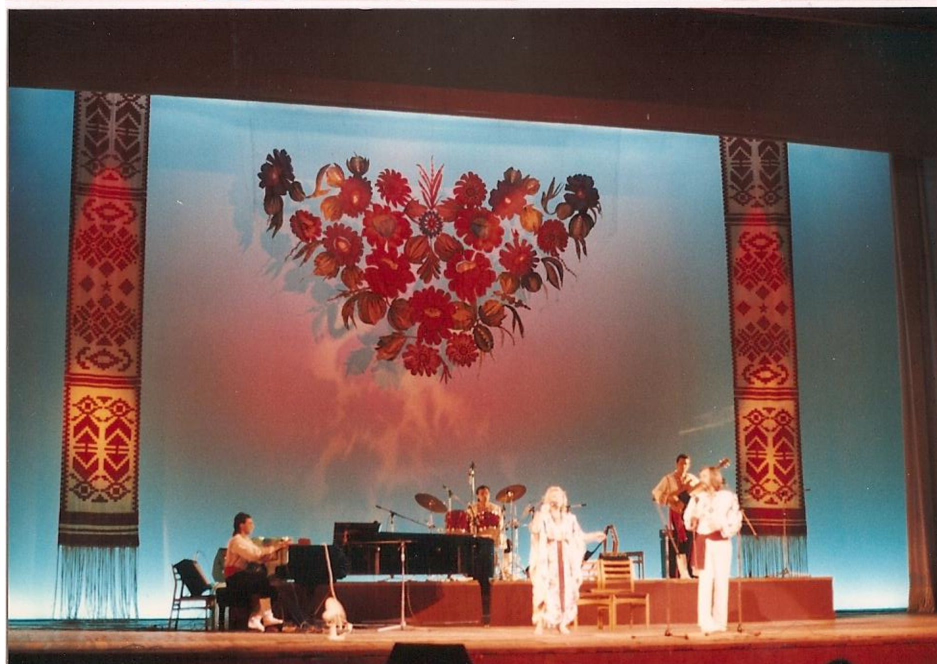
Kiev
1988



Extreme Photoemission: Soft and Hard X-Ray Photoemission and ARPES with Standing-Wave Excitation

Informal group meeting to discuss new results

Gruppo

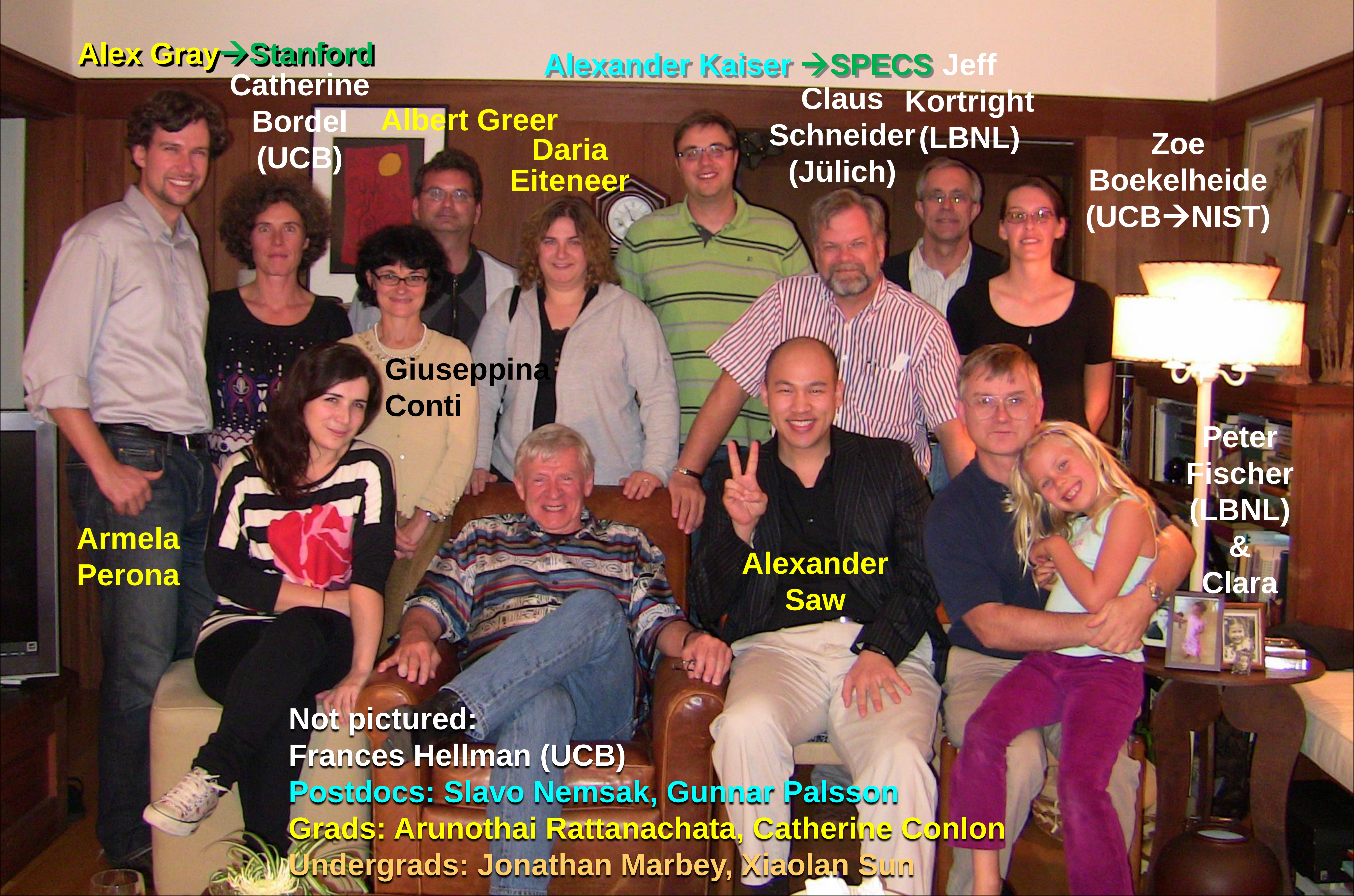
Extreme Photoemission: Soft and Hard X-Ray Photoemission and ARPES with Standing-Wave Excitation

Chuck Fadley
Dept. of Physics, UC Davis
and
Materials Sciences Division
Lawrence Berkeley National Laboratory

Supported by:
DOE: LBNL Materials Sciences Division
"Nanoscale Magnetic Materials"
ARO-Multi-University Research Initiative:
"Emergent Phenomena at Mott Oxide Interfaces"
Peter Grünberg Institute, PGI 9, Jülich Research Center
Humboldt Foundation, Germany
Soleil Synchtron-APTCOM Project

V. V. Nemoshkalenko Memorial Conference and Workshop

Group Members and Some Close Collaborators



Other Institutions and Collaborators

The Advanced Light Source

Julich Research Center

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

A. Gray[1,2], A. Kaiser[1,2,&], G. Conti[1,2], C. Papp[1,2,*], B. Balke[1,2,+], S. Ueda[3,4], Y. Yamashita[3,4], K. Kobayashi[3,4], M. Gorgoi[5], S.-H. Yang[6], L. Plucinski[7], S. Döring[8], U. Berges[8], M. Huijben[9,10], D. Buergler[7], F. Hellman[2,11], E. Rotenberg[12], A. Bostwick[12], J. Minar[13], J. Braun[13], H. Ebert[13], P. Krüger[14], J. Fujii[15], G. Panaccione[15], C. Caspers[7], M. Mueller[7], B.C. Sell[1,2,#], M. W. West[2], M. Press[2], F. Salmassi[2], J.B. Kortright[2], E. Gullikson[2], S.S.P. Parkin[6], A. Gloskovskii[16], W. Drube[16], F. Kronast[5], C. Westphal[8], V. Strocov[18], M. Kobayashi[18], J.-P. Rueff[19], C.M. Schneider[7], R. Ramesh[2,9,11], J. Son[17], P. Moetakef[17], S. Stemmer[17], A. Janotti[17], C. Van der Welle[17], R. Pentcheva[20]

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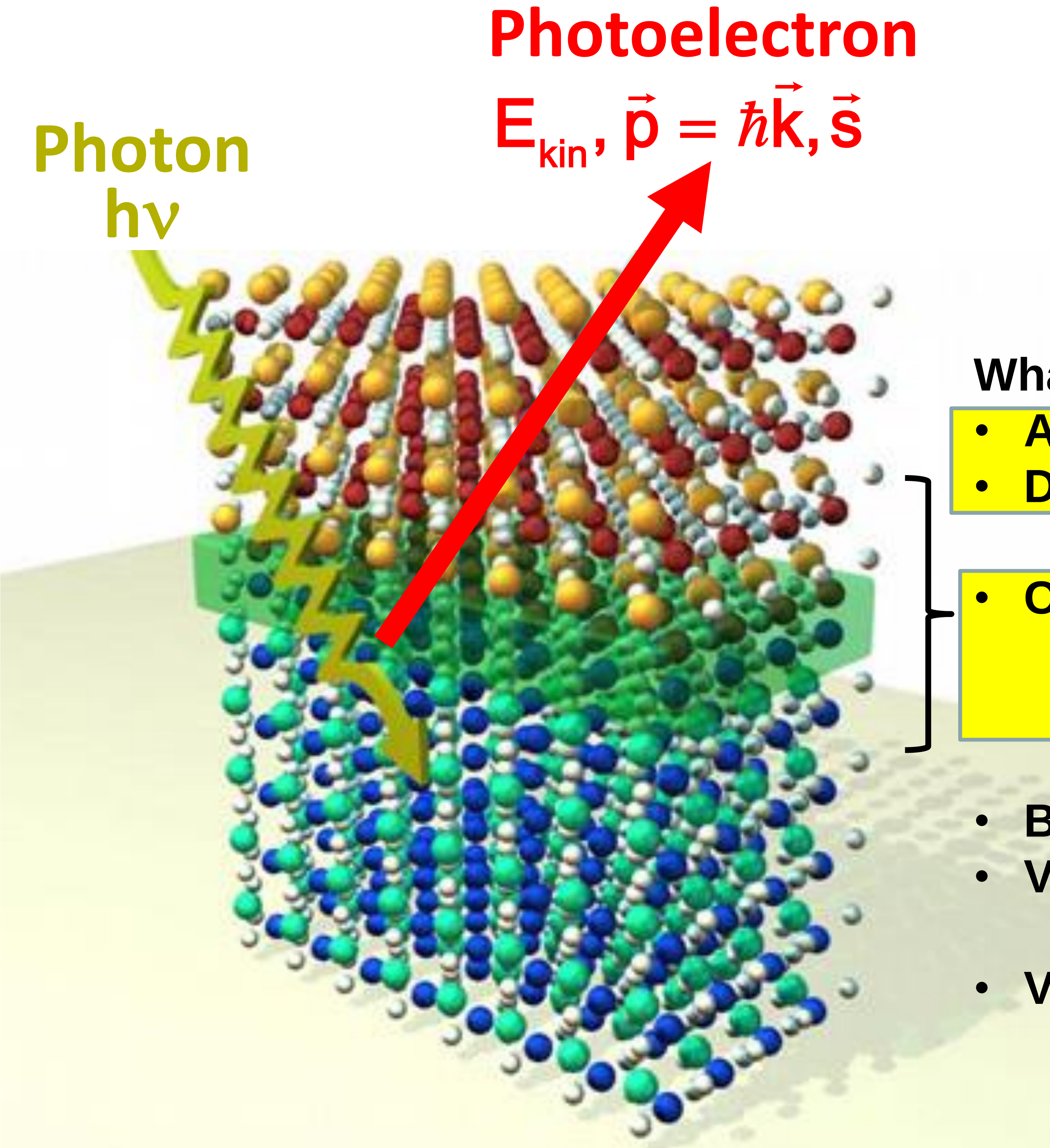
[1]Physics, UC Davis; [2]Mat. Sci. Div., LBNL; [3]SPring-8; [4]NIMS; [5]HZB-BESSY Berlin; [6]IBM Almaden; [7]Research Center Jülich; [8]Physics, Tech. Univ. Dortmund; Physics; [9]Mat. Sci., UC Berkeley; [10]Univ. of Twente; [11] Physics, UC Berkeley; [12]ALS, LBNL; [13]Phys. Chem., Univ. Munich; [14]Univ. Bourgogne, Dijon; [15]TASC, Trieste; [16]Hasylab, Hamburg; [17]UC Santa Barbara; [18]SLS: [19]Soleil; [20]Earth and Enviro. Science, Univ. Munich; Pres. address: [&]SPECS; [*]Univ. Erlangen; [+]Univ. Mainz; [#]Wright-Patterson AFB

Photoemission from complex bulk materials, buried layers, interfaces



TEM+EELS

What do we want to know?

- **Atomic structure, lattice distortions**
- **Depth profiles of composition and optical properties**
- **Core-levels→element-specific binding energies, charge states electronic configurations, magnetic moments/magnetization**
- **Band offsets**
- **Valence-band densities of states bandgaps, behavior near E_F**
- **Valence-band dispersions, via depth-resolved ARPES**

Photoemission in complex heterostructures and materials

Core photoemission→XPS, X-ray photoelectron diffraction-XPD,…
Valence photoemission→
Higher energy a/o temperature→Densities of states-DOSs
Lower energy a/o temperature→Band mapping, Angle-resolved photoemission-ARPES
are very powerful techniques, but they:

- **are sometimes too strongly influenced by surface effects, if bulk or buried layer/interface properties are to be studied**

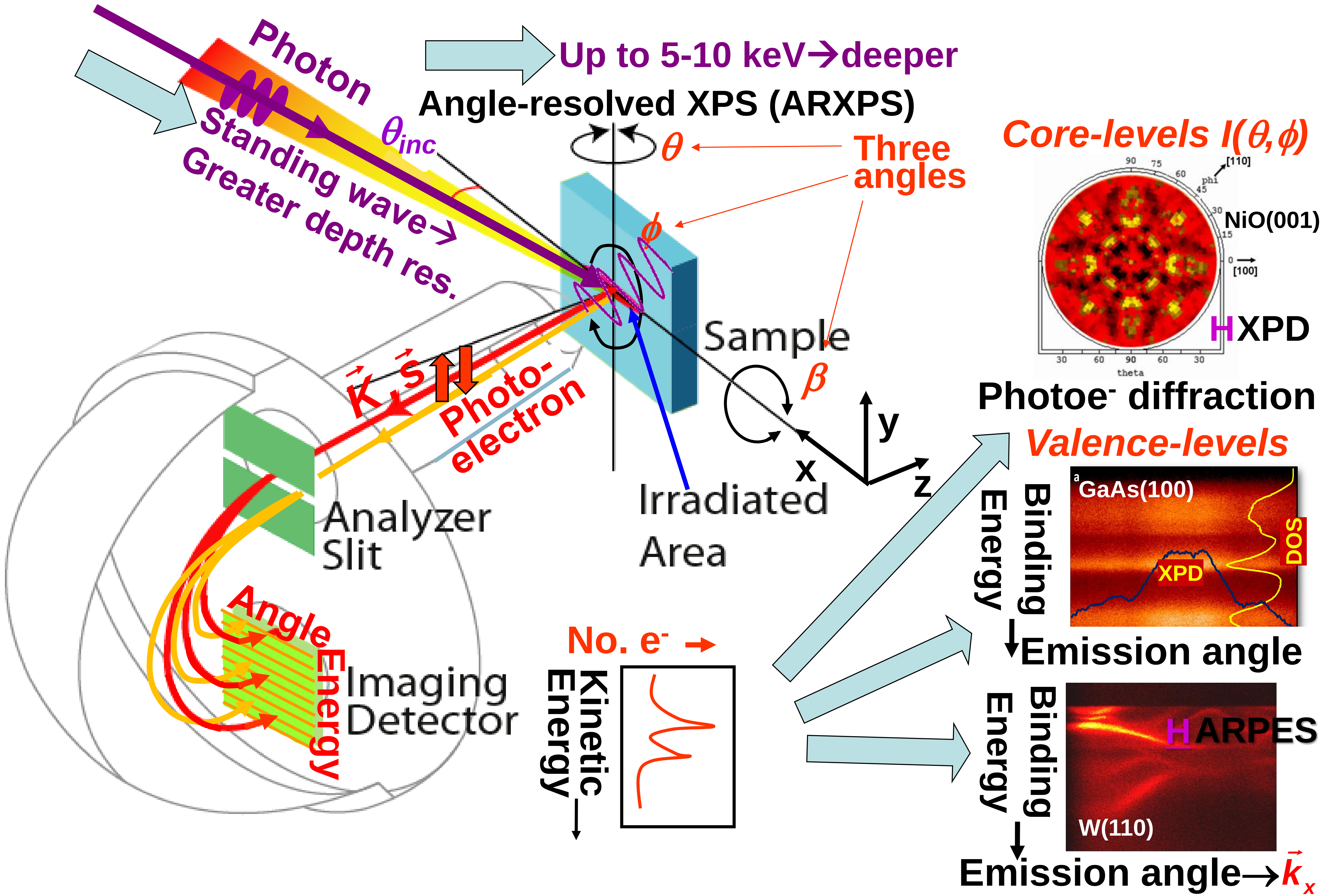
- **may not be able to selectively and <u>quantitatively</u> see bulk, buried-layer or interface properties**

Two ways to address these limitations:

- **use of <u>harder x-ray excitation</u> (HAXPES, HXPS) for deeper probing: core (HXPD) and valence DOSs or hard x-ray ARPES or "HARPES"**

- **use of <u>soft and hard</u> x-ray <u>standing waves</u> to selectively look below the surface, including ARPES**

X-ray photoemission: some key elements



Photoemission in complex heterostructures and materials

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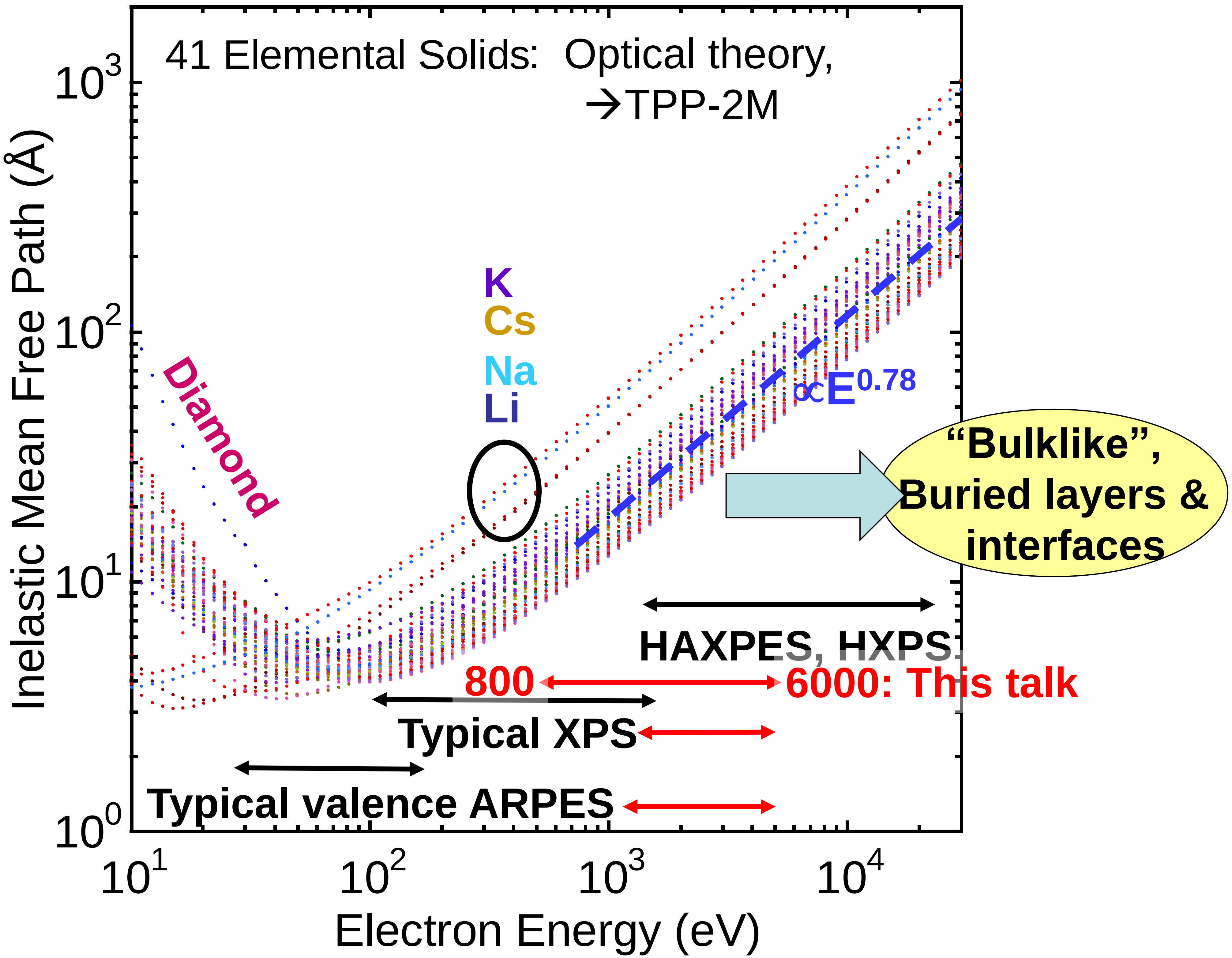
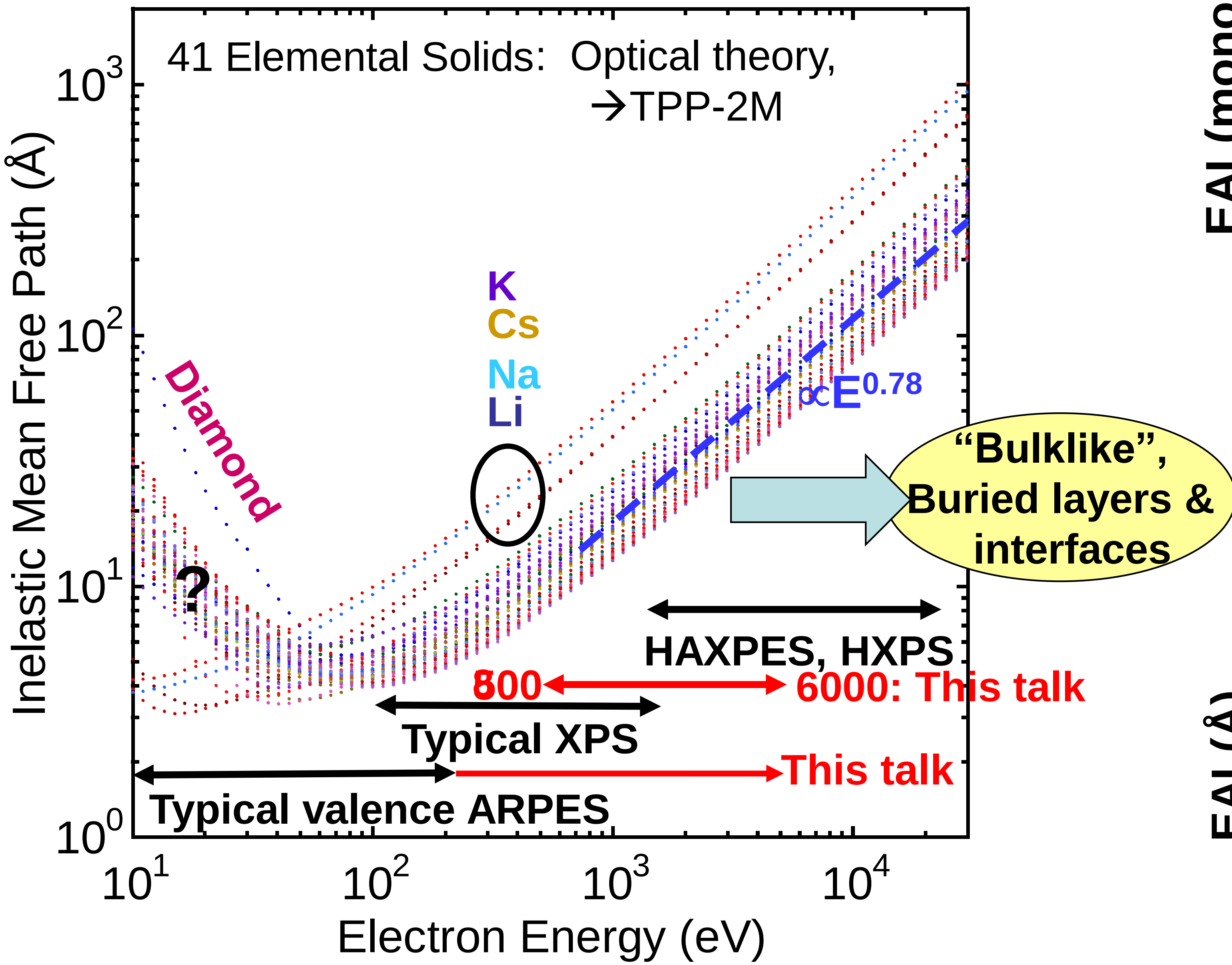
Why do we want to go to 5-10 keV in XPS?

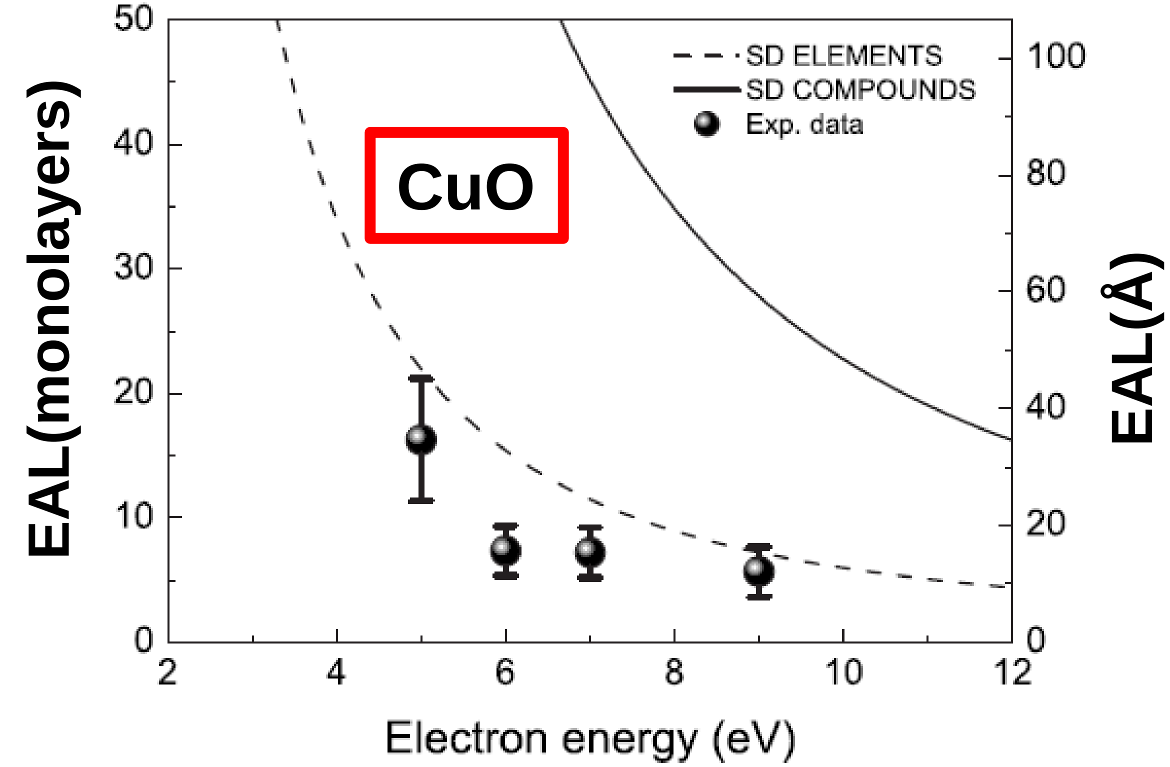


Tanuma, Powell, Penn, Surf. and Interf. Anal. 43, 689 (2011)

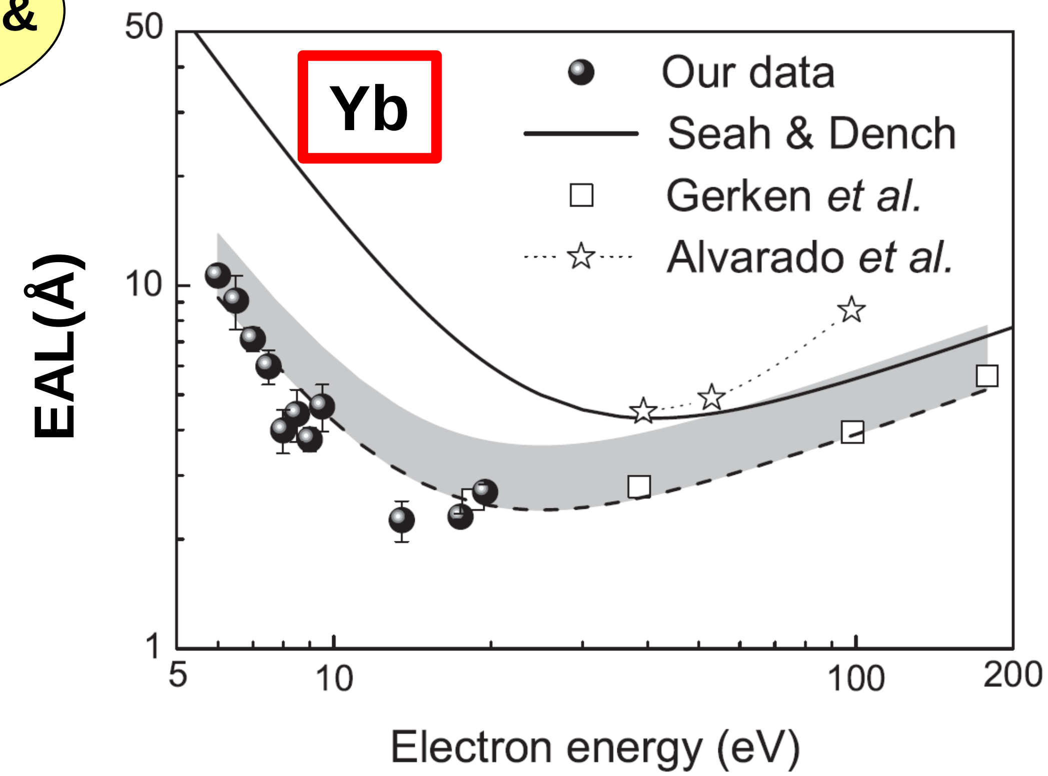
Why do we want to go to 5-10 keV in XPS?



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



Offi et al., PRB 77, 201101R (2008)



Offi et al., J. Phys.: Cond. Matt. 22 (2010) 305002

→The only certain way to obtain more bulk sensitivity

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

Past workshops:

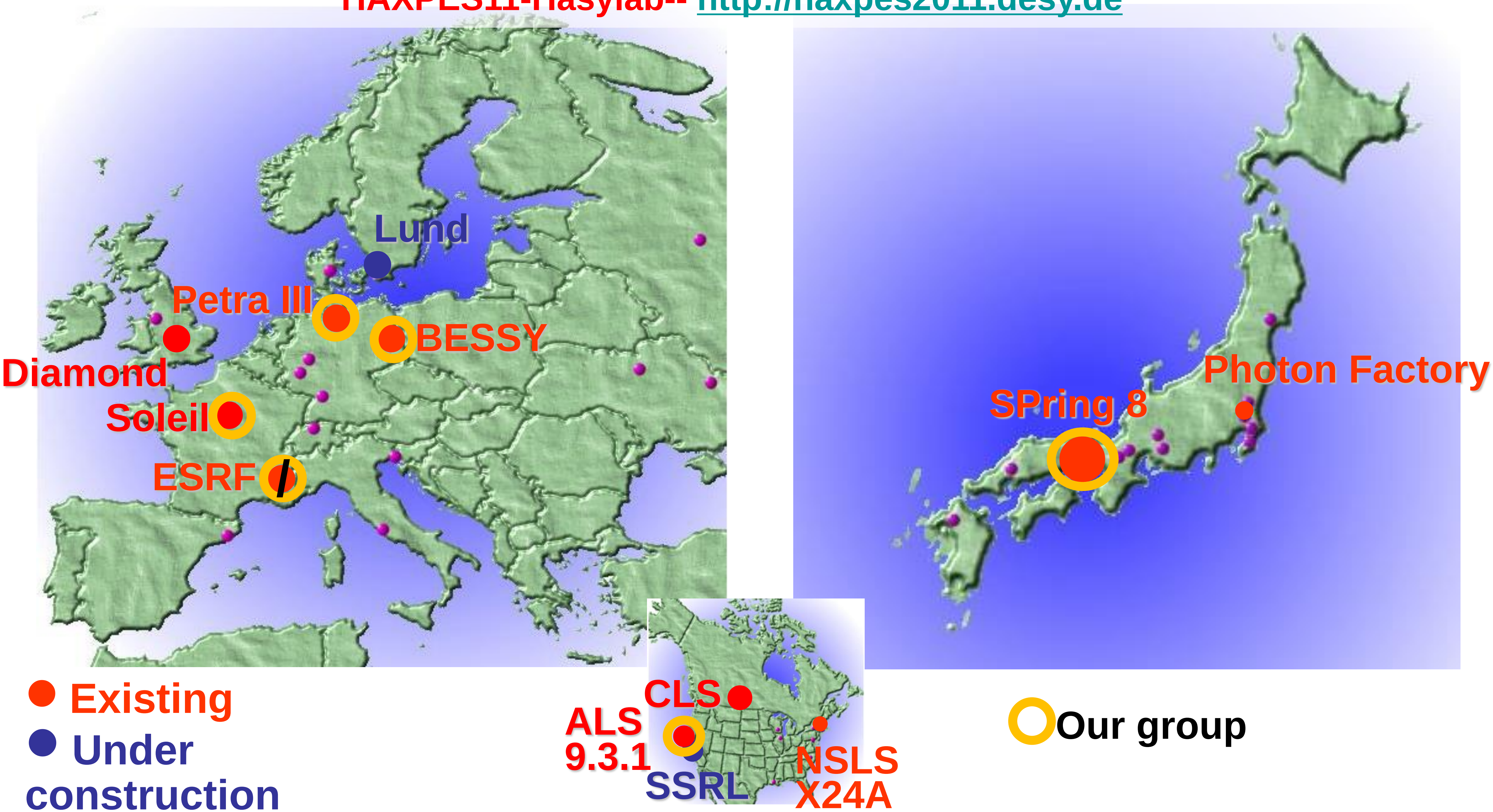
HAXPES03, ESRF--Nucl. Inst. and Meth. A, Volume 547, Issue 1, Pages 1-238 (2005)

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

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

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

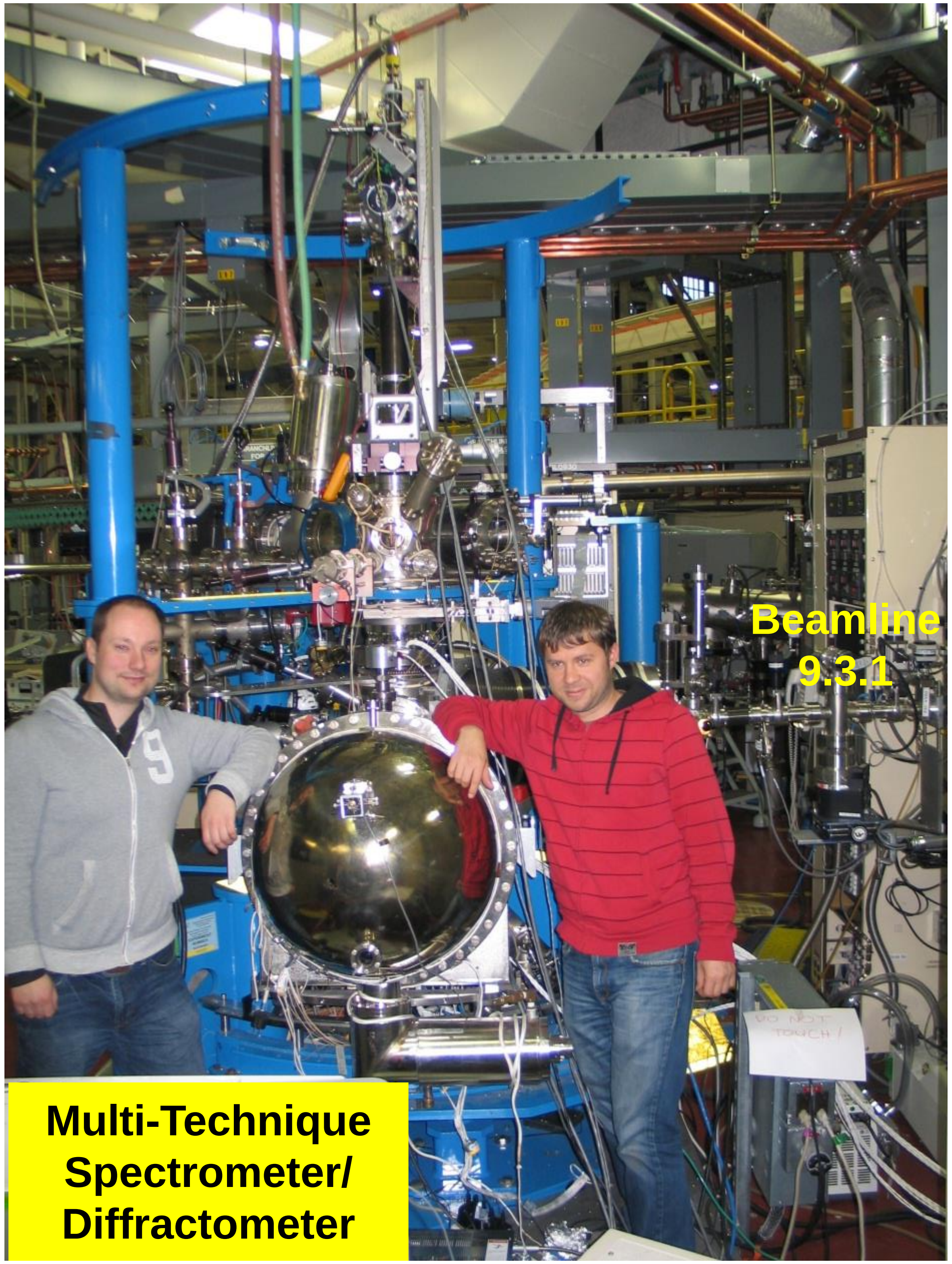
HAXPES11-Hasylab-- http://haxpes2011.desy.de



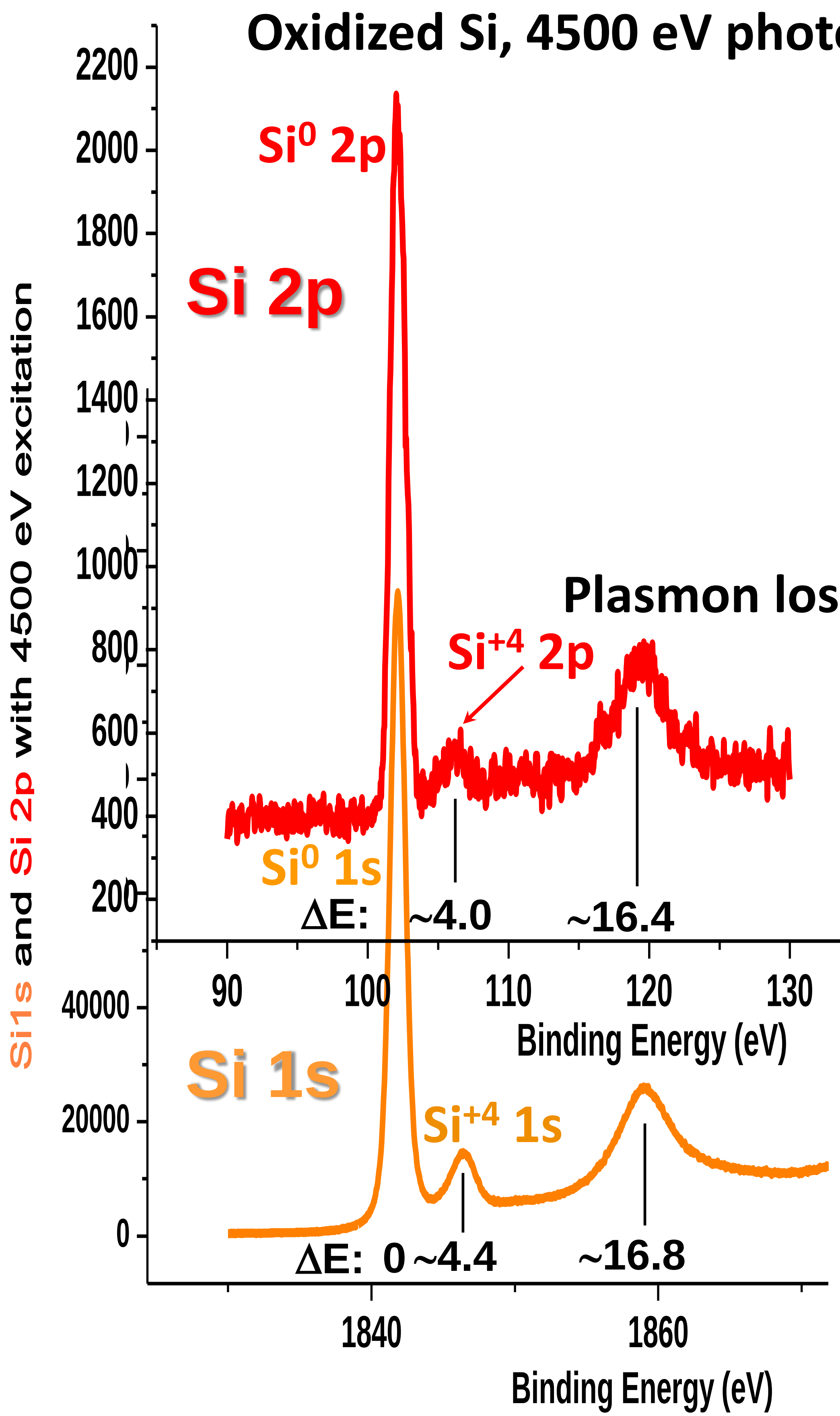
References to prior papers on hard x-ray photoemission systems at other facilities:

1. "X-Ray Photoelectron Spectroscopy and Diffraction in The Hard X-Ray Regime: Fundamental Considerations and Future Possibilities", C. S. Fadley, Nuclear Instruments and Methods A 547, 24-41 (2005), review in special issue edited by J. Zegenhagen and C. Kunz –overview.
2. "Bulk electronic properties of the bilayered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ from hard-x-ray photoemission", F. Offi, P. Torelli, M. Sacchi, P. Lacovig, A. Fondacaro, G. Paolicelli, S. Huotari, G. Monaco, C.S. Fadley, J.F. Mitchell, G. Stefani, and G. Panaccione, Phys. Rev. B 75, 014422 (2007) --ESRF.
3. "Temperature-dependent electronic structure of the colossal magnetoresistive manganite $La_{0.7}Sr_{0.3}MnO_3$ from hard x-ray photoemission", F. Offi, N. Mannella, T. Pardini, G. Panaccione, A. Fondacaro, P. Torelli, M.W. West, J.F. Mitchell, and C.S. Fadley, Phys. Rev. B 77, 174422 (2008) --ESRF.
4. "High energy photoelectron diffraction: model calculations and future possibilities", A. Winkelmann, J. Garcia de Abajo and C.S. Fadley, New J. Phys. 10, 113002 (2008) – theoretical study.
5. "Interface properties of magnetic tunnel junction $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ superlattices studied by standing-wave excited photoemission spectroscopy", 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, and C. S. Fadley, Phys. Rev. B 82, 205116 (2010) –SPring-8 and ALS.
6. "Band Gap and Electronic Structure of an Epitaxial, Semiconducting Cr0.80Al0.20 Thin Film", Z. Boekelheide, A. X. Gray, C. Papp, B. Balke, D. A. Stewart, S. Ueda, K. Kobayashi, F. Hellman, and C. S. Fadley, Phys. Rev. Letters 105, 236404 (2010).
7. "X-ray Photoelectron Spectroscopy : Progress and Perspectives", C.S. Fadley, invited review, Journal of Electron Spectroscopy and Related Phenomena 178–179, 2 (2010), 30 pp., 35 figs –review, with ESRF, BESSY, and SPring-8 results discussed.
8. "Hard x-ray photoemission using standing-wave excitation applied to the MgO/Fe interface", Sven Döring, Frank Schönbohm, Ulf Berges, Reinert Schreiber, Daniel E. Bürgler, Claus M. Schneider, Mihaela Gorgoi, Franz Schäfers, Christian Papp, Benjamin Balke, Charles S. Fadley, Carsten Westphal, Phys. Rev. B 83, 165444 (2011) --BESSY.
9. "Hard X-ray Photoemission Study of Near-Heusler Fe_xSi_{1-x} Alloys", A. X. Gray, J. Karel, J. Minar, C. Bordel, H. Ebert, J. Braun, S. Ueda, Y. Yamashita, L. Ouyang, D. J. Smith, K. Kobayashi, F. Hellman, and C. S. Fadley, Phys. Rev. B 83, 195112 (2011) –SPring-8.
10. "Insulating State of Ultrathin Epitaxial $LaNiO_3$ Thin Films Detected by Hard X-ray Photoemission", A. X. Gray, A. Janotti, J. Son, J. M. LeBeau, S. Ueda, Y. Yamashita, K. Kobayashi, A. M. Kaiser, C. G. Van de Walle, S. Stemmer, and C. S. Fadley, Phys. Rev. B, 84, 075104 (2011) --SPring-8.
11. "Probing bulk electronic structure with hard X-ray angle-resolved photoemission", A. X. Gray, C. Papp, S. Ueda, B. Balke, Y. Yamashita, L. Plucinski, J. Minár, J. Braun, E. R. Ylvisaker, C. M. Schneider, W. E. Pickett, H. Ebert, K. Kobayashi and C. S. Fadley, Nature Materials 10, 759 (2011); see also companion News and Views article: D. L. Feng, Nature Materials 10, 729-730 (2011) --SPring-8.
12. "Identification of different electron screening behavior between bulk and surface of (Ga,Mn)As as detected by soft and hard x-ray photoemission", J. Fujii, M. Sperl, S. Ueda, K. Kobayashi, Y. Yamashita, M. Kobata, P. Torelli, F. Borgatti, M. Utz, C.S. Fadley, A. Gray, G. Monaco, C.H. Back, G. van der Laan, and G. Panaccione, Phys. Rev. Letters 107, 187203 (2011) --SPring-8.
13. "Chemical Stability of the Magnetic Oxide EuO directly on Silicon observed by Hard X-ray Photoemission Spectroscopy", C. Caspers, M. Müller, A. X. Gray, A. M. Kaiser, A. Gloskovskii, C. S. Fadley, W. Drube, and C. M. Schneider, Phys. Rev. B 84, 205217 (2011) –Petra III
14. "Electronic structure of EuO spin filter tunnel contacts directly on silicon", C. Caspers, M. Müller, A. X. Gray, A. M. Kaiser, A. Gloskovskii, C. S. Fadley, W. Drube, and C. M. Schneider, Phys. Status Solidi, Rapid Research Letters, 5 , 441 (2011) –Petra III.
15. "Electronic Structure Changes across the Metamagnetic Transition in $Fe_{0.50}Rh_{0.50}$", A. X. Gray, D. W. Cooke, P. Krüger, C. Bordel, A. M. Kaiser, S. Ueda, Y. Yamashita, C.M. Schneider, K. Kobayashi, F. Hellman, and C. S. Fadley, Phys. Rev. Letters 108, 257208 (2012)–SPring-8.
16. "Non-destructive investigation of delta-doped La:$SrTiO_3$-layers by hard x-ray photoelectron spectroscopy", A. M. Kaiser, A. X. Gray, G. Conti, B. Jalan, A. Kajdos, A. Gloskovskii, S. Ueda, Y. Yamashita, K. Kobayashi, W. Drube, S. Stemmer, and C. S. Fadley, Applied Phys. Letters 100, 261603 (2012)--SPring-8 and Petra III.
17. "Observation of boron diffusion in an annealed Ta/CoFeB/MgO magnetic tunnel junction with standing-wave hard x-ray photoemission", A.A. Greer, A. X. Gray, S. Kanai, A. M. Kaiser, S. Ueda, Y. Yamashita, C. Bordel, G. Palsson, N. Maejima, S.-H. Yang, G. Conti, K. Kobayashi, S. Ikeda, F. Matsukura, H. Ohno, C. M. Schneider, J. B. Kortright, F. Hellman, and C. S. Fadley, Appl. Phys. Letters 101, 202402 (2012). –Spring-8
18. "Bulk Electronic Structure of the Dilute Near-Ferromagnetic Semiconductor $Ga_{1-x}Mn_xAs$ via Hard X-Ray Angle-Resolved Photoemission" A. X. Gray, J. Minar, S. Ueda, P. R. Stone, Y. Yamashita, J. Fujii, J. Braun, L. Plucinski, C. M. Schneider, G. Panaccione, H. Ebert, O. D. Dubon, K. Kobayashi, and C. S. Fadley, Nature Materials 11, 957 (2012).--SPring-8
19. "Nondestructive characterization of a TiN metal gate: chemical and structural properties by means of standing-wave hard x-ray photoemission spectroscopy", C. Papp, G. Conti, B. Balke, S. Ueda, Y. Yamashita, H. Yoshikawa, S.L. He, C. Sakai, Y.S. Uritsky, K. Kobayashi, J.B. Kortright, C.S. Fadley, Journal of Applied Physics 112, 114501 (2012).
20. "Looking Deeper: Angle-Resolved Photoemission with Soft and Hard X-rays", Charles S. Fadley, Synchrotron Radiation News 25, 26 (2012)-Spring-8
21. "Hard X-ray Photoemission with Angular Resolution and Standing-Wave Excitation", C. S. Fadley, invited review, Journal of Electron Spectroscopy, to appear—BESSY, SPring-8 and Petra III

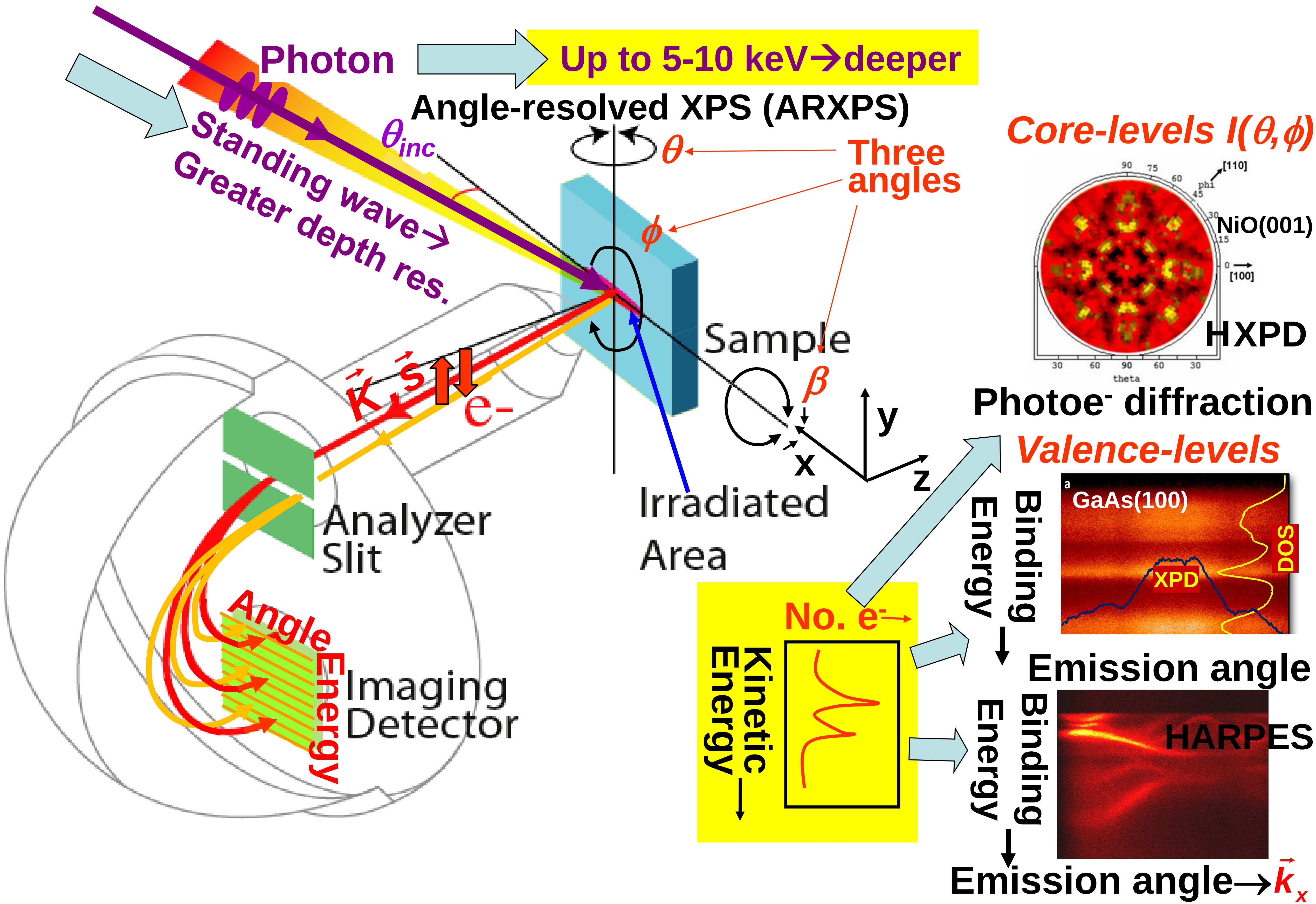
Hard X-Ray Photoemission at the LBNL Advanced Light Source—First Results, March, 2012



Gunnar Palsson　　Slavomir Nemsak



X-ray photoemission: some key elements



Hard x-rays, soft x-rays, and standing waves: Some example studies

6.0 keV

CrAl, FeRh:

Core-level fine structure and density of states measurements of bulk materials

3.2 & 6 keV

W; GaAs, $Ga_{1-x}Mn_xAs$:

SPring8
Petra III

Core-level fine structure and angle-resolved photoemission

How high can we go in energy?→Bulk electronic structure!

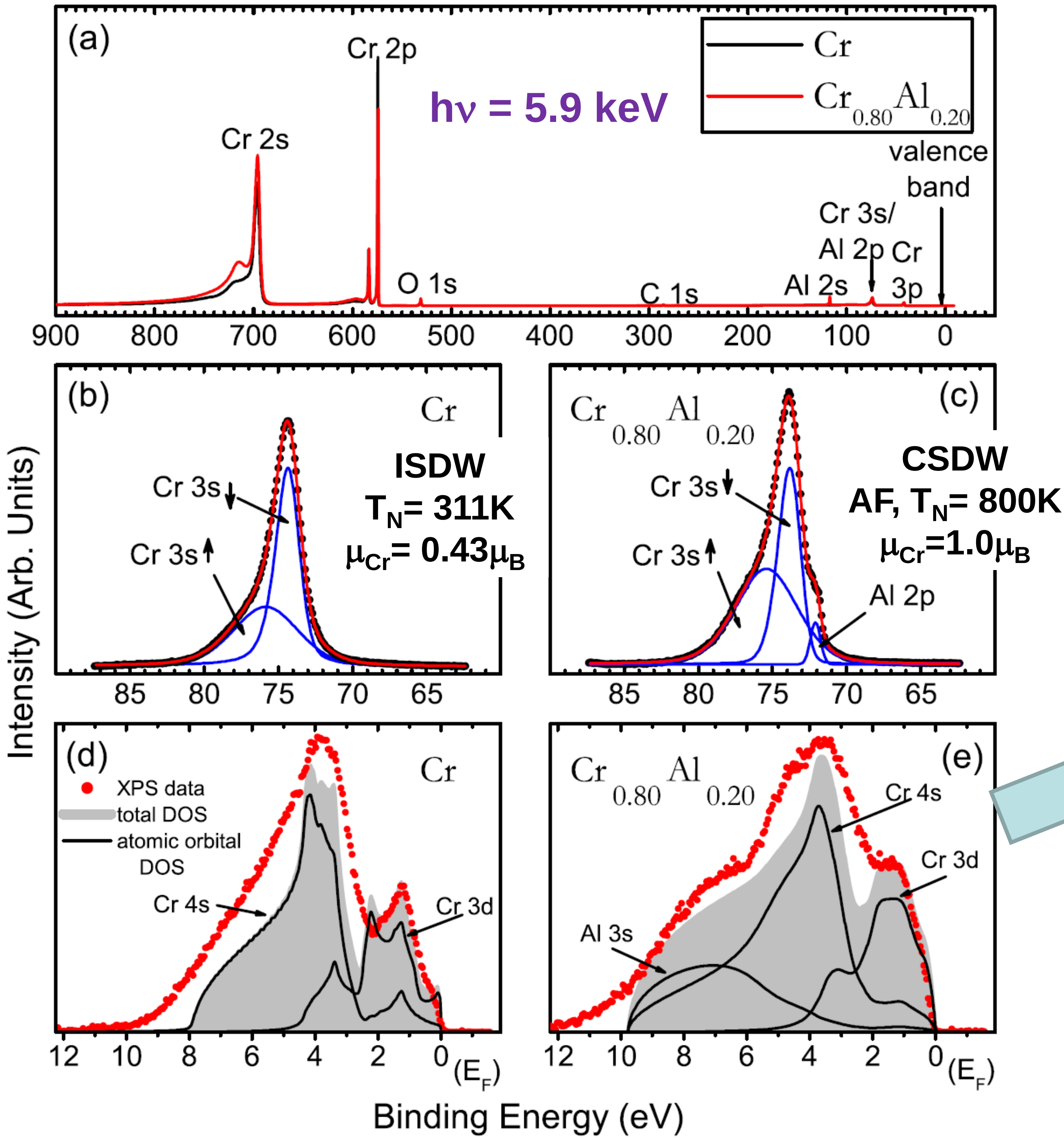
0.8 & 6 keV

$SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$ multilayer:

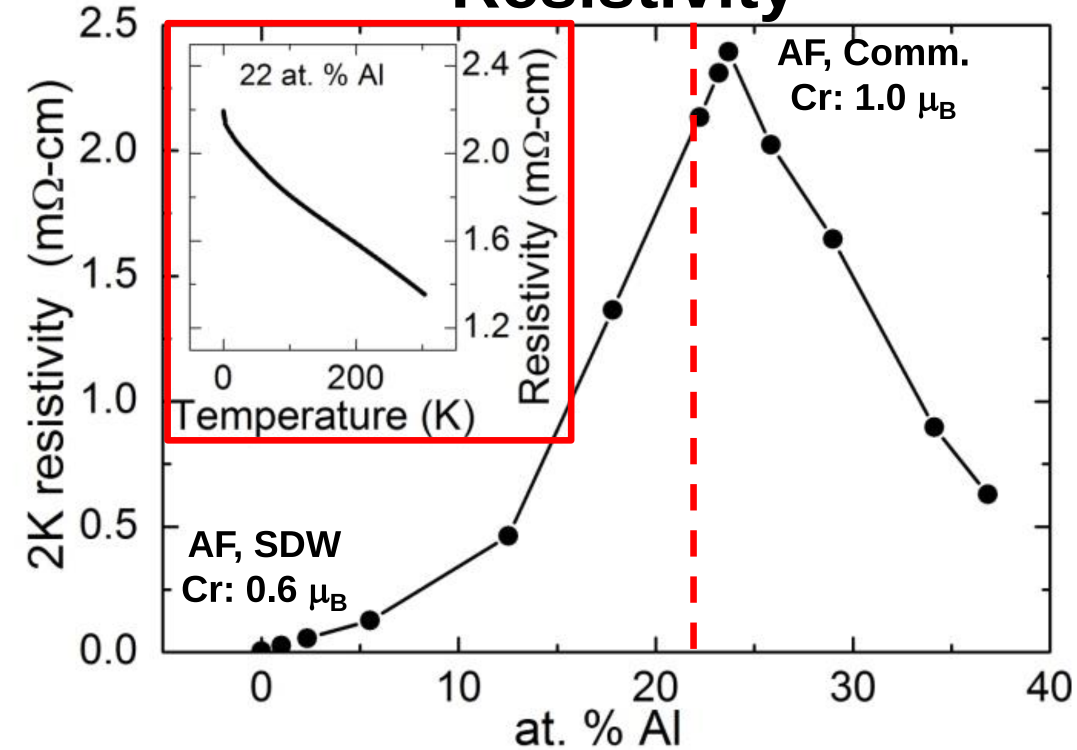
ALS
SPring8
SLS

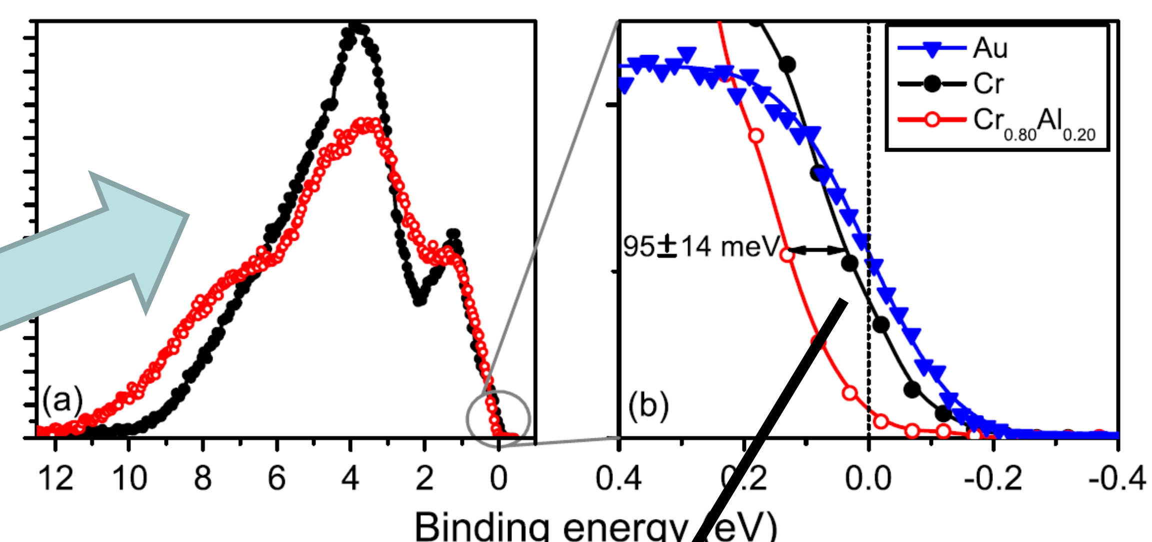
Standing-wave depth-resolved composition, dielectric properties, bonding, and band structure

Opening of the Gap in an Epitaxial Semiconducting $Cr_{0.80}Al_{0.20}$ Thin Film



Resistivity

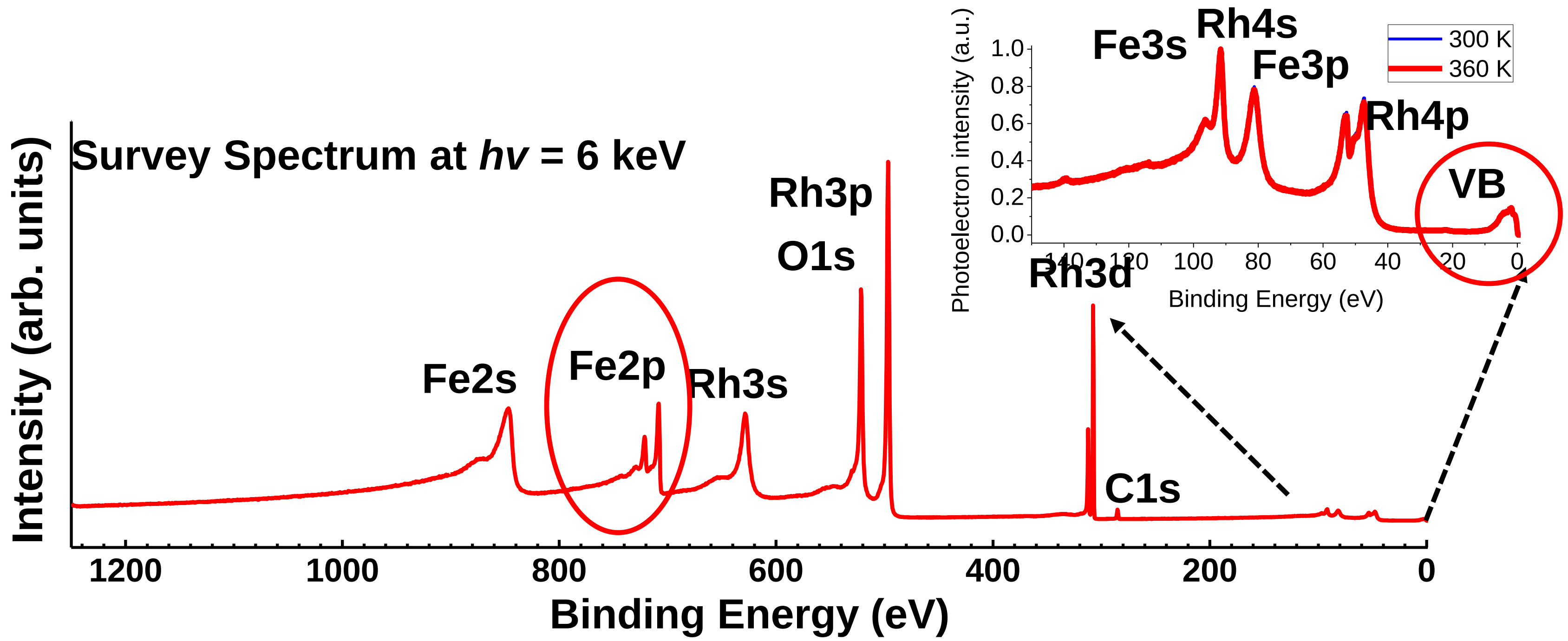


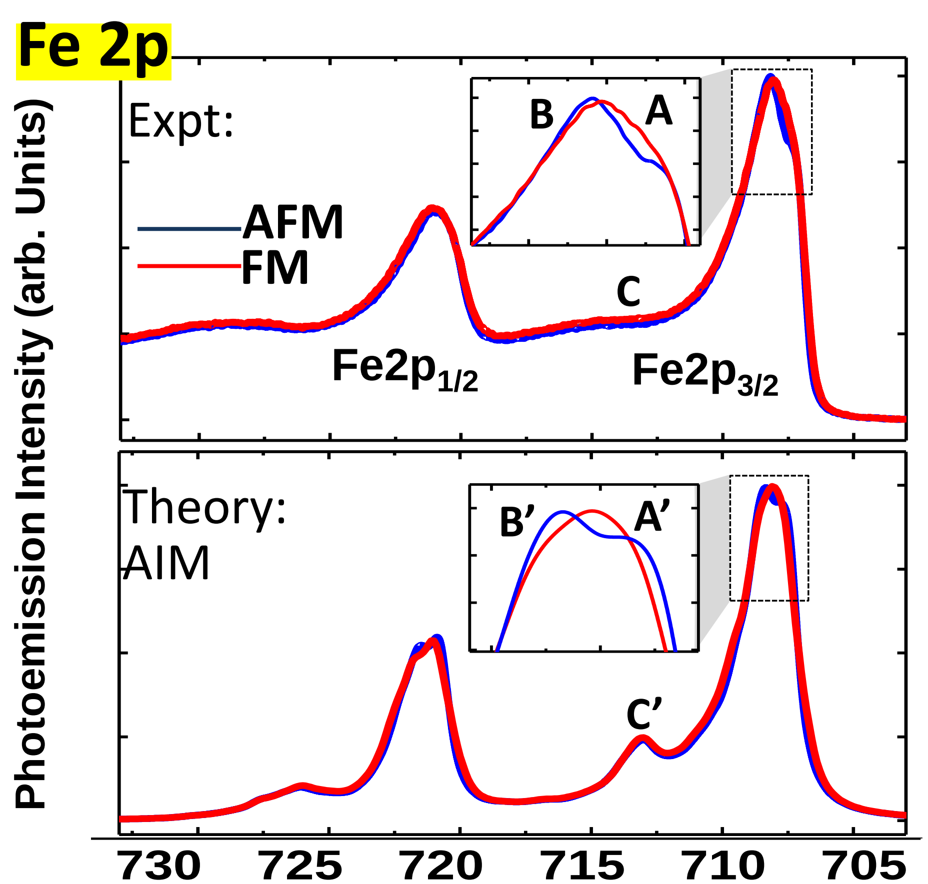


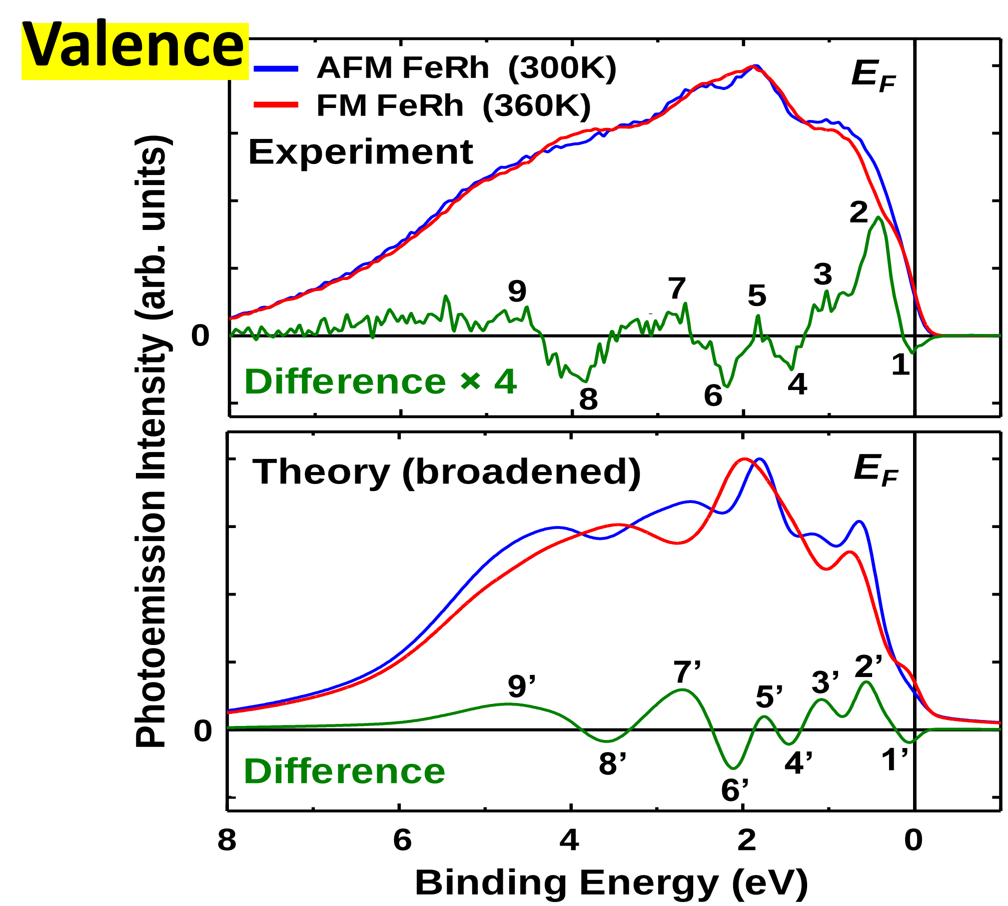
Opening of semiconducting gap

Boekelheide, Gray et al.. PRL 105, 236404 (2010)-SPring-8

FeRh—Metamagnetic transition from AF (low T) to FM (high T) at ~330 K, thermally-assisted magnetic recording

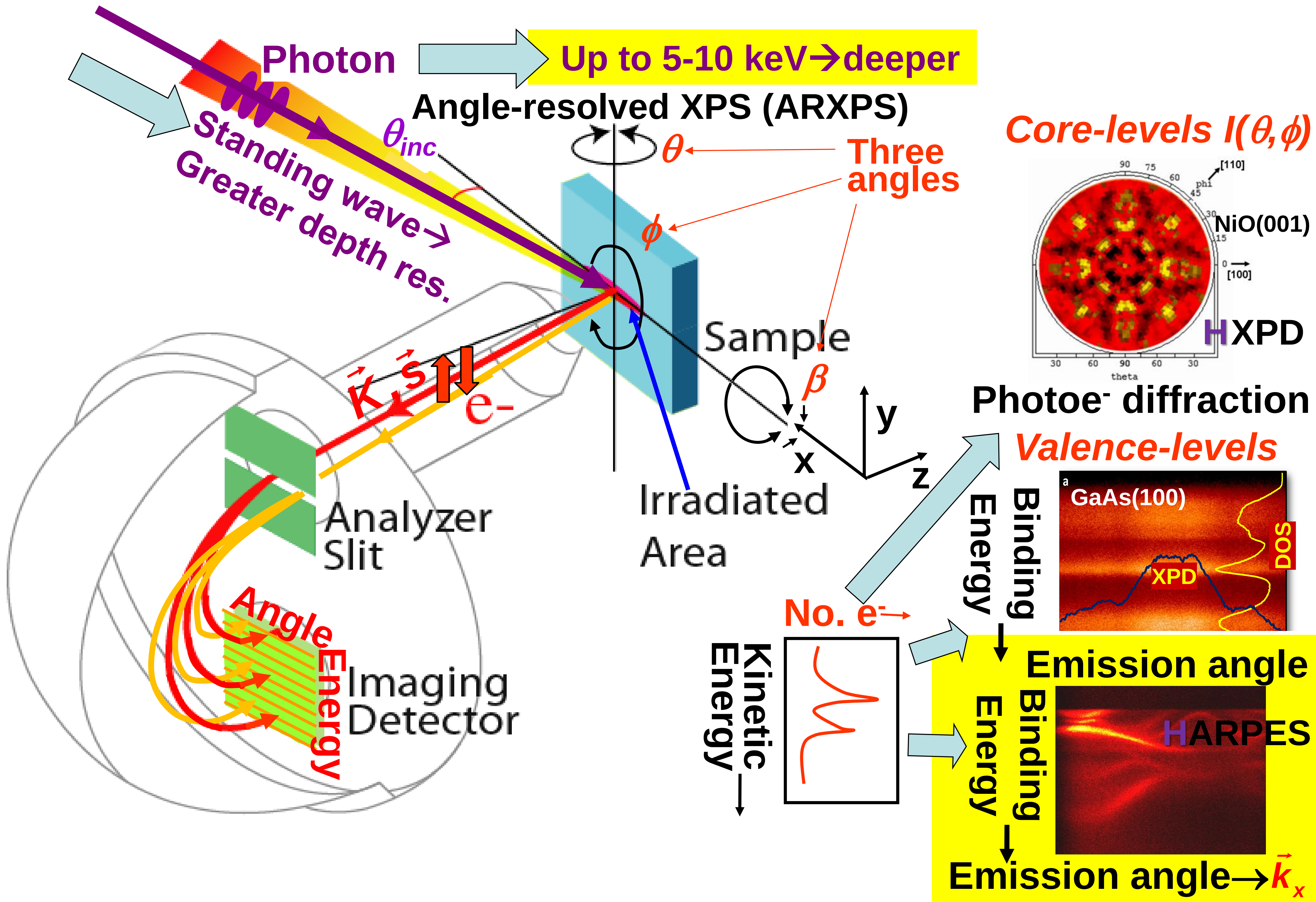




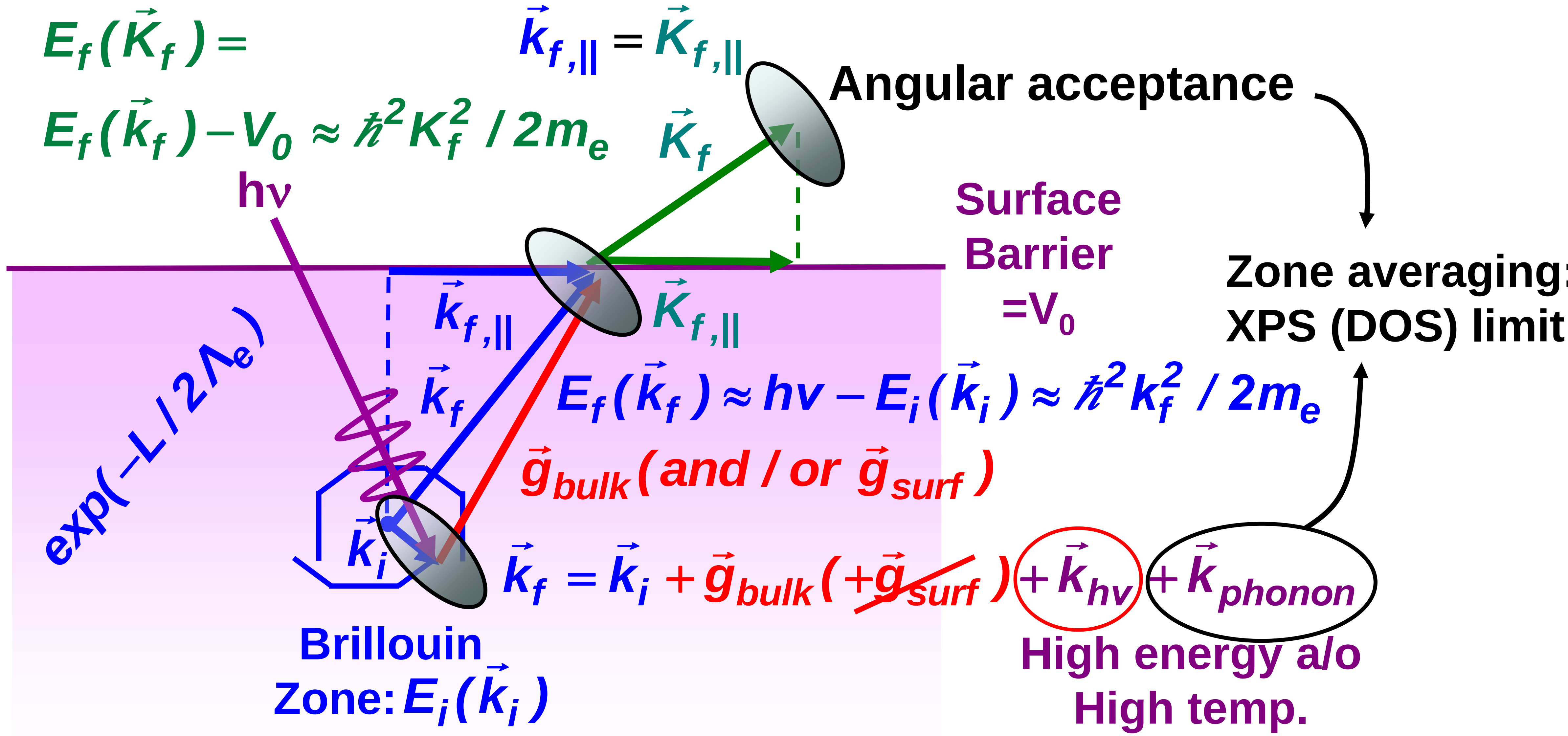


Gray et al., Phys. Rev. Letters 108, 257208 (2012)-Spring-8

X-ray photoemission: some key elements



ARPES—How high can we go in energy and temperature?



Fraction DTs ≈ Debye-Waller factor = $W(T) \approx \exp[-(k^f)^2 \langle u^2(T) \rangle]$

$\approx \exp[-C_1 (k^f)^2 T/(m\Theta_D^2)] \approx \exp(-C_2 E_{kin} T)$

$W \approx 1$

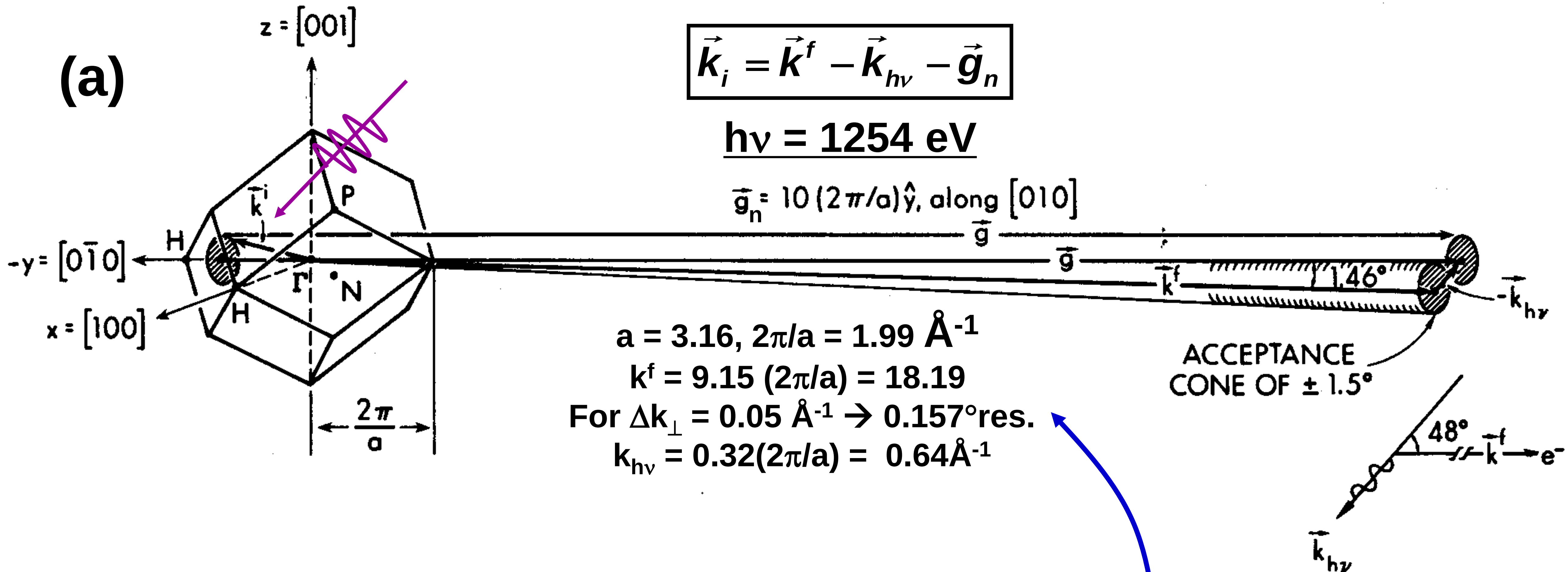
ARPES → bands, quasiparticles (Low hν, Low T, High angul. Res.)

$W \approx 0$

XPS → DOS+XPD (High hν, High T, Low angul. Res.)

Shevchik, Phys. Rev. B 16, 3428 (1977)
Hussain….CF, Phys. Rev. B 34 (1986) 5226

Angle-Resolved Photoemission at High Energy--



$$\vec{k}_i = \vec{k}^f - \vec{k}_{h\nu} - \vec{g}_n$$

hν = 1254 eV

a = 3.16, 2π/a = 1.99 Å^{-1}
k^f = 9.15 (2π/a) = 18.19
For $\Delta k_\perp$ = 0.05 Å^{-1} → 0.157°res.
$k_{h\nu}$ = 0.32(2π/a) = 0.64Å^{-1}

Hussain et al.….CF, Phys. Rev. B 22 3750 (1980) Phys. Rev. B 34, 5226 (1986)

Shevchik, Phys. Rev. B 16, 3428 (1977)

Additional effects at higher energies:

- **Non-dipole--the photon momentum** $k_{h\nu}$ *→easy to allow for*
- **Angular acceptance→B.Z. averaging** *→need better angular res.*
- **Lattice recoil→phonon creation→more B.Z. averaging,**

Fraction DTs ≈ Debye-Waller factor = $W(T) \approx \exp[-(k^f)^2 \langle u^2(T)\rangle]$

$\approx \exp[-C_1 (k^f)^2 T/(m\Theta_D^2)] \approx \exp(-C_2 E_{kin} T)$ *→need cryocooling*

→the "XPS limit" of full B.Z. averaging and D.O.S. sensitivity

→core-like photoelectron diffraction

Alvarez et al., PRB 54, 14703 (1996)

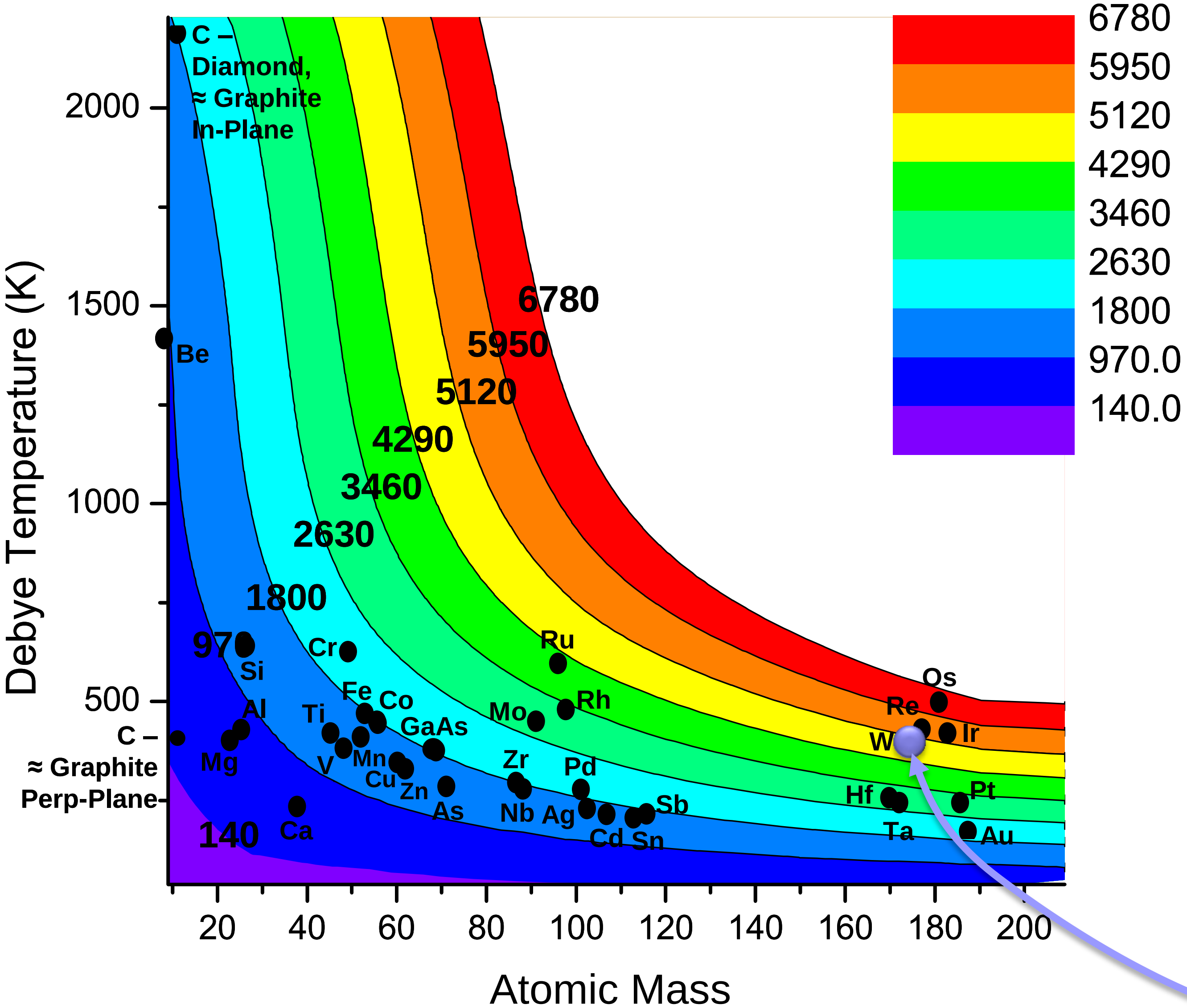
- **Recoil →peak shifts and broadening:**

$$E_{recoil}(eV) \approx \left[\frac{m_e}{M}\right] E_{kin} \approx 5.5 \times 10^{-4} \left[\frac{E_{kin}(eV)}{M(amu)}\right]$$

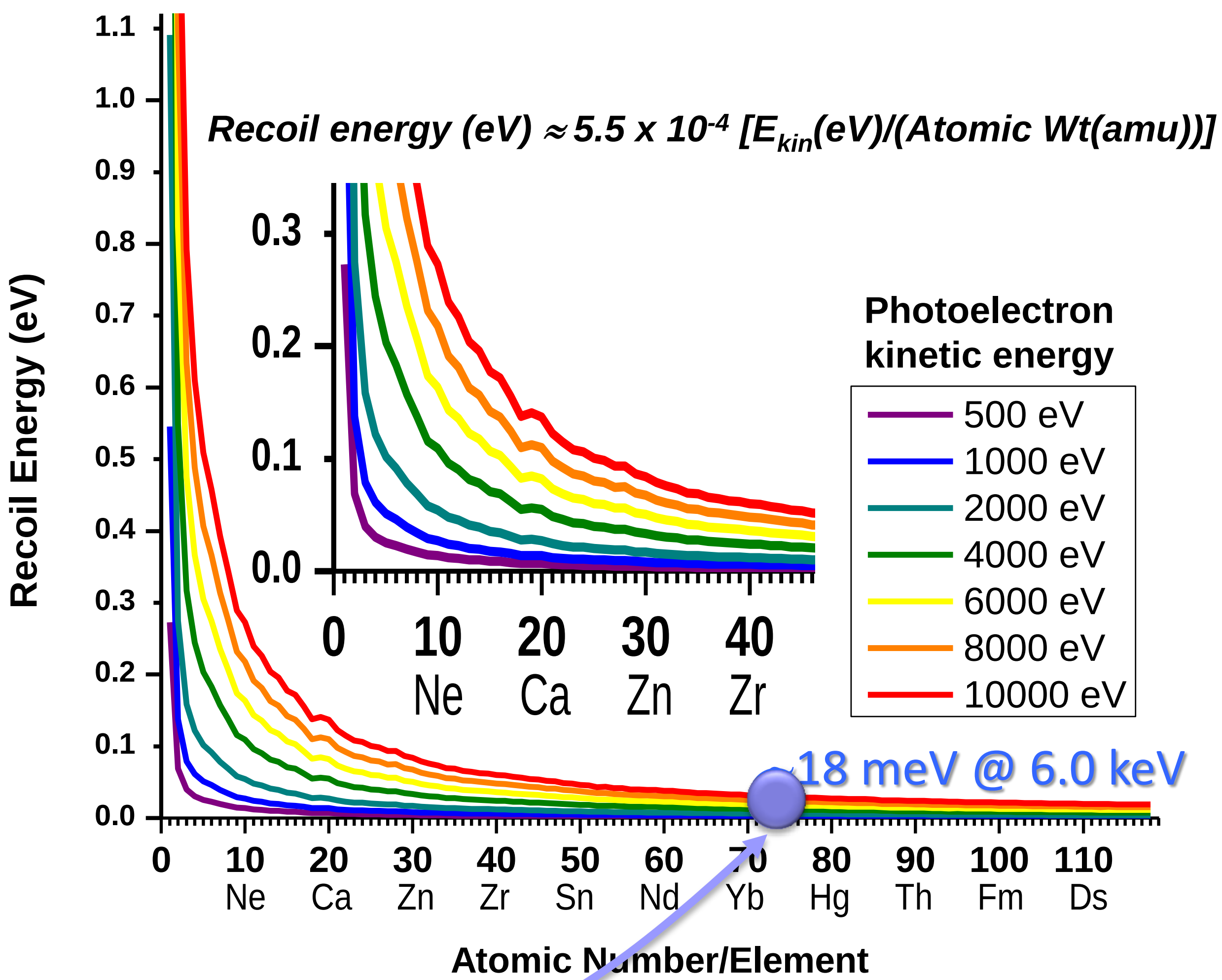
Takata et al., Phys. Rev. B 75, 233404 (2007)

ARPES→HARPES-How high can we go? Photoemission Debye-Waller Factors and Recoil Energies

Photon energy for ~50% DTs = O.5 D-W @ 20K

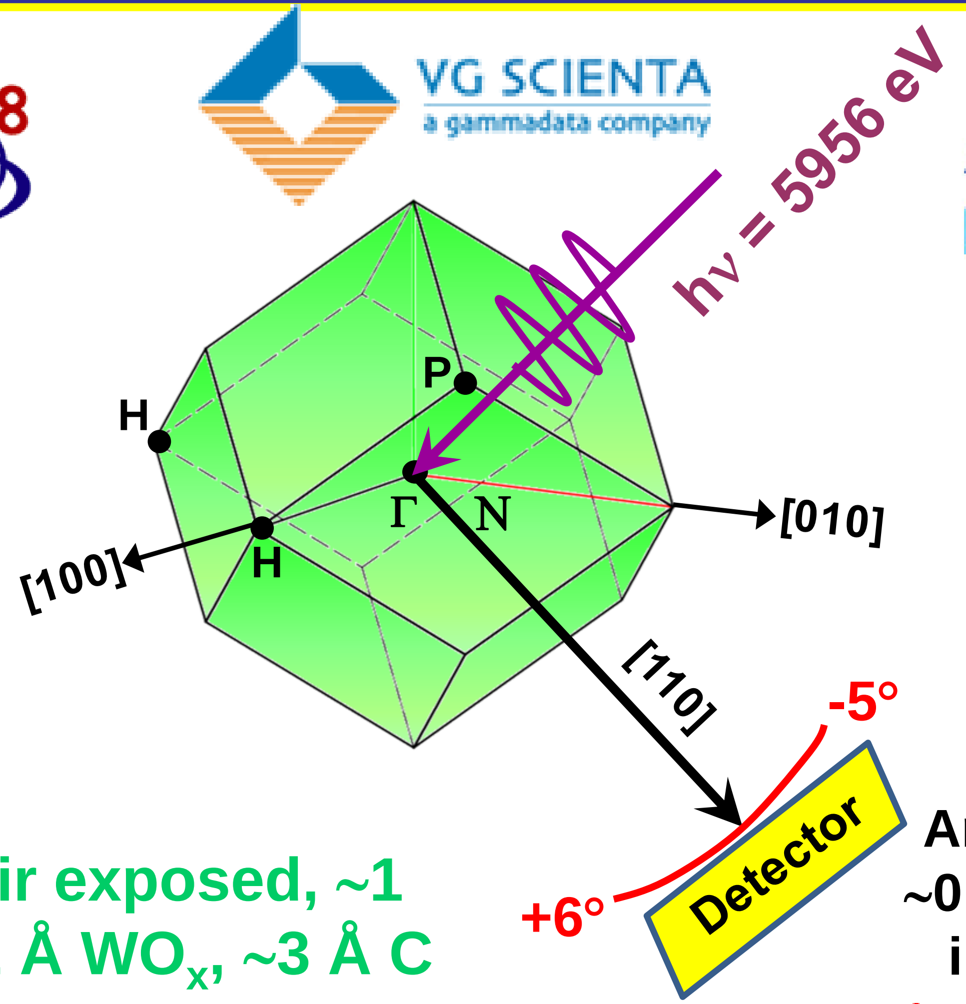


Recoil energy for all atoms and different photon energies



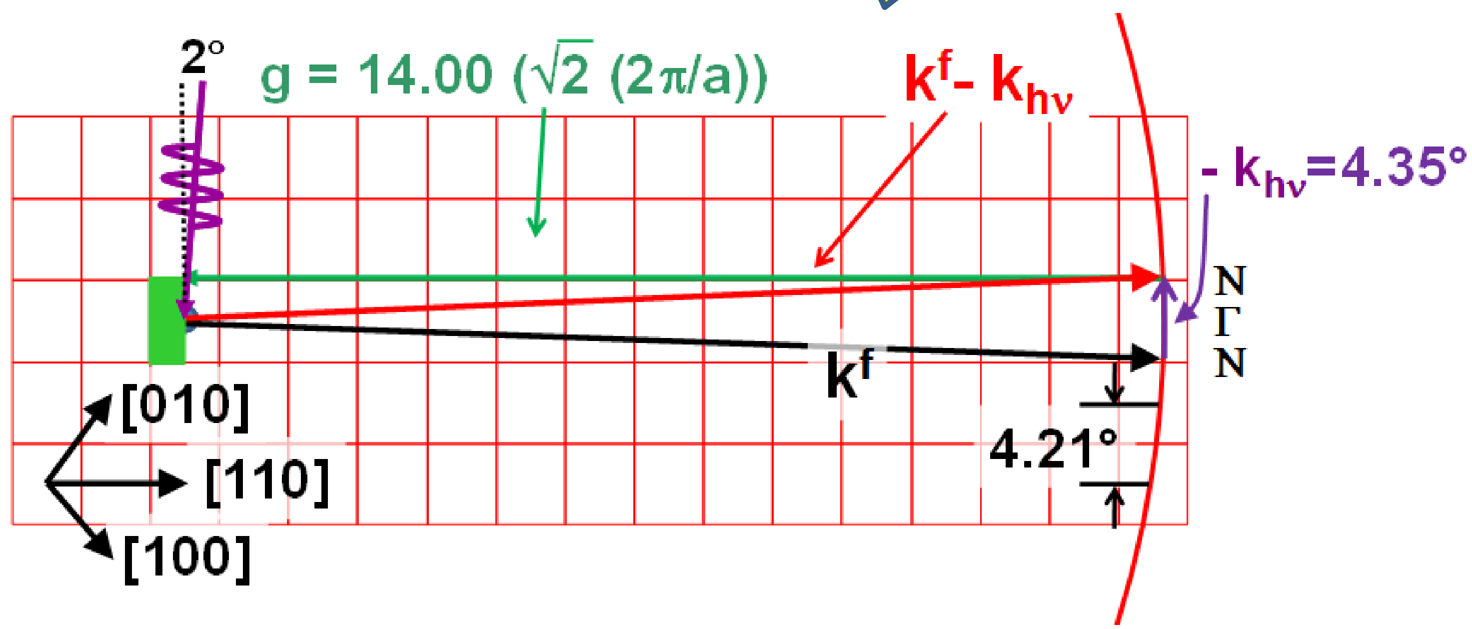
C. Papp. L. Plucinski, et al., Phys. Rev. B 84, 045433 (2011)

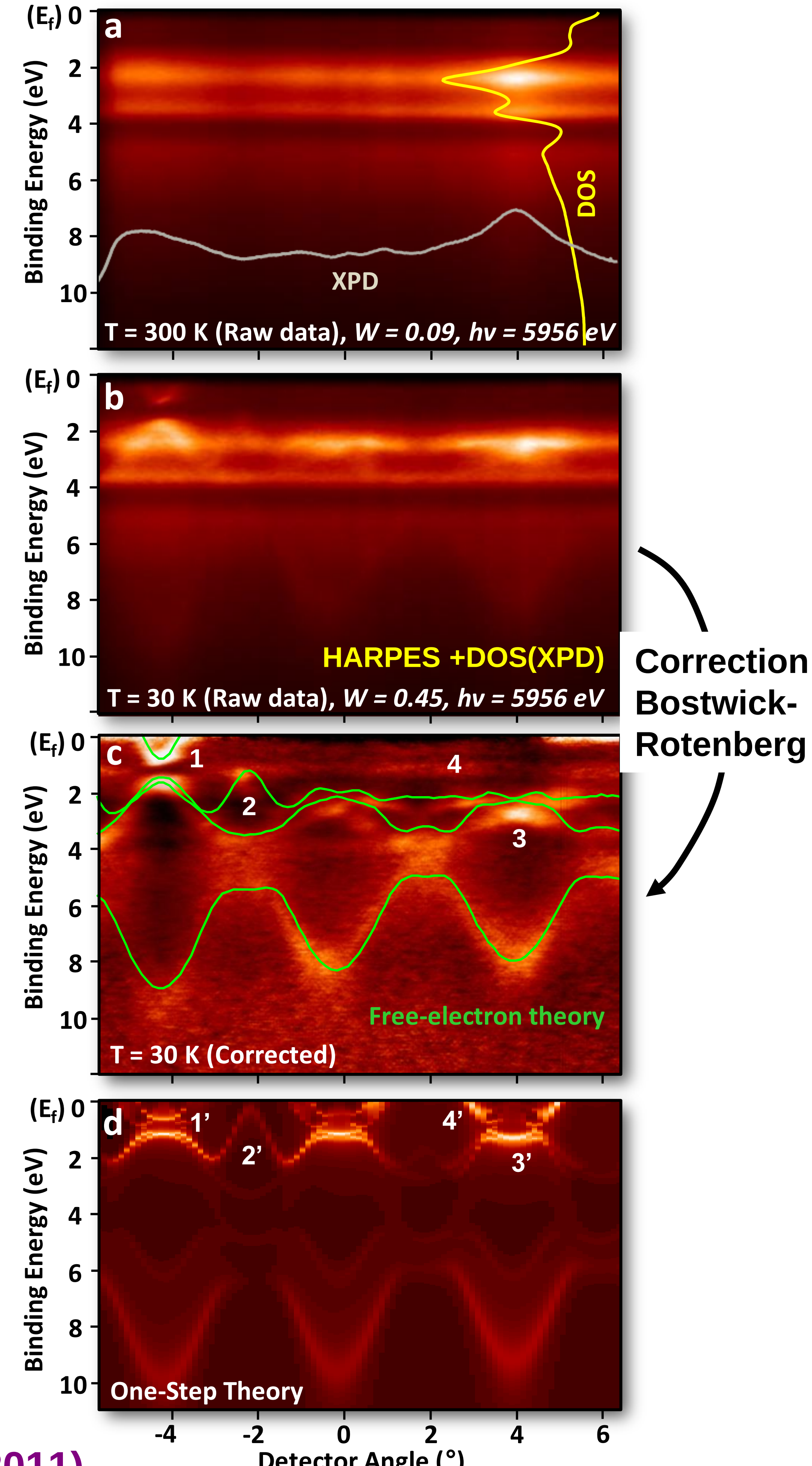
Hard x-ray ARPES for W(110): 6.0 keV



Ang. Res.: ~0.2°→0.02° in future

W(110)-air exposed, ~1 year, ~12 Å WO_x, ~3 Å C

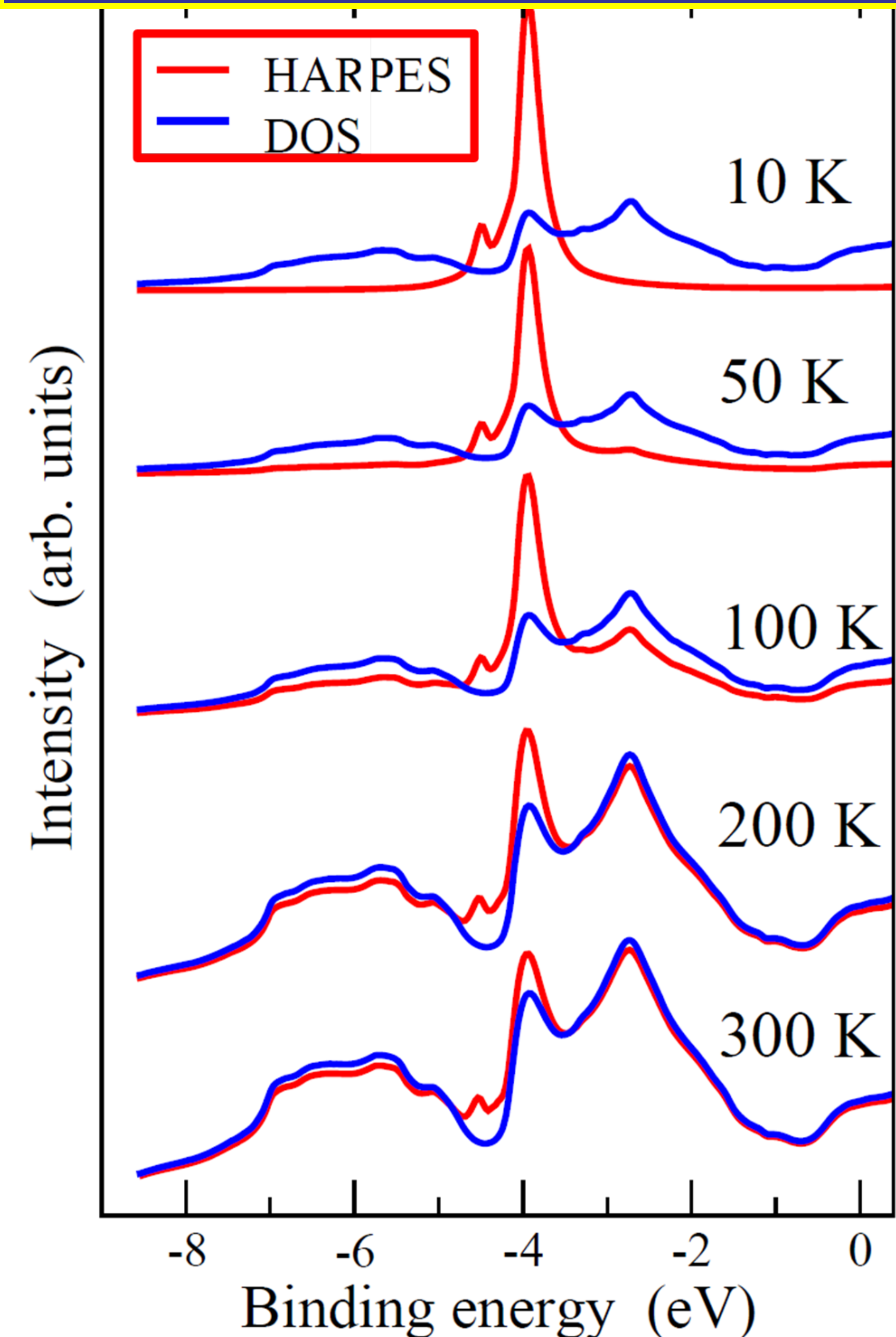


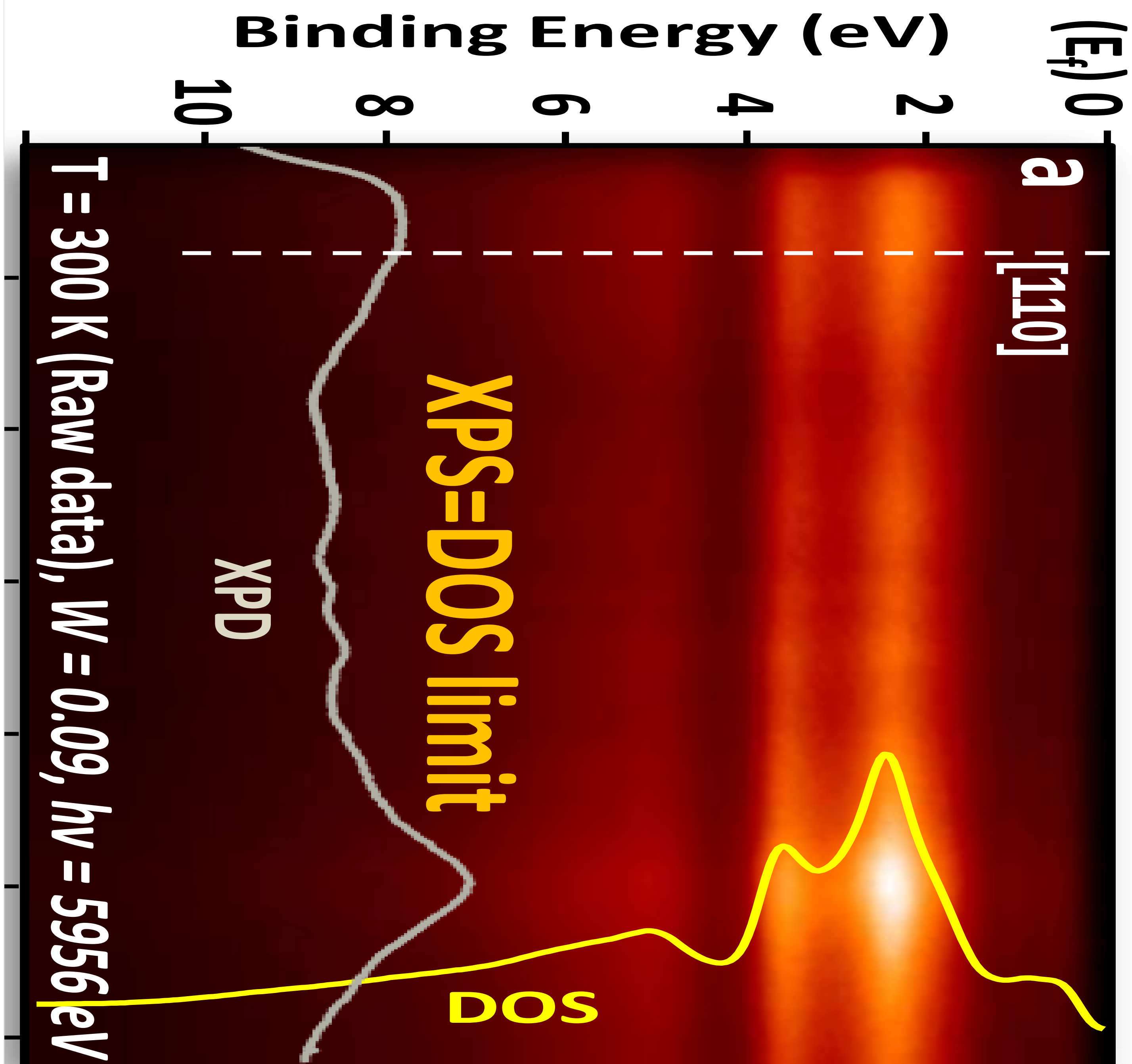


Correction: Bostwick-Rotenberg

Gray, Minar et al., Nature Mat. 10, 759 (2011);
Plus *News and Views*, Feng, Nature Mat. 10, 729-730 (2011)

Hard x-ray ARPES for W(110):
One-step theory with phonons (Braun, Minar, Ebert) vs expt. (Gray et al.)



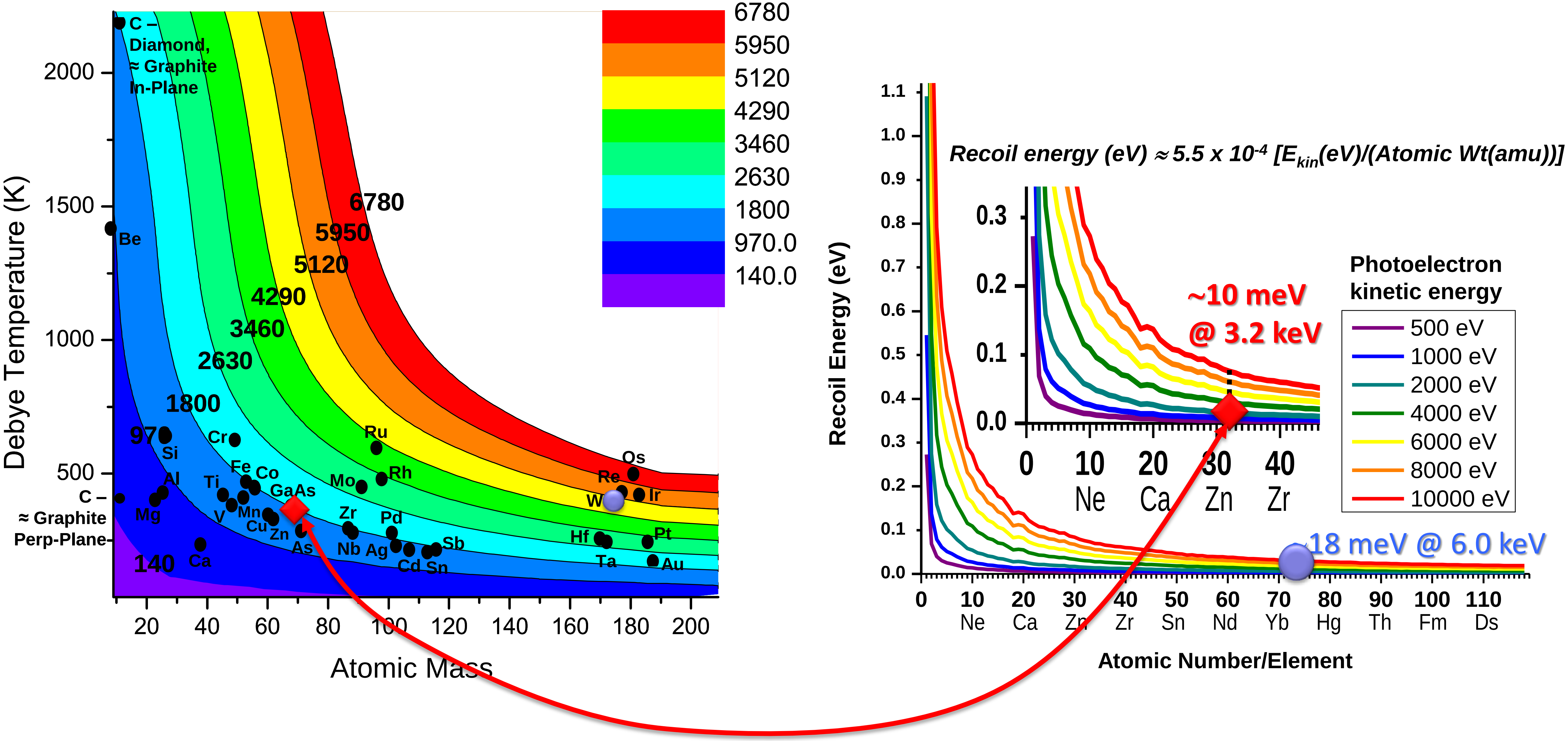


Braun et al., to be published

ARPES→HARPES-How high can we go? Photoemission Debye-Waller Factors and Recoil Energies

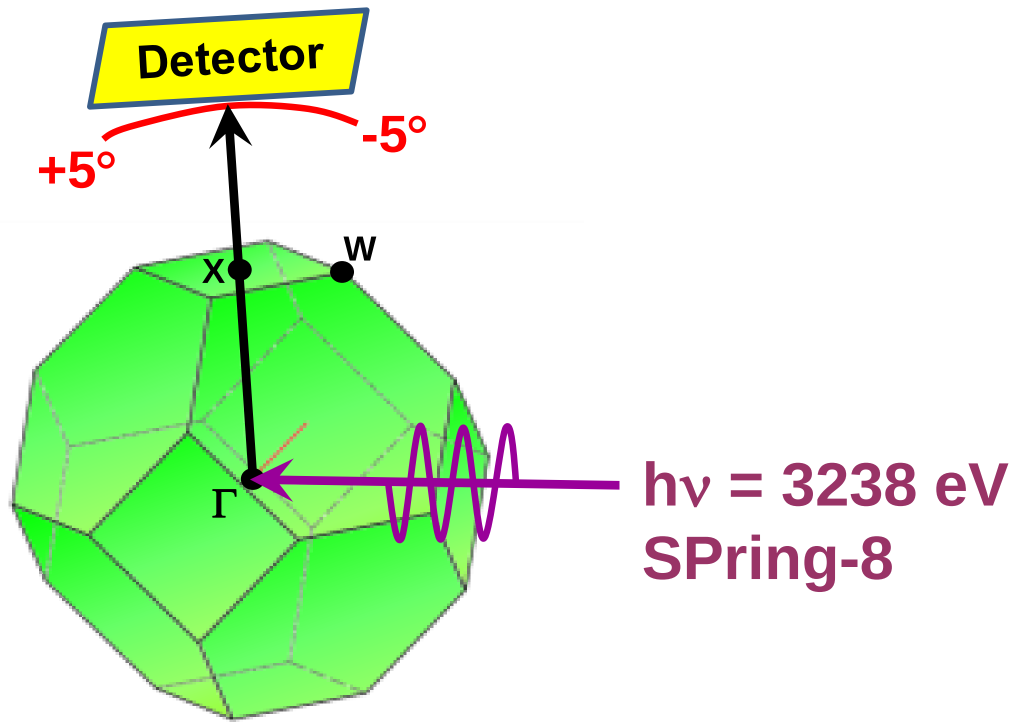
Photon energy for ~50% DTs = O.5 D-W @ 20K

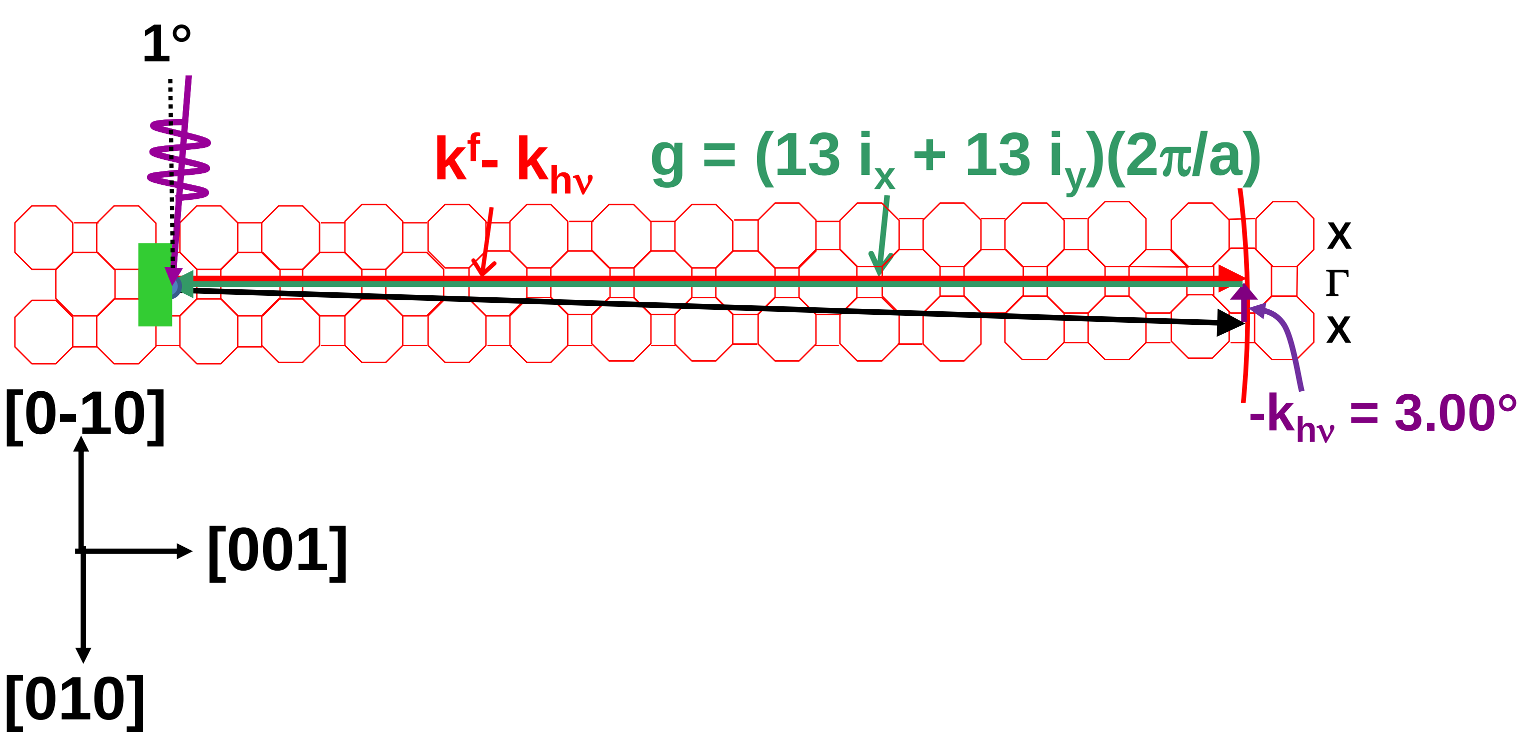
Recoil energy for all atoms and different photon energies

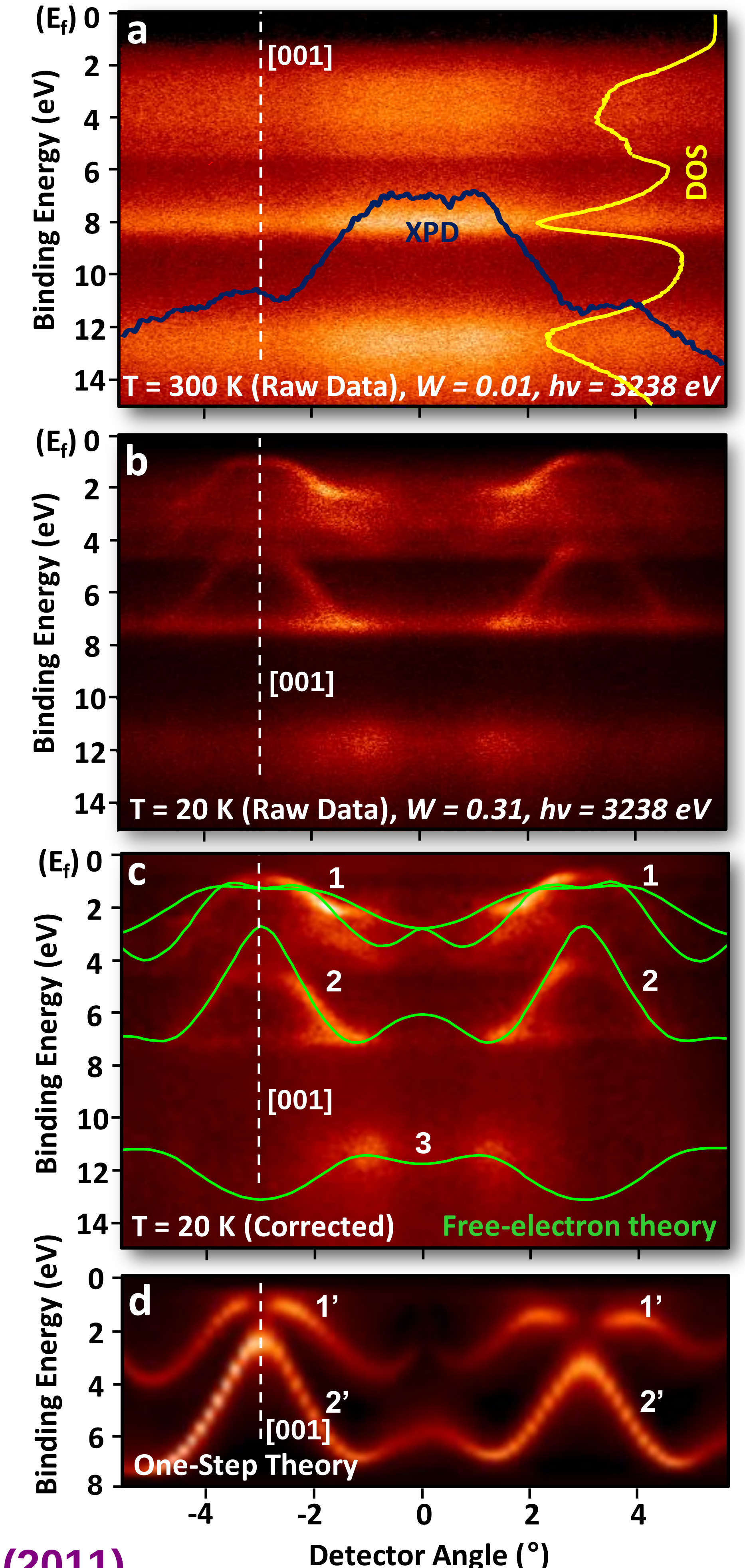


C. Papp. L. Plucinski, et al.,
Phys. Rev. B 84, 045433 (2011)

Hard x-ray ARPES for GaAs(001): 3.2 keV



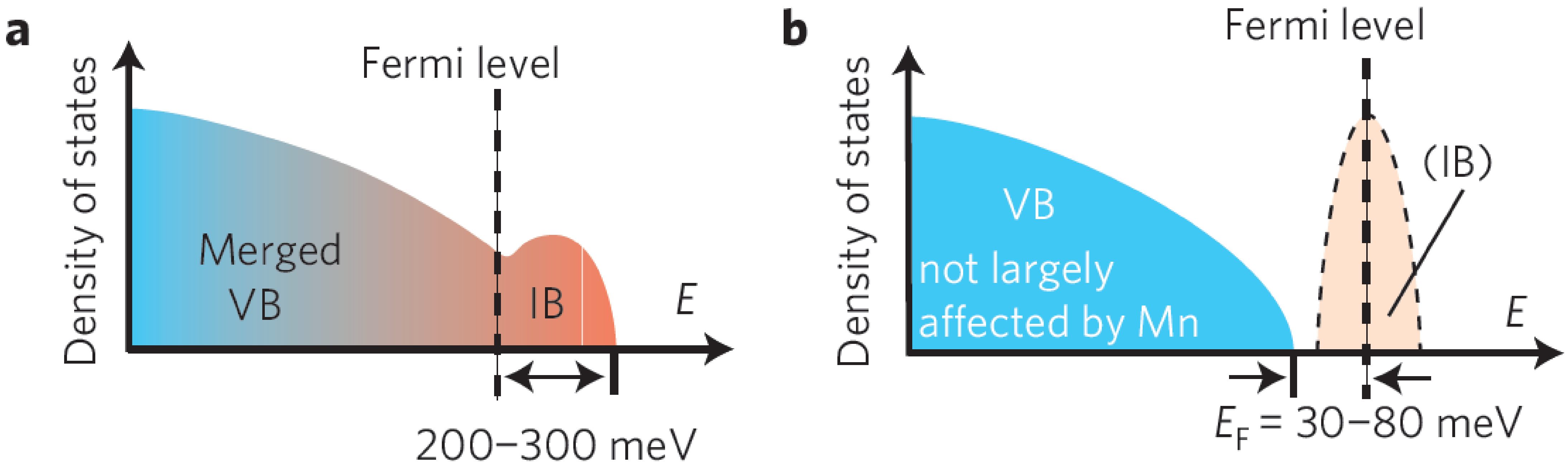




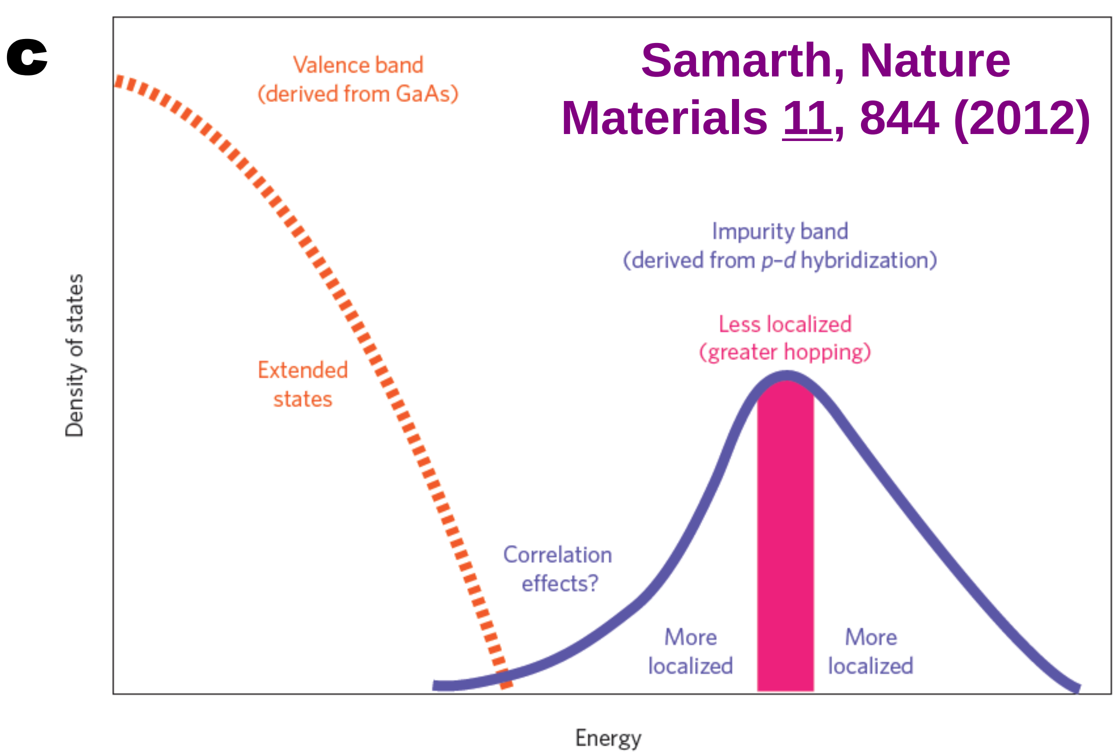
Gray, Minar et al., Spring-8, Nature Materials 10, 759 (2011)

Hard x-ray ARPES--GaAs and the dilute magnetic semiconductor $Ga_{0.97}Mn_{0.03}As$

How does Mn alter the GaAs electronic structure so as to produce ferromagnetic coupling? Differing views:



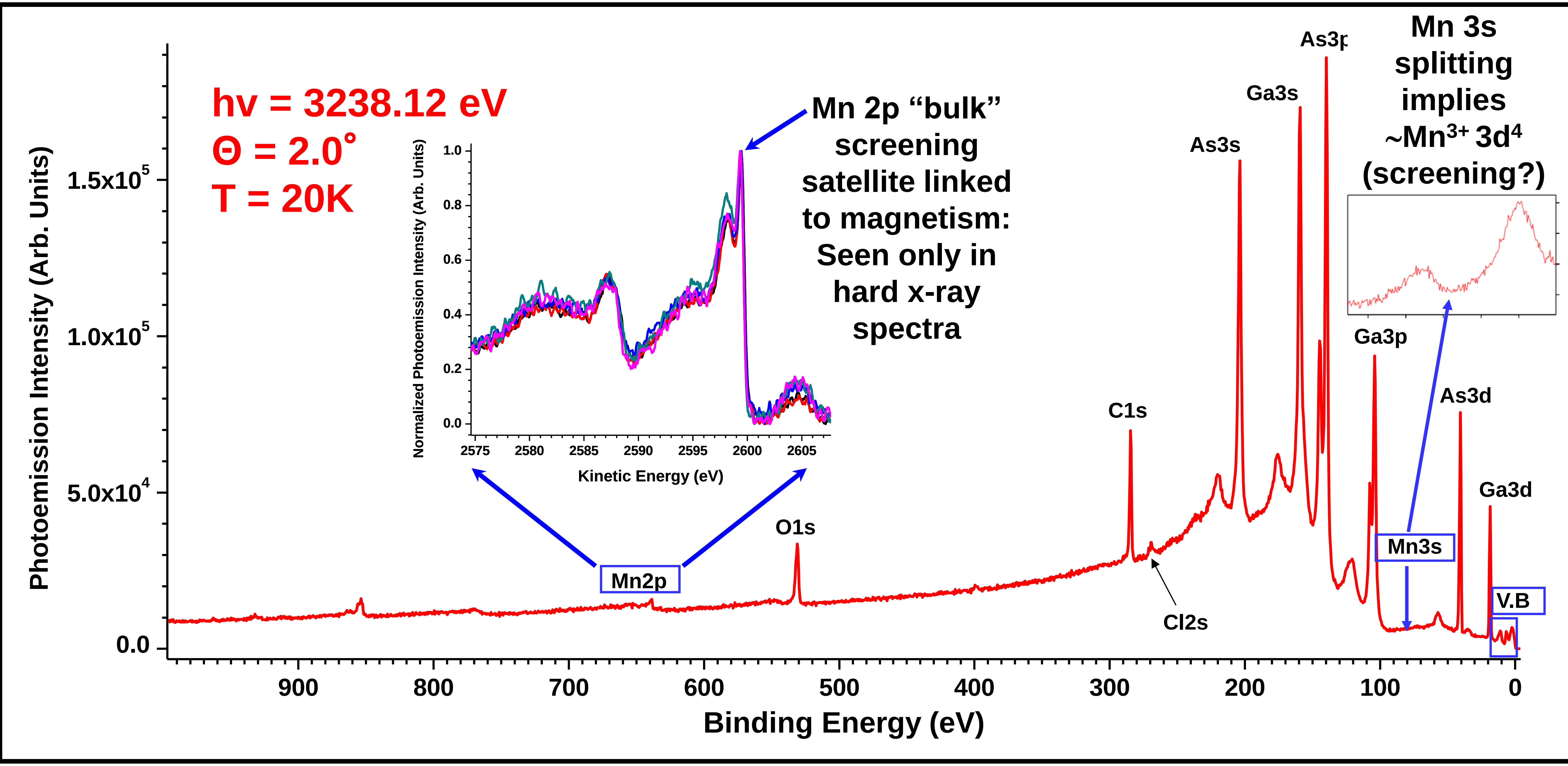
Ohya et al., Nature Physics 7, 342 (2011)



Samarth, Nature Materials 11, 844 (2012)

?

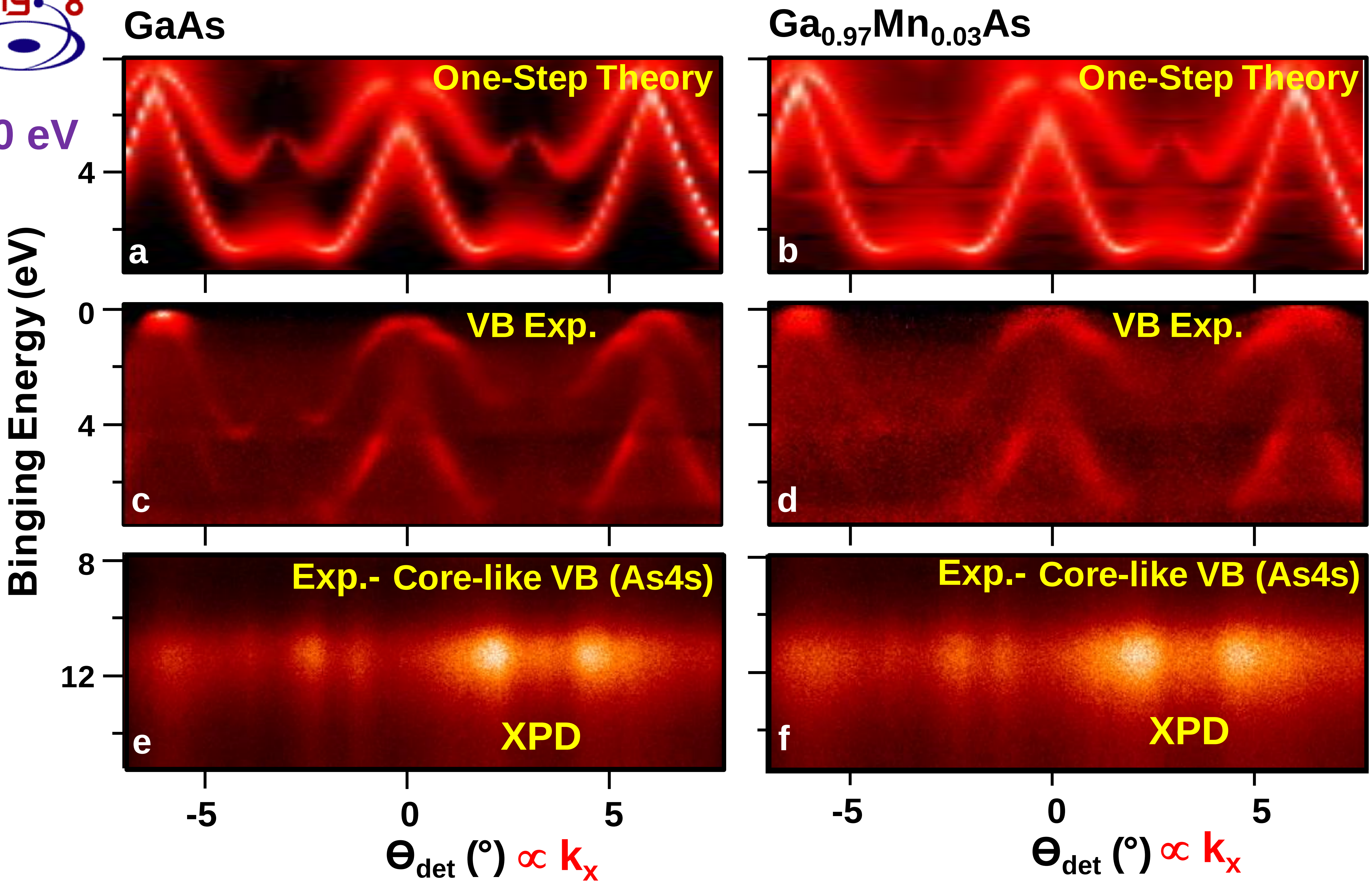
E.g.-GaAs doped with Mn: a magnetic semiconductor $Ga_{0.96}Mn_{0.04}As$--HXPS: T = 20K, Broad Survey



Samples: Stone, Dubon
Expt.-Gray, Papp, Ueda, Yamashita, Kobayashi
Theory- Pickett, Ylvisaker, Minar, Braun, Ebert

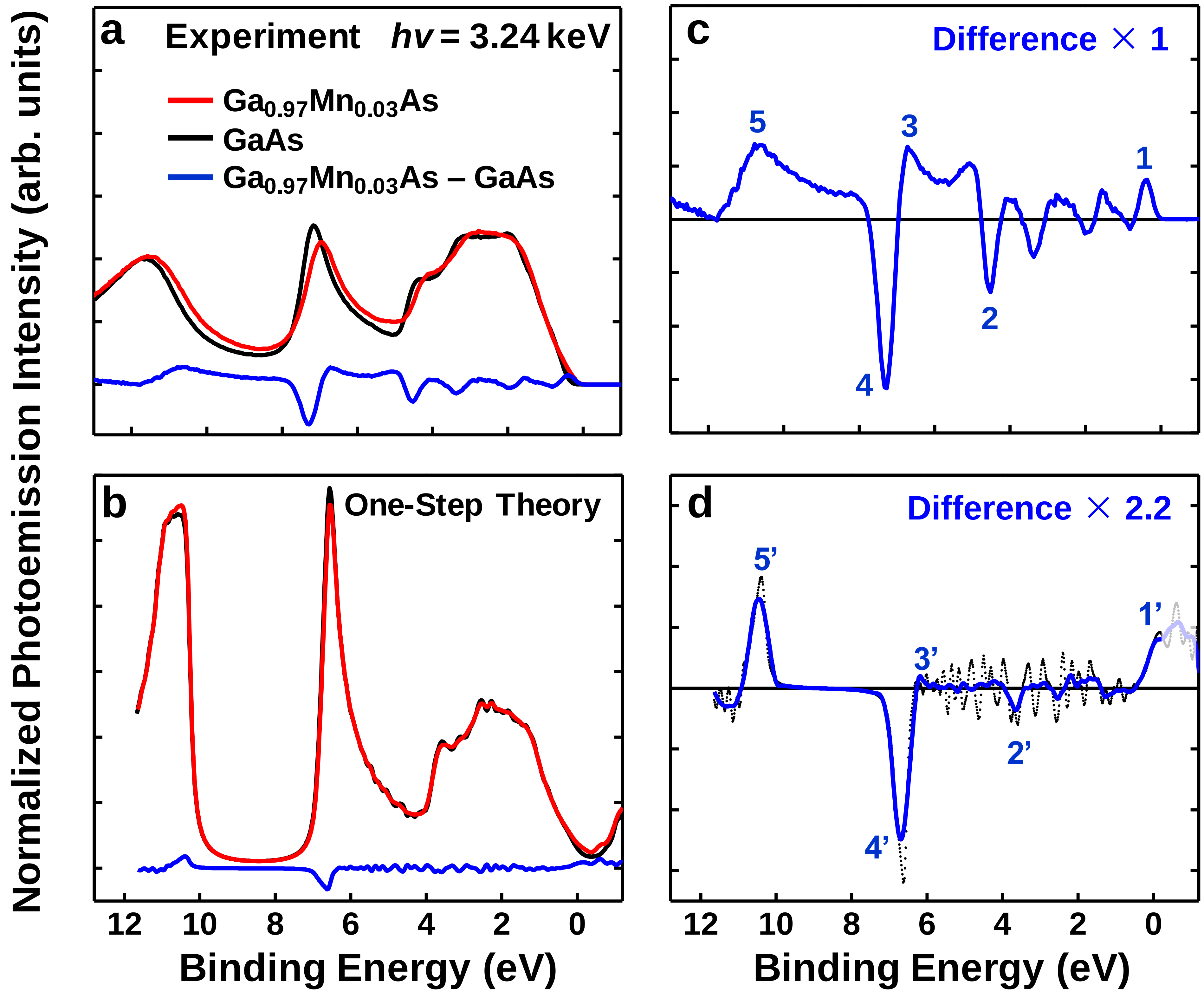
Hard x-ray ARPES--GaAs and DMS $Ga_{0.97}Mn_{0.03}As$
Comparing Experiment and One-Step KKR Theory

3,200 eV



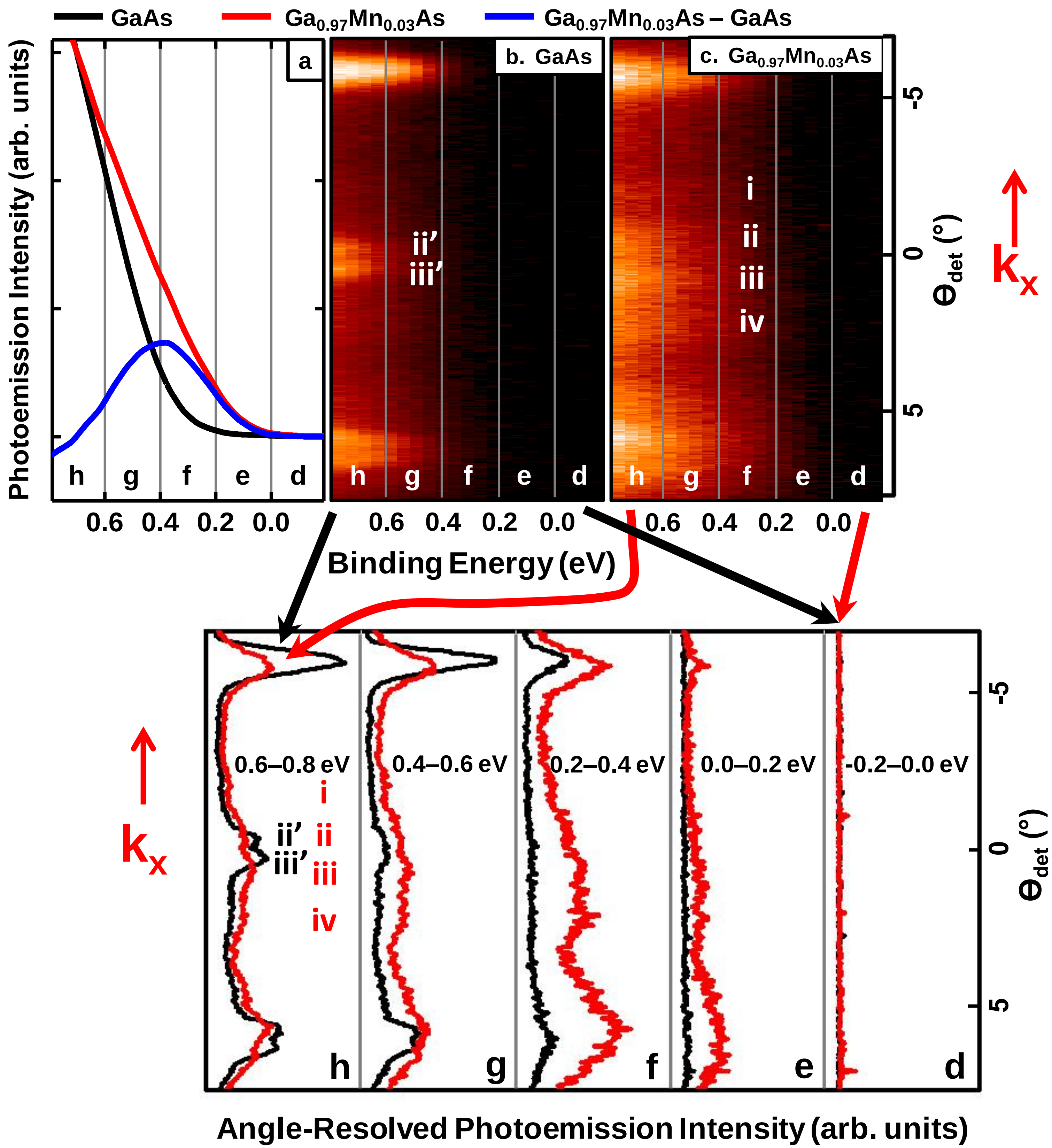
Gray et al., Nature Materials 11, 957 (2012)

GaAs and $Ga_{0.97}Mn_{0.03}As$
Angle-Integrated Hard X-Ray ARPES @ 3.2 keV
Experiment and One-Step KKR Theory



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

GaAs and $Ga_{0.97}Mn_{0.03}As$
Hard X-Ray ARPES @ 3.2 keV
Experiment near E_F



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

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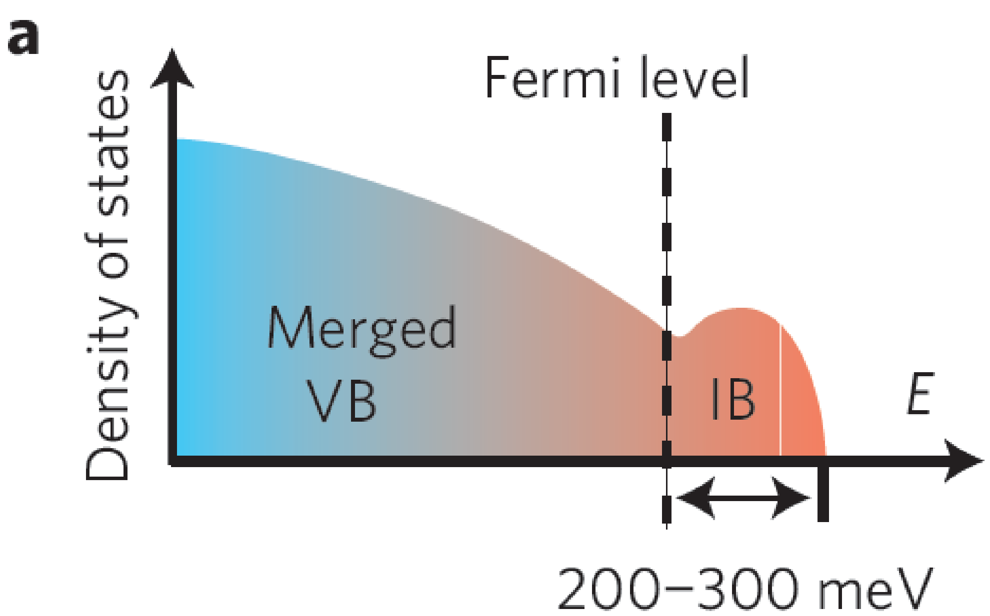
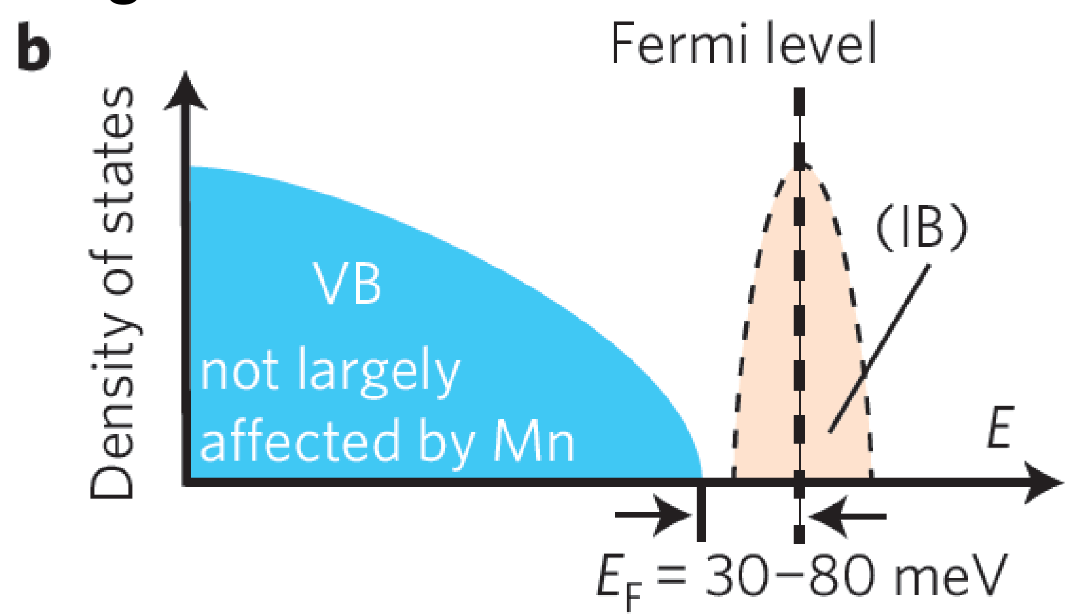
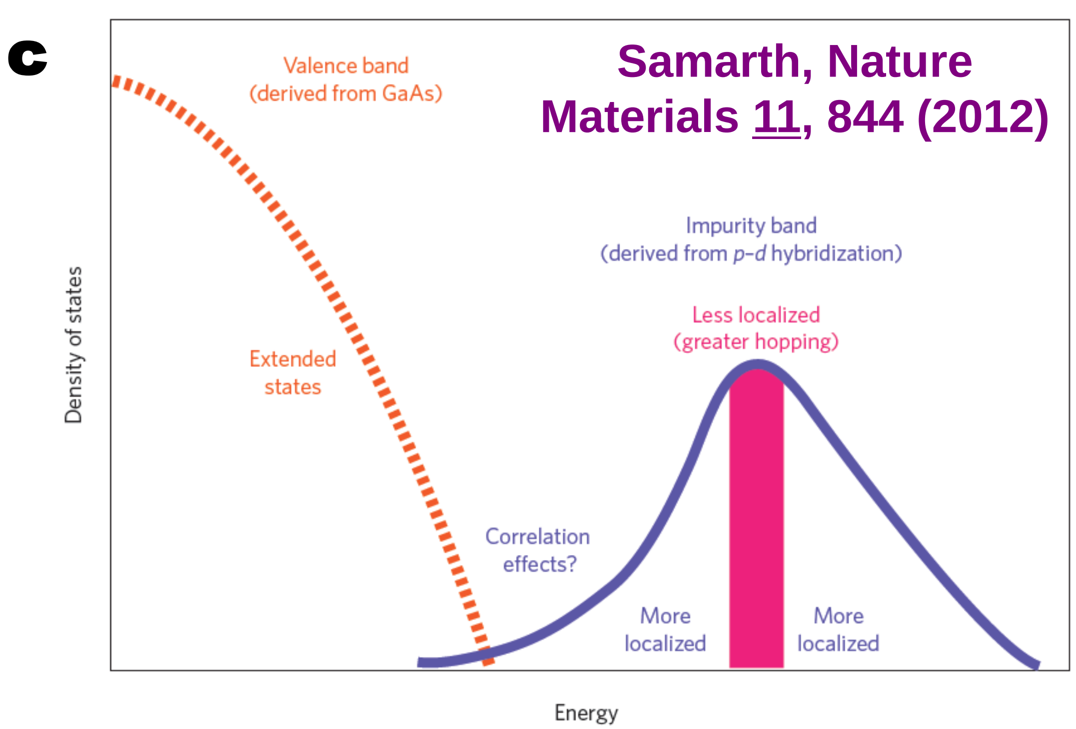
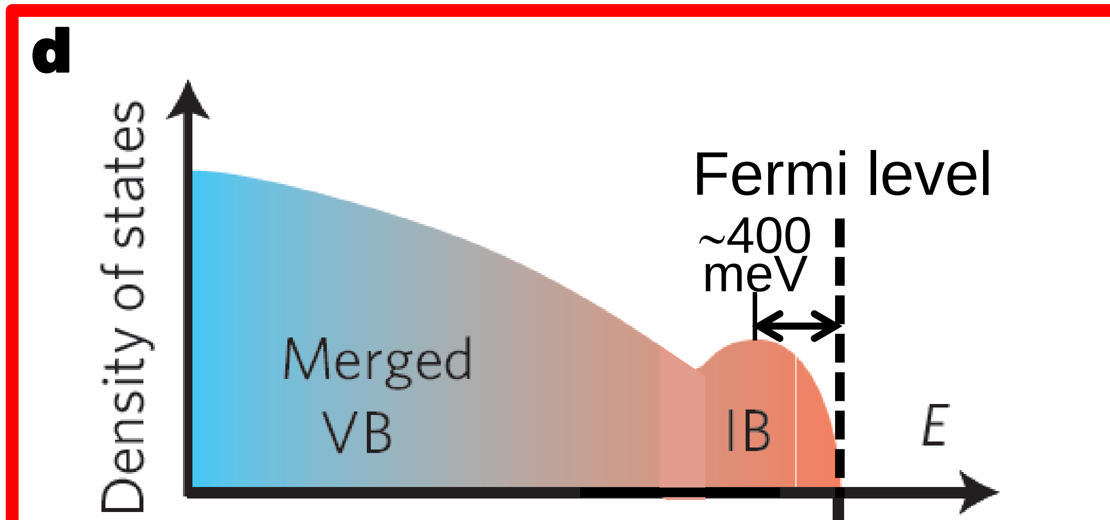




Ohya et al., Nature Physics 7, 342 (2011)



Samarth, Nature Materials 11, 844 (2012)



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

Photoemission in complex heterostructures and materials

Core photoemission→XPS, X-ray photoelectron diffraction-XPD,…
Valence photoemission→
Higher energy a/o temperature→Densities of states-DOSs
Lower energy a/o temperature→Band mapping, Angle-resolved photoemission-ARPES
are very powerful techniques, but they:

- **are sometimes too strongly influenced by surface effects, if bulk or buried layer/interface properties are to be studied**

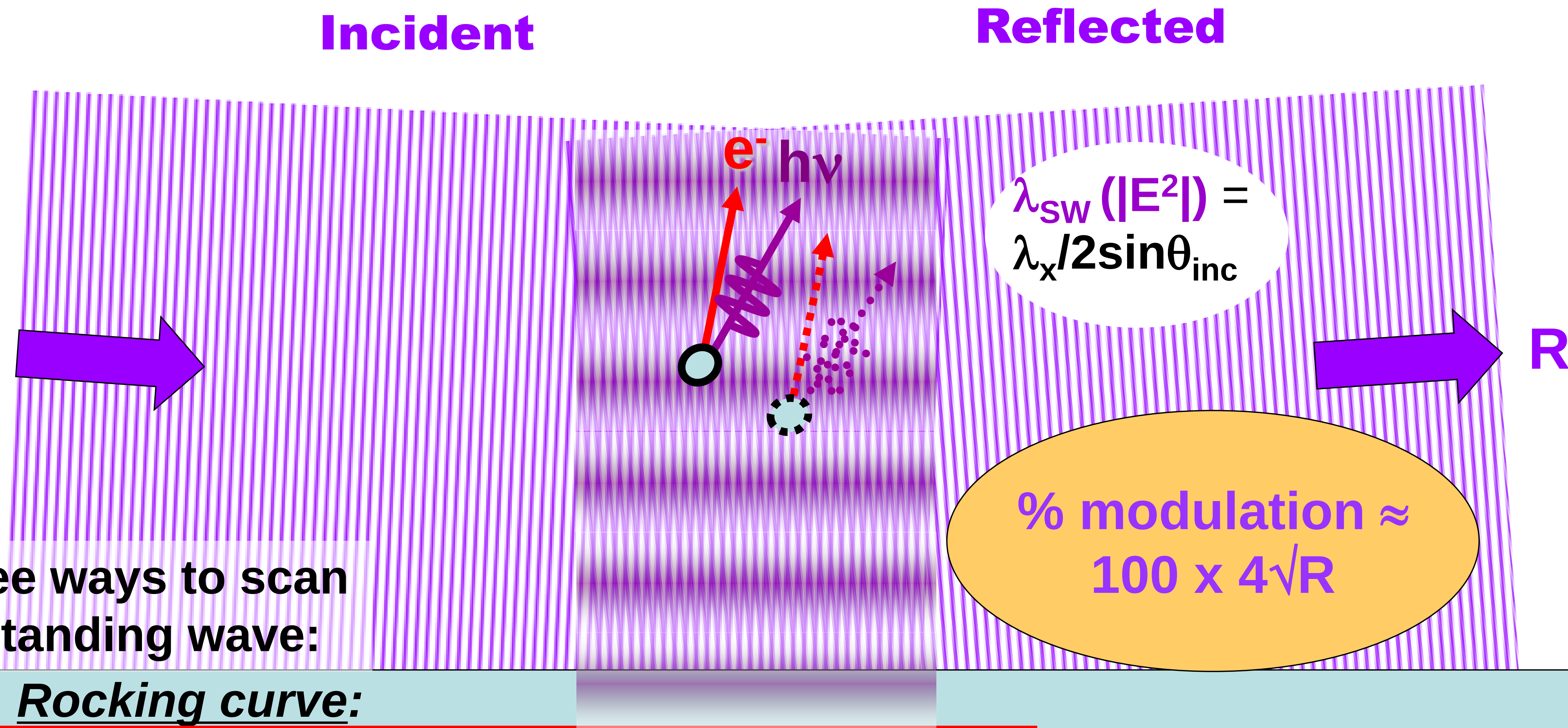
- **may not be able to selectively and quantitatively see buried-layer and interface properties**

Two ways to address these limitations:

- **use of harder x-ray excitation (HAXPES, HXPS) for deeper probing: core (HXPD) and valence DOSs or hard x-ray ARPES or "HARPES"**

- **use of soft and hard x-ray standing waves to selectively look below the surface, including ARPES**

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



Three ways to scan a standing wave:

1. Rocking curve:

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

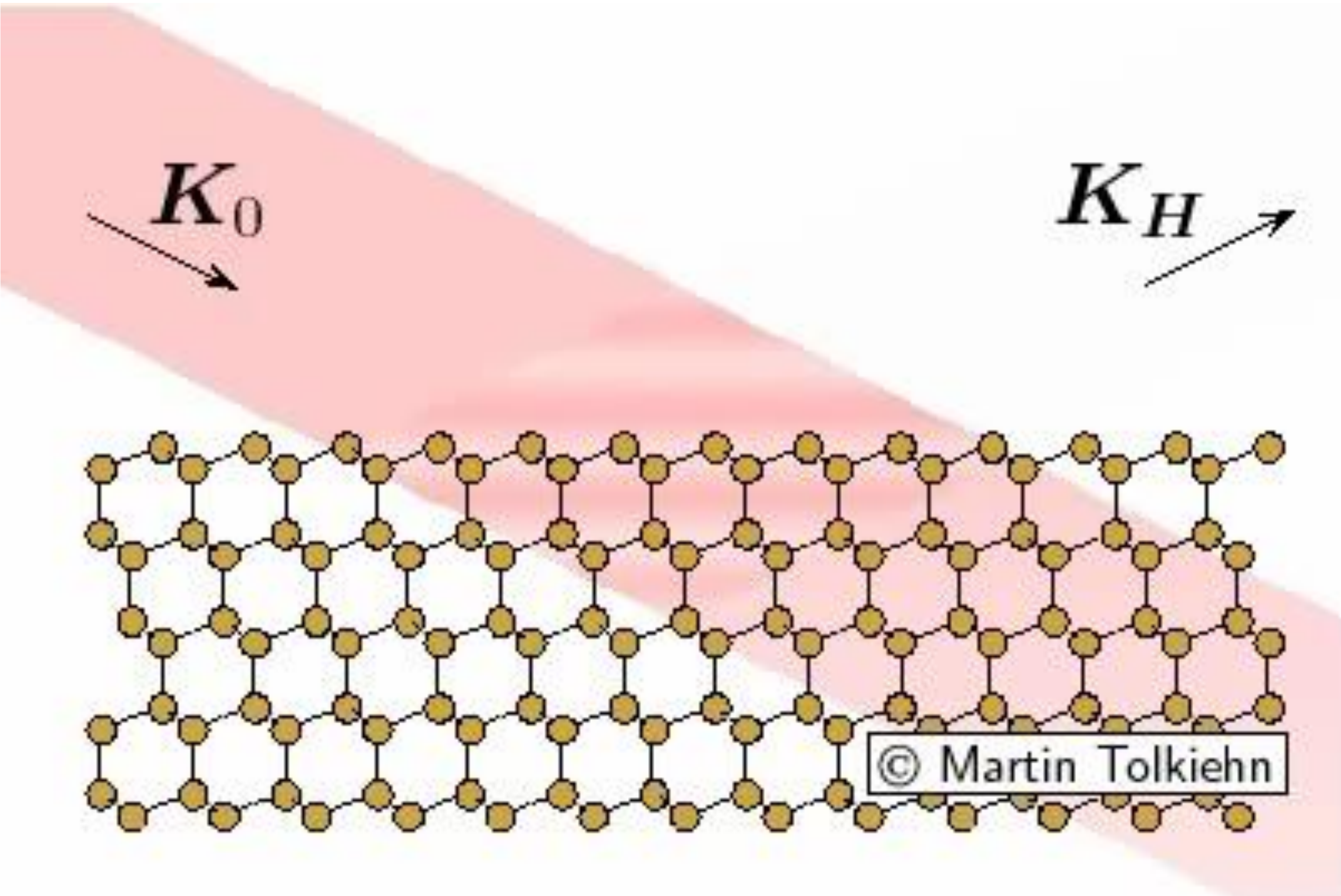
2. Photon energy scan:

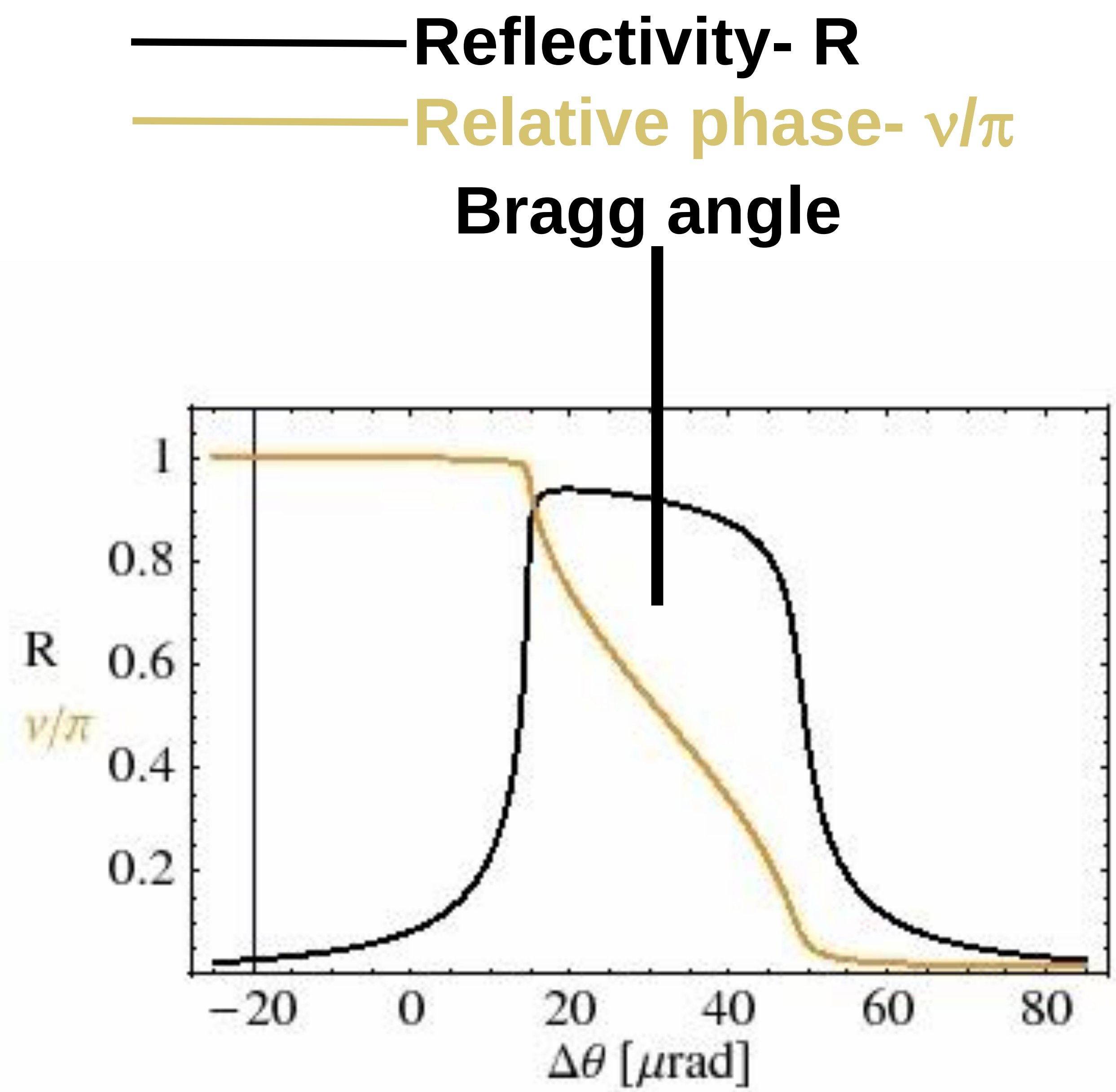
$$I(hv) \propto 1 + R(hv) + 2\sqrt{R(hv)}\, f \cos[\varphi(hv) - 2\pi P]$$

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





+Same general forms if photon energy is scanned

With thanks to Martin Tolkiehn, Dimitri Novikov, DESY

Hard x-rays, soft x-rays, and standing waves: Some example studies

6.0 keV

CrAl, FeRh: SPring8

Core-level fine structure and density of states measurements of bulk materials

3.2 & 6 keV

W; GaAs, $Ga_{1-x}Mn_xAs$: SPring8 Petra III

Core-level fine structure and angle-resolved photoemission

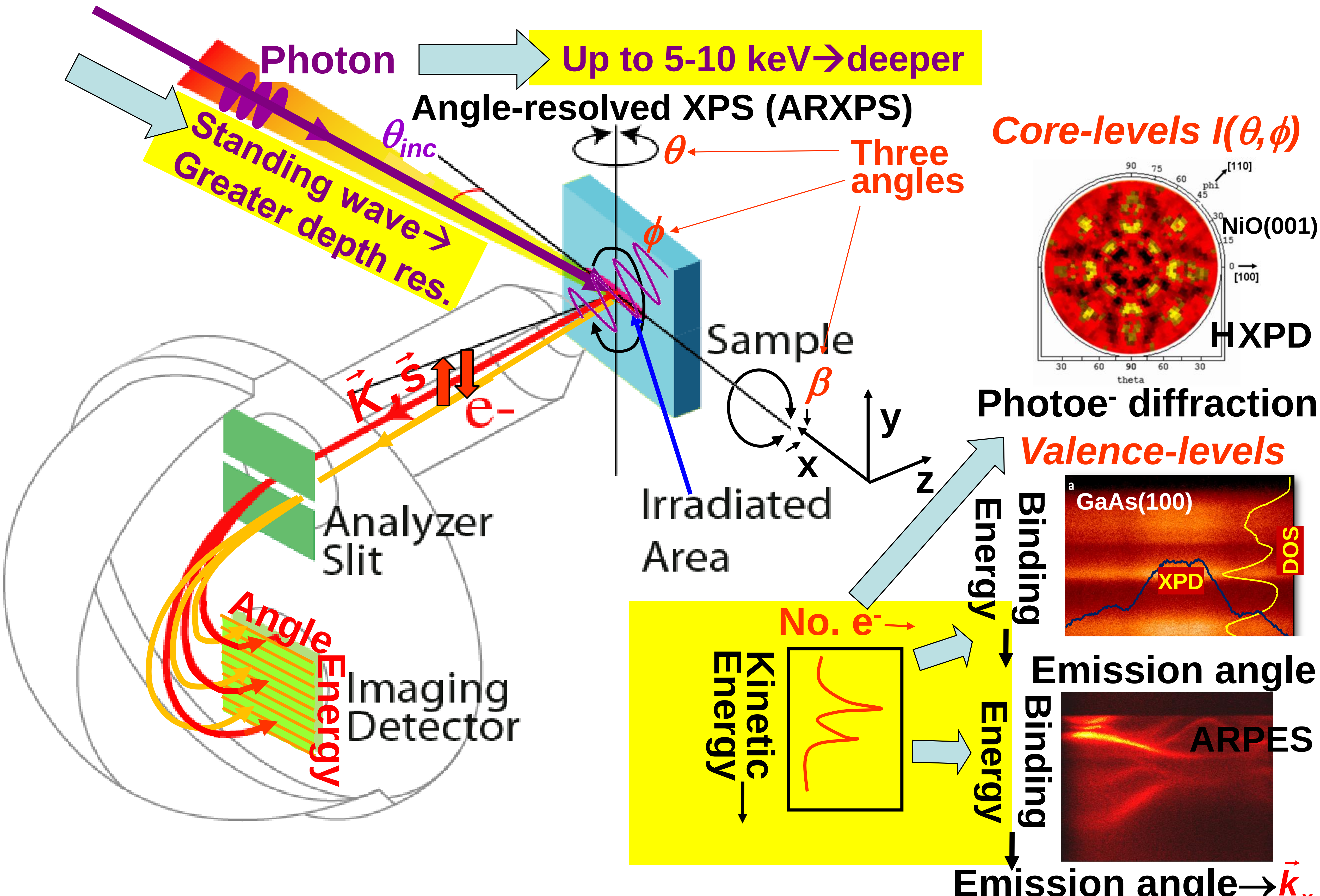
How high can we go in energy?→Bulk electronic structure!

0.8 & 6 keV

$SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$ multilayer: ALS SPring8 SLS

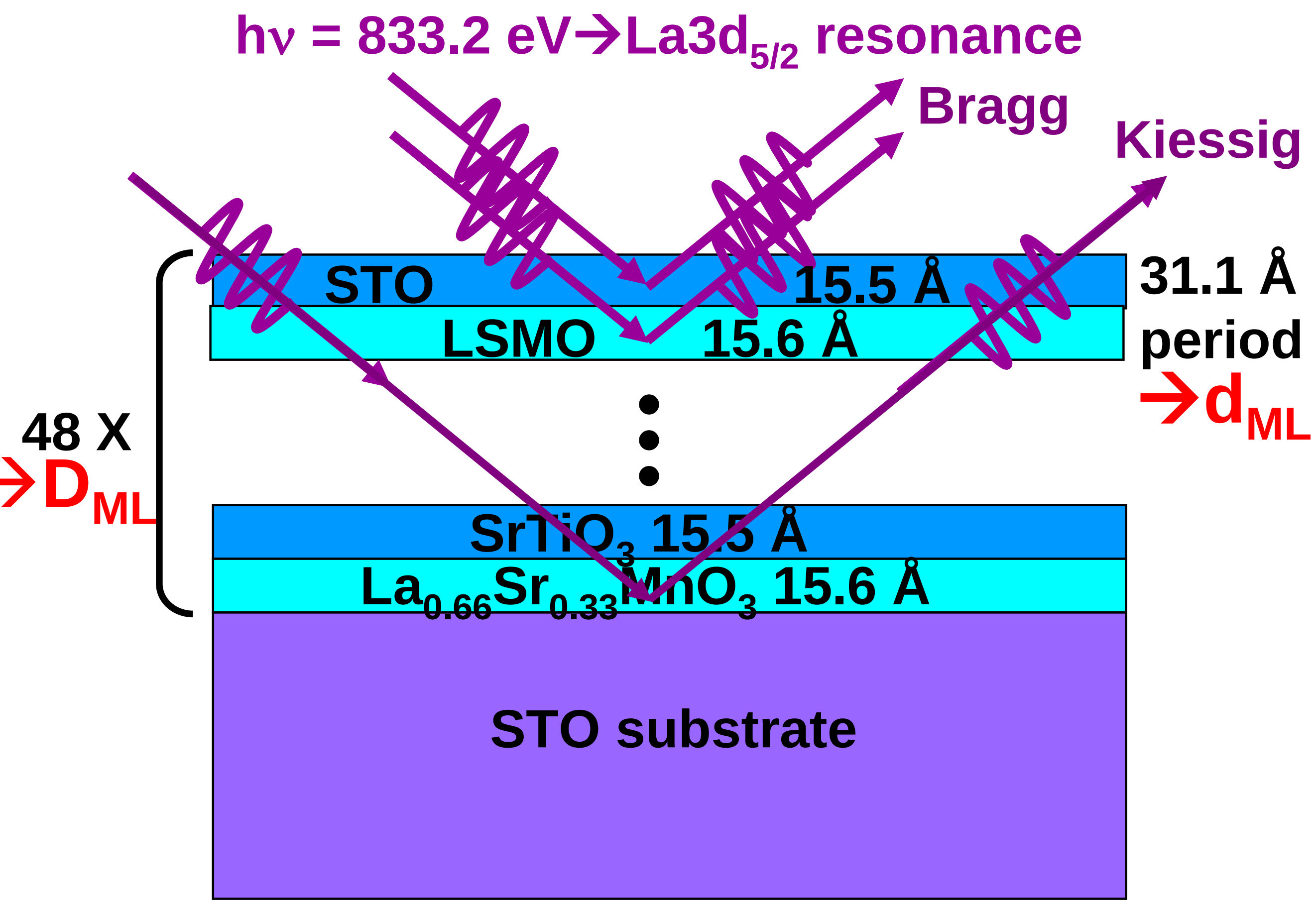
Standing-wave depth-resolved composition, dielectric properties, bonding, and band structure

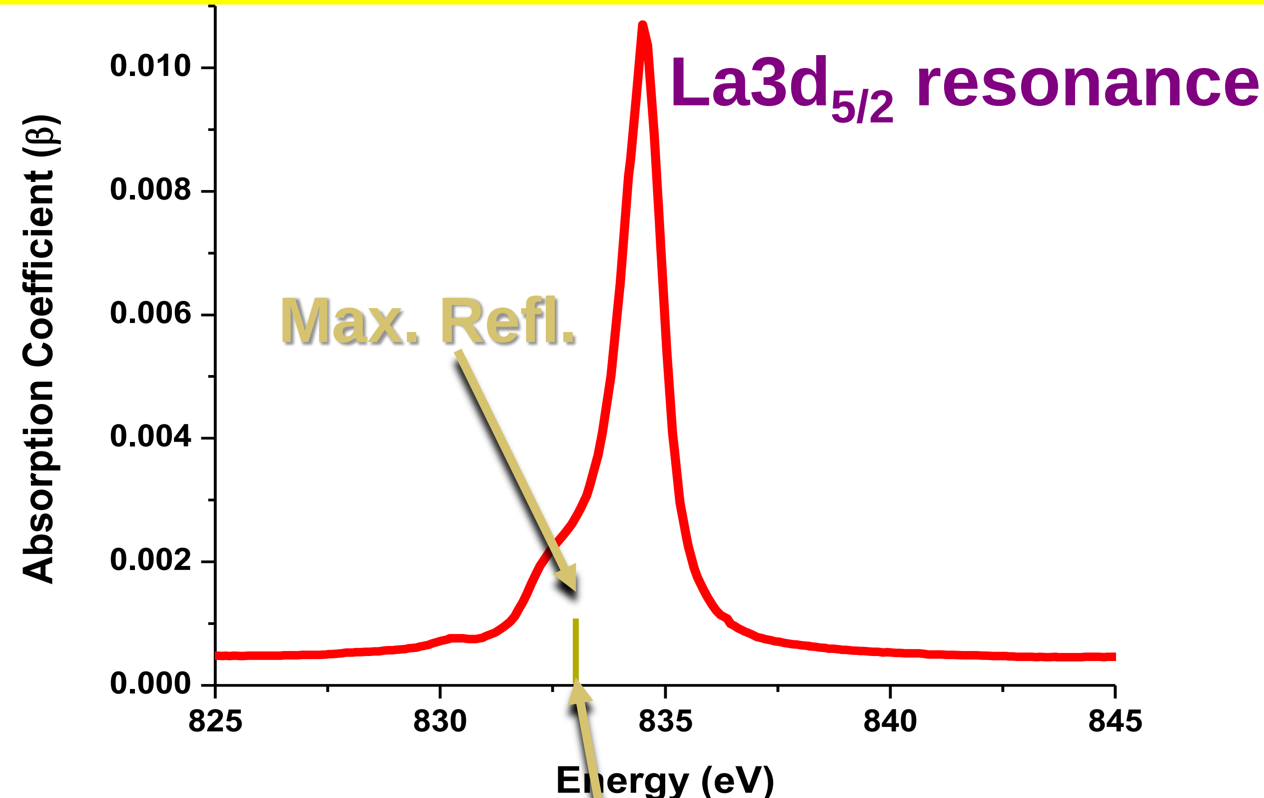
X-ray photoemission: some key elements

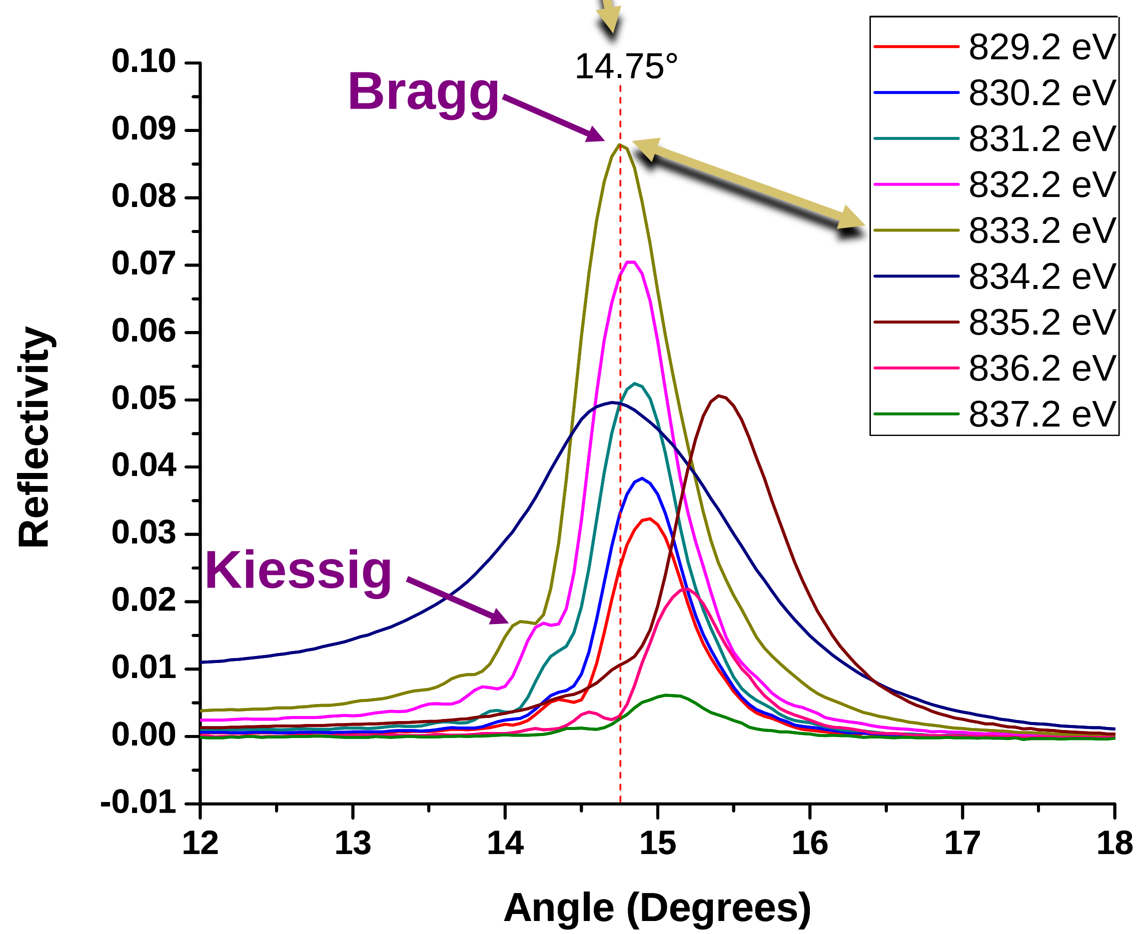


Case study: Standing wave/rocking curve analysis of an epitaxial $SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ interface: Resonant soft x-ray excitation

The Advanced Light Source



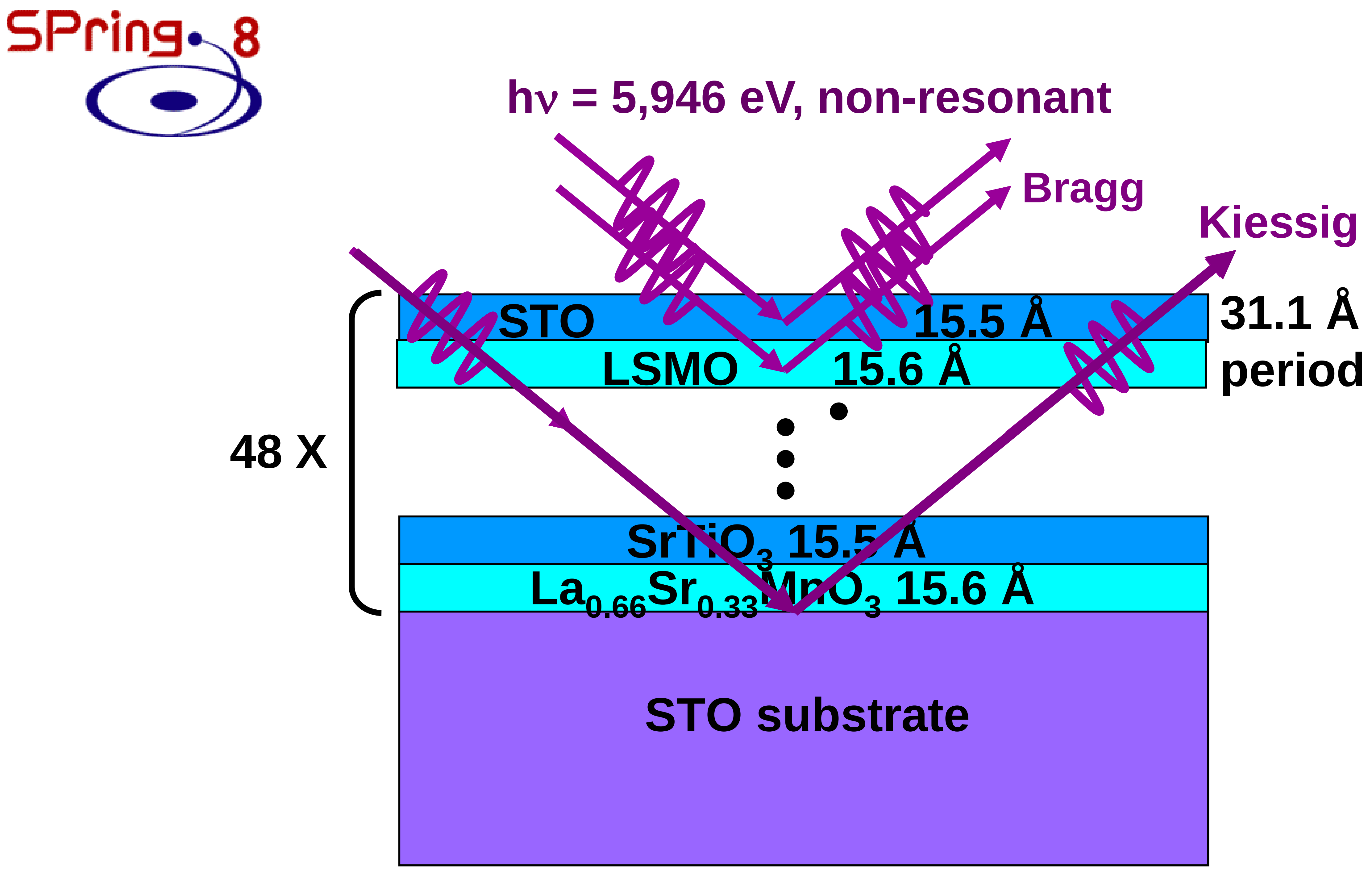




$$\lambda_x = 2d_{ML}\sin\theta_{Bragg}$$

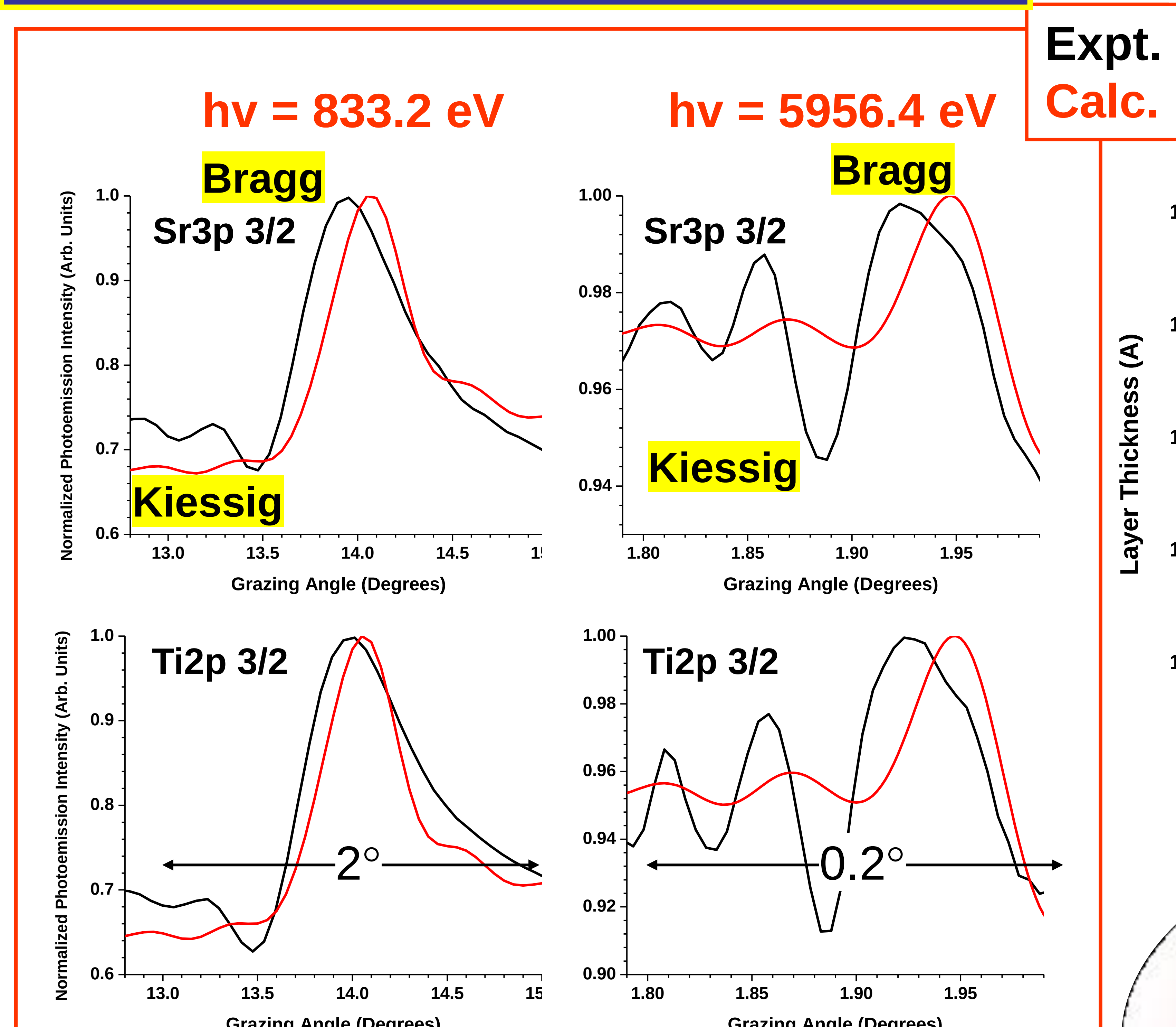
Gray et al., Phys. Rev. B 82, 205116 (2010)
Samples: Ramesh, Huijben

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

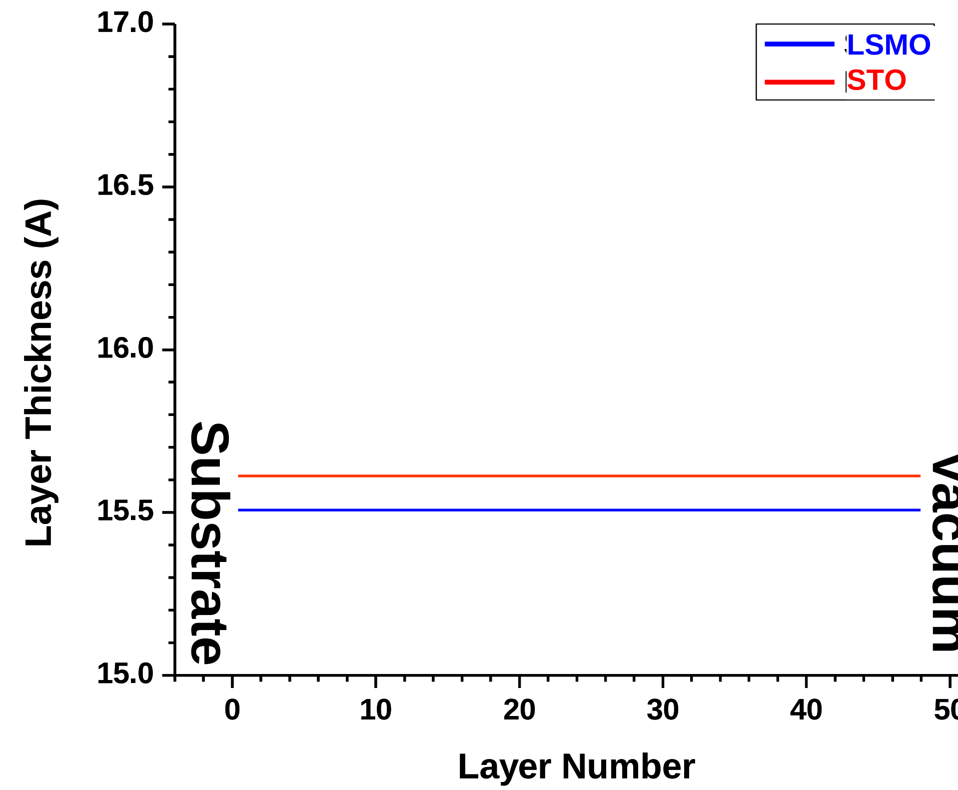


Gray et al., Phys. Rev. B 82, 205116 (2010)
Samples: Ramesh, Huijben

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



Ideal Bilayer Thickness Gradient Profile



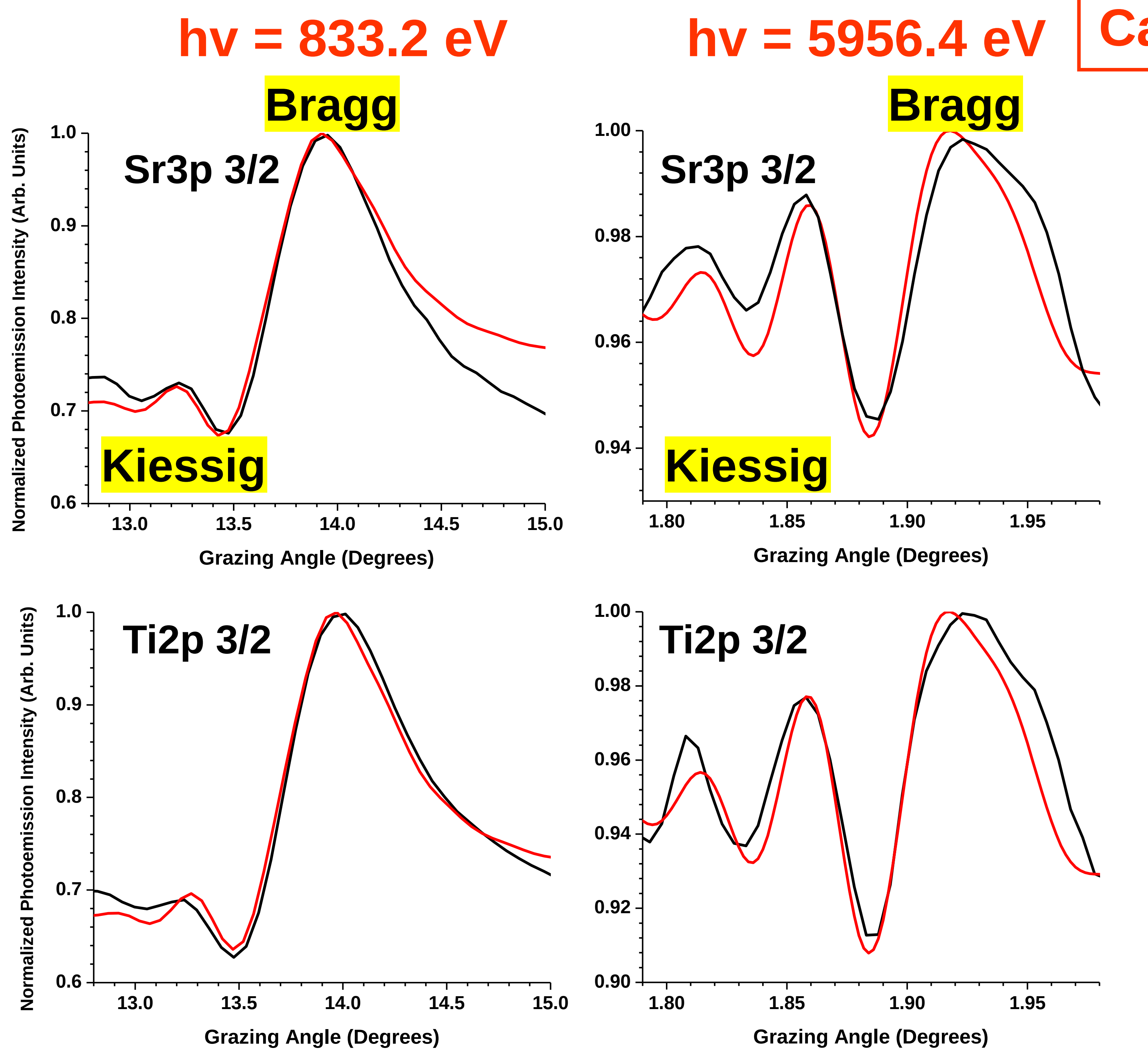
- Relative amplitude of the predicted Kiessig fringes does not agree with experiment
- Strong Kiessig fringes predicted on both sides of the rocking curves, esp. 5.9 keV

The Advanced Light Source

SPring-8

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

Exp.
Calc.

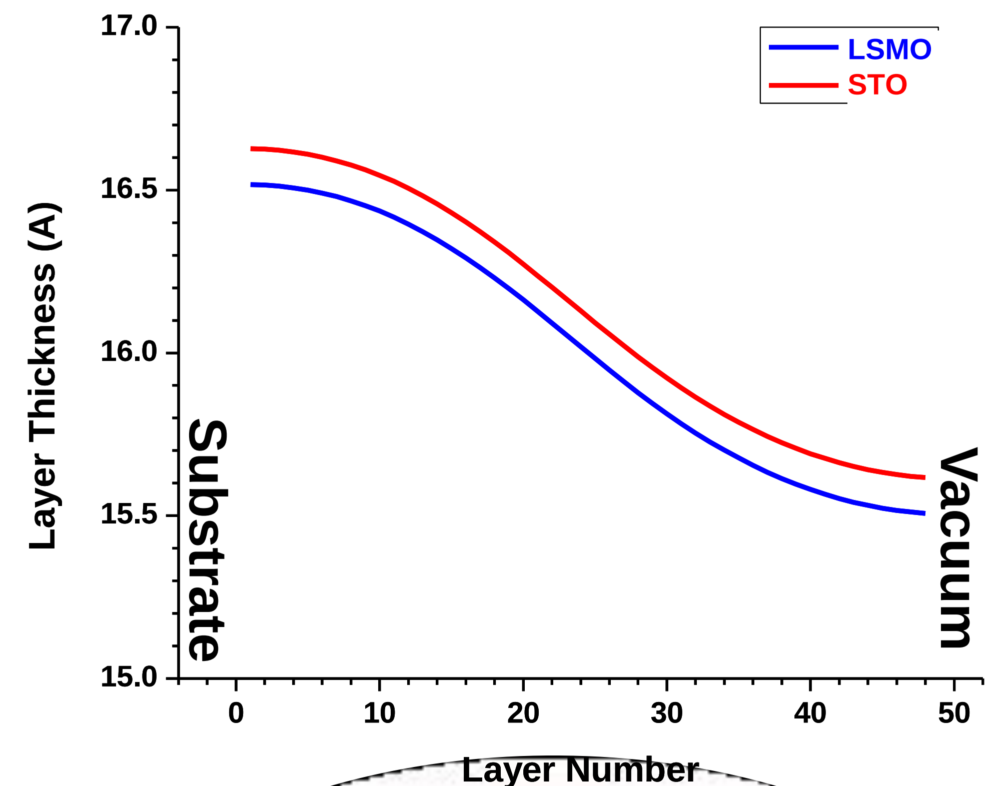


BEST FIT

The Advanced Light Source

SPring-8

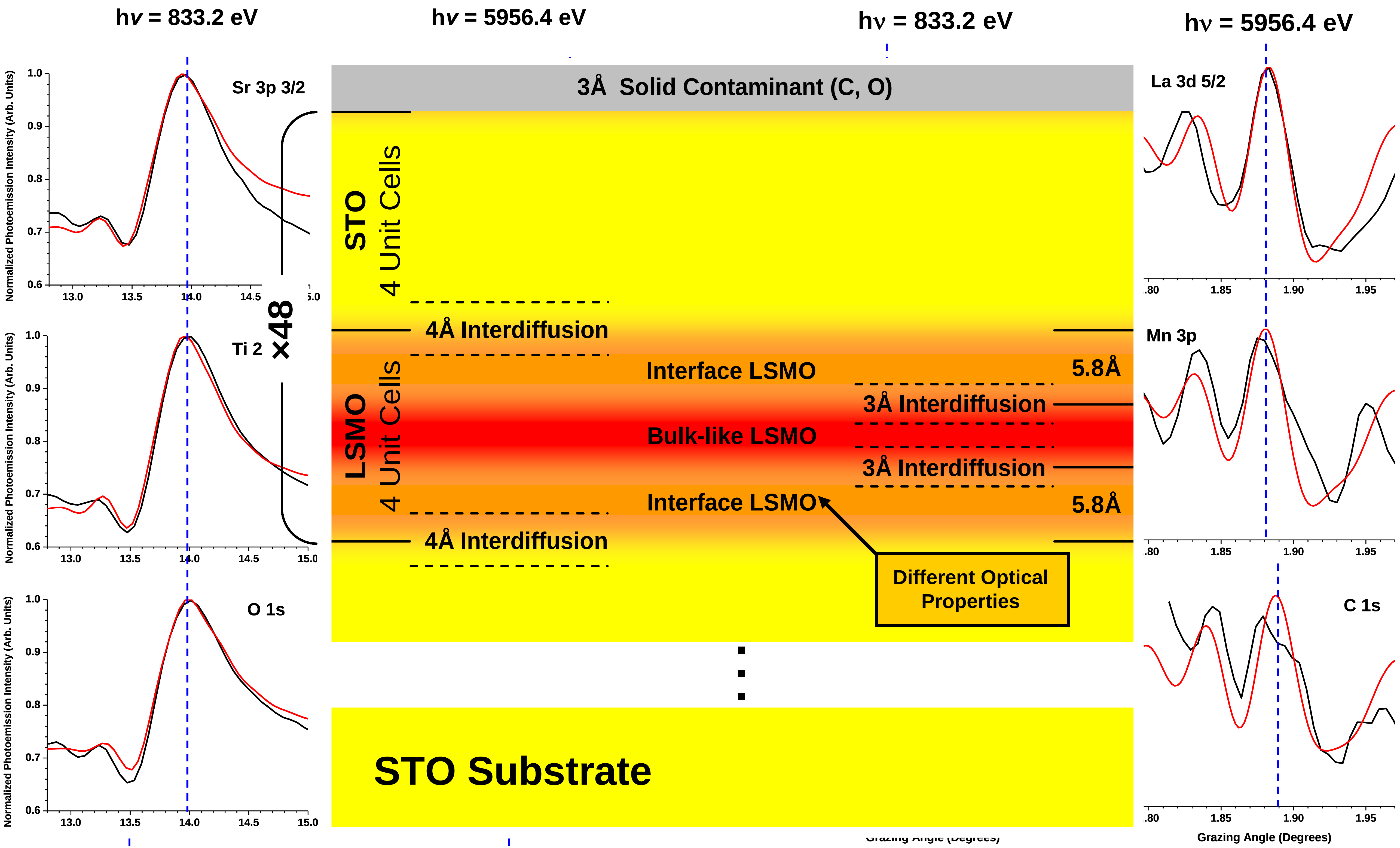
Bilayer Thickness Gradient Profile



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

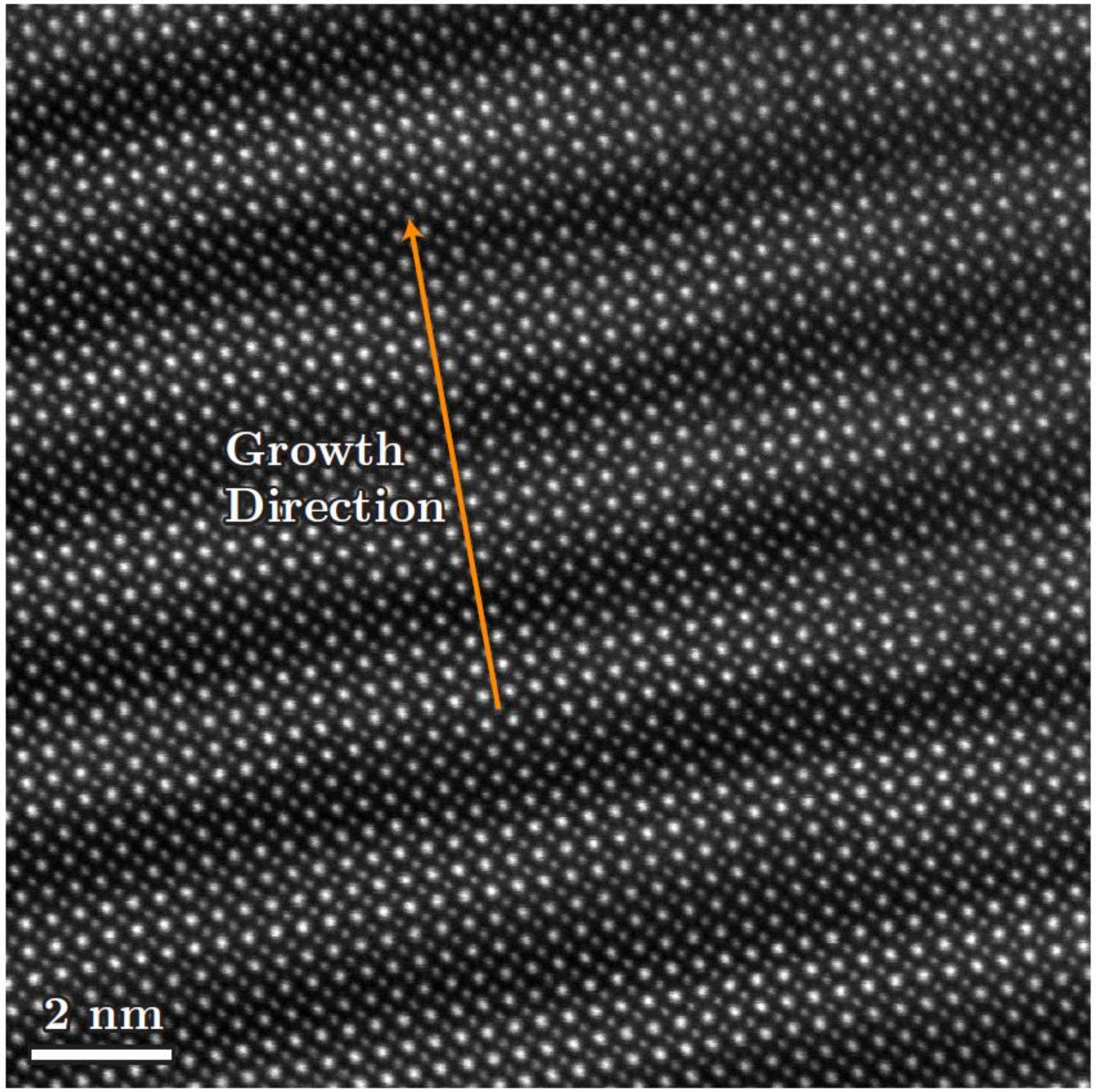
Gray et al., Phys. Rev. B 82, 205116 (2010)

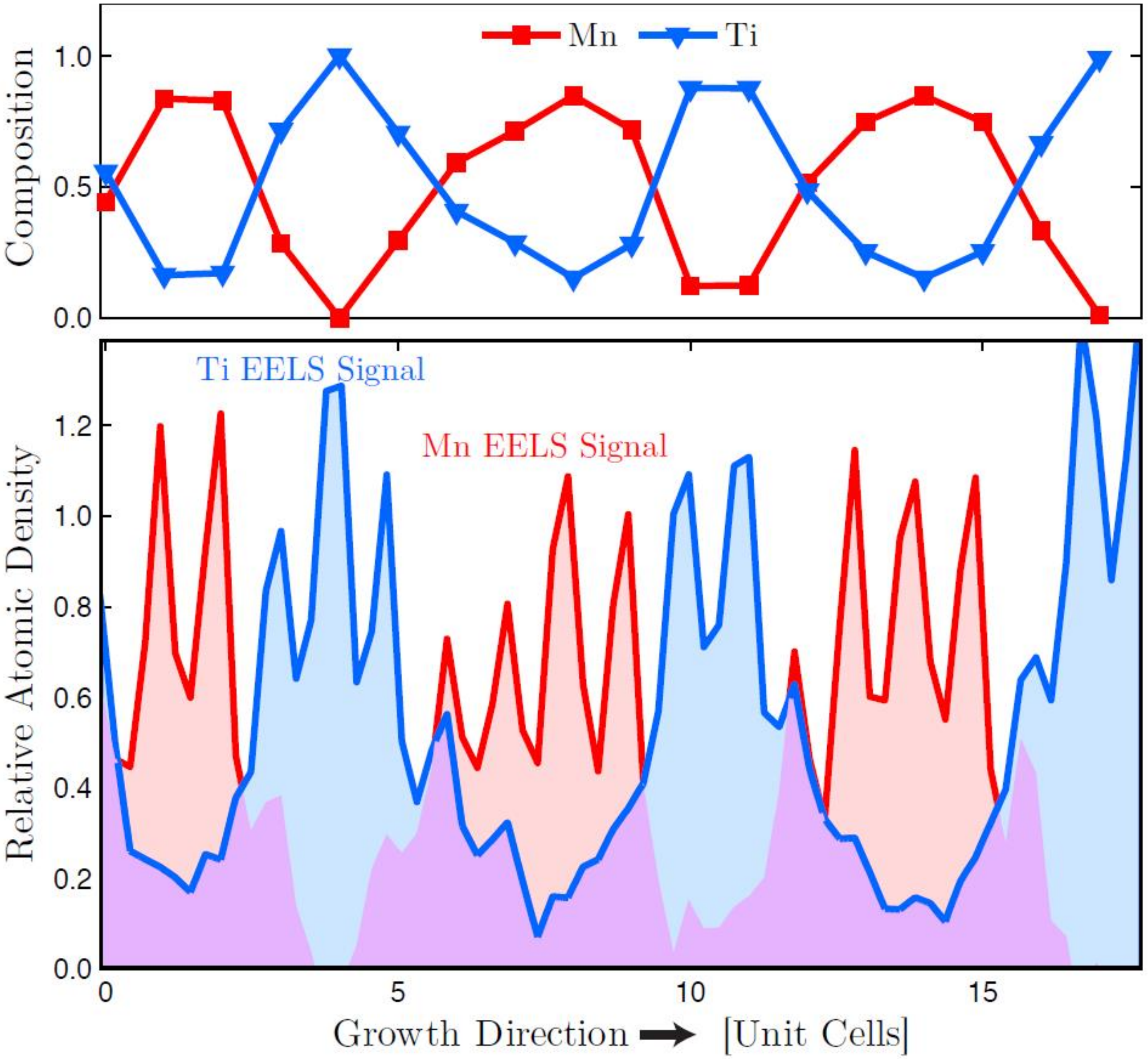
Fitting of Rocking Curves—All Elements Present, Soft and Hard X-rays



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

TEM with EELS-Confirms Conclusions of Standing-Wave Photoemission

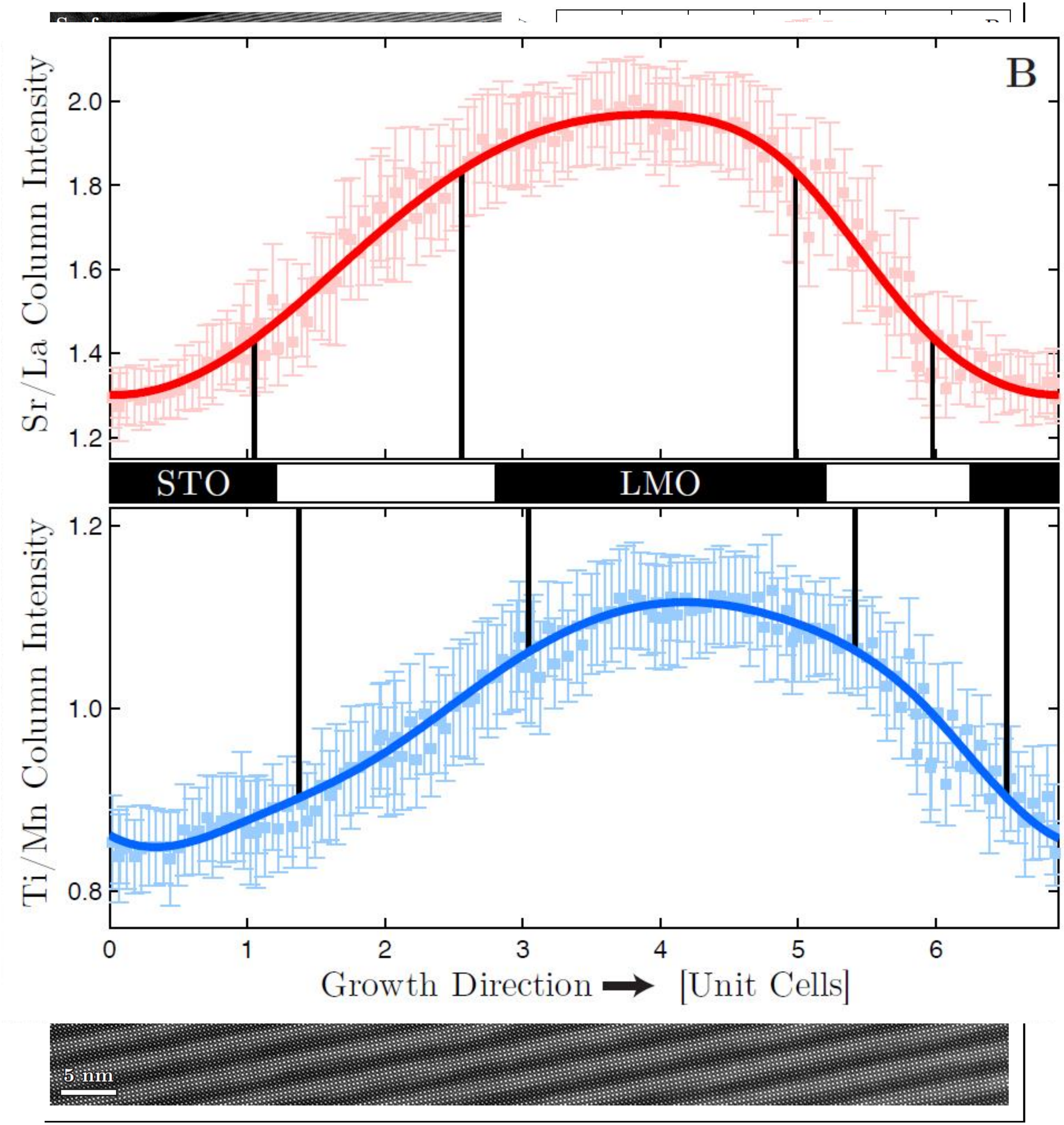




Also confirms change in bilayer spacing from top to bottom

Measurements at Nat'l. Center for Electron Microscopy, LBNL by
J. Ciston, C. Ophus, M. Mancuso

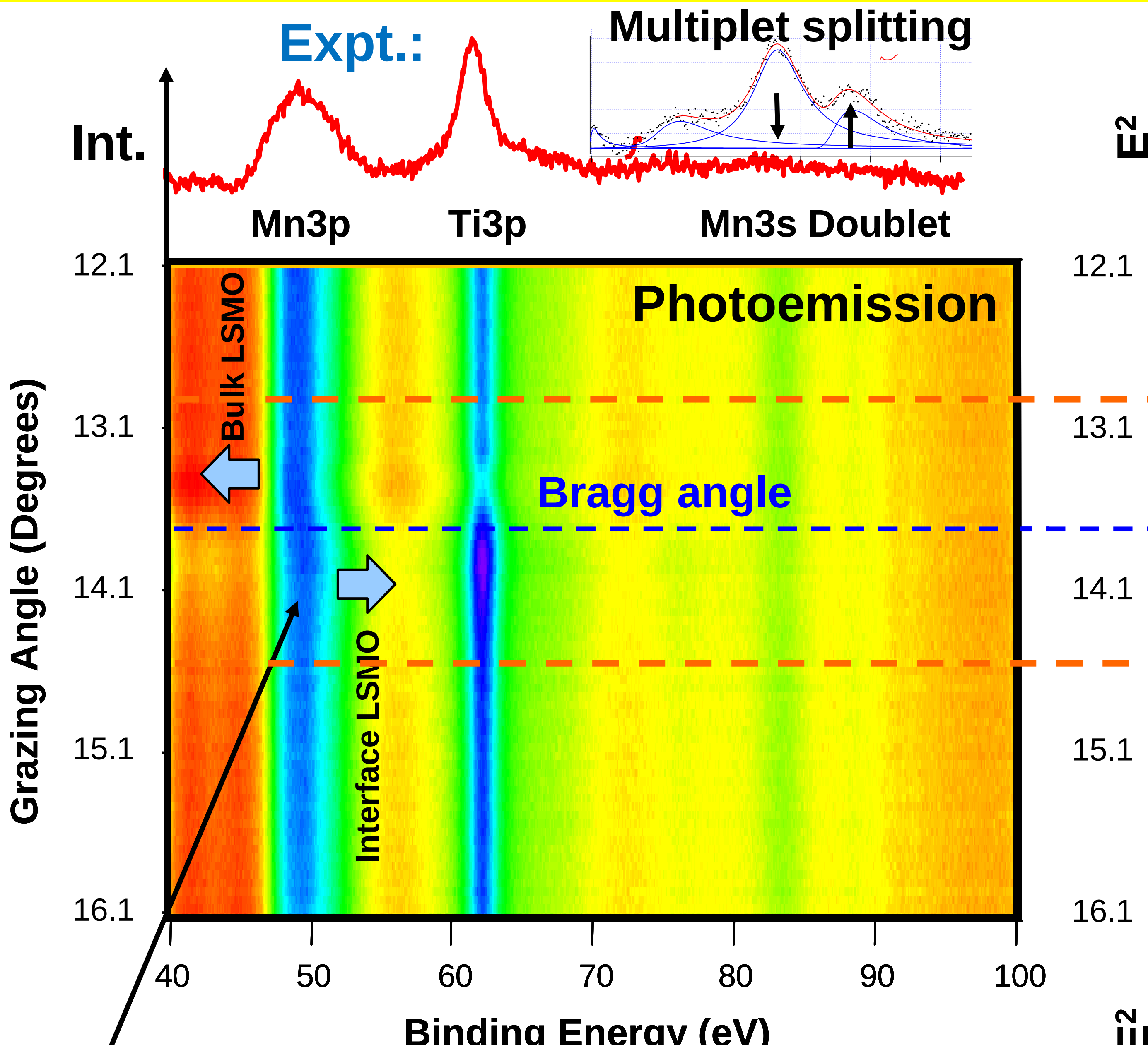
TEM with EELS-Confirms Conclusions of Standing-Wave Photoemission

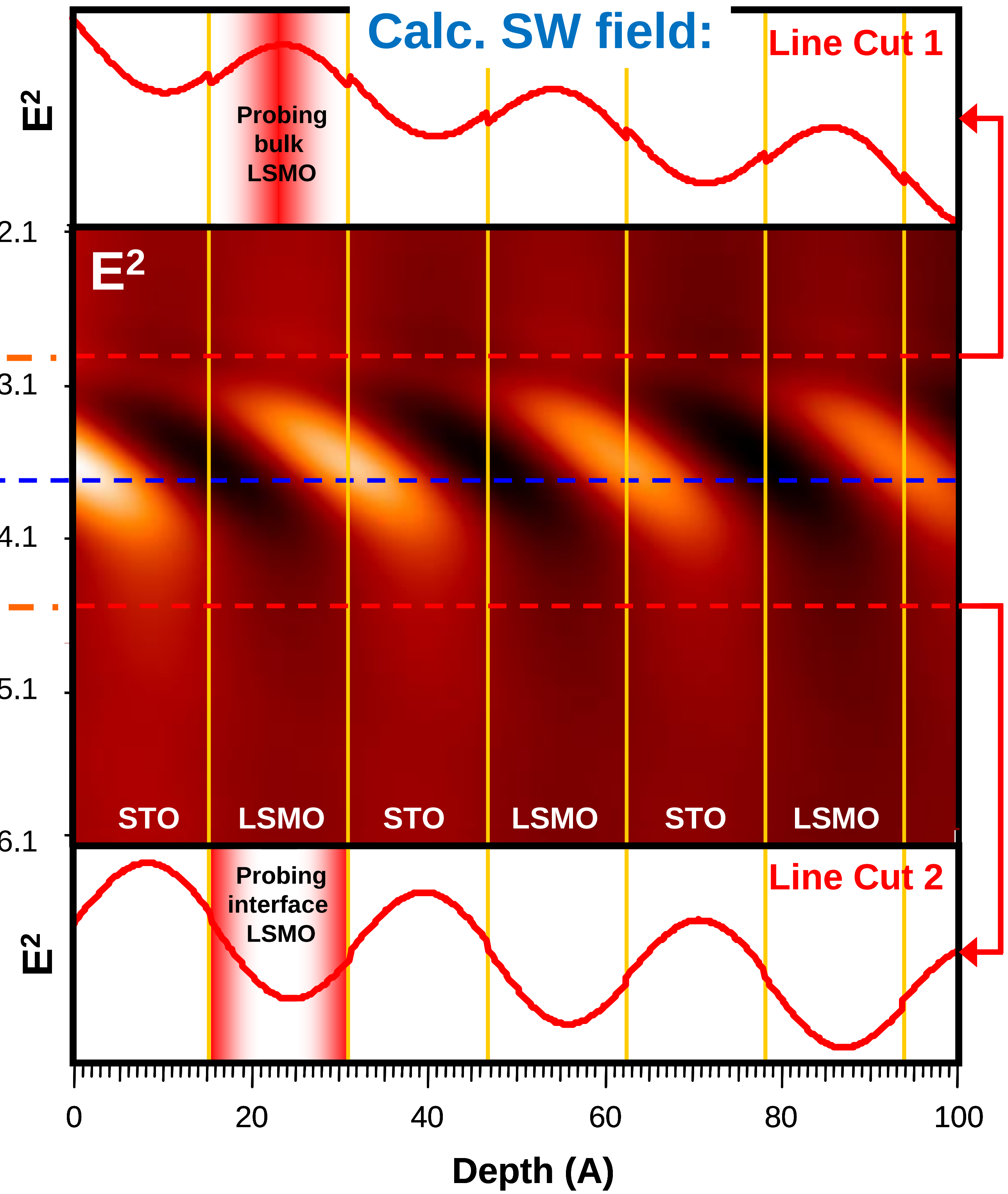


- Top and bottom interfaces of difference thicknesses
- Photoemission most sensitive to top interface

Measurements at Nat'l. Center for Electron Microscopy, LBNL by J. Ciston, C. Ophus, M. Mancuso

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

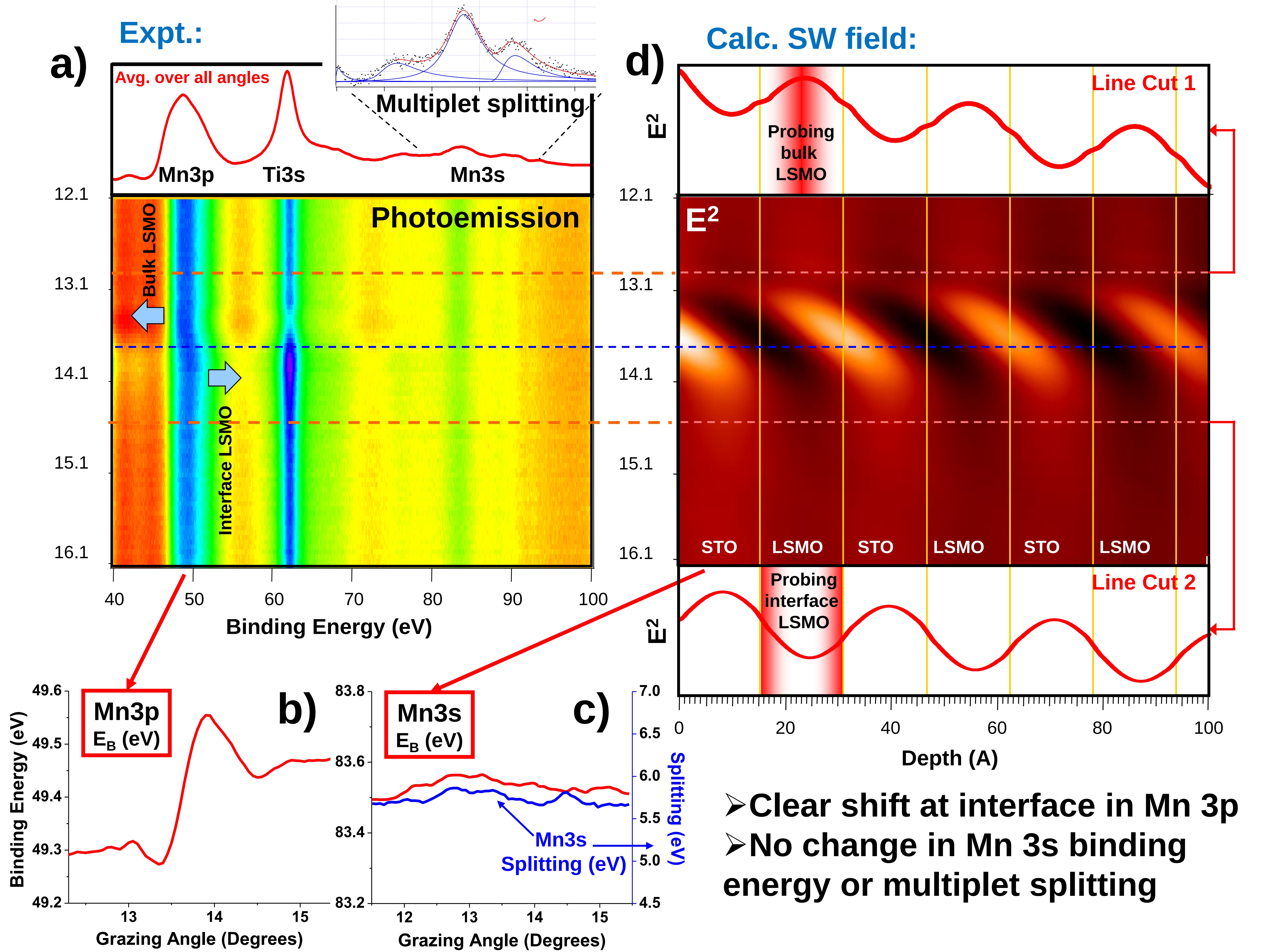




- ➢Clear chemical/final-state shift at interface seen in Mn 3p
- ➢No change in Mn 3s
- ➢No change in Ti 3p—near surface

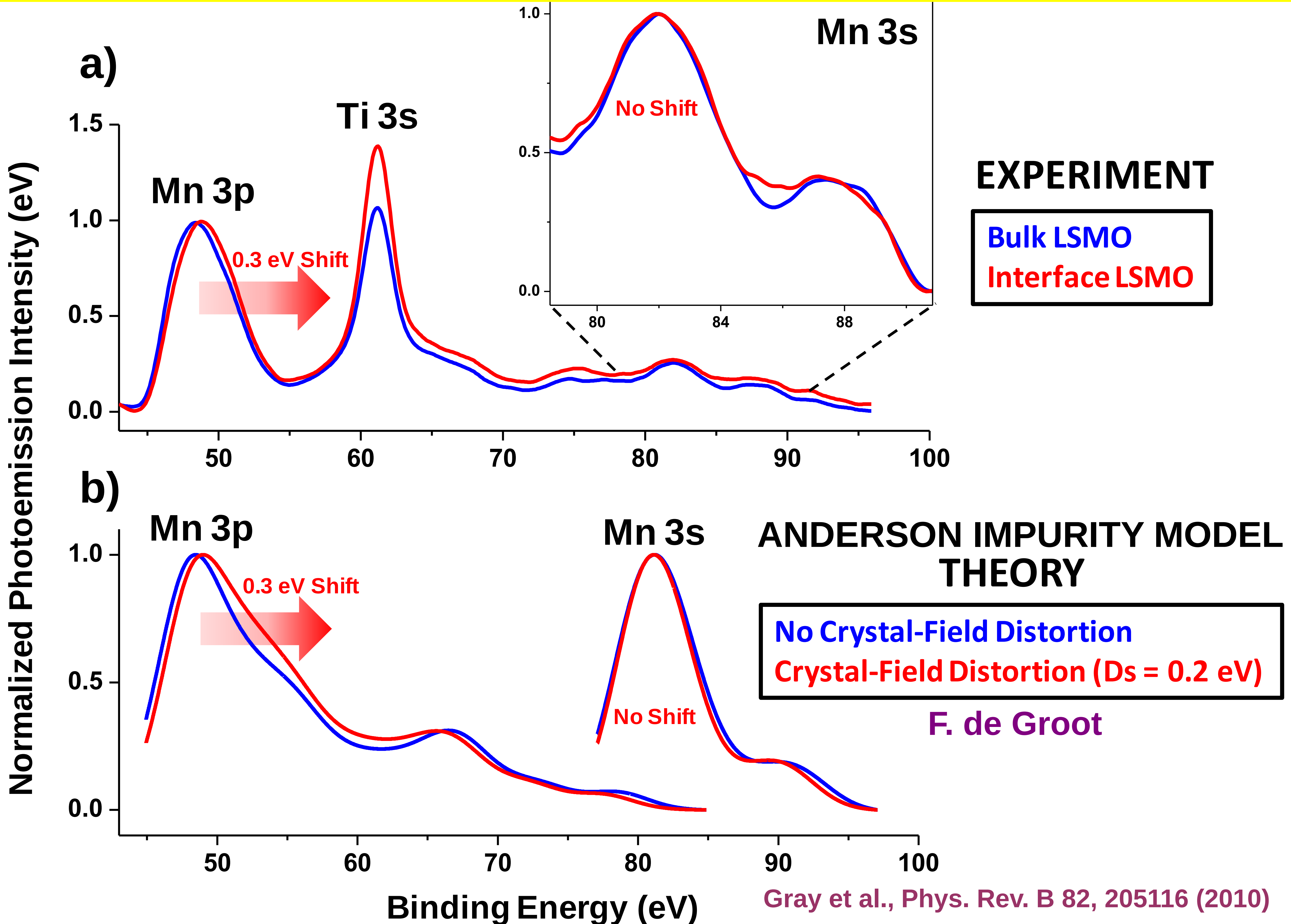
The Advanced Light Source

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



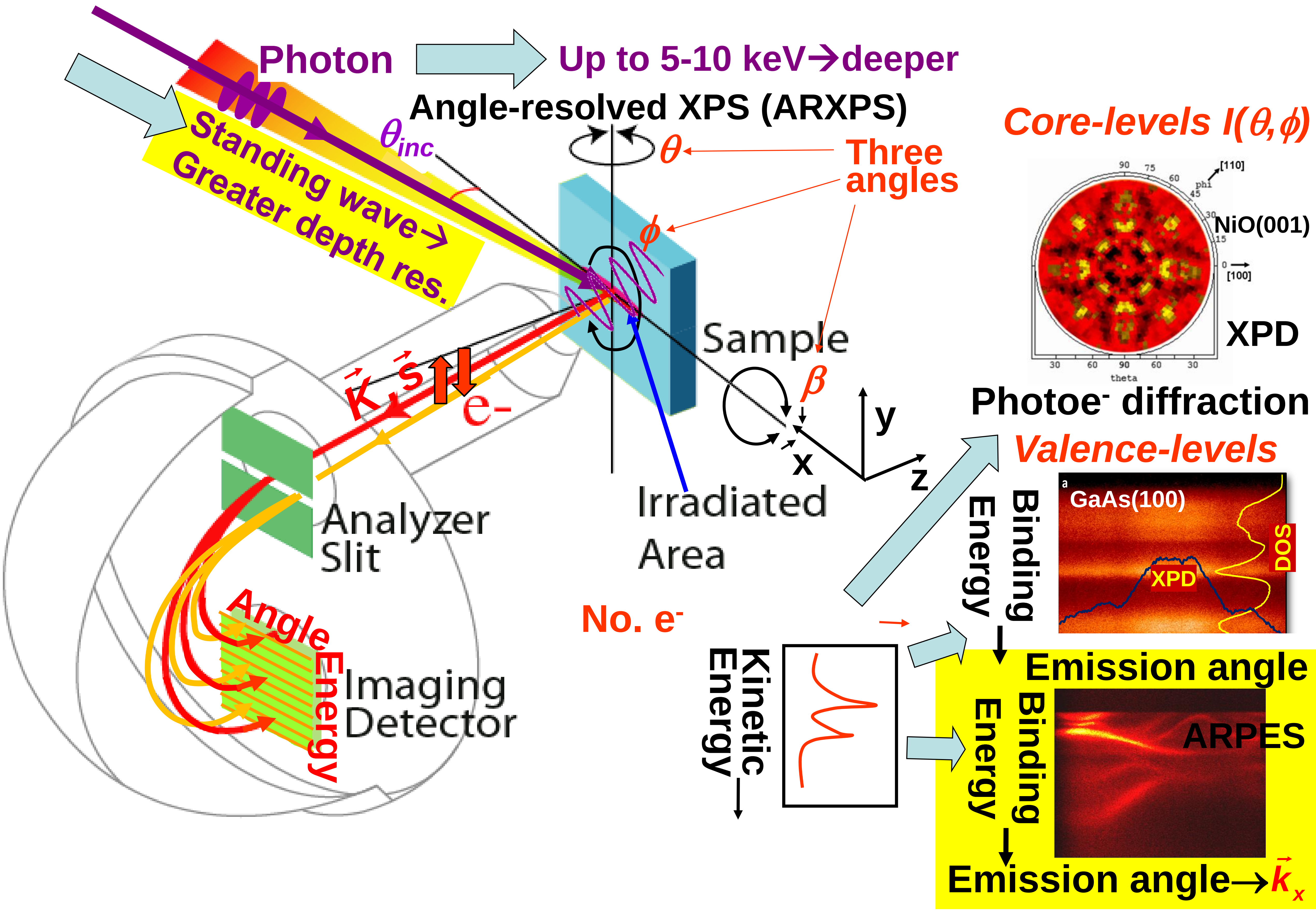
- ➢Clear shift at interface in Mn 3p
- ➢No change in Mn 3s binding energy or multiplet splitting

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

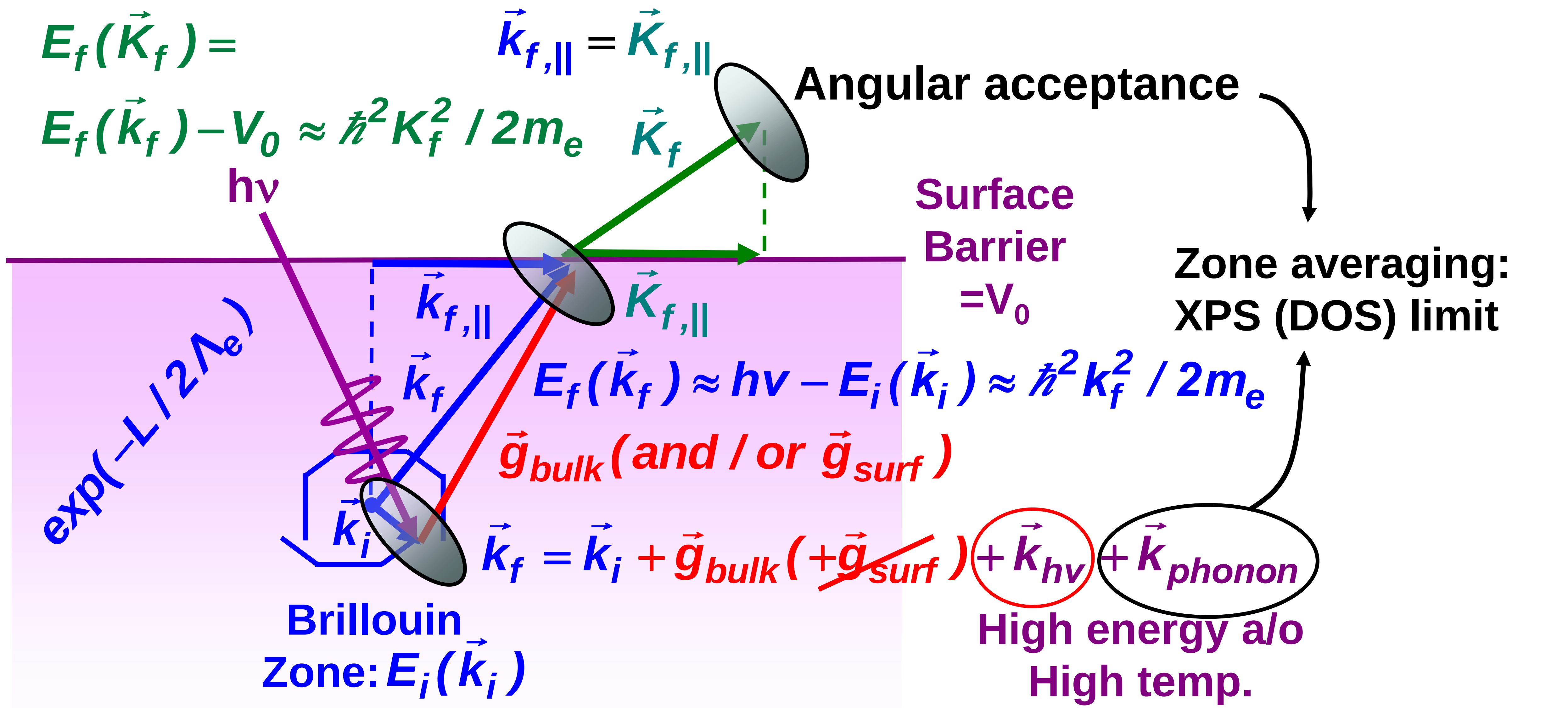


Gray et al., Phys. Rev. B 82, 205116 (2010)

X-ray photoemission: some key elements



ARPES—How high can we go in energy and temperature?



Fraction DTs ≈ Debye-Waller factor = $W(T) \approx \exp[-(k^f)^2 \langle u^2(T) \rangle]$

$\approx \exp[-C_1 (k^f)^2 T / (m\Theta_D^2)] \approx \exp(-C_2 E_{kin} T)$

$W \approx 1$

ARPES → bands, quasiparticles (Low hν, Low T, High angul. Res.)

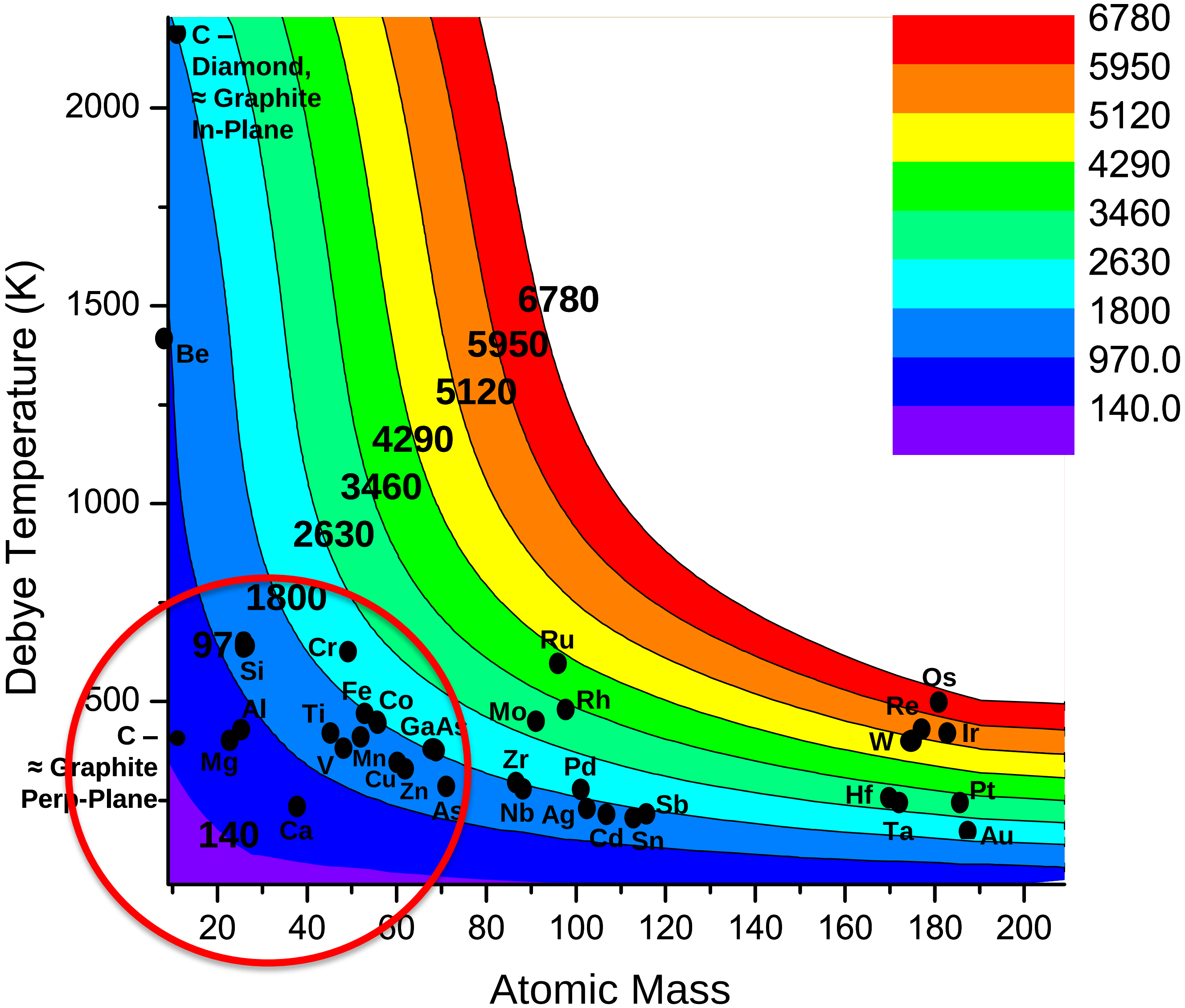
$W \approx 0$

XPS → DOS+XPD (High hν, High T, Low angul. Res.)

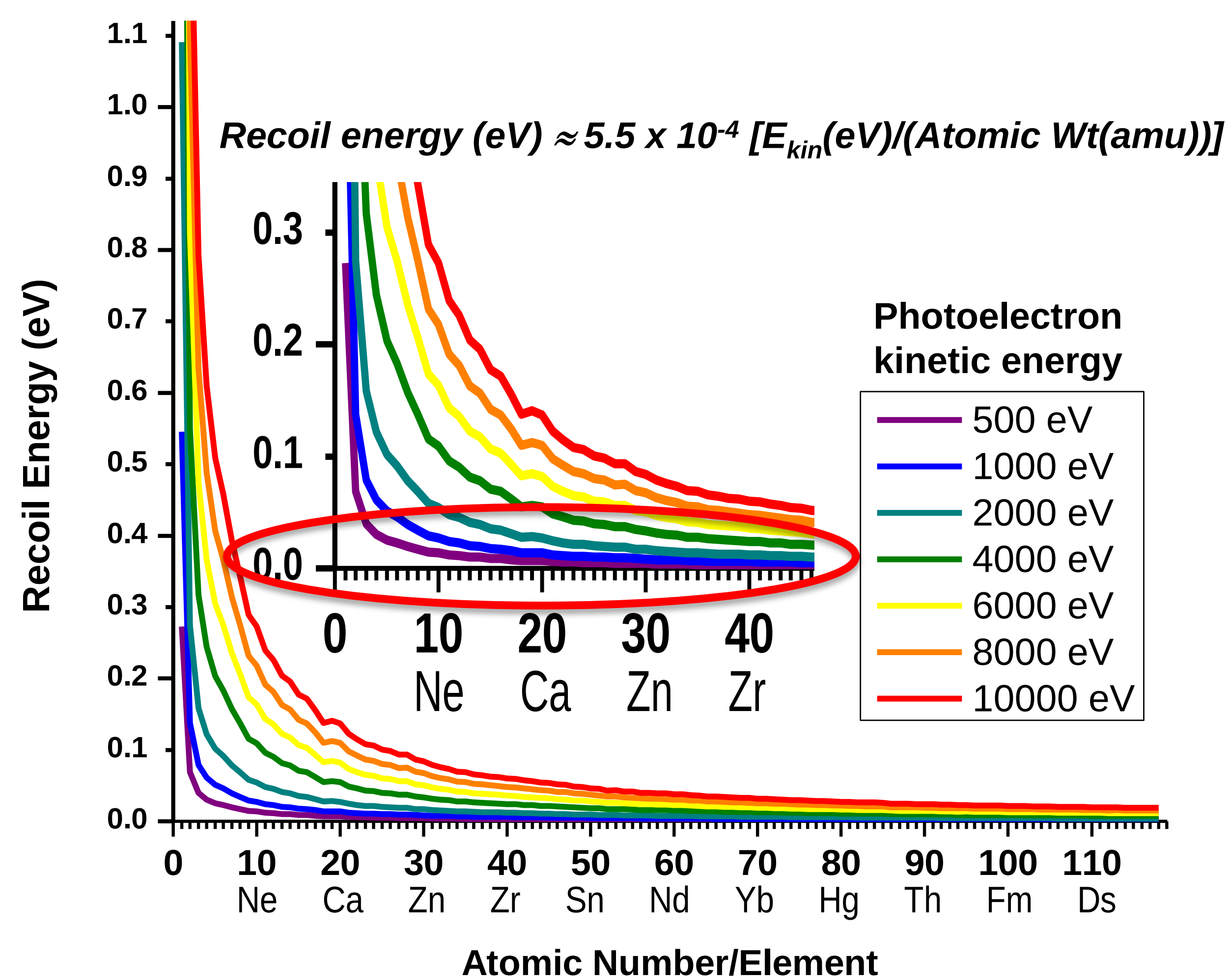
Shevchik, Phys. Rev. B 16, 3428 (1977)
Hussain….CF, Phys. Rev. B 34 (1986) 5226

ARPES→HARPES-How high can we go? Photoemission Debye-Waller Factors and Recoil Energies

Photon energy for ~50% DTs = O.5 D-W @ 20K

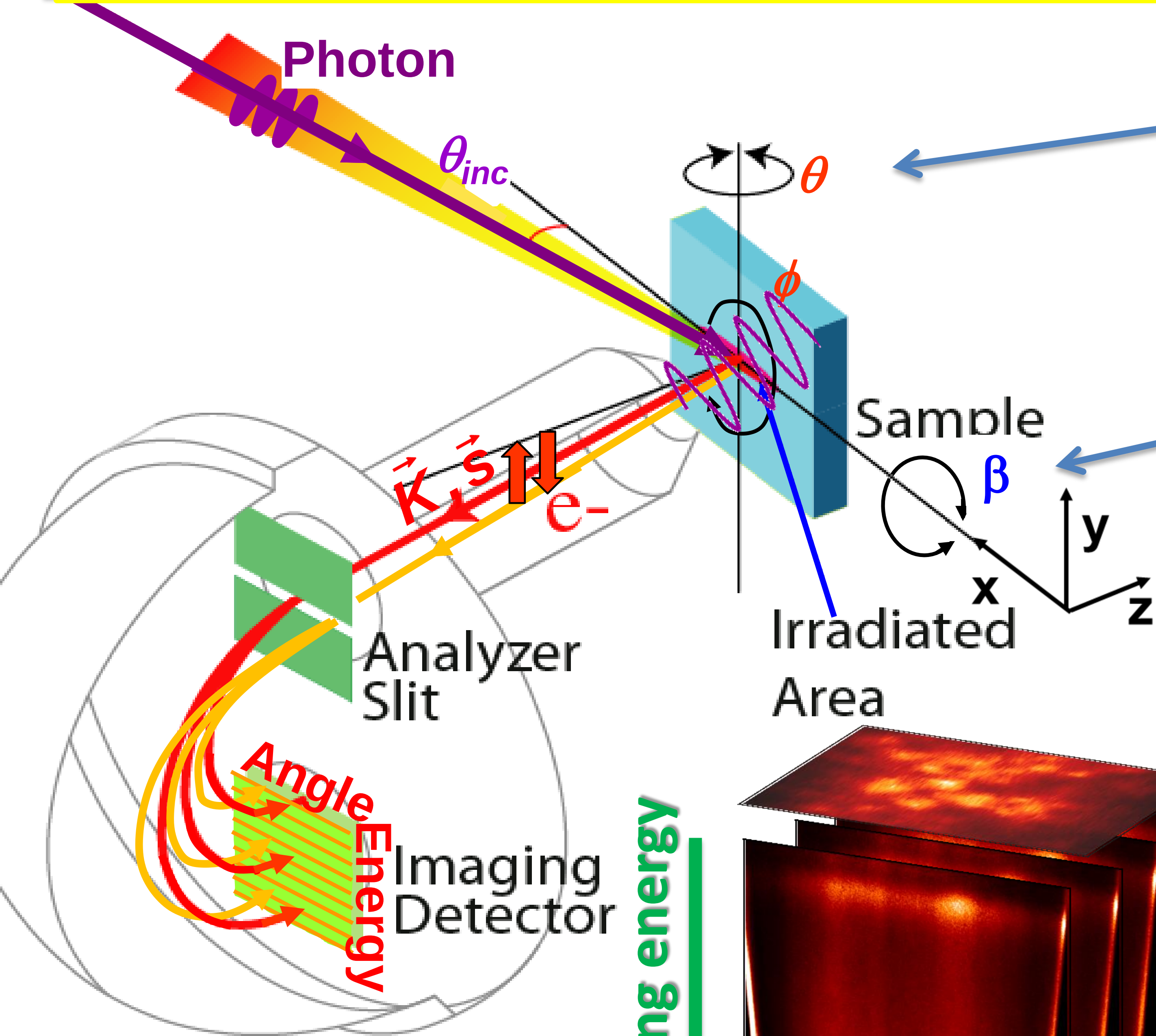


Recoil energy for all atoms and different photon energies



C. Papp. L. Plucinski, et al.,
Phys. Rev. B 84, 045433 (2011)

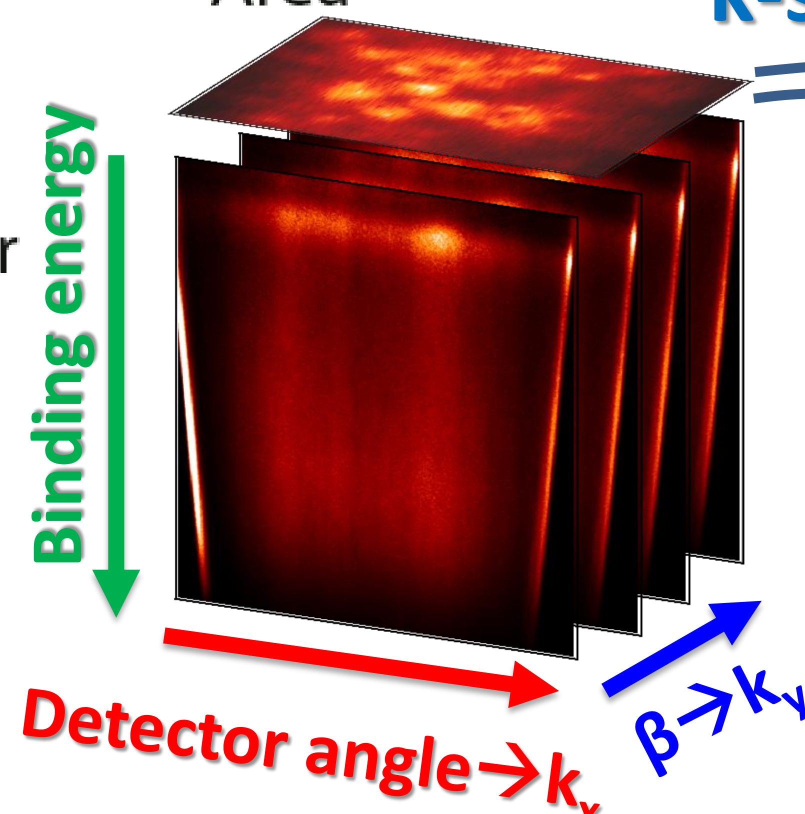
Standing-wave angle-resolved photoemission

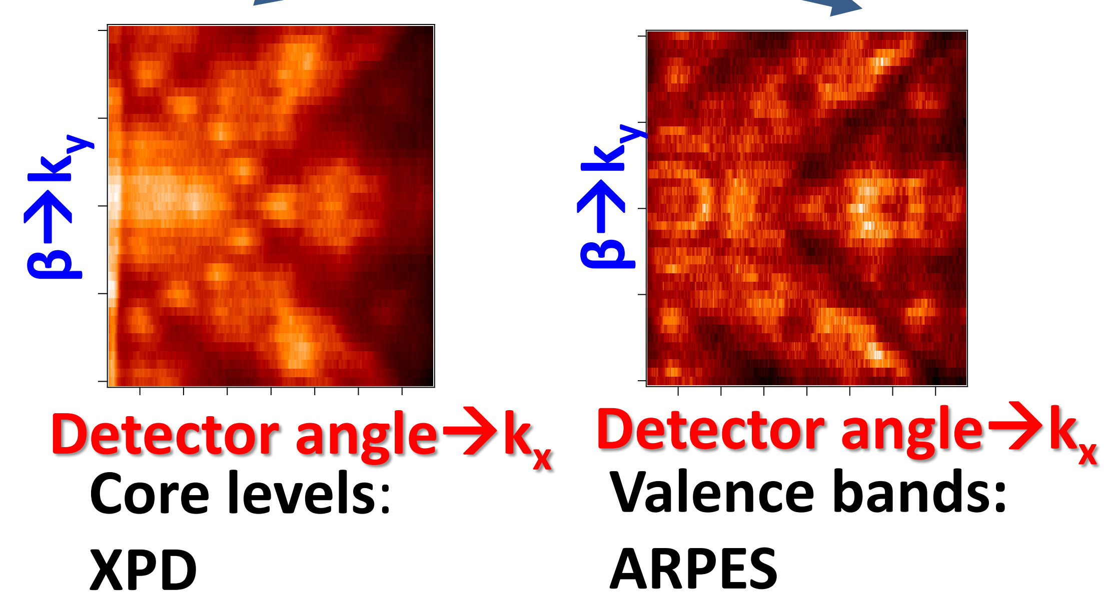


Variation of Θ_{inc}:
Change of incidence angle
⇨Standing wave sweeps

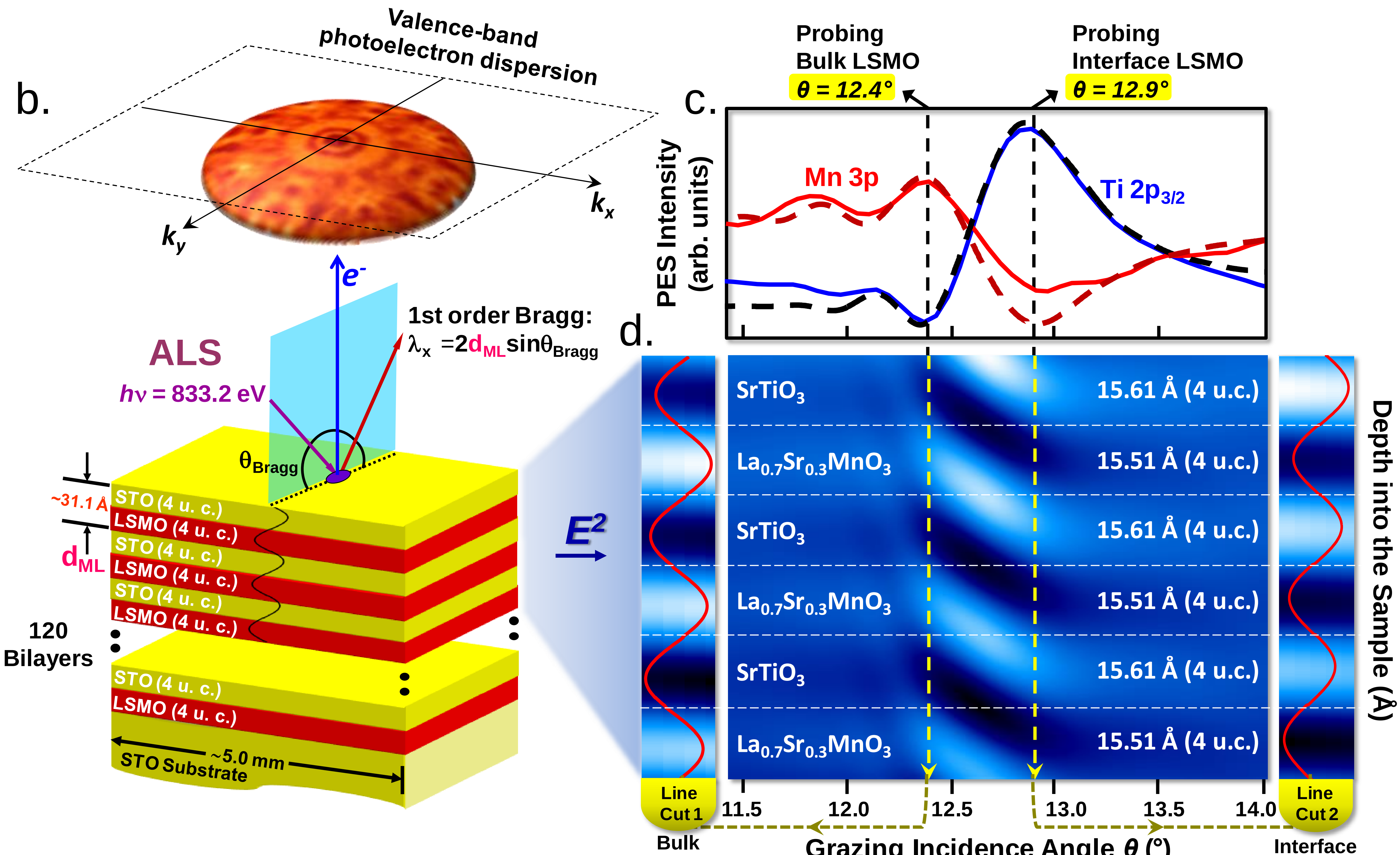
Variation of β:
Change of takeoff angle
⇨ Electron energies for
different $\mathbf{k}_y$ vectors

k-space mapping





Depth-Resolved Soft X-Ray ARPES?

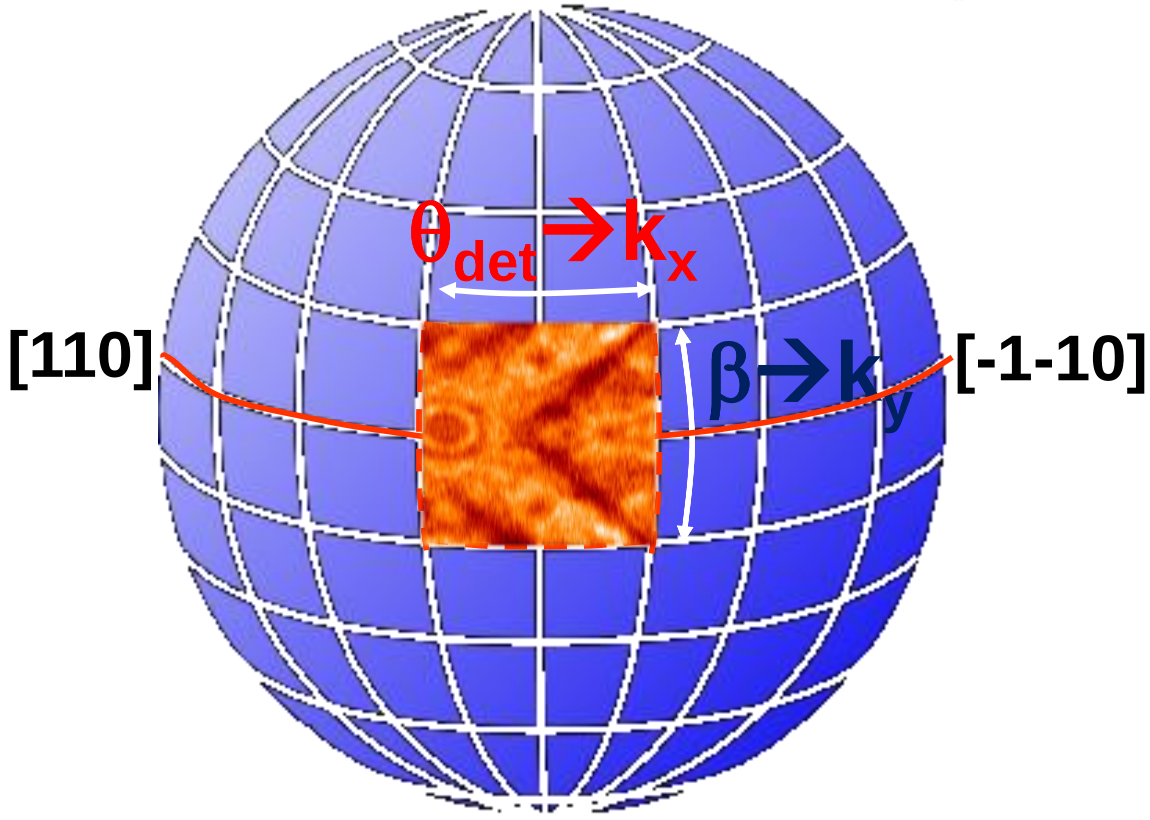


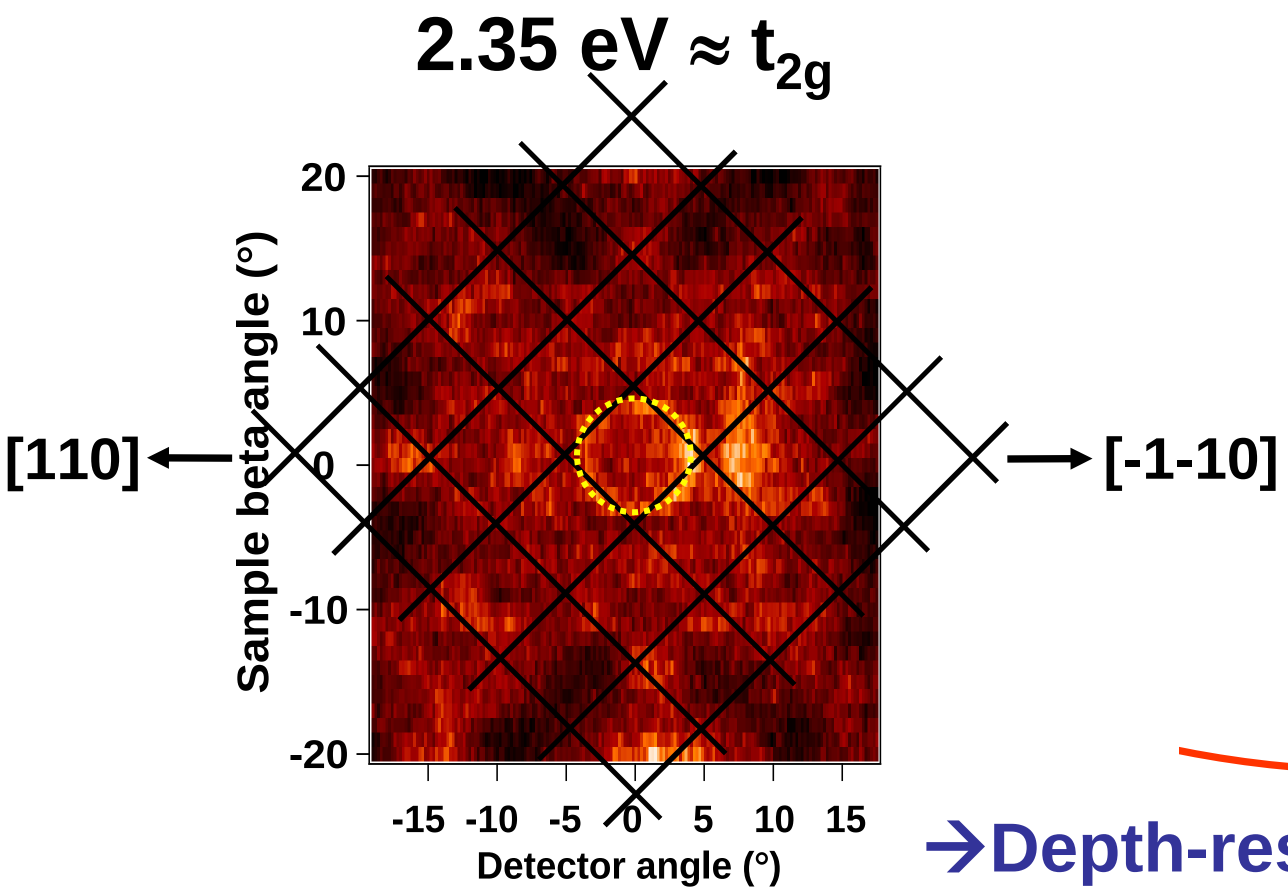
Sample: Huijben, Ramesh

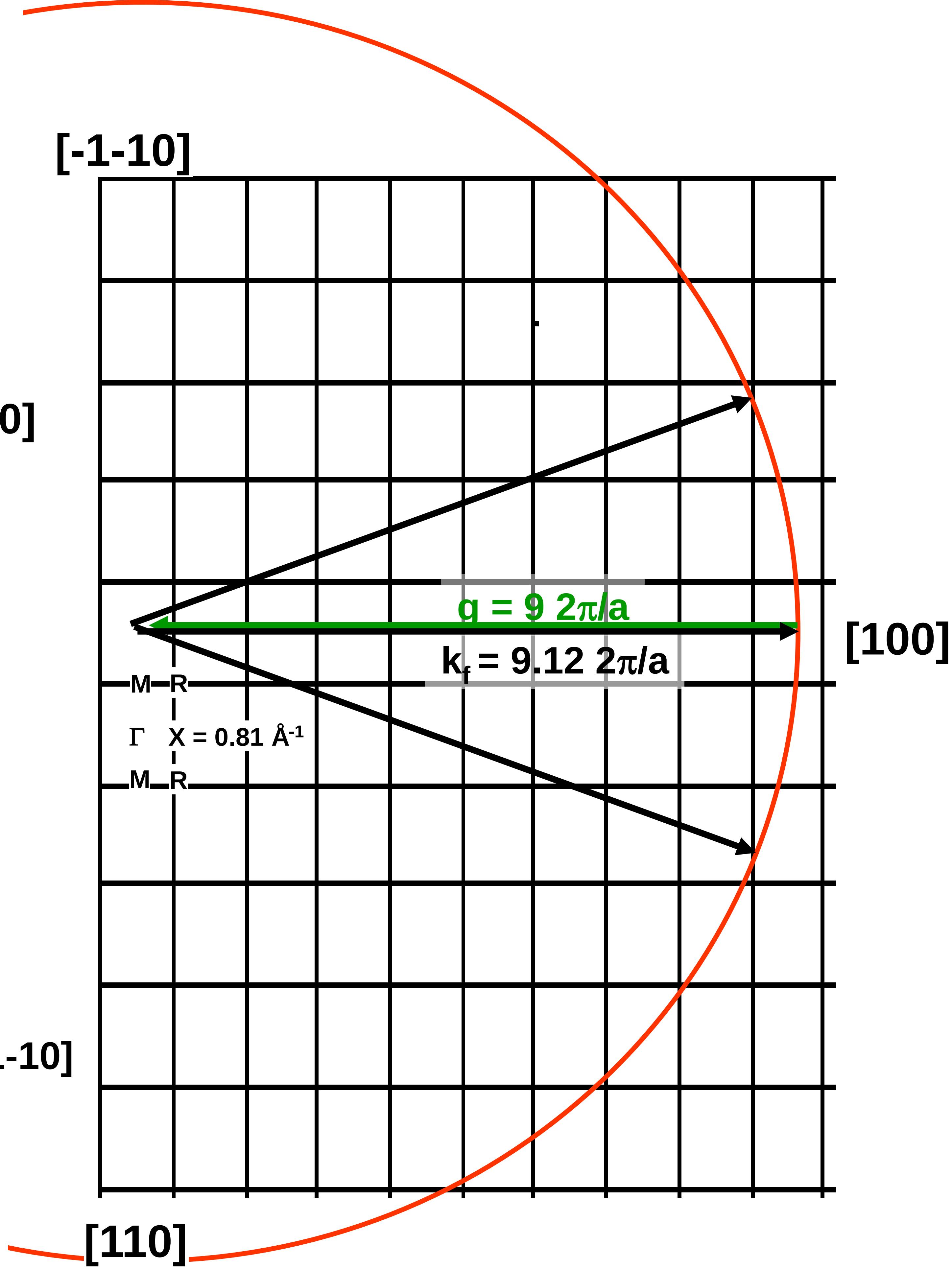
Experiment: Gray, Papp, Bostwick, Rotenberg, Ueda, Yamashita, Kobayashi

Theory: Minar, Braun, Ebert, Plucinski, Yang

STO/LSMO ARPES in k-space: 833 eV, 20K



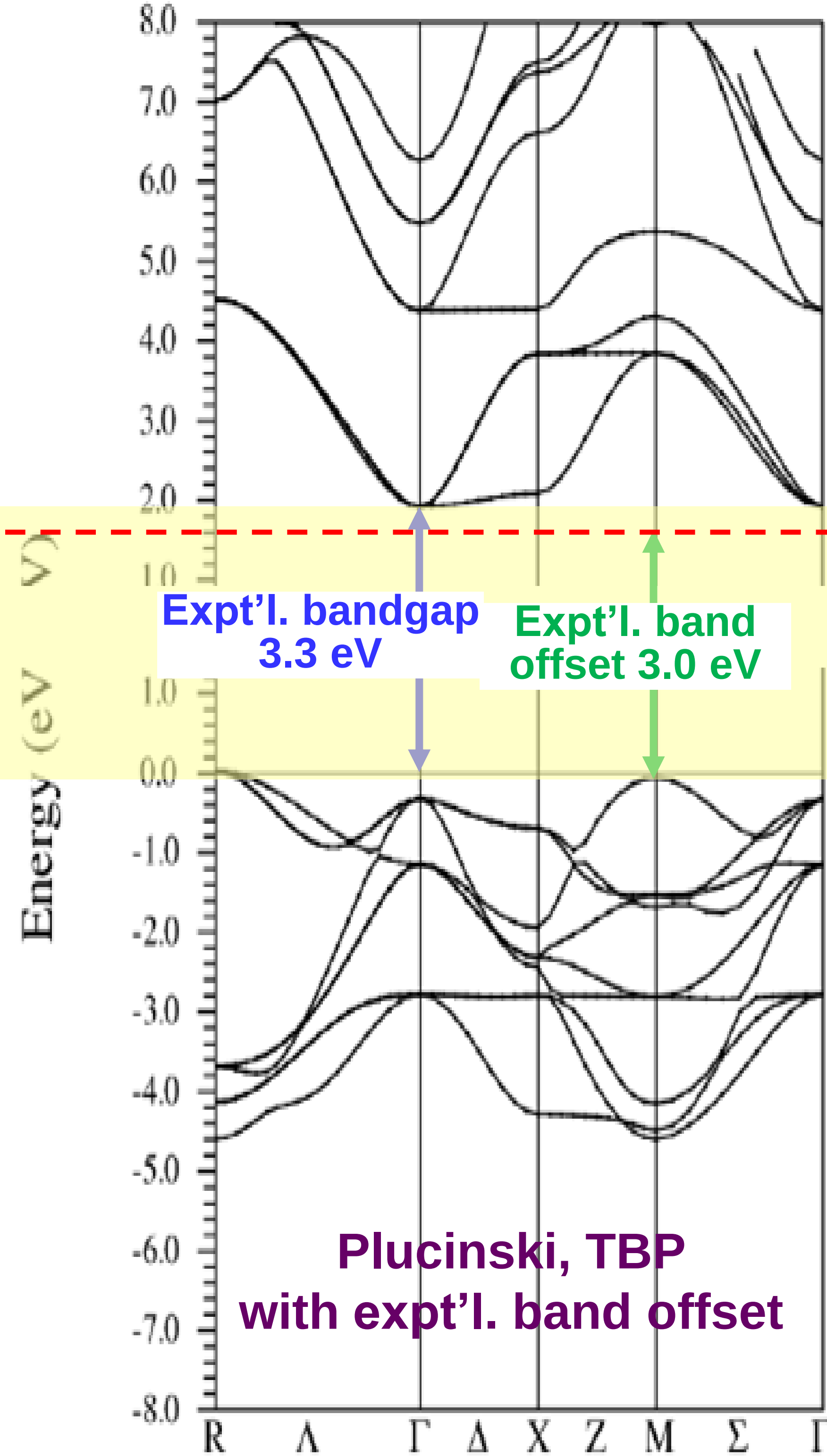




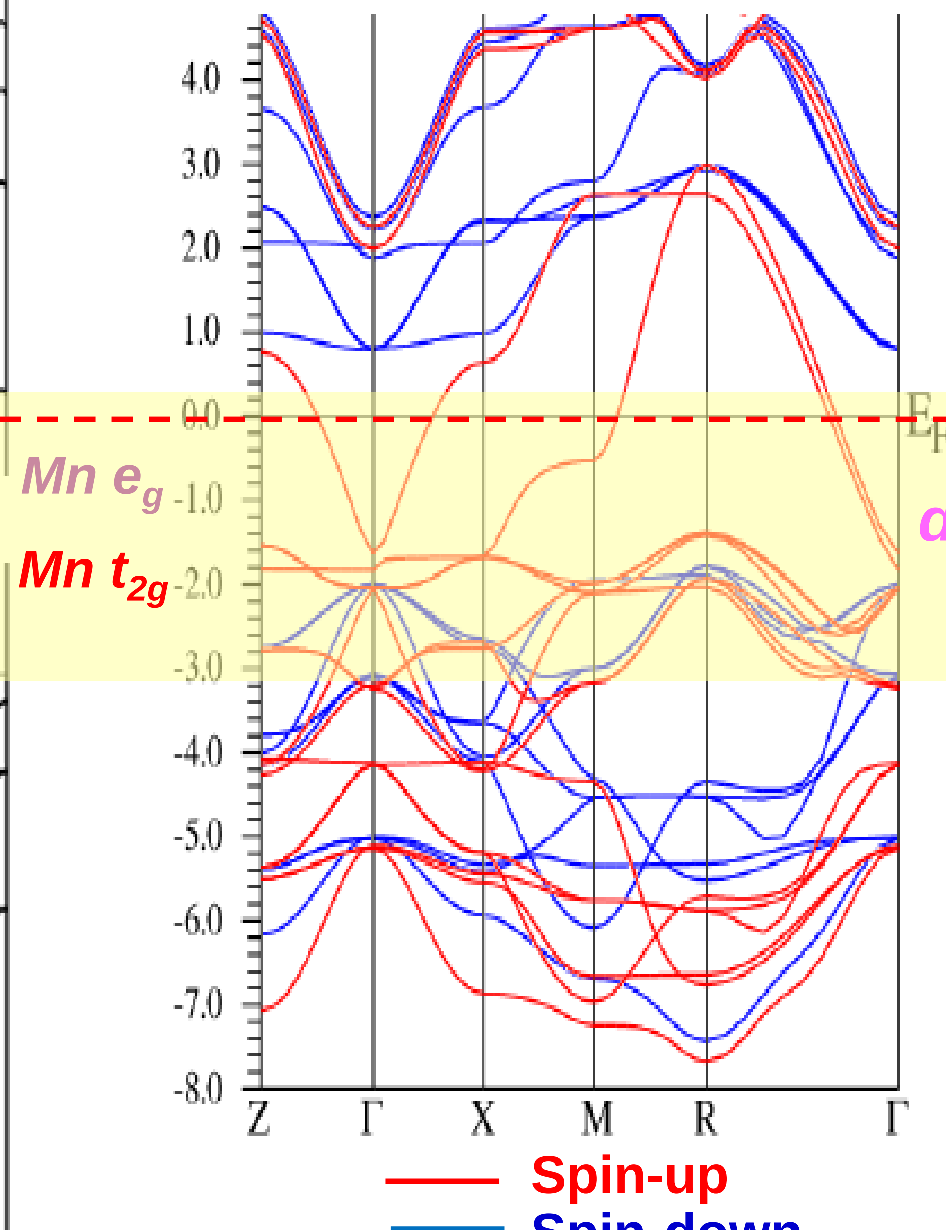
→Depth-resolved/interface band structure?

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

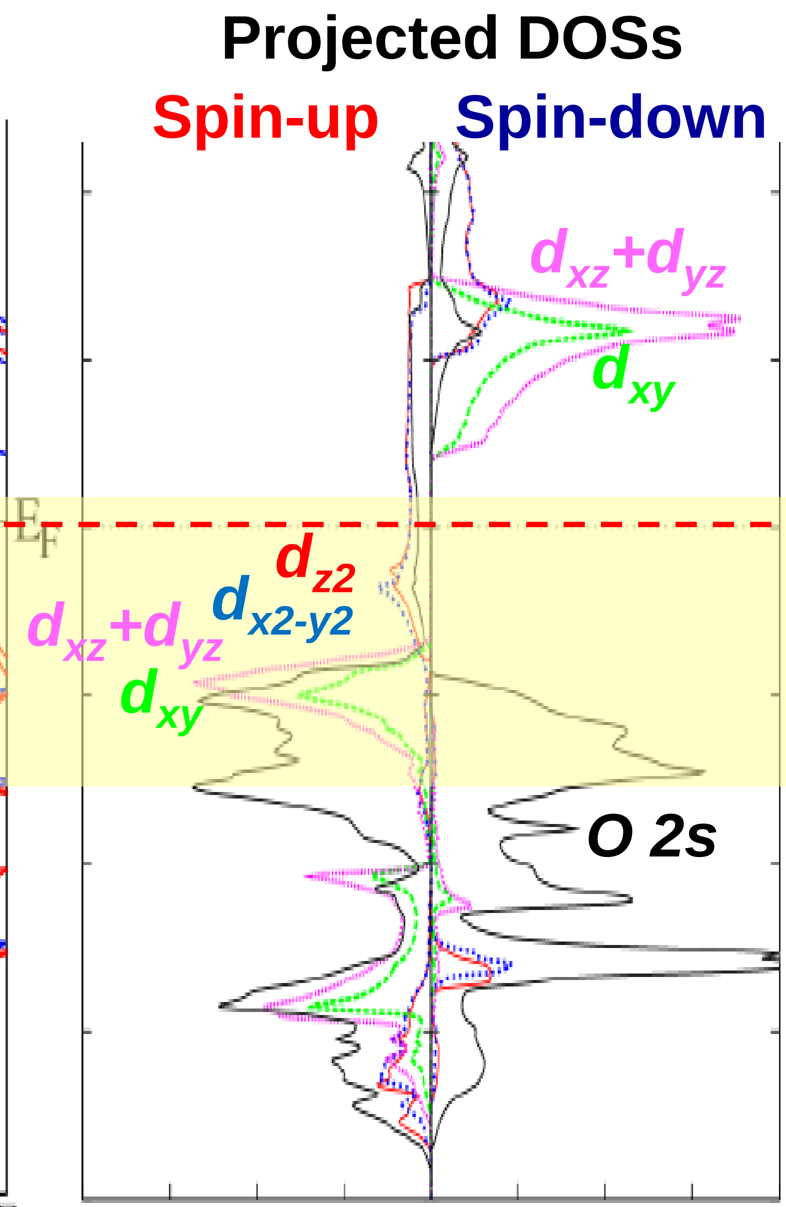
$SrTiO_3$-band insulator



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

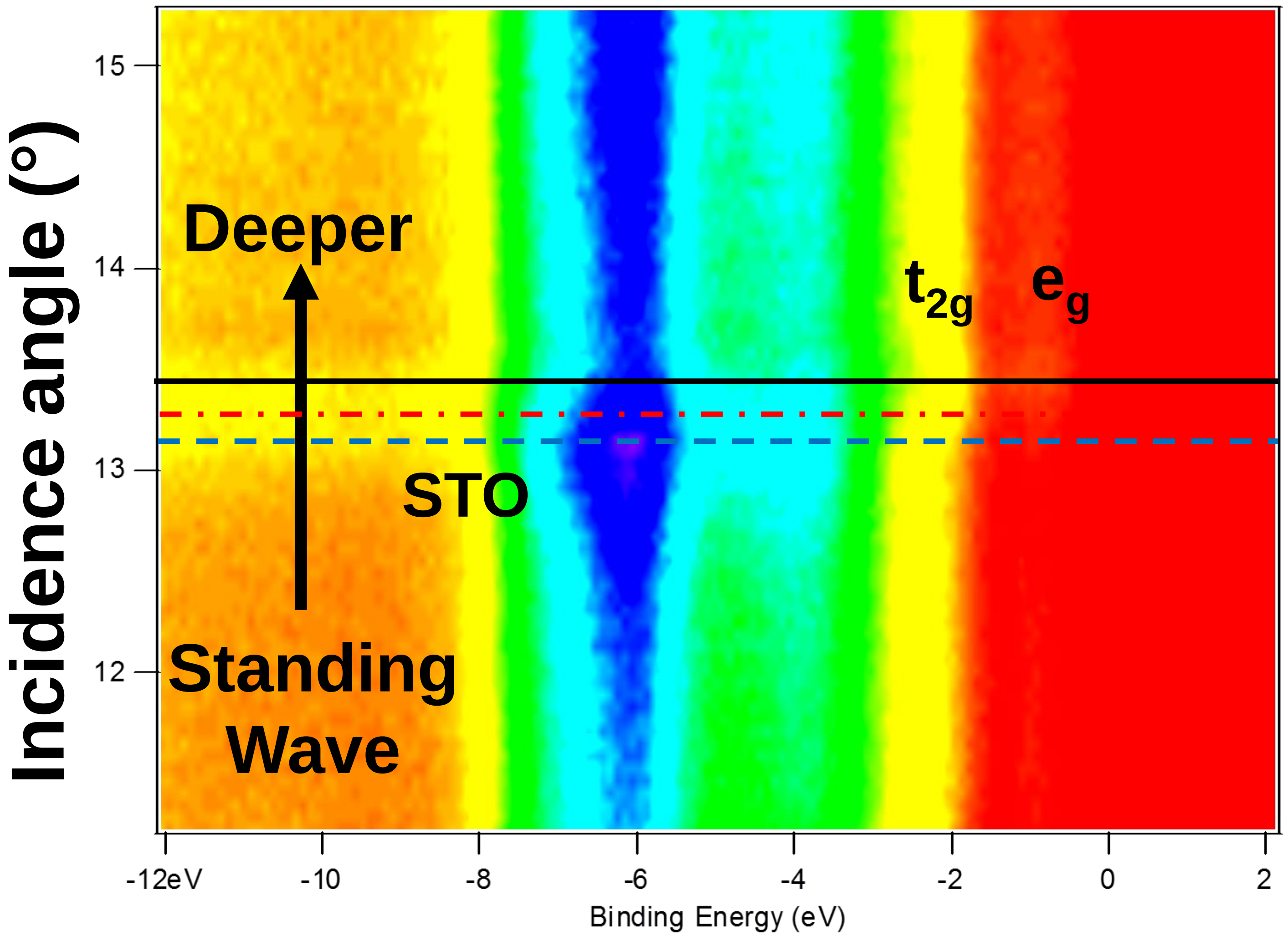


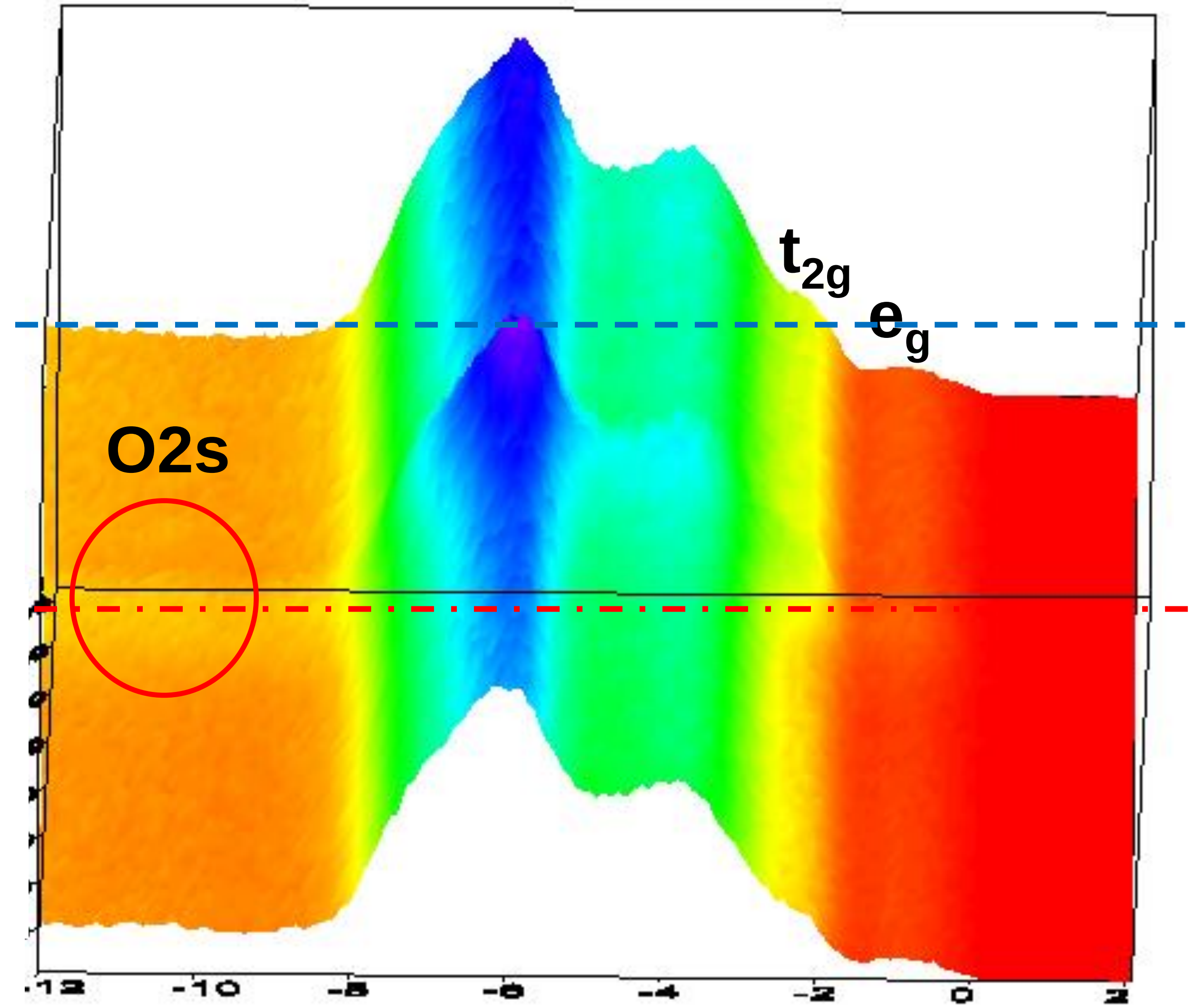
Chikamatsu et al., PRB 73, 195105 (2006); Plucinski, TBP



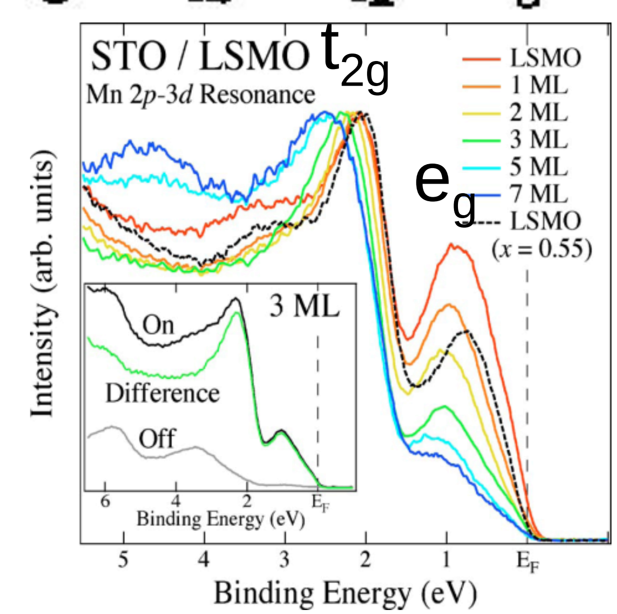
Zheng, Binggeli, J. Phys. Cond. Matt. 21, 115602 (2009) Plucinski, TBP

STO/LSMO-Standing wave/rocking curves of valence region: 833 eV, 300K
Debye-Waller ≈ 0.013→ DOS limit





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

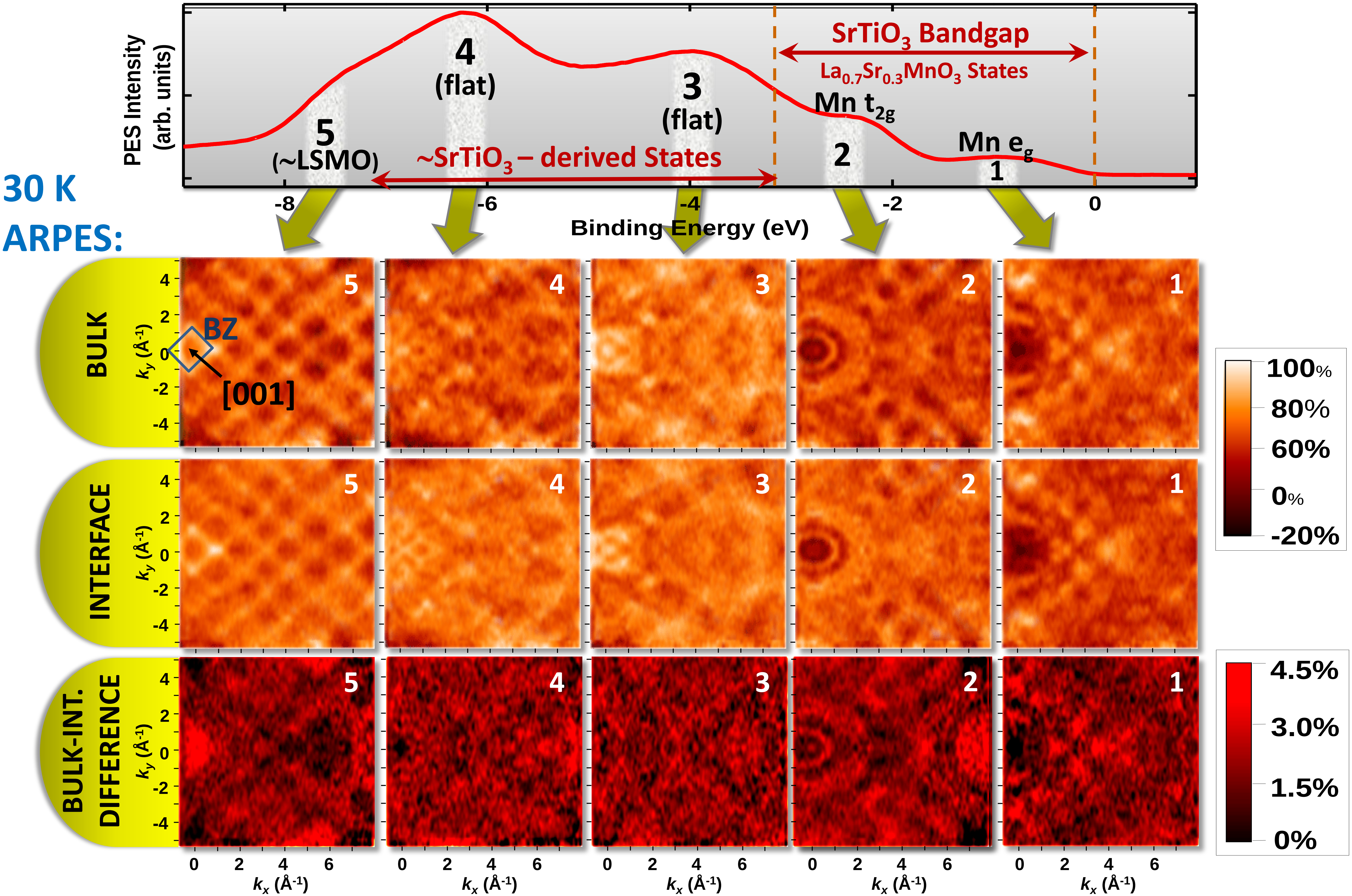


The Advanced Light Source

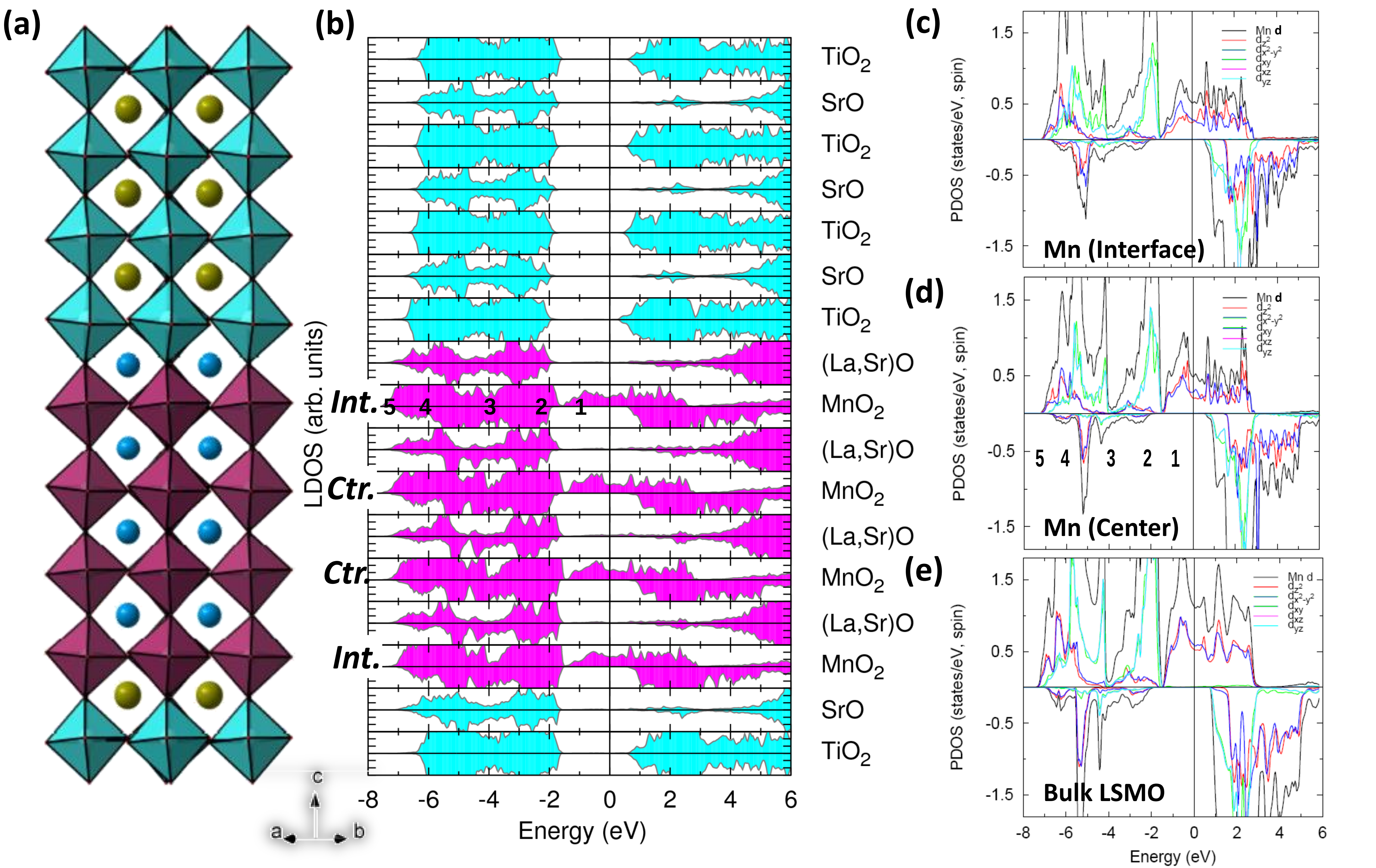
Prior resonant PS: Fujimori et al., J.A.P 99, 08S903 (2006)

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

Room-Temperature DOS Spectrum, Standing-wave LSMO emphasis:

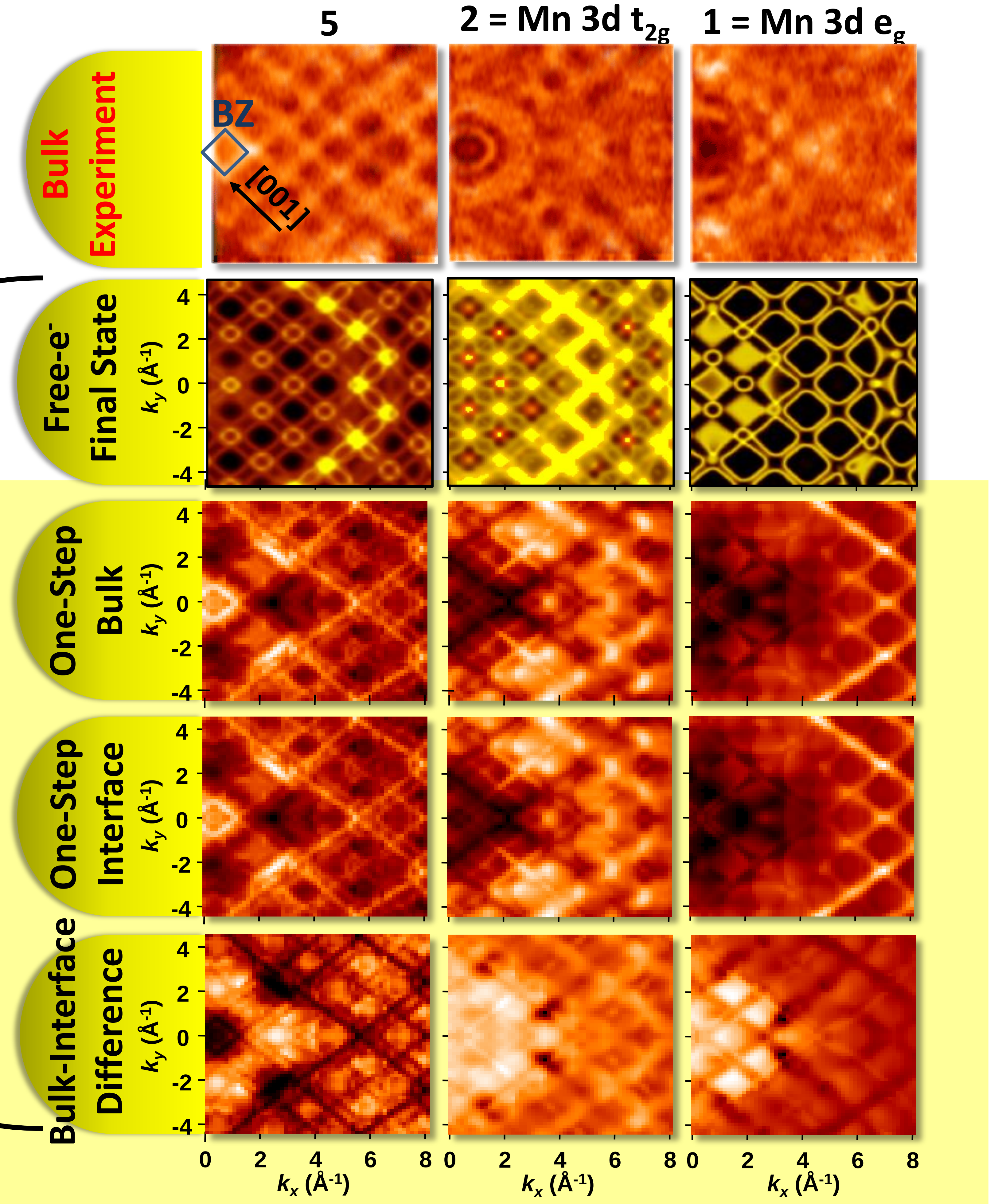


STO/LSMO- Full-multilayer all-electron full-potential APW calculations using LDA/GGA+U (Wien2k) of density of states



Doenning, Pentcheva, TBP

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

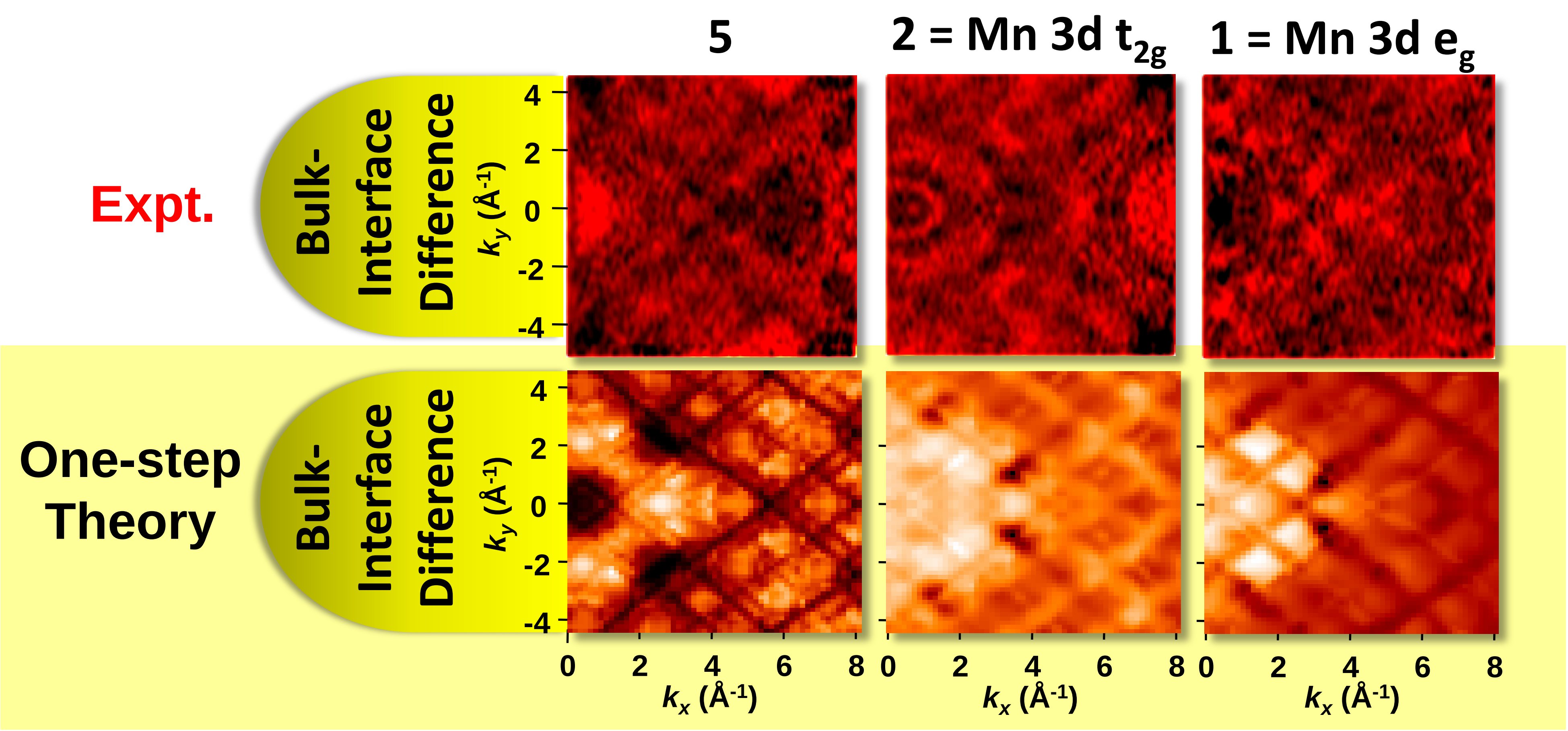


Theory:
Ground-state band structure→k-conserving free-e⁻ final state
Plucinski

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

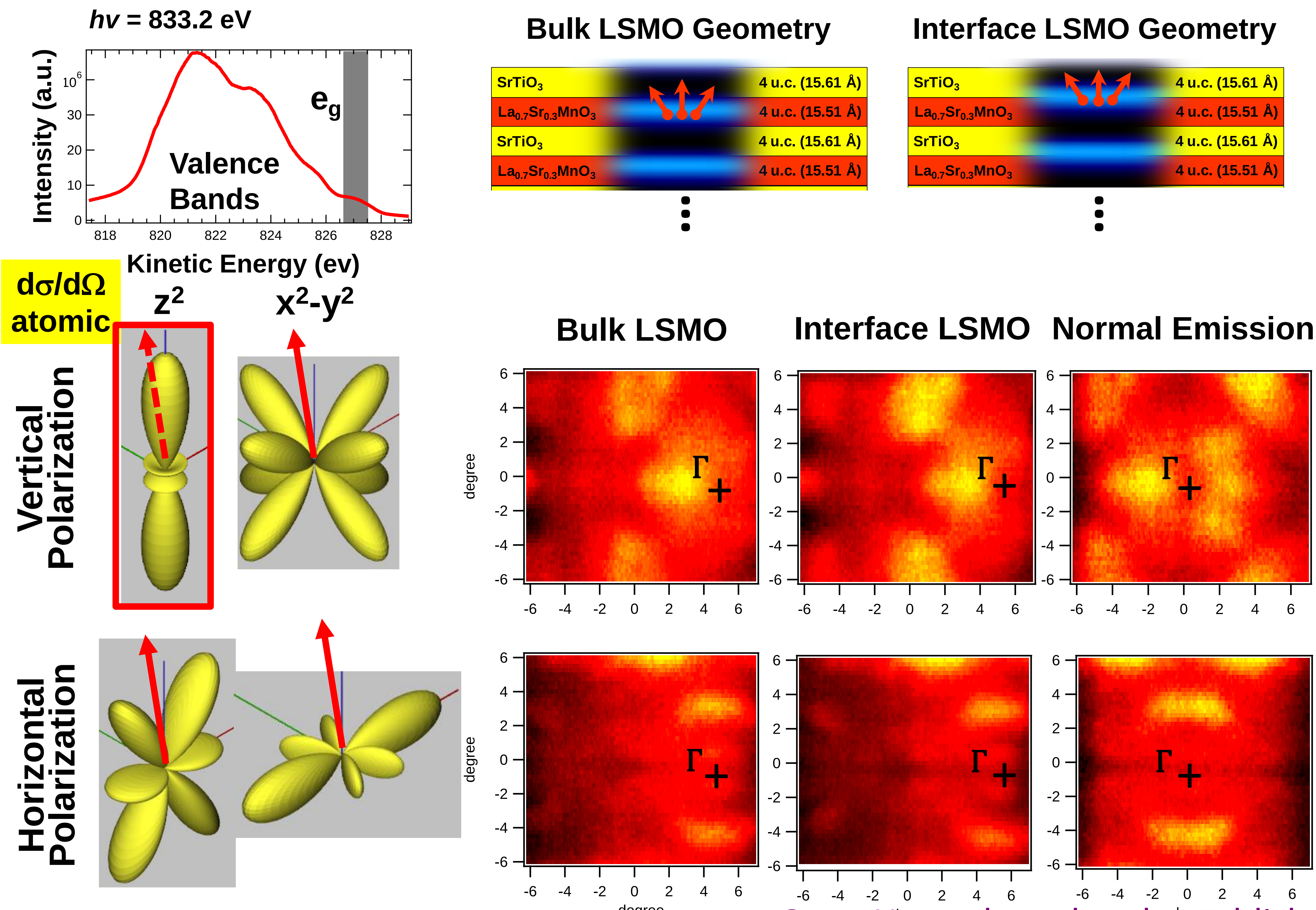
Gray et al., Phys. Rev. B 82, 205116 (2010), and TBP

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



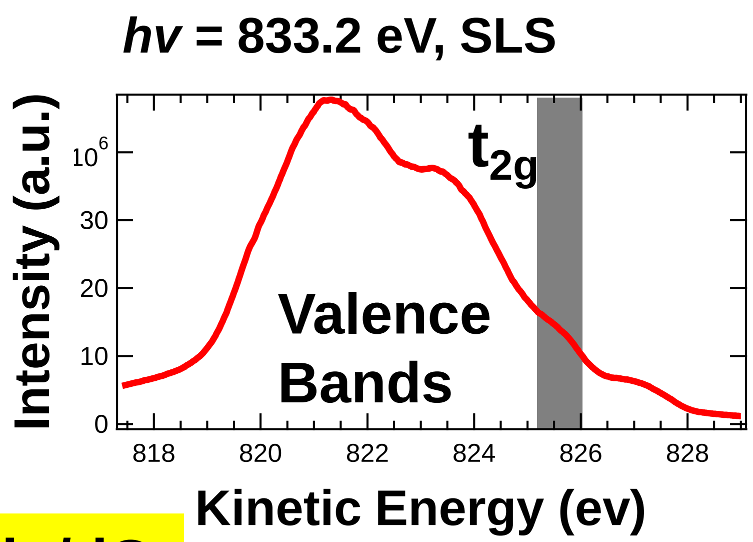
Further calculations in progress with relaxed atomic positions and multilayer roughness at interface (Pentcheva)
Gray et al., Phys. Rev. B 82, 205116 (2010), and TBP

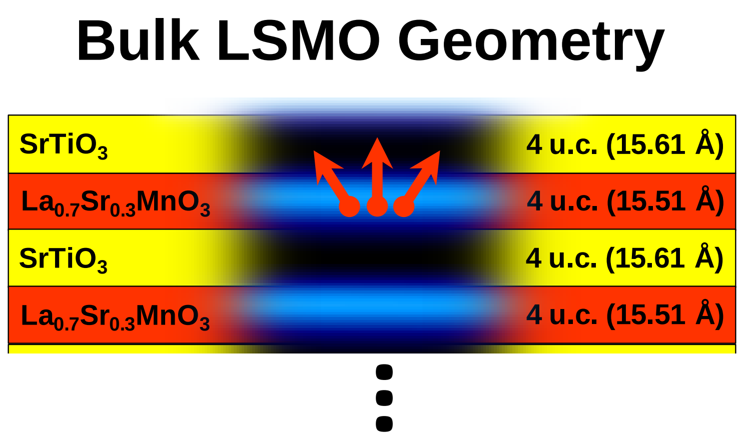
$[SrTiO_3/La_{0.7}Sr_{0.3}MnO_3]_{120}$ Variable-Polarization SWARPES

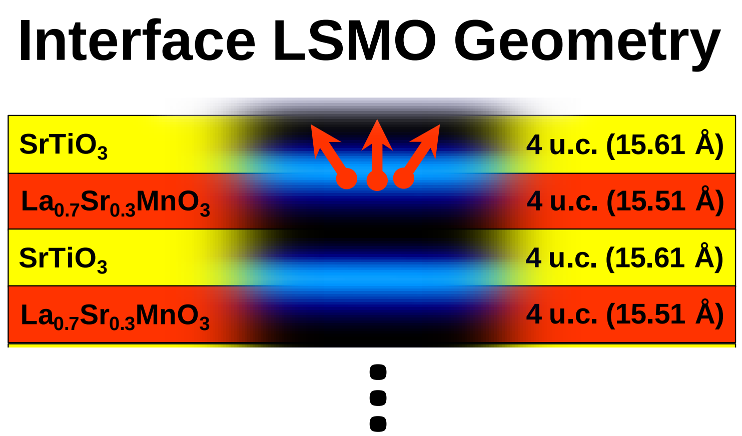


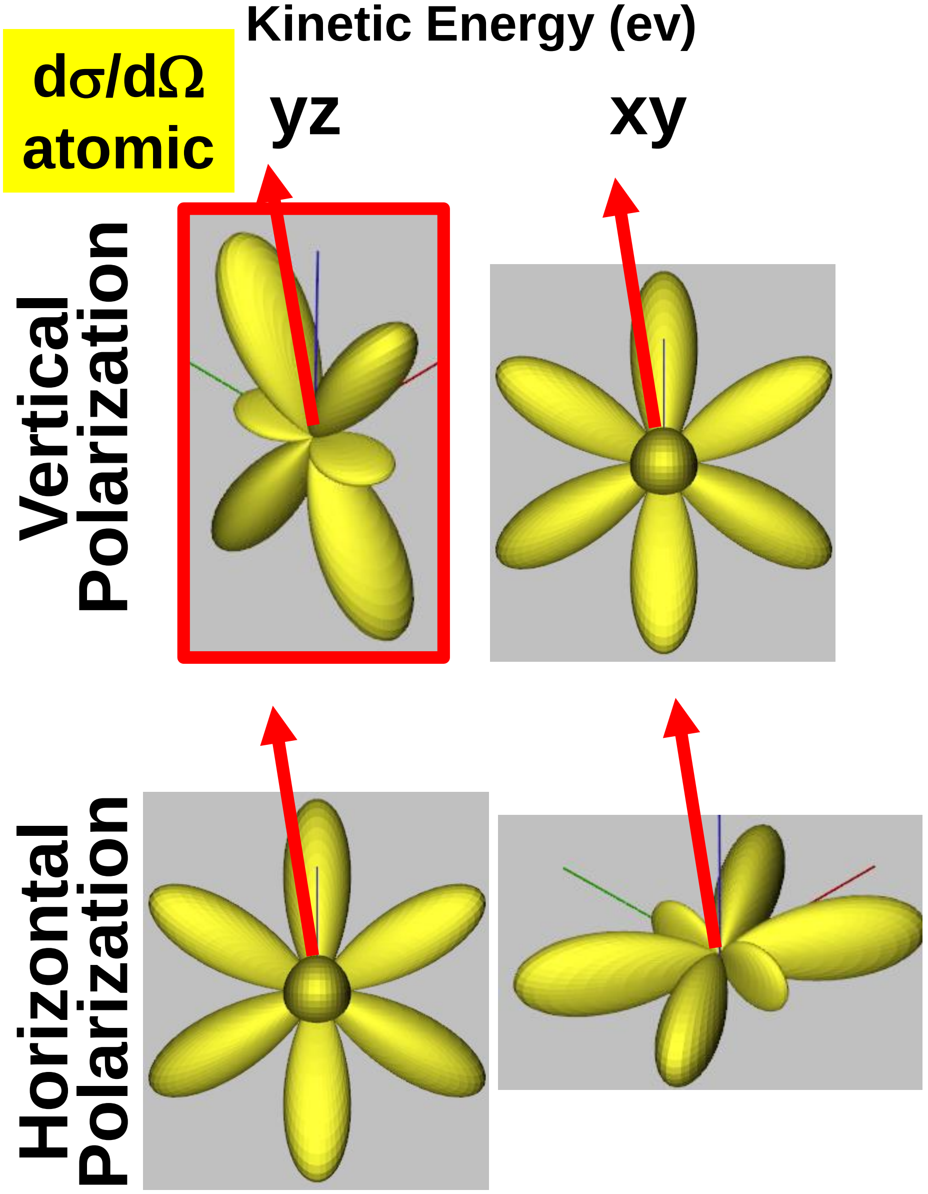
Gray, Nemsak et al. to be published

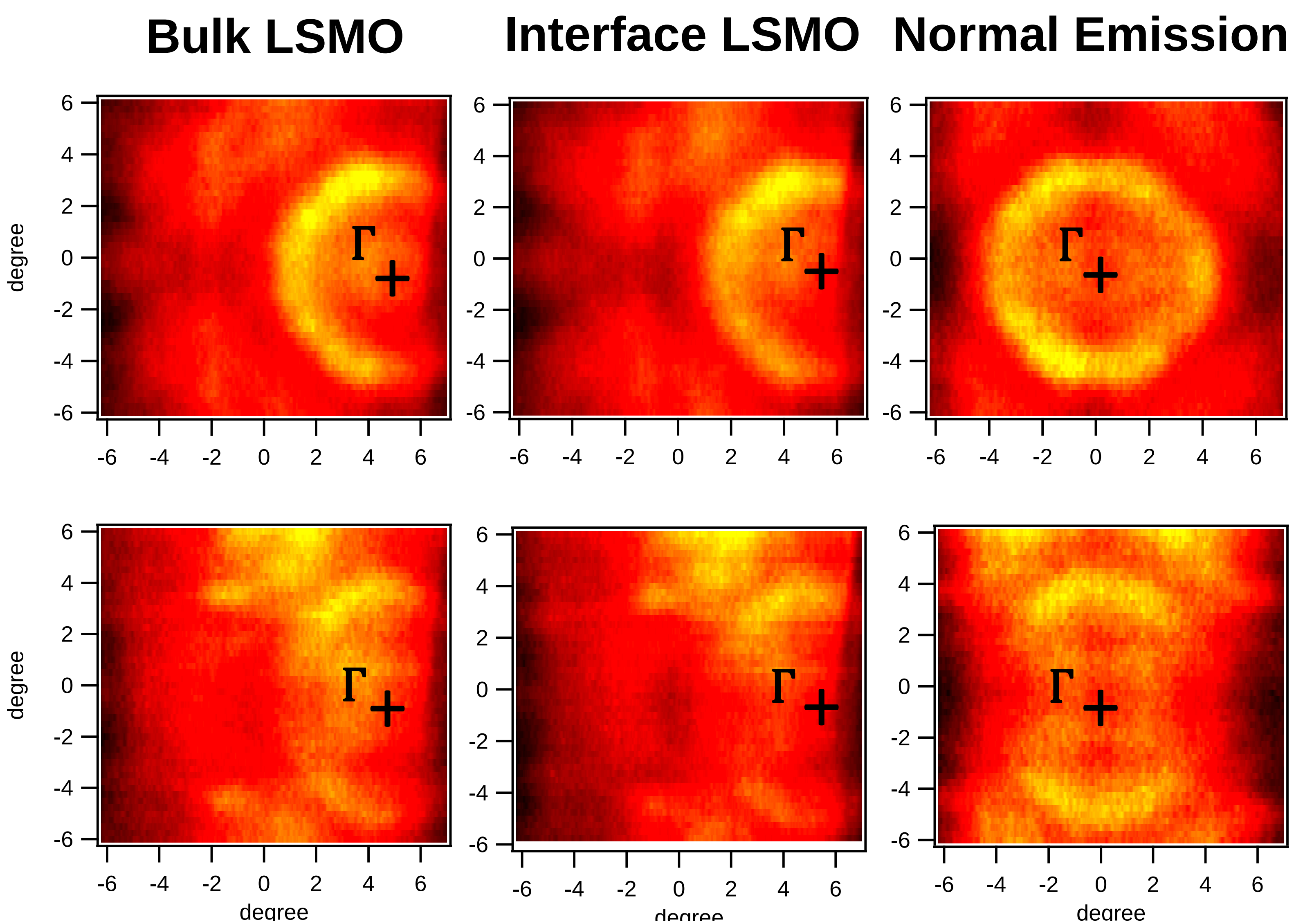
$[SrTiO_3/La_{0.7}Sr_{0.3}MnO_3]_{120}$ Variable-Polarization SWARPES











Gray, Nemsak et al., TBP

Summary

- Hard x-ray excitation to 5-10 keV permits probing to depths of ~100 Å: bulk properties and buried interfaces
- Hard x-ray photoemission (HAXPES, HXPS) is rapidly growing worldwide, with recent overviews at:
  - C.F., Nuclear Instr. & Meth. A 547, 24-41 (2005); 601, 8 (2009);
  - J. Elect. Spect. 178–179, 2 (2010) and to appear;
  - K. Kobayashi, Nuclear Inst. & Meth. A 601, 32 (2009);
  - L. Kover, J. Elect. Spect. 241, 178-179, (2010)
  - Hamburg HAXPES Conf.- http://haxpes2011.desy.de
- HARPES is possible in the multi-keV regime: W, GaAs
- One-step theory of ARPES (Ebert et al.) used for quantitative interpretation, including phonon effects via CPA
- HARPES of GaAs and GaMnAs permits determining nature of Mn perturbation of the electronic structure
- Combining soft and hard x-ray excitation, standing waves, and ARPES (SWARPES) yields depth-resolved composition, optical properties, and electronic structure for $SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$ multilayer, wider application to other multilayer systems (see also talk by Strocov)
- SARPES and HARPES emerging as new more bulk-sensitive probes of electronic structure (see also Strocov talk)
  - CF, Synchrotron Radiation News 25, 26 (2012)