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

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

Measurements

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A. Rattanachata[1,2]
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A. Bostwick[6]
L. Morescini[6]
E. Gullikson[6]
S. Ueda[7]
Y. Yamashita[7]
K. Kobayashi[7]
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M. Kobayashi[8]
J. Fujii[9]
G. Panaccione[9]
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Sample Synthesis

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G. Rijnders[10]
D. H. A. Blank[10]
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O. D. Dubon[11]
J. Son[12]
S. Stemmer[12]

Theory

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J. Braun[13]
H. Ebert[13]
L. Plucinski[14]
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S.-H. Yang[16]
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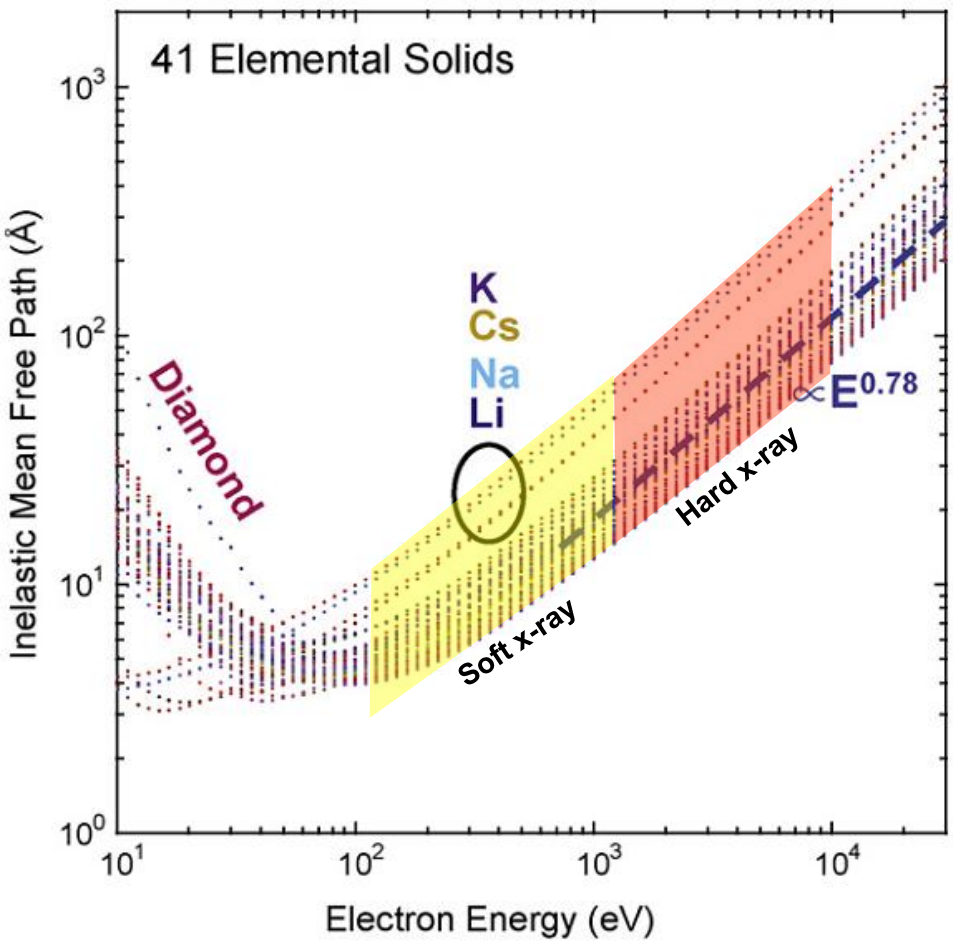
Outline

- **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?

Inelastic Mean-Free Path VS E_{kin}



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

With multi-keV excitation

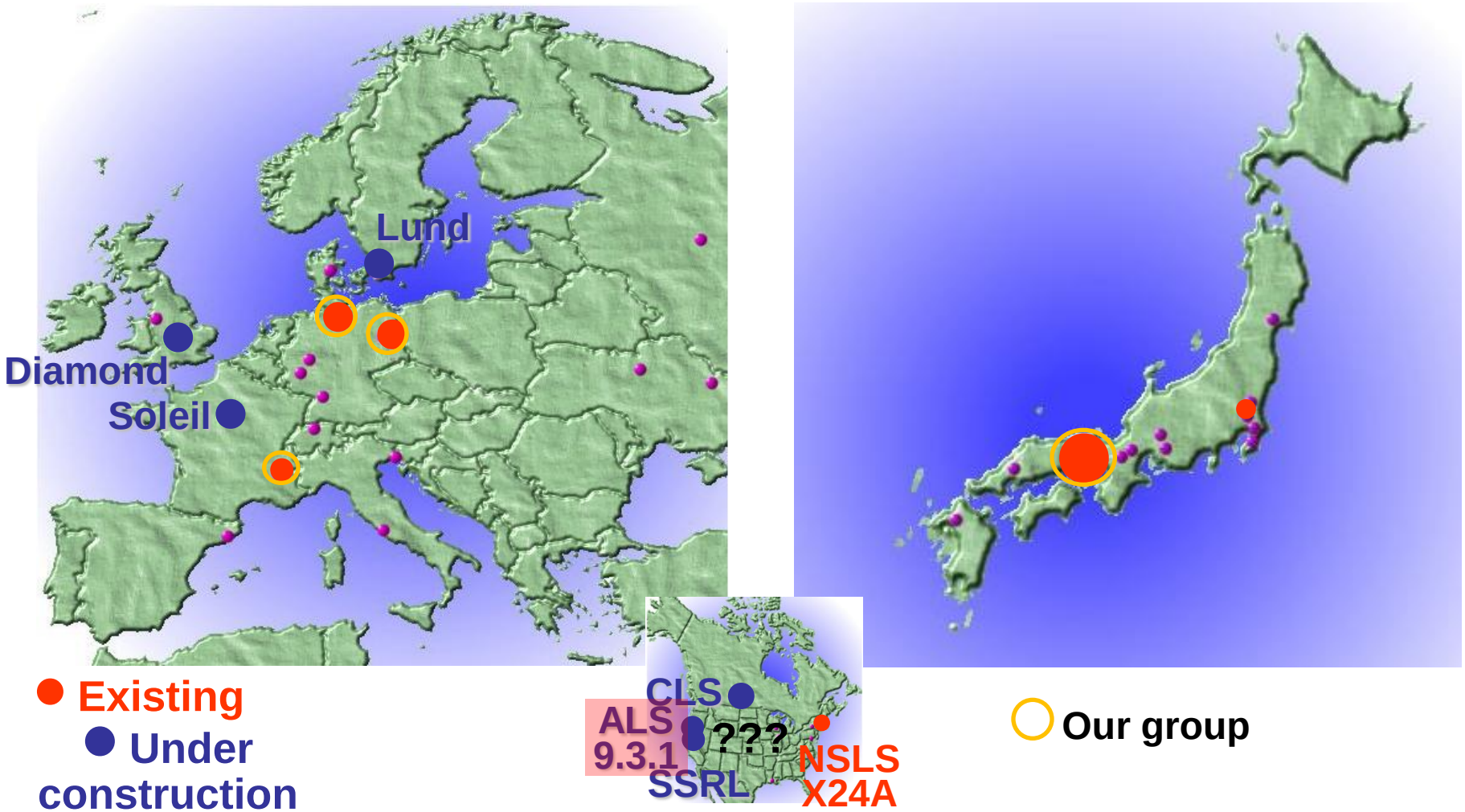
~ 4-5× deeper than soft x-ray XPS

We can obtain more accurate BULK electronic structure

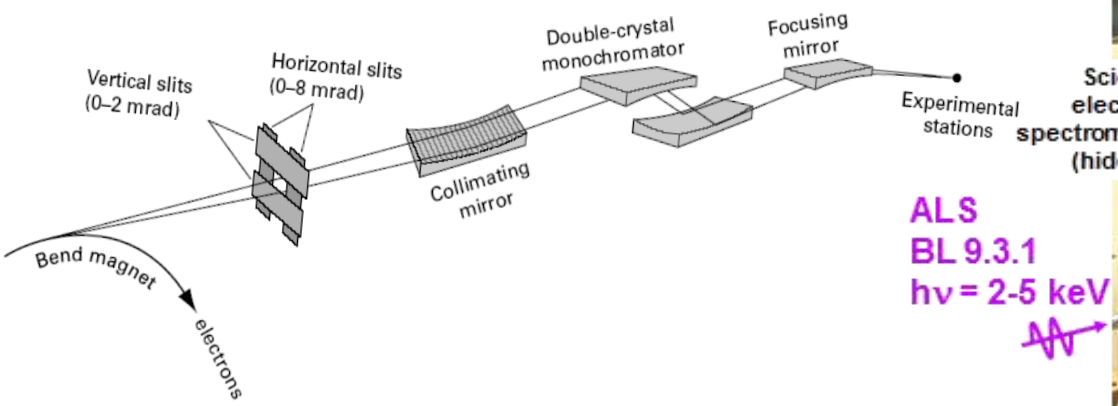
Energy resolutions down to 50 meV (→10 meV in future)
Angular resolutions to 0.2° (→0.02° in future)

S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 43, 689 (2010).

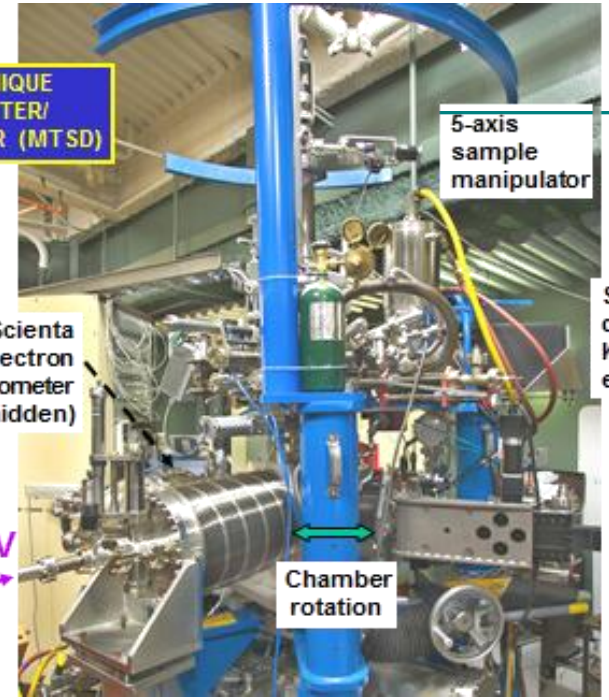
Places to do HAXPES



Facility for hard x-ray photoemission at the ALS: Based largely on existing beamline and end station-in progress

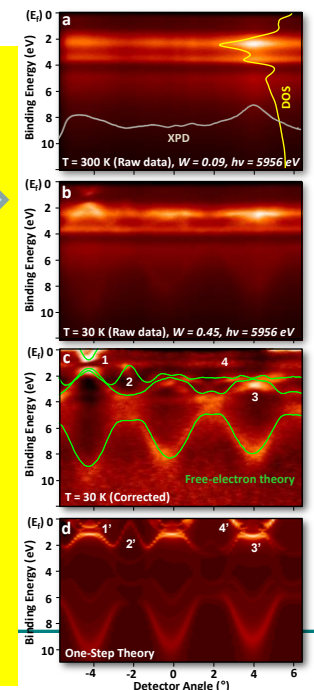


ALS
BL 9.3.1
hν = 2-5 keV



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

ARPES at 3-6 keV: A.X. Gray et al., Nature Materials 10, 759 (2011); D.L. Feng, *News and Views*, ibid., 10, 729 (2011)



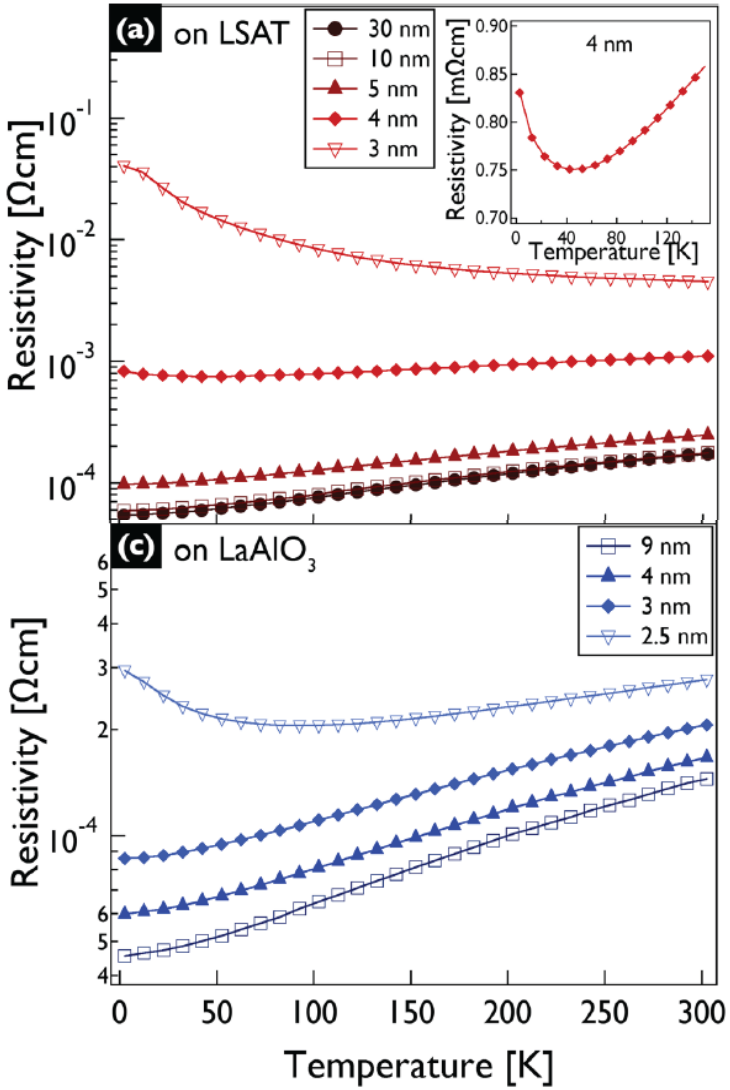
4th International HAXPES Workshop, DESY, Hamburg, Sept. 2011
http://haxpes2011.desy.de,
With most talks available at:
https://indico.desy.de/materialDisplay.py?materialId=slides&confId=3713

Reviews:
Kobayashi, NIMA 601, 32 (2009)
Fadley, JESRP 178–179 2–32 (2010

Application of HAXPES

Mott Behavior in $LaNiO_3$ Epitaxial Thin Films

Conductivity (J. Son, S. Stemmer)



J. Son et al., APL 96, 062114 (2010)

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

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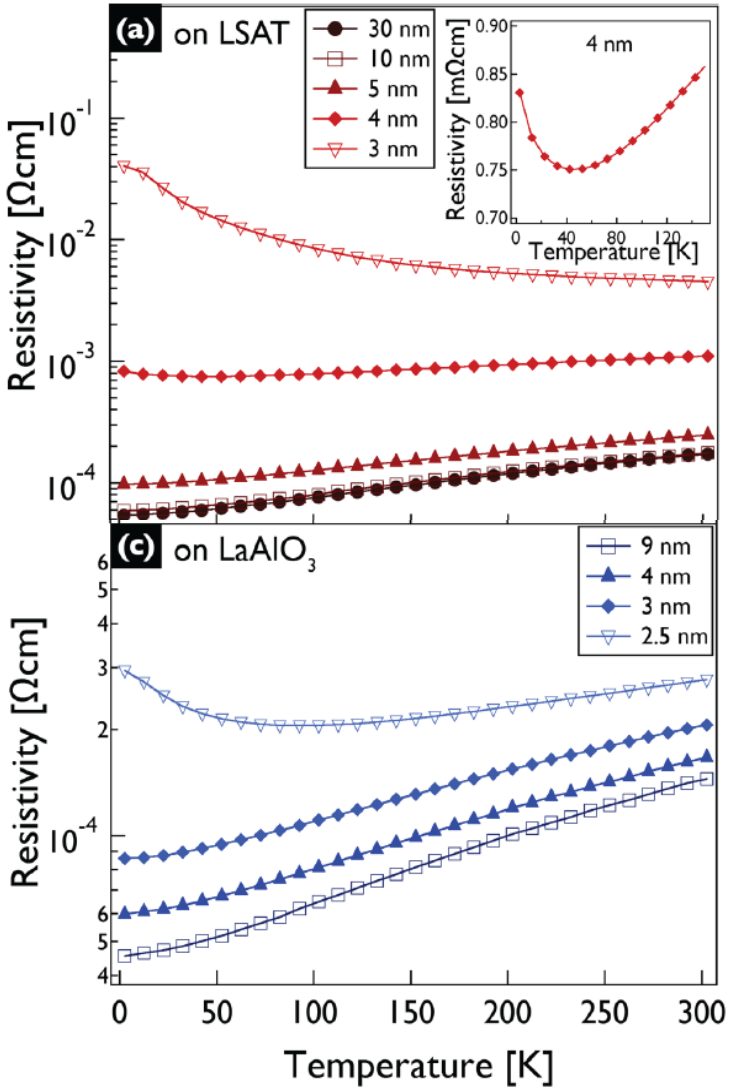
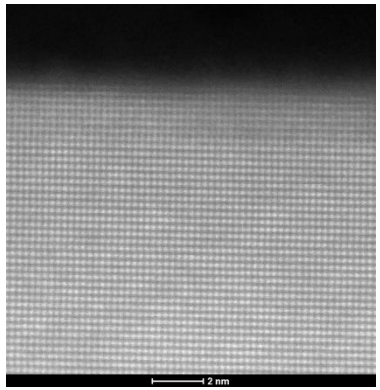
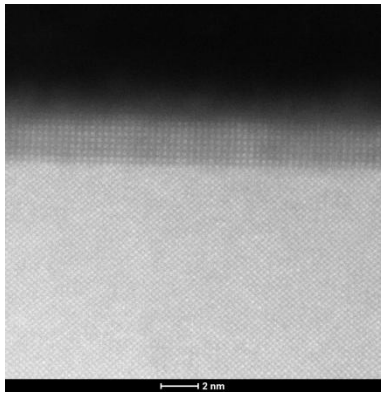


J. Son et al., APL 96, 062114 (2010)

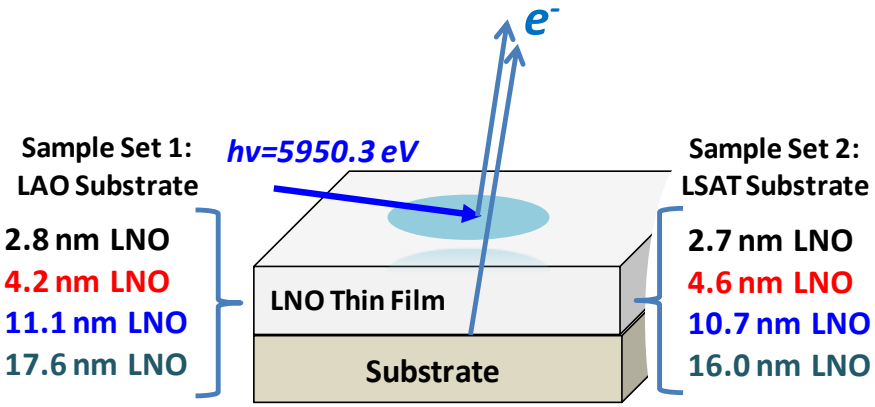
Epitaxial layers with TEM thickness det'n. (J. Son, J. LeBeau, S. Stemmer)



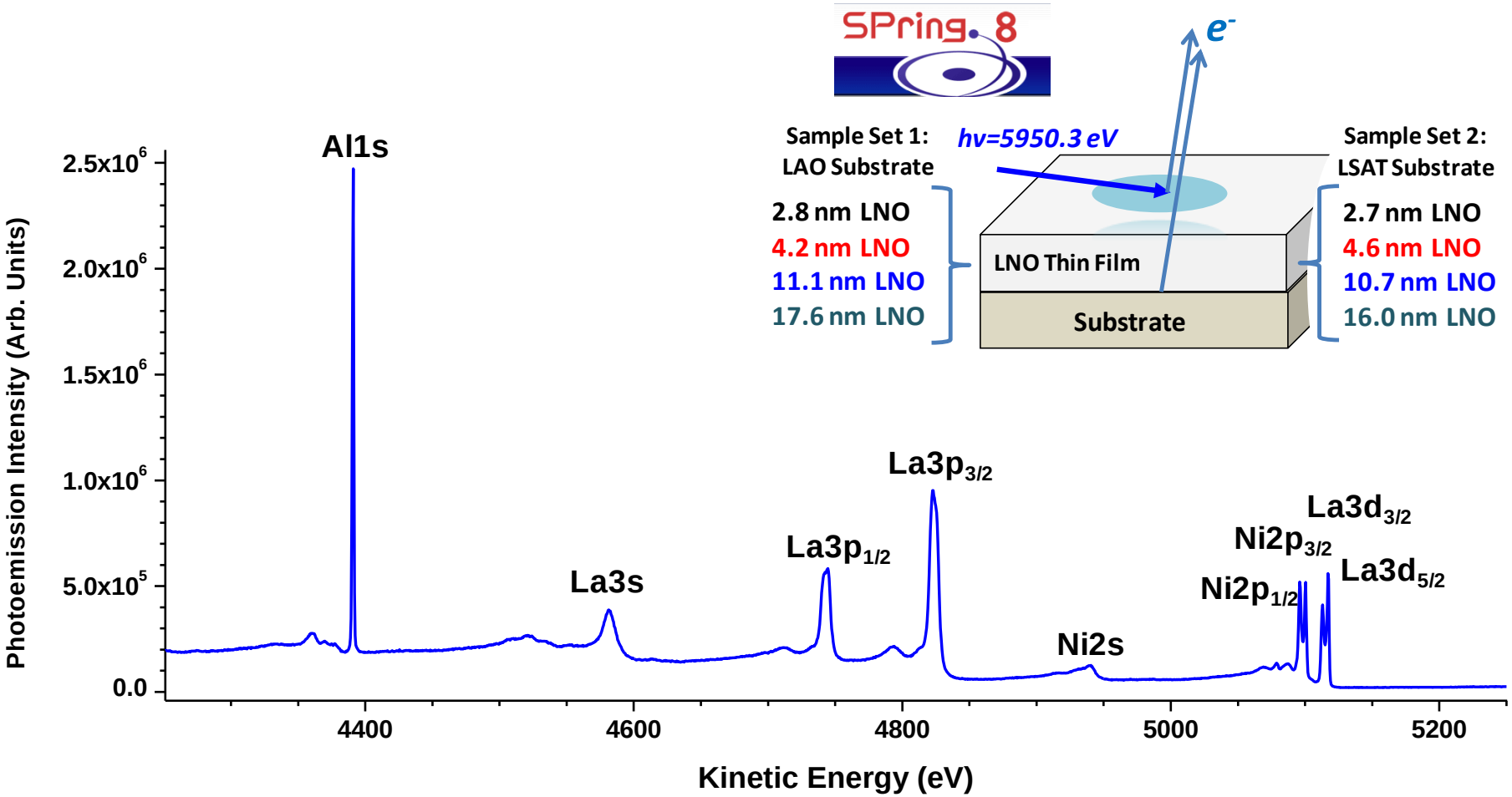
LNO/LAO
~ 7 unit cells = 2.8 nm



LNO/LSAT
~ 7 unit cells = 2.7 nm



Hard X-ray Photoemission at *hv*=5.95 keV



Probing ~70 Å into the sample

Experiment with S. Ueda, K. Kobayashi

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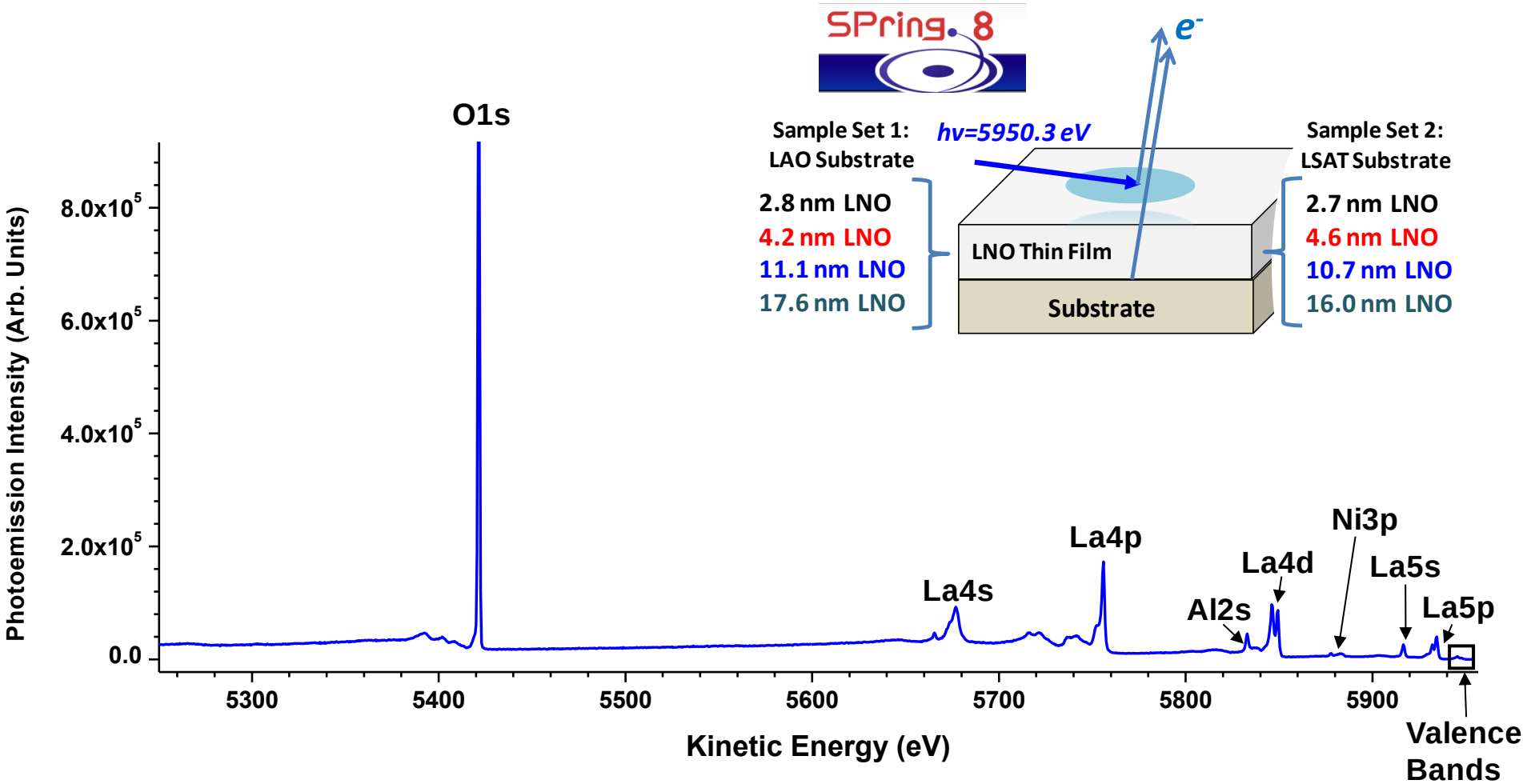

Probing ~70 Å into the sample

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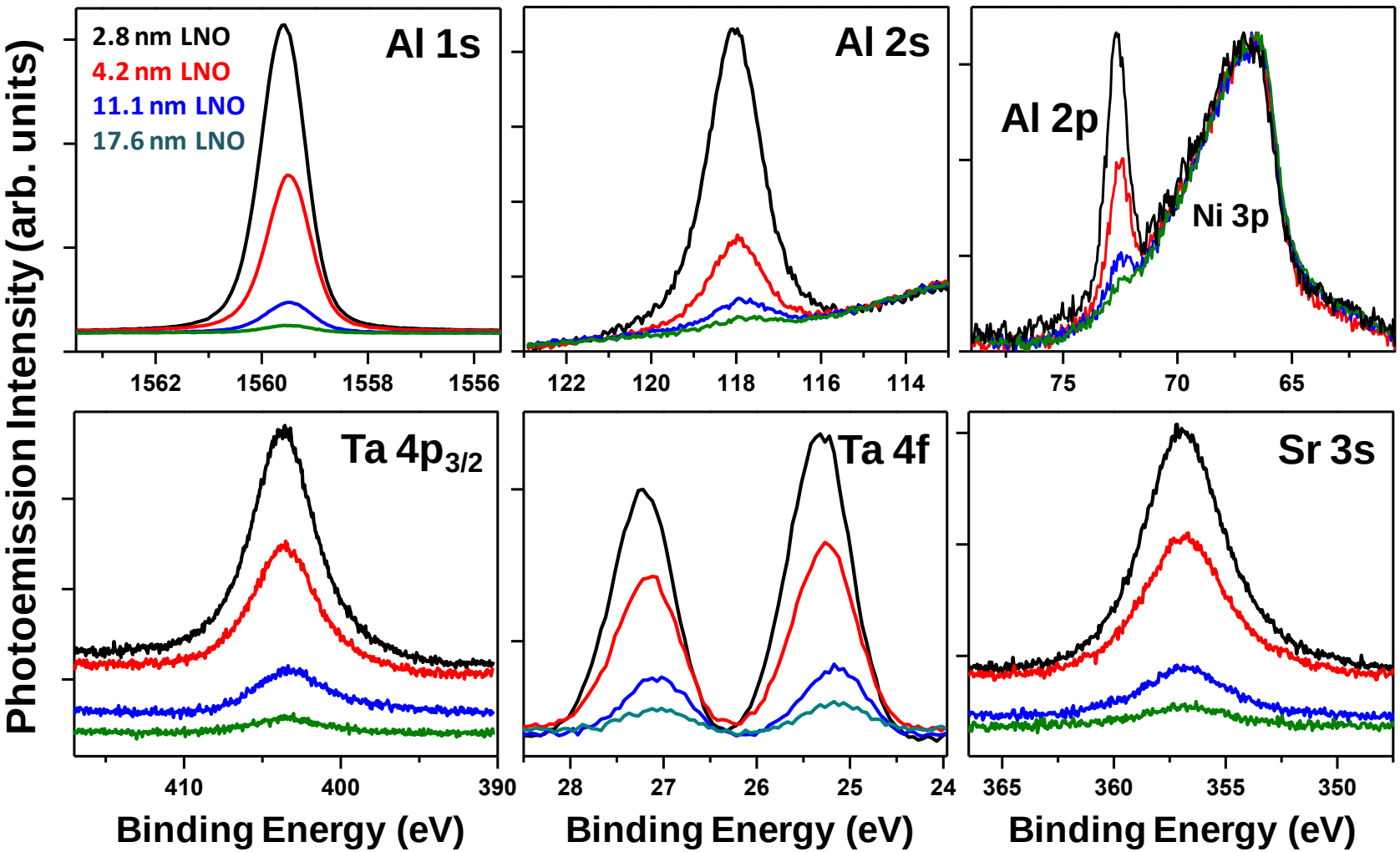
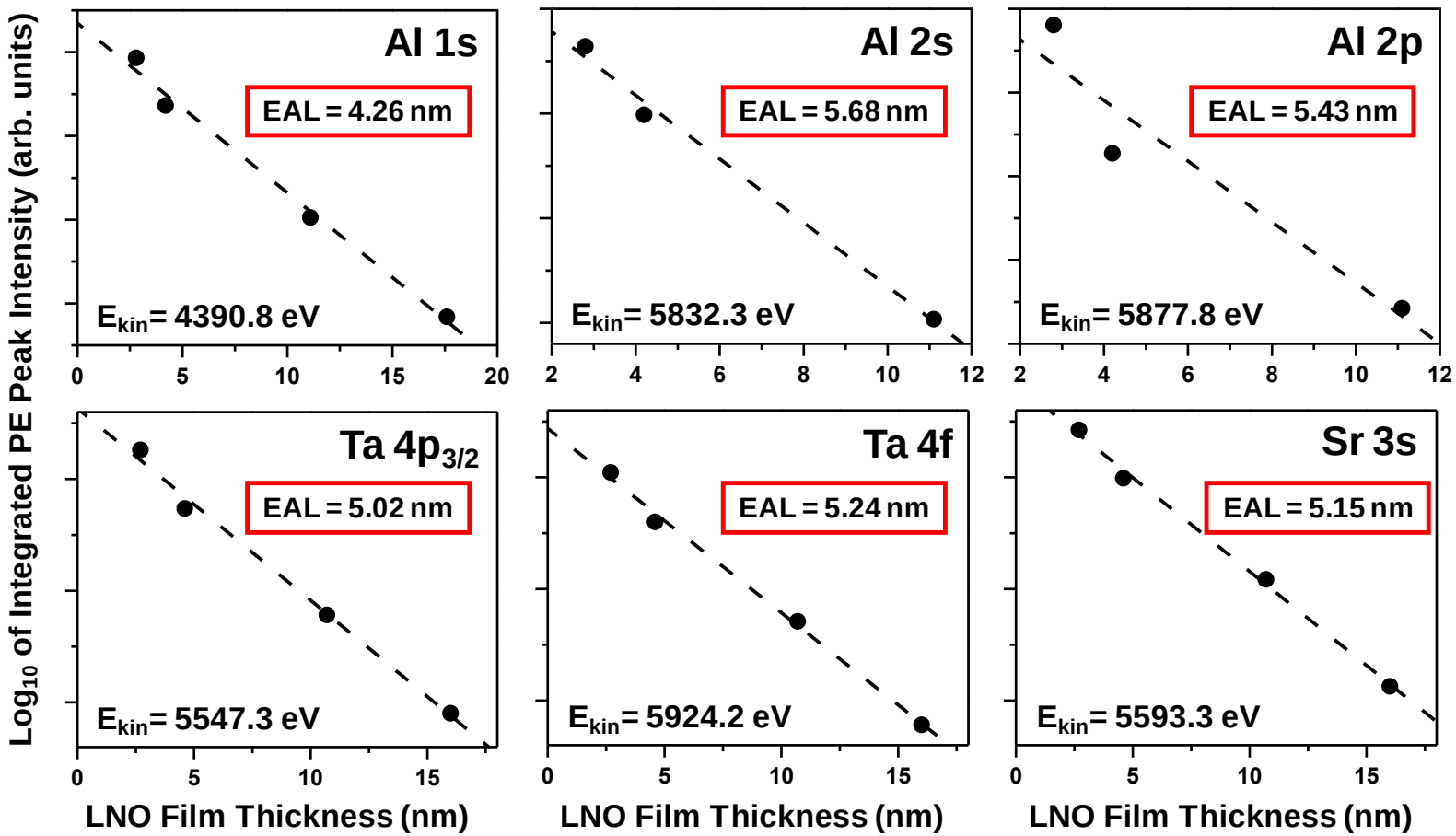
Substrate Core-Peak Photoemission Spectra

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

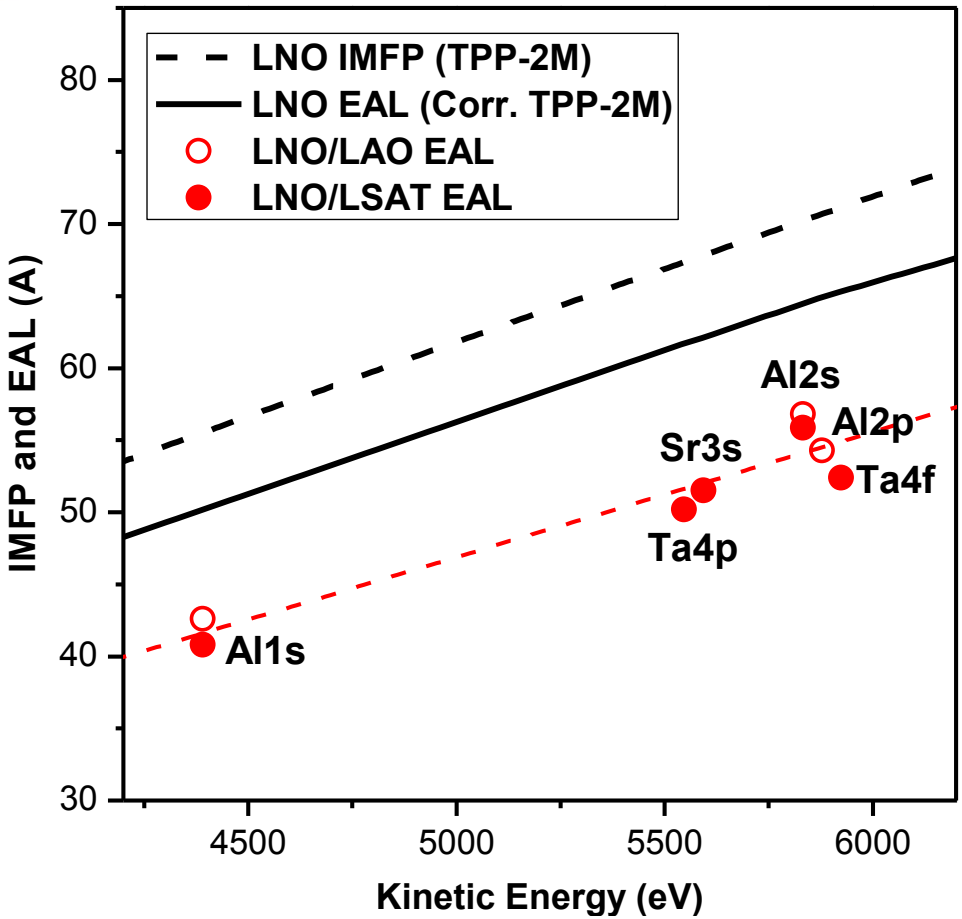


Calculating Effective Attenuation Lengths

Effective attenuation lengths for the photoelectrons can be calculated by analyzing core peak intensities according to: $I_{substrate} \propto e^{-t/\Lambda_{EAL}}$



Experimentally Determined EALs



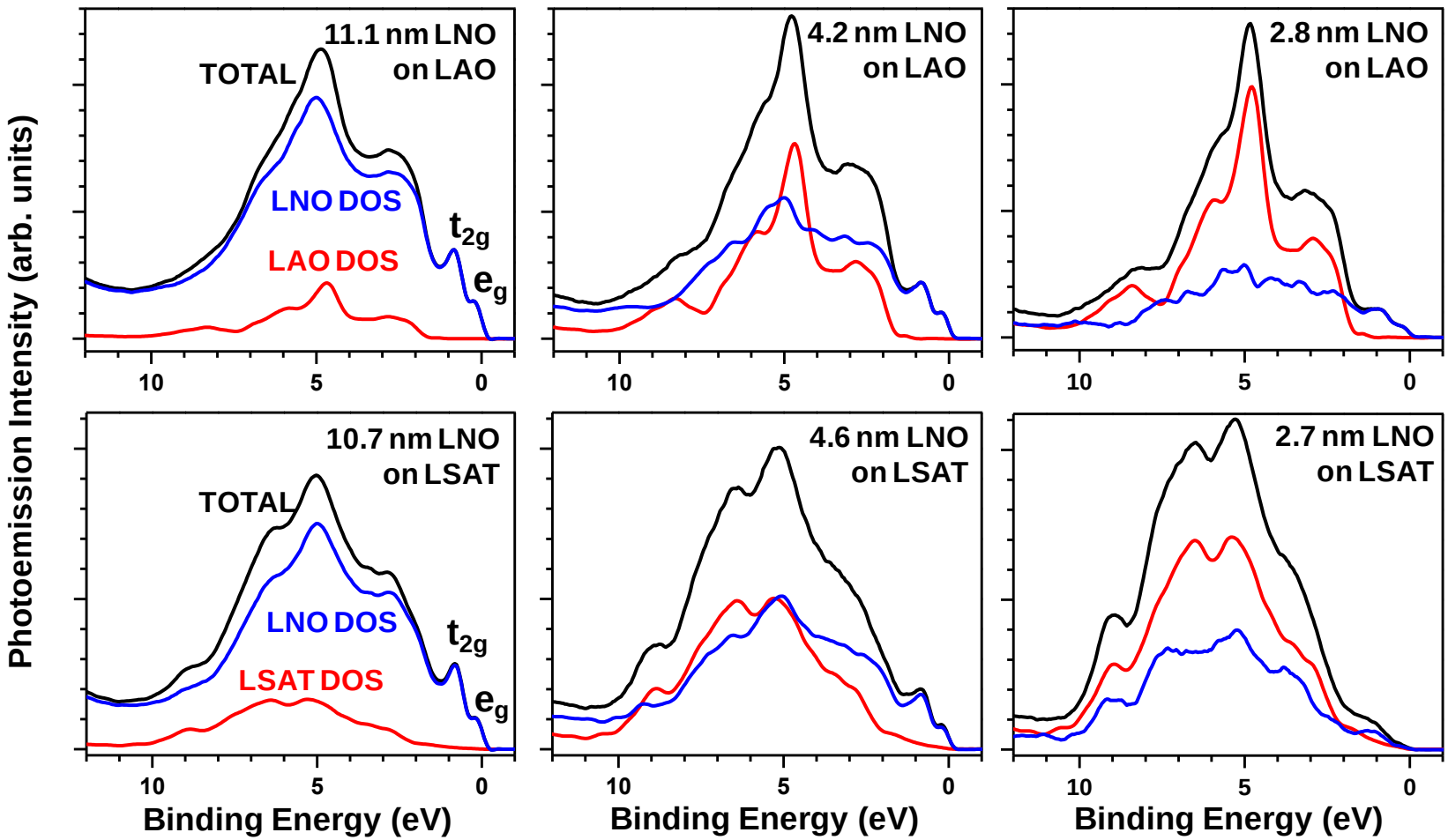
S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.* 43, 689 (2011).
A. Jablonski and C. J. Powell, J. Vac. Sci. Technol. A 27, 253 (2009).

- **LNO EALs within ~20% of the much-used semi-empirical TPP-2M formula, if corrected for elastic scattering**

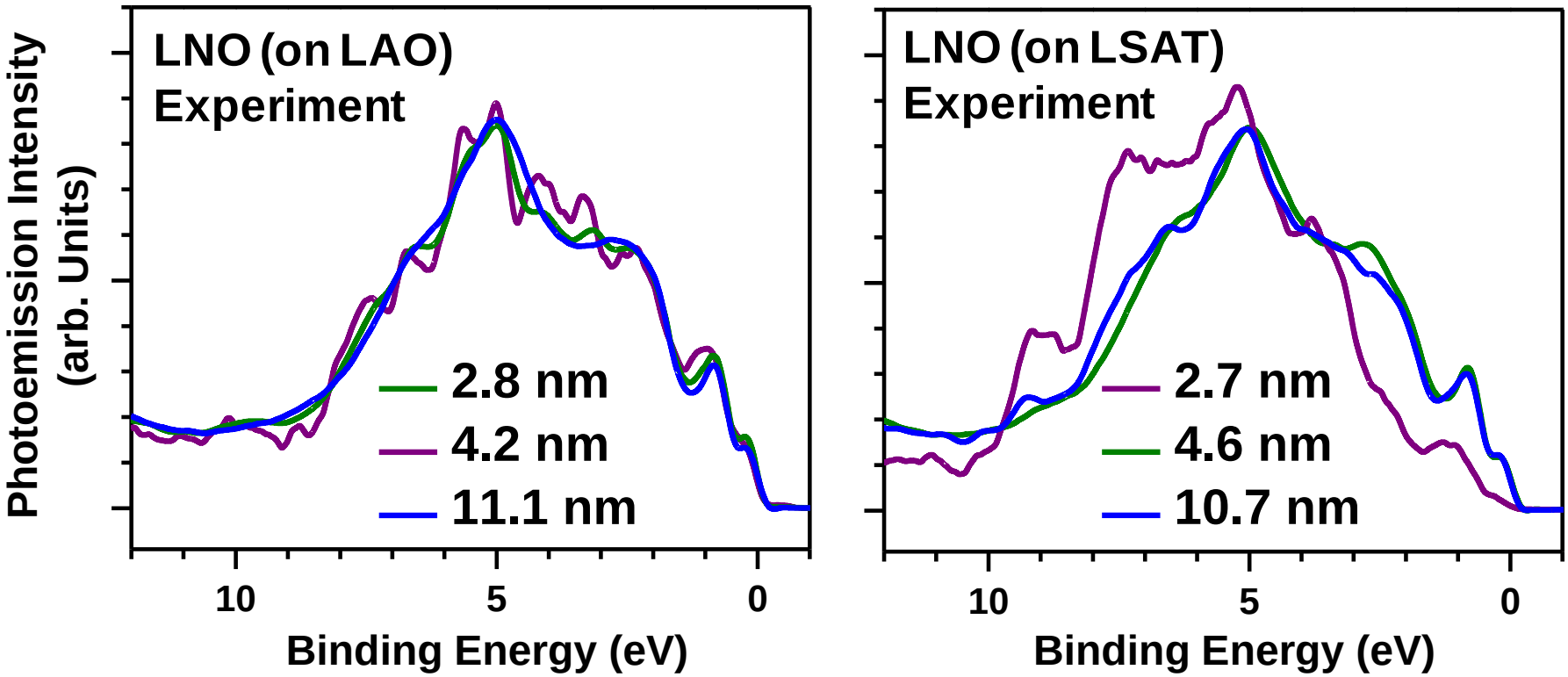
- **Remaining expt./theory discrepancy may be due to lack of resonant absorption edges in theory: an effect not considered previously**

Valence-Band Decomposition

Valence band spectra can now be decomposed into the film and substrate DOS components using the EALs and $I_t^{(0)} = [1 - e^{-t/\Lambda_{EAL}}] I_{LNO,t} + e^{-t/\Lambda_{EAL}} I_{LAO(LSAT),t}$



Thickness and Substrate Dependence of LNO DOS



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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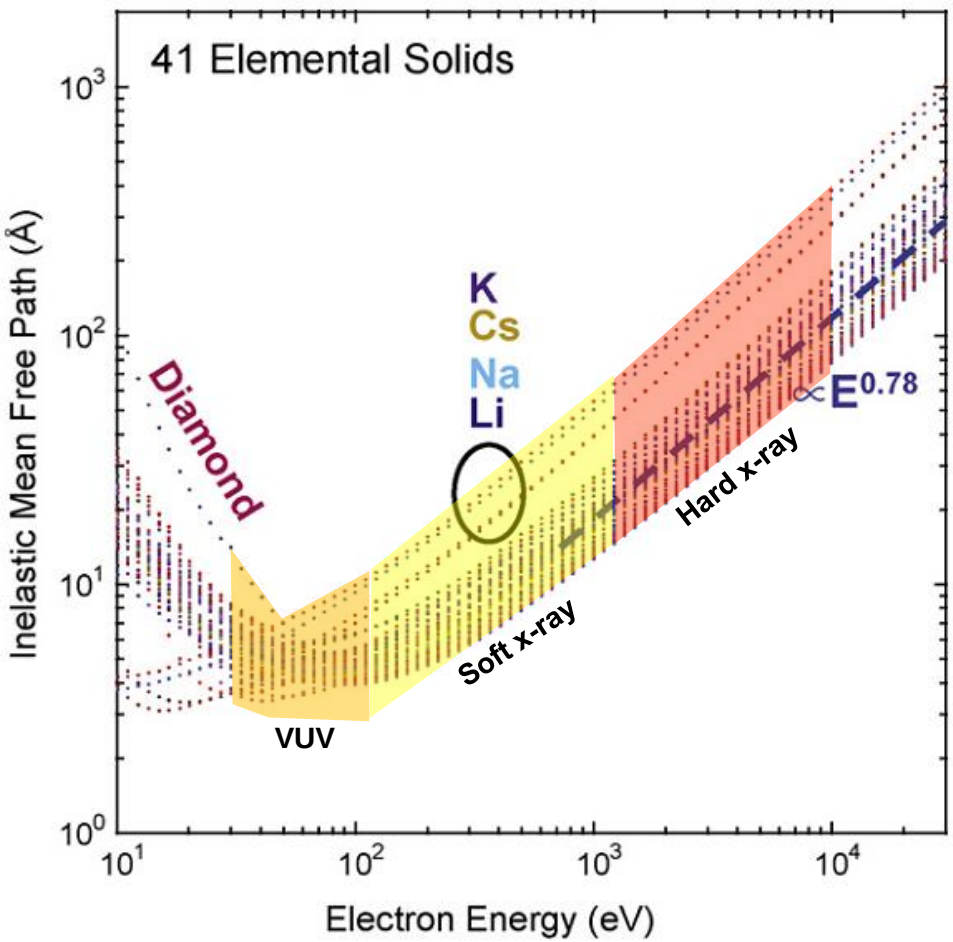


Traditional ARPES is heavily influenced by surface effects

With multi-keV excitation

~ 5-20× deeper than ARPES

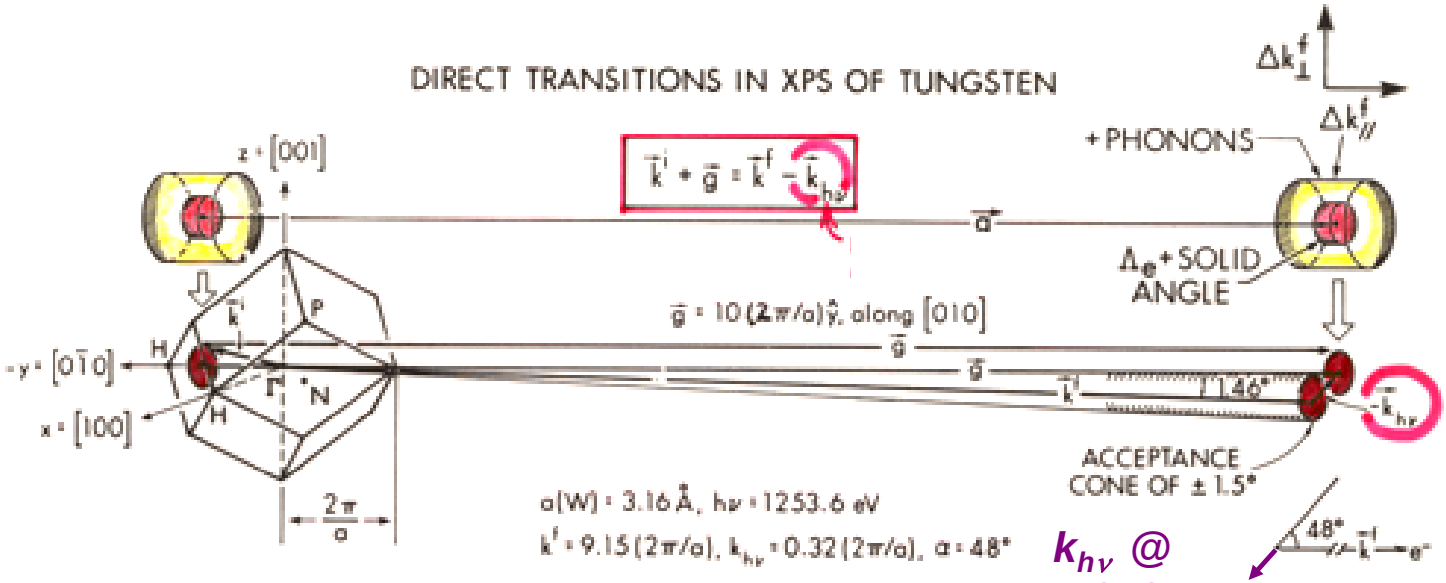
⇩

We can obtain more accurate BULK electronic structure

S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 43, 689 (2010).

Angle-Resolved Photoemission at High Energies

What and Where is the "XPS Limit"?



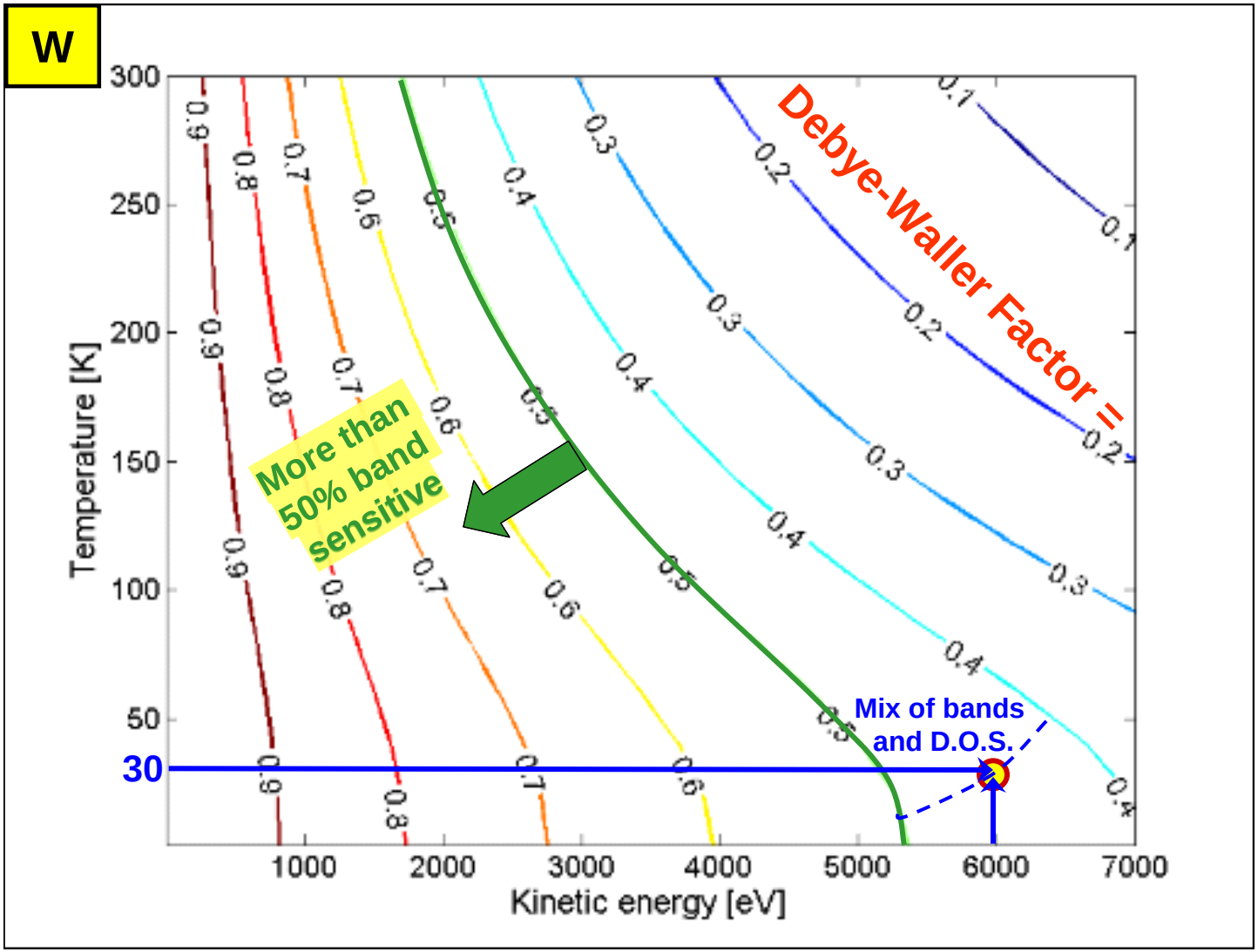
$k_{h\nu}$ @ 1,253 eV

Hussain et al., Phys. Rev. B 22, 3750 (1980)

- Low photoelectric cross sections → d- and f- states are suppressed
- Magnitude of the wavevector associated with the final photoelectron momentum increases. → Brillouin zone averaging
- The magnitude of the photon momentum cannot be ignored anymore. → 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

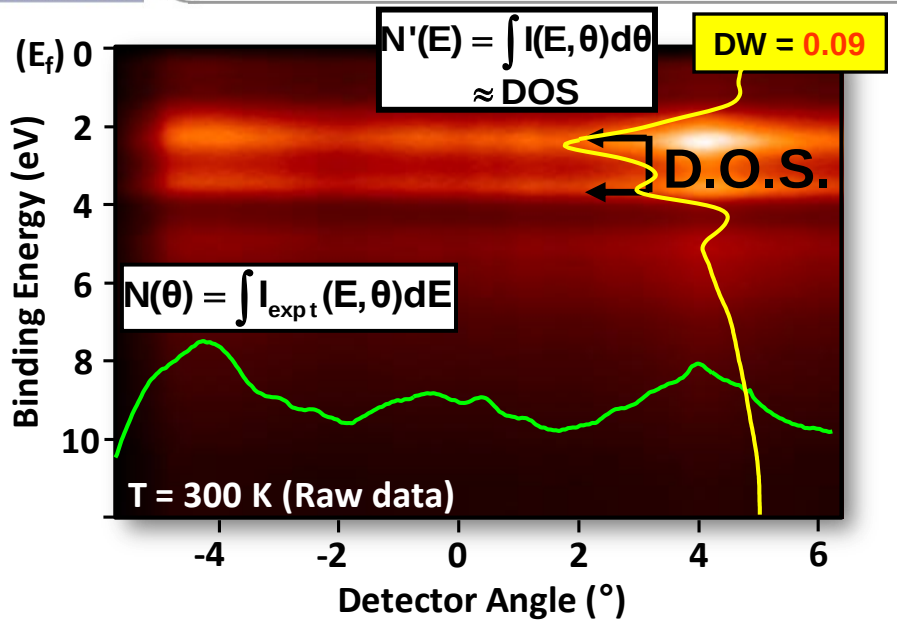
The Debye-Waller Factor

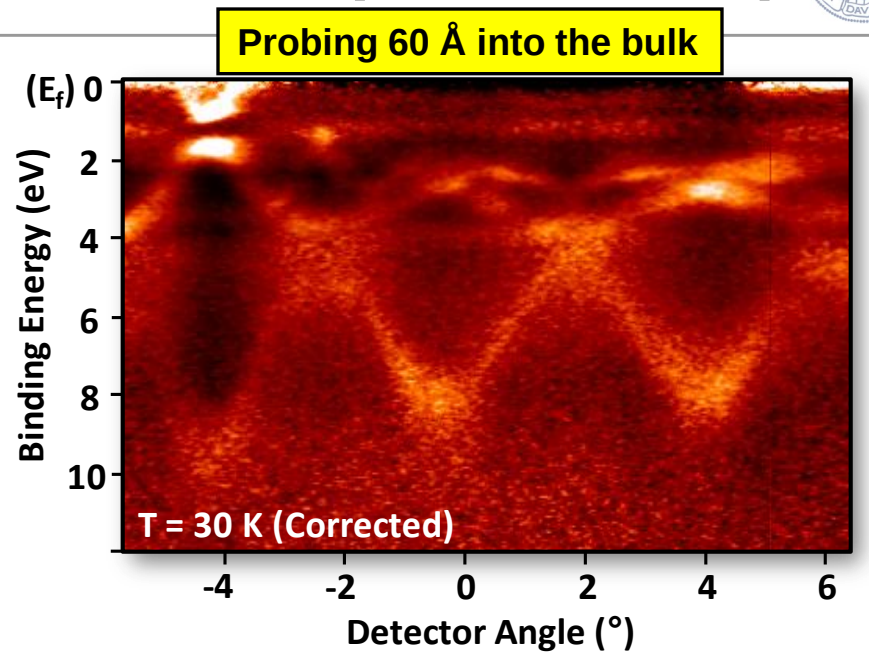
Estimate of the Fraction of Direct Transitions

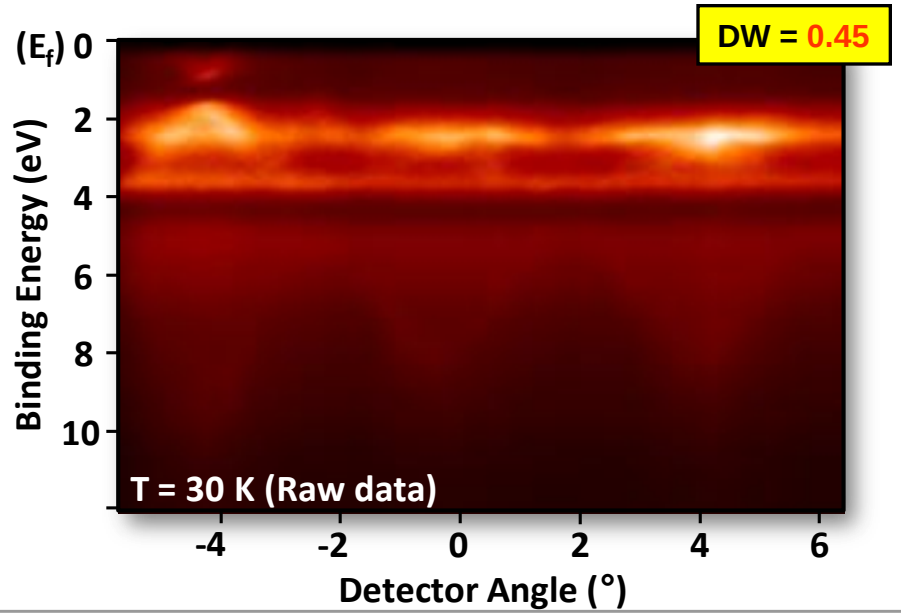


L. Plucinski, et al. PRB 78, 035108 (2008)

W(110) First Experimental Data (*hv*=5.95keV)







Gray et al., Nature Mat. 10, 759 (2011)

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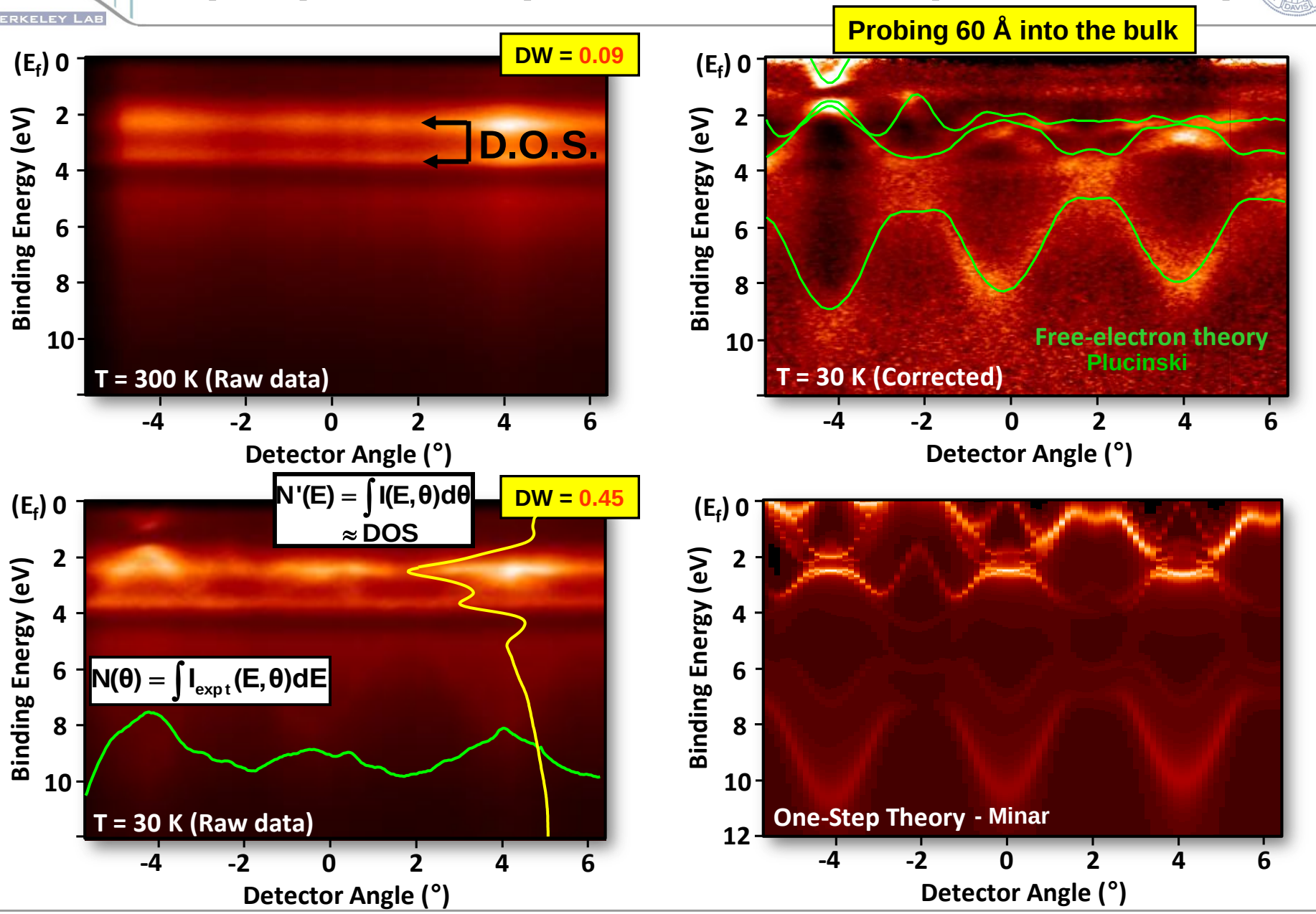
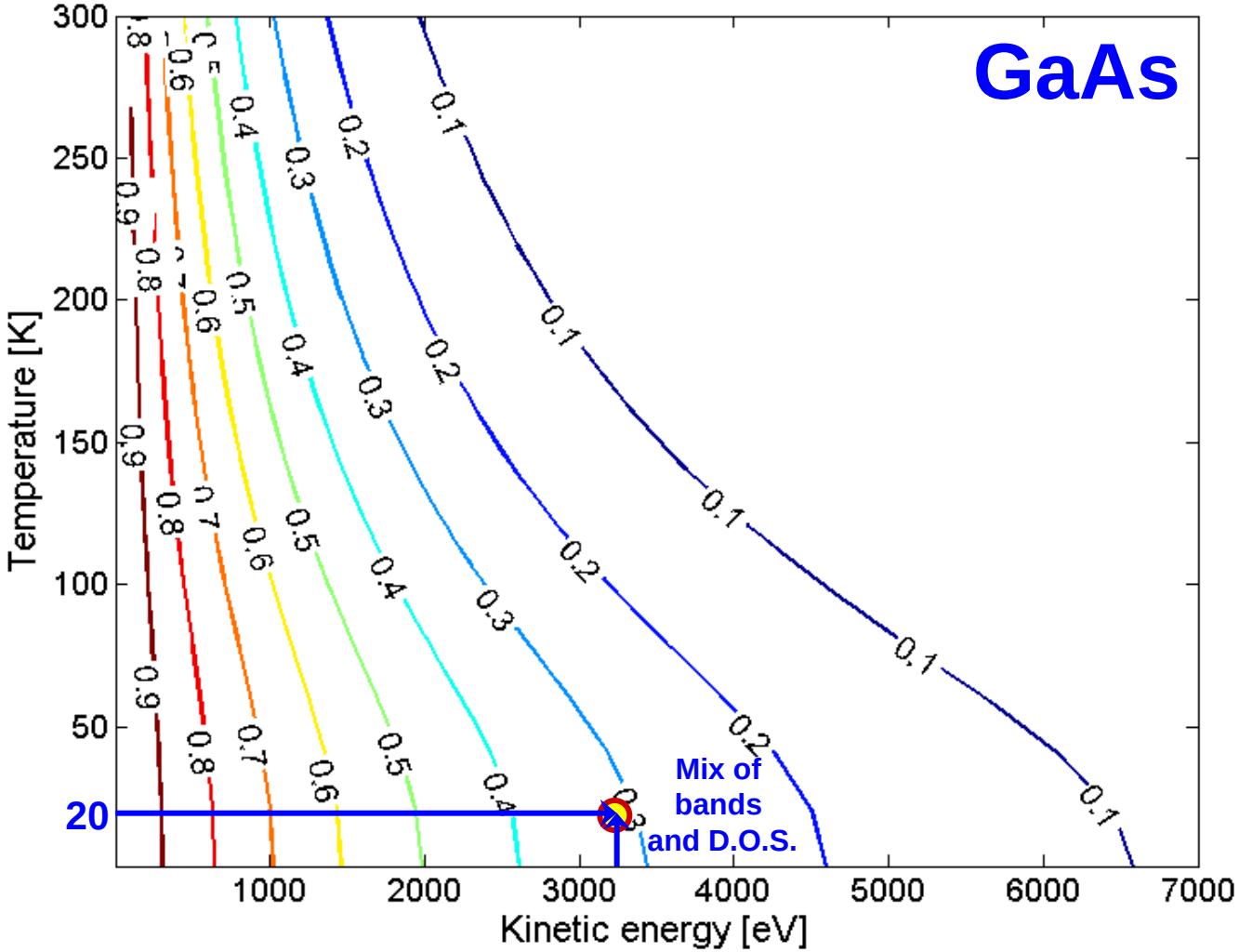


The Debye-Waller Factor

Estimate of the Fraction of Direct Transitions: GaAs



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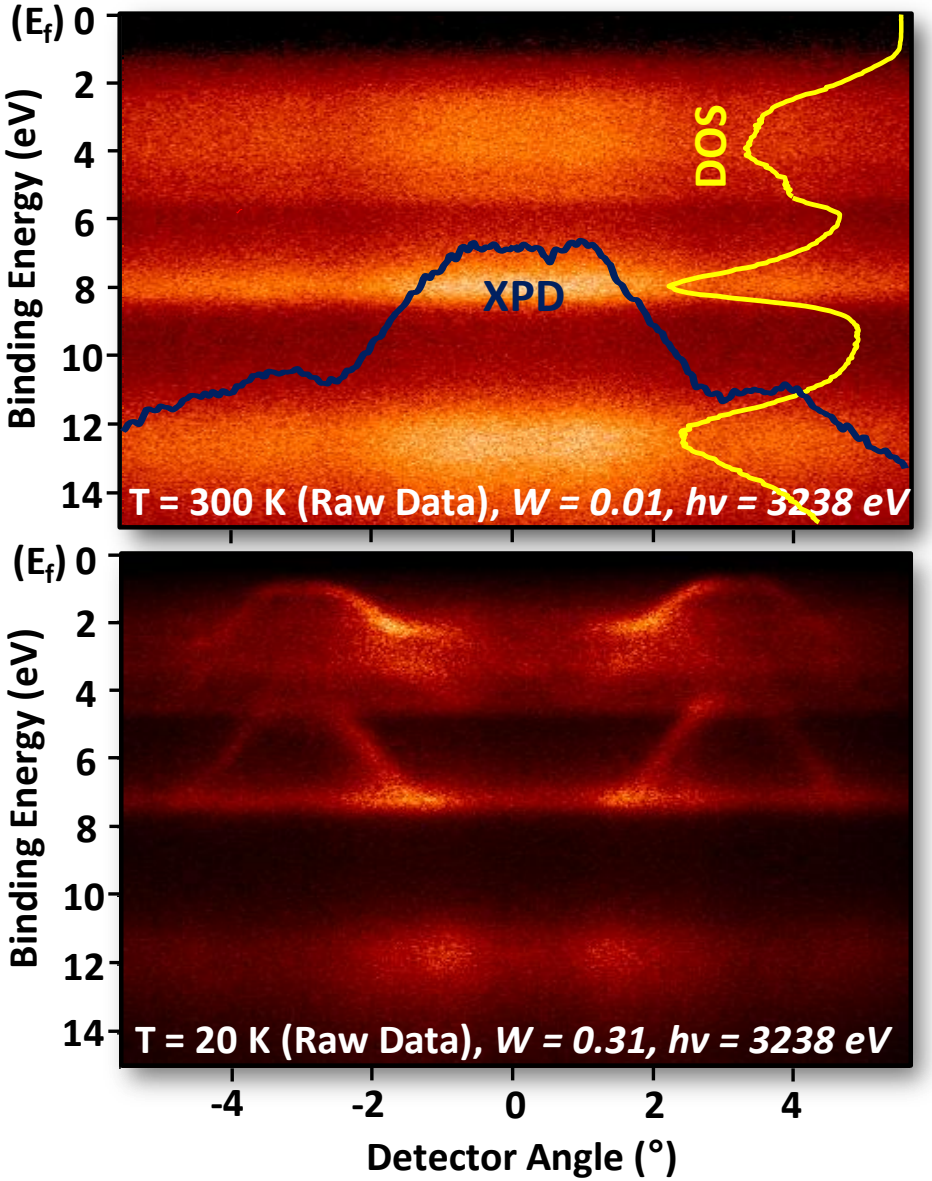
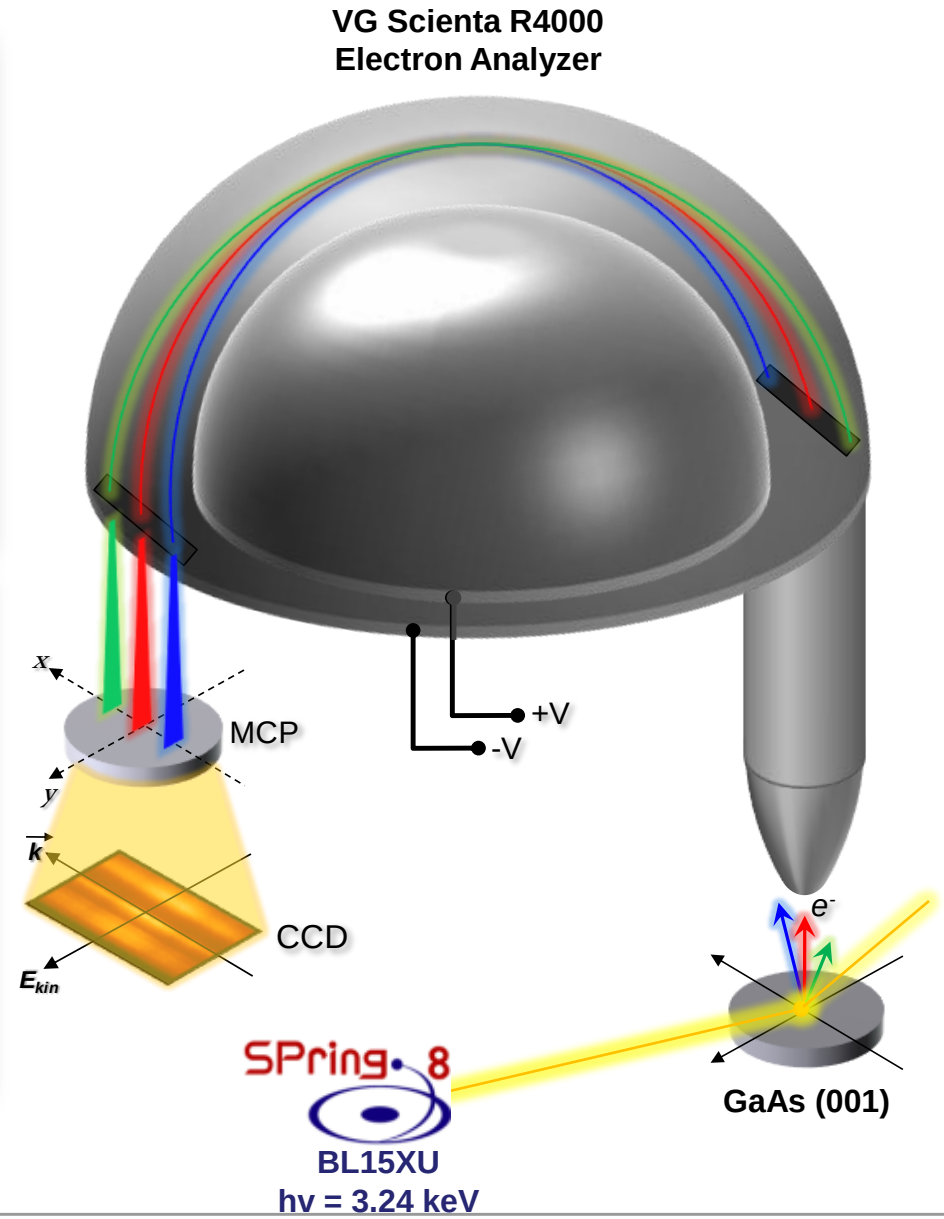
HARPES of GaAs (*hv* = 3.24 keV, IMFP = 57Å)





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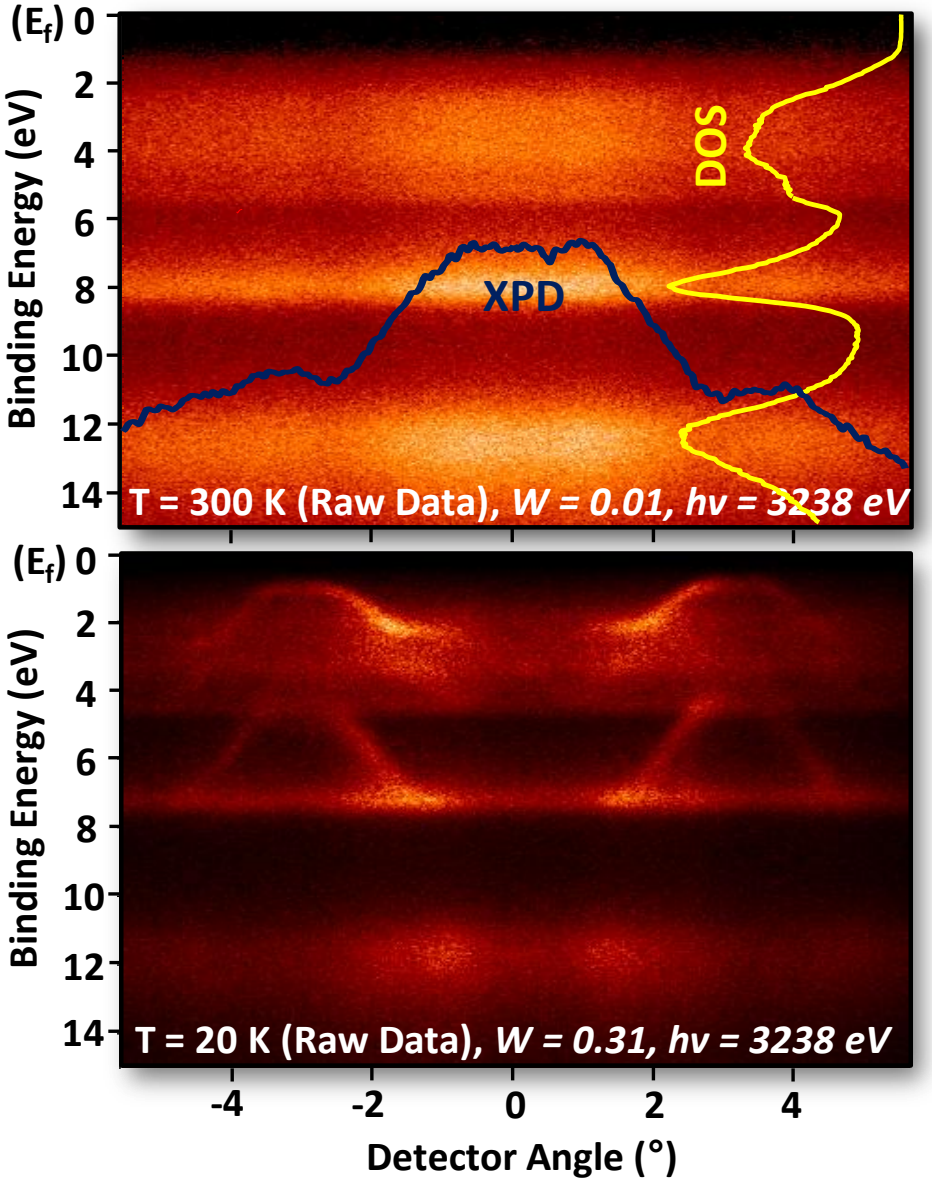

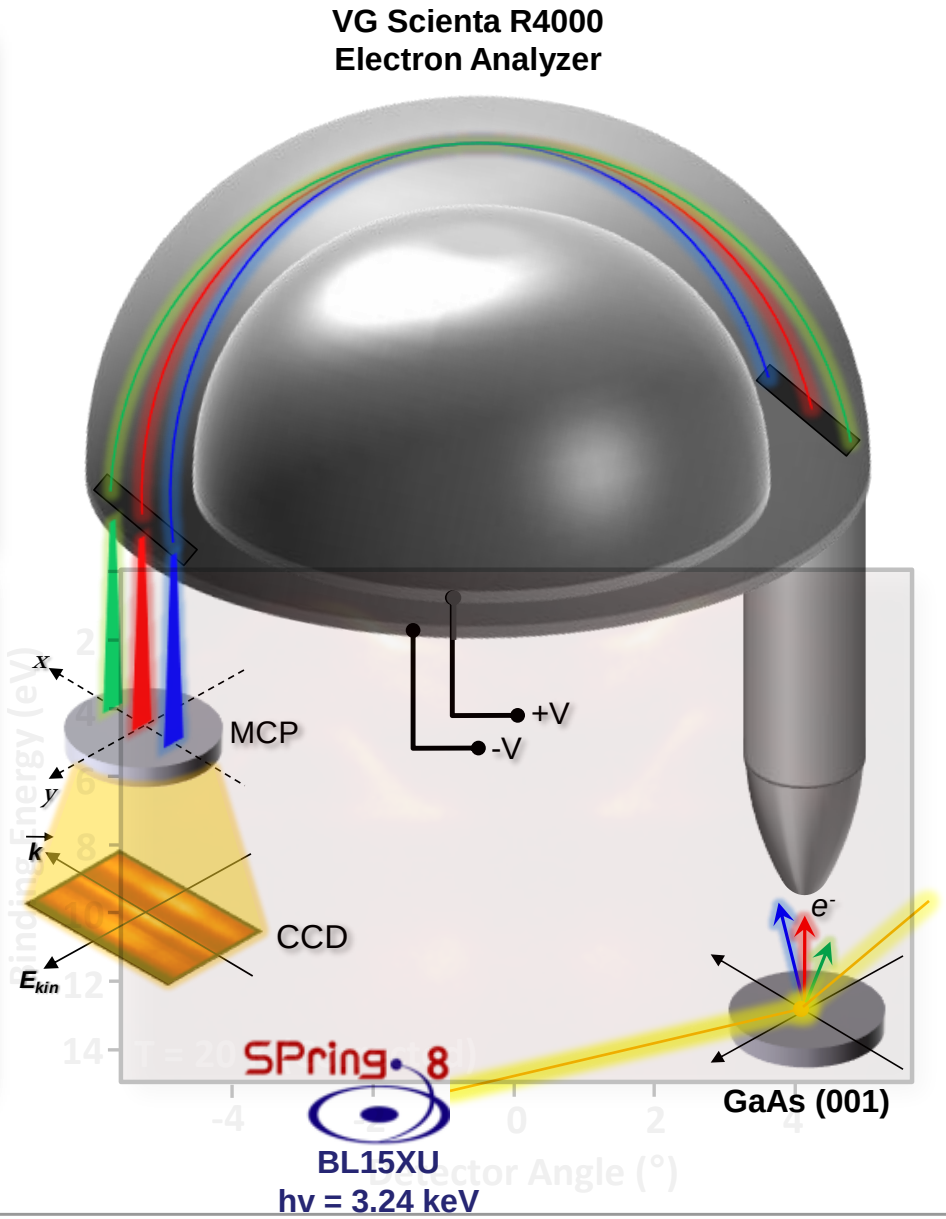

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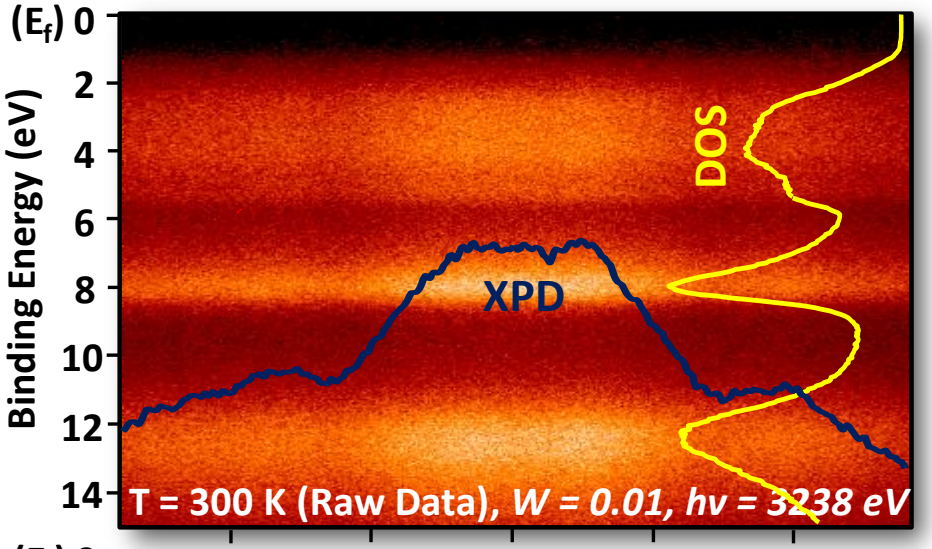

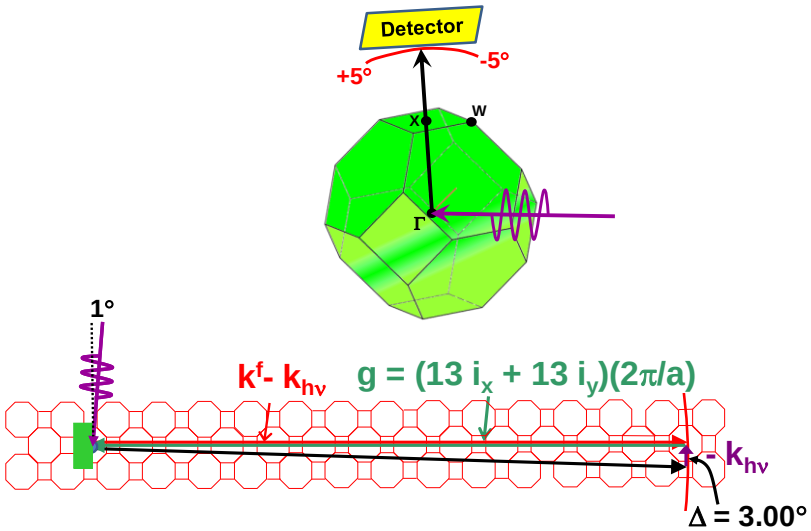

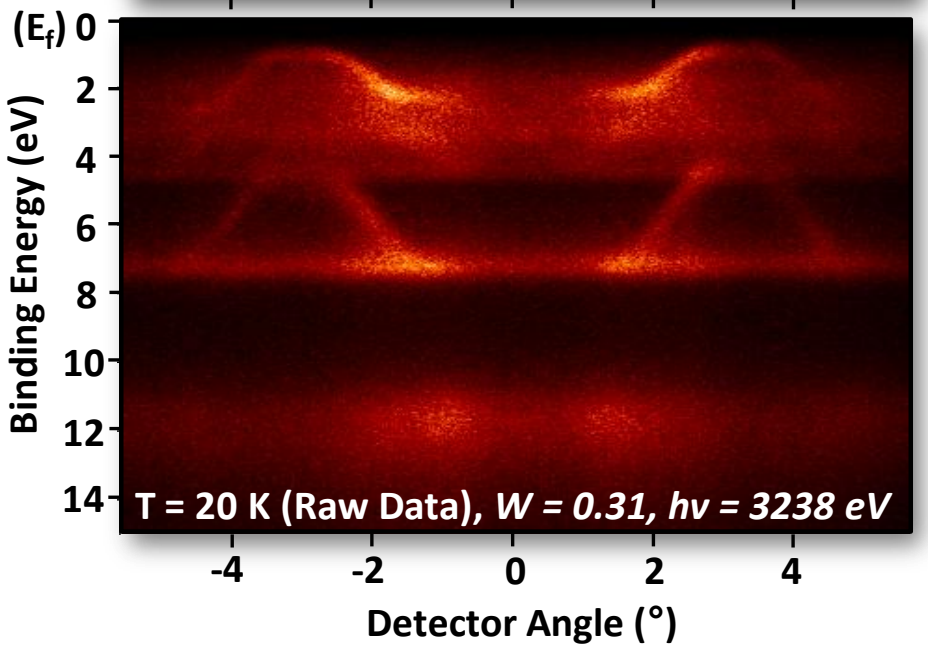

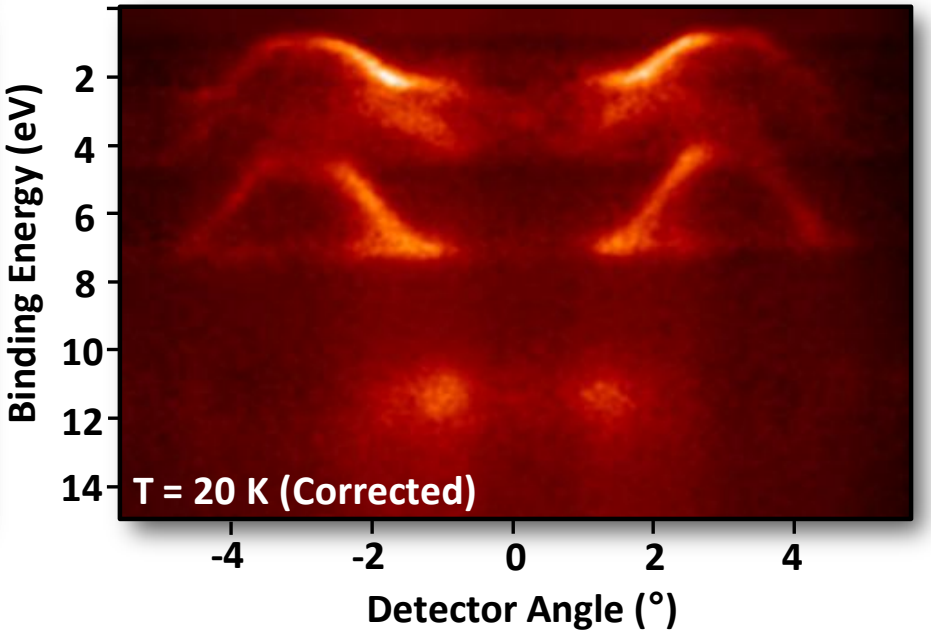

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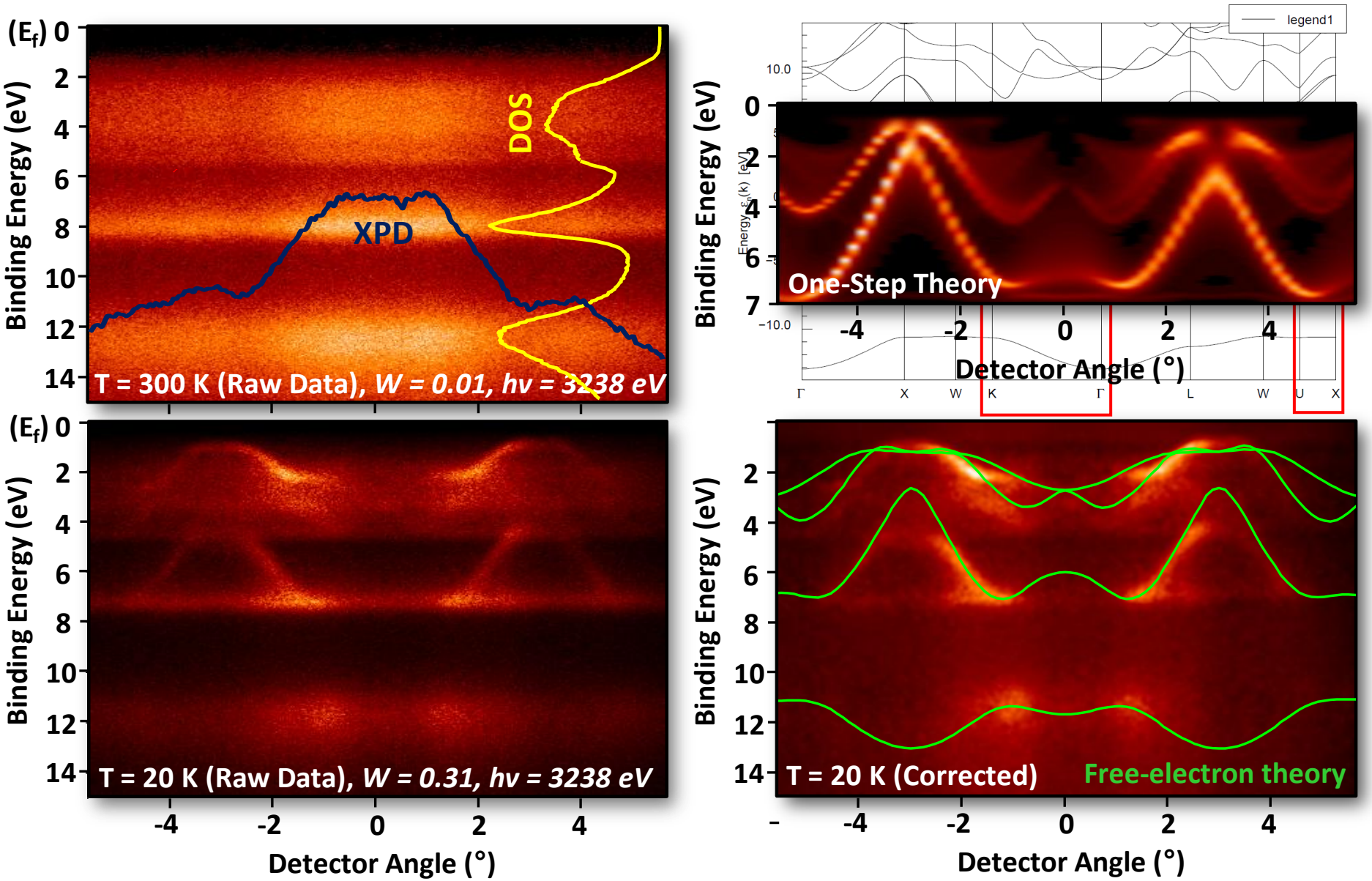
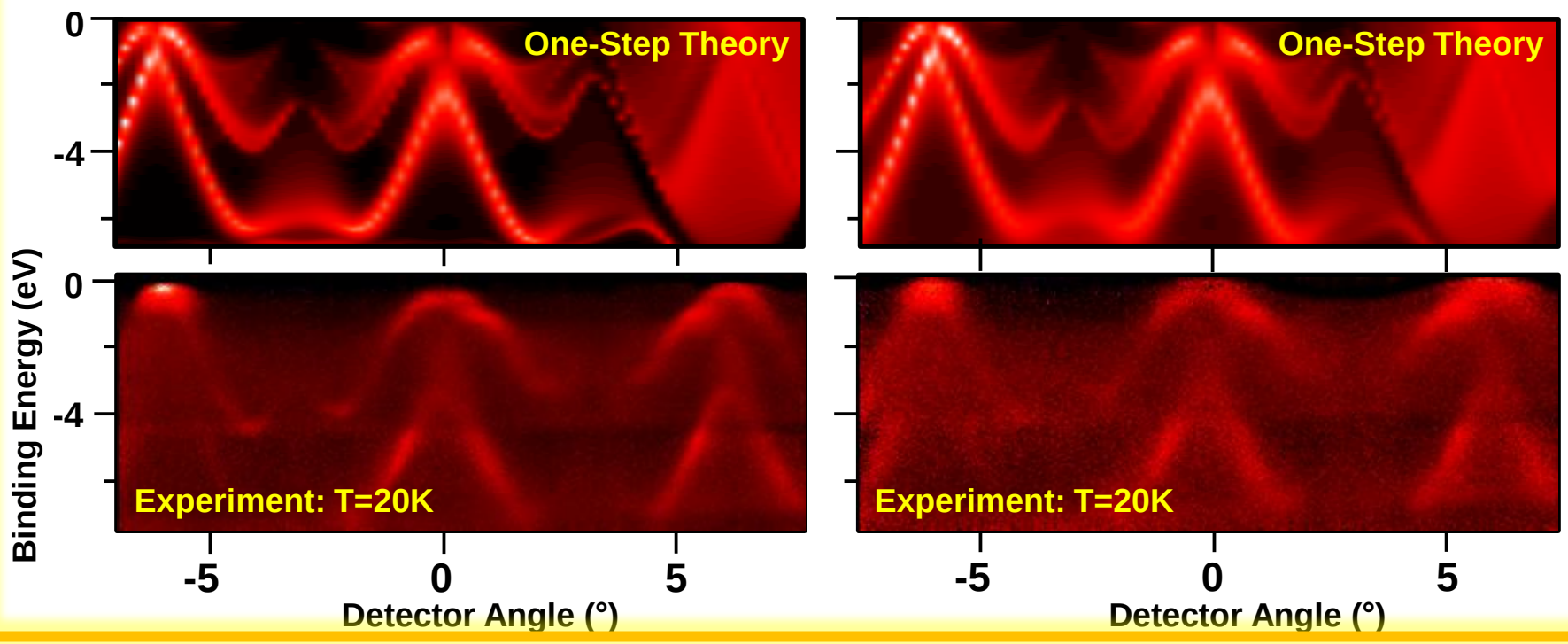
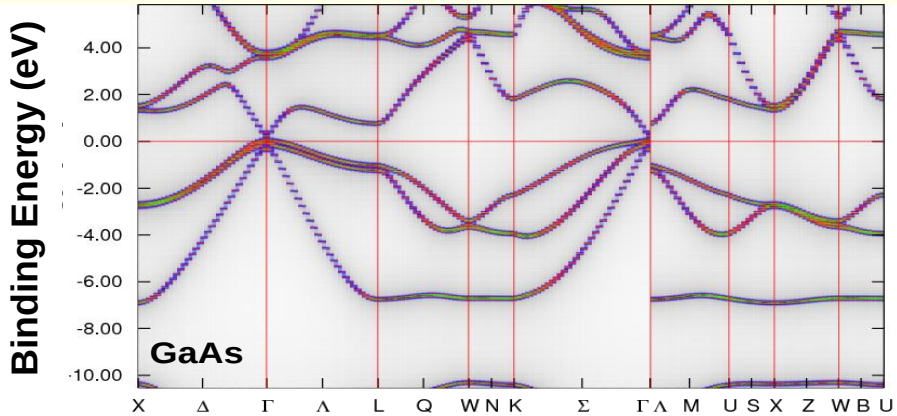
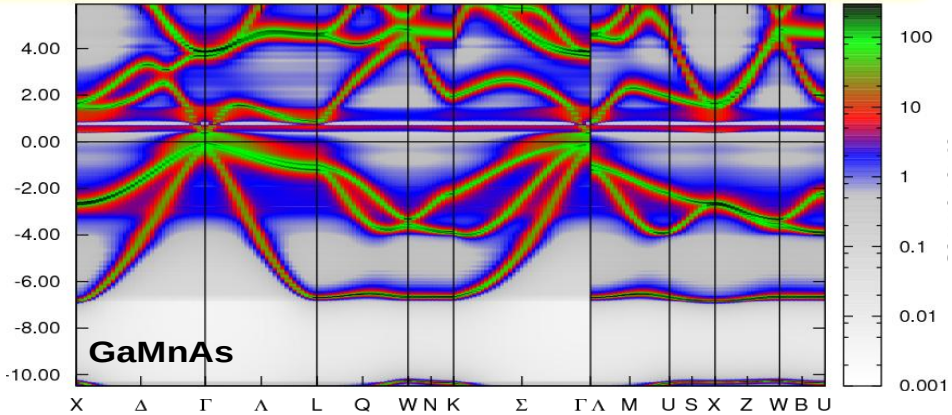


HARPES of (Ga,Mn)As (*hv* = 3.24 keV)







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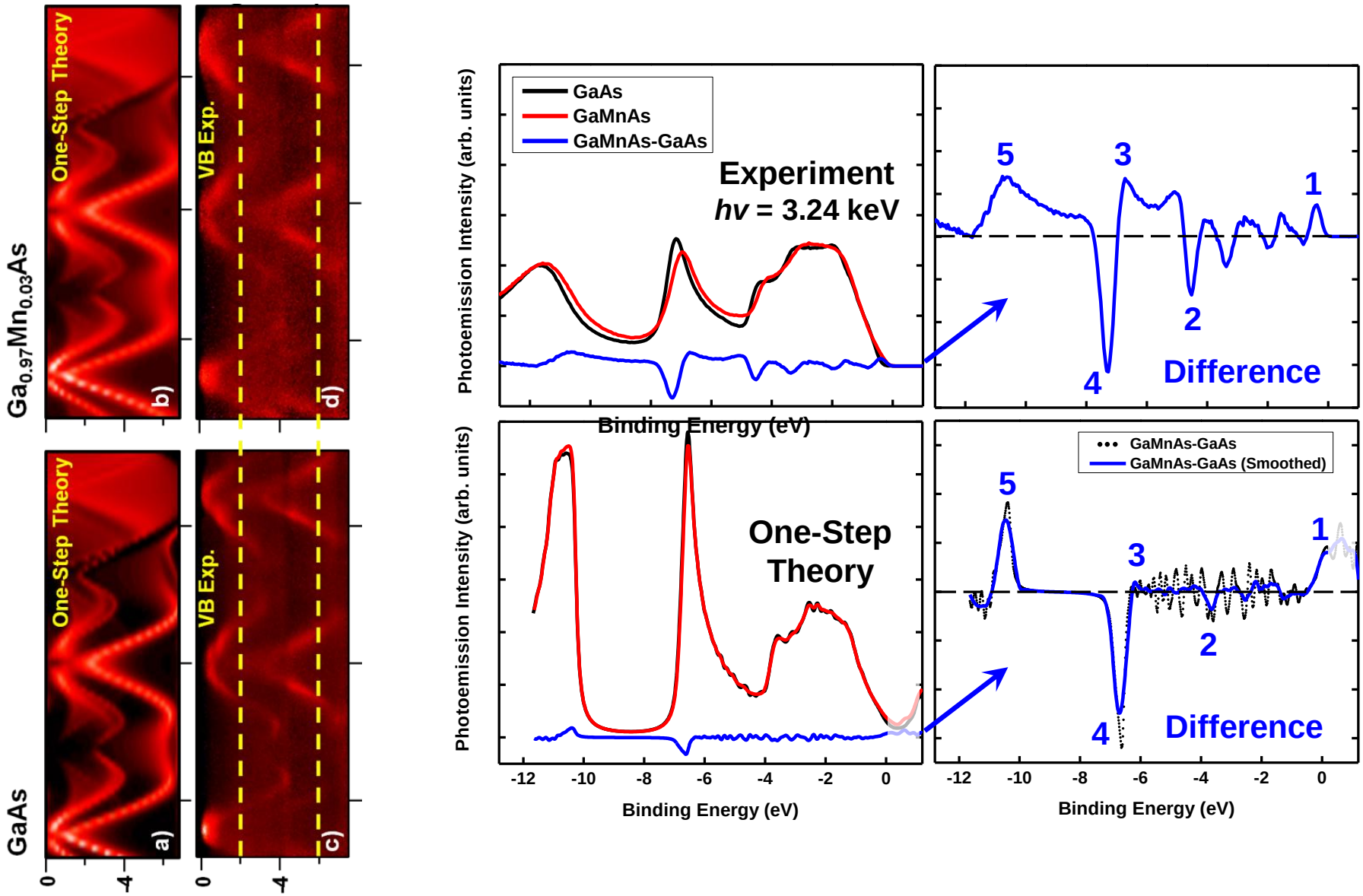

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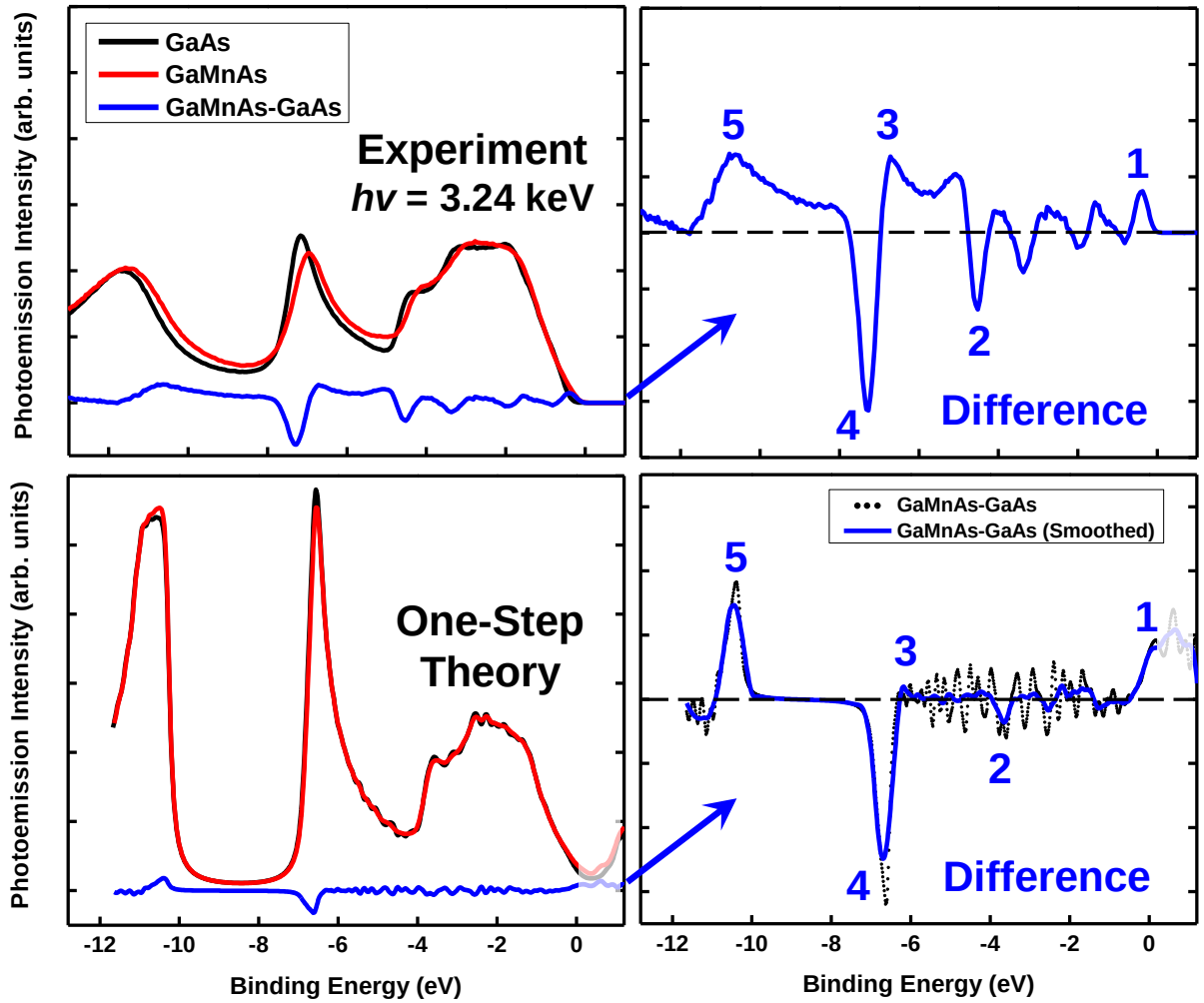

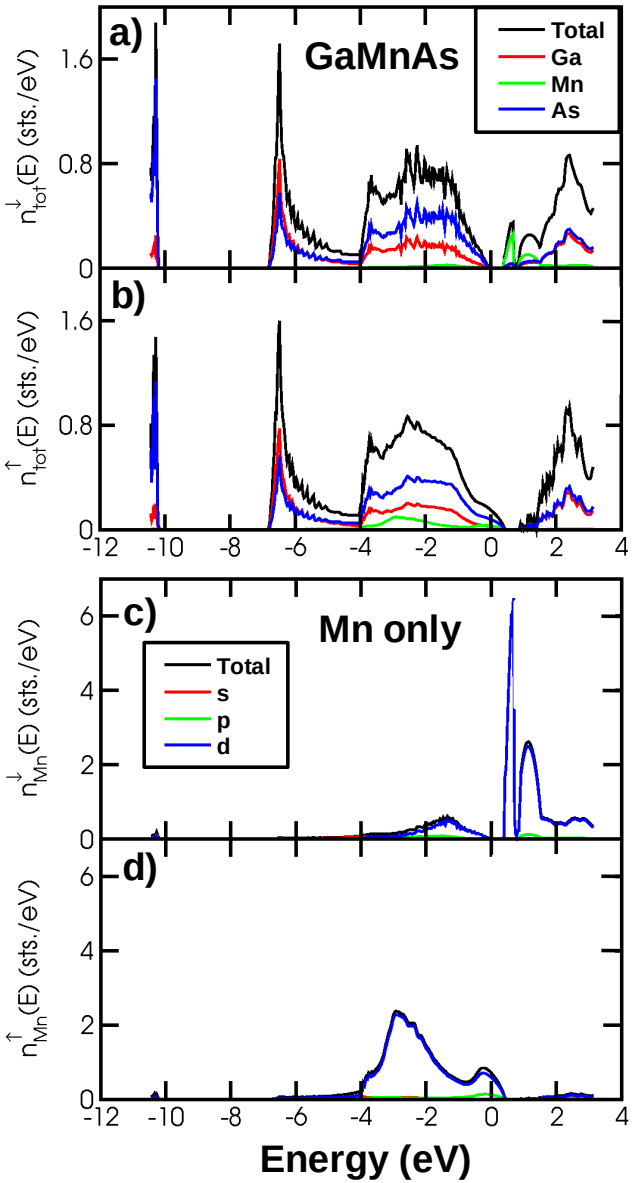

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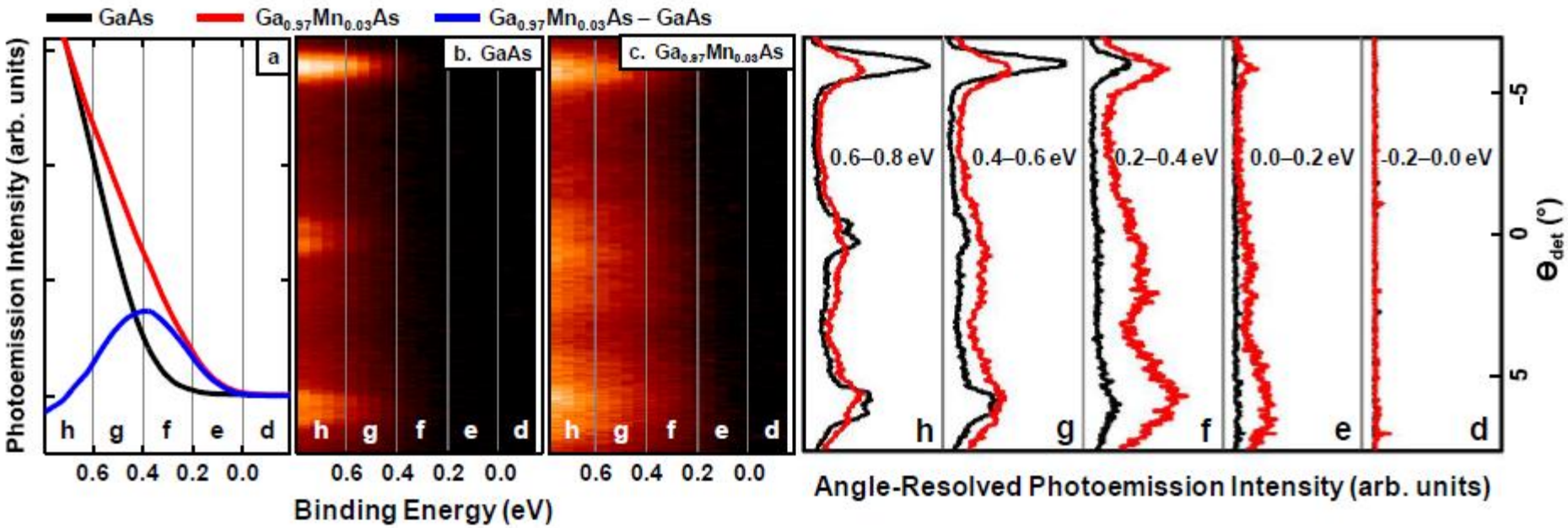

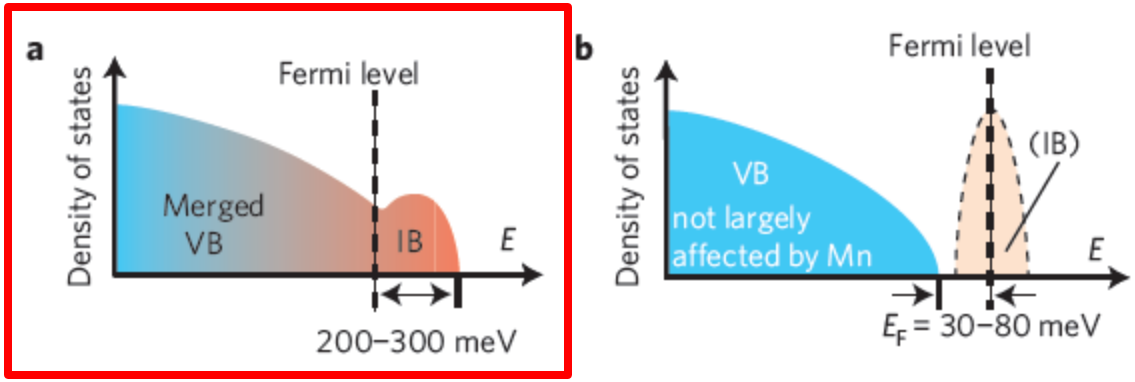

S. Ohya et al., Nature Physics 7, 342 (2011)

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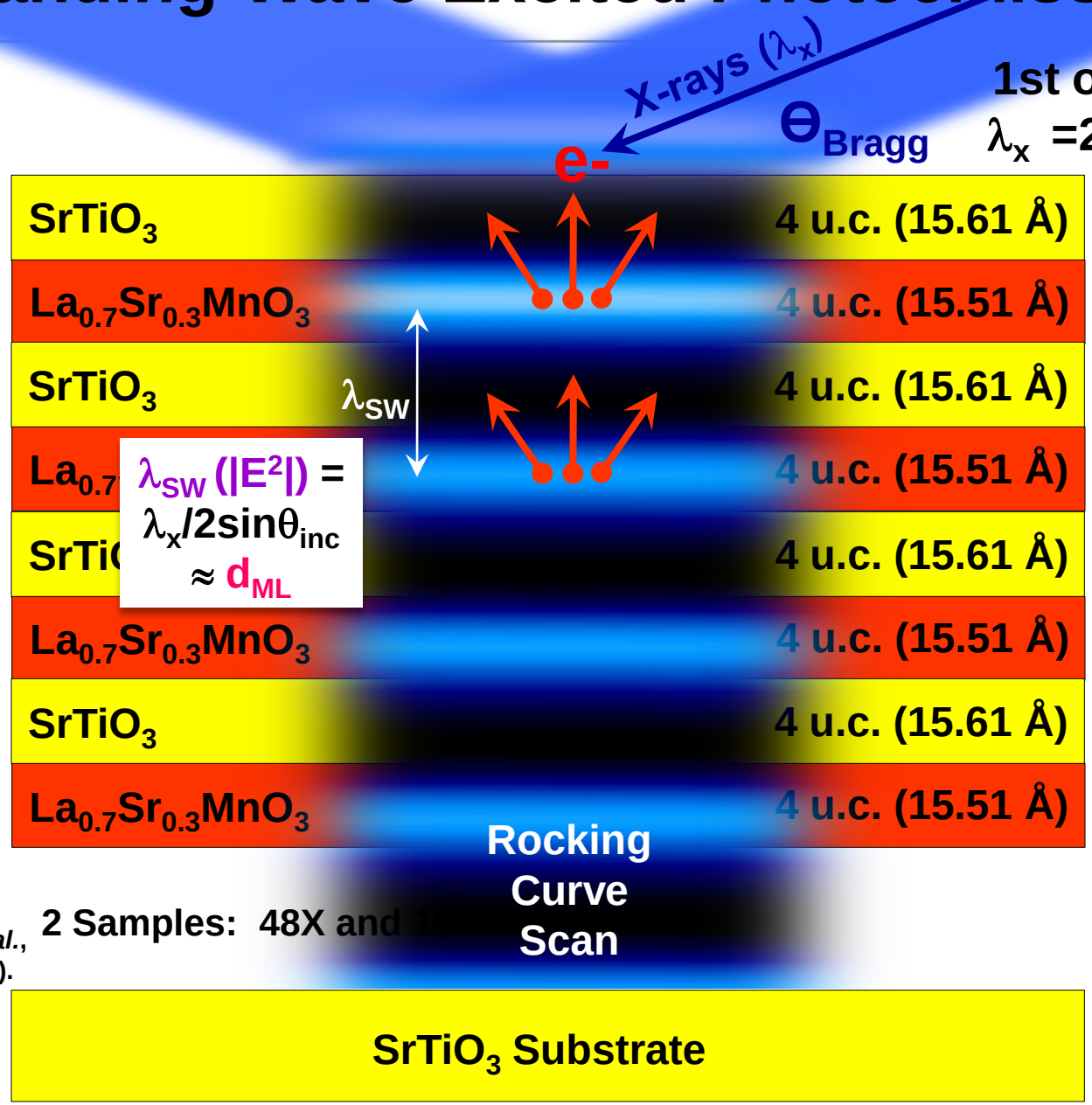
  - Metal-to-Insulator Transition in $LaNiO_3$
- Hard X-ray Angle-Resolved Photoemission (HARPES)
  - W, GaAs, and $Ga_{0.97}Mn_{0.03}As$
- **Standing-Wave Excited Photoemission (SWARPES)**
  - **$La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ Interface**
- **Summary and Future Outlook**

Standing-Wave Excited Photoemission



1st order Bragg:

$\lambda_x = 2d_{ML}\sin\theta_{Bragg}$

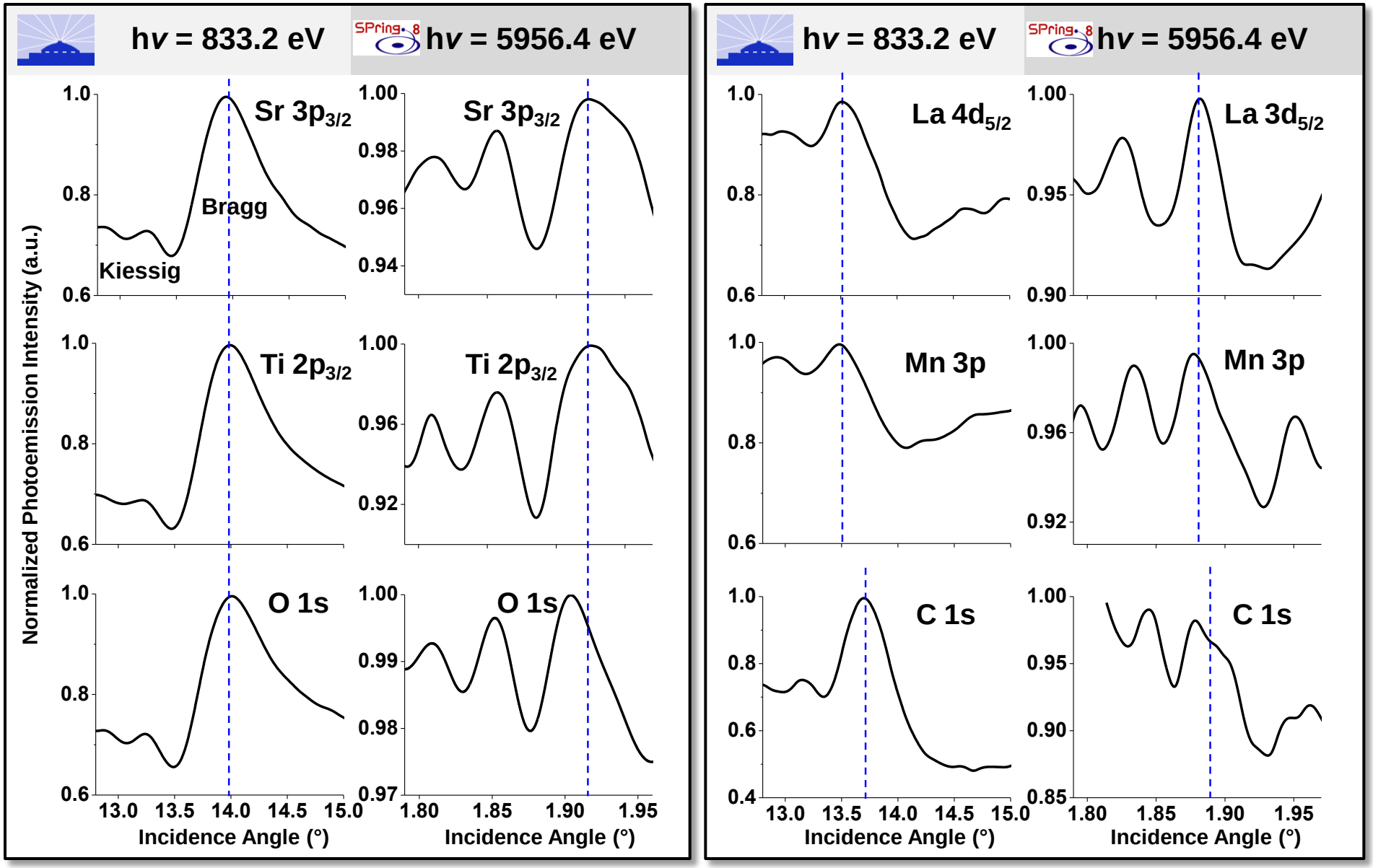
d_{ML}

$h\nu$ = 833.2 (ALS-(La $3d_{5/2}$ res.) and 5956 eV (SPring-8)

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

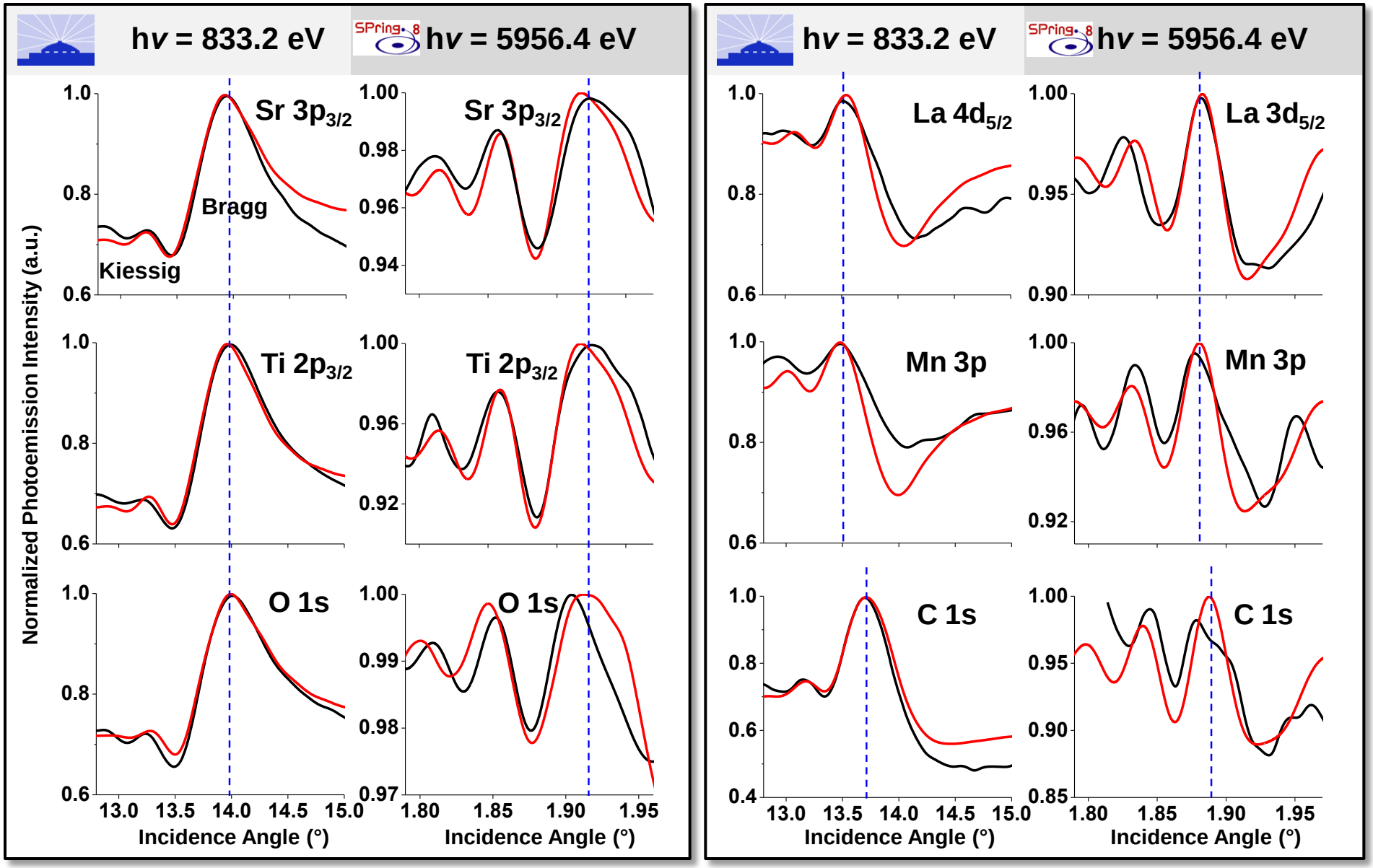
Sample: M. Huijben, D. H. A. Blank R. Ramesh

Experimental Results



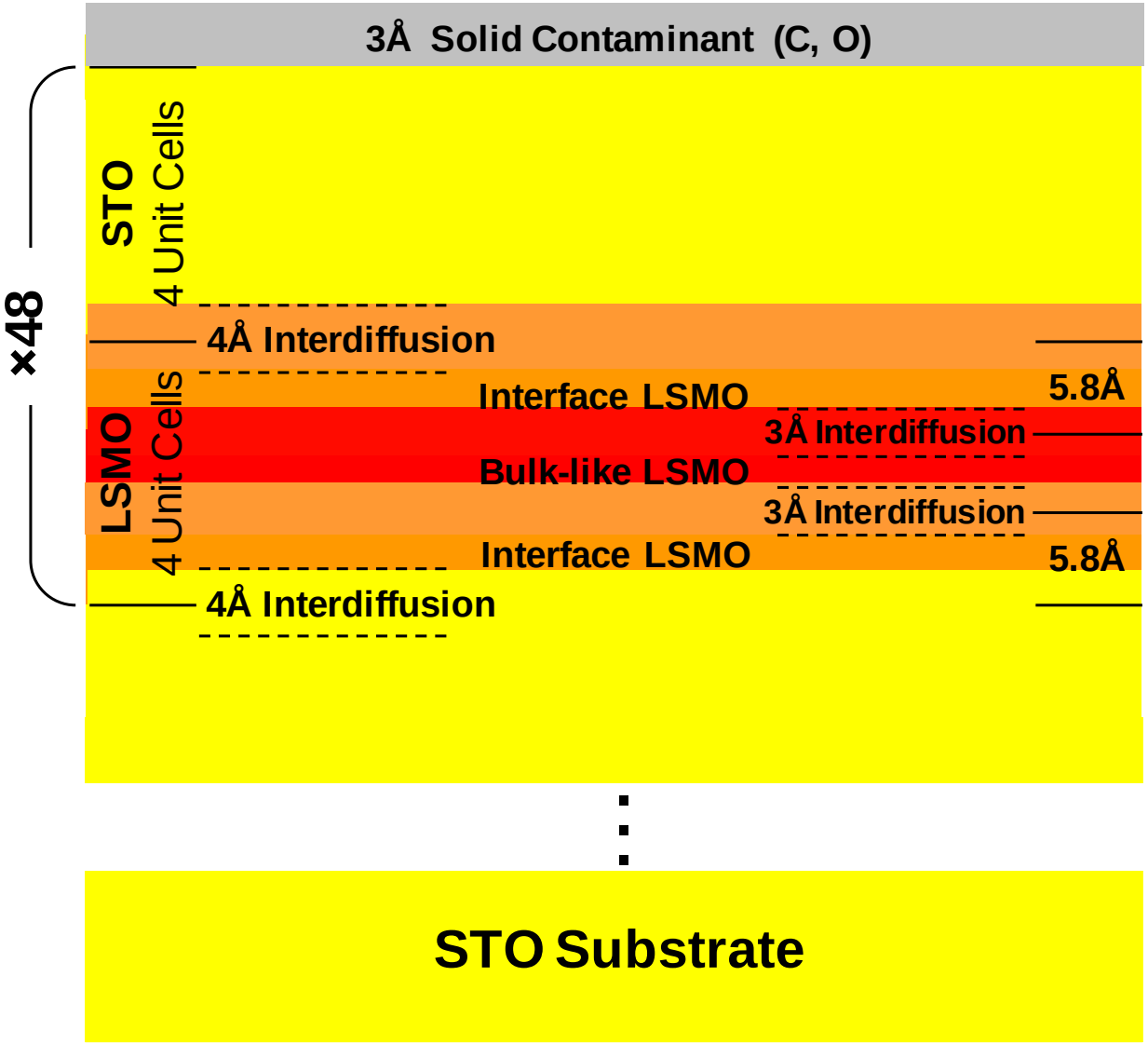
Fitting to X-ray Optical Calculations

Exp.
Cal.



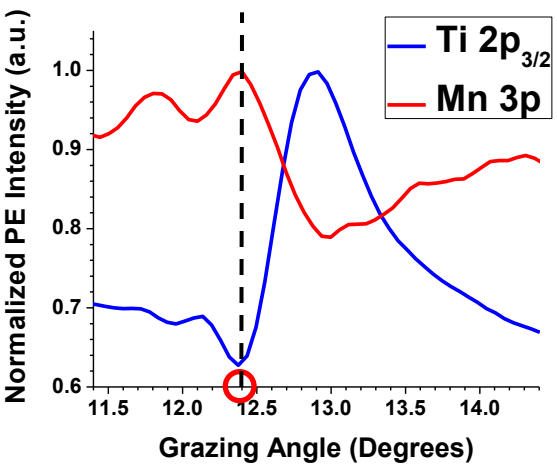
S. H. Yang, A. X. Gray *et al.*, JESRP (submitted).

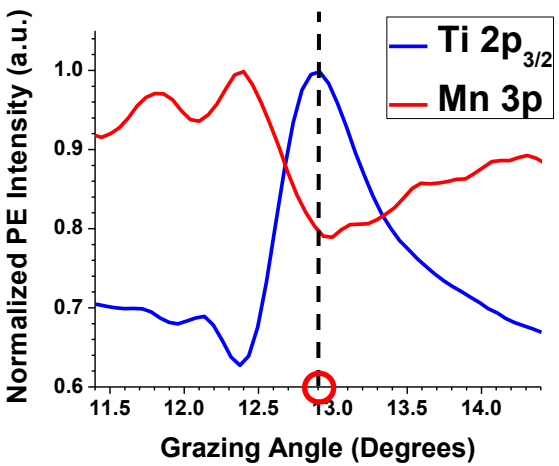
Resulting Structure for the $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ Interface and Multilayer



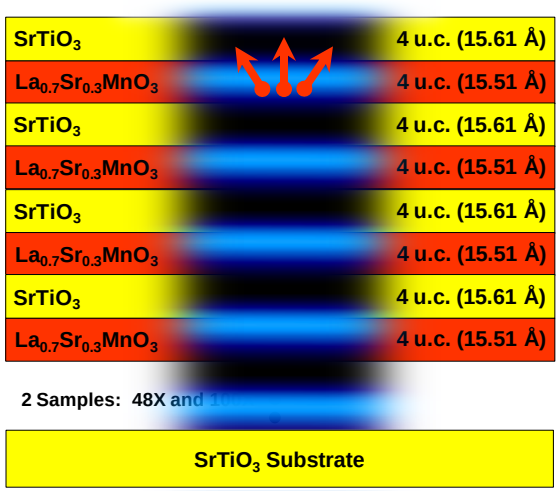
- Interface has interdiffusion/ roughness and altered dielectric constant
- Average multilayer period changes by about -1 Å or -6% from top to bottom

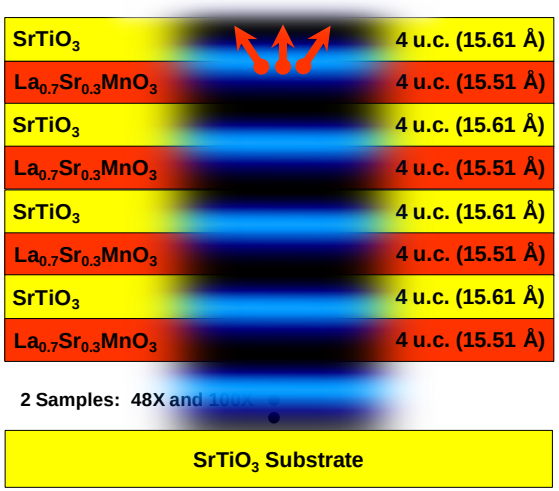
Standing-Wave Excited ARPES (SWARPES)





Probing Bulk LSMO

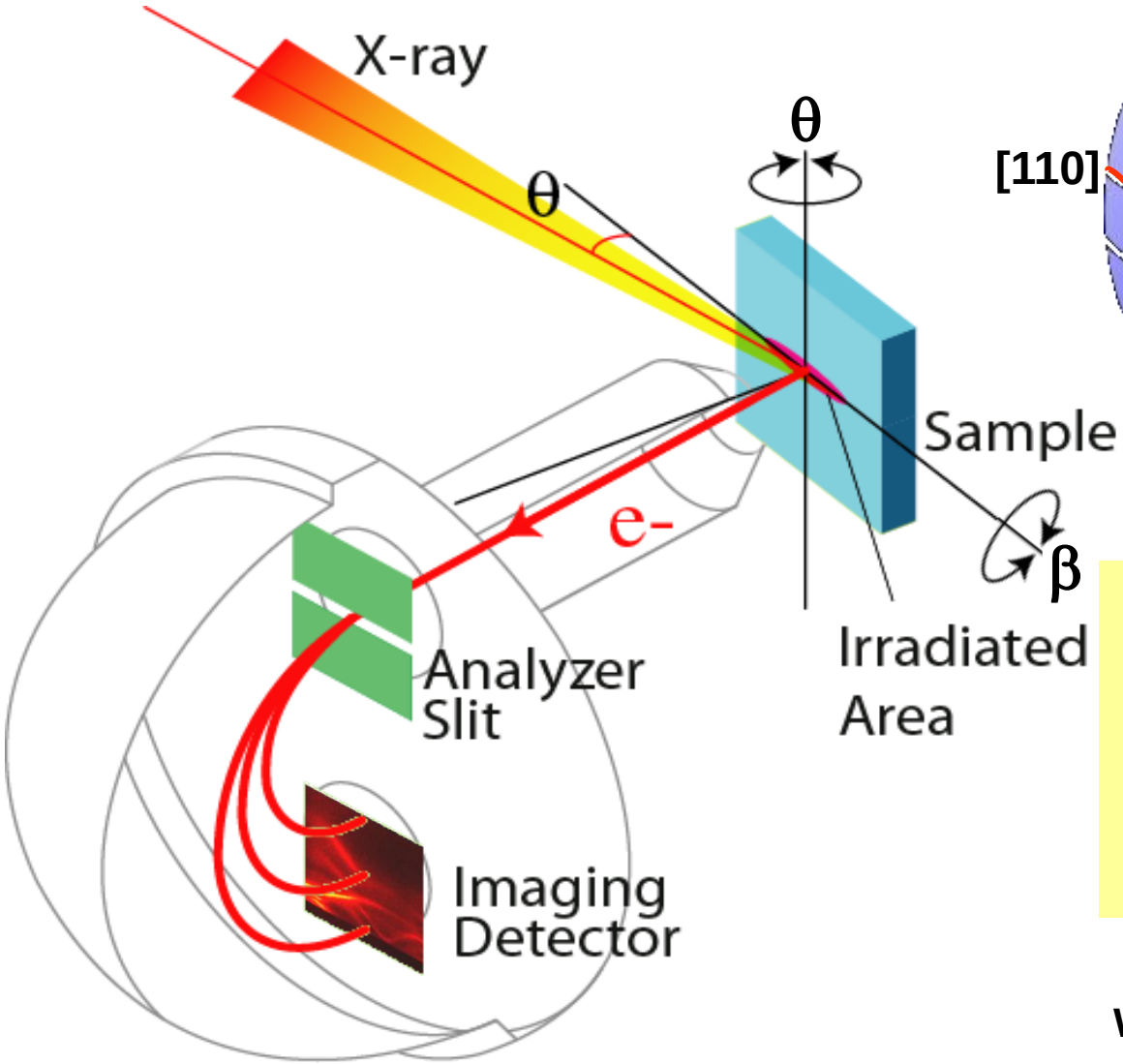


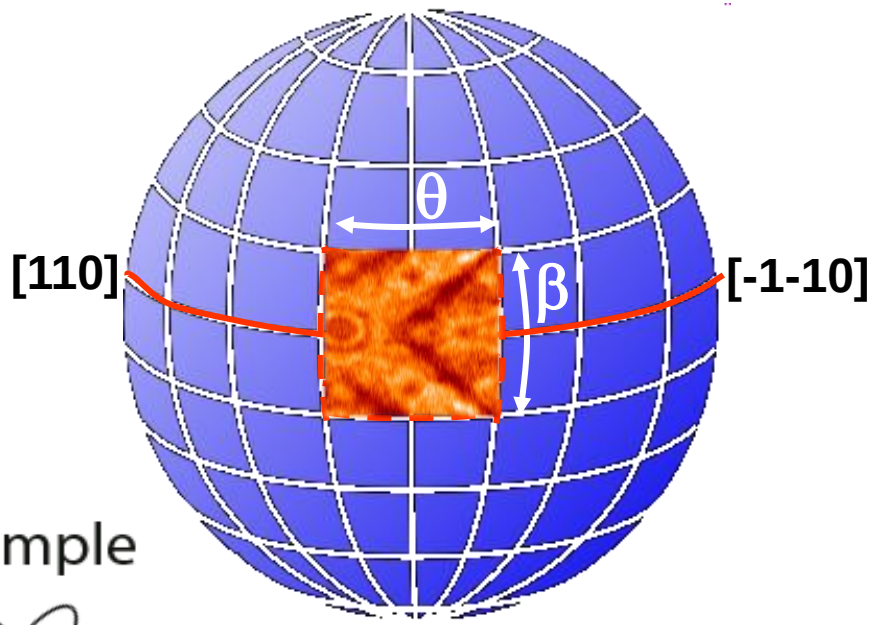


Probing Interface LSMO

A. X. Gray, J. Minár *et al.*,
(in preparation)

Standing-Wave Excited ARPES (SWARPES)



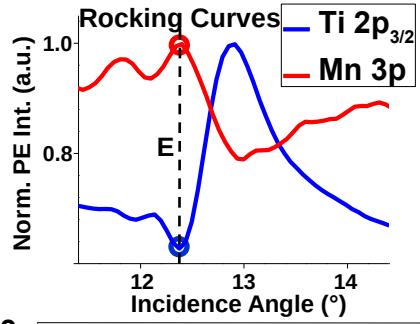


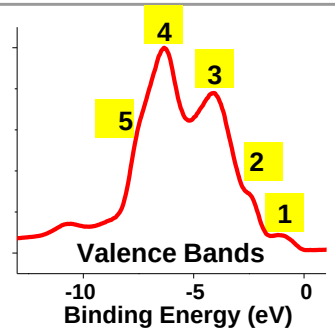
hν = 833.2 eV (still)
T = 20 K
~ARPES limit with
Photoemission Debye-Waller
W(20K)→
~75% k-conserving transitions

Beamline 7.0 ALS
With A. Bostwick, E. Rotenberg

Depth-Resolved ARPES: Bulk LSMO

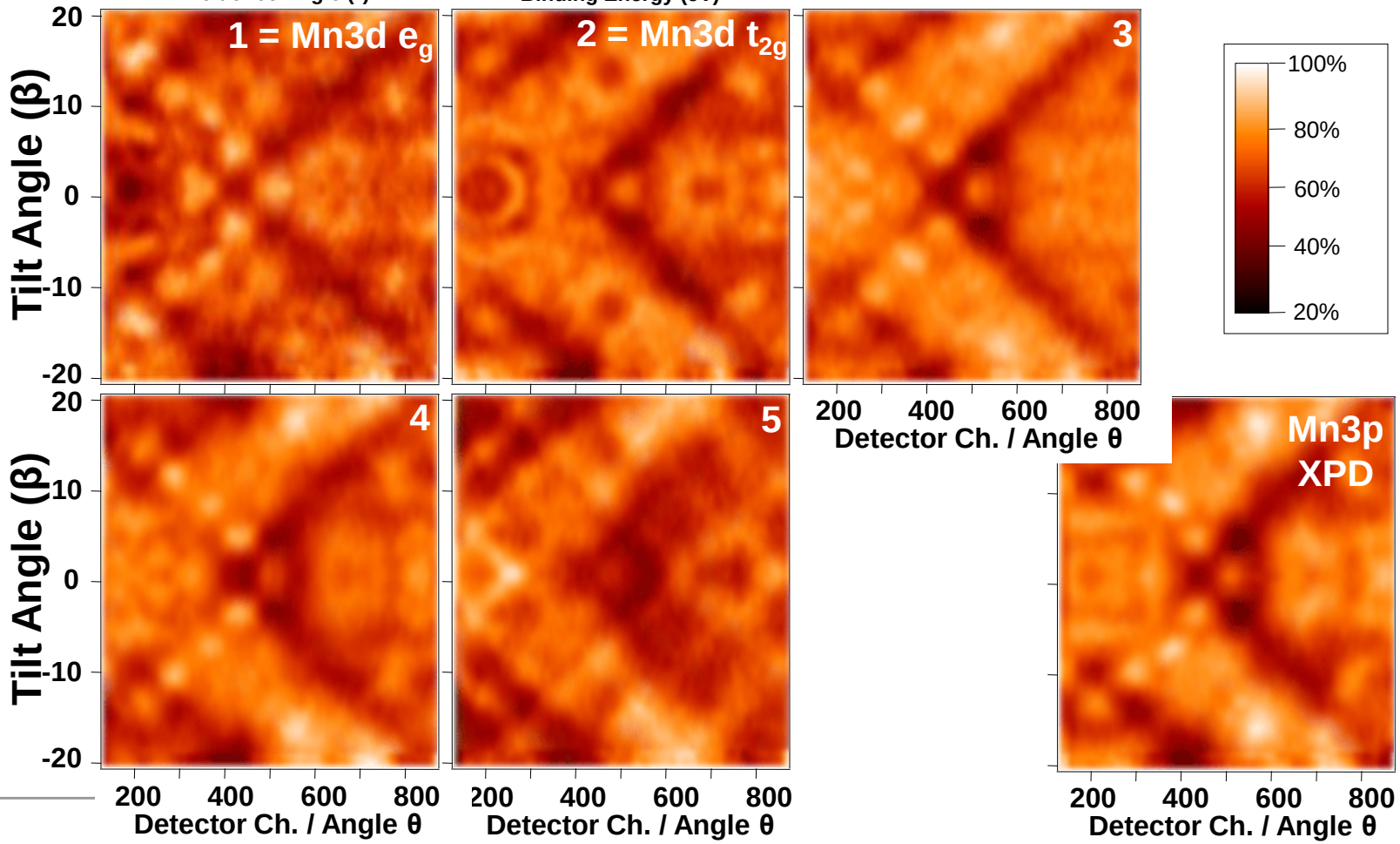
Probing **Bulk** LSMO (max. Bulk sensitivity)





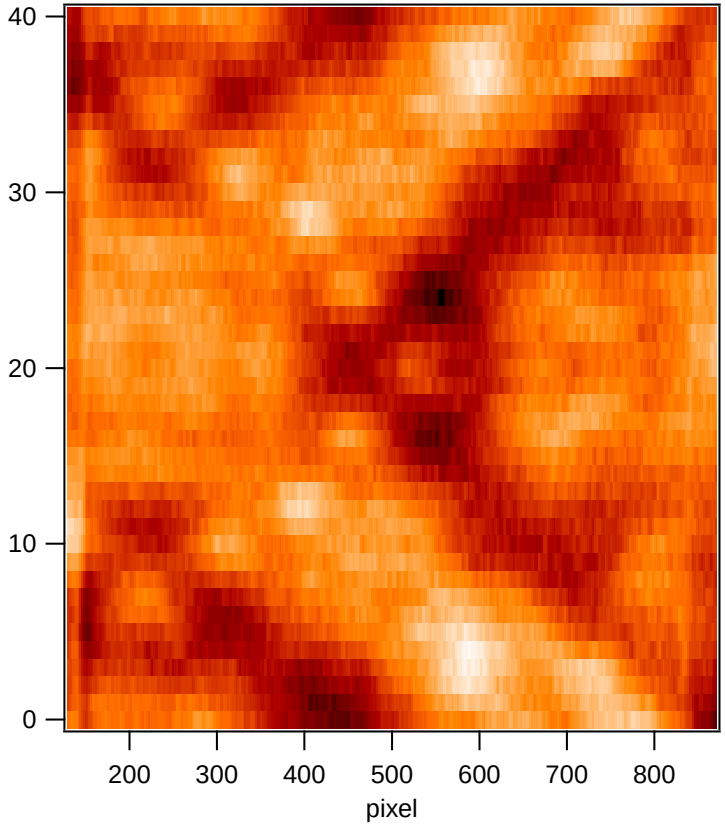
hv = 833.2 eV

T = 20 K



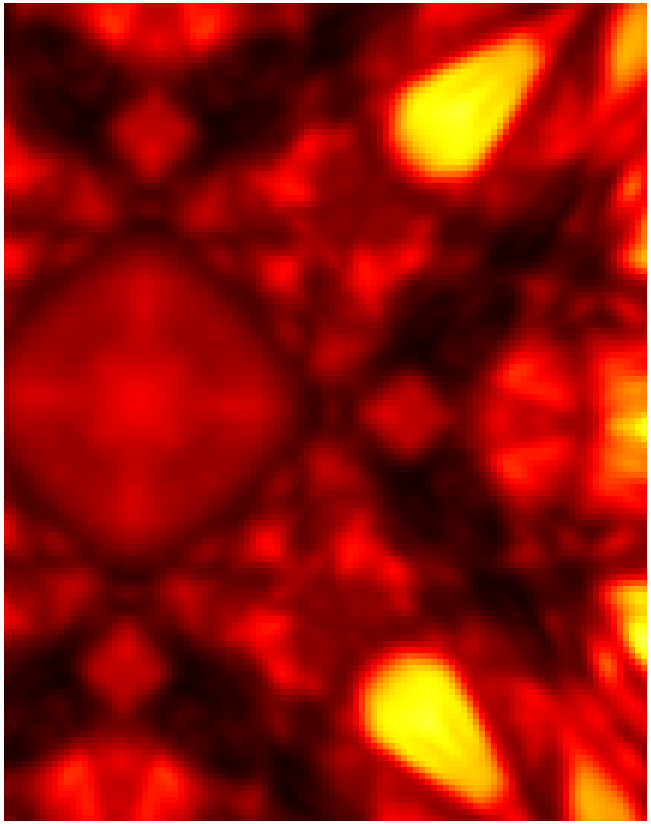
X-Ray Diffraction Effects in the Data

Experiment: Mn 3p



Experiment: Fadley Group

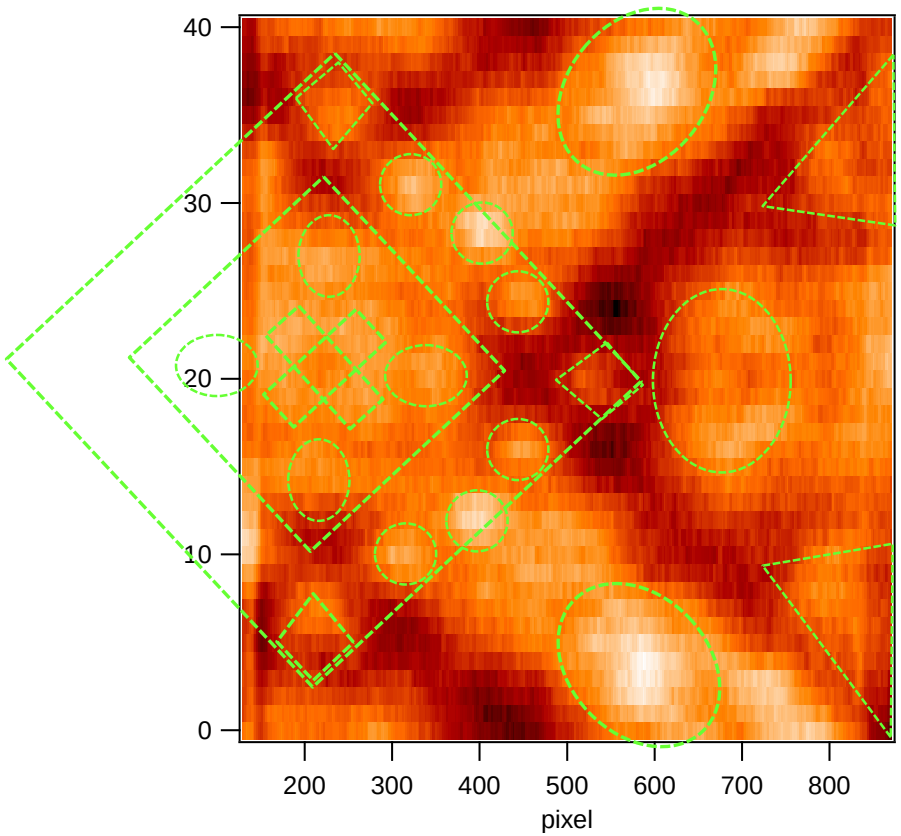
XPD Theory: Mn3p



Theory: A. Winkelmann

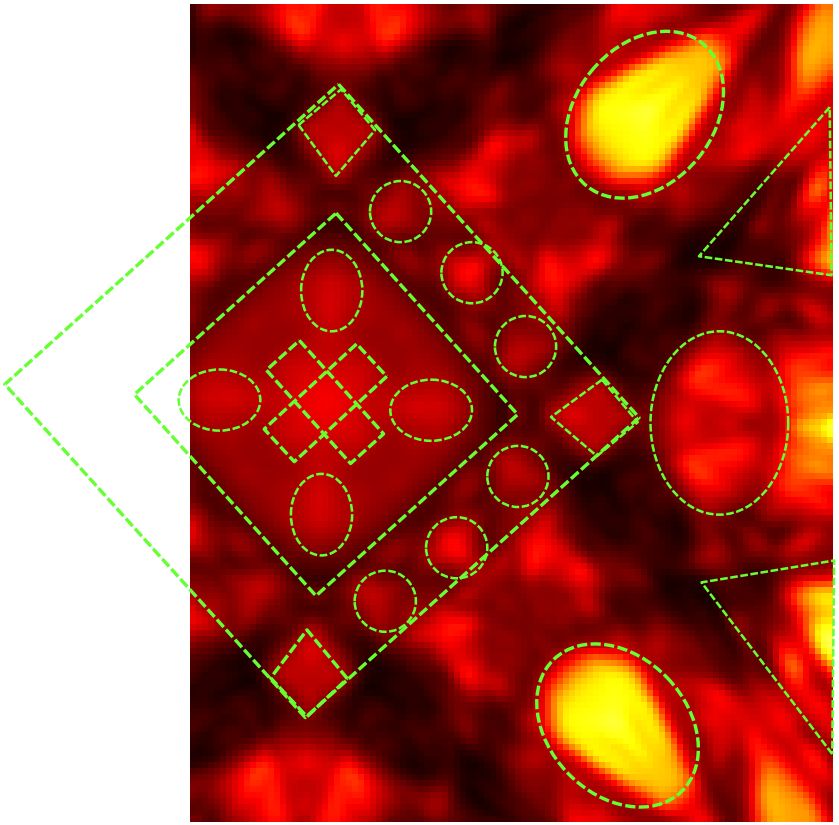
X-Ray Diffraction Effects in the Data

Experiment: Mn 3p



Experiment: Fadley Group

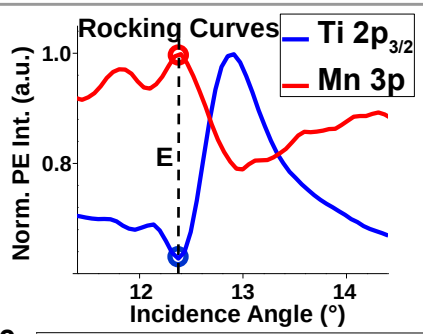
XPD Theory: Mn3p

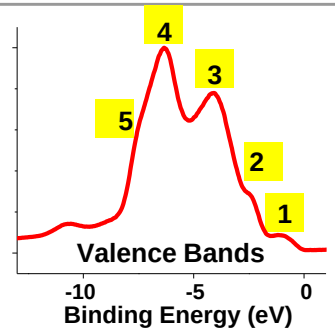


Theory: A. Winkelmann

Depth-Resolved ARPES: Bulk LSMO

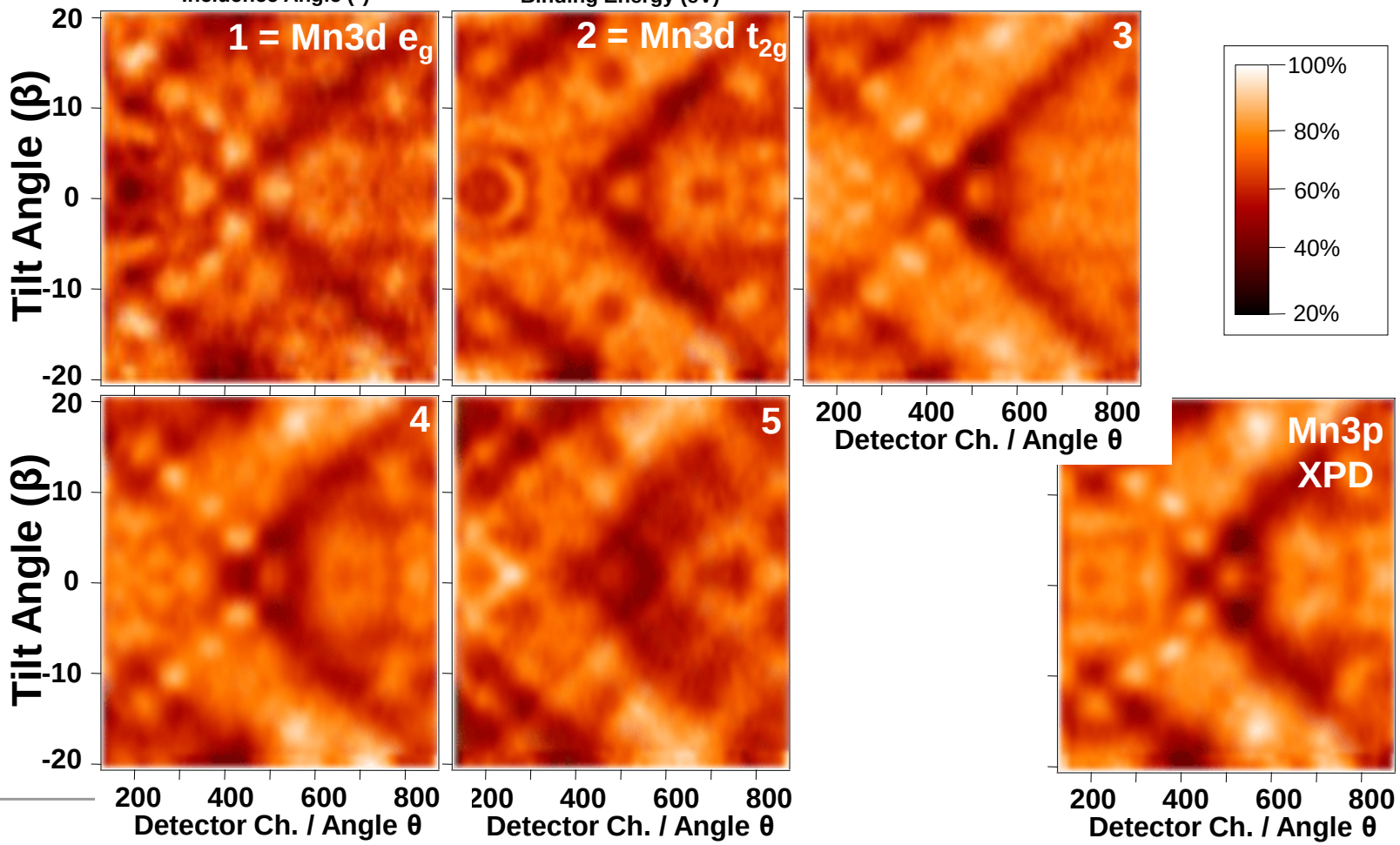
Probing **Bulk** LSMO (max. Bulk sensitivity)





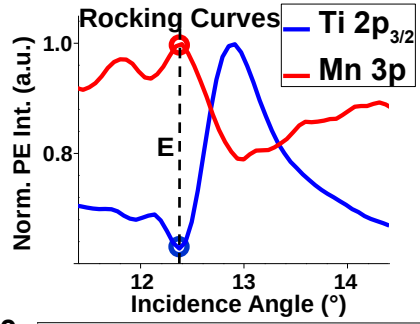
hv = 833.2 eV

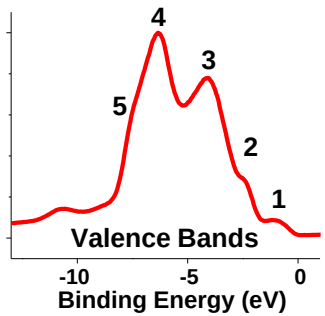
T = 20 K



Depth-Resolved ARPES: Bulk LSMO

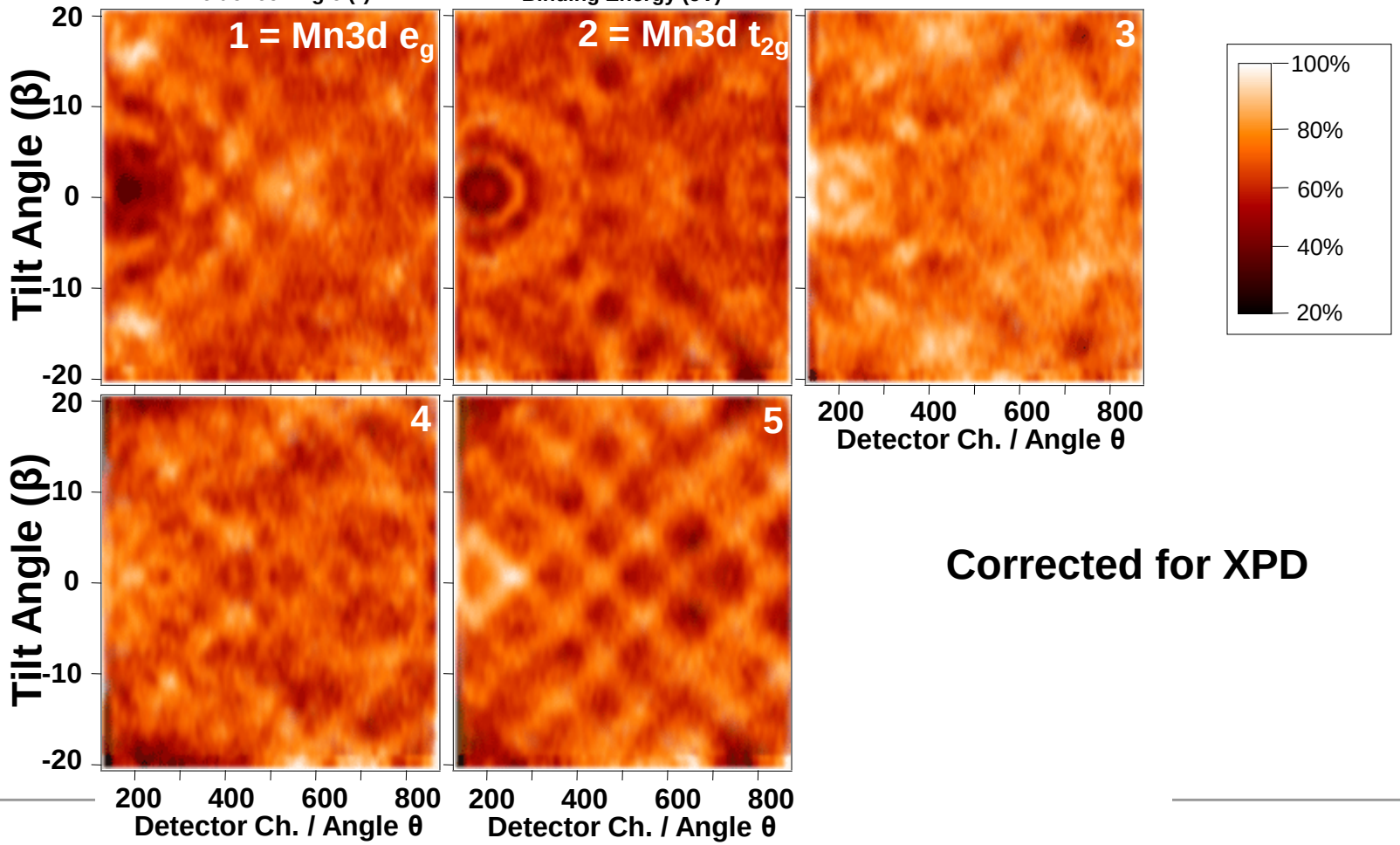
Probing **Bulk** LSMO (max. Bulk sensitivity)





hv = 833.2 eV

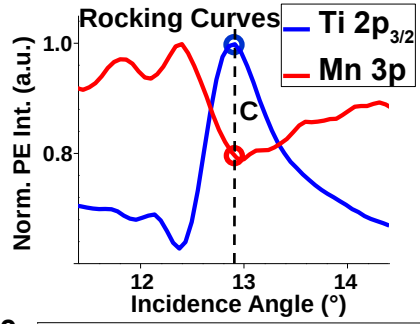
T = 20 K

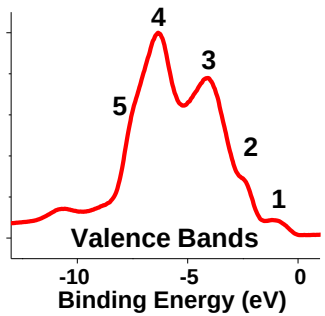


Corrected for XPD

Depth-Resolved ARPES: Interface LSMO

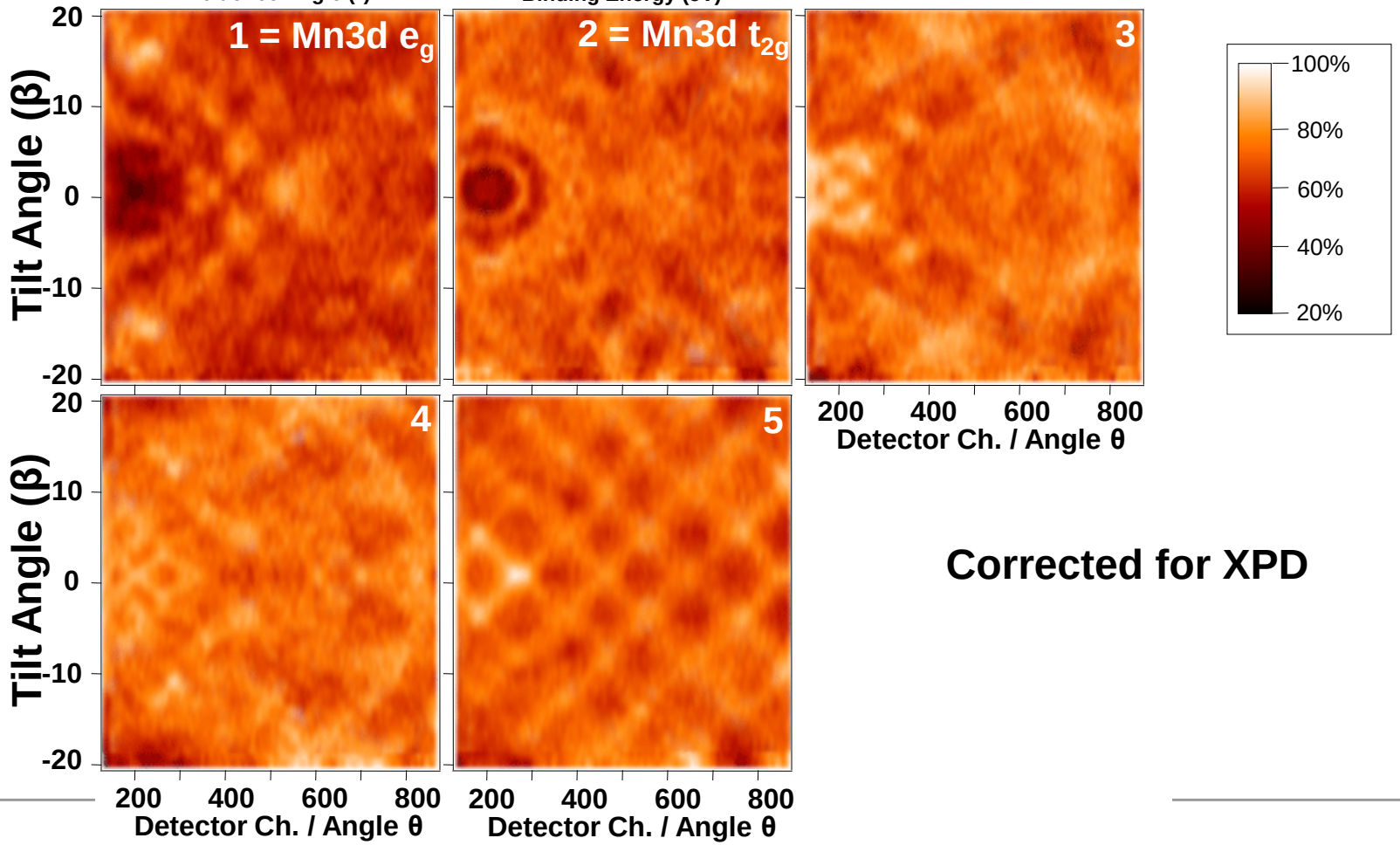
Probing Interface LSMO (max. Interface sensitivity)





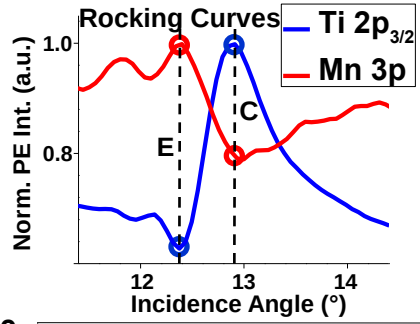
hv = 833.2 eV

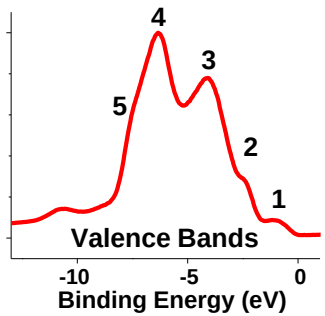
T = 20 K



Corrected for XPD

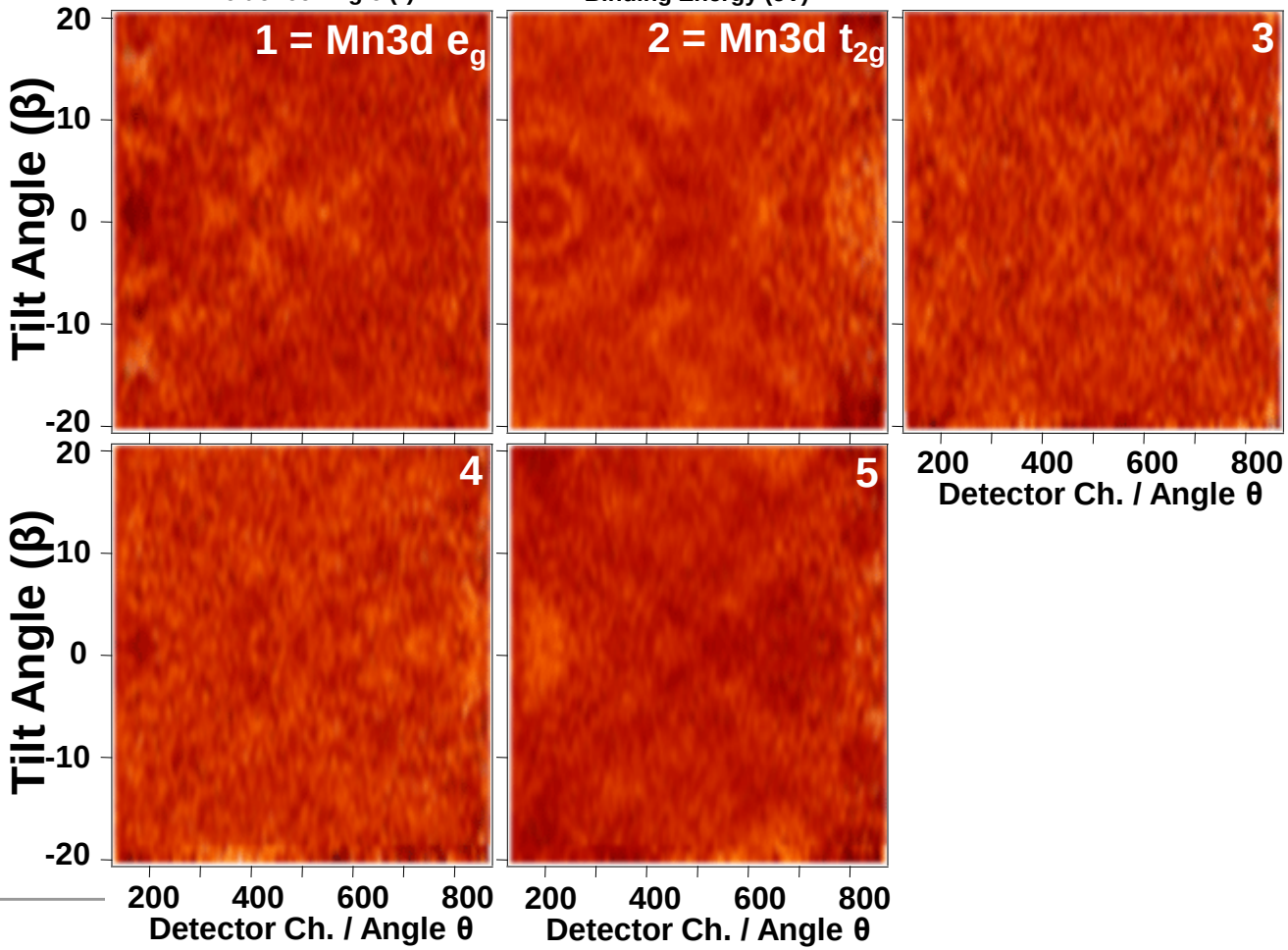
Depth-Resolved ARPES: Bulk - Interface

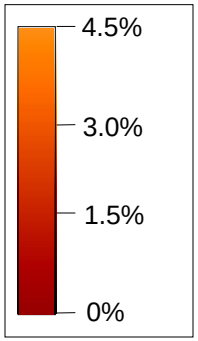




hv = 833.2 eV

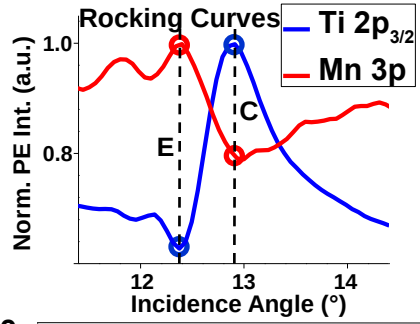
T = 20 K

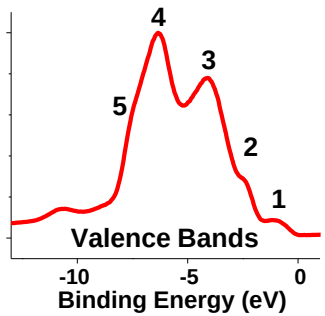




Depth-Resolved ARPES: Bulk - Interface

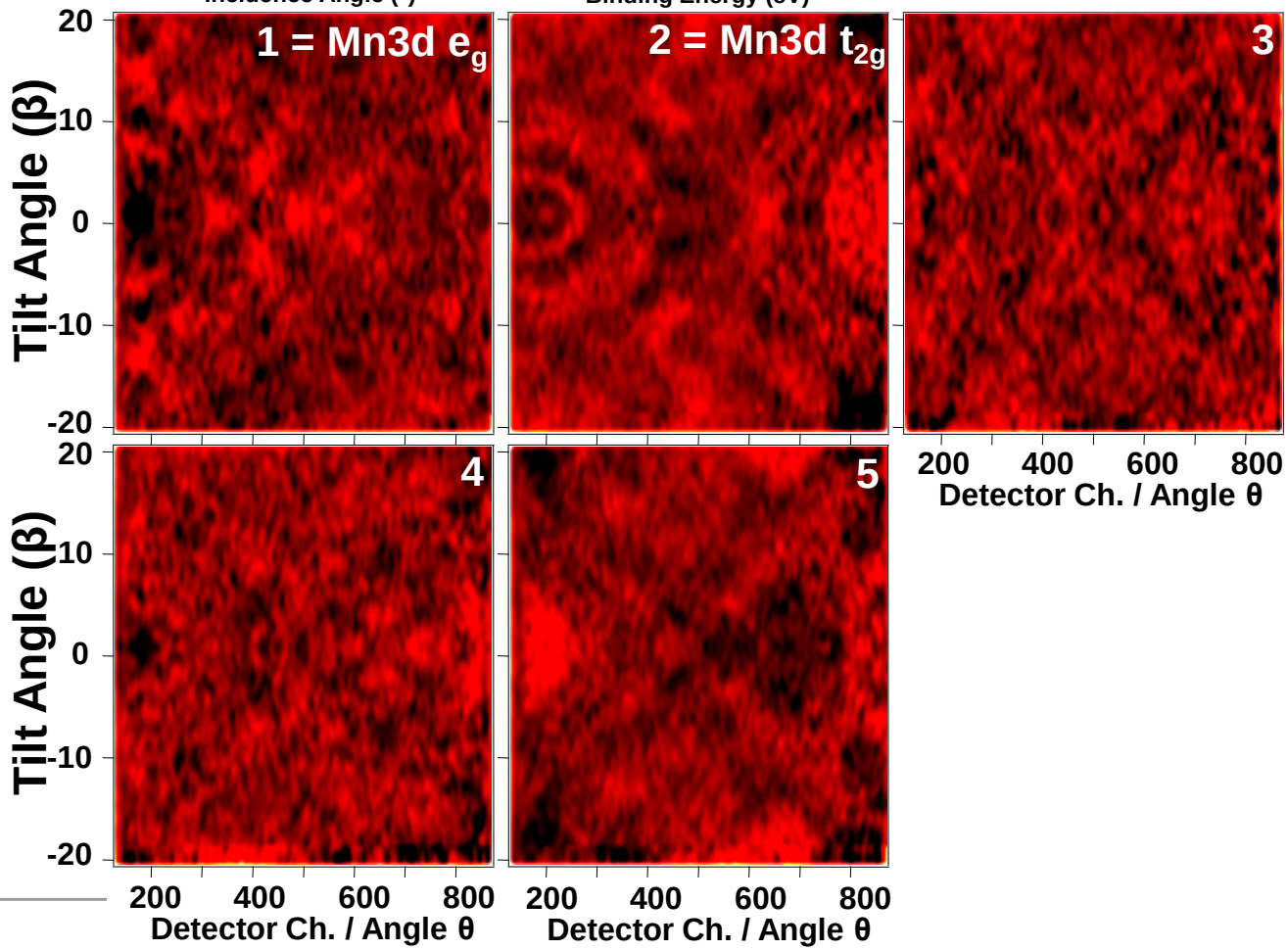
Enhanced Contrast

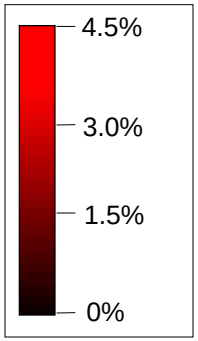




hv = 833.2 eV

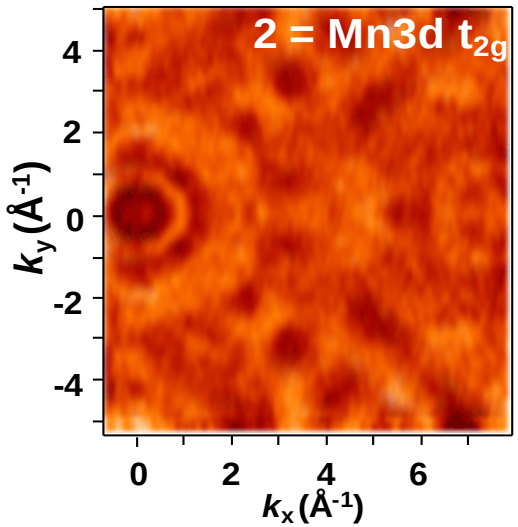
T = 20 K



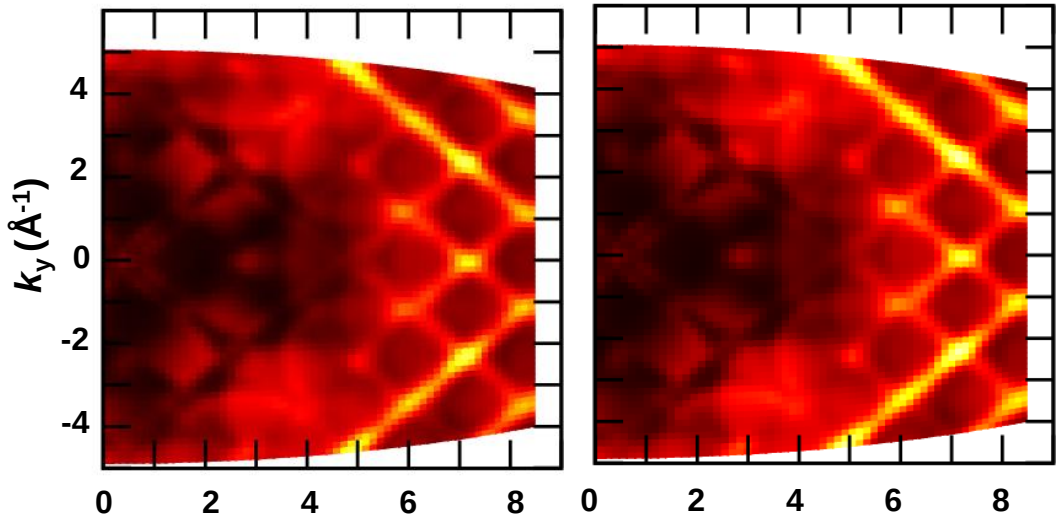


First comparison to one-step photoemission theory for STO/LSMO

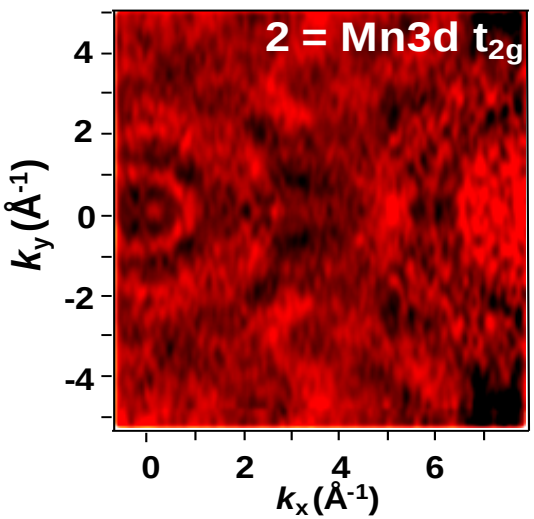
Experiment:
t_{2g}: Bulk LSMO



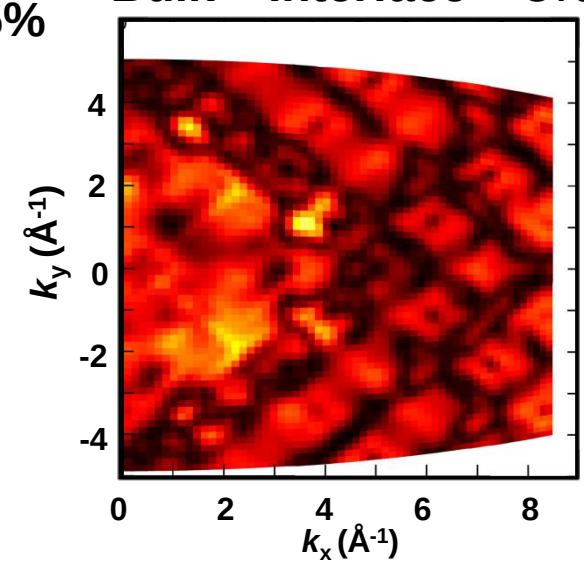
One-Step Theory, LDA+U, with SW E-field profile:
t_{2g}: Bulk LSMO **Interface LSMO**



Bulk – Interface- ~5%



Bulk – Interface- ~8%

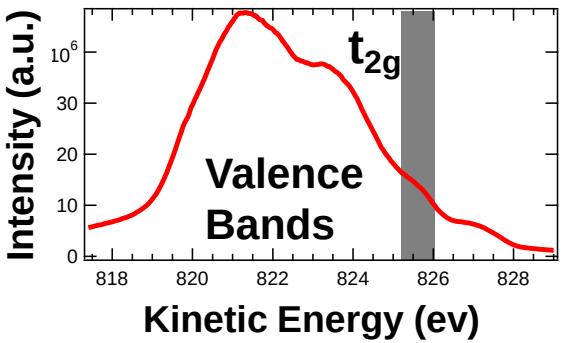


Calculations with more complex Interface relaxations in progress- Minar, Braun, Ebert

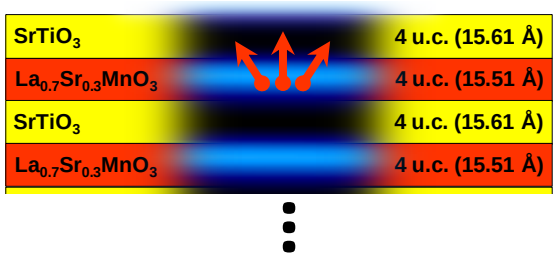
A. Gray et al., TBP

$[SrTiO_3/La_{0.7}Sr_{0.3}MnO_3]_{120}$ Variable-Polarization SWARPES

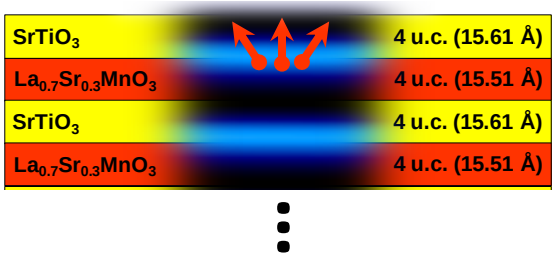
hv = 833.2 eV, SLS



Bulk LSMO Geometry



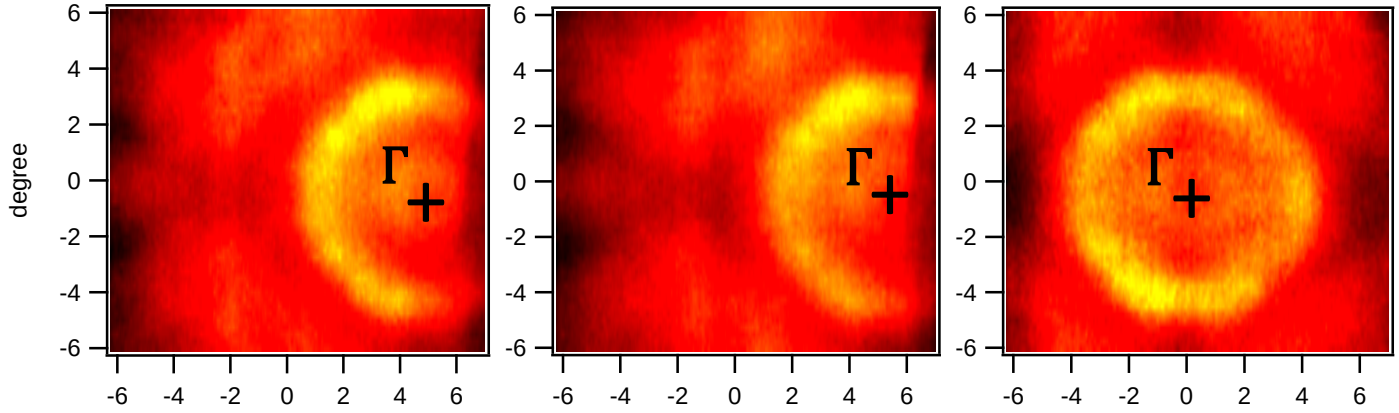
Interface LSMO Geometry



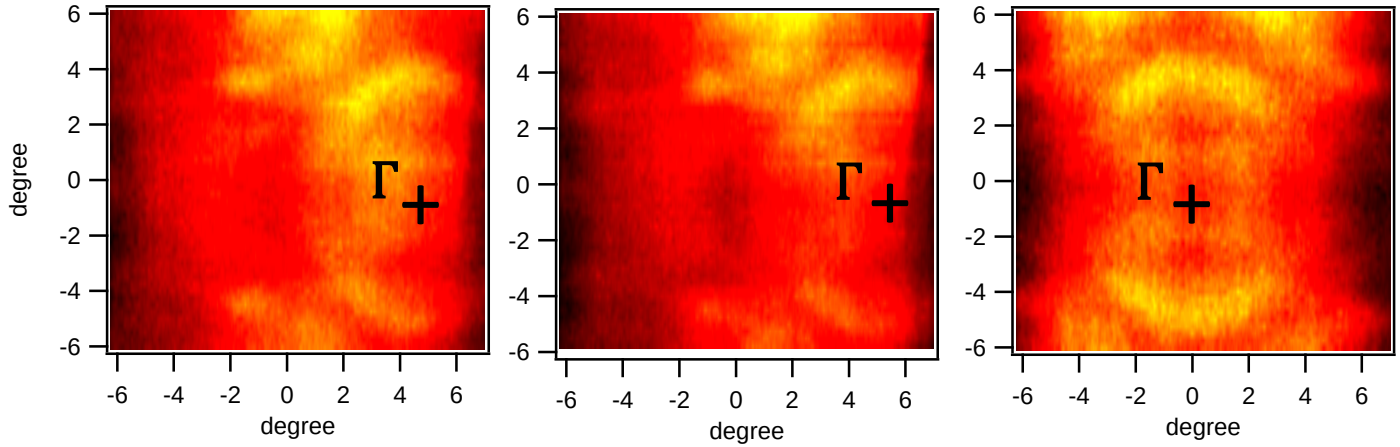
Bulk LSMO | **Interface LSMO** | **Normal Emission**

From SLS ADRESS

Vertical Polarization



Horizontal Polarization

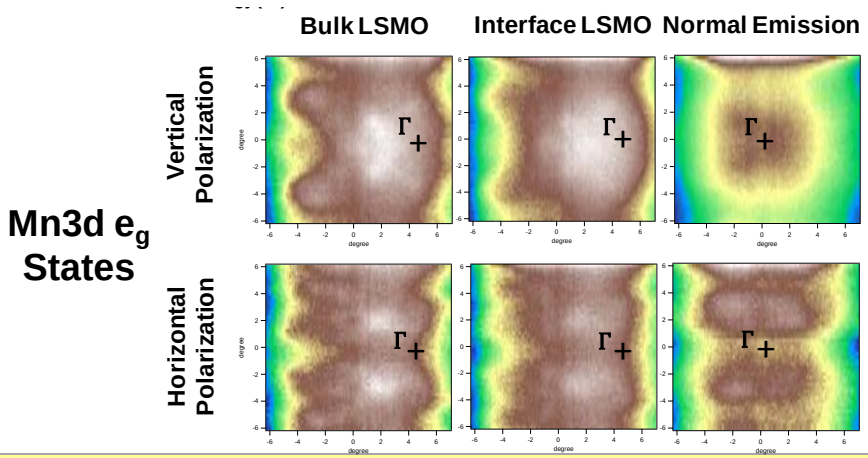


A. Gray et al., TBP

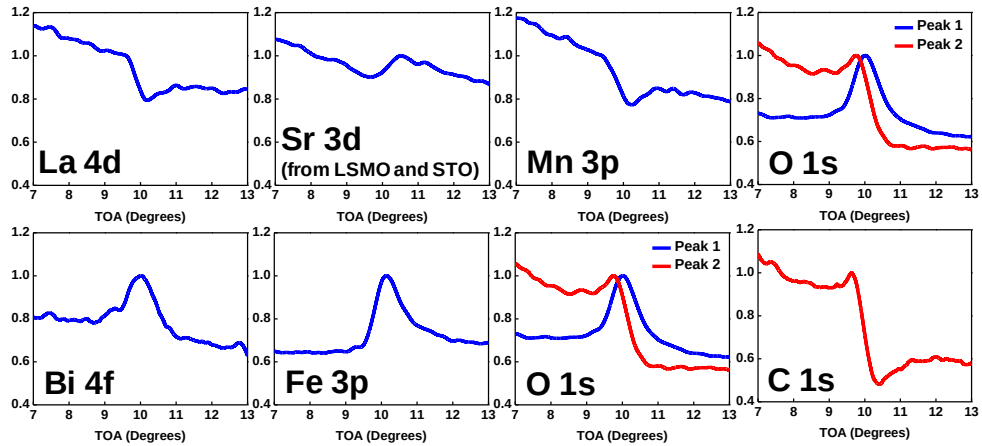
Most Recent SWARPES Measurements (SLS)

Depth-Resolved Electronic Structure of Exchange-Bias $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ Superlattice

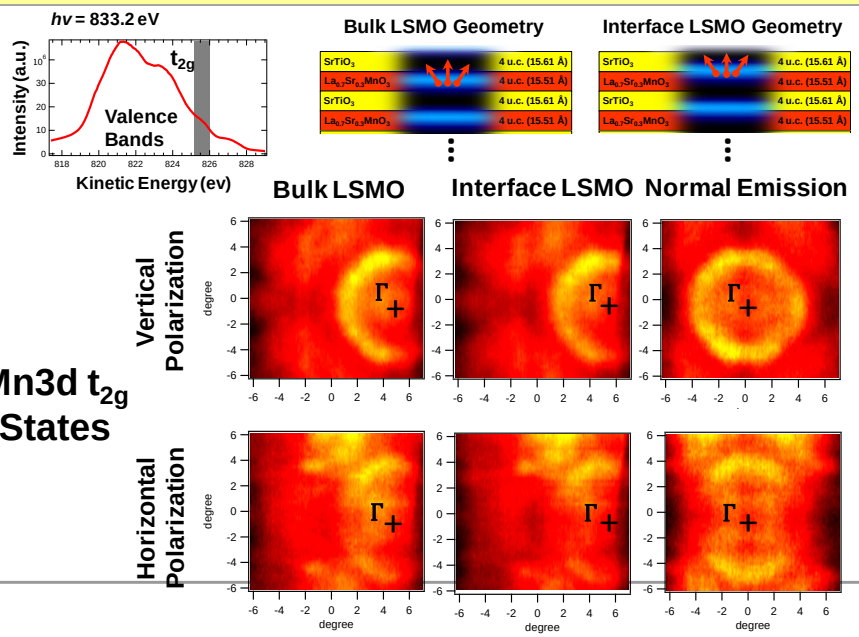
Standing-Wave ARPES of the Valence Bands



Core-Level Rocking Curves: Interface Profile

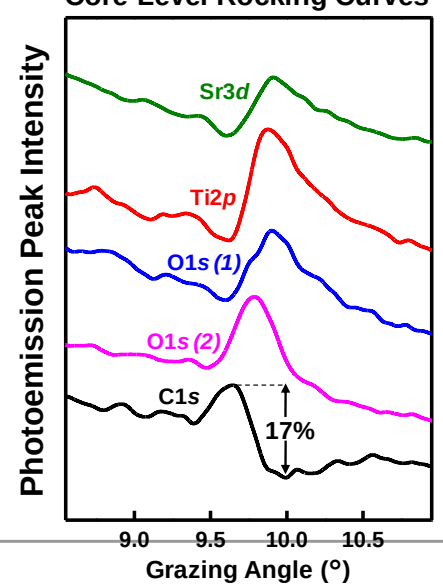


Polarization-Dependent Standing-Wave ARPES of $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ Magnetic Tunnel Junction

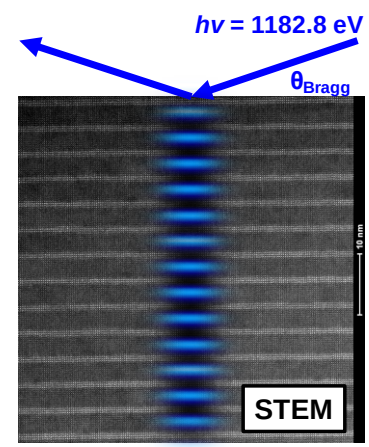


Depth-Resolved Electronic Structure of Mott-Hubbard $GdTiO_3/SrTiO_3$ Superlattice

Core-Level Rocking Curves



Standing-Wave Excited Photoemission



Sample: S. Stemmer (UCSB)

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)**