Surfaces & Interfaces (II) [Millis]

- We shall consider explicitly superlattice of perovskite \( \text{ABO}_3 \)
  \- perovskite: \( A \) sits on corner of cubic lattice
  \- \( B \) sits on center of cubic lattice
  \- \( O \) sits on the faces of cubic lattice
- We shall assume \( B \) transition metal, \& \( A = \text{La, Sr, ...} \)
- The general superlattice is \( \text{001} \) (along cubic axes)
  - Homometallic: "\( A \)" changes, "\( B \)" stays the same
    - e.g. \( \text{LaTiO}_3 / \text{SrTiO}_3 \)
  - Heterometallic: "\( B \)" changes ("\( A \)" may or may not change)
    - case A: hard wall, e.g.
      - case B: different correlated material, e.g. \( \text{LaMnO}_3 / \text{YBa}_2\text{Cu}_2\text{O}_7 \)

- Fabrication methods (all variation on film)
  \- Oxide epitaxy
  \- MBE
  \- Pulsed Laser Deposition

- Image can be obtain because different atoms have different cross sections.
  \- But reality is often less "clean & clean" than the image suggests.

- Consider
  \[ 2^+ \ 3^+ \ 3^+ \ 3^+ \ 2^+ \ 2^+ \ 2^+ \]
  \[ \text{Sr} \ \text{La} \ \text{La} \ \text{Sr} \ \text{Sr} \ \text{Sr} \ \text{...} \]
  \[ \text{Ti} \ \text{Ti} \ \text{Ti} \ \text{Ti} \ \text{Ti} \ \text{Ti} \ \text{Ti} \ \text{...} \]
  \[ \text{naive:} \ 0.5 \ 1 \ 1 \ 0.5 \ 0 \ 0 \ 0 \]

- \( \text{LaTiO}_3 \) is Mott insulator, \( \text{SrTiO}_3 \) is band insulator
The charge distribution can be measured by TEM/EELS. Look for inelastic processes, in particular.

\[ \text{Ti: } 2p \rightarrow 3d \]

The Ti state with (say) +0.5 charge can be decomposed into superposition of +0 & +1 charge (not clear why it is just superposition).

Result: LA

One can also measure longitudinal Hall resistance to find carrier density.

Get \( \frac{2}{3} \) carrier per LA naively. Still close to \( \sim 1 \) as expected.

Now it is also possible to do optical measurement (drude peak).

In above TEM can truly resolve individual layers, while Hall probe/optical measure involve averaging between layers.

Magnetization can be seen at interface.

Consider LaMnO\(_3\)/YBa\(_2\)Cu\(_3\)O\(_7\).

Orbital occupation can be measured using polarized light.

| Bulk: holes found in \( |x^2-y^2| \) state |
| Interface: holes found ALSO in \( 13z^2-r^2 \) state |
Consider electrostatics of these superlattices.

Most ABO$_3$ perovskites are polar $\Rightarrow$ charges build up at termination of interface. 

\[ \text{e.g. } \text{LaAlO}_3 \quad \text{Al} - O - \text{Al} + 1 \]

\[ \text{La} - O - \text{Al} + 1 \]

Intuitively, this is why, from a material science perspective, for thicker polar layer in superlattice, quality of interface reduces.

To cure, introduce dipole layer at the end: \( C: \frac{1}{2} -1 +1 \ldots -1 +1 -\frac{1}{2} \)

This is why electron microscopy is hard to do in these materials, since the interface adjusts itself to produce the desired polar charge.

Sawatzky's insight is that in superlattice, the $\pm \frac{1}{2}$ charge layer can be obtained by having an 2D $e^-$ gas in the interface (hence interface $\Rightarrow$ more metallic)

Question: Do we have ion transfer or $e^-$ transfer?

For $\text{SrTiO}_3/\text{LaAlO}_3$, we have p-type $\&$ n-type

\[ \begin{array}{c}
\text{p-type:} & \text{Ti} & \text{Sr} & \text{Al} & \text{La} \\
\text{n-type:} & \text{Sr} & \text{Ti} & \text{La} & \text{Al}
\end{array} \]

For n-type find $-0.6 \, e^-$ & $\sim 0.15$ O vacancy

For p-type find $0 \, e^-$ & $\sim 0.3$ O vacancy

$\Rightarrow$ for some reason the material does not want to dope interface with holes.

Hetrometaltlic interface is less sharp than homometaltlic.

For $\text{LaAlO}_3/\text{SrTiO}_3$, the interface goes superconducting, but mobile carriers $\sim 0.1$ per cell.

Similarly, Hall measurement shows fewer mobile carriers.
SrTiO₃ is a bulk SC, but can only support few carriers.

Matching \( \Rightarrow \) can get interface SC up to 16 layers.

Consider \( LaAlO_3/SrTiO_3 \)

\[
E_p = n\Delta + \frac{1}{2} E_{comp} n^2 \sim e^2/\epsilon
\]

At the other surface, we need surface charge \( n_{surf} \) to make surface dipole cancel \( \Delta n \)

Combining,

\[
E = n\Delta + \frac{1}{2} E_{comp} n^2 - N E_p (1-2n)n + \frac{1}{2} E_p \left[ N(1-2n)^2 \right] \]

\[
\Rightarrow \quad n_{cell} = \left( \frac{N E_p + 2 N^2 E_{D} - \Delta}{E_{comp} + 4 N E_p + 4 N^2 E_{D}} \right)
\]

In experiment,

Classically,

\[
E = \Delta \sum_j n_j + \frac{1}{2} E_p \sum_j n_j^2 + \frac{2\pi e^2}{\epsilon c} \sum_{j \neq k} n_j n_k |j-k|
\]

Putting all \( n \) in \( 0^{th} \) layer, \( E = n\Delta + \frac{1}{2} E_p n^2 \)

If we have \( n=5 \) in layer 0, \& \( \delta \) in layer 1

\[
\Delta E = \delta (E_p - E_0) n + O(\delta^2)
\]

Thus only delocalized charge \( \delta \) \( E_0 \) \( E_p \) [hard!]

We've neglected e-hopping which will produce the desired charge spreading.