Looking for Leverage in New ARPES Beamlines

National Synchrotron Light Source II Workshop
Session on “Photoemission”
Wednesday, July 18, 2007

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Some experiences with assessing and avoiding surface effects in photoemission spectroscopy of correlated electron materials

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electron removal (and addition) to study single-particle behavior of many-body system

Spectroscopy of energy and momentum dependence of spectral weight

$$\rho(k,\omega) = \frac{1}{\pi} \text{Im} \left[ \frac{1}{\omega - \varepsilon_k - \Sigma(k,\omega)} \right]$$

of single particle Green’s function

Both processes together give unbound hole/electron pair the RIGHT WAY TO DEFINE INSULATOR GAP!
Einstein’s photoelectric effect to measure removal part of $\rho(k,\omega)$

Undulator device inserted in synchrotron electron beam gives intense light.
Photoemission spectroscopy (and its inverse) to measure $\rho(k,\omega)$ or $k$-summed $\rho(\omega)$

Angle variation moves on spherical k-space surfaces.

Vary photon energy to change $k_z$

Full electronic structure @ fixed photon energy —3D data set—

Cross-section resonances at core level absorption edges = RESPES

High photon energy gives Larger elastic escape depth $\Rightarrow$ Greater bulk sensitivity

angles, energies $\Rightarrow k$
Fermi Surface Mapping of a 3D metal

ALS – early 1990’s
E. Rotenberg, J. D. Denlinger

Cu (100) $h\nu=83$ eV

k-space (repeated zones)

Constant energy measurement surface

- Plane wave final state
- Surface refraction included
  ($inner potential = 8.8$ eV)
ARPES data acquisition for three dimensional materials

- For a fixed photon-energy:

(1) Parallel angle detection (unit of acquisition)
(2) Vary sample or detector angle
(3) Assemble volume electronic structure
(4) Extract $E_F$ slice, i.e. "Fermi Surface" map
(5) Assemble $hv$-dependent 3D data set of FS maps
Anderson impurity model and emergent Kondo behavior

- **Ground State Singlet**
- Spin entropy quenched for $T \ll T_{\text{Kondo}}$

- $N_f$ fold degenerate local orbital hybridized to conduction band
  - Binding energy $\varepsilon_f$
  - Hybridization $\Delta (\varepsilon) = \pi D(\varepsilon) V(\varepsilon)^2$
  - Local Coulomb Interaction $U_{ff}$
  - Spin orbit splitting $\Delta_{\text{LS}}$

**Low Energy Scale $T_K$:**

$(U_{ff} \rightarrow \infty, f^0 \leftrightarrow f^1, \Delta_{\text{LS}}=0, )$

$k_B T_K = E_F \exp (-1/J)$

$J = N_f \Delta / \pi \varepsilon_f$

- Very fast dependence on $J$ !
- Ground State Singlet
- Spin entropy quenched for $T \ll T_{\text{Kondo}}$
Quasi-particle of Anderson impurity model

Kondo / Suhl-Abrikosov resonance

A Fermi energy peak implied by Friedel Sum Rule (Langreth) for fixed $n_f$

$$\rho_f(\omega=E_F) = \rho_f^0(\omega=E_F)$$

Effective mass = band mass / $Z$

Can be very large for small $T_K$
Spectra from photoemission and x-ray inverse photoemission (Xerox PARC) samples: (Maple, UCSD) 

Allen et al PRB 1983

Fig. from Allen et al Adv. in Physics 1985

Spectral theory: Gunnarsson & Schönhammer PRL 1983

“Kondo Volume Collapse”

Ce $\alpha$ phase $E_K$ large $\gamma$ phase $E_K$ small

Allen & Martin PRL ’82 Allen & Liu PRB ‘92
Some historical perspective

Fallout from Ce RESPES on 2 eV binding energy and Kondo resonance findings of 1978-1981

- You don’t measure the right thing.
  “Not the binding energy in the ground state.”
  “High energy photon too brutal for delicate Kondo physics”
  fundamental misunderstandings--mostly gone now.

- You have crummy resolution.     wow, Scienta

- Couldn’t you do it k-resolved? making real progress.

- You only measure the surface. even larger issue now
  (Suga SPring-8 beamline really important step forward)
Ever more important exactly because of:

- improved resolution
- emphasis on ARPES
- more sophisticated questions asked—e.g. Fermi surfaces, lineshapes, FL vs. NFL

Two general issues:

- surface/bulk electronic structures, how different?
- surface inhomogeneous?
Surface effects

My General Impressions:

- understanding for solid samples still mostly ad hoc, empirical, but starting to understand some principles

- microscopy really scary—but also correlation between spectrum quality and visual appearance low
  e.g. Seamus Davis STM for cuprates

- small measurement area really important

- still must consider on case by case basis --- can’t reliably predict or generalize
Surface effects – some general principles

Reduced coordination the basic origin of bulk/surface difference

Surface states from altered potential

long lived if occur in energy gap
of bulk band structure projected to surface

study theoretically with repeated slab calculations

Particularly likely on polar non-neutral surfaces
Surface effects for strongly correlated systems

- Reduces bandwidth on surface
  \[ \Rightarrow \text{reduced } t/U \]

- Surface cohesive energy less than bulk
  \[ \Rightarrow \text{surface binding energy } |E| \text{ of local orbital increased} \]
  B. Johansson, PRB 19, 6615 (1979)
  and so ....
  \[ |E(\text{corner atom})| > |E(\text{edge atom})| > |E(\text{smooth surface})| \]

Experimental Verification by M. Domke et al, PRL 56, 1287 (1986)

Smooth Tm metal surfaces: shifted surface trivalent peaks
Rough Tm metal surfaces: also show trivalent peaks
Mott-Hubbard metal-insulator transition
new view from “Dynamic Mean Field Theory”
(Vollhardt, Metzner, Kotliar, Georges ≈ 1990)

DMFT: lattice ⇒ a self-consistent
Anderson impurity model (exact
in ∞ dimensions -- finds Σ(k,ω) = Σ(ω) )

Hubbard model for
Mott transition

Kondo physics—moment loss &
Suhl-Abrikosov/Kondo resonance
Mott-Hubbard metal-insulator transition
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And. Imp.  Bath elec

hopping t  repulsion U

U/t small  U/t large
T-dependent LDA + DMFT (QMC) theory compared to PM phase low $h\nu$ photoemission for $V_2O_3$.

- $U=5.0\text{eV}, T=1160\text{ K}$
- $U=5.0\text{eV}, T=700\text{ K}$
- $U=5.0\text{eV}, T=300\text{K}$
- \text{Schramme et al.}
  $h\nu=60\text{eV}, T=300\text{K}$

LDA + DMFT (QMC) at 1160K compared favorably to 300K 60 eV data (Held et al, PRL ‘01)

But theory peak sharpens up with decreasing T.

Shows large disagreement with data for same T.
Early evidence of bulk/surface difference for $V_2O_3$

J.-H. Park thesis
NSLS “dragon” beamline (Univ. of Michigan 1994)

Systematic reduction of near $E_F$ peak in metallic phase for low photon energy relative to high photon energy implies surface effect
Qualitative energy dependence of inelastic mean free path

Curve not really “universal”

Seah and Dench (1979)
Early evidence of bulk/surface difference for $V_2O_3$

Systematic reduction of near $E_F$ peak in metallic phase for low photon energy relative to high photon energy implies surface effect but resolution not good at high photon energy at that time.

J.-H. Park thesis NSLS “dragon” beamline (Univ. of Michigan 1994)

Early evidence of bulk/surface difference for $V_2O_3$
Angle integrated bulk sensitive spectra for Mott transition in $(V_{1-x}Cr_x)_2O_3$

Experiment: SPring-8 BL 25SU (S. Suga)
- \(h\nu = 500-700\) eV total \(\Delta E \approx 90\) meV
- Cleaved single crystals from P. Metcalf, Purdue


“Kondo peak” theory and experiment in M phase

Previous work, 30 years NO M phase peak

Surface layer more correlated than bulk
Crystal structure and surface layer

- Crystal structure:
  - \( a = 4.95 \text{ Å} \)
  - \( c = 14.0 \text{ Å} \)

- Surface-layer thickness = 2.44 Å

- (10\bar{1}2) cleavage plane

- \( d = 4.95 \text{ Å} \)

- Vanadium
- Oxygen
Small spot also essential for large $E_F$ peak!

With small spot can select probing point to avoid steps, edges, strain as much as possible.

$E_F$ peak much reduced with larger spot.

Difference for 300 eV to 500 eV range even larger.

Steps, edges have even lower coordination than smooth surface.
High photon energy ARPES is possible!
E.g. \( \text{Sr}_{2-x}\text{Ca}_x\text{RuO}_4 \) (\(x=0, 0.2\)) Sekiyama et al, cond-mat/0402614

EDC’s for various directions in Brillouin zone

Fermi surface maps: (b) and (d) are schematic comparisons to theory

Low photon energy -- quench surface states to see bulk electronic structure
High photon energy -- just cleave and measure
Have tried to FS map by ARPES at SPring-8

Hints of data but just not enough beamtime to do systematic job.
LDA for LaRu$_2$Si$_2$ and CeRu$_2$Si$_2$ compared

Overview from summary and review papers by Zwicknagl and her collaborators

band 4
Z- hole pocket

La

Ce
LaRu$_2$Si$_2$

3D Fermi surface mapping

Full 3D character of FS observed by fine-angle maps at fixed photon energies & by fine photon-energy-step $k_z$-dependent slice at fixed angle.

samples from J.L. Sarrao (LANL)
**Fermi volume change at Kondo temperature: the f-electron in CeRu$_2$Si$_2$**

Luttinger counting theorem $\Rightarrow$

- f-electrons counted in Fermi volume IF magnetic moments quenched (as in Kondo effect)

Conjecture (Fulde & Zwicknagl, 1988)

- f-electrons excluded from FS above Kondo temperature $T_K$

Difficult to test with low-T dHvA.

Paradigm (dHvA) (Tautz et al, 1995)

- **large Z-point hole FS** $f^0$ LaRu$_2$Si$_2$

- **reduced "pillow" hole FS** counts $\approx \frac{1}{2}$ Ce f-electron in Kondo CeRu$_2$Si$_2$ --at temperature below $T_K$

- $\mathbf{LDA}$ "band 4" hole Fermi surface no f-electron

- $\mathbf{\approx \frac{1}{2}}$ extra f-electron here

( $\approx \frac{1}{2}$ f-electron in other multiply-connected complex FS piece)
CeRu$_2$Si$_2$ ARPES good and bad cleaves
Evidence that bulk behavior can be seen in 4d RESPES of this material

(a) and (b) ARPES from center of normal emission Z-point

(d) Ce 3d edge RESPES with 0.2 eV resolution (consistent with SPring-8 data)

(c) angle summed 4d edge RES-ARPES

J. D. Denlinger et al, Physica B 312-313, 670 (2002)
CeRu$_2$Si$_2$ why bulk at low $\nu$?

Two cleavage planes -- with and without Ce i.e. buried active layer -- important for Bi 2212 cuprate

- Atomic layer stacking in XRu$_2$Si$_2$ structure + preferential cleave between Ru-Si $\Rightarrow$ no surface (less coordinated) rare-earth atoms (except for steps / surface roughness)
- Bulk-like spectra obtained at even 100 eV similar lineshape to high photon energy spectra
Same large hole FS for LaRu$_2$Si$_2$ and CeRu$_2$Si$_2$ for $T \approx 120K > 6T_K \Rightarrow f$-electrons excluded from FS!

XRu$_2$Si$_2$ review: J. D. Denlinger et al, JESRP 117, 8 (2001)

Same conclusion from 2d angular correlation of positron annihilation studies—(Monge et al, PRB, 2002) but didn't actually measure the "pillow"
More surface effects: EuB$_6$

Time dependent relaxation of a polar surface

- Covalent bonded B$_6$
- Ionic bonding: Eu$^{2+}$ & B$_6^{(2-)}$

### Time-dependent size of X-point electron pocket

- Time-dependent surface-shifted Eu 4f state →

### Surface slab calculation:
1. Surface state in bulk gap
2. Surface-shifted Eu 4f

→ Surface slab calculation:
1. Surface state in bulk gap
2. Surface-shifted Eu 4f

- Covalent bonded B$_6$
- Ionic bonding: Eu$^{2+}$ & B$_6^{(2-)}$

**Model**

- t = 0 (Cleave)
  - Statistically 50% Eu-terminated
- t < t$^*$
  - Clustering of mobile surface Eu atoms
- t > t$^*$
  - Residual gas adsorption

w/ Z. Fisk (UC Irvine), B. Delley (Paul-Scherrer Institut), R. Monnier (ETH-Zurich)
EuB$_6$ --kill surface effects to see bulk

- **Surface:** electron-rich Eu-termination $\Rightarrow$ X-point electron pockets
  + higher binding energy-shifted Eu 4f state
- **Bulk:** hole-like pockets just touch $E_F$ (p-type) $\Rightarrow$
  observe exchange splitting for $T<T_C$
  $\Rightarrow$ bulk Ferromagnetism in EuB$_6$ likely from superexchange (like EuO)

w/ Z. Fisk (UC Davis), B. Delley (Paul-Scherrer Institut), R. Monnier (ETH-Zurich)
EuB$_6$ bulk valence band exchange splitting now observable below ferromagnetic $T_c$
YbBiPt

- 8 maps span full FS along <111> oriented cleave surface probed; bulk very near Yb 3+
- 3-fold symmetry & $k_z$-stacking observed in Fermi surface
- First ARPES Fermi surface map of any Yb-compound
- Small photon spot essential to get this data

heaviest Fermions
$\gamma \sim 8000 \text{ mJ/mol-K}$

FIG. 2. Low-temperature specific heat $C_p(T)$ of YbBiPt between 0.09 and 0.85 K. Inset: Same data as $C_p/T$ vs $T$. w/ Z. Fisk (UC Irvine)
Surface effects always lurking

- "Ordinary" surface states are present (polar surfaces particularly unstable)

- Correlated systems especially vulnerable because of sensitivity to changes in bandwidth/U

- Steps and edges and other surface inhomogeneities can greatly enhance bulk to surface differences

- Buried active surfaces can give bulk data but usually require a "lucky cleave"

High photon energies and very small photon spots offer best protection