Emerging Photoemission Techniques for Probing Buried Layers and Interfaces: HAXPES, HARPES and SWARPES

Alexander Gray
Department of Physics, University of California, Davis
Materials Sciences Division, Lawrence Berkeley National Laboratory
Currently at SLAC National Accelerator Laboratory

Funded by the U.S. Department of Energy, U.S. Army Research Office, and the Humboldt Foundation
# Measurements

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<tr>
<th>Authors</th>
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<tr>
<td>A. X. Gray(^1,2)</td>
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<tr>
<td>C. Papp(^3)</td>
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<td>B. Balke(^4)</td>
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<td>G. Conti(^2)</td>
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<td>D. Eiteneer(^1,2)</td>
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<td>A. Greer(^1,2)</td>
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<td>A. Rattanachata(^1,2)</td>
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<td>S. Nemšák(^1,2)</td>
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<td>S. Döring(^5,14)</td>
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<td>E. Rotenber(^6)</td>
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<td>A. Bostwick(^6)</td>
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<td>L. Morescini(^6)</td>
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<td>E. Gullikson(^6)</td>
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<td>S. Ueda(^7)</td>
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<td>Y. Yamashita(^7)</td>
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<td>K. Kobayashi(^7)</td>
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<td>V. N. Strokov(^8)</td>
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<td>M. Kobayashi(^8)</td>
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<td>J. Fujii(^9)</td>
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<td>G. Panaccione(^9)</td>
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<td>C. M. Schneider(^14)</td>
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<td>C. S. Fadley(^1,2)</td>
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# Sample Synthesis

<table>
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<tr>
<td>M. Huijben(^10)</td>
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<td>D. H. A. Blank(^10)</td>
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<td>P. R. Stone(^11)</td>
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<td>O. D. Dubon(^11)</td>
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<td>J. Son(^12)</td>
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<td>S. Stemmer(^12)</td>
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# Theory

<table>
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<tr>
<td>J. Minár(^13)</td>
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<td>J. Braun(^13)</td>
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<td>H. Ebert(^13)</td>
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<td>L. Plucinski(^14)</td>
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<td>A. Winkelmann(^15)</td>
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<td>S.-H. Yang(^16)</td>
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<td>A. Janotti(^9)</td>
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<td>C. Van de Walle(^12)</td>
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<td>F. M. F. de Groot(^17)</td>
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# Institutions

\(^1\)UC Davis, \(^2\)LBNL, \(^3\)University of Erlangen, \(^4\)University of Mainz, \(^5\)University of Dortmund, \(^6\)ALS, \(^7\)SPRING-8, \(^8\)SLS, PSI, \(^9\)TASC, Elettra, \(^10\)University of Twente, \(^11\)UC Berkeley, \(^12\)UCSB, \(^13\)Ludwig-Maximilians-Universität München, \(^14\)Research Center Jülich, \(^15\)MPI Halle, \(^16\)IBM Almaden, \(^17\)Utrecht University

*Funded by the U.S. Department of Energy, U.S. Army Research Office, and the Humboldt Foundation*
Outline

• Hard X-ray Photoemission (HAXPES)
  • Metal-to-Insulator Transition in LaNiO$_3$

• Hard X-ray Angle-Resolved Photoemission (HARPES)
  • W, GaAs, and Ga$_{0.97}$Mn$_{0.03}$As

• Standing-Wave Excited ARPES (SWARPES)
  • La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ Interface

• Summary and Future Outlook
Hard X-ray Photoemission (HAXPES)
How much Deeper does Photoemission Probe with Hard X-Rays?

Traditional soft X-ray XPS is heavily influenced by surface effects

With multi-keV excitation

~ 4-5× deeper than soft x-ray XPS

We can obtain more accurate BULK electronic structure

Energy resolutions down to 50 meV (→10 meV in future)
Angular resolutions to 0.2° (→0.02° in future)

Places to do HAXPES

- Diamond
- Soleil
- Lund

- Existing
- Under construction

- ALS 9.3.1
- CLS
- SSRL
- NSLS X24A
- Our group

11/20/2011
Materials Science Division. Fadley Group.
Facility for hard x-ray photoemission at the ALS: Based largely on existing beamline and end station-in progress

(~5-10x faster than BL X24A at NSLS-1-the only HXPS show in the US)


4th International HAXPES Workshop, DESY, Hamburg, Sept. 2011
http://haxpes2011.desy.de,
With most talks available at:
https://indico.desy.de/materialDisplay.py?materialId=slides&confId=3713

Reviews:
Kobayashi, NIMA 601, 32 (2009)
Conductivity (J. Son, S. Stemmer)

Mott Materials

- For ultra-thin films, strong electron correlations cause an insulating state when conventional theory predicts metallic behavior.

- This has great promise for applications, if the transition can be controlled.

- Materials are on the verge of metal-to-insulator transition.

- Dramatic Changes in properties: electrical, optical and magnetic.

- Among the least understood phenomena in condensed matter physics.

Mottronics

J. Son et al., APL 96, 062114 (2010)
Application of HAXPES
Mott Behavior in LaNiO$_3$ Epitaxial Thin Films

Conductivity (J. Son, S. Stemmer)

Epitaxial layers with TEM thickness det’n.
(J. Son, J. LeBeau, S. Stemmer)

Sample Set 1:
LAO Substrate

Sample Set 2:
LSAT Substrate

J. Son et al., APL 96, 062114 (2010)
Hard X-ray Photoemission at $h\nu=5.95$ keV

Probing ~70 Å into the sample

Experiment with S. Ueda, K. Kobayashi

11/20/2011
Materials Science Division. Fadley Group.
Hard X-ray Photoemission at $hv=5.95$ keV

Probing $\sim 70$ Å into the sample

Experiment with S. Ueda, K. Kobayashi
Substrate Core-Peak Photoemission Spectra

Core peaks originating from the substrate lose intensity as the overlayer thickness becomes larger: $I_{\text{LSAT}} \propto e^{t_{\text{LNO}}/\Lambda_{\text{EAL,LNO}}}$

- 2.8 nm LNO
- 4.2 nm LNO
- 11.1 nm LNO
- 17.6 nm LNO

Al 1s

Al 2s

Al 2p

Ni 3p

Ta 4p$_{3/2}$

Ta 4f

Sr 3s

Binding Energy (eV) 1562 1560 1558 1556

Binding Energy (eV) 122 120 118 116 114

Binding Energy (eV) 75 70 65

Binding Energy (eV) 410 400 390

Binding Energy (eV) 28 27 26 25 24

Binding Energy (eV) 365 360 355 350
Effective attenuation lengths for the photoelectrons can be calculated by analyzing core peak intensities according to: $I_{\text{substrate}} \propto e^{-t/E_{\text{AL}}}$.
LNO EALs within ~20% of the much-used semi-empirical TPP-2M formula, if corrected for elastic scattering

Remaining expt./theory discrepancy may be due to lack of resonant absorption edges in theory: an effect not considered previously

Valence-band spectra can now be decomposed into the film and substrate DOS components using the EALs and

\[ I^{(0)}_t = [1 - e^{-t/\Delta_{EAL}}] I_{LNO,t} + e^{-t/\Delta_{EAL}} I_{LAO(\text{LSAT}),t} \]
A gap opening consistent with a metal-to-insulator transition is observed for the thinnest (2.7 nm) LaNiO$_3$ film on an LSAT substrate.

Gray et al., PRB 84, 075104 (2011)
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Hard X-ray Angle-Resolved Photoemission (HARPES)
How much Deeper does Photoemission Probe with Hard X-Rays?


Traditional ARPES is heavily influenced by surface effects
With multi-keV excitation

~ 5-20× deeper than ARPES

We can obtain more accurate BULK electronic structure
Angle-Resolved Photoemission at High Energies
What and Where is the “XPS Limit”? 

- Low photoelectric cross sections $\rightarrow$ d- and f- states are suppressed
- Magnitude of the wavevector associated with the final photoelectron momentum increases. $\rightarrow$ Brillouin zone averaging
- The magnitude of the photon momentum cannot be ignored anymore. $\rightarrow$ Must consider shifts due to photon-electron interactions
- Recoil can shift energies and broaden features, esp. lighter atoms
- The effects of phonon creation and annihilation must be considered

The Debye-Waller Factor
Estimate of the Fraction of Direct Transitions

Debye-Waller Factor =

More than 50% band sensitive

Mix of bands and D.O.S.

W(110) First Experimental Data ($h\nu=5.95\text{keV}$)

Detector Angle ($^\circ$)

-4 -2 0 2 4 6

Binding Energy (eV)

0 2 4 6 8 10

T = 300 K (Raw data)

T = 30 K (Corrected)

DOS

$\approx$$\int I(E, \theta)d\theta$

$N' (E) = \int I(E, \theta)d\theta$

$D.W. = 0.09$

$D.W. = 0.45$

Probing 60 Å into the bulk

Gray et al., Nature Mat. 10, 759 (2011)
W(110) First Experimental Data ($h\nu=5.95\text{keV}$)

- **Detector Angle ($\theta$)**
  - $-4 -2 0 2 4 6$
  - **DW = 0.09**
  - **D.O.S.**
  - **T = 300 K (Raw data)**

- **Binding Energy (eV)**
  - $0 2 4 6 8 10$

- **Probing 60 Å into the bulk**

- **Detector Angle ($\theta$)**
  - $-4 -2 0 2 4 6$
  - **DW = 0.45**
  - **T = 30 K (Corrected)**

- **DOS**
  - $\approx \int N(E) I(E, \theta) d\theta$

- **Free-electron theory**
  - Plucinski

- **One-Step Theory**
  - Minar

- **T = 30 K (Raw data)**
  - $-4 -2 0 2 4 6$

- **T = 30 K (Corrected)**
  - $-4 -2 0 2 4 6$

- **Exp t**
  - $N(\theta) \approx \int l(E, \theta) d\theta$

- **Exp t**
  - $N'(E) I(E, \theta) d\theta$
The Debye-Waller Factor
Estimate of the Fraction of Direct Transitions: GaAs

HARPES of GaAs ($h\nu = 3.24$ keV, IMFP = 57Å)

Detector Angle (°)

Binding Energy (eV)

T = 300 K (Raw Data), $W = 0.01$, $h\nu = 3238$ eV

T = 20 K (Raw Data), $W = 0.31$, $h\nu = 3238$ eV

VG Scienta R4000
Electron Analyzer

GaAs (001)

BL15XU
$hv = 3.24$ keV

SPRIng+ 8
HARPES of GaAs ($h\nu = 3.24$ keV, IMFP = 57Å)

T = 300 K (Raw Data), $W = 0.01$, $h\nu = 3238$ eV

T = 20 K (Raw Data), $W = 0.31$, $h\nu = 3238$ eV

VG Scienta R4000 Electron Analyzer

HARPES of GaAs ($h\nu = 3.24$ keV, IMFP = 57Å)

T = 20 K (Corrected)

11/20/2011

Materials Science Division. Fadley Group.
HARPES of GaAs ($h\nu = 3.24$ keV, IMFP = 57Å)

T = 300 K (Raw Data), $W = 0.01$, $h\nu = 3238$ eV

T = 20 K (Raw Data), $W = 0.31$, $h\nu = 3238$ eV

T = 20 K (Corrected)

Detector Angle (°)

11/20/2011

Materials Science Division. Fadley Group.
HARPES of GaAs \((h\nu = 3.24\ \text{keV}, \ \text{IMFP} = 57\text{Å})\)

- For the raw data at 300 K, the parameters are: \(T = 300\ \text{K}\), \(W = 0.01\), \(h\nu = 3238\ \text{eV}\).

- For the raw data at 20 K, the parameters are: \(T = 20\ \text{K}\), \(W = 0.31\), \(h\nu = 3238\ \text{eV}\).

- For the corrected data at 20 K, the parameters are: \(T = 20\ \text{K}\), \(W = 0.31\), \(h\nu = 3238\ \text{eV}\), with the addition of the free-electron theory label.
HARPES of (Ga,Mn)As \((h\nu = 3.24\text{ keV})\)
HARPES of (Ga,Mn)As ($hv = 3.24$ keV)

Experiment

$hv = 3.24$ keV

Difference

One-Step Theory

GaAs

Ga$_{0.97}$Mn$_{0.03}$As

Ga$_{0.95}$Mn$_{0.05}$As

Experiment

One-Step Theory

Photoemission Intensity (arb. units)

Binding Energy (eV)

GaAs

GaMnAs

GaMnAs-GaAs

GaMnAs-GaAs (Smoothed)
HARPES of (Ga,Mn)As \((hv = 3.24\text{ keV})\)

**Experiment**
\((hv = 3.24\text{ keV})\)

**One-Step Theory**

**Difference**

**GaMnAs**

**Mn only**
HARPES of (Ga,Mn)As ($h\nu = 3.24$ keV)

S. Ohya et al., Nature Physics 7, 342 (2011)
Outline

• Hard X-ray Photoemission (HAXPES)
  • Metal-to-Insulator Transition in LaNiO₃

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  • W, GaAs, and Ga₀.₉₇Mn₀.₀₃As

• Standing-Wave Excited Photoemission (SWARPES)
  • La₀.₇Sr₀.₃MnO₃/SrTiO₃ Interface

• Summary and Future Outlook
Standing-Wave Excited Photoemission

<table>
<thead>
<tr>
<th>Material</th>
<th>4 u.c. (Å)</th>
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<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>15.61</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$</td>
<td>15.51</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>15.61</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$</td>
<td>15.51</td>
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<tr>
<td>SrTiO$_3$</td>
<td>15.61</td>
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<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$</td>
<td>15.51</td>
</tr>
</tbody>
</table>

1st order Bragg:
\[ \lambda_x = 2d_{ML}\sin \theta_{Bragg} \]

\[ \lambda_{SW} = \frac{\lambda_x}{2\sin \theta_{inc}} \approx d_{ML} \]

\[ h\nu = 833.2 \text{ (ALS- (La 3d}_{5/2}\text{ res.)}} \]
and
5956 eV (SPring-8)

2 Samples: 48X and 100X

Sample:
M. Huijben,
D. H. A. Blank
R. Ramesh

A. X. Gray, C. Papp et al.,
PRB 82, 205116 (2010).

SrTiO$_3$ Substrate
Experimental Results

$$h\nu = 833.2 \text{ eV}$$

$$h\nu = 5956.4 \text{ eV}$$

- Sr 3p$_{3/2}$
- Bragg
- Kiessig
- Ti 2p$_{3/2}$
- O 1s

- La 4d$_{5/2}$
- Mn 3p
- C 1s

Incidence Angle (°)
Fitting to X-ray Optical Calculations

Exp. Cal.

hv = 833.2 eV

<table>
<thead>
<tr>
<th>Sr 3p\textsubscript{3/2}</th>
<th>Ti 2p\textsubscript{3/2}</th>
<th>O 1s</th>
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</thead>
<tbody>
<tr>
<td>Bragg</td>
<td>Kiessig</td>
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hv = 5956.4 eV

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<tr>
<th>Sr 3p\textsubscript{3/2}</th>
<th>Ti 2p\textsubscript{3/2}</th>
<th>O 1s</th>
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<tbody>
<tr>
<td>La 4d\textsubscript{5/2}</td>
<td>Mn 3p</td>
<td></td>
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1.80 1.85 1.90 1.95

0.85 0.90 0.95 1.00

C 1s

13.0 13.5 14.0 14.5 15.0

0.85 0.90 0.95 1.00

C 1s

S. H. Yang, A. X. Gray et al., JESRP (submitted).
Resulting Structure for the \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3 \) Interface and Multilayer

- Interface has interdiffusion/roughness and altered dielectric constant
- Average multilayer period changes by about -1 Å or -6% from top to bottom
Standing-Wave Excited ARPES (SWARPES)

Probing Bulk LSMO

Probing Interface LSMO

A. X. Gray, J. Minár et al., (in preparation)
Standing-Wave Excited ARPES (SWARPES)

\[ h\nu = 833.2 \text{ eV (still)} \]
\[ T = 20 \text{ K} \]
\[ \sim \text{ARPES limit with Photoemission Debye-Waller} \]
\[ W(20\text{K}) \rightarrow \sim 75\% \text{ k-conserving transitions} \]

Beamline 7.0 ALS
With A. Bostwick, E. Rotenberg
Depth-Resolved ARPES: Bulk LSMO

Probing Bulk LSMO (max. Bulk sensitivity)

$\nu = 833.2$ eV

$T = 20$ K
X-Ray Diffraction Effects in the Data

Experiment: Mn 3p

XPD Theory: Mn3p

Experiment: Fadley Group

Theory: A. Winkelman
X-Ray Diffraction Effects in the Data

Experiment: Mn 3p

XPD Theory: Mn3p

Theory: A. Winkelman
Probing **Bulk LSMO** (max. Bulk sensitivity)

- **hv** = 833.2 eV
- **T** = 20 K

**Depth-Resolved ARPES: Bulk LSMO**

**Rocking Curves**: Ti 2p$_{3/2}$, Mn 3p

**Valence Bands**: 1, 2, 3, 4, 5

**Tilt Angle (β)**: 0°, 10°, 20°

**Detector Ch. / Angle θ**: 200, 400, 600, 800

**Color Scale**:
- 100%
- 80%
- 60%
- 40%
- 20%
Depth-Resolved ARPES: Bulk LSMO

Probing Bulk LSMO (max. Bulk sensitivity)

$hv = 833.2 \text{ eV}$
$T = 20 \text{ K}$

Corrected for XPD
Depth-Resolved ARPES: Interface LSMO

Probing Interface LSMO (max. Interface sensitivity)

$\text{hv} = 833.2 \text{ eV}$

$T = 20 \text{ K}$

Corrected for XPD
Depth-Resolved ARPES: Bulk - Interface

- $h\nu = 833.2 \text{ eV}$
- $T = 20 \text{ K}$

**Rocking Curves**

- **Ti 2p$_{3/2}$**
- **Mn 3p**

**Valence Bands**

- Incidence Angle (°)
- Binding Energy (eV)

**Tilt Angle ($\beta$)**

- 1 = Mn3d $e_g$
- 2 = Mn3d $t_{2g}$

**Detector Ch. / Angle $\theta$**

- 3
- 4
- 5

**Color Scale**

- 4.5%
- 3.0%
- 1.5%
- 0%
Enhanced Contrast

$hv = 833.2 \text{ eV}$

$T = 20 \text{ K}$

$1 = \text{Mn3d } e_g$

$2 = \text{Mn3d } t_{2g}$

$3$

$4$

$5$

Detector Ch. / Angle $\theta$
First comparison to one-step photoemission theory for STO/LSMO

Experiment:
t_{2g}: Bulk LSMO

One-Step Theory, LDA+U, with SW E-field profile:
t_{2g}: Bulk LSMO

Calculations with more complex Interface relaxations in progress-
Minar, Braun, Ebert

A. Gray et al., TBP
[SrTiO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$]$_{120}$ Variable-Polarization SWARPES

$h \nu = 833.2$ eV, SLS

Bulk LSMO Geometry

Interface LSMO Geometry

Valence Bands

Kinetic Energy (eV)

Intensity (a.u.)

From SLS ADRESS

Vertical Polarization

Horizontal Polarization

Normal Emission

A. Gray et al., TBP
Most Recent SWARPES Measurements (SLS)

Depth-Resolved Electronic Structure of Exchange-Bias BiFeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ Superlattice

Standing-Wave ARPES of the Valence Bands

Core-Level Rocking Curves: Interface Profile

Polarization-Dependent Standing-Wave ARPES of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ Magnetic Tunnel Junction


Intensity (a.u.)
hv

815 820 825 830
0.0
0.2
0.4
0.6
0.8
1.0

Average
828 826 824 822 820 818 eV

Substrate
13 12 10 9 8

Substrate
12 11 9

Substrate
8

Substrate
7

Interface LSMO
12

Interface LSMO
8

Interface LSMO

Mn3d $e_g$
States

Mn3d $t_{2g}$
States

Vertical
Polarization

Horizontal
Polarization

Valence
Bands

Kinetic Energy (ev)

Intensity (a.u.)

hv = 833.2 eV

Bulk LSMO Geometry

Interface LSMO Geometry

Valence
Bands

Kinetic Energy (ev)

Intensity (a.u.)

hv = 1182.8 eV

θ$_{Bragg}$

Sample: S. Stemmer (UCSB)

Standing-Wave Excited Photoemission

Core-Level Excited Photoemission

Sr3d

O1s (1)

O1s (2)

C1s

17%
Summary

• Hard X-ray Photoemission (HAXPES)
  • Probing deeper into the bulk
  • Characterization of buried layers and interfaces

• Hard X-ray Angle-Resolved Photoemission (HARPES)
  • Band mapping in keV regime
  • True bulk electronic band structure
  • No need for surface cleaning, in-situ cleaving, etc.

• Standing-Wave Excited ARPES (SWARPES)
  • Depth-selective probe of buried layers and interfaces
  • Chemical and electronic structure profiling
  • Interface-specific changes in the electronic structure

• Soon to come – HAXPES and HARPES at ALS (9.3.1)