_{n=0} \]

If top layer is phase incoherent with lower layer

Scat prob: \( \frac{1}{4} \mid f_{n=0} \mid^2 + \mid f_{n=0} \mid^2 \)

Decays slowly. \( \Delta \) not (or more slowly) decays at all

This picture oversimplified, but general idea seems to work

\( \rightarrow \text{Hill} \)
So far: different manifestations of old physics

Most intriguing possibility: some new physics

ex) proposal: Khaliullin. PRL 07
\[ e^{-x^2-y^2} \rightarrow 1e^- - (2x) \Rightarrow \text{high } T_c \]

Recall high-\( T_c \) \( \equiv \) \( 3z^2-r^2 \) filled \( 2e^- \)

Inference: 1 carrier in \( x^2-y^2 \) band is good for HTSC

Qn: How else might you get this

He says: Take \( \text{LaNi}_x \text{O}_3 \) \( \Rightarrow \) 3 holes n d-shell

Mott insulator, 4 holes n d-shell. Bad

\[ \equiv \text{t}z^2 \]

Put in appropriate environment.

split \( \text{d}\)-level far enough away

that \( e^- \) only n \( x^2-y^2 \)

Qn: Can this work?
Discussion so far:
- surfaces (all controlled)
  - QM: How "passivate" a TMO surface
  - speculation

Rest of lectures: super-lattice. Apparently better controlled system

"Oxide epitaxy" = "careful pulsed laser deposition"

Idea: shoot calibrated "puffs" of ions
- substrate at substrate, under appropriate oxygen pressure. Monitor result by high class scatterer
- can grow many "materials by design"

So far: mainly studied variants on "ABO\textsubscript{3}"
perovskite structure.
- B site: simple cubic lattice. Latt. par ∼ 4\AA
- 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 super-lattice: chage only A