New Directions in Hard and Soft X-Ray Photoemission with Synchrotron Radiation, Including Standing Wave Excitation

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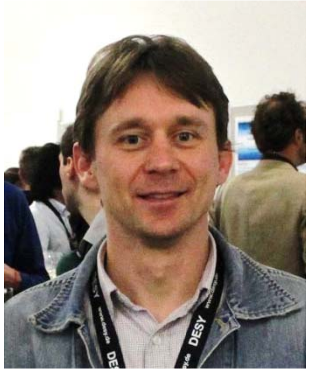
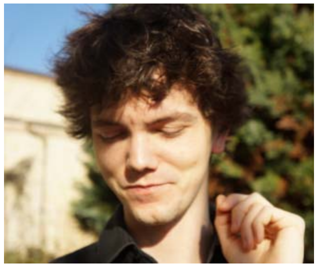
DOE: LBNL Materials Sciences Division
"Nanoscale Magnetic Materials" and LDRD
DOE, BES, Materials Sciences, X-Ray Scattering Program
ARO-Multi-University Research Initiative:
"Emergent Phenomena at Mott Oxide Interfaces"
Peter Grünberg Institute, PGI 6, Jülich Research Center
APTCOM Project, Triangle de Physique, Paris

Seminar at the Federal University of Parana State, 7 April 2016

The Core Group: Berkeley/Davis



Lukasz Plucinski
→Jülich



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Shi-Chieh Lin

Jared Garst

Alexander
Saw

Postdocs

Senior
Scientist

Grad
students

1-2 External
Student Visitors

+ experimental and theoretical collaborators at LBNL, UCB, UCD, in the U.S., Europe, and Asia

Other Institutions and Collaborators

The Advanced Light Source

PETRA III

Experiments/Data Analysis   Sample Synthesis/Charac.   Theory/Modeling

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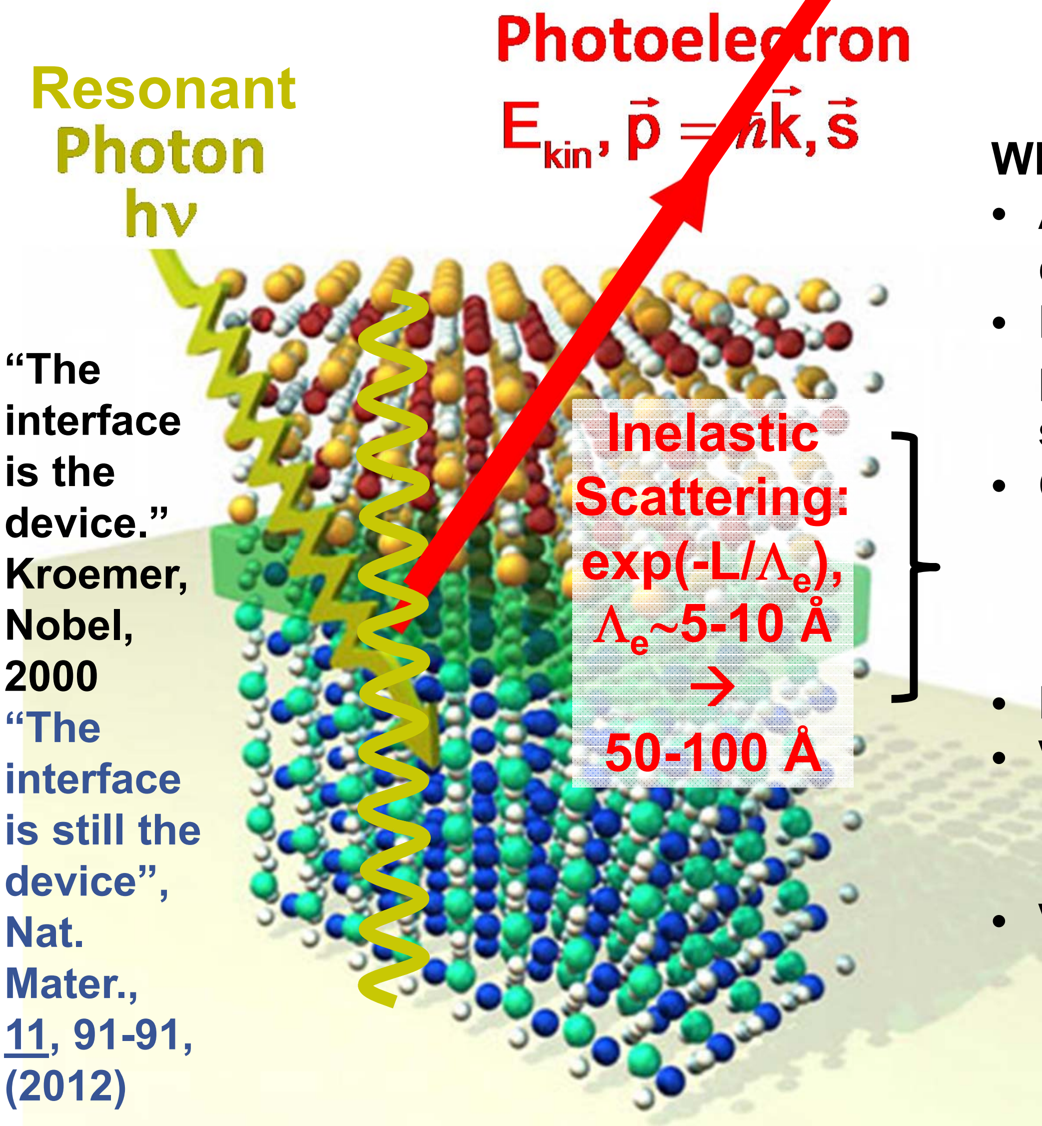
Julich Research Center

Photoemission from surfaces, complex bulk materials, buried layers, interfaces



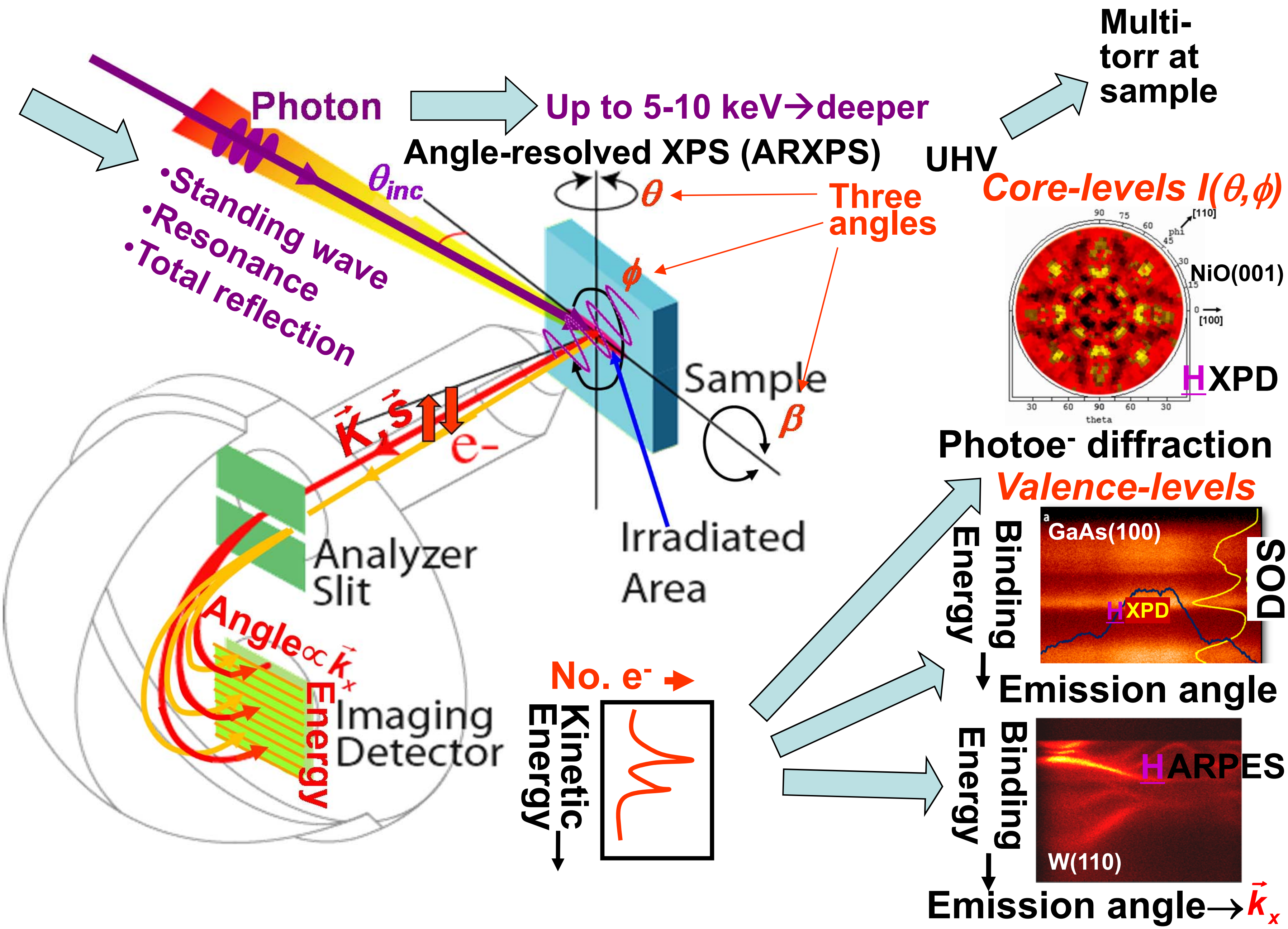
"The interface is the device." Kroemer, Nobel, 2000

"The interface is still the device", Nat. Mater., 11, 91-91, (2012)

What do we want to know?

- **Atomic structure, lattice/octahedral distortions**
- **Depth profiles of composition, optical properties, magnetization, from surface inward, and at interfaces**
- **Core-levels→element-specific**
  binding energies, charge states
  electronic configurations,
  magnetic moments/magnetization
- **Band offsets, depth-dependent pot'ls.**
- **Valence-band densities of states,**
  element-resolved, behavior near E_F
  (XPS limit)
- **Valence-band dispersions, via**
  depth-, angle-, and element-resolved photoemission (ARPES limit)
- **Lateral resolution in all of the above through microscopy**

X-ray photoemission: some key elements



Photoemission from complex materials, heterostructures, and interfaces

Three ways to address the limitations of traditional photoemission:

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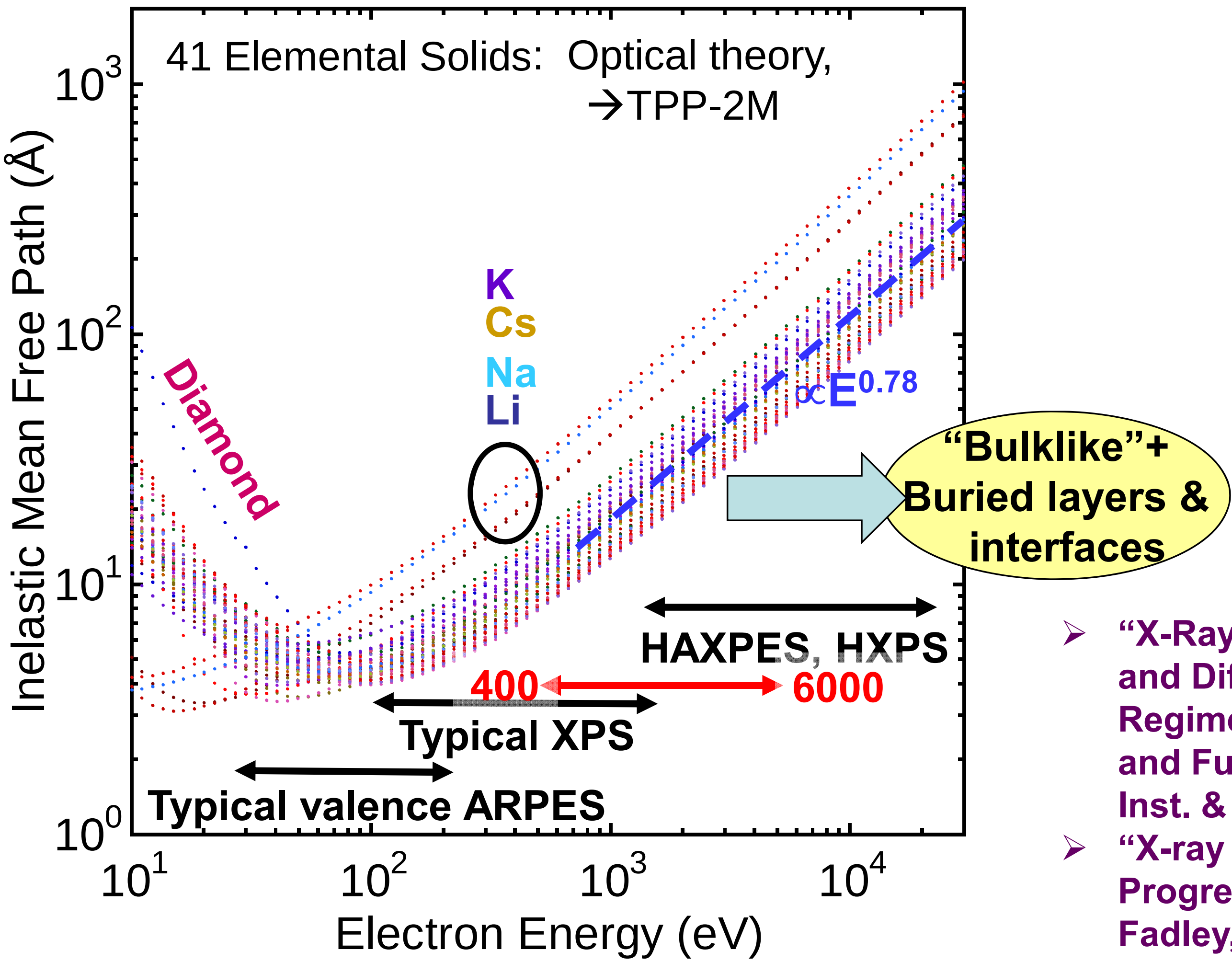
- **Use of soft and hard x-ray standing waves, total reflection, other x-ray optical effects, resonant excitation, to selectively look below the surface, at buried interfaces, including ARPES**

- **Use of differentially-pumped systems to provide multi-Torr ambient pressure photoemission, more real-world conditions for studying surface chemical processes, catalysis, electrochemistry**

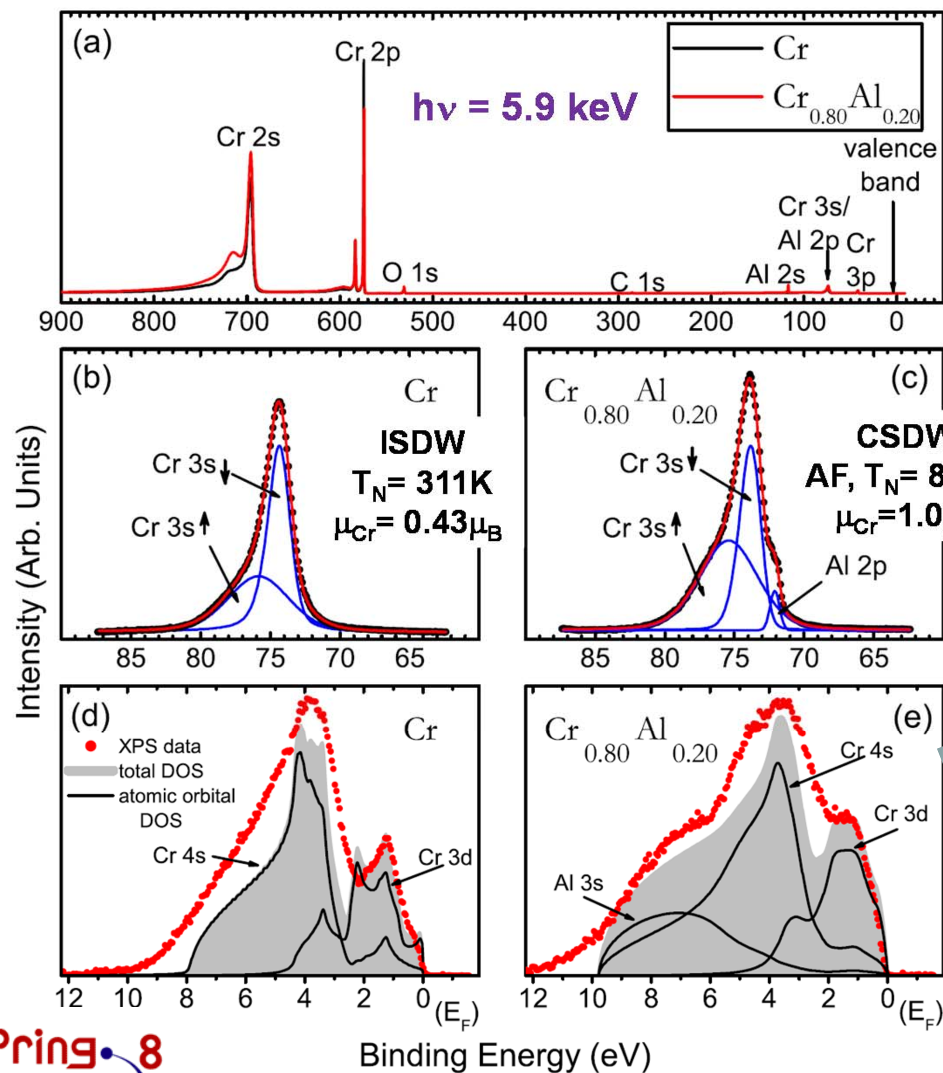
The reason for higher photon energies

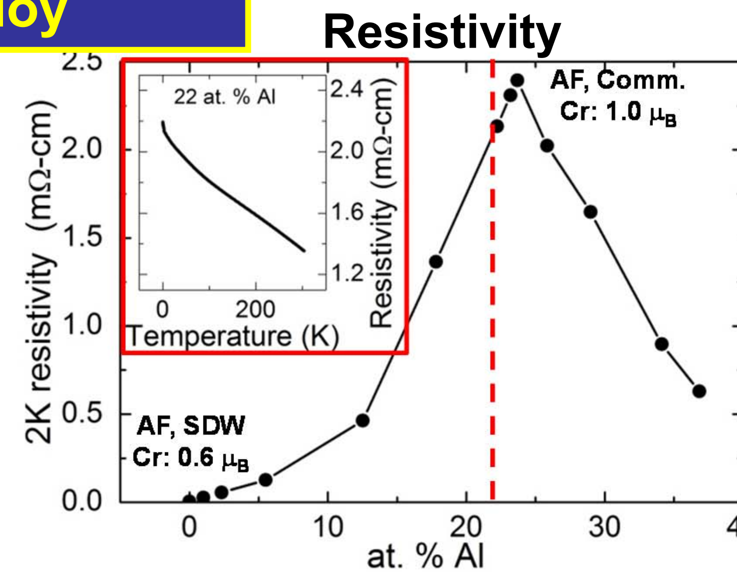


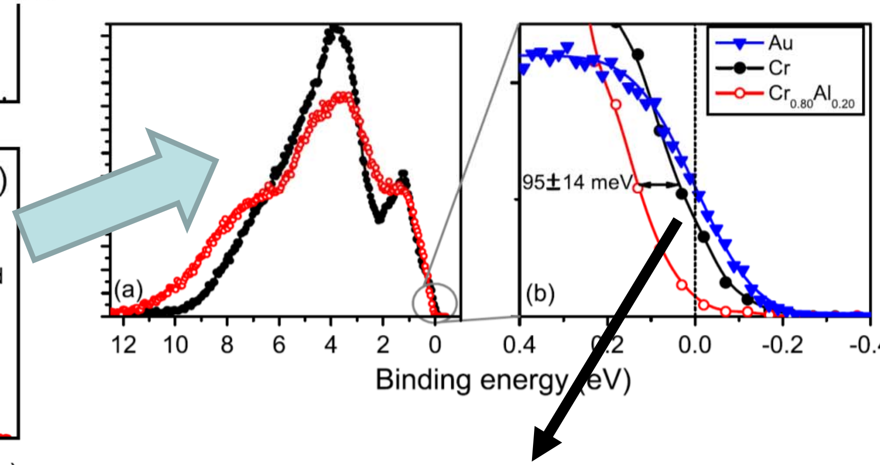
Tanuma, Powell, Penn, Surf. and Interf. Anal. 43, 689 (2011)

- "X-Ray Photoelectron Spectroscopy and Diffraction in The Hard X-Ray Regime: Fundamental Considerations and Future Possibilities", CSF, Nuc. Inst. & Meth. A 547, 24-41 (2005)
- "X-ray Photoelectron Spectroscopy : Progress and Perspectives", C.S. Fadley, invited review, J. Electron Spectrosc. 178–179, 2 (2010),
- "Looking Deeper: Angle-Resolved Photoemission with Soft and Hard X-rays", CSF, Synchrotron Radiation News 25, 26 (2012)

Hard x-ray photoemission example: Opening of a semiconducting gap in the “bulk” of a magnetic CrAl alloy





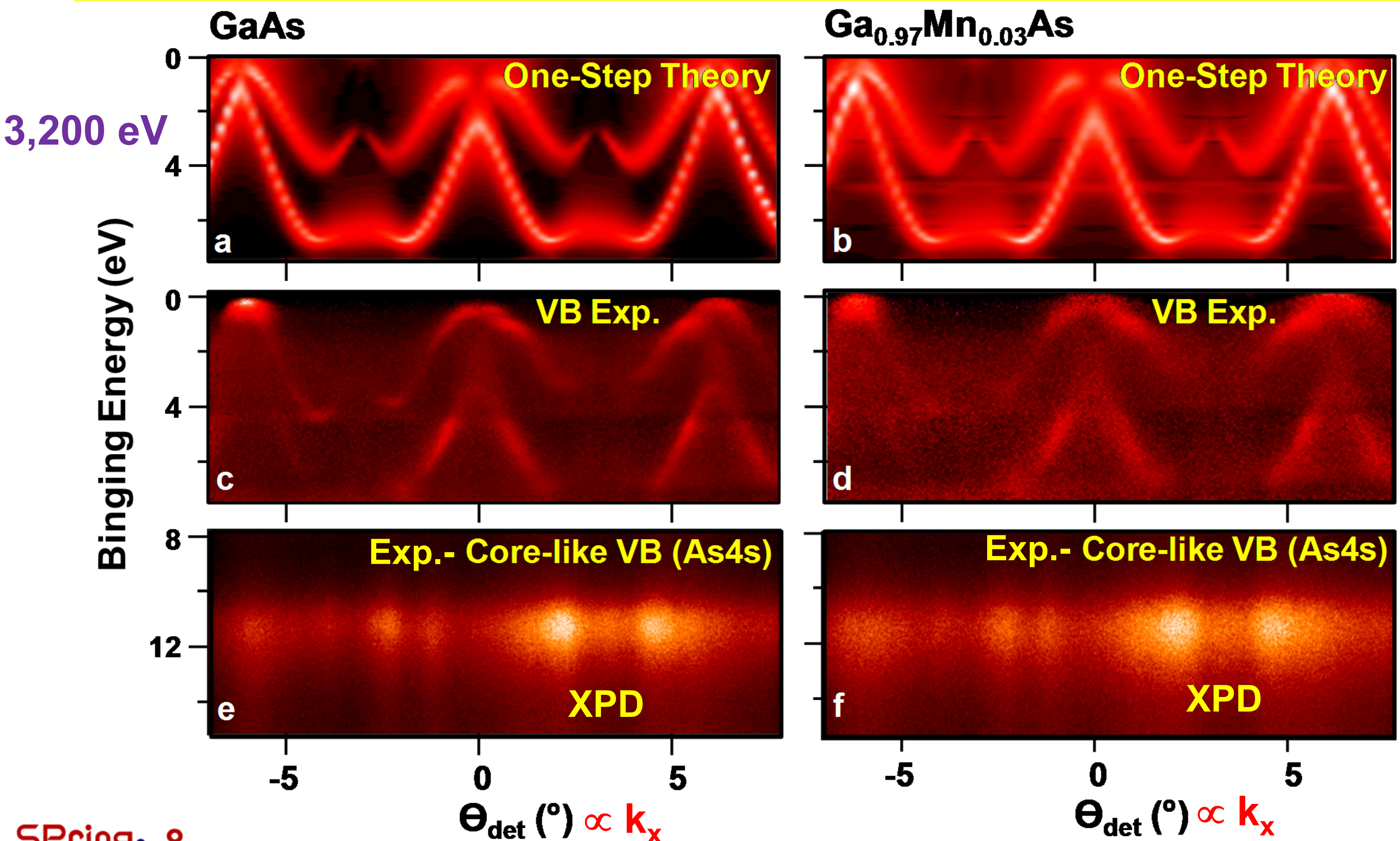


Opening of ~90 meV semiconducting gap

SPring-8

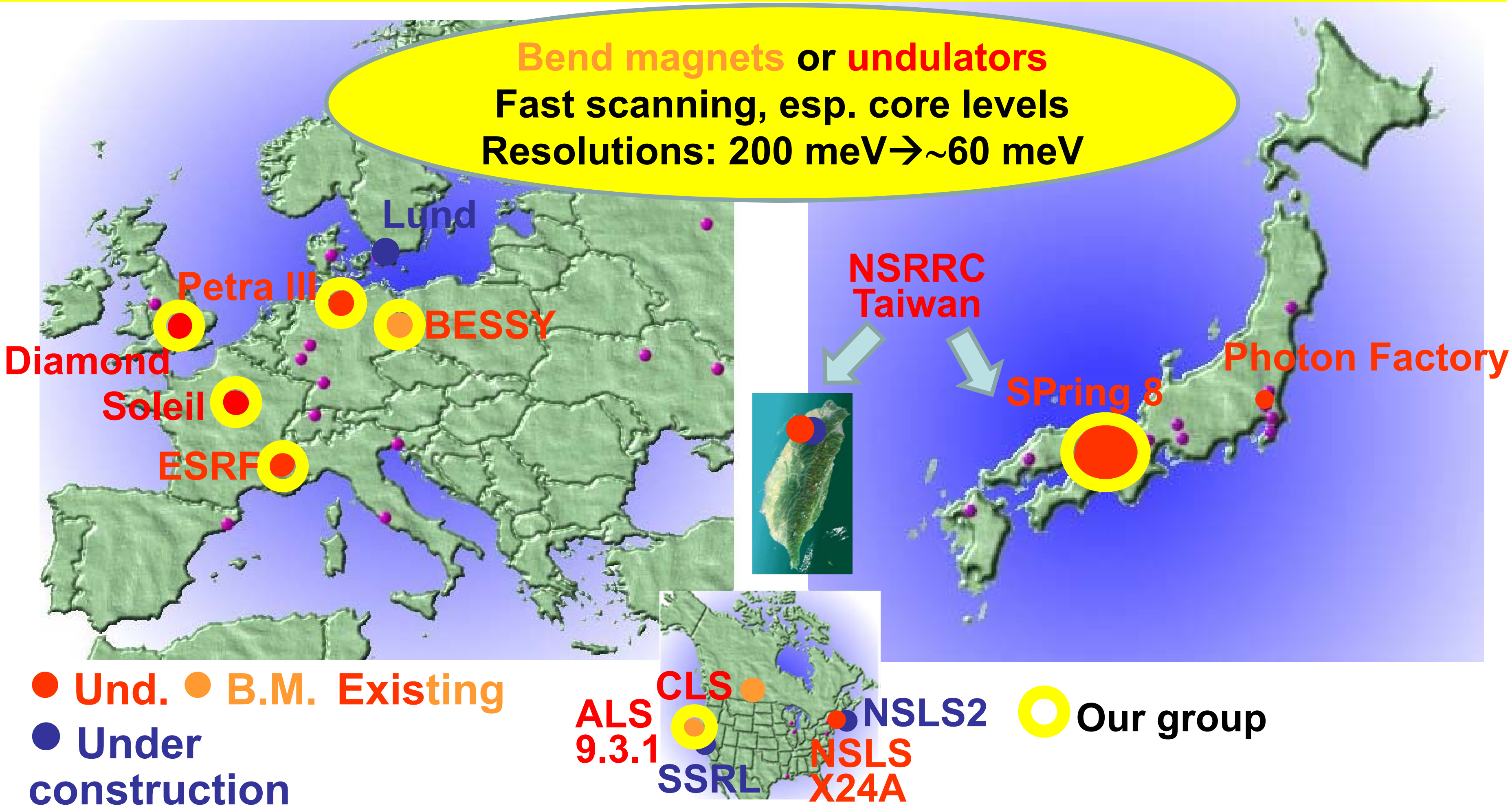
Boekelheide, Gray et al. (Hellman, Fadley Groups) PRL 105, 236404 (2010)

Hard x-ray ARPES--GaAs and DMS $Ga_{0.97}Mn_{0.03}As$
Comparing Experiment (3.2 keV, 30K) and One-Step KKR Theory



Gray et al., Nature Materials 11, 957 (2012)

Hard X-Ray Photoemission (HXPS, HAXPES, HX-PES, HIKE...) in the World



Workshops/conferences:

HAXPES03, ESRF--Nucl. Inst. and Meth. A, Volume 547, Issue 1, Pages 1-238 (2005)

HAXPES06, SPring8-- http://haxpes2006.spring8.or.jp/program.html

HAXPES-ALS-- http://ssg.als.lbl.gov/ssgdirectory/fedorov/workshops/index.html

HAXPES09-NSLS-- http://www.nsls.bnl.gov/newsroom/events/workshops/2009/haxpes/

HAXPES11-DESY-- http://haxpes2011.desy.de

HAXPES13-Uppsala-- http://www-conference.slu.se/haxpes2013/

HAXPES15-Taiwan-- http://www.nsrrc.org.tw/haxpes-2015/

7th International Conference on Hard X-Ray Photoemission

HAXPES 2017

11-15 September, 2017
At LBNL
Sponsors: LBNL & SLAC

Co-Chairs: C. Fadley, Z. Hussain, P. Pianetta

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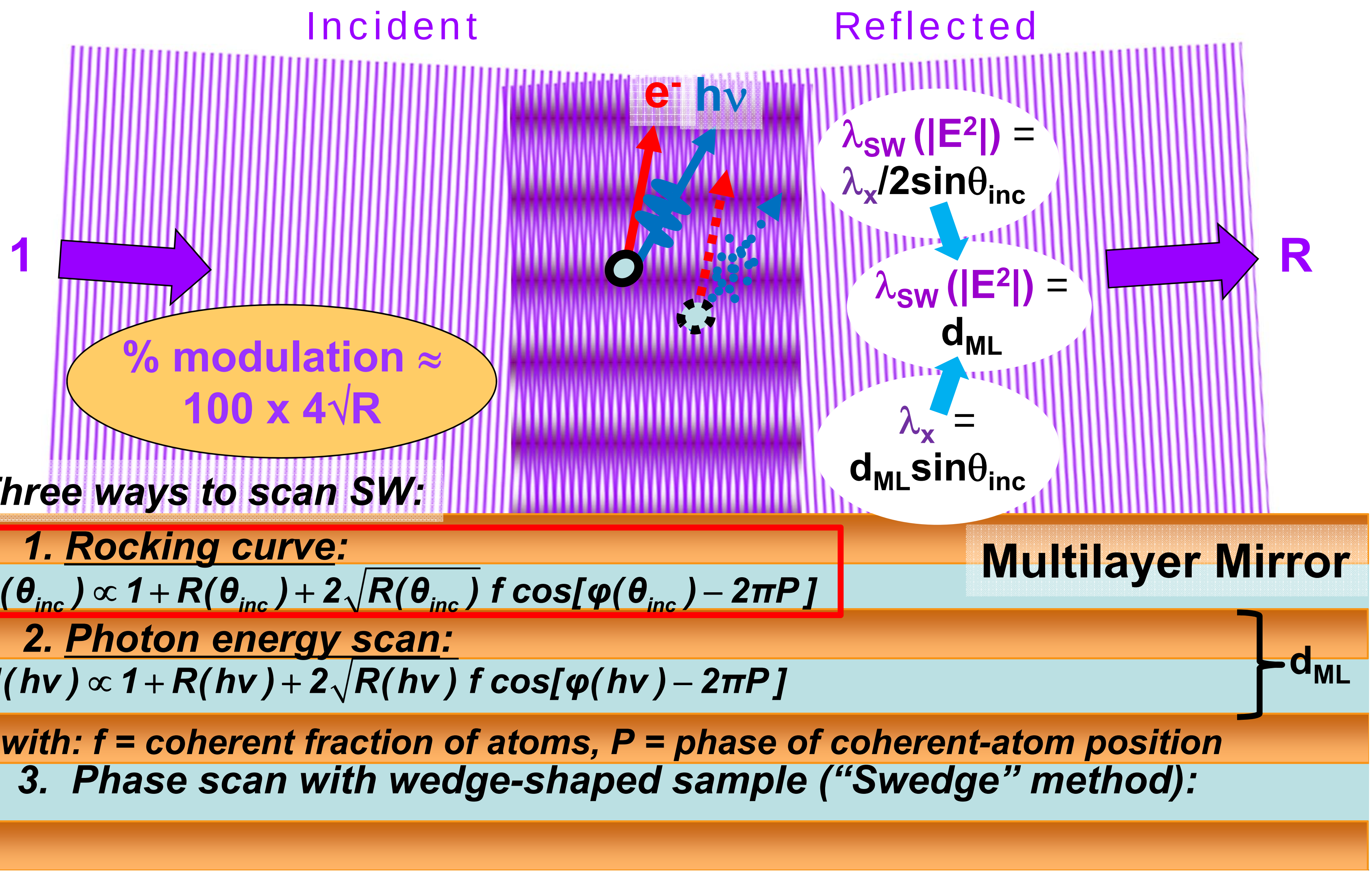
Three ways to scan a standing wave formed in reflection from single-crystal Bragg planes, or a multilayer mirror



Three ways to scan SW:

1. Rocking curve:

$$I(\theta_{inc}) \propto 1 + R(\theta_{inc}) + 2\sqrt{R(\theta_{inc})}\, f \cos[\varphi(\theta_{inc}) - 2\pi P]$$

2. Photon energy scan:

$$I(h\nu) \propto 1 + R(h\nu) + 2\sqrt{R(h\nu)}\, f \cos[\varphi(h\nu) - 2\pi P]$$

with: f = coherent fraction of atoms, P = phase of coherent-atom position

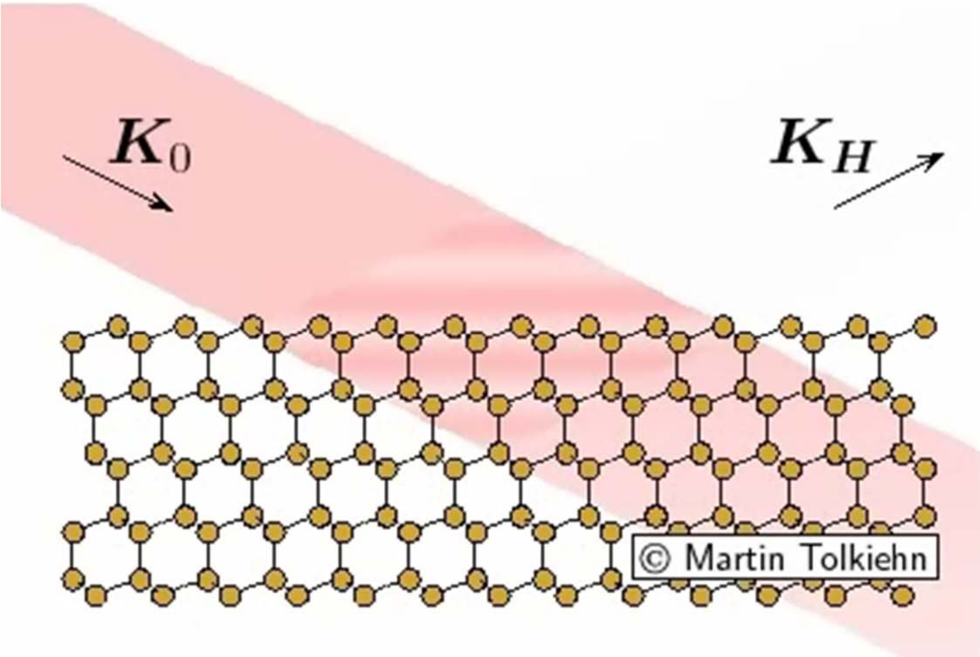
3. Phase scan with wedge-shaped sample ("Swedge" method):

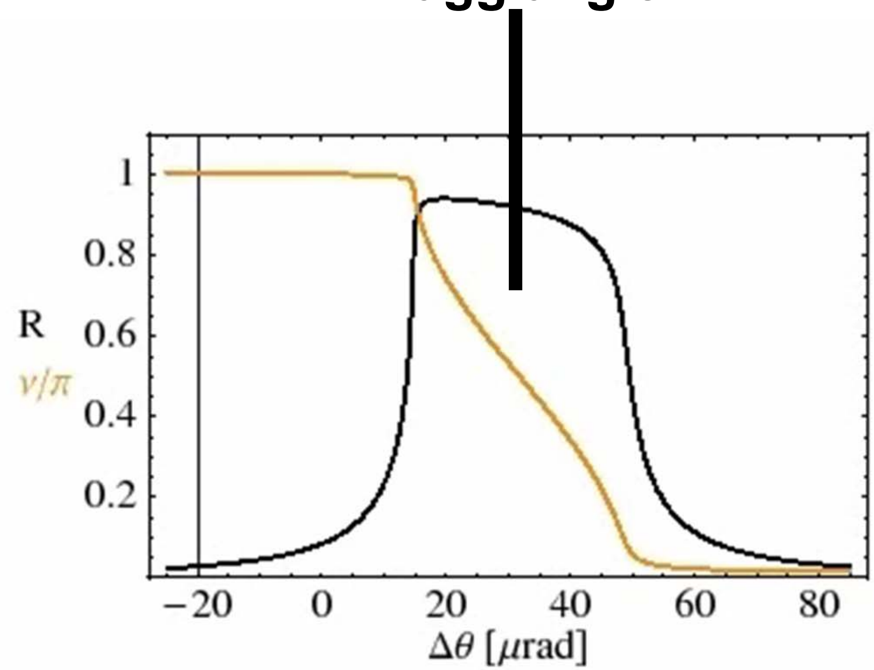
Standing Wave Behavior During a Rocking Curve or Photon-Energy Scan

Reflectivity- R

Relative phase- ν/π

Bragg angle



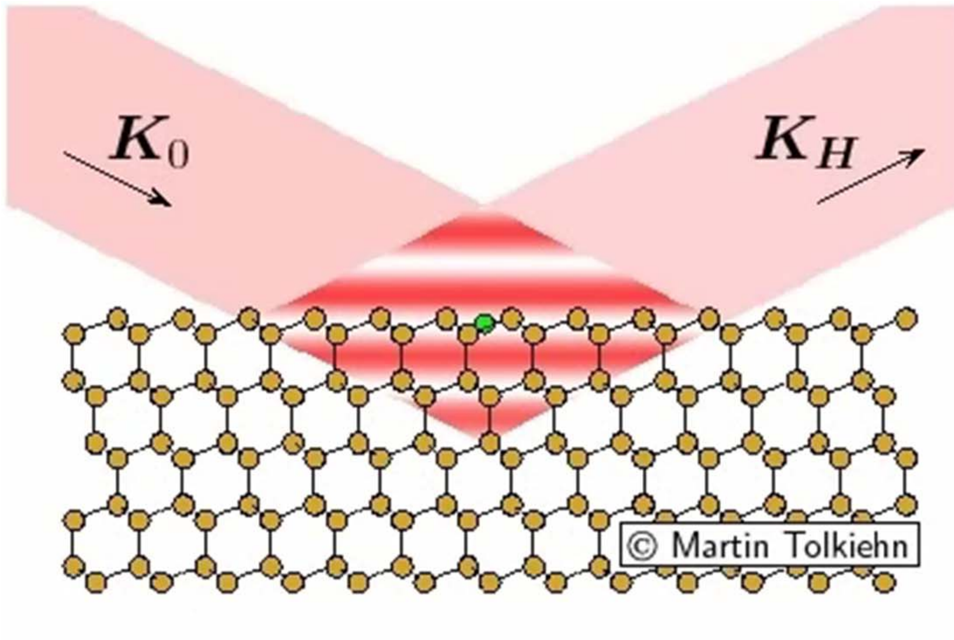


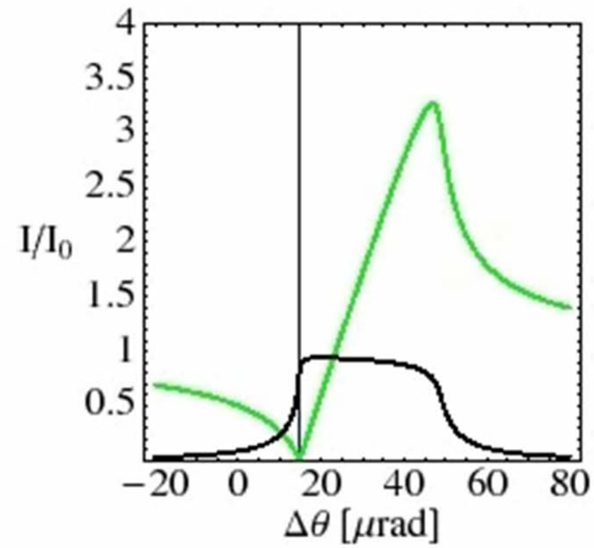
+Same general forms if photon energy is scanned

With thanks to Martin Tolkiehn, Dimitri Novikov, DESY

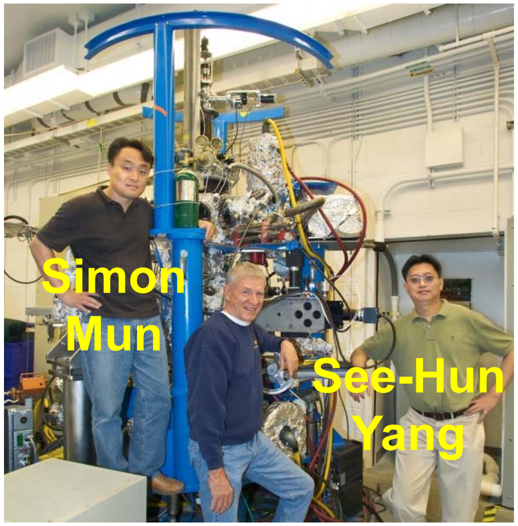
Form of rocking curve is unique to position of emitter

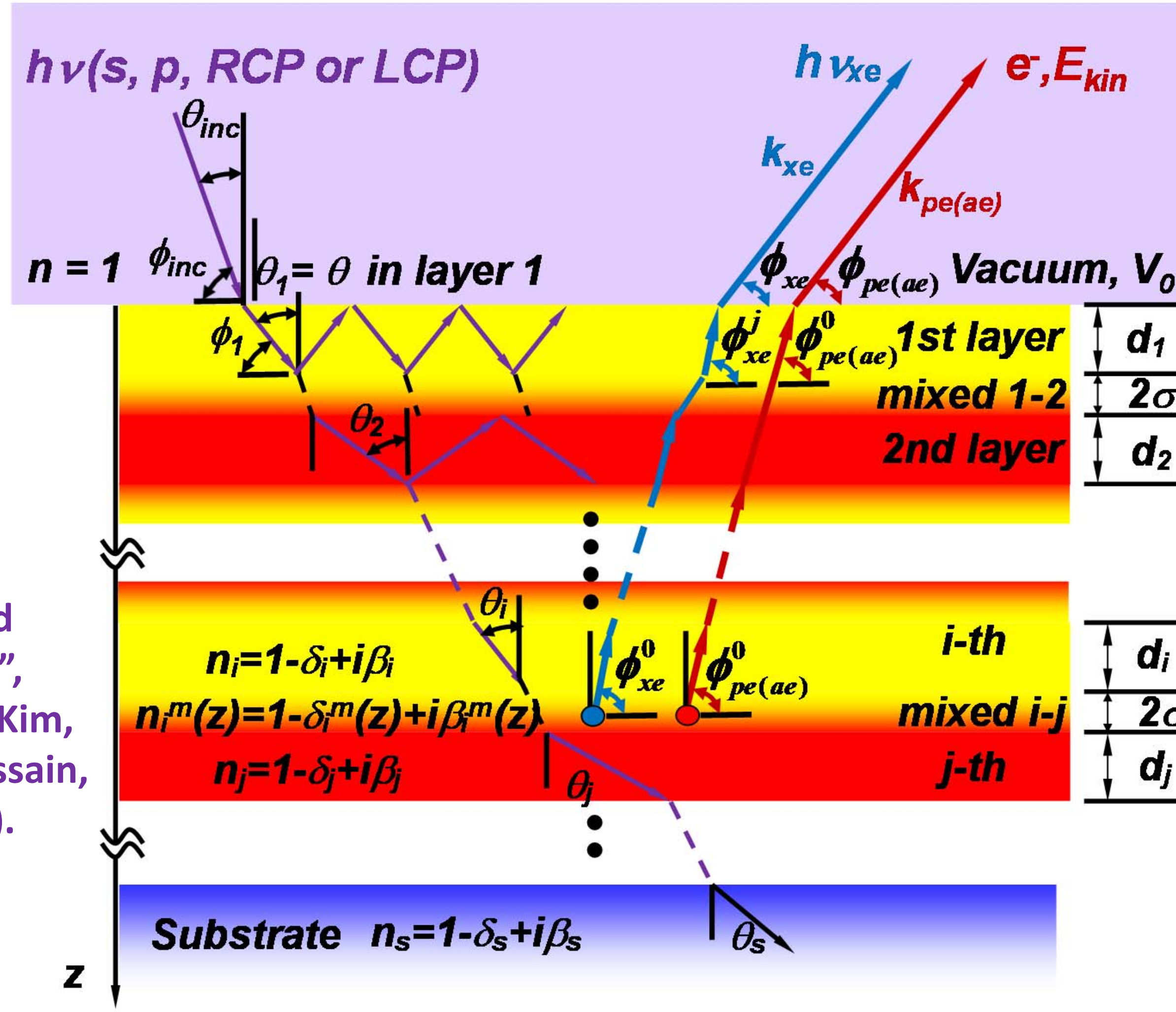
Intensity vs atomic position





X-ray optical effects in photoelectron or x-ray emission from a multilayer structure

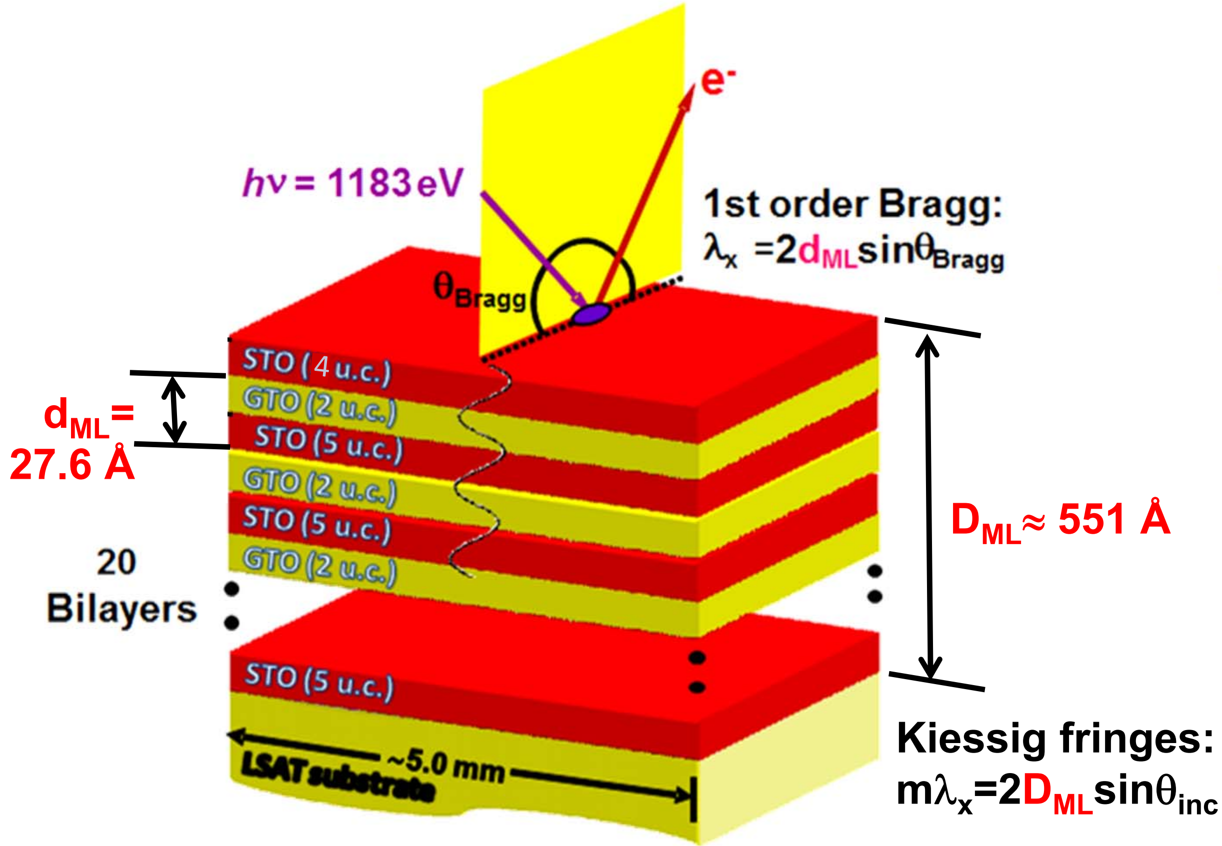




"Depth-resolved photoemission spectroscopy from surface and buried layers with soft X-ray standing waves", S.-H. Yang , B.S. Mun, A.W. Kay S.-K. Kim, J.B. Kortright, J.H. Underwood, Z. Hussain, C.S. Fadley, Surf. Sci. 461, L557 (2000).

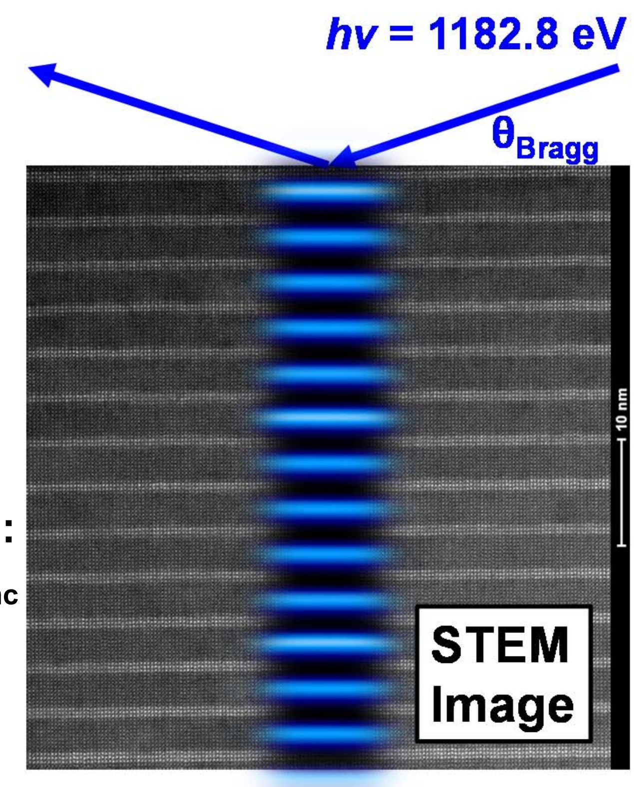
"Making use of x-ray optical effects in photoelectron-, Auger electron-, and x-ray emission spectroscopies: total reflection, standing-wave excitation and resonant effects", S.-H. Yang et al., J. Appl. Phys. 113, 073513 (2013); downloadable Yang XRO software package: https://sites.google.com/a/lbl.gov/yxro/home

Multilayer GTO/STO – Resonance effects



4 u.c. STO/[2 u.c. GTO/5 u.c. STO]$_{20}$
STO: c = 3.934 Å; GTO: c = 3.941 Å

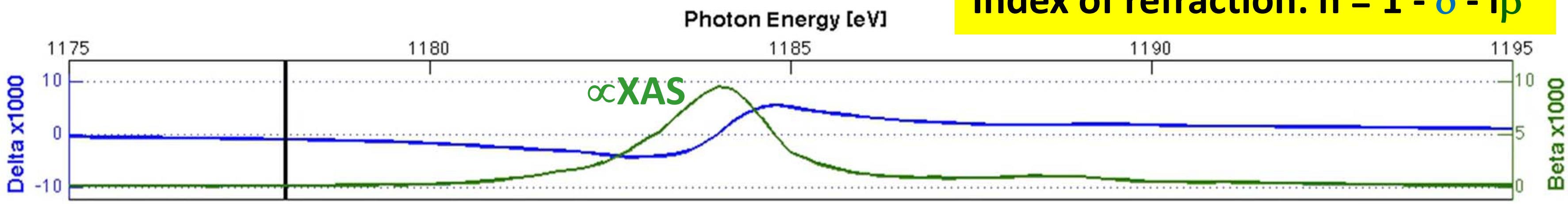
Standing-Wave Excited Photoemission



P. Moetakef, S. Stemmer,
UCSB

Resonant effects: $SrTiO_3/GdTiO_3$ multilayer
Sweeping the photon energy through the Gd M_5 resonance

Index of refraction: $n = 1 - \delta - i\beta$



Going above the edge: A new trick to focus better on buried interfaces→ Observing a 2D electron gas at the STO/GTO interface

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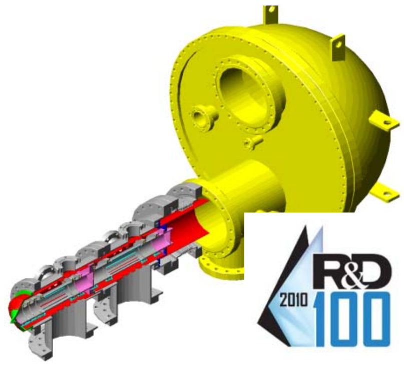
Ambient Pressure XPS→HXPS Systems

1st Gen

2000: Differentially-pumped electrostatic transfer lens allows operation at p ~ 5 torr (equilibrium vapor pressure of water at 0 °C)

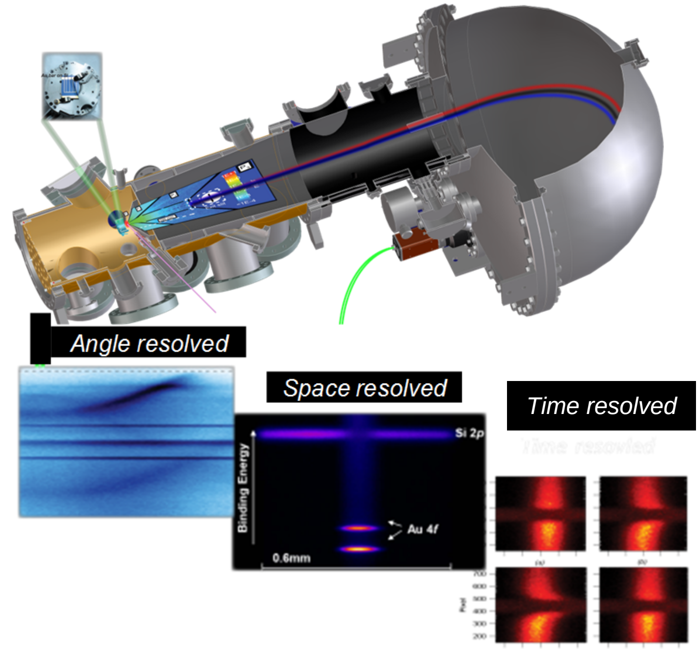
D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

2nd Gen



2005: The first commercial system from Specs. Installed at ALS and BESSY

3rd Gen



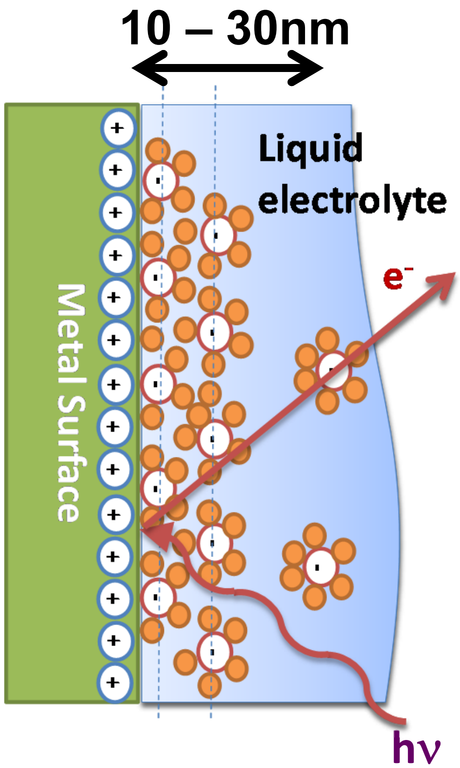
2009: Fast 2D detector and superior electron transmission from Scienta Hipp 4000 installed at ALS BL9.3.2.
New Specs at BL 11.0.2

M.E. Grass, P.G. Karlsson, F. Aksoy, M. Lundqvist, B. Wannberg, B.S. Mun, Z. Hussain, Z. Liu, Rev. Sci. Instrum. 81, 053106 (2010)

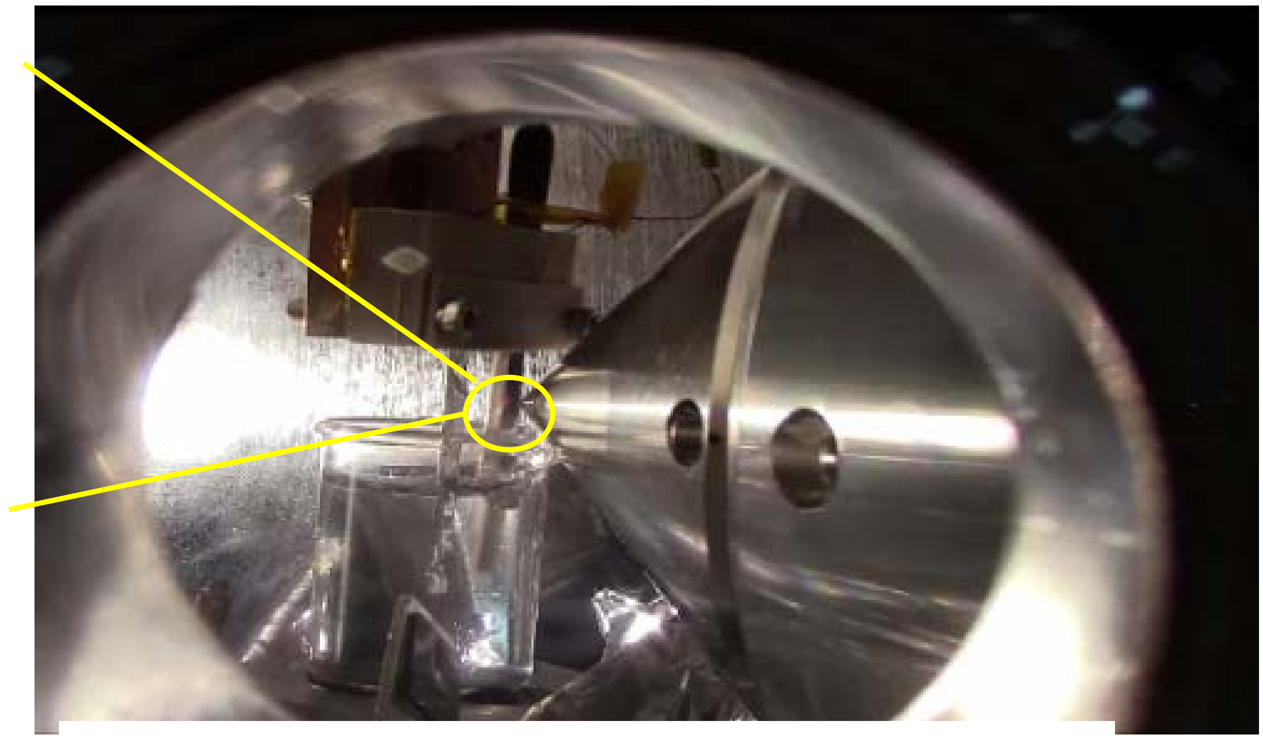
AP XPS/HXPS systems in use/
in commissioning or construction:
ALS, BESSY, ALBA, MAXLAB, SSRL, NSLS, Soleil, Photon Factory, Sirius...
First hard x-ray endstation @ ALS BM, + soft/hard x-ray @ EMIL-BESSY
→100 Torr, even 1 atm (Nilsson, SSRL)

Berkeley Lab

Looking *in operando* at the solid-liquid interface of an electrode
The dip-stick method with hard x-rays→higher pressures



20 Torr, Room Temperature:
"Dipstick Method"



Axnanda, Crumlin, Mao, Rani, Chang, Karlsson, Edwards, Lundqvist, Moberg, Ross, Hussain, Liu, Scientific Reports 5, 09788 (2015)

ALS

Soft → hard x-rays and standing waves: a few example studies

Fe/MgO-tunnel junction

Depth-resolved composition, chemical states, magnetization

$SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$-tunnel junction

Depth-resolved composition, dielectric properties, bonding, k-resolved electronic structure

$SrTiO_3/GdTiO_3$-2D electron gas

Depth-resolved composition, charge states, k-resolved electronic structure

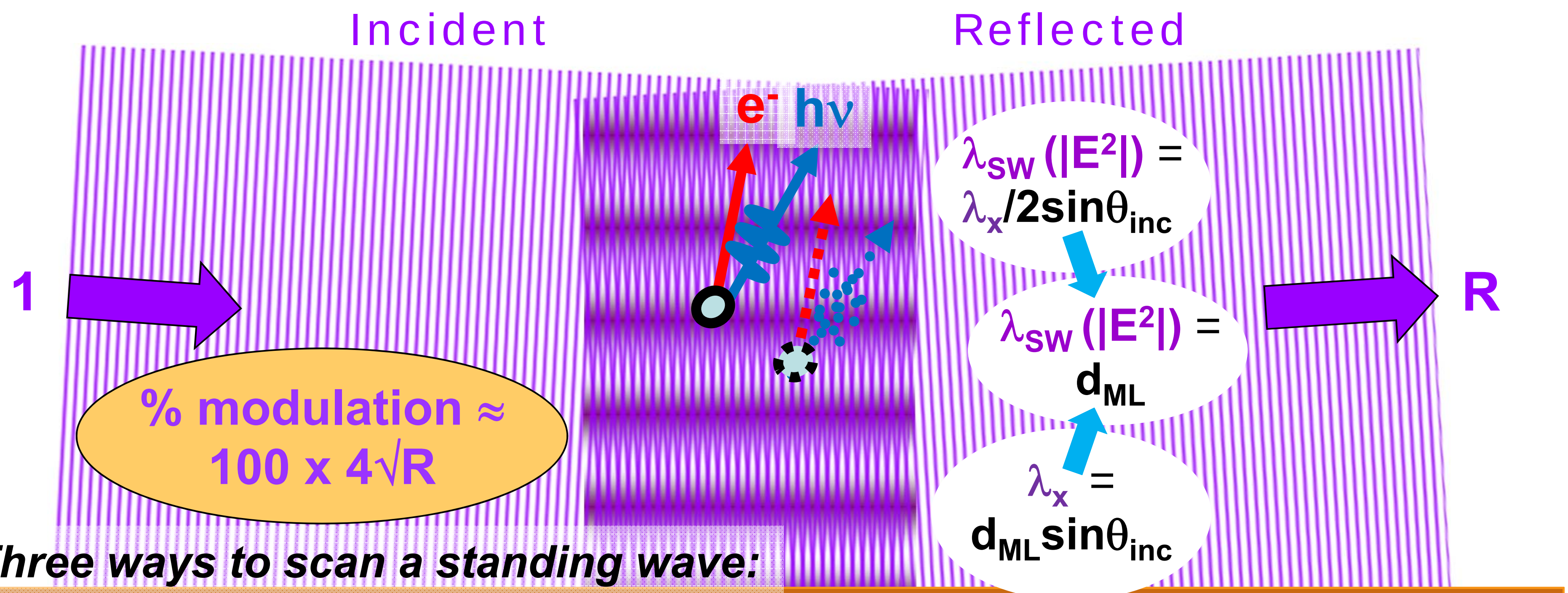
$BiFeO_3/(Ca,Ce)MnO_3$ interface (Ferroelectric/Mott insulator)

Depth-resolved electronic structure from near-total-reflection (NTR) angle scans

Fe_2O_3 reacting with NaOH, CsOH, and H_2O

Using standing wave XPS to probe the solid/gas and solid/liquid interface: some first ambient pressure results

Three ways to scan a standing wave formed in reflection from single-crystal Bragg planes, or a multilayer mirror



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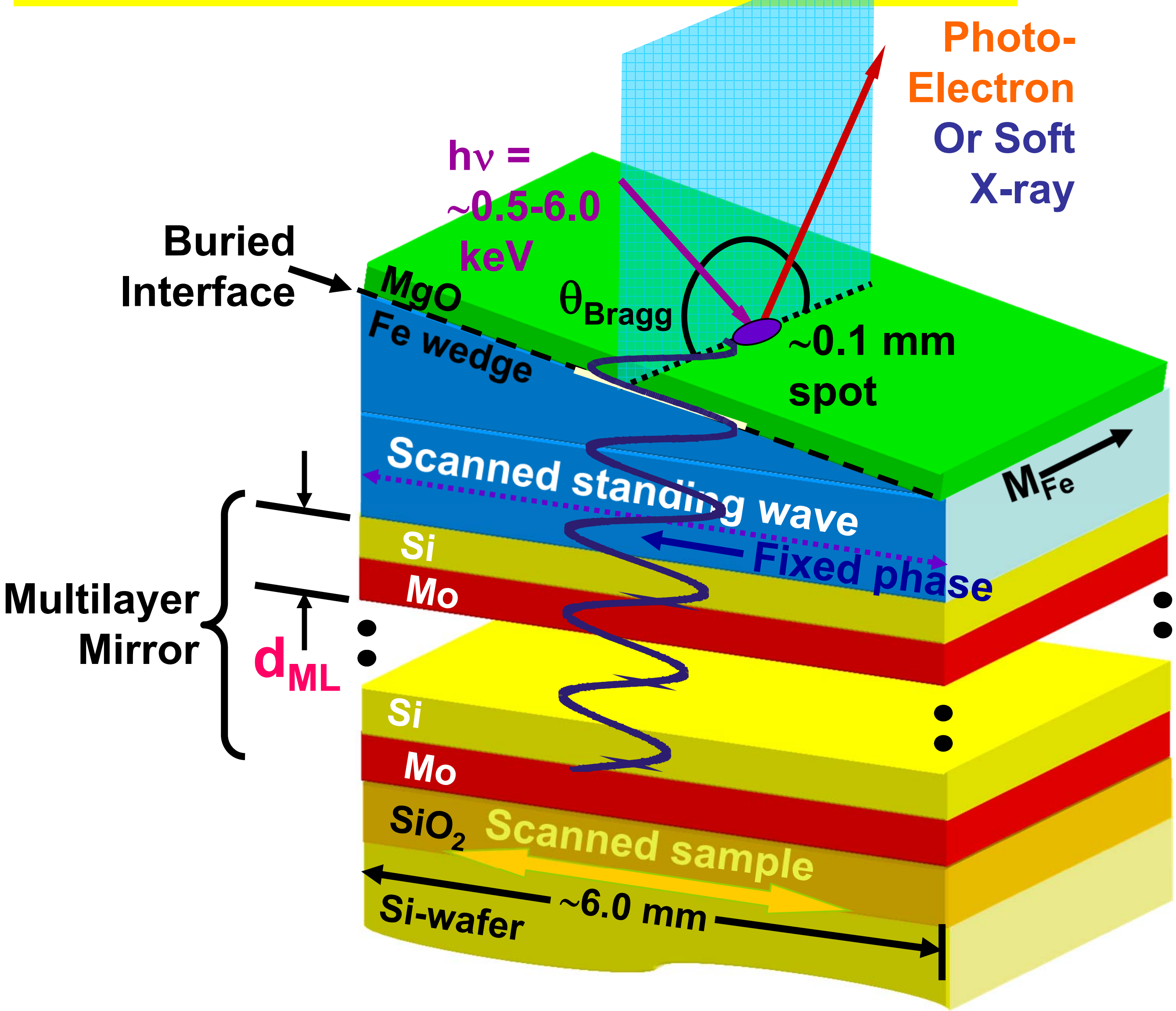
with: f = coherent fraction of atoms, P = phase of coherent-atom position

Phase scan with wedge-shaped sample ("Swedge" method):

Probing Buried Interfaces: The Standing Wave-Wedge ("Swedge") Method

Example: The MgO/Fe magnetic tunnel junction interface

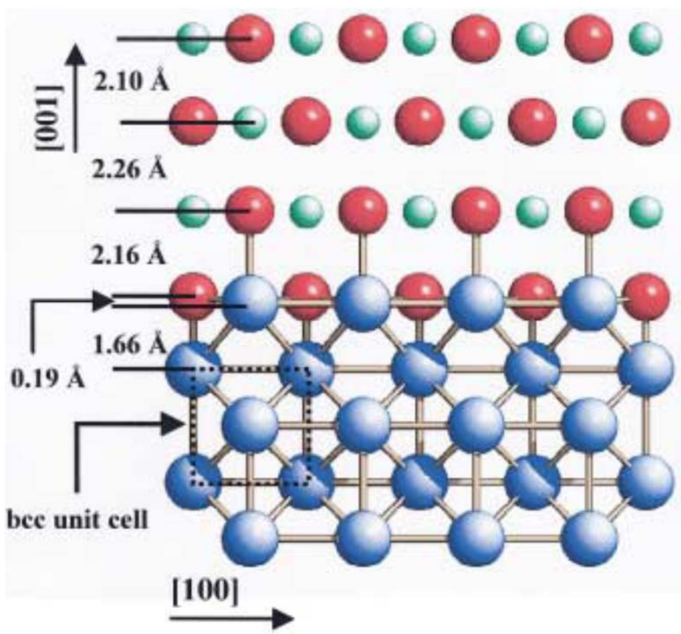


λ_{SW} ($|E^2|$) = $\lambda_x/2\sin\theta_{inc}$ $\approx$ d_{ML}

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

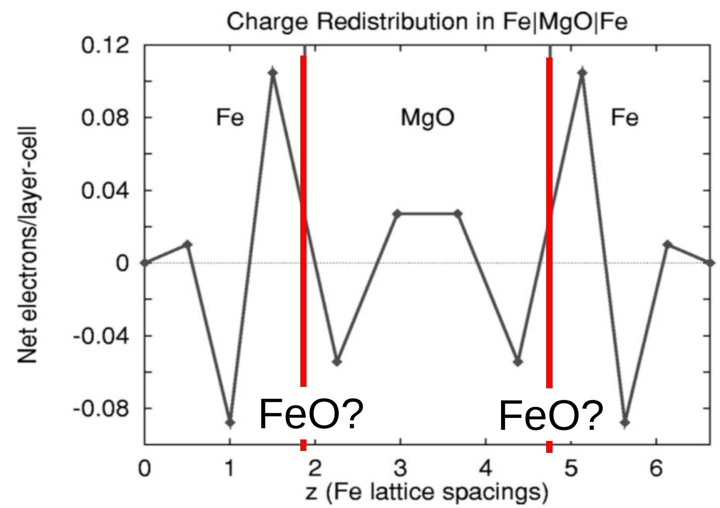
S.-H. Yang et al., Phys. Rev. B 84, 184410 (2011)

MgO/Fe tunnel junction- the real interface



Meyerheim PRL 87, 076102 (2001).

- *Is there FeO at the interface?*
- *What is the density of states at the interface?*
- *Δ_1 band controls tunneling? Can we see bands at epitaxial interfaces? (Soleil-June, 2014!)*



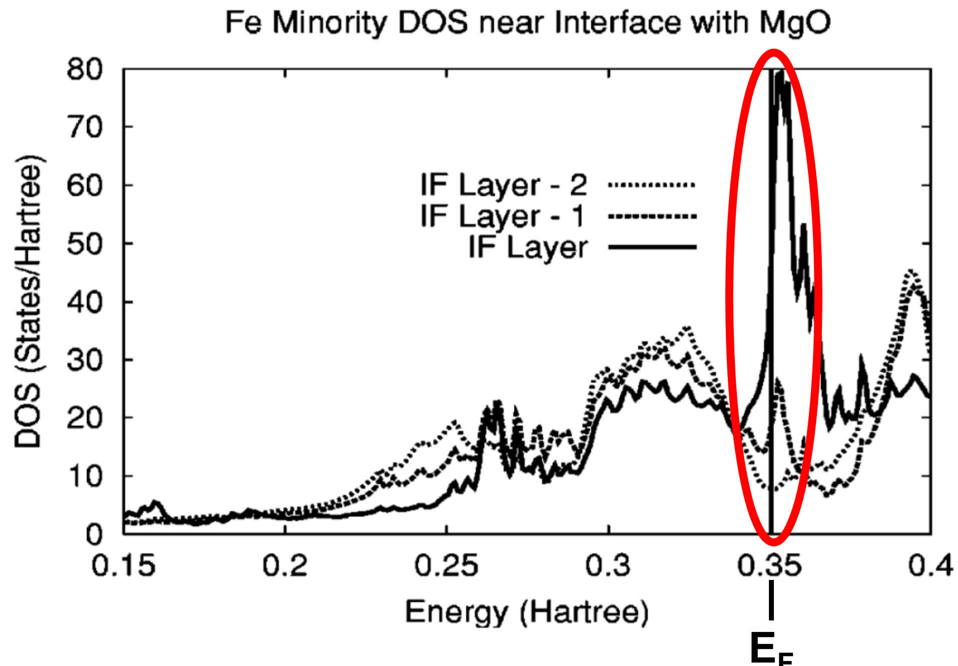
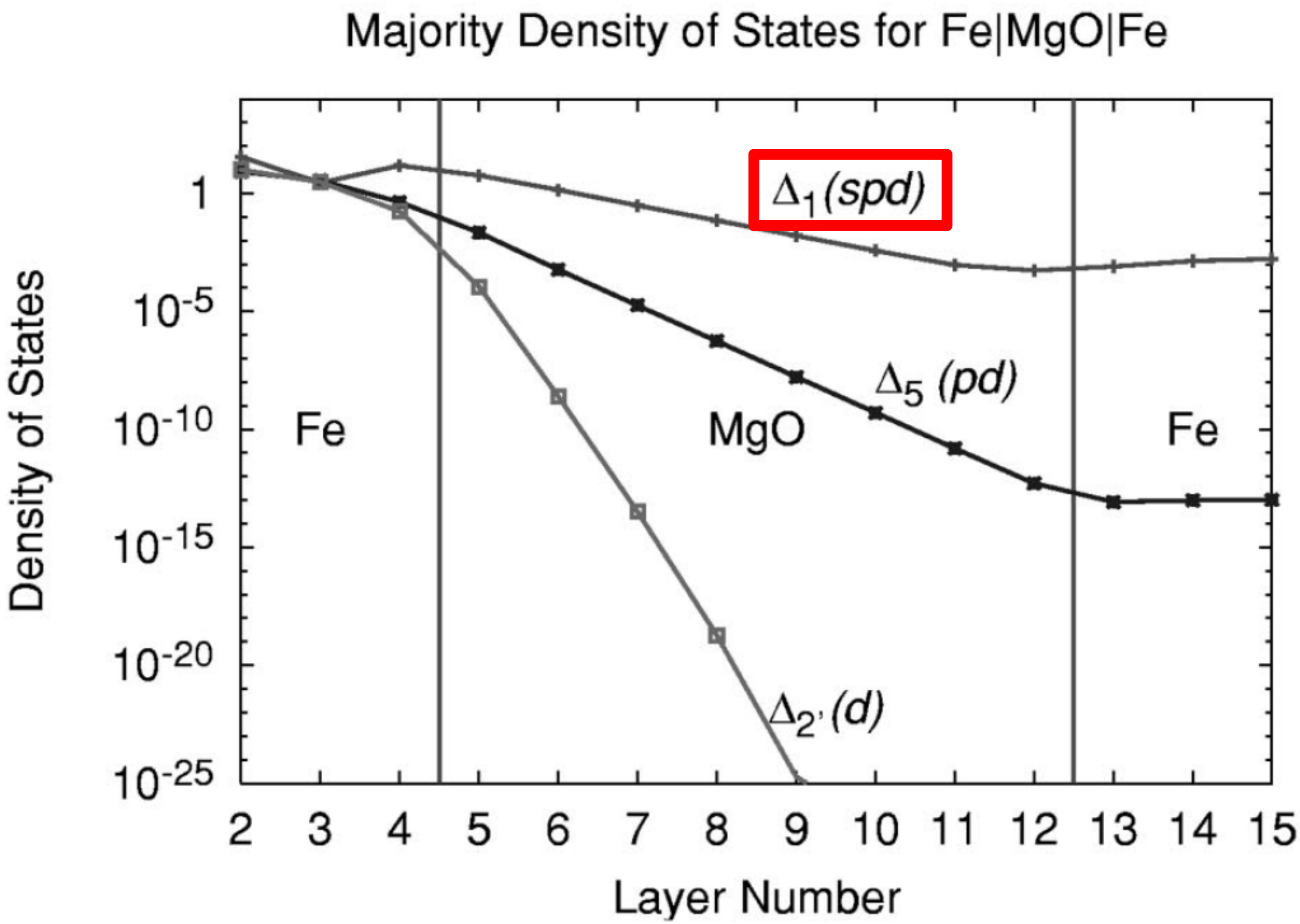


FIG. 3. Density of states for each atomic layer of Fe(100) near an interface with MgO. One hartree equals 27.2 eV.

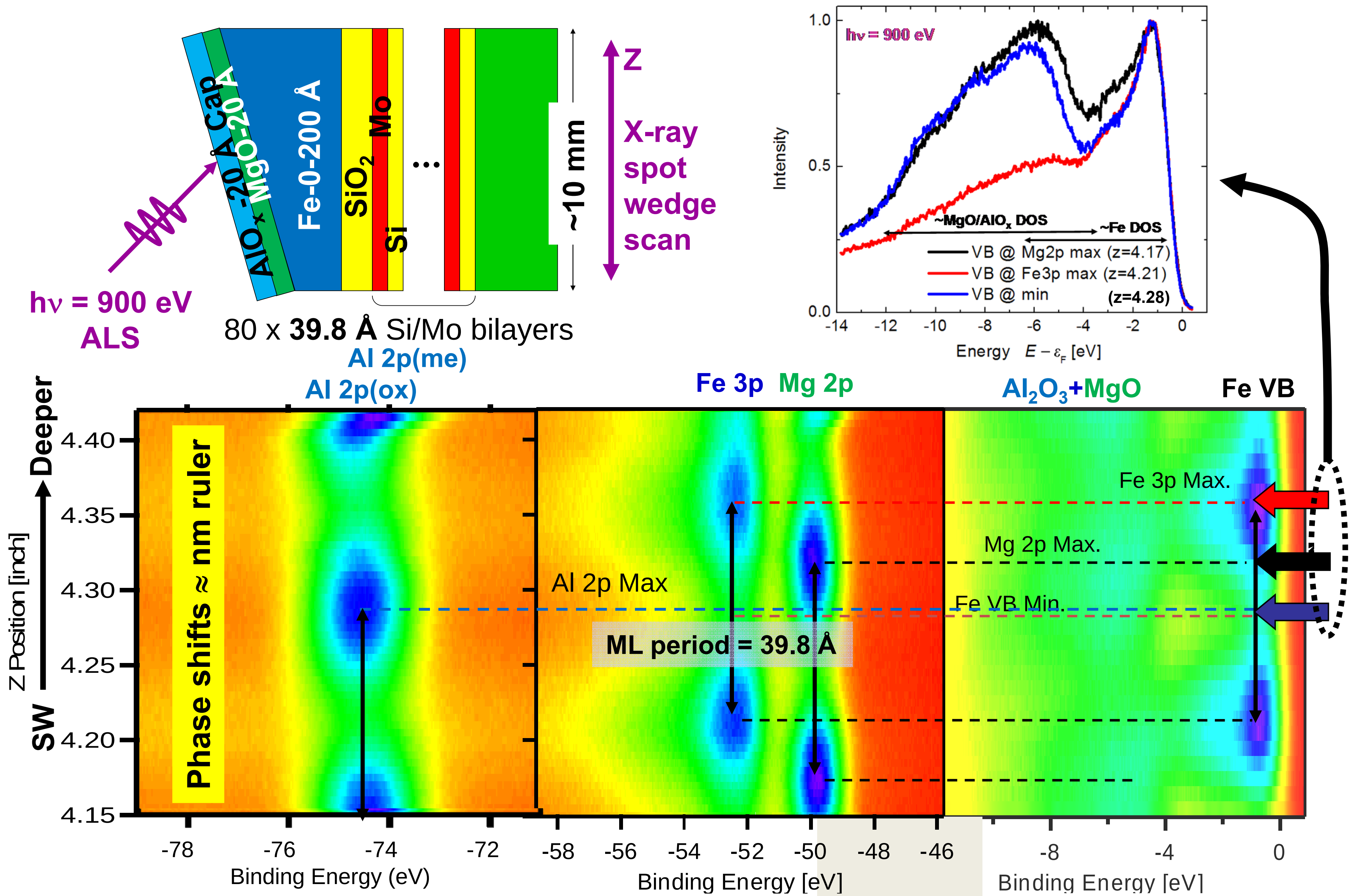
Butler et al.,PRB 63, 054416 (2001);
Mathon & Umerski, PRB 63, 220403 (2001);
Mertig et al., PRB 73, 214441 (2006)

MgO/Fe tunnel junction-Δ_1 states dominant in tunneling for ideal interface



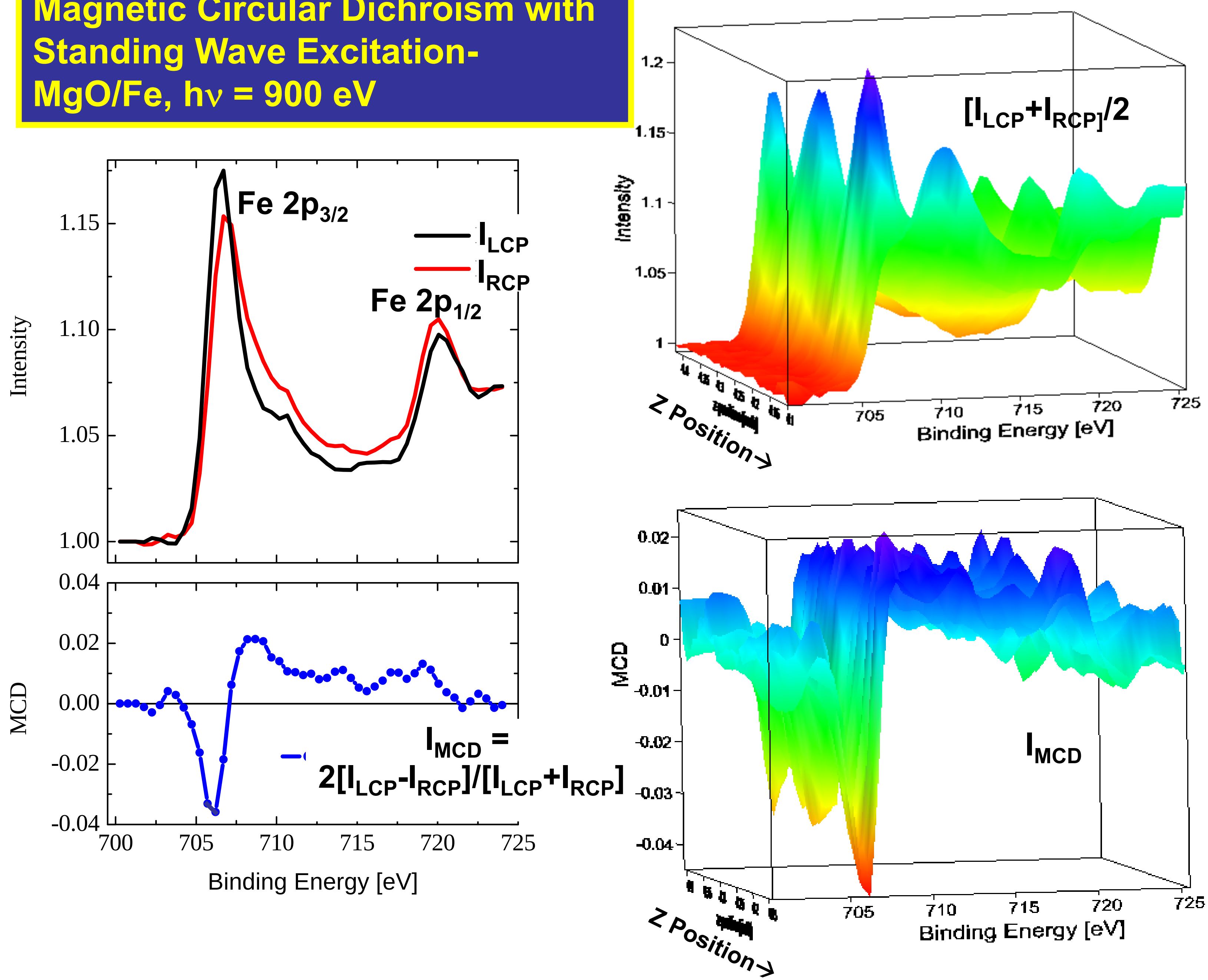
Butler et al.,PRB 63, 054416 (2001)

Soft x-ray standing-wave wedge scans through a magnetic tunnel junction

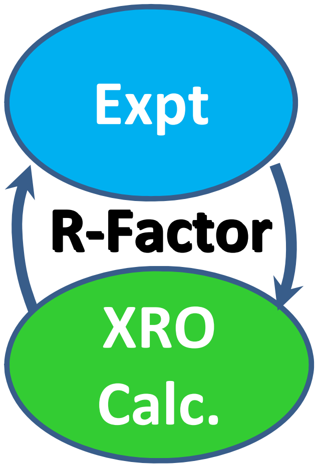


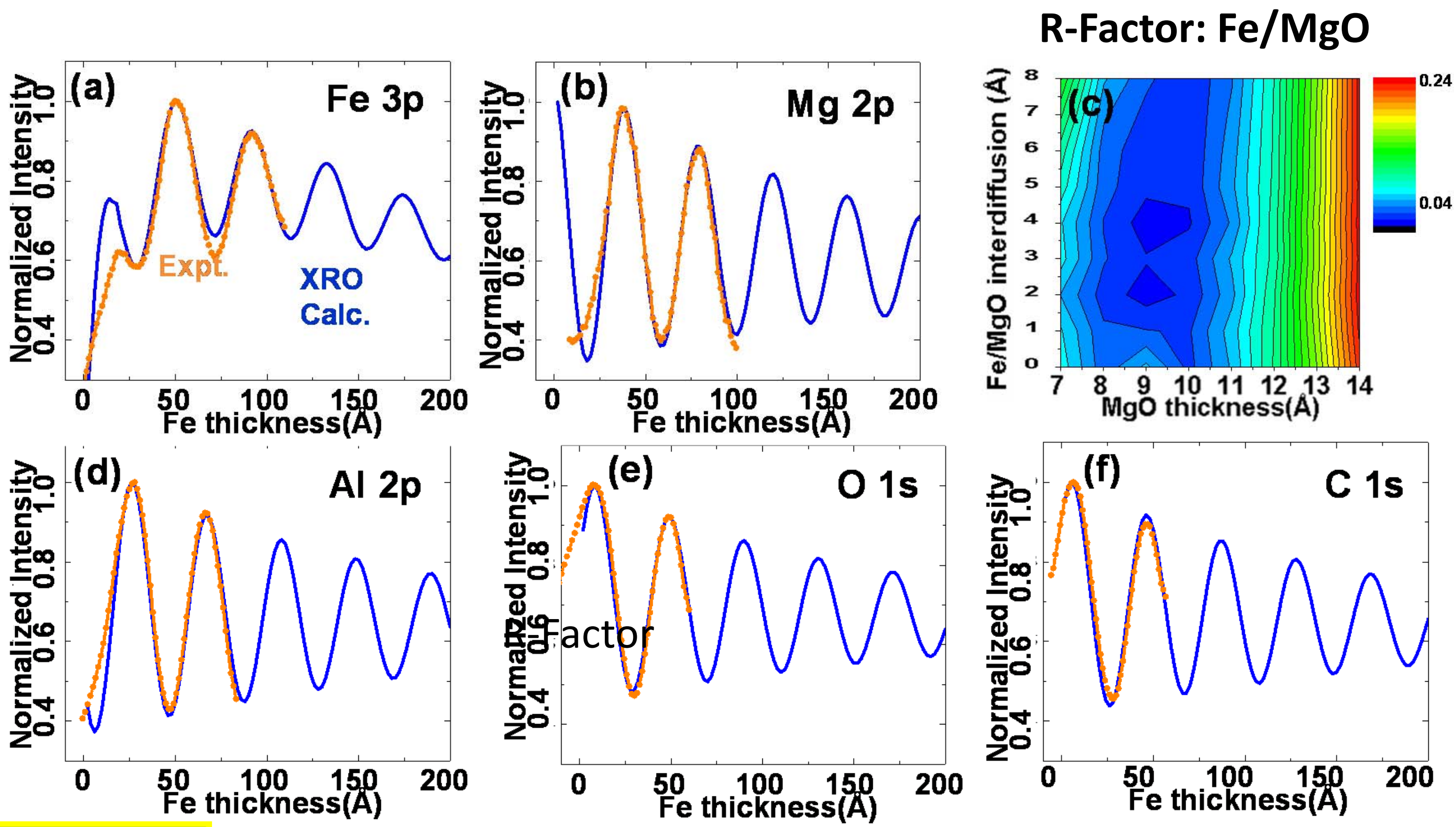
Yang et al., Phys. Rev. B 84, 184410 (2011)

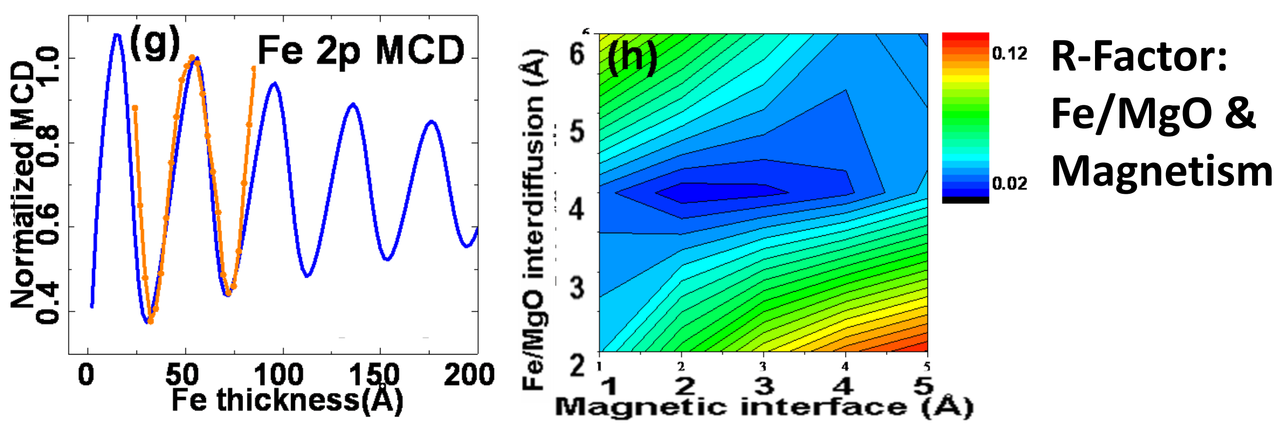
Magnetic Circular Dichroism with Standing Wave Excitation- MgO/Fe, hν = 900 eV



Yang, Balke et al., Phys. Rev. B 84, 184410 (2011)



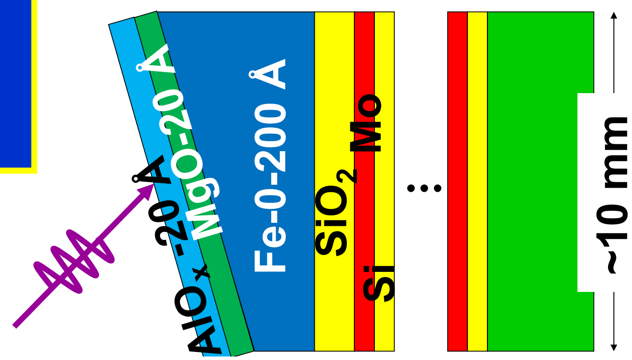


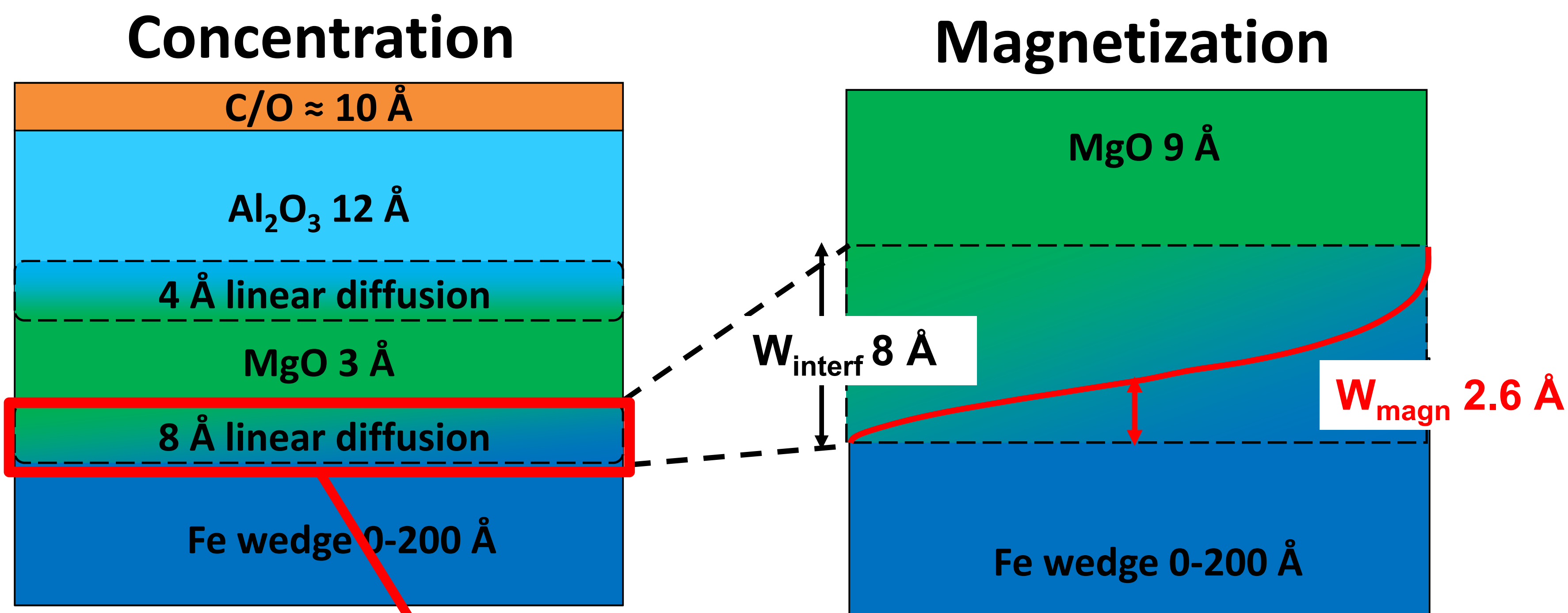


Standing wave/wedge analysis of an Fe/MgO tunnel junction multilayer: final fits of expt. to x-ray optical calcs.

Balke, Yang et al., Phys. Rev. B 84, 184410 (2011)

Final profiles of concentration and magnetization

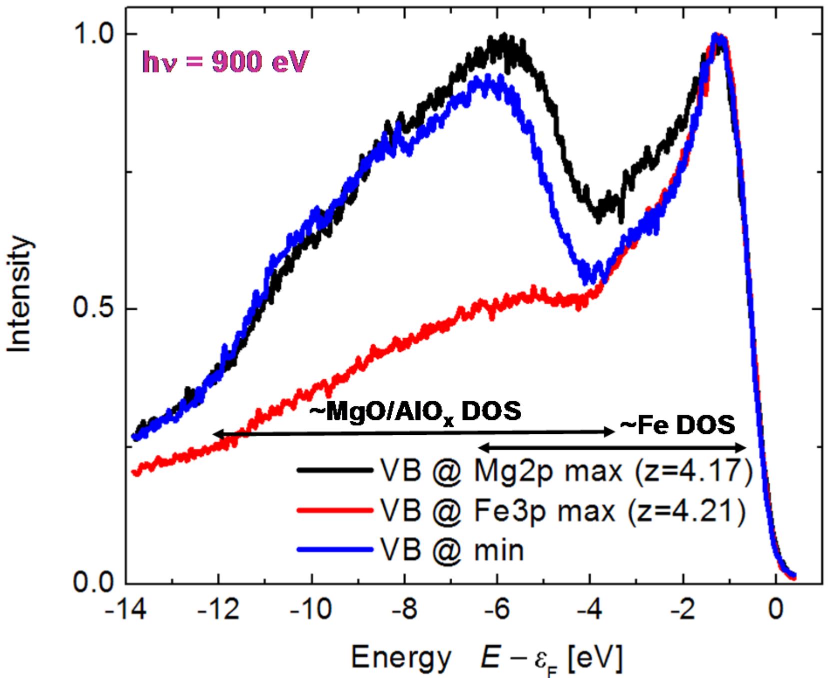




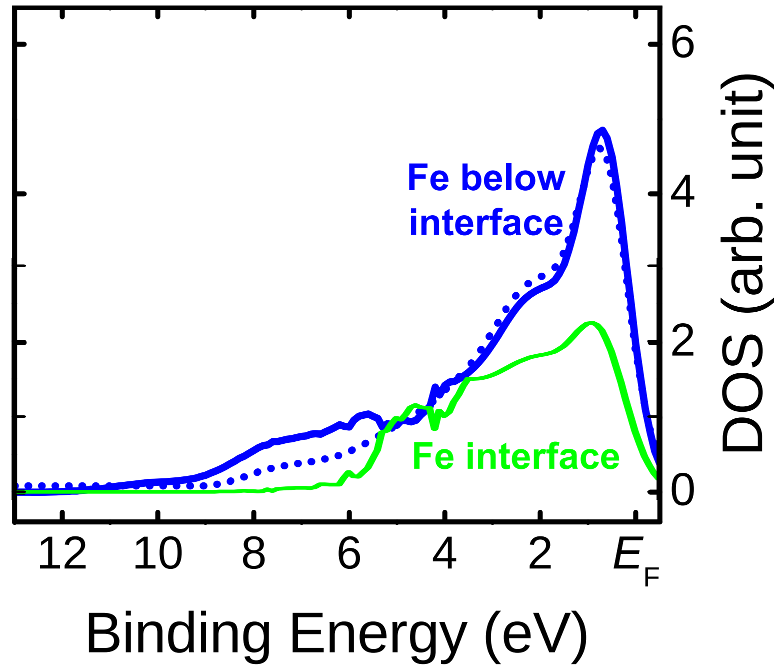
And what is the density of states in this interface region?

Yang, Balke et al., Phys. Rev. B 84, 184410 (2011)

Standing wave/wedge derivation of depth-dependent densities of states: Fe/MgO tunnel junction



→Oxidation at the Fe/MgO interface



Self-consistent X-ray optical modeling of layer-resolved densities of states

Yang, Balke et al., Phys. Rev. B 84, 184410 (2011)

Conclusions: Standing-Wave Soft X-Ray Photoemission of the Fe/MgO Interface

- Measured the depth distribution of concentration <u>and magnetization</u> (via core-level PMCD) through the interface with ca. ±2 Å resolution
- Resolved the density of states into interface and bulk Fe components, indicating Fe oxidation at the interface
- Demonstrated the standing-wave wedge approach as a new and powerful way to study buried interfaces.

Yang, Balke et al., Phys. Rev. B <u>84</u>, 184410 (2011)

Soft → hard x-rays and standing waves: a few example studies

Fe/MgO-tunnel junction

Depth-resolved composition, chemical states, magnetization

$SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$-tunnel junction

Depth-resolved composition, dielectric properties, bonding, k-resolved electronic structure

$SrTiO_3/GdTiO_3$-2D electron gas

Depth-resolved composition, charge states, k-resolved electronic structure

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Depth-resolved electronic structure from near-total-reflection (NTR) angle scans

Fe_2O_3 reacting with NaOH, CsOH, and H_2O

Using standing wave XPS to probe the solid/gas and solid/liquid interface: some first ambient pressure results

$SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$
A classic magnetic tunnel junction

$SrTiO_3$
- Band insulator (E_g=3.4 eV)
- Low temperature superconductor

$La_{0.7}Sr_{0.3}MnO_3$
- Half-metallic ferromagnet
- Colossal magnetoresistive material

Alex Gray
→Stanford
→Temple U.

$SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$ interface
- What does the interface look like?
- How are bonding and atomic/electronic structure at the interface different?

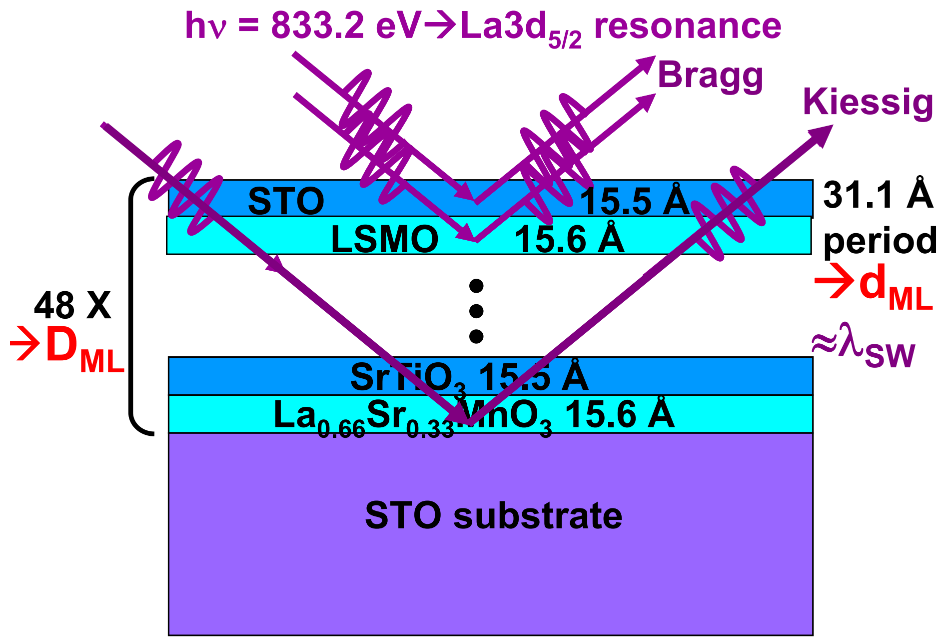
A. X. Gray, C. Papp, B. Balke, S.-H. Yang, M. Huijben, E. Rotenberg, A. Bostwick, S. Ueda, Y. Yamashita, K. Kobayashi, E. M. Gullikson, J. B. Kortright, F. M. F. de Groot, G. Rijnders, D. H. A. Blank, R. Ramesh, CSF, PRB 82, 205116 (2010); EPL 104, 17004 (2013)

BERKELEY LAB The Advanced Light Source SPring-8 NIMS IBM
UNIVERSITY OF TWENTE

Standing wave/rocking curve analysis of an epitaxial $SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ interface: near-resonant soft x-ray excitation

The Advanced Light Source

BL 7.0.2

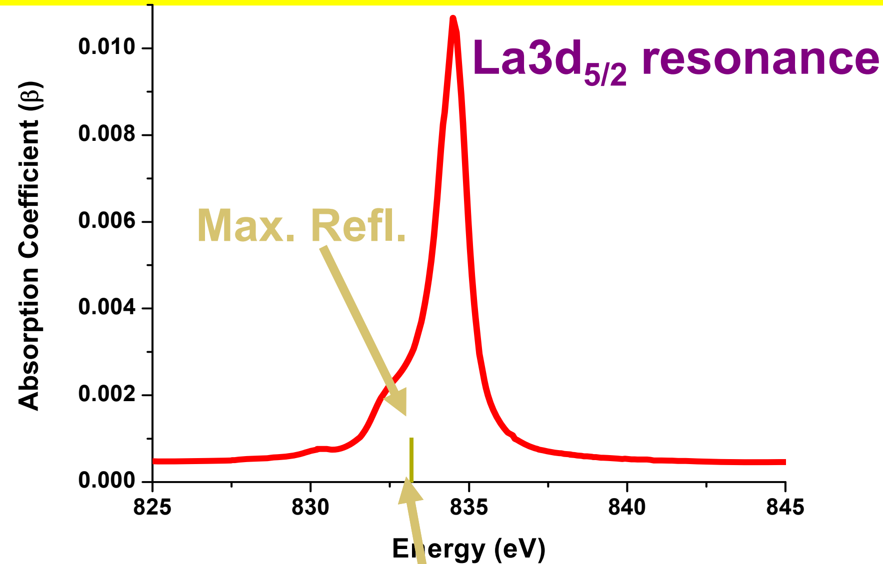


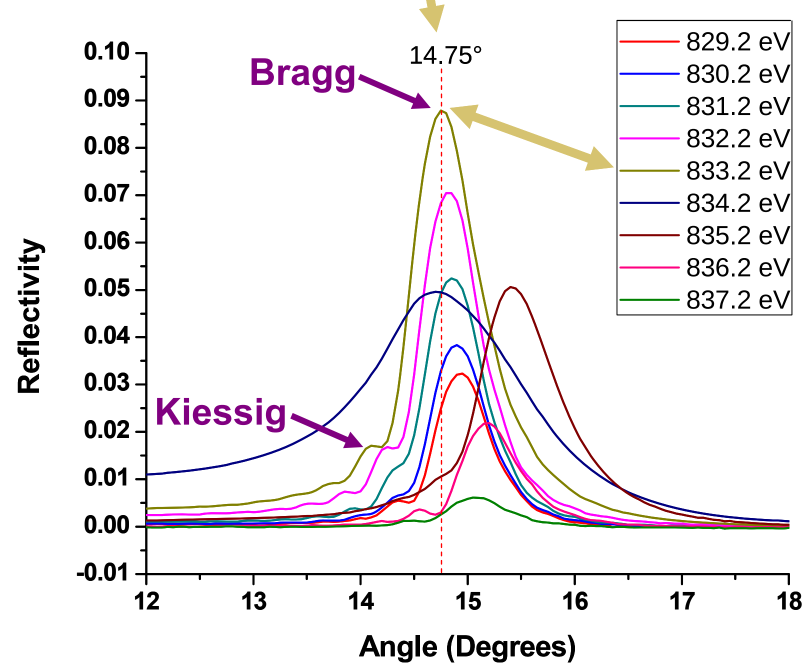
$$\lambda_x = 2 d_{ML} \sin\theta_{Bragg}$$

$$m\lambda_x = 2 D_{ML} \sin\theta_{Kiessig}$$

Gray et al., Phys. Rev. B 82, 205116 (2010); Europhysics Letters 104, 17004 (2013)

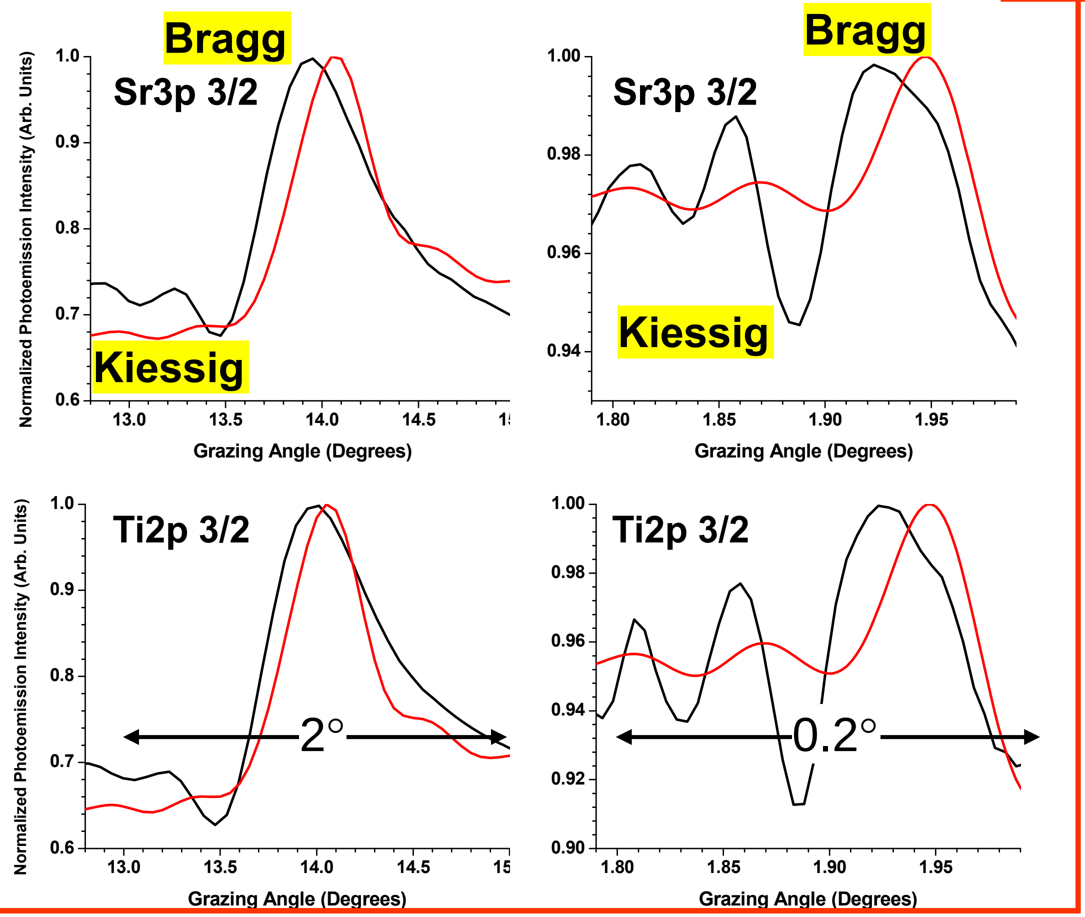
Samples: Ramesh, Huijben



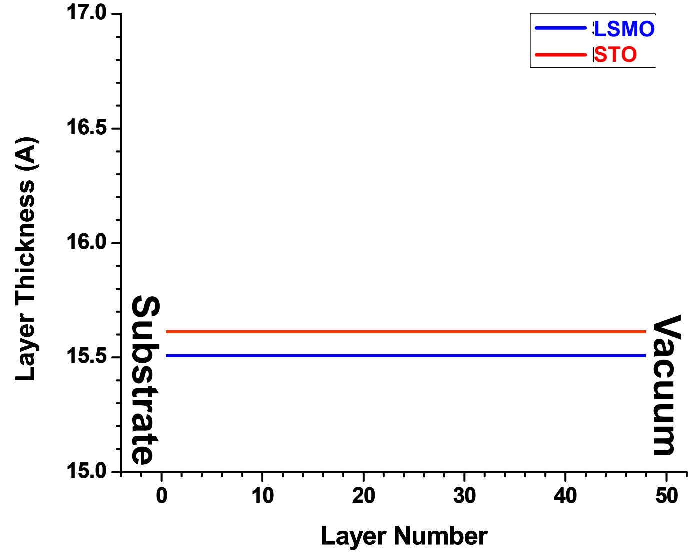


$SrTiO_3$/$La_{0.67}Sr_{0.33}MnO_3$ Multilayer
Analysis of Rocking Curves

Expt.
Calc.



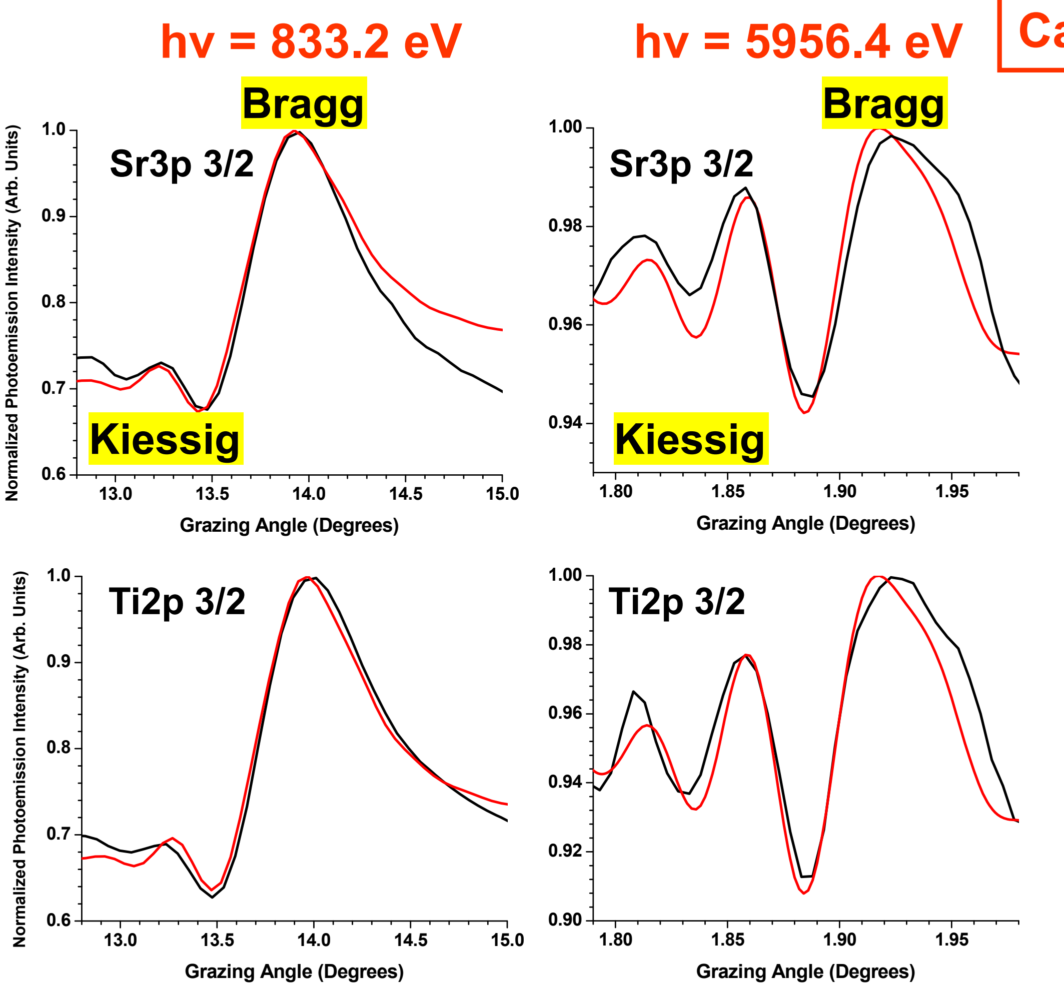
Ideal Bilayer Thickness Gradient Profile



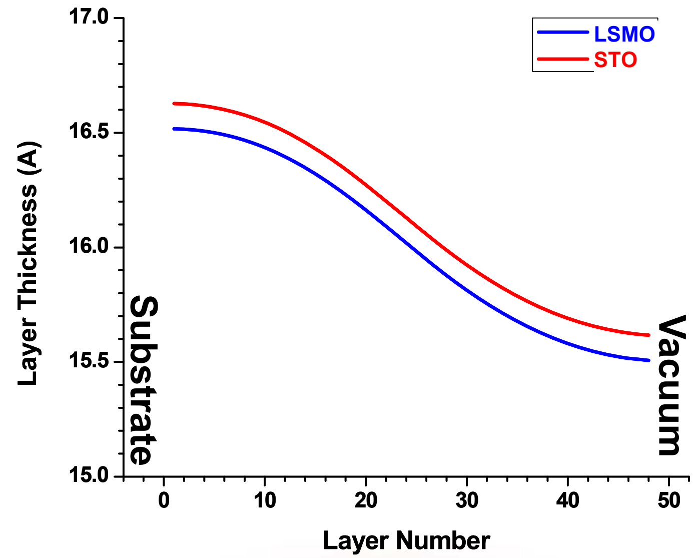
- Relative amplitude of the predicted Kiessig fringes does not agree with experiment
- Strong Kiessig fringes predicted on both sides of the rocking curves, esp. 5.9 keV

$SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ Multilayer
Analysis of Rocking Curves

Exp.
Calc.



Bilayer Thickness Gradient Profile



→Average multilayer d_{ML} changes by about -2 Å ≈ -6% from top to bottom

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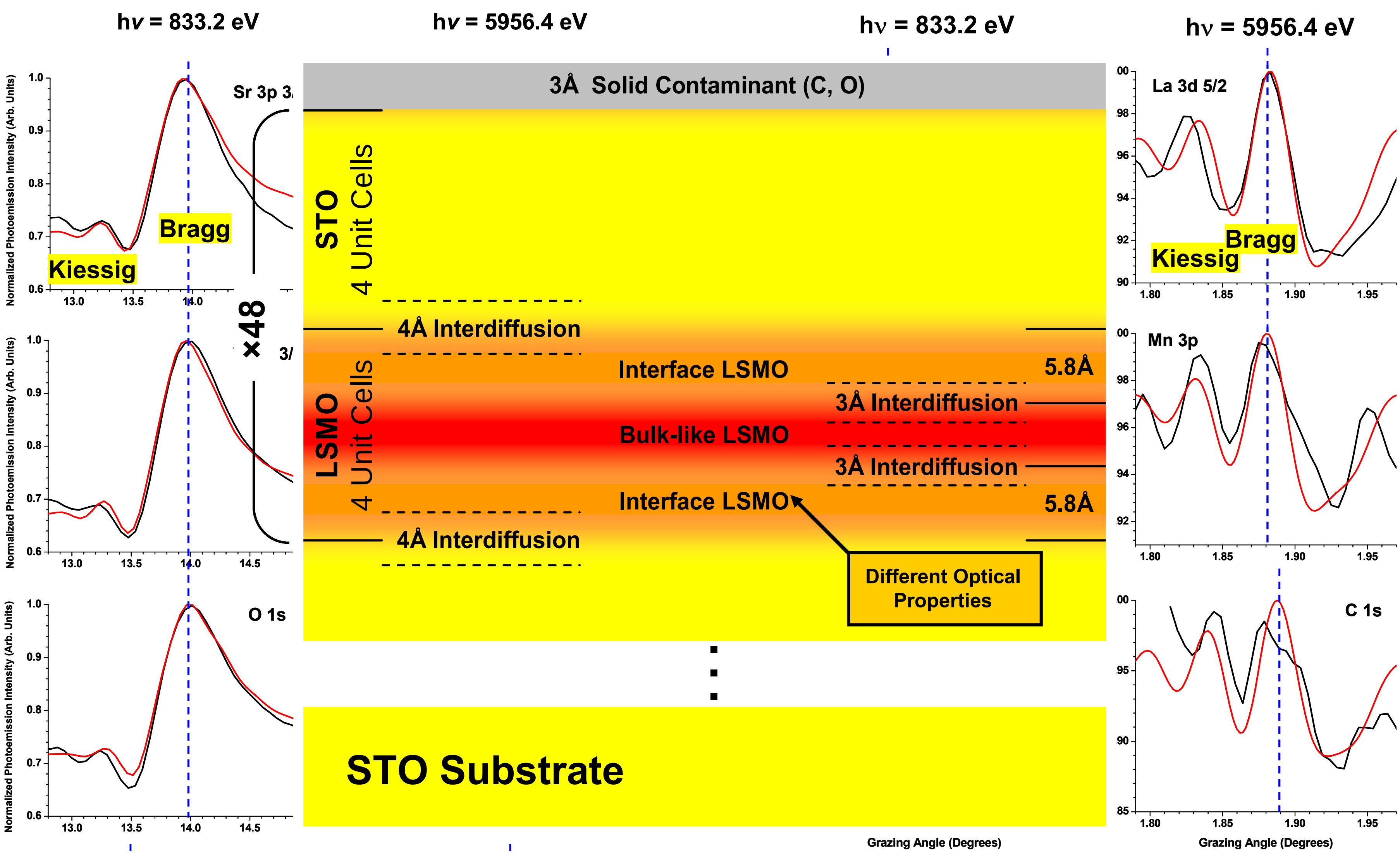
BEST FIT

SPring-8

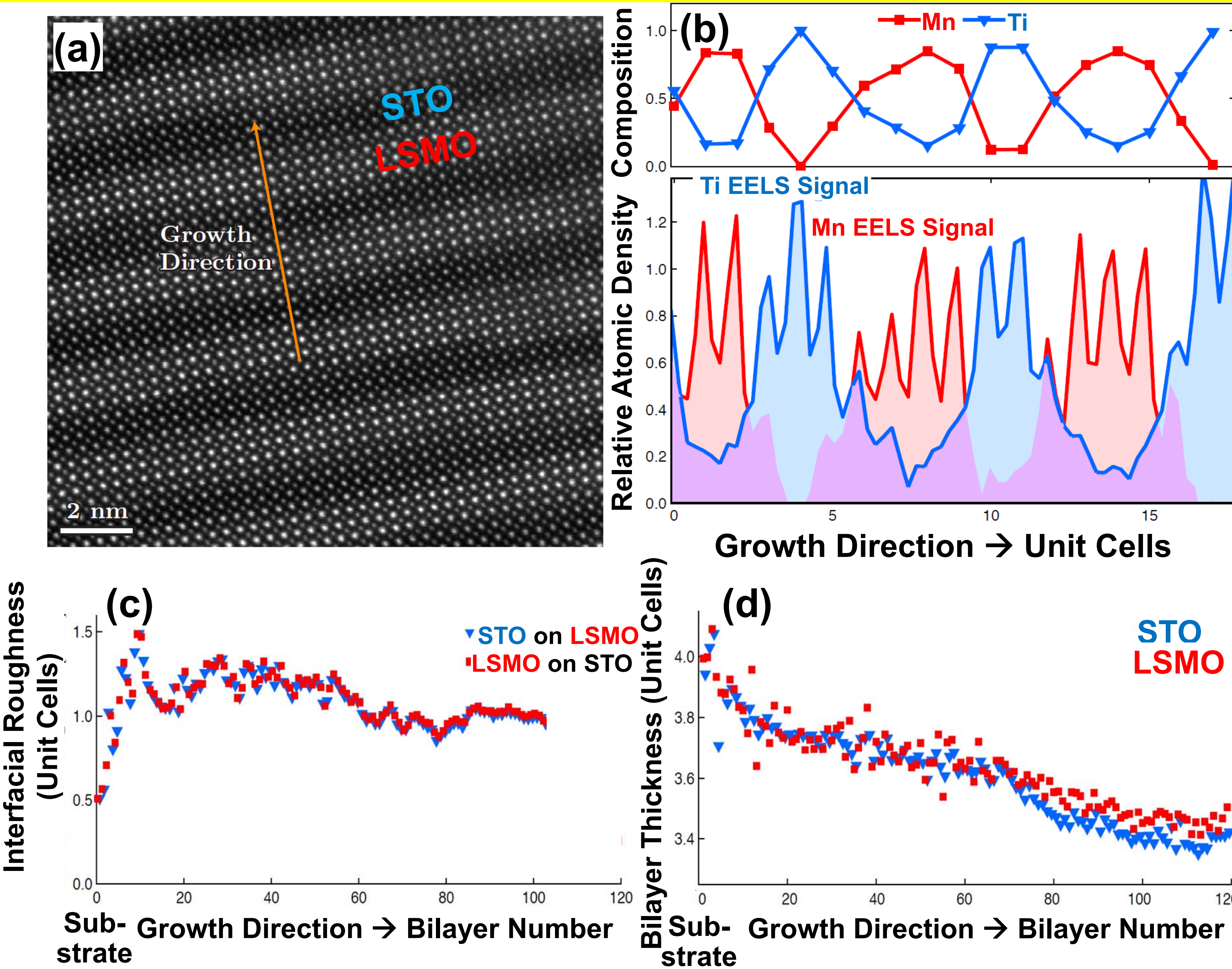
Gray et al., Phys. Rev. B 82, 205116 (2010)

Fitting of Rocking Curves—All Elements Present, Soft and Hard X-rays



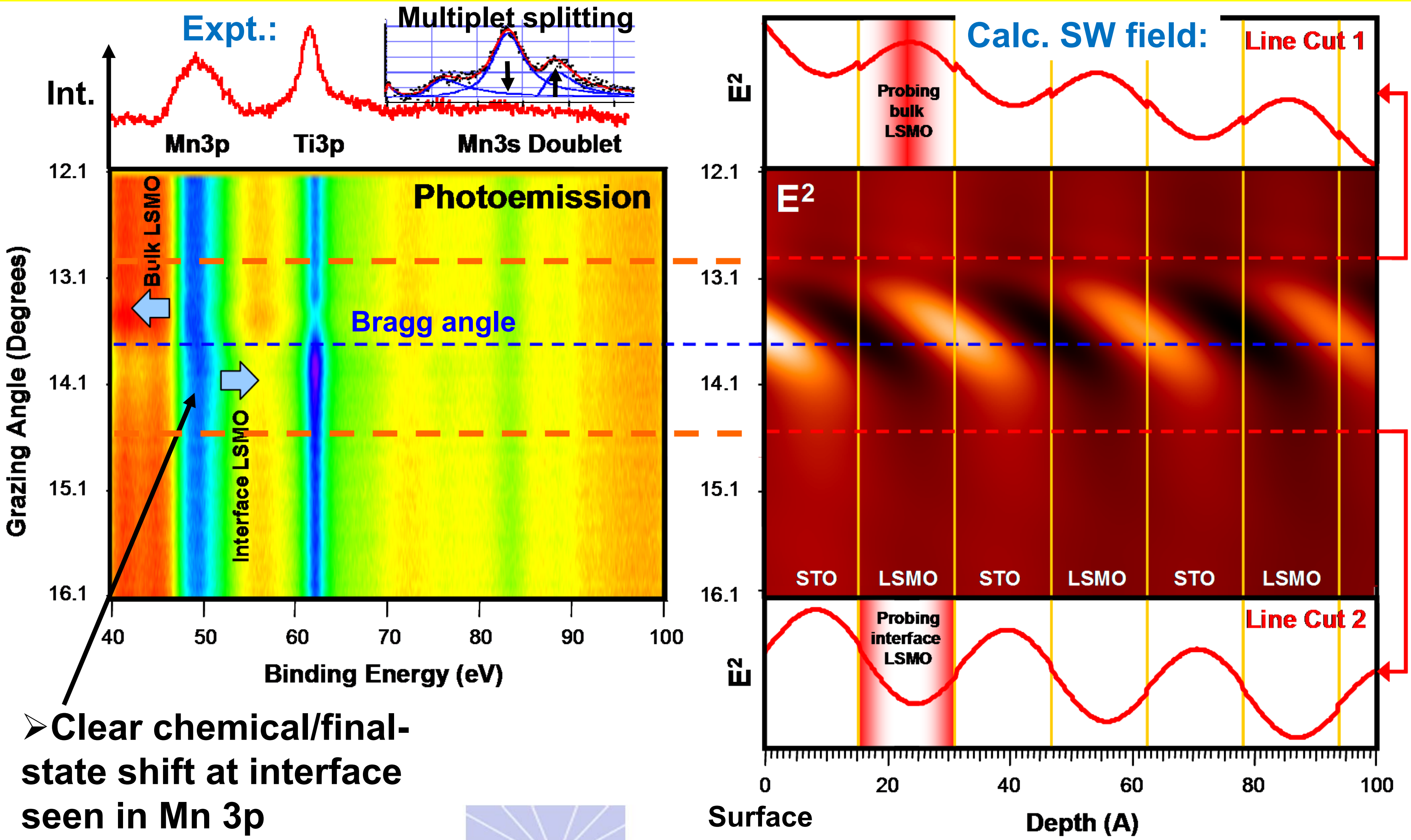
Gray et al., Phys. Rev. B 82, 205116 (2010)

TEM with EELS+HAADF-Confirms Conclusions of Standing-Wave Photoemission



J. Ciston et al. NCEM, LBNL, EPL 104, 17004 (2013)

STO/LSMO-Resonant soft x-ray standing wave/rocking curves at 833 eV: core photoelectron peaks compared to calculated standing-wave field



- Clear chemical/final-state shift at interface seen in Mn 3p
- No change in Mn 3s
- No change in Ti 3p—near surface

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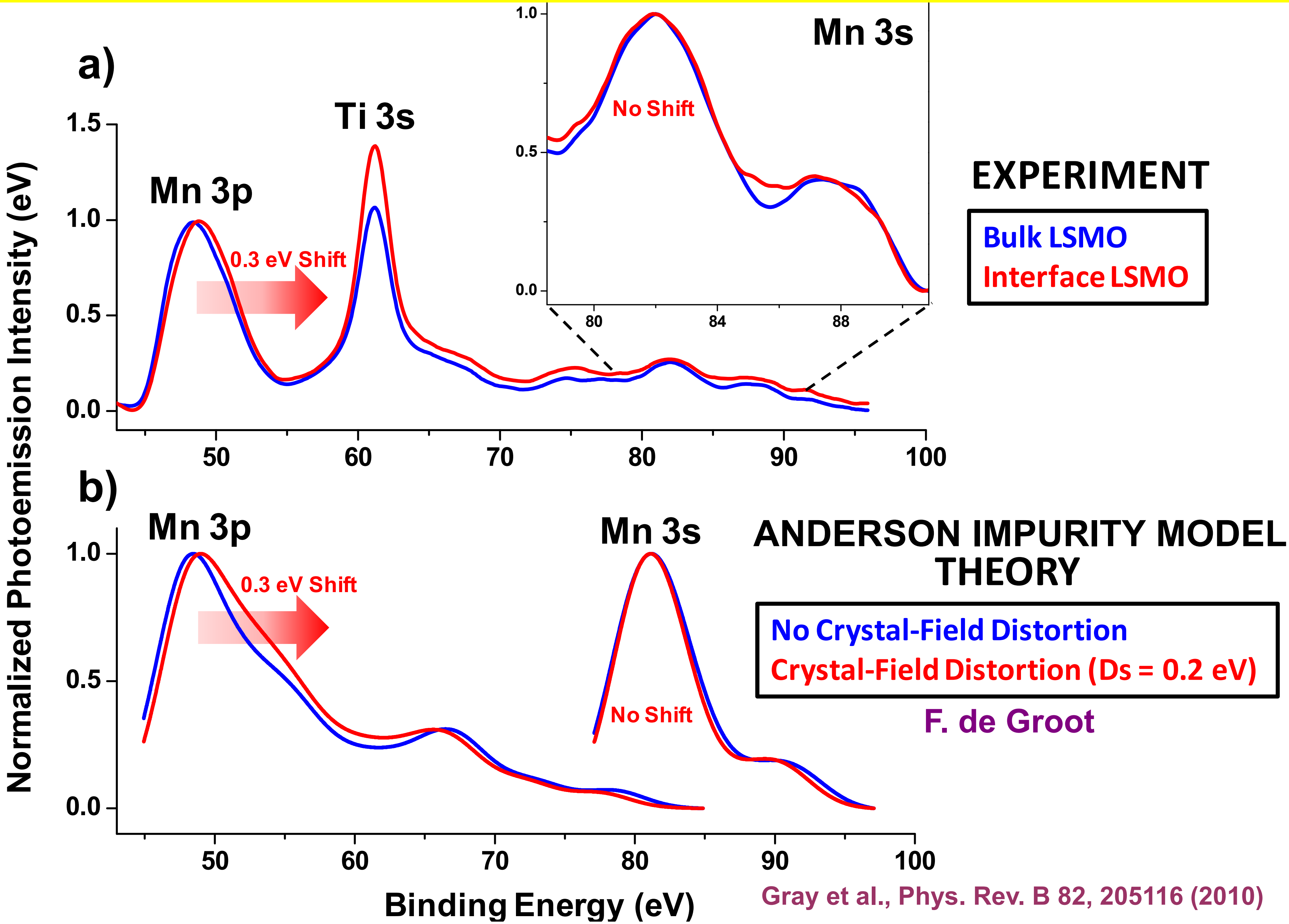
Gray, Yang et al., Phys. Rev. B 82, 205116 (2010)

STO/LSMO-Explaining the Difference Between Mn 3p and Mn 3s behavior

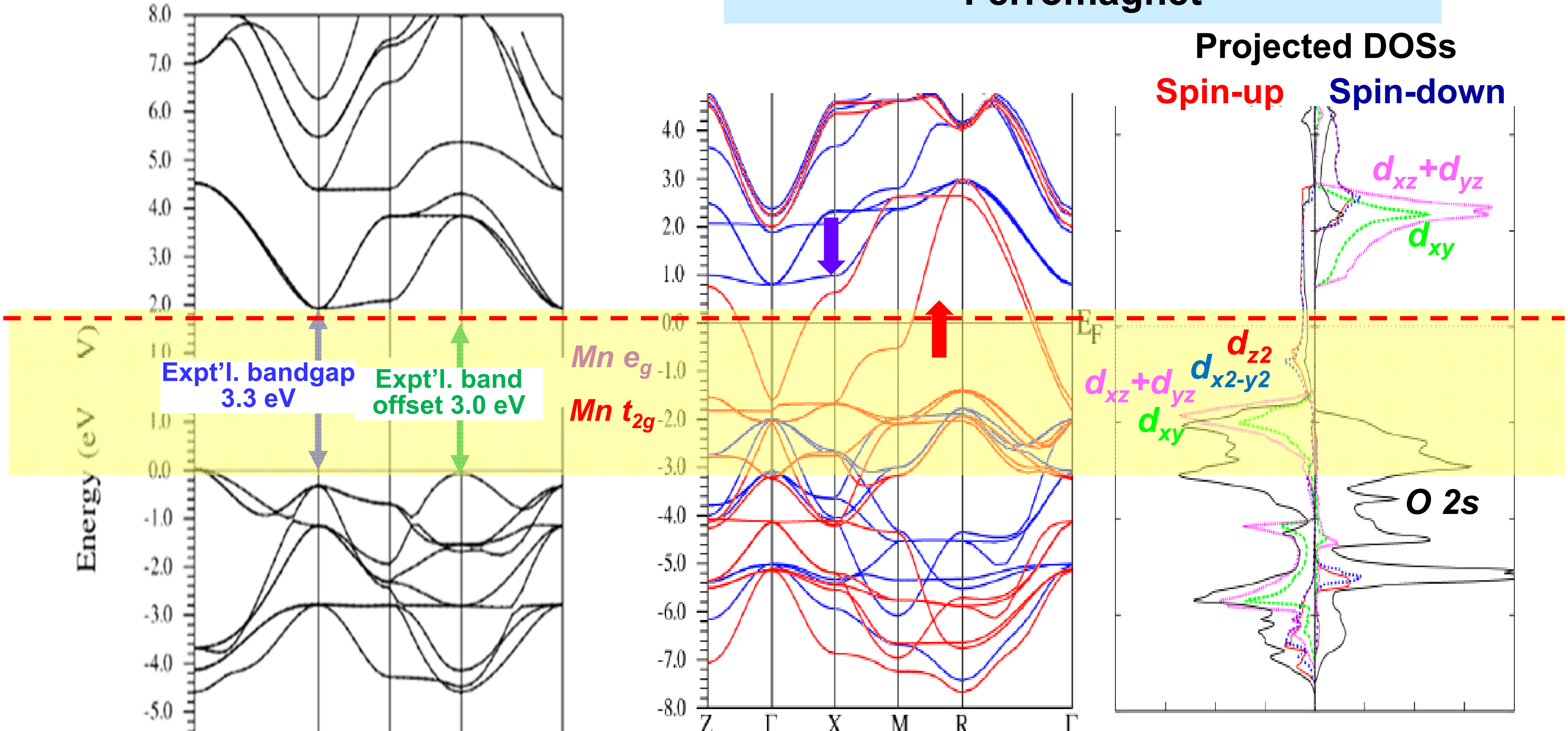


Gray et al., Phys. Rev. B 82, 205116 (2010)

$SrTiO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ band structures and DOS

$SrTiO_3$-band insulator

$La_{0.67}Sr_{0.33}MnO_3$- Half-Metallic Ferromagnet

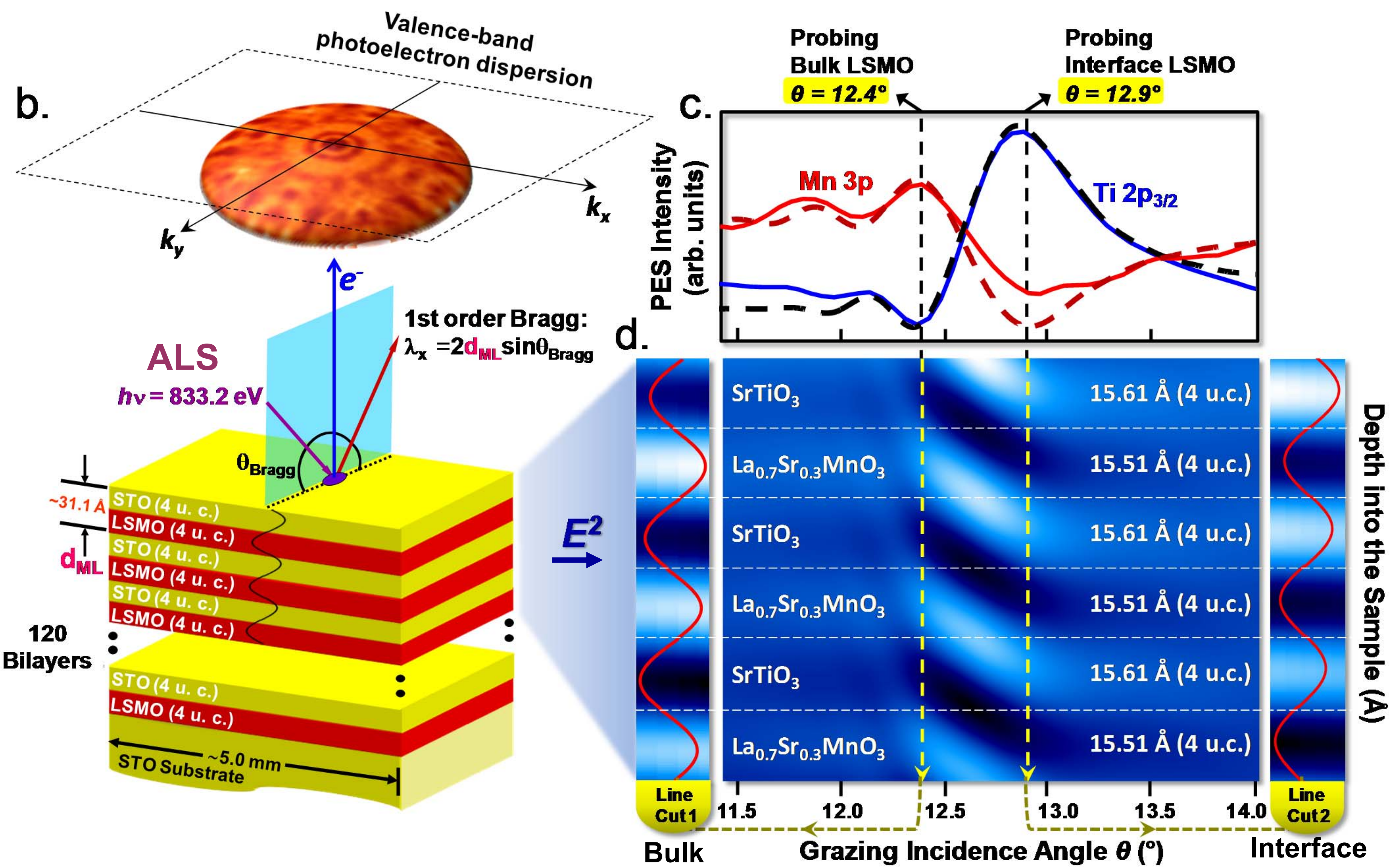


Plucinski, Wien2k,TBP with expt'l. band offset

Spin-up
Spin-down
Chikamatsu et al., PRB 73, 195105 (2006); Plucinski, TBP

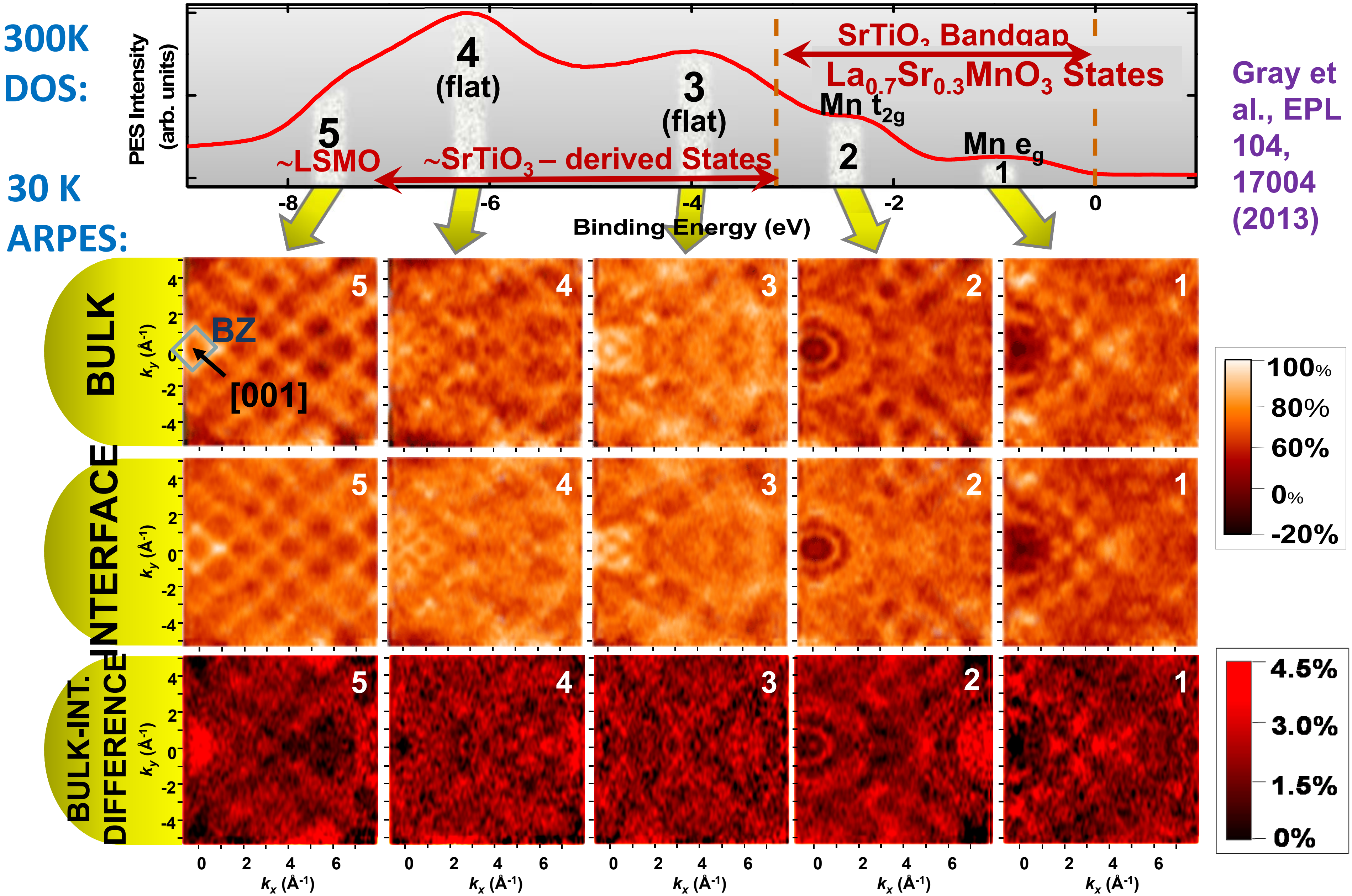
Zheng, Binggeli, J. Phys. Cond. Matt. 21, 115602 (2009) Plucinski, TBP

Depth-Resolved Soft X-Ray ARPES? Cryocooling to supress phonon smearing: DW factor



ALS BL 7.0.2

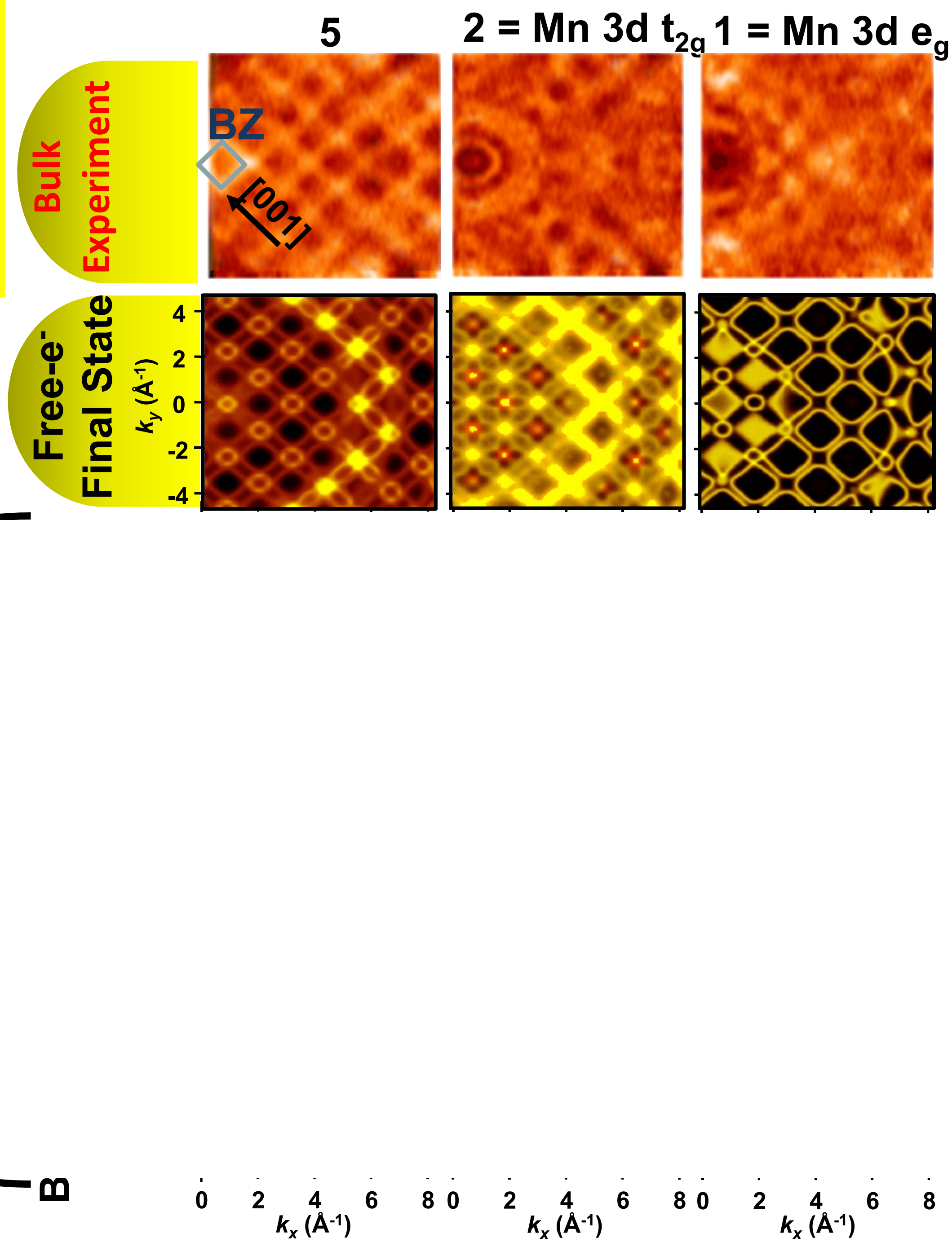
STO/LSMO Depth-resolved ARPES: hν=833 eV, RT (DW = 0.13) and 30K (DW = 0.75)



Gray et al., EPL 104, 17004 (2013)

First test case:
STO/LSMO
Depth-resolved ARPES:
hν=833 eV, 20K-
Expt. vs Theory

Theory:
Ground-state band structure→k-conserving free-e⁻ final state
Plucinski



Theory:
One-step, t-reversed LEED, spin-polarized relativistic KKR, alloy CPA
Minar, Braun, Ebert

Gray et al., Phys. Rev. B 82, 205116 (2010); Europhysics Letters 104, 17004 (2013)

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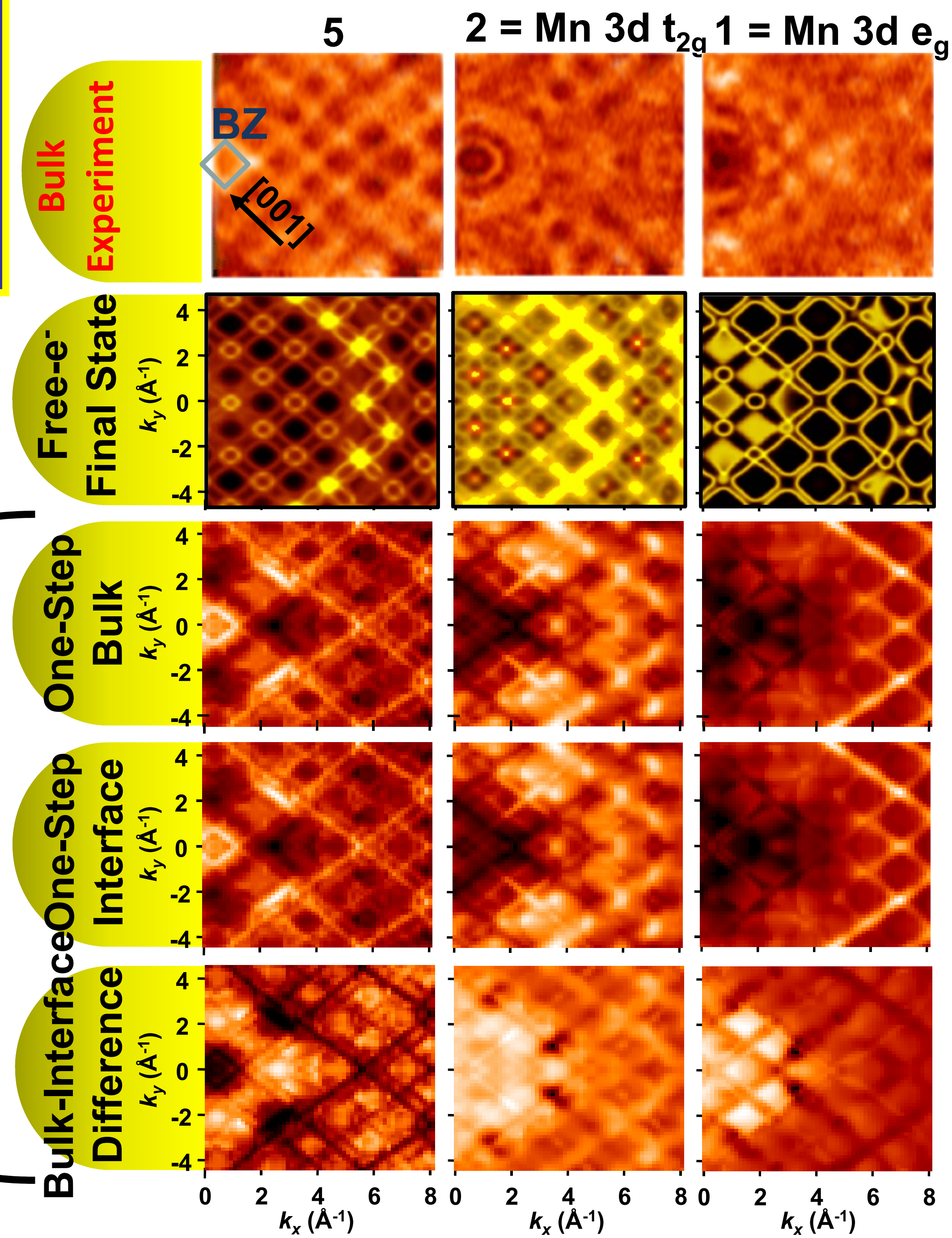

Gray et al., Phys. Rev. B 82, 205116 (2010); Europhysics Letters 104, 17004 (2013)

Conclusions: Soft and Hard X-Ray Standing-Wave PS and ARPES of $SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$

- Depth distribution of concentration and index of refraction through the interface with ca. ±2 Å resolution, confirmed by TEM/EELS/HAADF
- Interface Mn 3p binding energy shift consistent with crystal field distortion via AIM calculations
- Interface-specific changes in <u>k-resolved</u> electronic structure
- Results qualitatively in agreement with free-electron final state and one-step theory
- Future applications to other interfaces

Gray et al., Phys. Rev. B 82, 205116 (2010);
Europhysics Letters 104, 17004 (2013)

Soft →hard x-rays and standing waves: a few example studies

Fe/MgO-tunnel junction

Depth-resolved composition, chemical states, magnetization

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$SrTiO_3/GdTiO_3$
An interface 2D electron gas

S. Nemšák et al., http://arxiv.org/abs/1508.01832

$SrTiO_3$
- Band insulator (E_g=2.3 eV)
- Low temperature superconductor

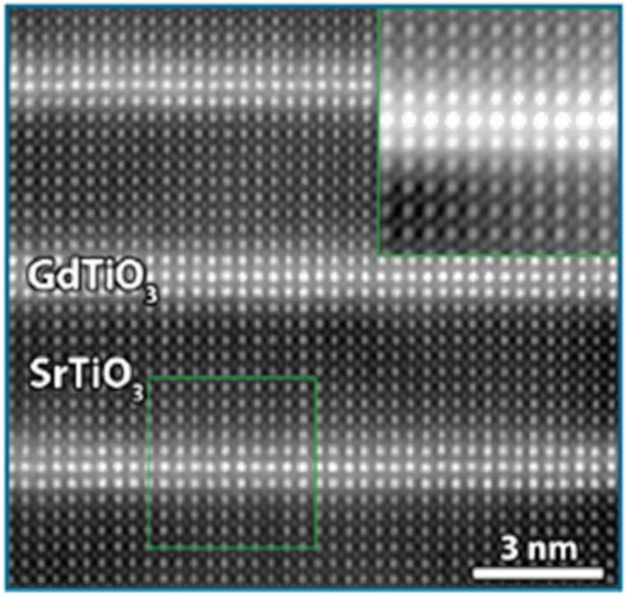
$GdTiO_3$
- Mott-Hubbard insulator

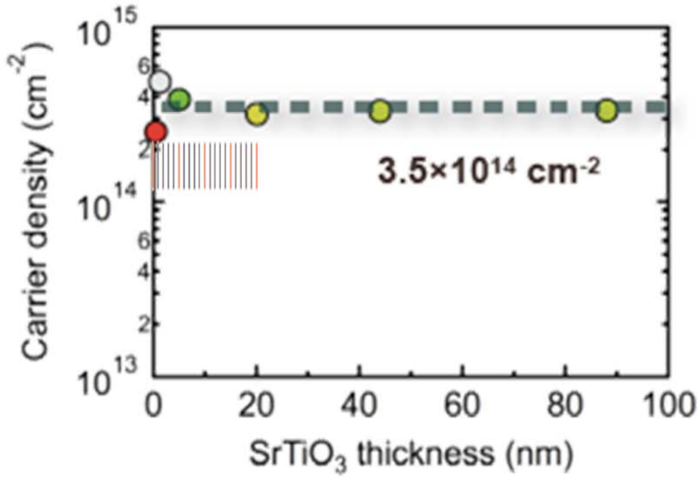
$GdTiO_3/SrTiO_3$ interface
- Two-dimensional electron gas (2DEG) at the interface between two insulators (*Appl. Phys. Lett.* ***99****, 232116, 2011*)
- Sheet carrier density on the order of $3x10^{14}$ cm^{-2}
- Ferromagnetism in the 2DEG at the interface (*Phys. Rev. X* ***2****,021014, 2012*)

S. Nemšák, G. Pálsson , A.X. Gray, D.Eiteneer, A.M. Kaiser, G. Conti, A.Y. Saw, A. Perona, A. Rattanachata, C. Conlon, A. Bostwick, V. Strocov, M. Kobayashi, W.Stolte, A. Gloskovskii, W. Drube , M.-C. Asencio, J. Avila, J. Son, P. Moetakef, C. Jackson, L. Bjaalie, A. Janotti, C. G. Van de Walle , J. Minar, J. Braun, H. Ebert, J.B. Kortright, S. Stemmer, and C. S. Fadley

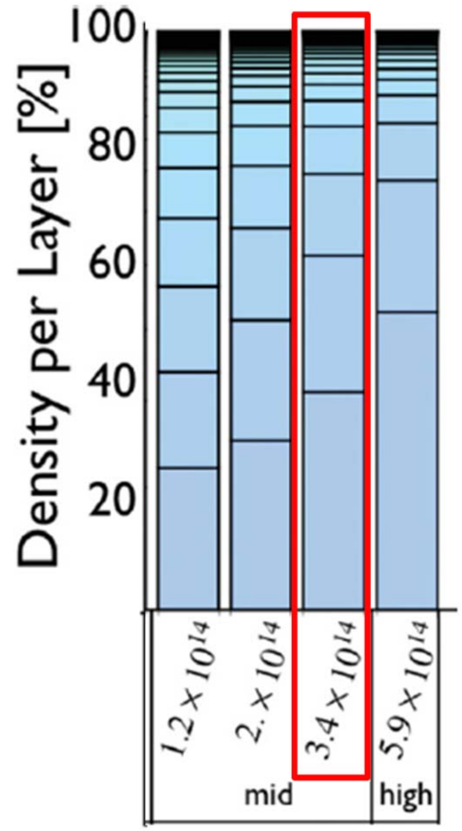
The Advanced Light Source | UCSB | SPring-8 | PAUL SCHERRER INSTITUT PSI | DESY | LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN | Julich Res. Ctr.

The STO/GTO 2D Electron Gas





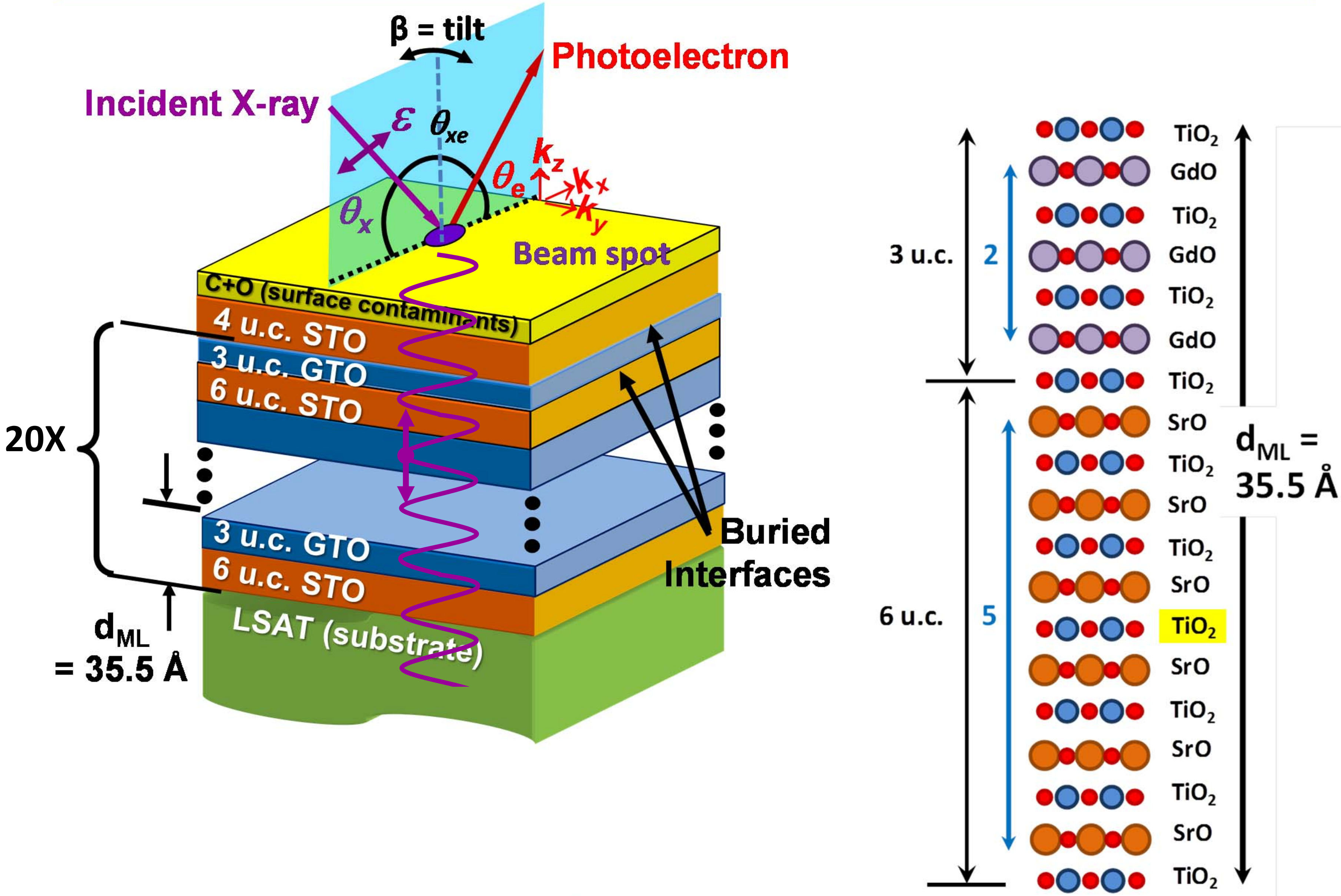
Appl. Phys. Lett. 99, 232116 (2011).
Stemmer et al.



Calculated carrier density (cm^{-2})
Khalsa and McDonald PRB 86, 125121 (2012)

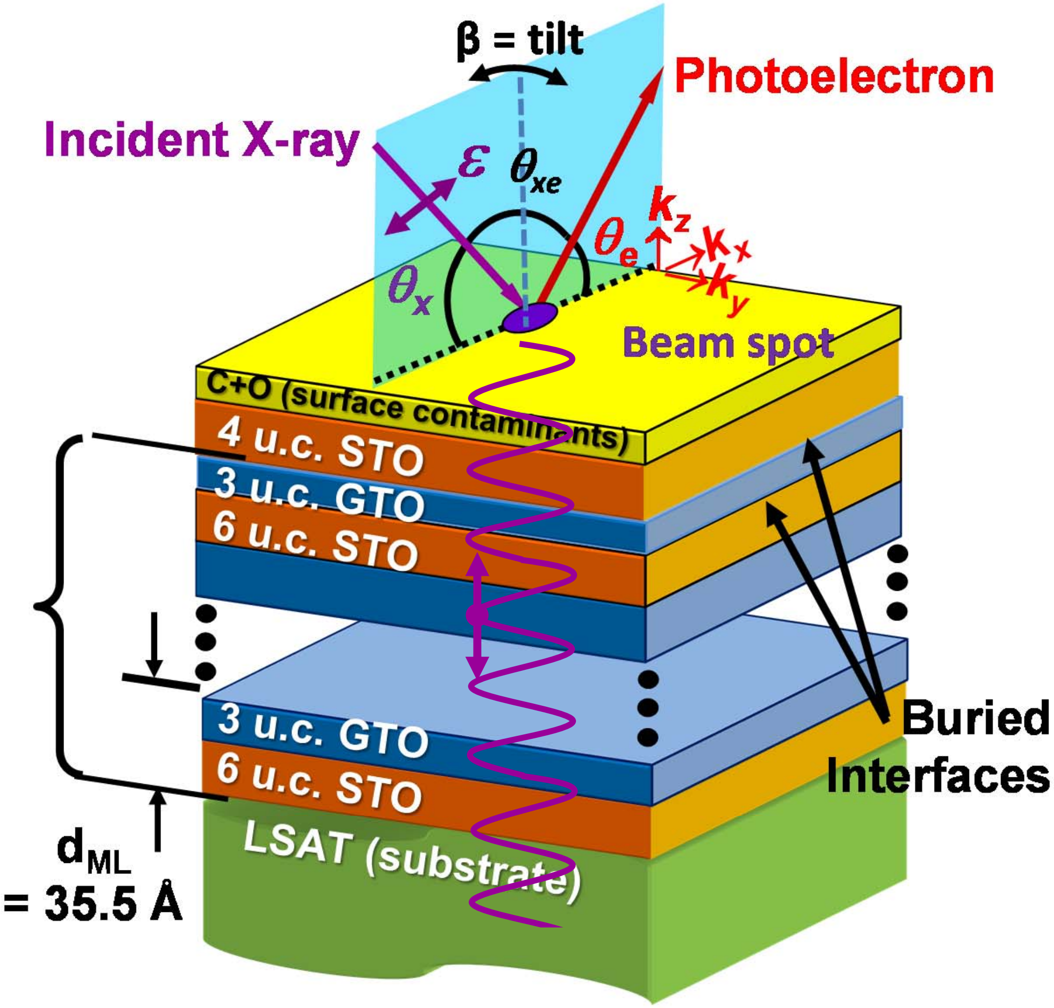
Can we see this 2DEG with standing wave ARPES, including its momentum dispersion and its depth distribution?

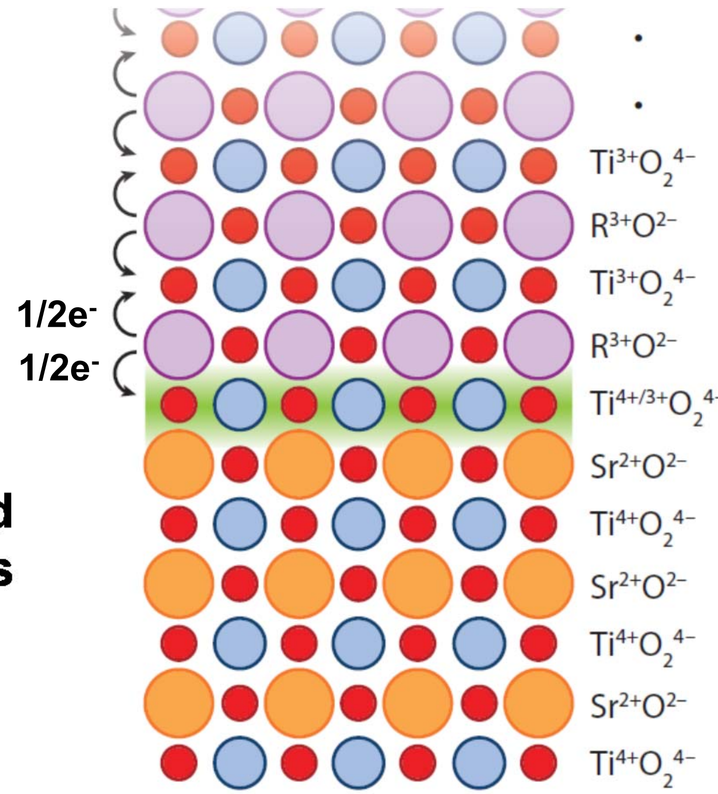
Multilayer GTO/STO



Samples: P. Moetakef,
S. Stemmer, UCSB

Multilayer GTO/STO

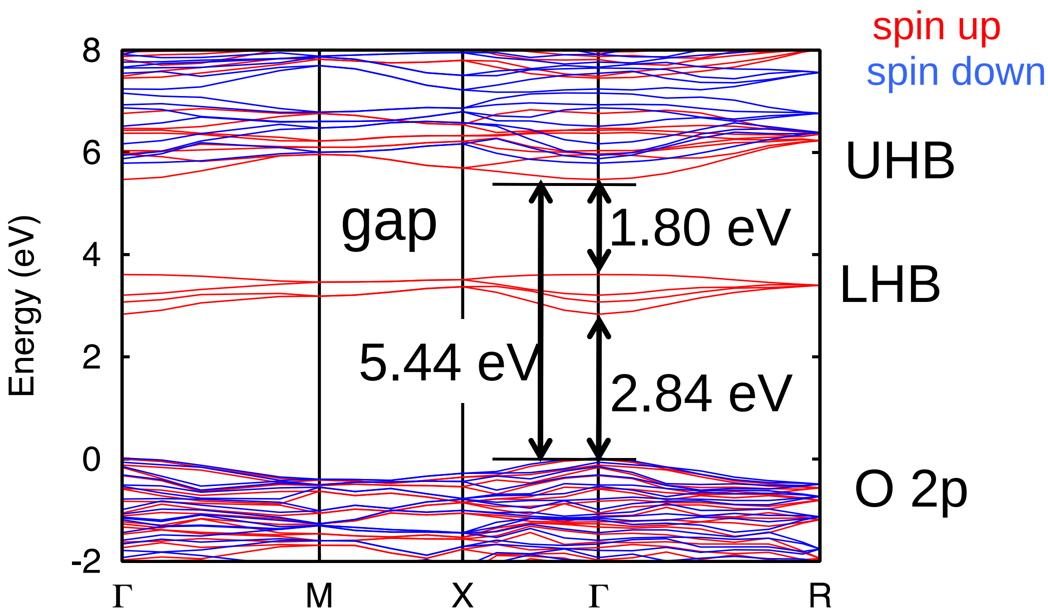


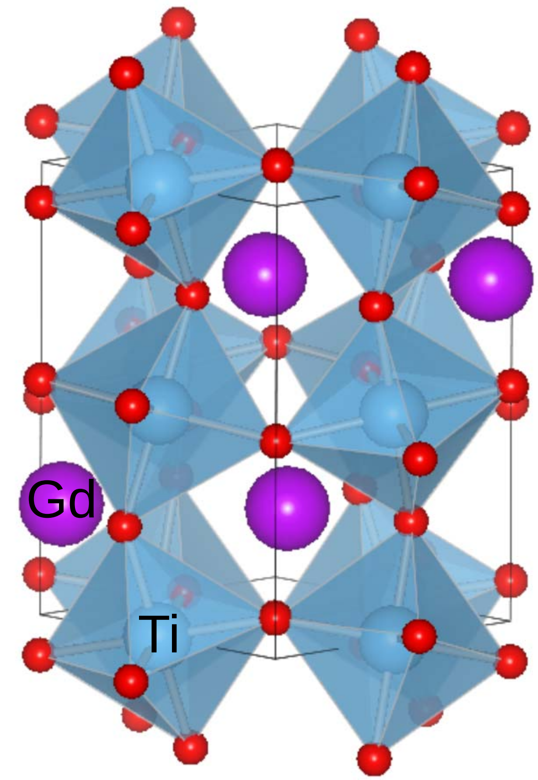


Stemmer, Allen
Annu. Rev. Mater. Res.
44:, 51–71 (2014)

P. Moetakef, S. Stemmer,
UCSB

Electronic structure of bulk $GdTiO_3$- LDA+hybrid functionals



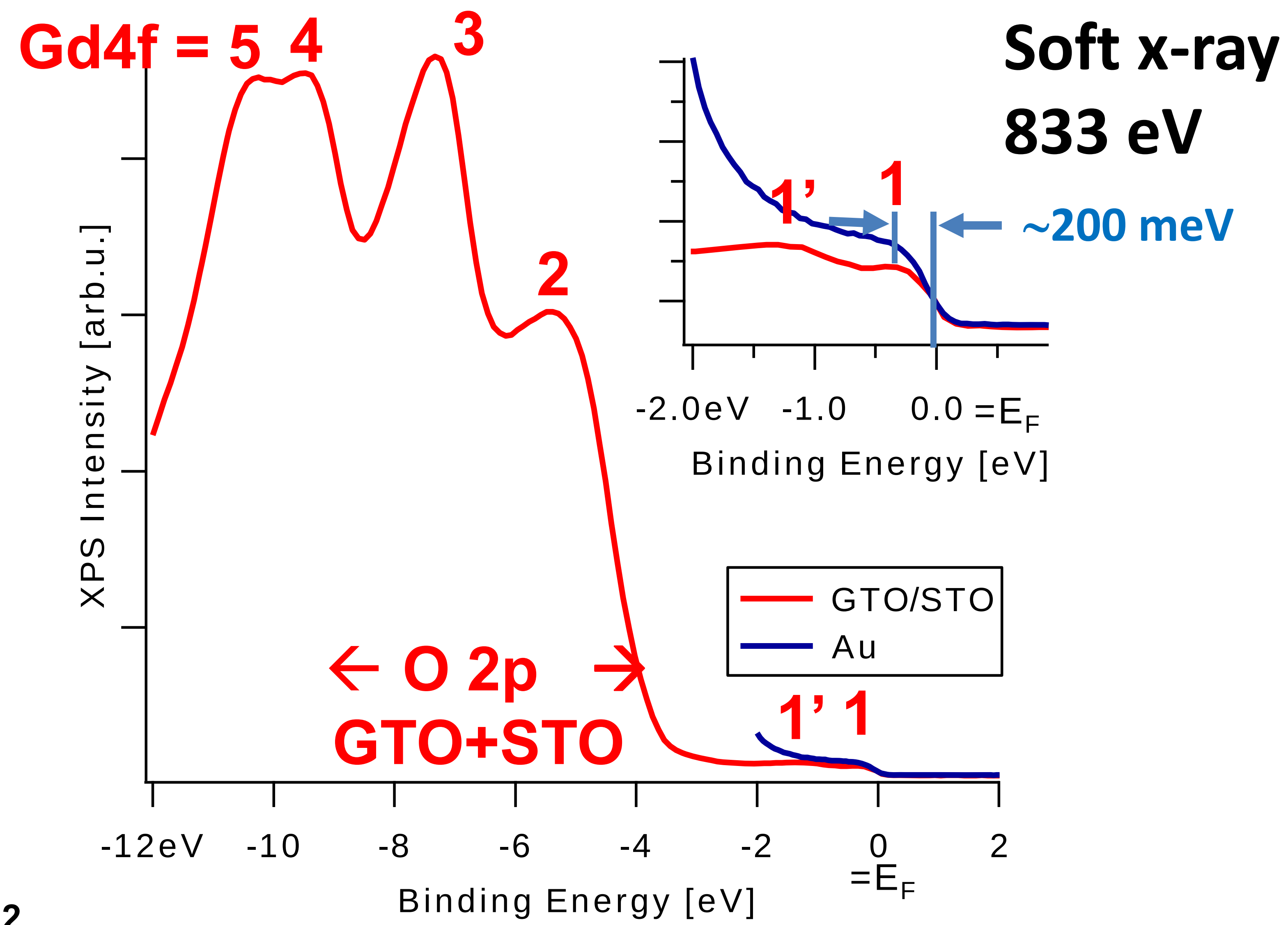


LHB width: 0.80 eV

4 bands compose LHB, one e^- for each Ti

L. Bjaalie, A. Janotti, C. Van de Walle
M32.7

GTO/STO multilayer:
Soft x-ray photoemission in the XPS limit @ 833 eV, 298K
→Matrix-element-weighted densities of states

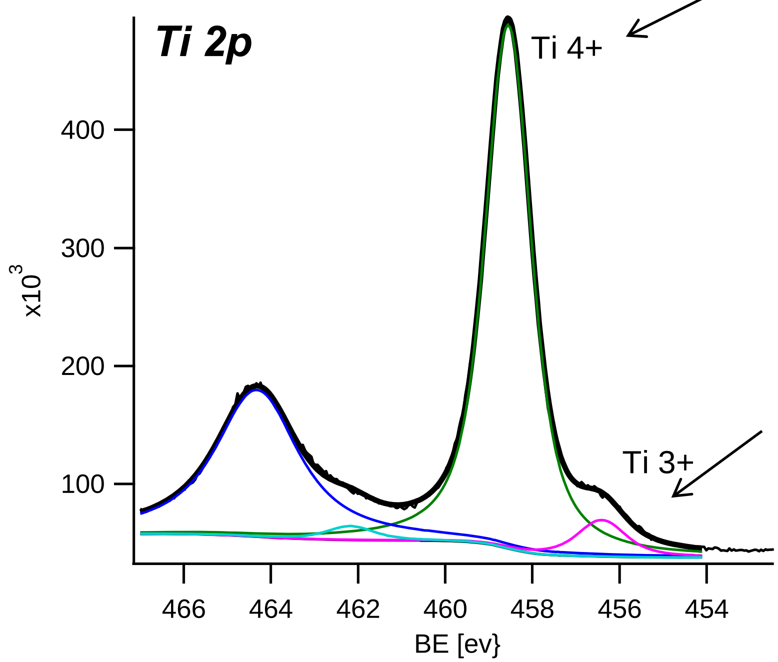


ALS BL 7.0.2

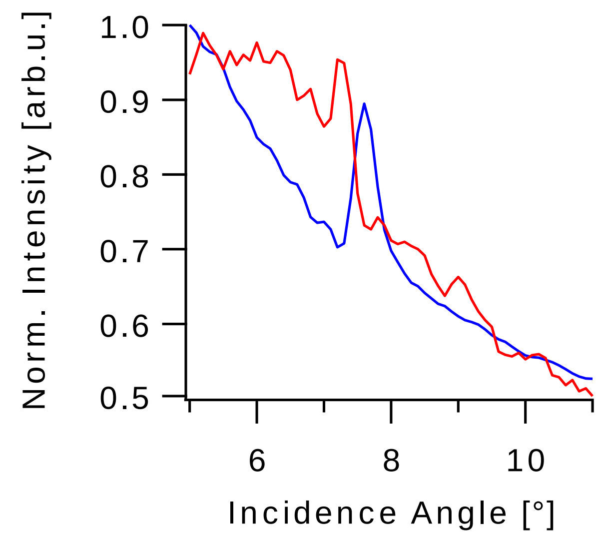
Standing-wave rocking curves: Ti 2p spectra, 1182 eV

SrTiO$_3$

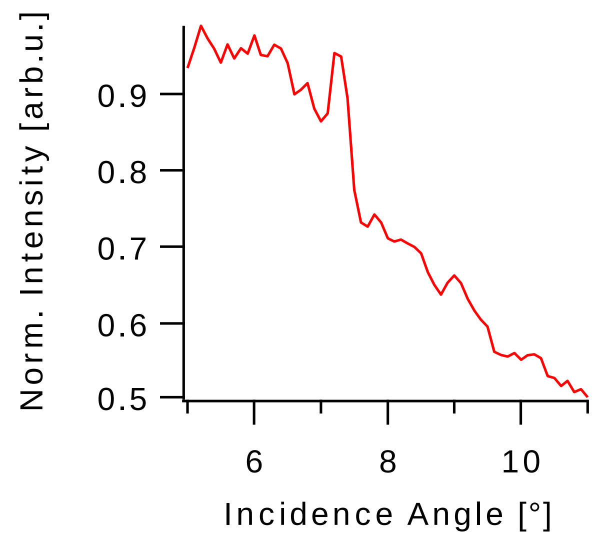
GdTiO$_3$



Ti^{4+} 2p rocking curve



Ti^{3+} 2p rocking curve

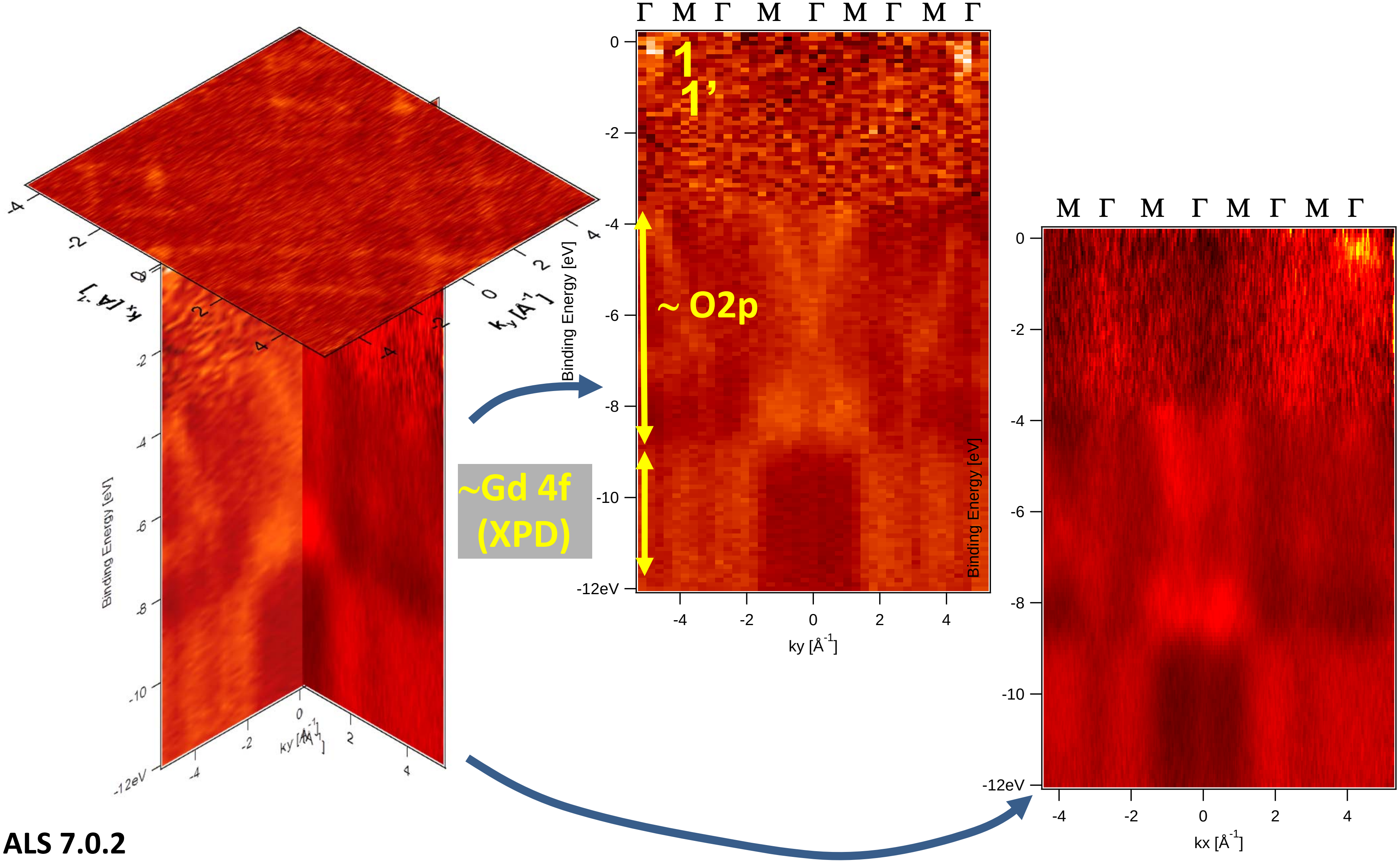


Rocking curves provide direct depth information

Swiss Light Source

Nemšák et al.

STO/GTO Standing-Wave ARPES @ 833 eV, 20 K



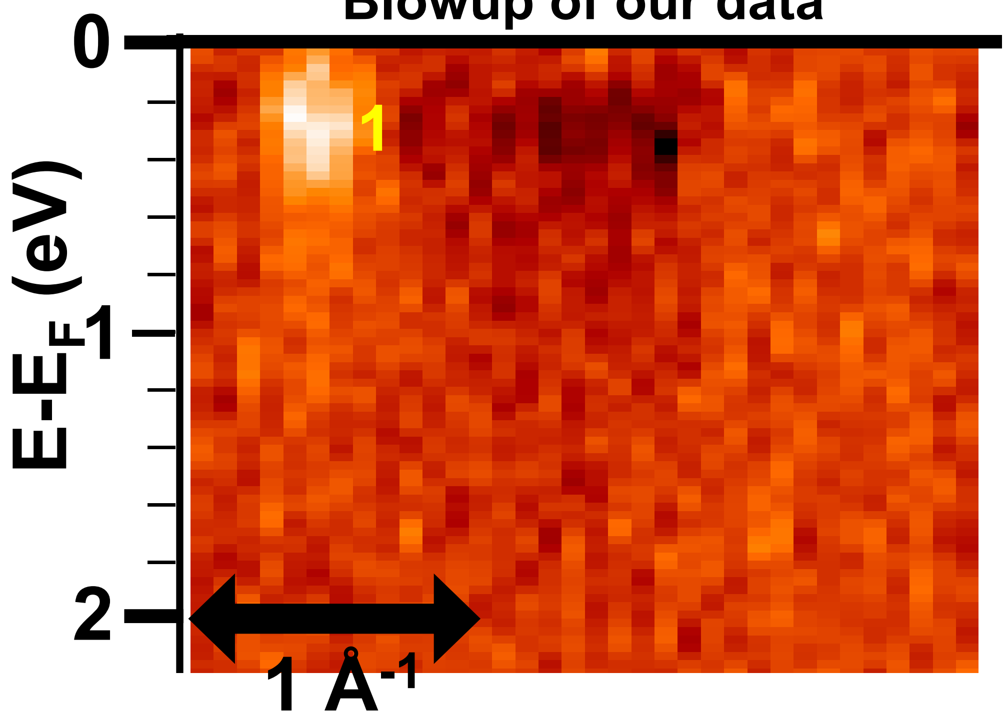
ALS 7.0.2

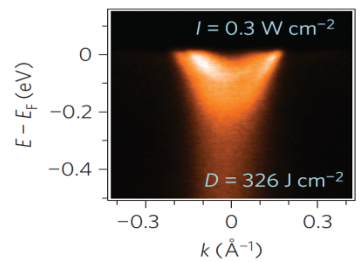
STO/GTO multilayer – Peak 1, 1' compared to 2DEG on STO

Creation and control of a two-dimensional electron liquid at the bare $SrTiO_3$ surface

W. Meevasana[1,2,3,4,5†], P. D. C. King[3†], R. H. He[1,2,6], S-K. Mo[1,6], M. Hashimoto[1,6], A. Tamai[3], P. Songsiriritthigul[4,5], F. Baumberger[3] and Z-X. Shen[1,2★]

Blowup of our data



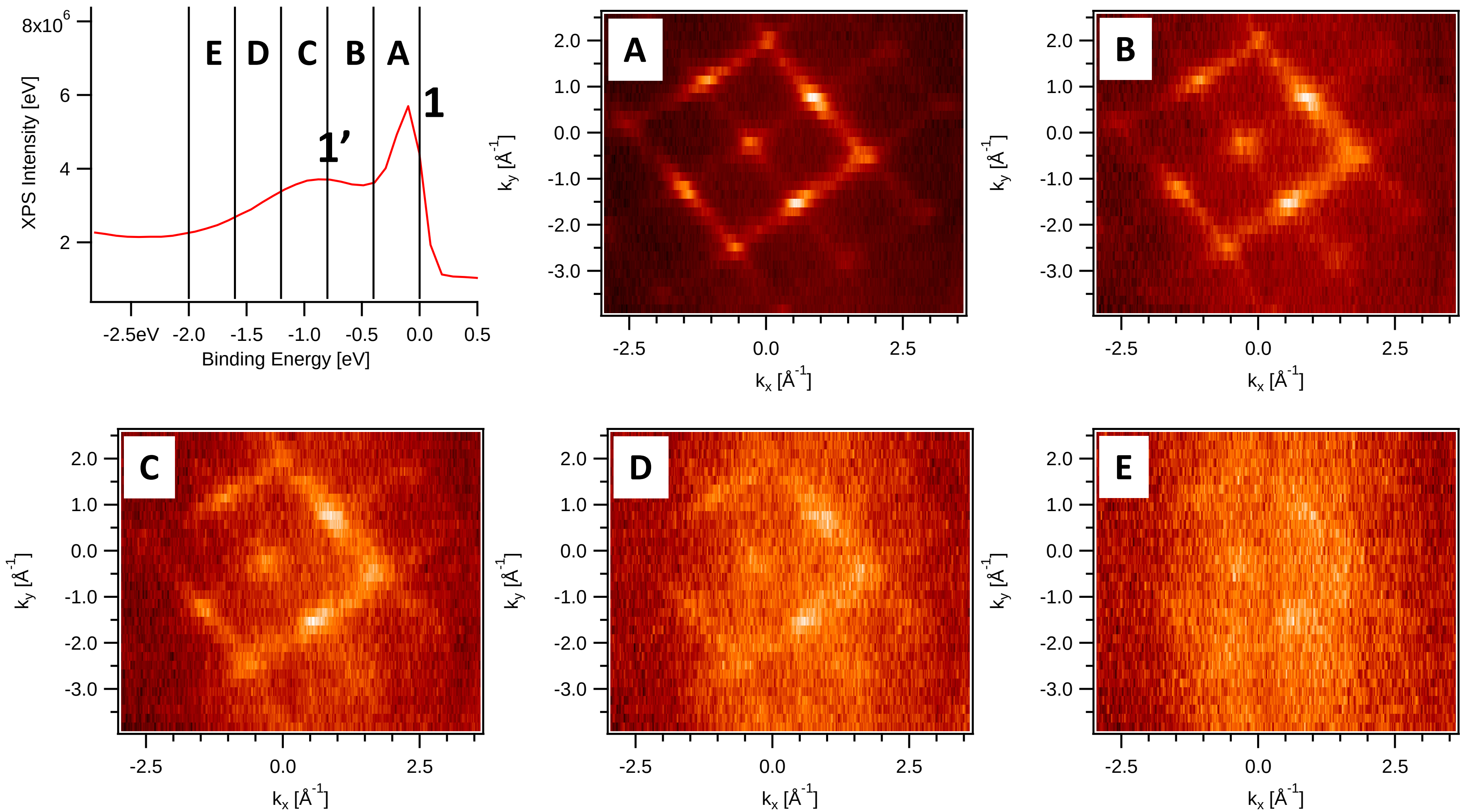


Same scales

Nature Materials 10 , 114 (2011)

→1 looks like interface 2DEG, but where is lower Hubbard band?

STO/GTO multilayer-Dispersion of Peaks 1 and 1’ : ARPES @ 465.2 eV (Ti resonant)



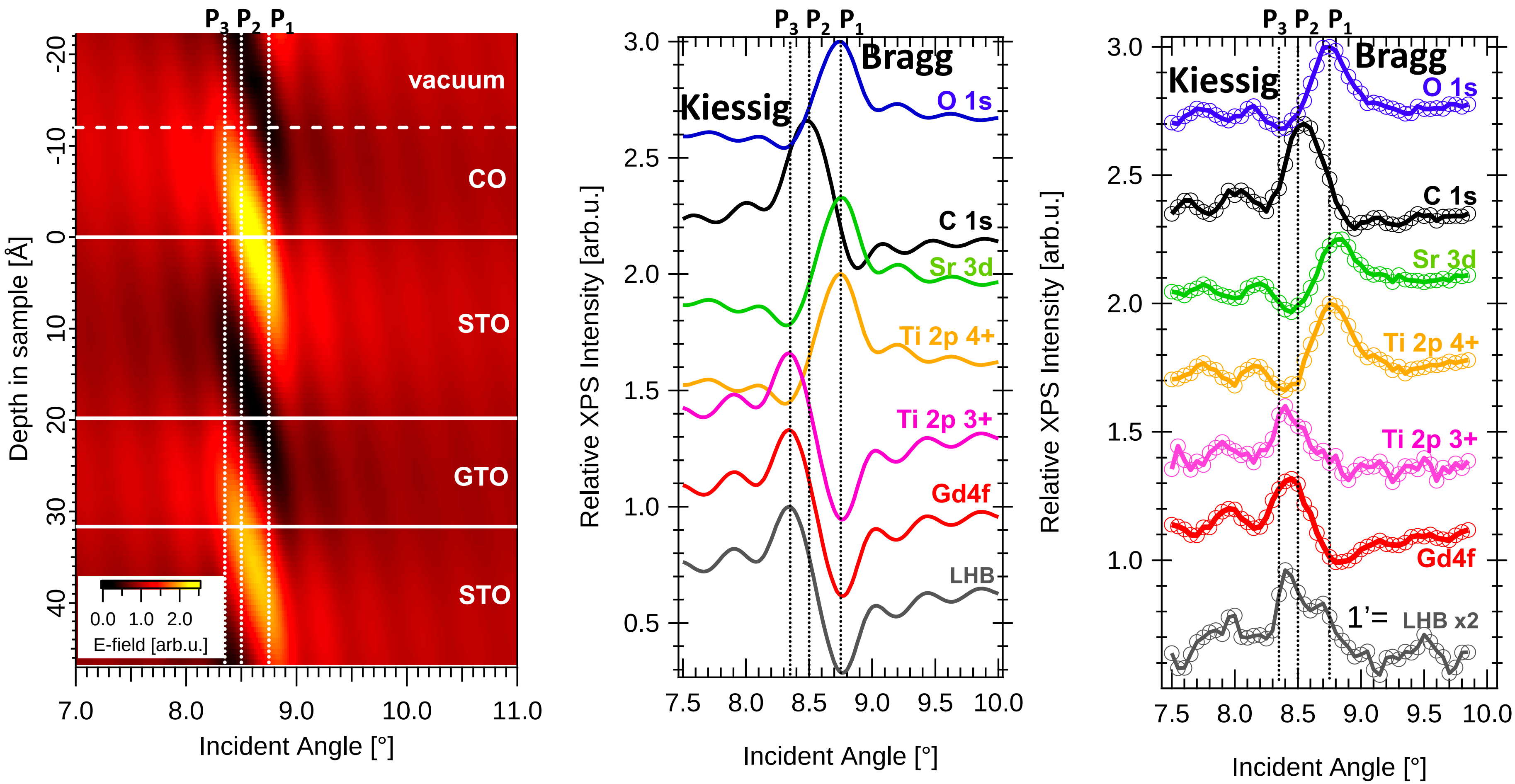
- 1, 1’ dispersions identical, states strongly mixed
- 1 has greater or different Ti character

ALS

Theoretical simulations vs. expt.—1182-just below Gd M_5 edge SW emphasizng STO

Rocking curves

Theory E^2 -field strength | **Theory** | **Experiment**

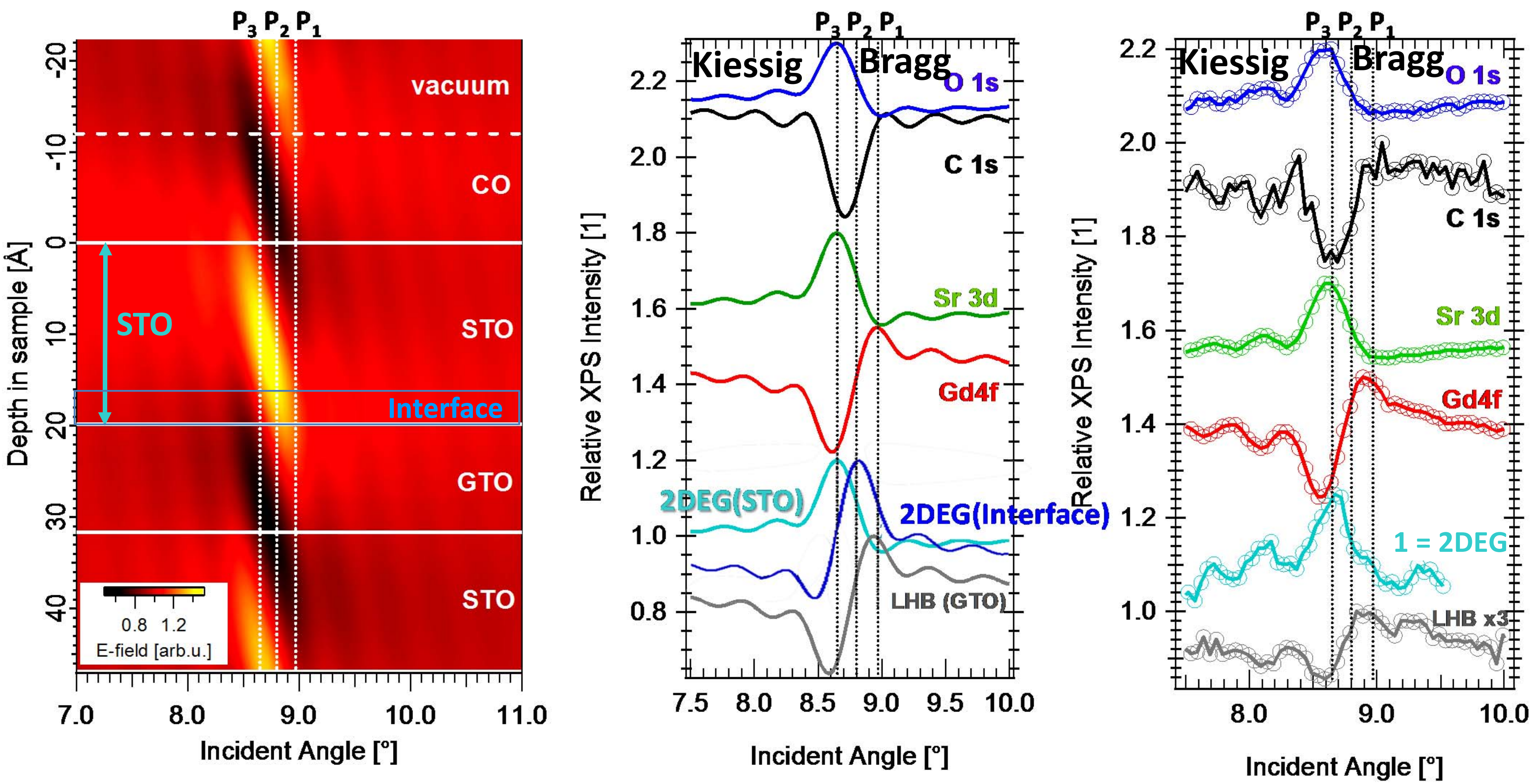


→Ti 4+ in STO, Ti 3+ in GTO, 1' = LHB in GTO

Theoretical simulations vs. expt.—1187-just above Gd M_5 edge SW emphasizng STO/GTO interface

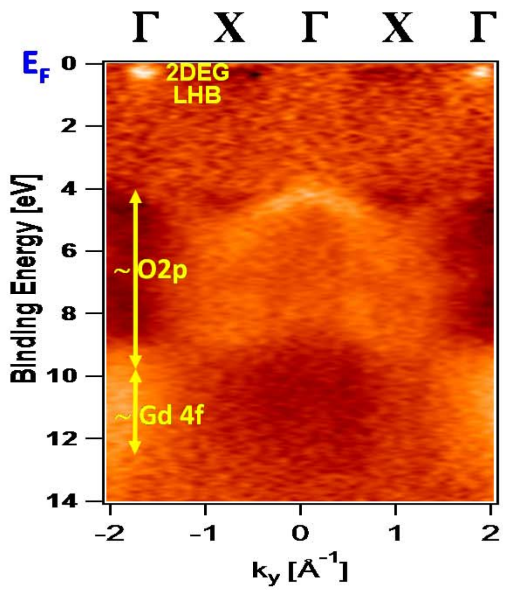
Rocking curves

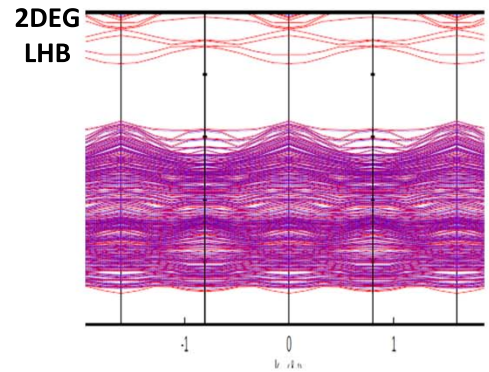
Theory: E^2 -field strength | Theory | Experiment

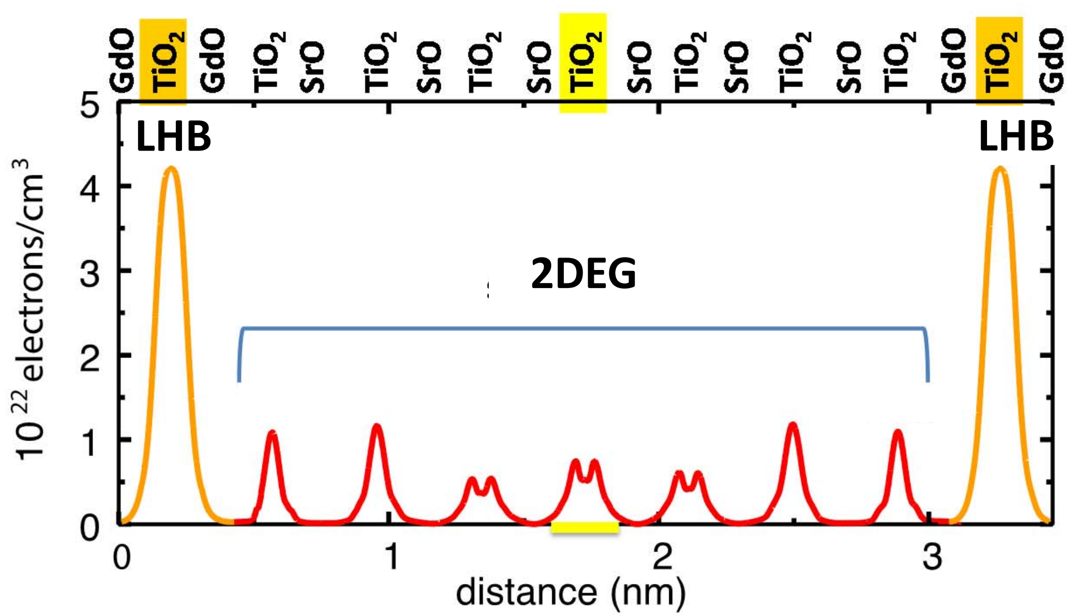


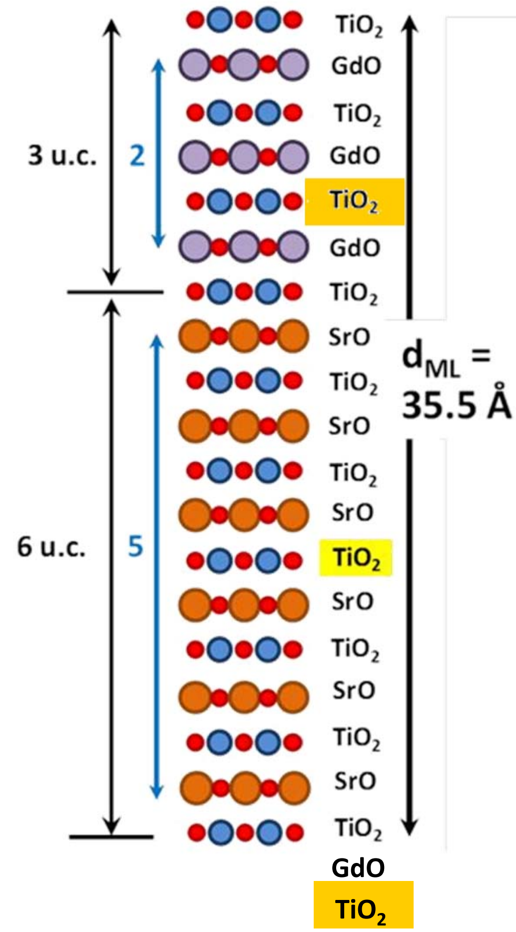
→Peak 1 = 2DEG & 2DEG occupies the full STO layer

Theory/expt. comparison: $(STO)_5(GTO)_2$ superlattice









LDA+hybrid functional theory agrees: 2DEG occupies full STO layer

A. Janotti, L. Bjaalie,
C. Van de Walle

S. Nemšák et al., http://arxiv.org/abs/1508.01832

Conclusions: Standing-Wave and Resonant XPS and ARPES of $SrTiO_3/GdTiO_3$

- k-resolved bands of GTO LHB and 2DEG, evidence for intermixing of the two
- 2DEG extends through the entire STO layer from standing-wave rocking curve analysis
- Results consistent with 2DEG tunneling subband spacing measurements and tight binding- or LDA + hybrid functional- calculations
- Rocking curve forms very sensitive measure of depth distributions near buried interfaces→future applications to other systems
- Bilayer data identify critical thickness for 2DEG formation

CSF and S. Nemšák,, J. Electron Spect. , 195, 409–422 (2014);
S. Nemšák, et al., Appl. Phys. Lett. 107 (23), 231602, 2015;
http://arxiv.org/abs/1508.01832

Soft → hard x-rays and standing waves: a few example studies

Fe/MgO-tunnel junction

Depth-resolved composition, chemical states, magnetization

$SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$-tunnel junction

Depth-resolved composition, dielectric properties, bonding, k-resolved electronic structure

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Depth-resolved composition, charge states, k-resolved electronic structure

Fe_2O_3 reacting with NaOH, CsOH, and H_2O

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$BiFeO_3/(Ca,Ce)MnO_3$ interface (Ferroelectric/Mott insulator)

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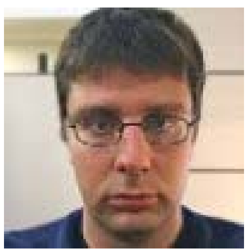
Standing wave photoemission from a liquid-like layer: CsOH and NaOH on Fe_2O_3

Slavo

S. Nemšák, A. Shavorskiy, O. Karslioglu, I. Zegkinoglou, A. Rattanachata, C.S. Conlon, A. Keqi, P.K. Greene, E.C. Burks, K. Liu, F. Salmassi, E.M. Gullikson, S.-H. Yang, K. Liu, H. Bluhm, C.S.F., Nature Comm. 5, 5441 (2014).



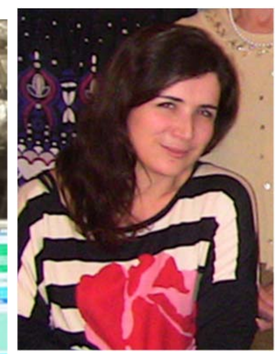
Andrey

Osman

Ioannis

Aru

Catherine



Armela

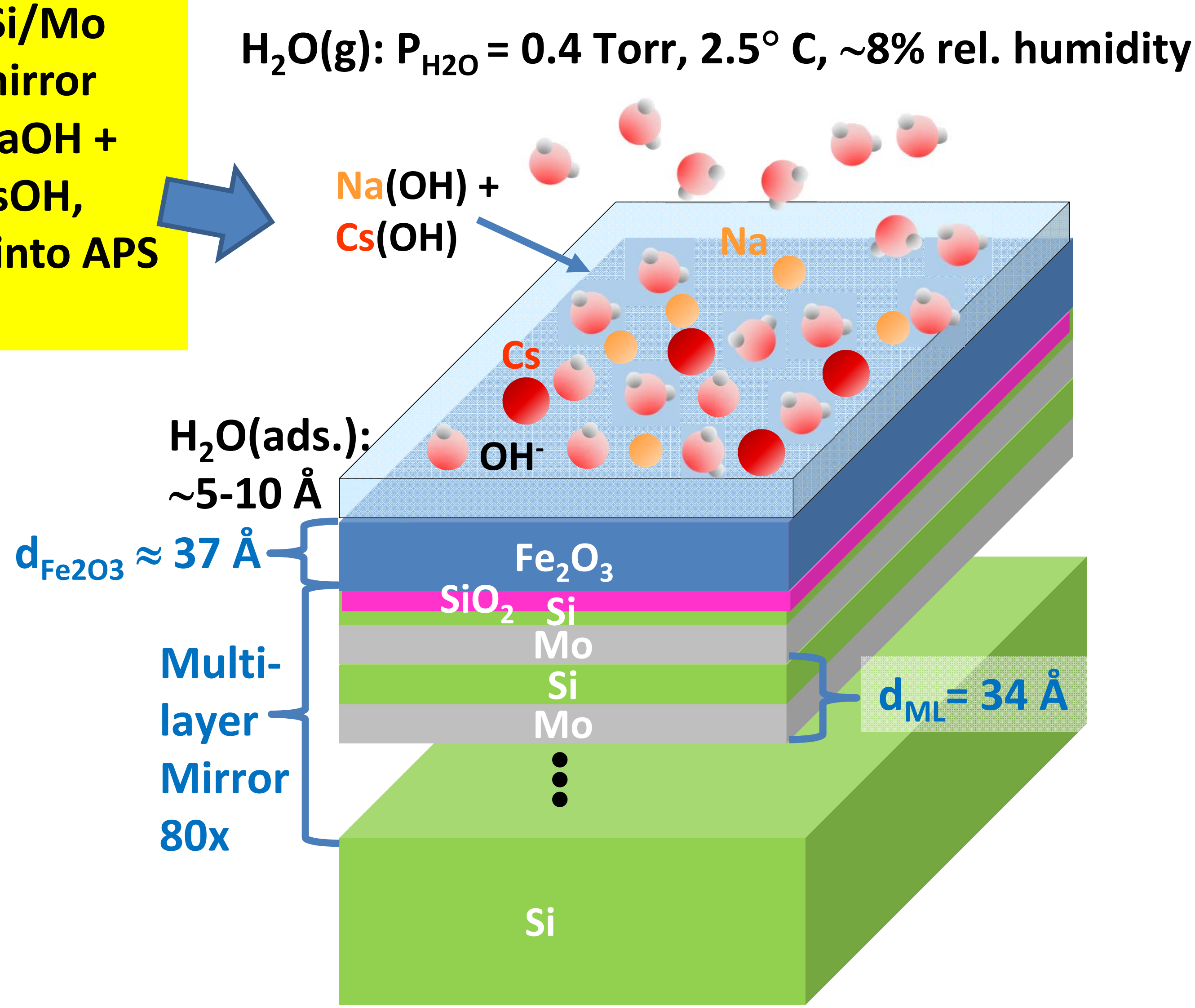
Hendrik

+Samples: Liu Group UCD

+Mirrors: CXRO LBNL

Standing-wave photoemission at the solid-liquid interface: some first experiments at ambient pressure

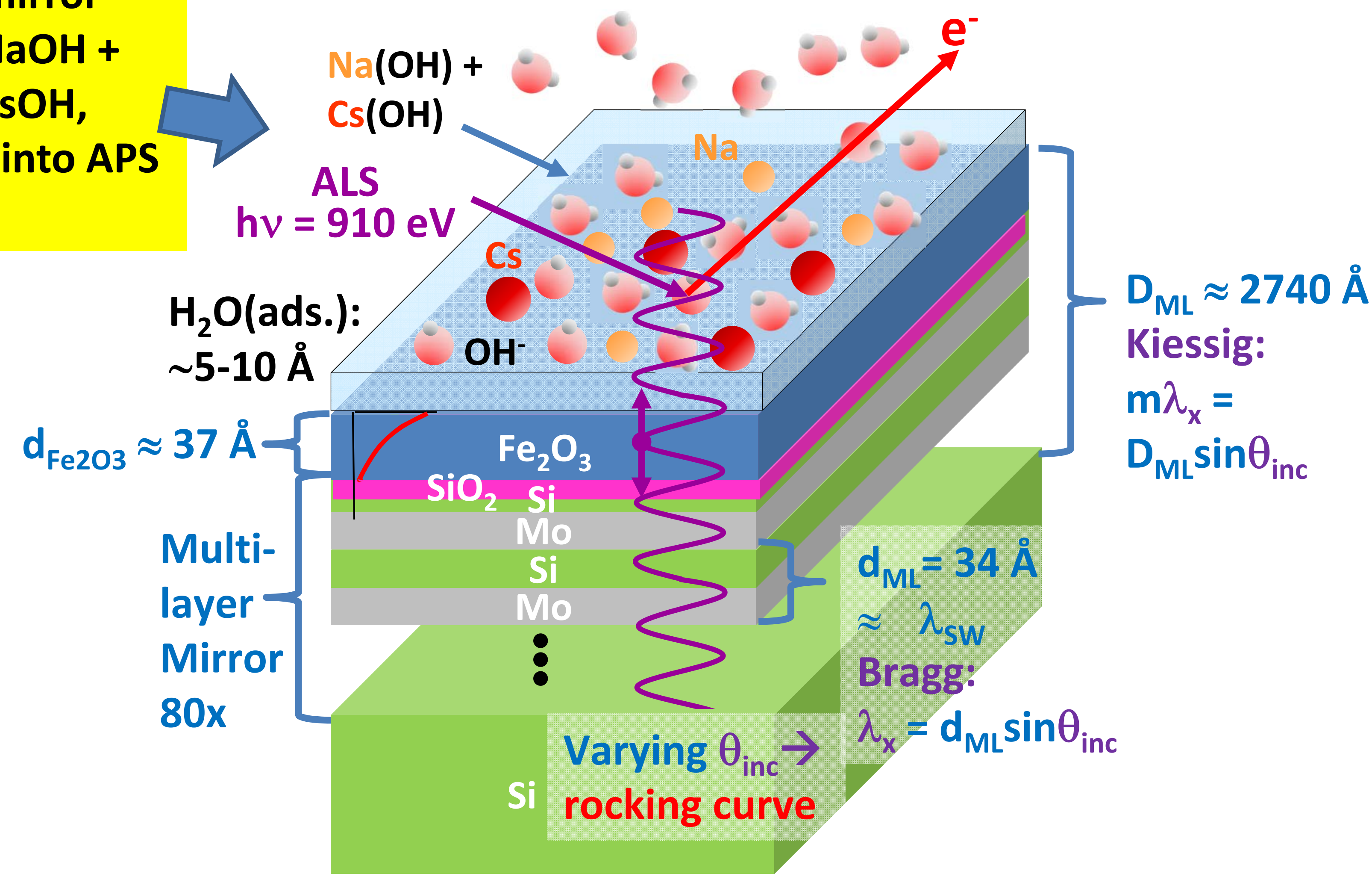
- Fe_2O_3 on Si/Mo multilayer mirror
- ~0.01M NaOH + ~0.01M CsOH, dried in air, into APS chamber



Standing-wave photoemission at the solid-liquid interface: some first experiments at ambient pressure

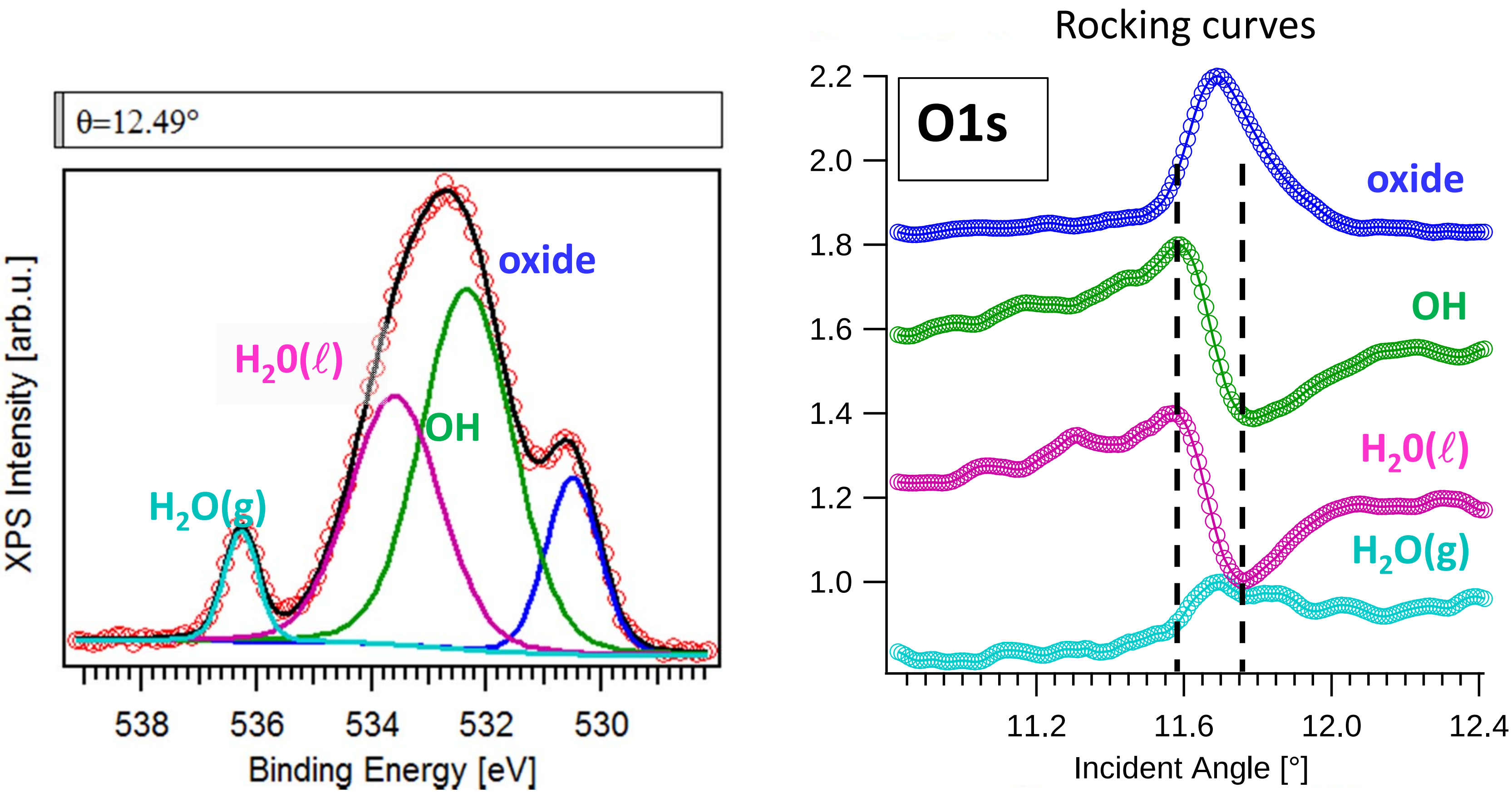
- Fe_2O_3 on Si/Mo multilayer mirror
- ~0.01M NaOH + ~0.01M CsOH, dried in air, into APS chamber

$H_2O(g)$: P_{H2O} = 0.4 Torr, 2.5° C, ~8% rel. humidity



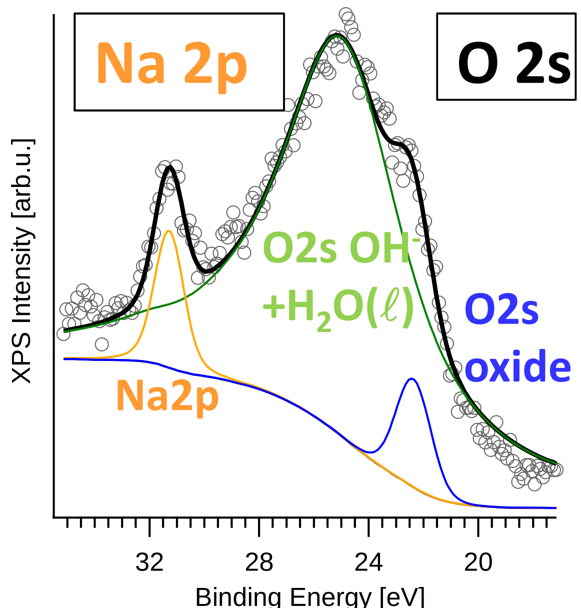
ALS BL 11.0.2

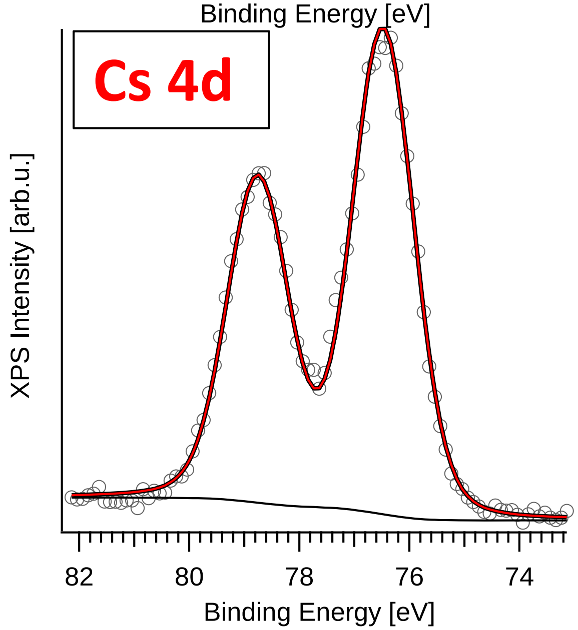
Rocking curves from the O 1s spectrum

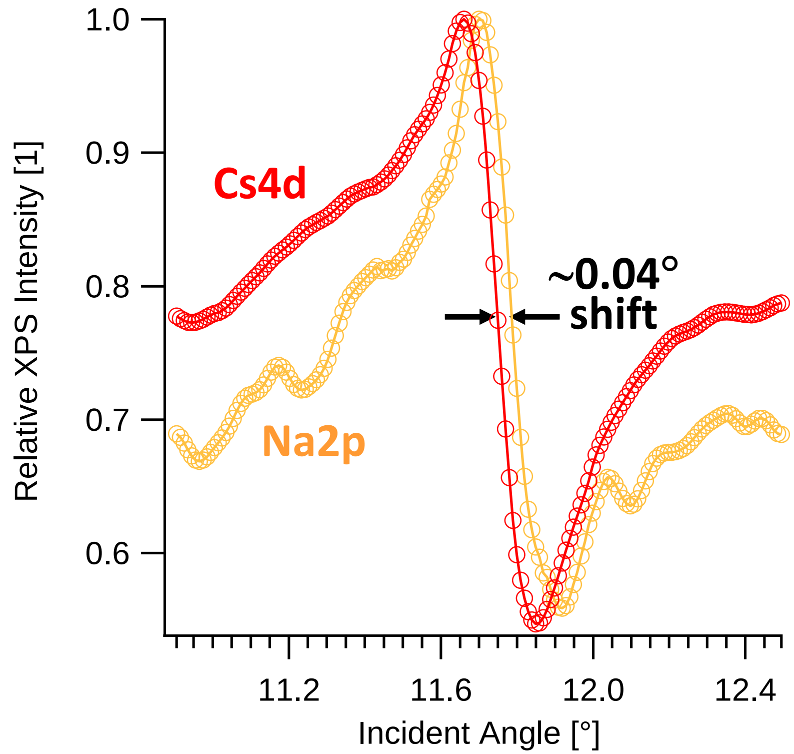


→ **Clearly four components in O 1s from rocking curve data**

Rocking curves for Na$^+$ and Cs+

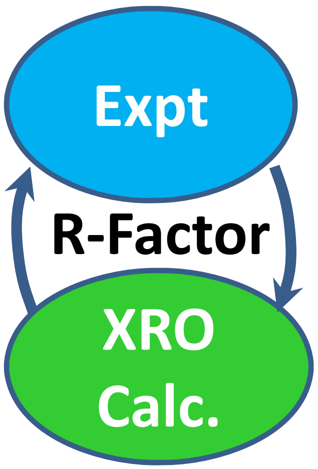


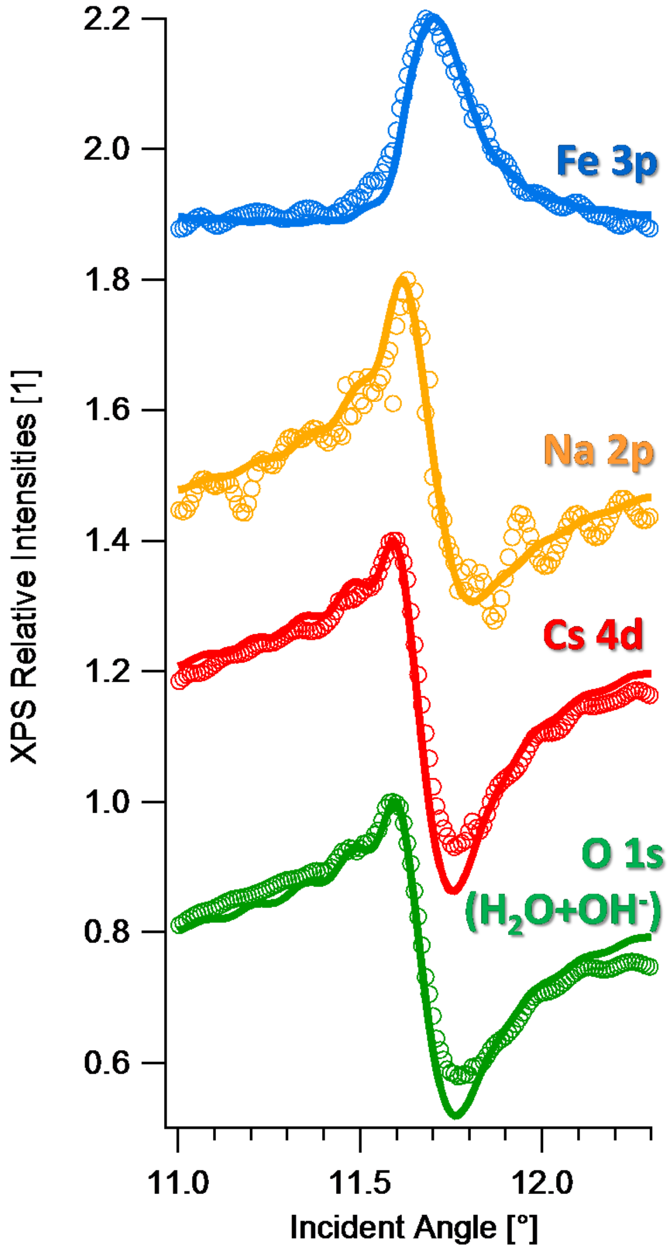


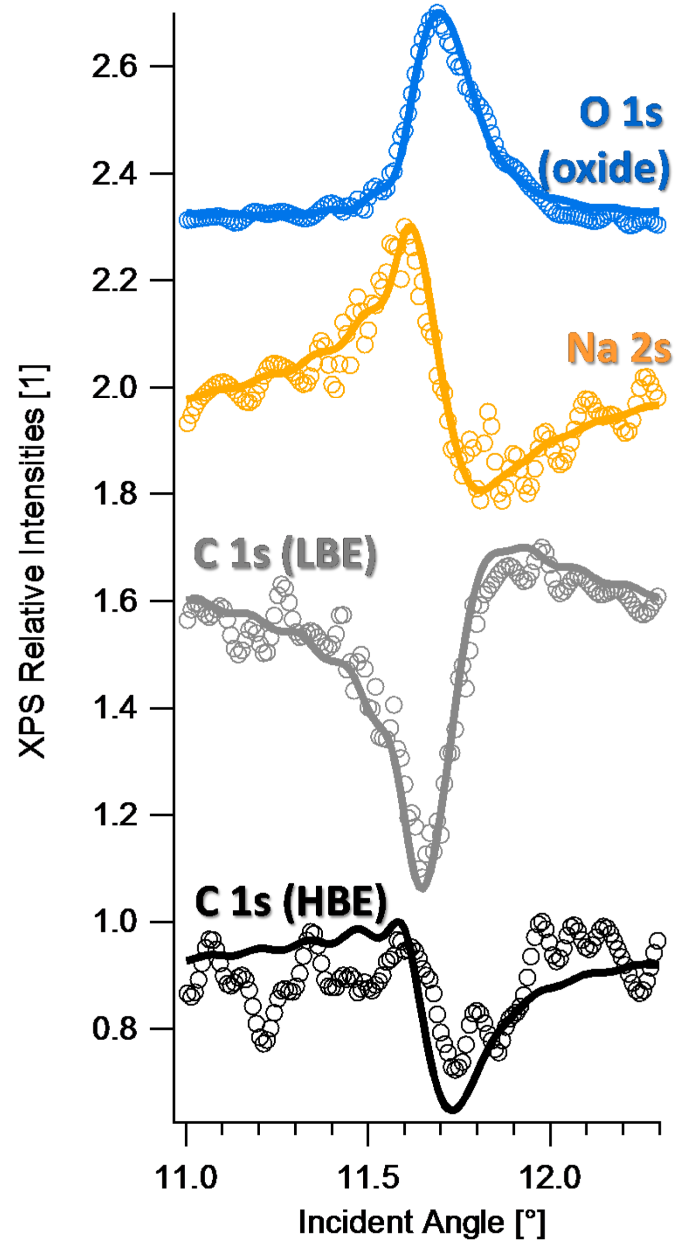


→ **Clear differences in position and wings of Cs and Na, indicating different depth distributions**

Final structure optimization after fitting x-ray optical calculations to rocking curves

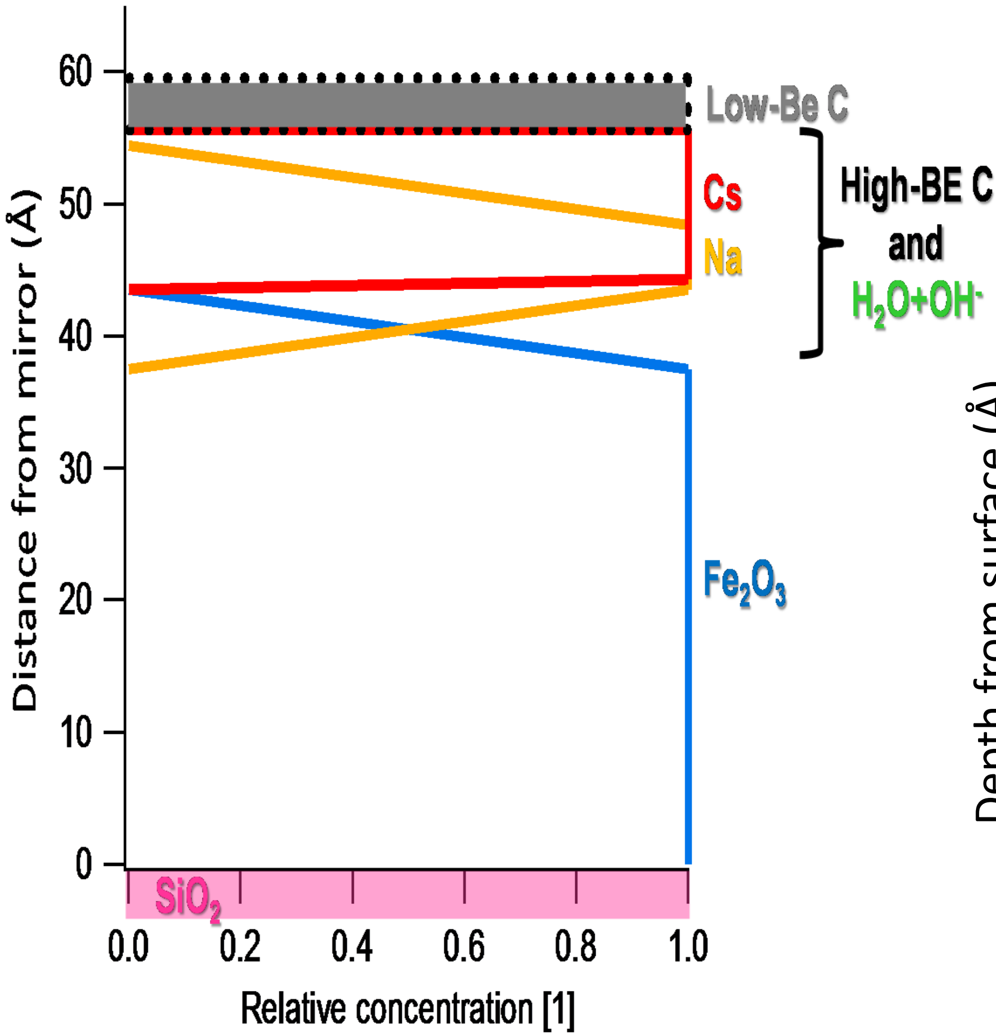


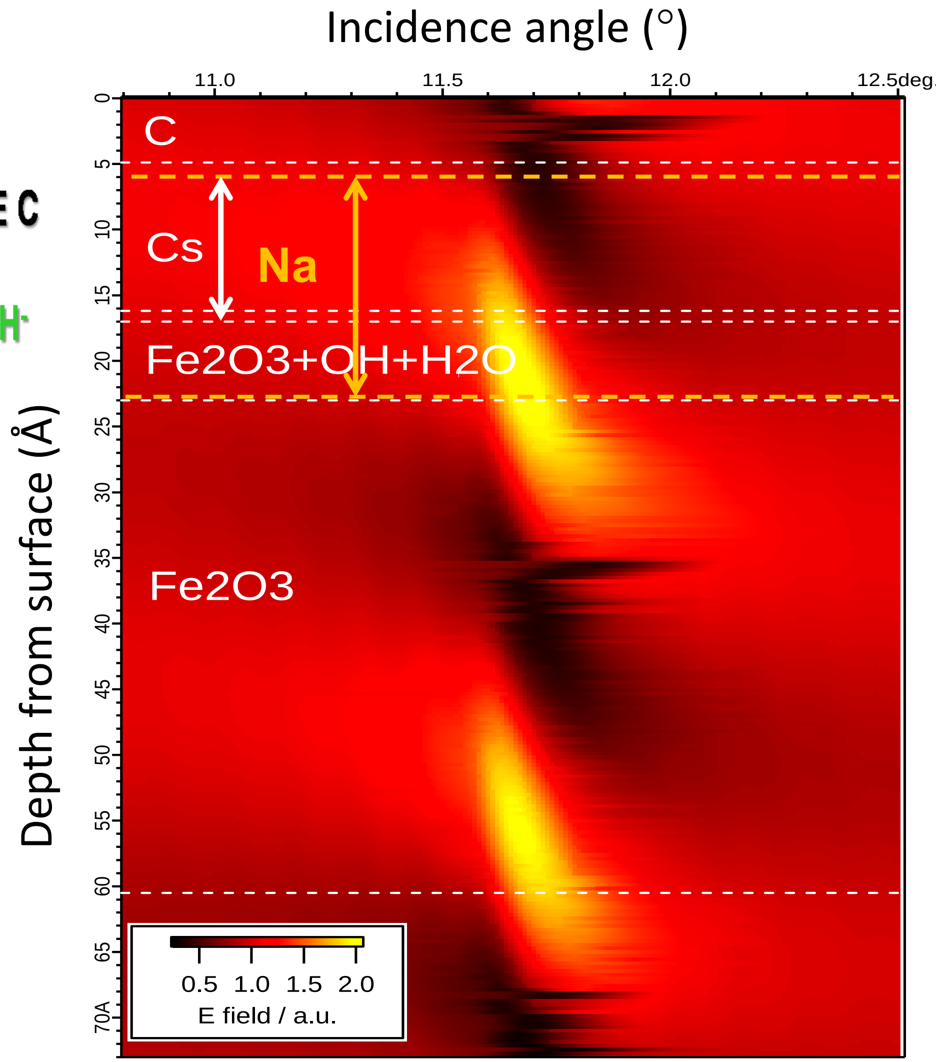




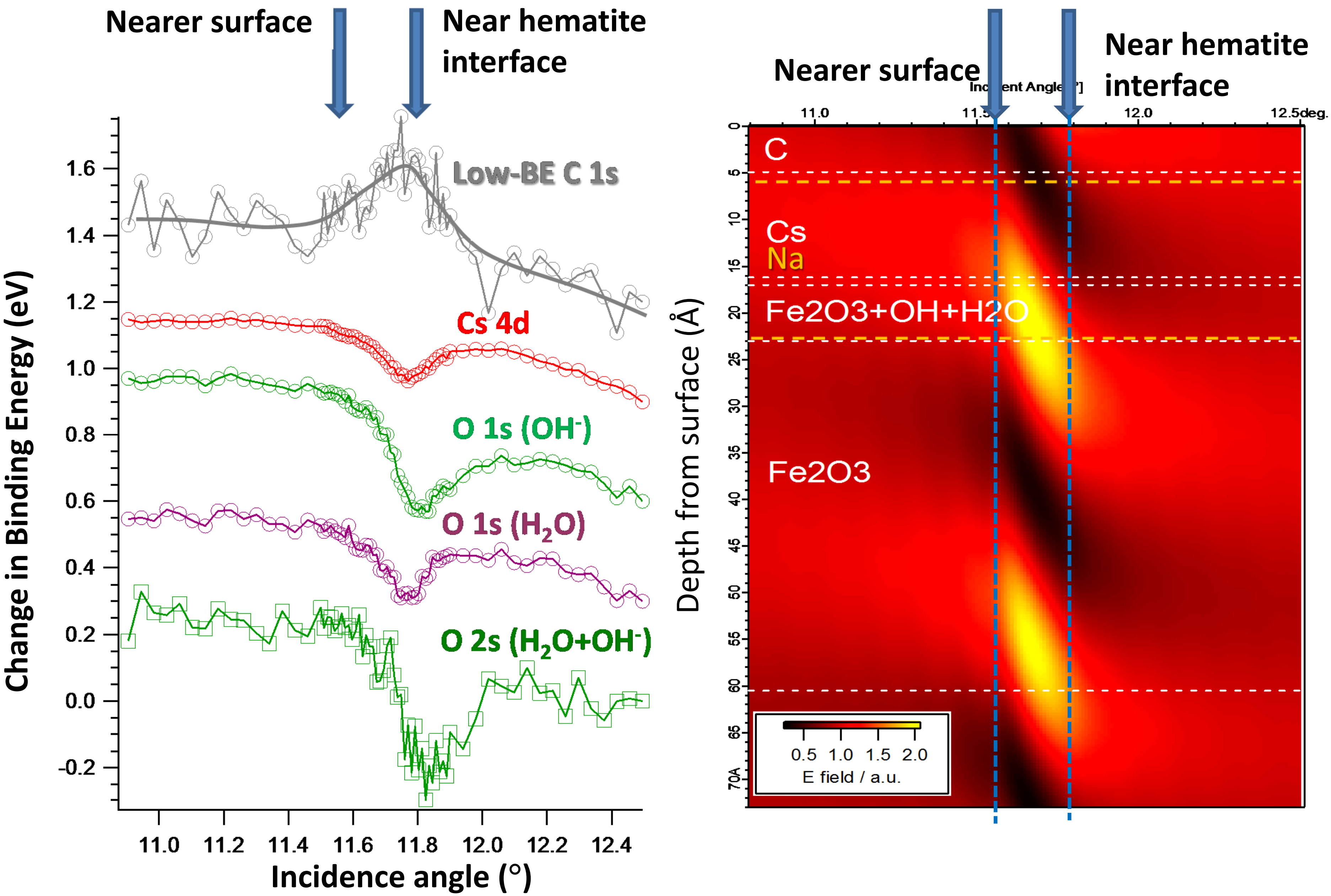
Nemšák

Final structure and the standing wave





Depth-dependent binding energies and the standing wave



Conclusions: Standing Wave Ambient Pressure Photoemission (SWAPPS) of NaOH + CsOH + H_2O on Fe_2O_3

From standing-wave rocking curves of all elements present:

- Fe_2O_3 surface--effective roughness of ~6 Å, agrees with AFM
- Na^+: average distance ~5.5 Å above Fe_2O_3, total distribution over ~11 Å
- Cs^+: larger average distance of ~9.5 Å above Fe_2O_3, total distribution over ~12 Å→ Cs^+ and Na^+ separated by ~ 5 Å.
- Low-binding-energy C: very thin ~5 Å layer on the surface of the sample →hydrocarbons?
- High-binding-energy C: spread over the entire depth range of the "wet" layer, H_2O+CO_2 → carboxylic or bicarbonate?
- OH^- + H_2O: Very nearly the same depth distribution
- Quantitative analysis for atomic concentrations possible
- Depth-dependent binding energies → depth dependent chemistry and potentials
- Provided that the sample can be grown on a multilayer mirror, SWAPPS a powerful new technique for looking at solid/solid and solid/liquid interaces, with resolution ~±2 Å

S. Nemšák, et al., Nature Comm. 5, 5441 (2014)

Soft → hard x-rays and standing waves: a few example studies

Fe/MgO-tunnel junction

Depth-resolved composition, chemical states, magnetization

$SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$-tunnel junction

Depth-resolved composition, dielectric properties, bonding, k-resolved electronic structure

$SrTiO_3/GdTiO_3$-2D electron gas

Depth-resolved composition, charge states, k-resolved electronic structure

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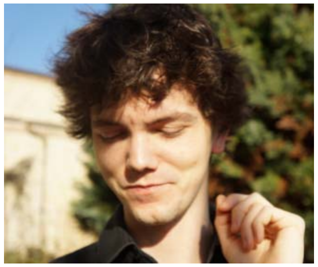
$BiFeO_3/(Ca,Ce)MnO_3$ interface (Ferroelectric/Mott insulator)

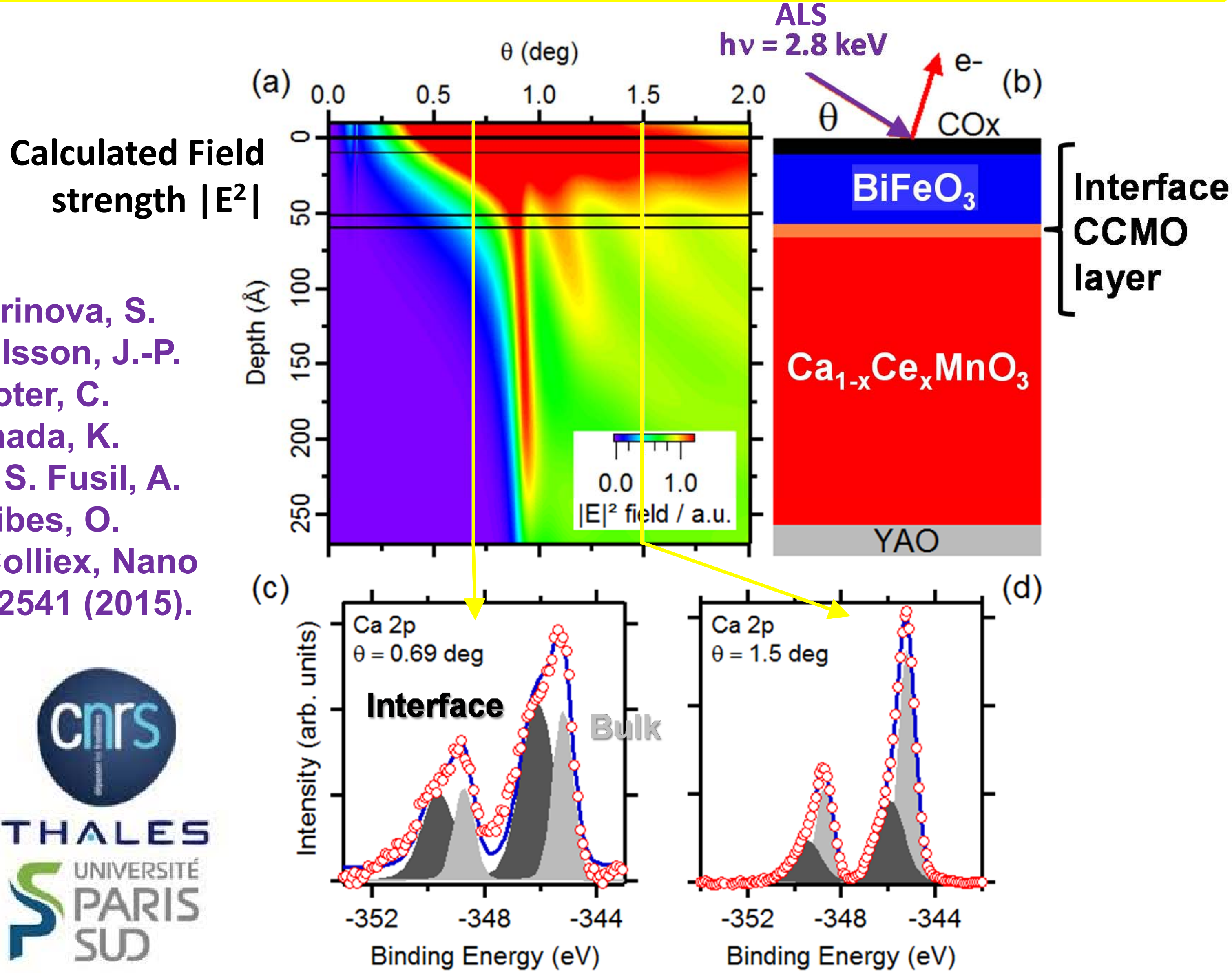
Depth-resolved electronic structure from near-total-reflection (NTR) angle scans

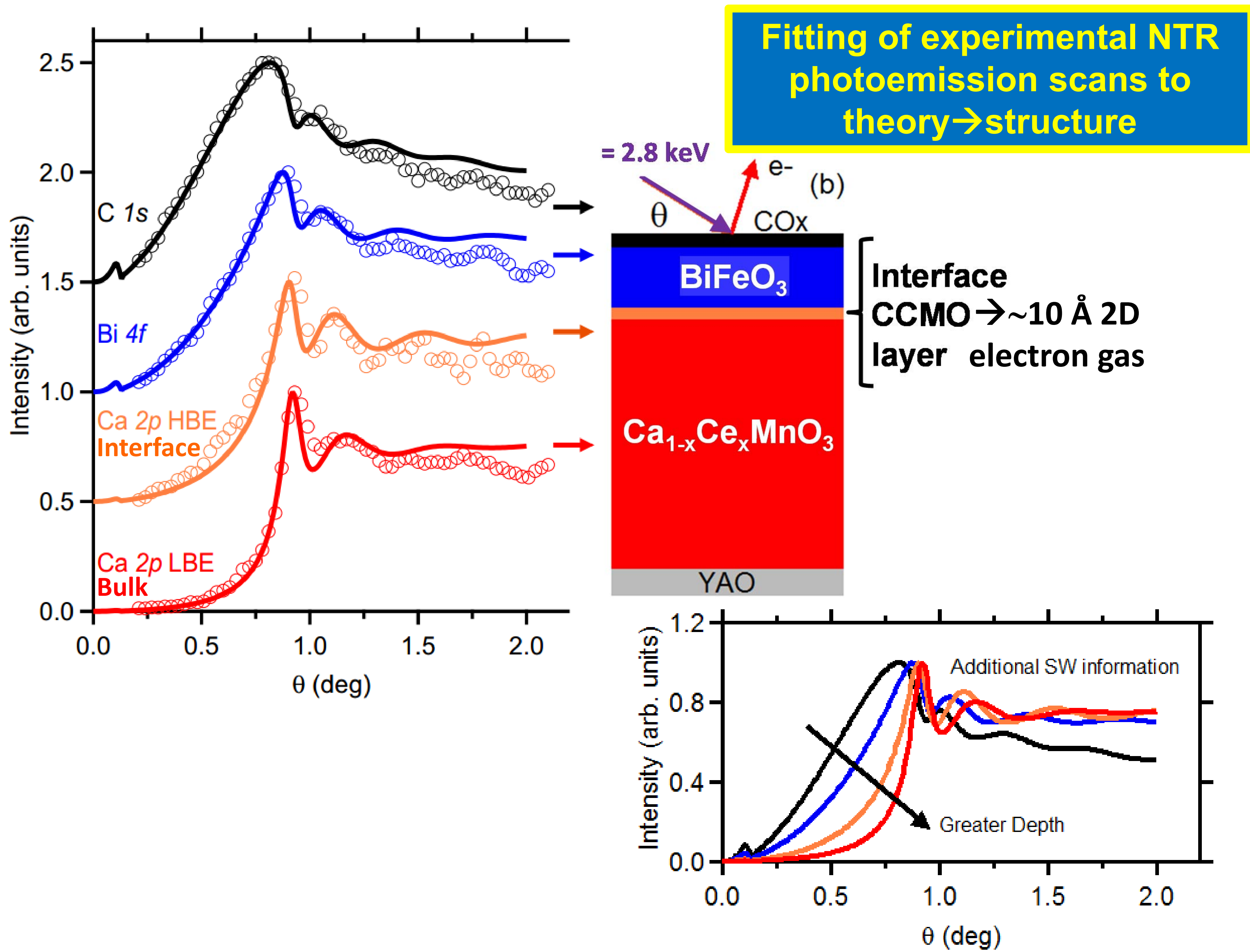
You don't need a multilayer!: Depth-resolved electronic structure at the $BiFeO_3$/(Ca,Ce)MnO_3 interface (Ferroelectric/Mott insulator) from near-total-reflection (NTR) angle scans



J. E. Rault, M. Marinova, S. Nemšák, G. K. Palsson, J.-P. Rueff, CSF, A. Gloter, C. Carrétéro, H. Yamada, K. March, V. Garcia, S. Fusil, A. Barthélémy, M. Bibes, O. Stéphan and C. Colliex, Nano Letters 15, 2533−2541 (2015).

The Advanced Light Source




Fitting of experimental NTR photoemission scans to theory→structure
Intensity (arb. units)
2.5
2.0
1.5
1.0
0.5
0.0
C 1s
Bi 4f
Ca 2p HBE
Interface
Ca 2p LBE
Bulk
0.0
0.5
1.0
1.5
2.0
θ (deg)
= 2.8 keV
e-
(b)
θ
COx
BiFeO3
Ca1-xCexMnO3
YAO
Interface
CCMO→~10 Å 2D
layer electron gas
Intensity (arb. units)
1.2
0.8
0.4
0.0
Additional SW information
Greater Depth
0.0
0.5
1.0
1.5
2.0
θ (deg)

Conclusions: Overall

- Combining soft and hard x-ray photoemission, with standing-wave excitation and resonant effects, is a powerful new suite of techniques for studying buried layers and interfaces, including solid/gas and solid/liquid at ambient pressures, and core-shell nanoclusters
- Future possibilities include:

  -Using hard x-rays for deeper interfaces and higher ambient pressures

  -Identifying particular angles/photon energies for different SW positions and doing time-dependent studies

  -For few-layer samples, or those which cannot be grown on a suitable mirror, going into total reflection, where standing waves are again produced

  -Varying polarization to select different orbital contributions, magnetism (via PMCD and XMCD)

  [-Doing the measurement in a photoelectron microscope (scanning photon energy) provides lateral resolution over devices (Gray, Kronast, et al., APL 97,062503 (2010))]