HAXPES09-Hard X-Ray Photoemission: Where are we and what does the future hold?

Chuck Fadley

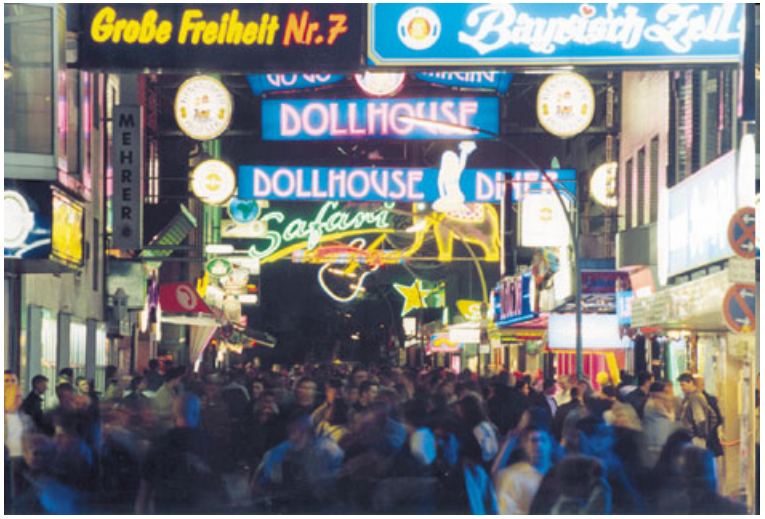
Convenient definition:
Soft x-rays: < 2 keV, grating monochromators
Hard x-rays: >2 keV, crystal monochromators

Many thanks to:

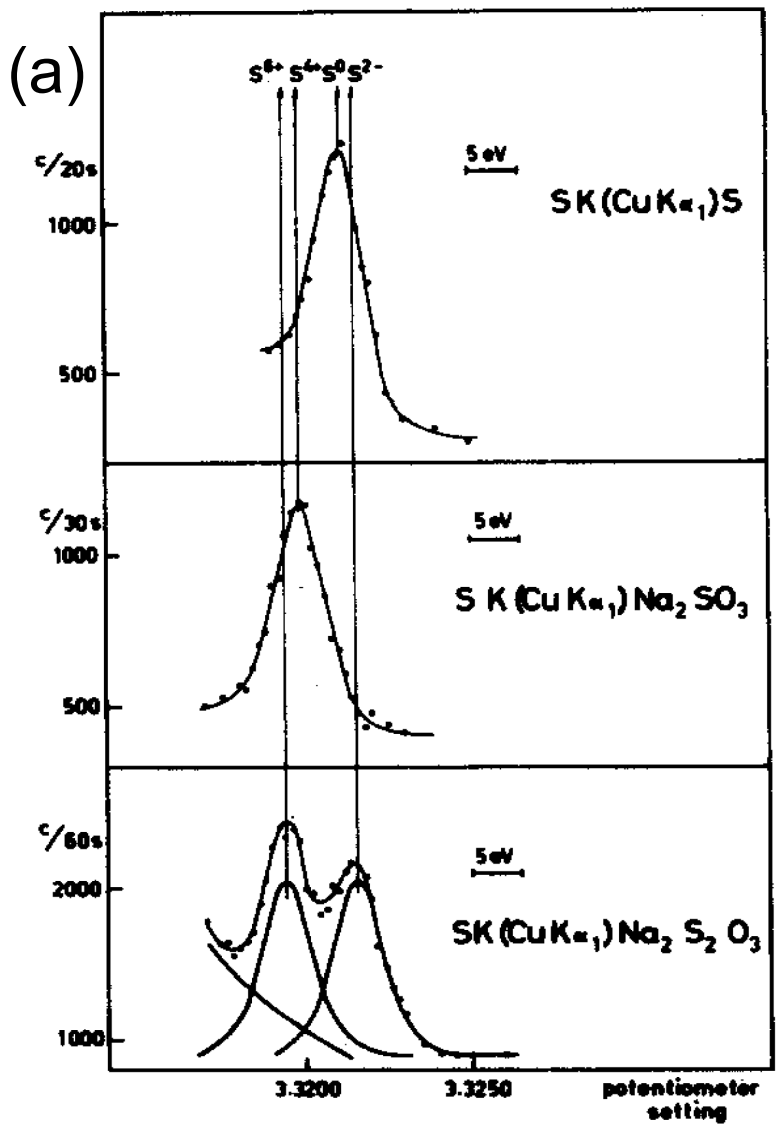
Joe Woicik—the buck stopped there
Dan Fischer—the money man
Elio Vescovo- the insider connection
David Starr
Barry Wells

Gretchen Cisko—program, travel and many other details
Mercy Baez —housing and many other things
Keisuke Kobayashi, Yasutaka Takata—the Japanese connection

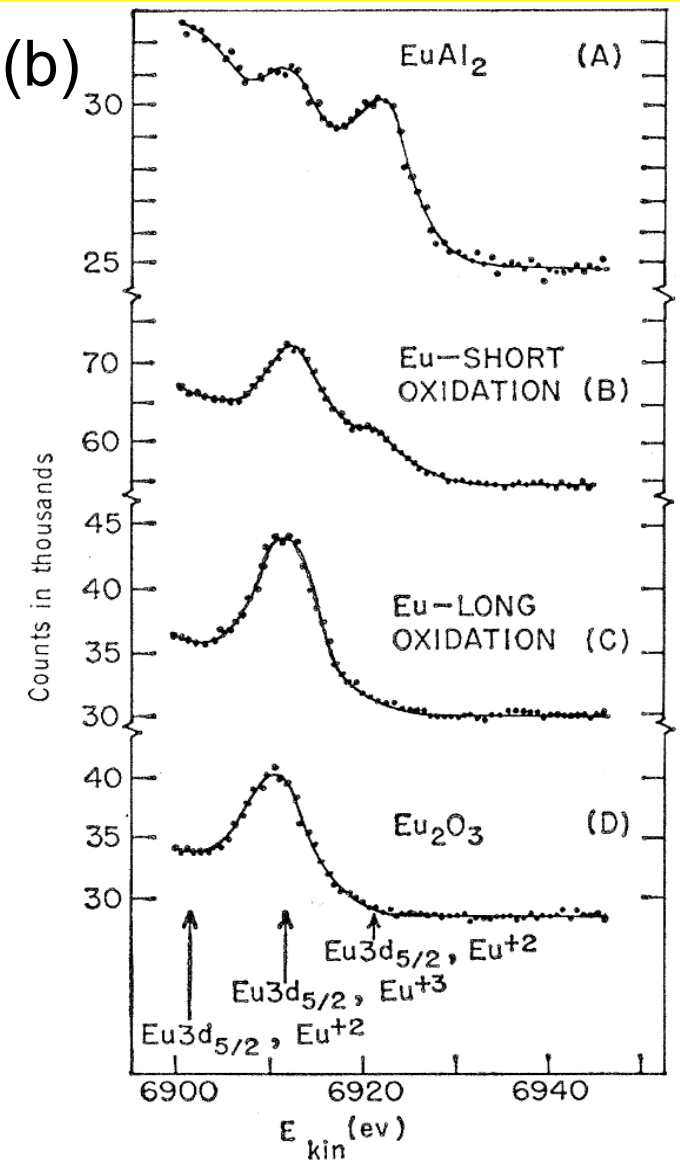
And looking ahead:
HAXPES11 in Hamburg
Local Organizing Committee (tentative):
Wolfgang Drube, Andrei Gloskowski, Gerhard Fecher, Claudia Felser, Ralph Claessen, Hubert Ebert, Mihaela Gorgoi, Franz Schäfers



Some early hard x-ray photoemission, CuKα @ 8.0 keV—The first chemical shifts



S. Hagstrom, C. Nordling, and K. Siegbahn, Physics Letters 9, 235 (1964).



C.S.F., S.B. Hagstrom, J.M. Hollander, M.P. Klein, D.A. Shirley, Science 157, 1571 (1967).

Hard x-ray photoemission with SR: the first experiment

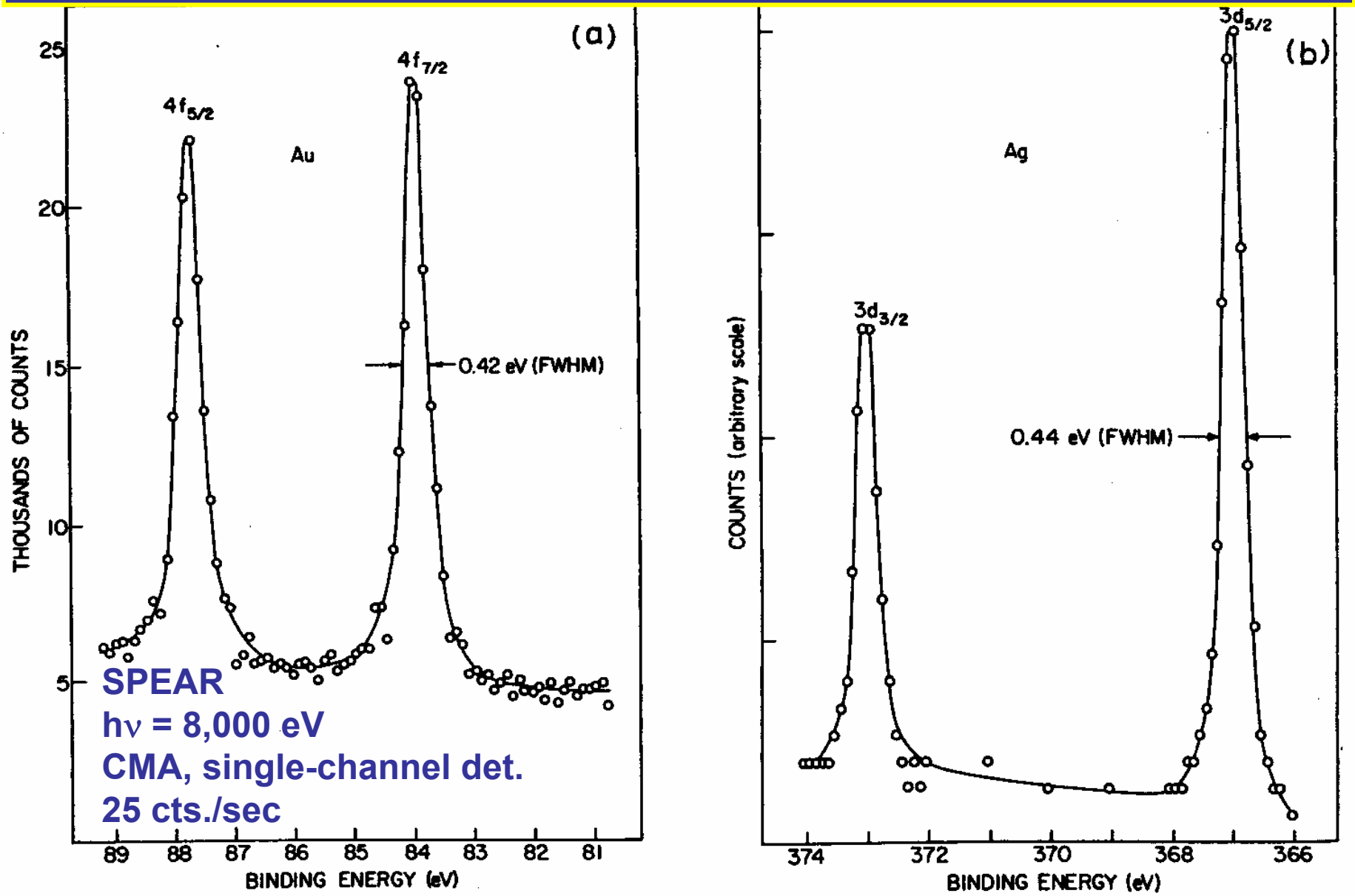
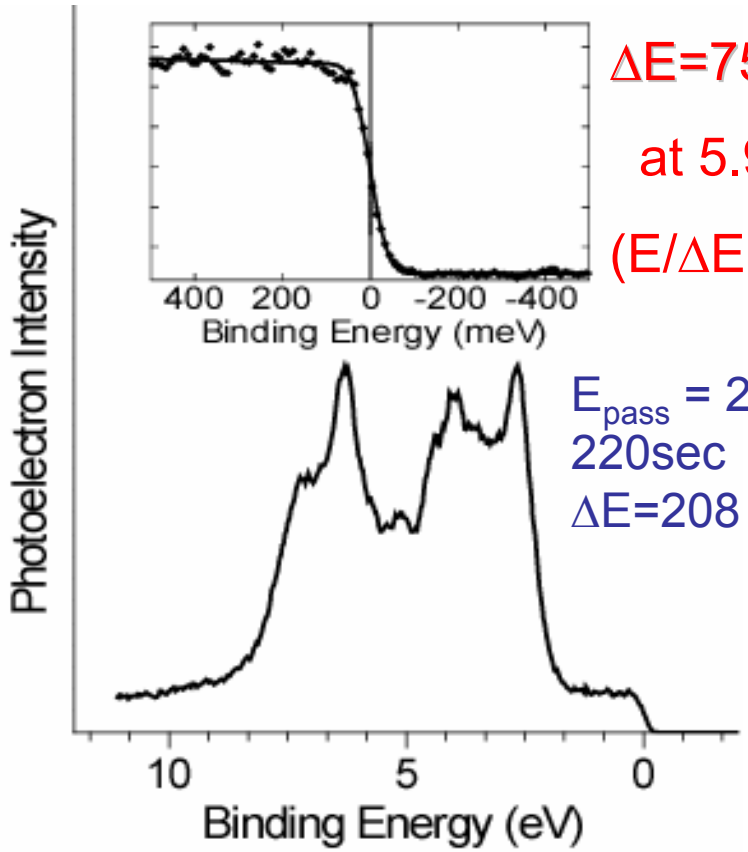


Figure 9. Electron distribution curves for the 4*f* doublet of gold (a) and the 3*d* doublet of silver (b).

Pianetta, Lindau, Nature 250, 214 (1974)

Fast forward to today @ SPring8 and other places

Au VB @ hν=5.95 keV

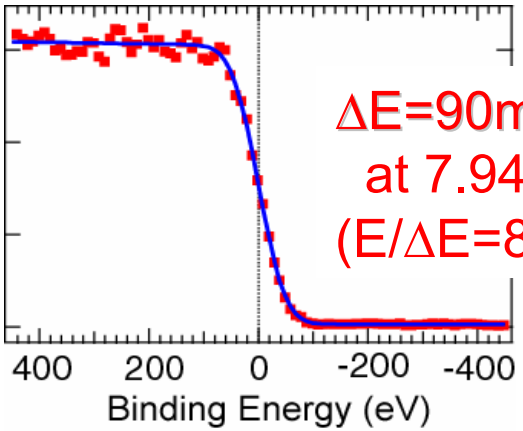


ΔE=75 meV

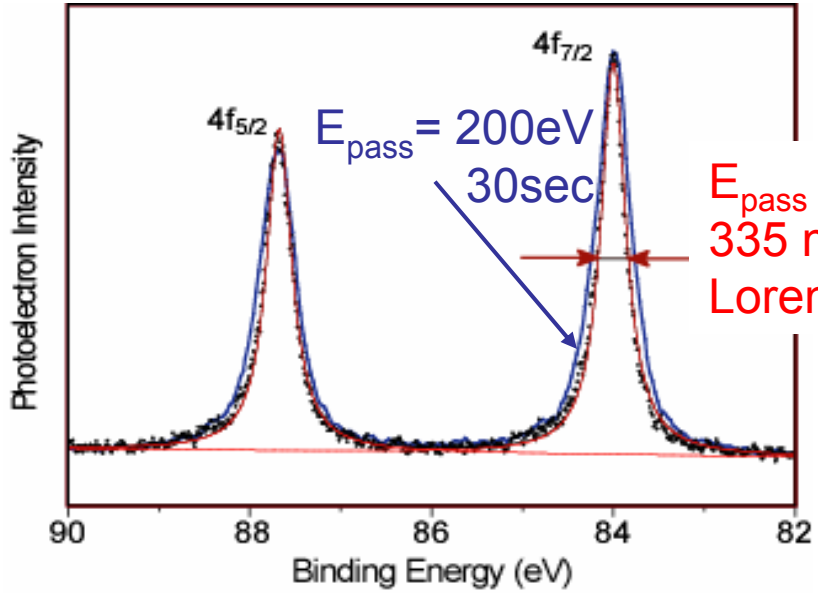
at 5.95keV

(E/ΔE=79000)

E_{pass} = 200eV
220sec
ΔE=208 meV



ΔE=90meV
at 7.94keV
(E/ΔE=88000)



E_{pass}= 200eV
30sec

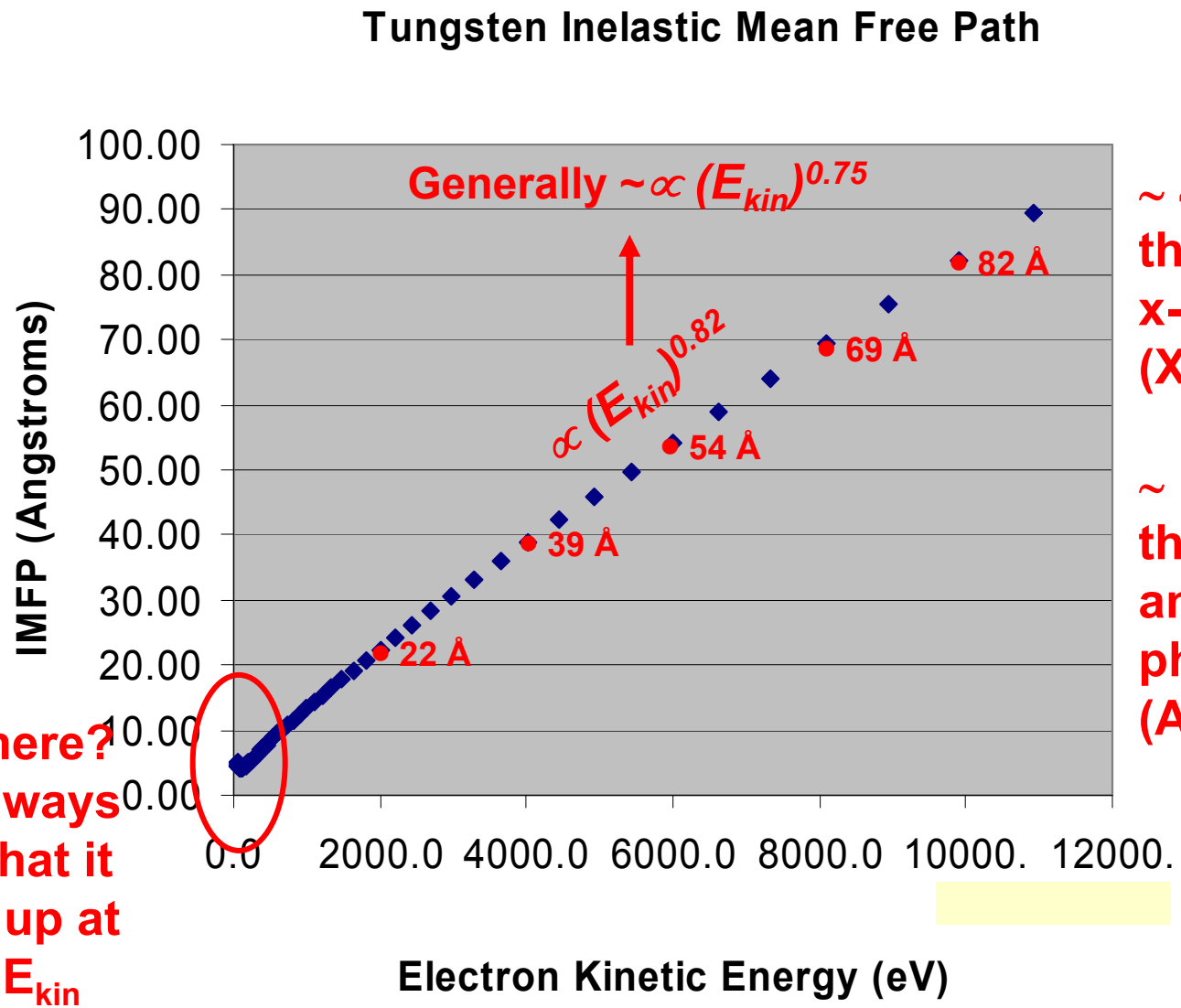
E_{pass} =50eV
335 meV
Lorentzian

Takata et al., Nuclear Instrum. and Methods. A547, 50 (2005)

HAXPES09: Ikenaga: (micron)^2 spot and +/- 30 deg, with same resolution and intensity + Polarization variation, e.g. via diamond ¼ wave plate, new undulators

How much deeper do we probe at 5-10 keV?

Typical elements: ~70-400 Å @ 10 keV



~ 4-5x deeper than normal x-ray photoem. (XPS)

~ 15-20x deeper than normal angle-resolved photoem. (ARPES)

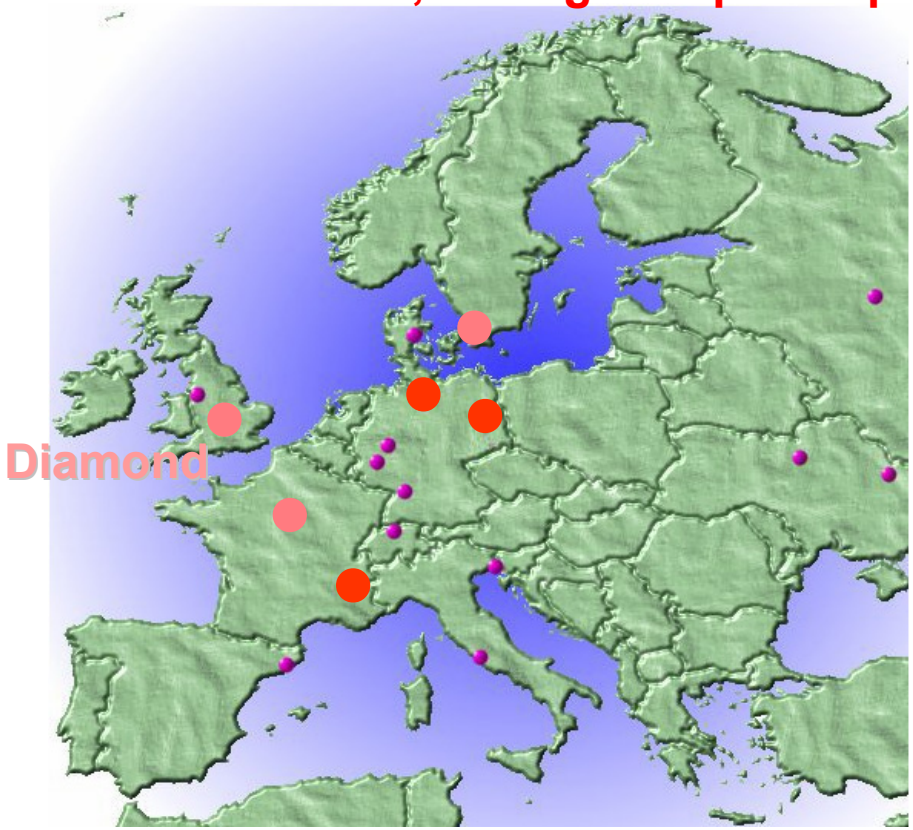
And here? Not always true that it turns up at low E_{kin}

C.J. Powell, S. Tanuma: both calculations and TPP-2M up to 30 keV
Plus simulations with the NIST SESSA program up to 20 keV

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

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

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



ESRF—Castro et al. Soleil—Rueff, Simon et al.
Panaccione et al.--VOLPE
Zegenhagen et al.
HASYLAB—Drube, Felser, Claessen et al.
BESSY---Gorgoi, Schaefers et al.—HIKE
Felser, Fecher et al.

SPring8—Kobayashi et al.
Takata, Shin et al.;
Suga et al.; Taiwan

U.S. Workshops:
October, 2008: ALS Users Meeting
A. Fedorov, C.F.
HAXPES09 @NSLS, May 20-22, 2009:
J. Woicik, D. Fischer, E. Vescovo, C.F.

Hard x-ray photoemission—applications areas

- High-k dielectrics, advanced semiconductor structures and materials→reactions at buried interfaces, stack profiles, band alignment

  (Conti, Drube, Garfunkel, Hughes, Herrera-Gomez, Lysaght, Yanagi, Zaima)
- Energy conversion devices: Photovoltaic cells, Fuel-cell electrodes, Li-ion batteries→interfaces and depth-resolved chemical states

  (Lysaght, Shikano, Zaima)
- Magnetic/spintronic multilayers→ interfaces, MCD, standing waves, spin resolution?,

  (Felser, Gorgoi, Papp/Balke, Ryan, Ueda, Zegenhagen)
- Strongly correlated, novel materials→surface vs bulk electronic structure in high TC, heavy Fermions, manganites, Heuslers

  (Chainani, Drube, Felser, Panaccione, Sawatzky, Suga, Taguchi, Tjeng…)
- Oxides, oxide interfaces, 2DEG, superconductivity, "Mottronics",…

  (Claessen, Panaccione, Rumaiz, Sawatzky, Tjeng, Zegenhagen)
- Catalysis, environmental, polymer science→depth distributions, high-pressure studies

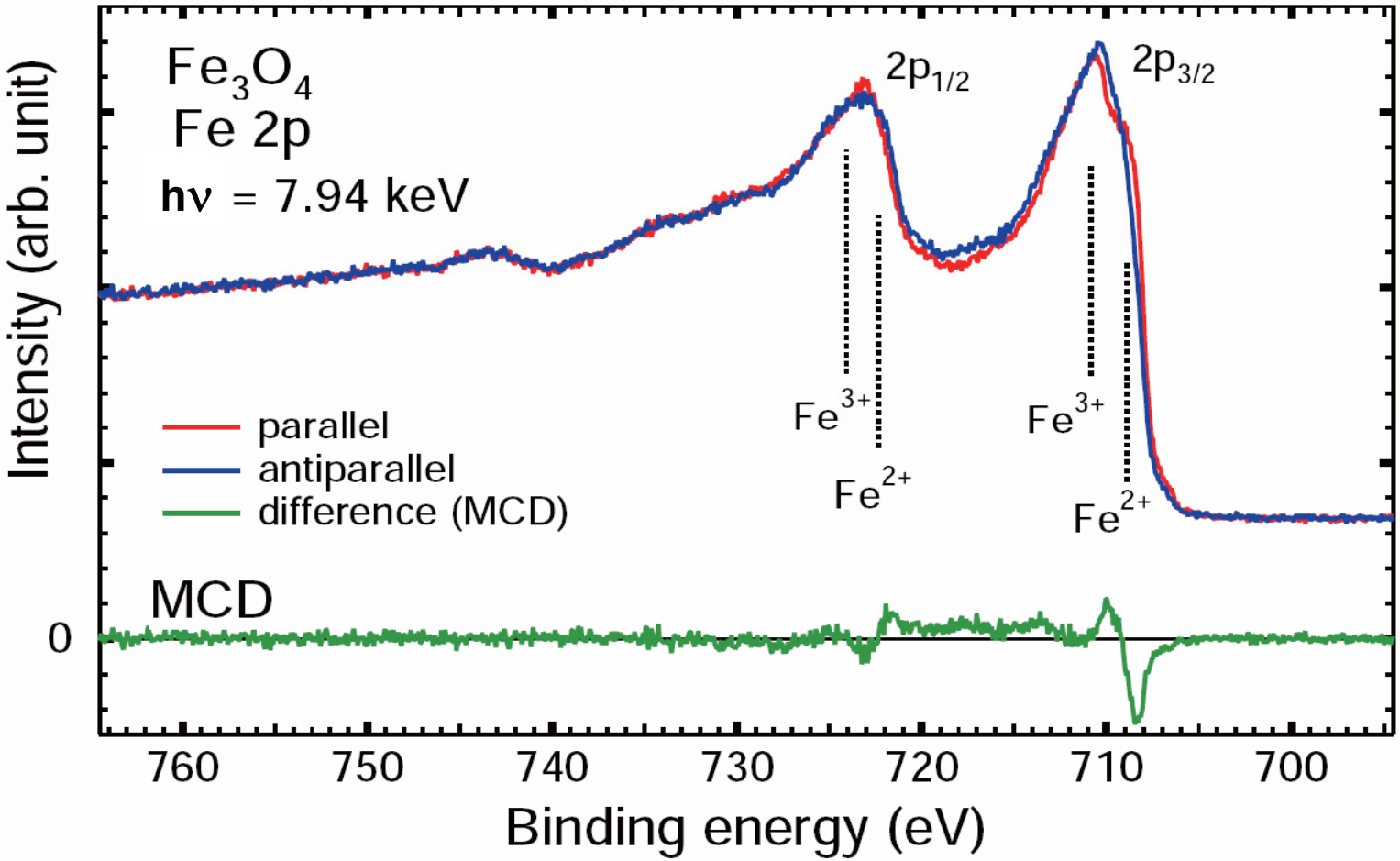
  (Bluhm, Bare, Mitchell)
- Lanthanide/Actinide systems→surface vs bulk electronic structure

  (Joyce)
- Atomic, molecular, cluster studies→non-dipole effects, recoil, many-electron, vibrational, rotational excitation

  (Lindle, Rosenberg, Simon)

HAXPES/HXPS is already a well-established technique for materials, nanostructure, nanomaterial, and device characterization!

Some first MCD data with hard x-ray excitation



S. Ueda et al., Appl. Phys. Exp. 1 (2008) 077003
SPring8-BL15XU

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Nondipolar Angular Distributions

$$\frac{d\sigma(h\nu)}{d\Omega} = \frac{\sigma(h\nu)}{4\pi}\left[1 + \frac{\beta}{2}(3\cos^2\theta - 1) + (\delta + \gamma\cos^2\theta)\sin\theta\cos\phi\right]$$

Lindle et al., Hemmers et al., Rad. Phys. and Chem. 70, 123-147 (2004) Guillemin et al., Rad. Phys. and Chem. 73, 311-327 (2005)
D.P. Woodruff, NIMA 547 (2005) 187–195
I. Vartanyants NIMA 547 (2005) 196–207

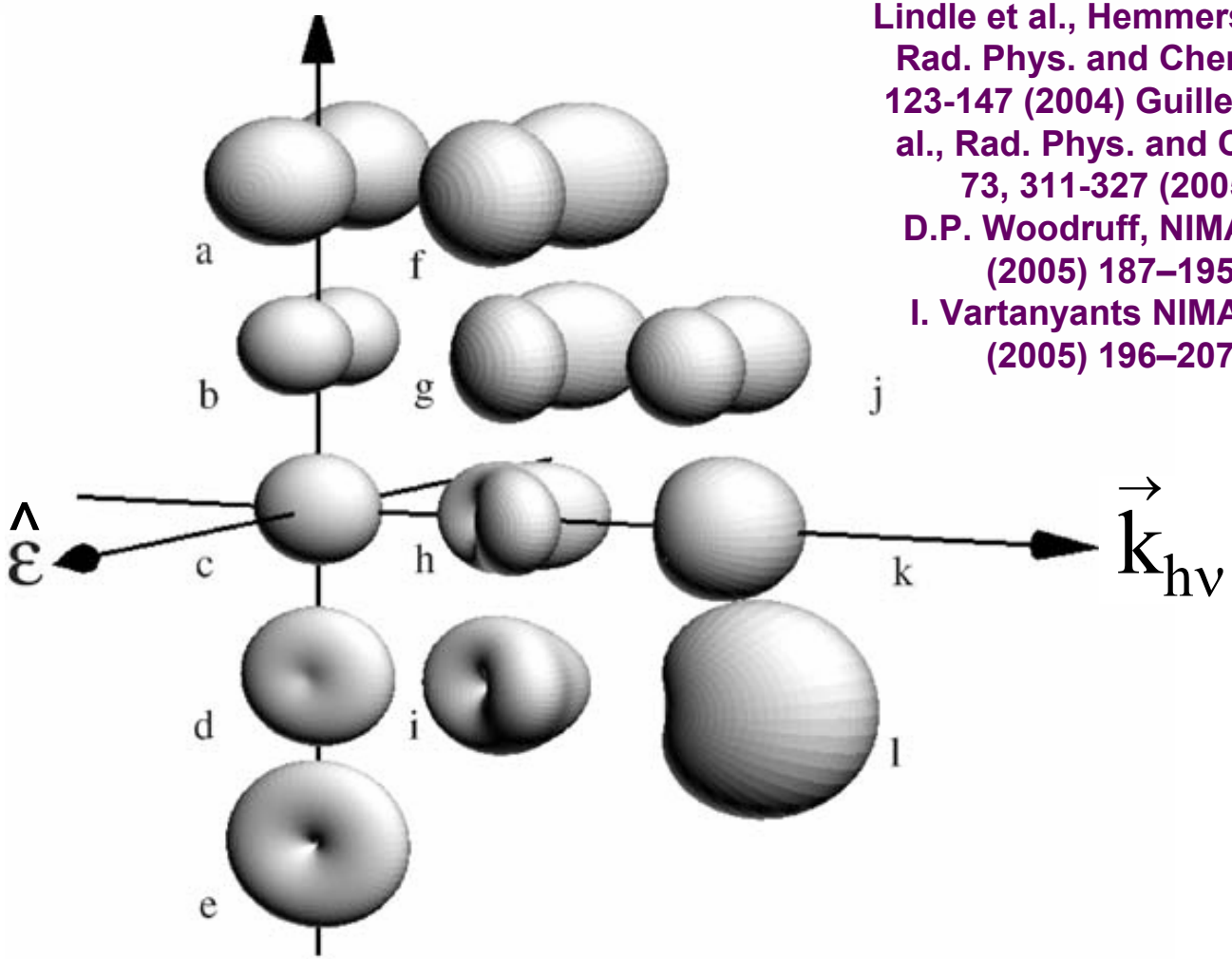
$\beta = 2$

1

0

-0.5

-1



γ,δ=0 γ large δ large

Hard x-ray photoemission—instrumentation

- Beamlines, spectrometers, microscopes—various new directions
  (Browning, Cai, Cholewa, Dierker, Drube, Hu, Ikenaga, Lee, Simon, Stefani; Focus, MBS, VG Scienta, SPECS)
- Detectors? OK, but ~20th century: need individual pixel counting at up to GHz integrated rates, 1D→2D with spin-the holy grail
  (Cholewa, instrument vendors)

Hard x-ray photoemission—basic effects and theory

- Inelastic mean free paths, effects of elastic scattering, peak fitting and analysis of ARXPS
  (Herrera-Gomez, Powell, Zaima,…)
- Cross sections, asymmetry parameters, non-dipole effects
  (Lindle, Yoshikawa, Zegenhagen,…)
- Anderson impurity model for core/valence levels
  (Chainani, Sawatzky, Suga, Taguchi,…)
- One-step ARPES theory with matrix elements, relativistic effects, spin resol.
  (Ebert, Rehr)
- Phonons! In recoil, in ARPES (UPS-band limit→XPS-DOS limit), in inelastic scattering→more development needed
  (Ebert, Kayanuma, Papp, Suga, Takata)

Hard x-ray photoemission—plusses and minusses

•**Plusses**

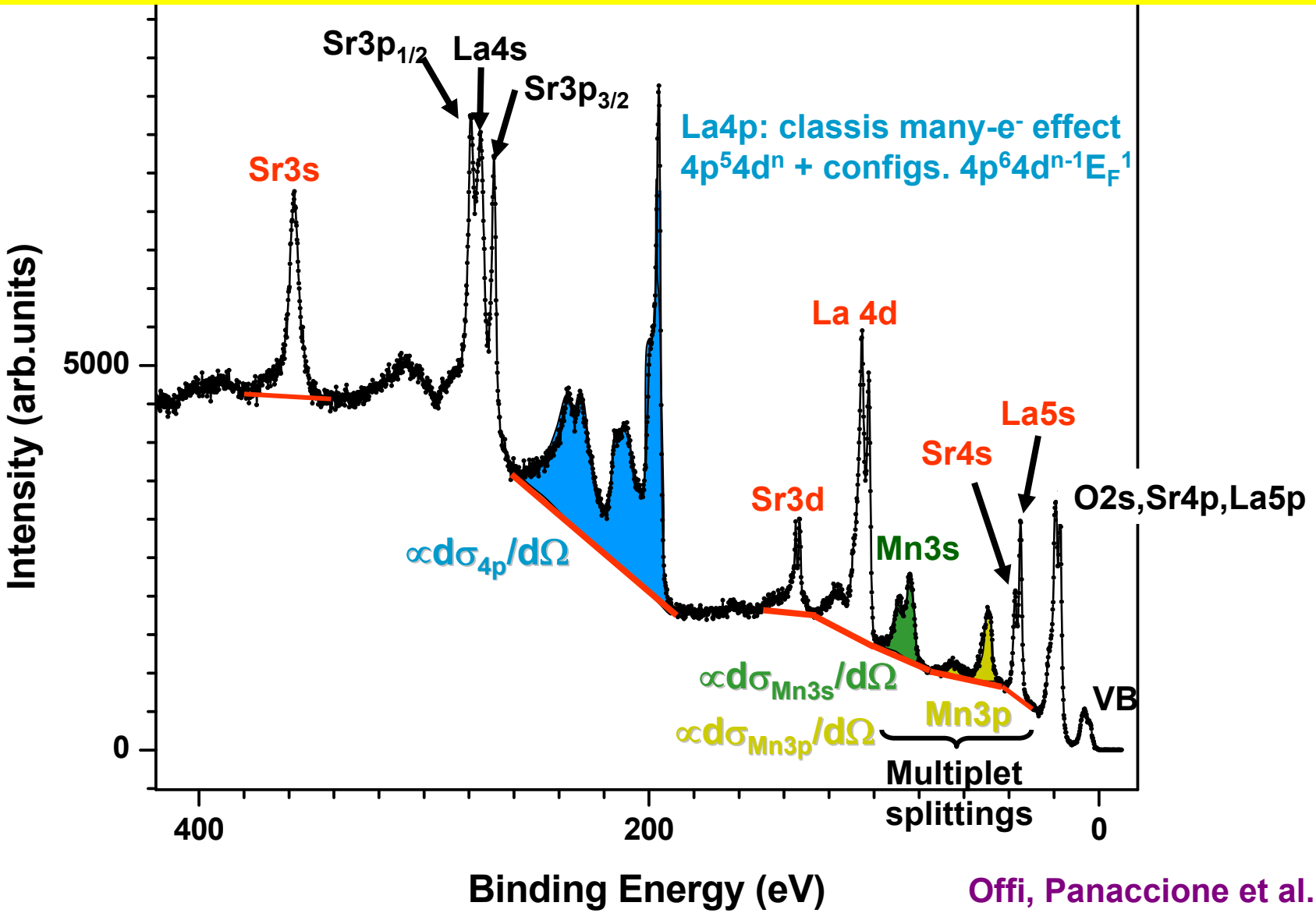
•More bulk sensitive spectra → a versatile tool for any new material, multilayer nanostructure

•Inelastic background less important & Augers more widely spread, less overlap

•Easier quantitative analysis via core spectra, but intensity drops for non-grazing incidence→rotateable analyzer or wide-angle lens

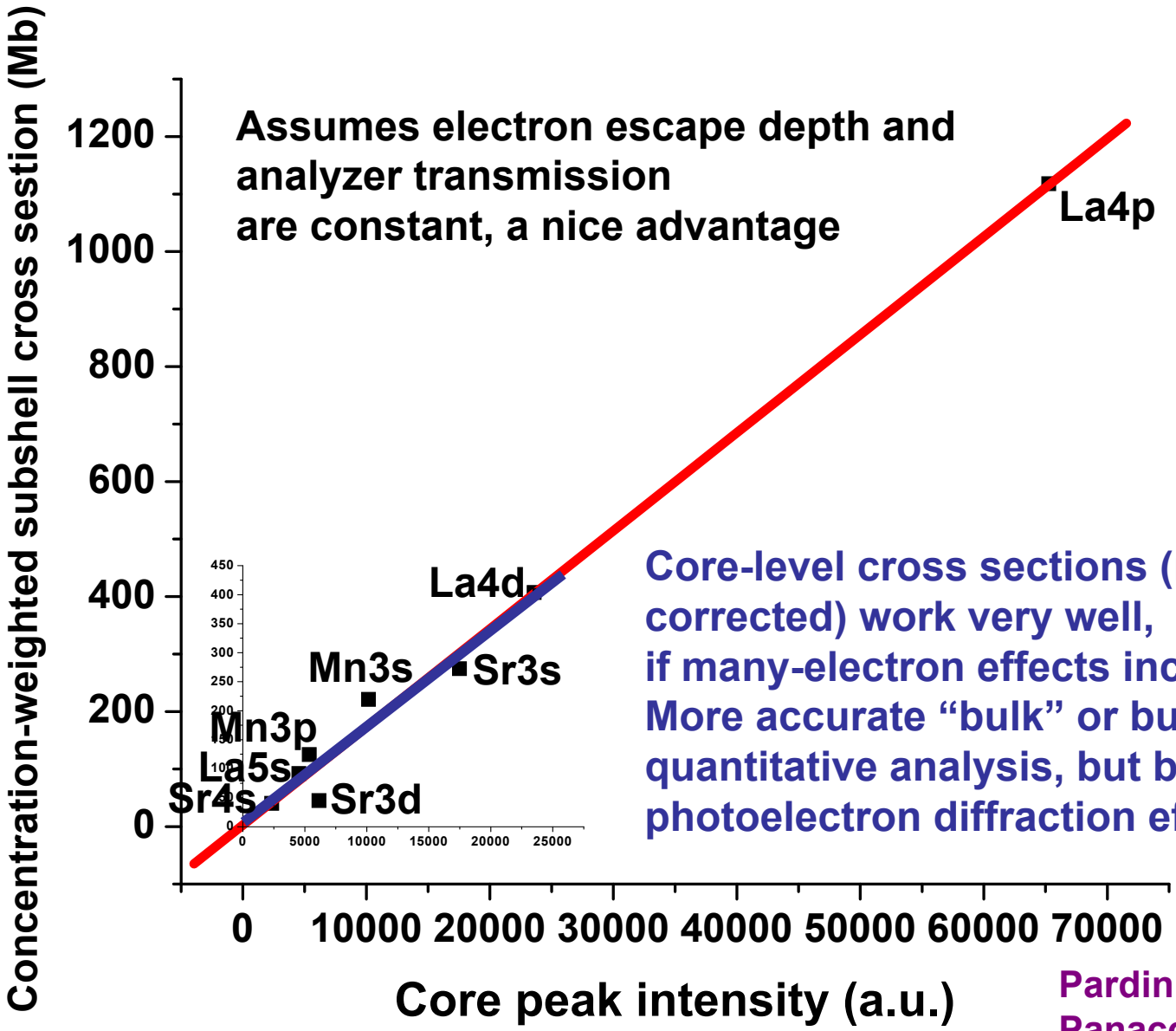
Minusses

Hard x-ray photoemission--Quantitative analysis of peak intensities using theoretical cross sections: $La_{0.7}Sr_{0.3}MnO_3$, $h\nu$ = 7700 eV



Offi, Panaccione et al., ESRF-VOLPE

Quantitative analysis of peak intensities using theoretical cross sections (Scofield): $La_{0.7}Sr_{0.3}MnO_3$, $h\nu$ = 7700 eV



Core-level cross sections (non-dipole corrected) work very well, if many-electron effects included→ More accurate "bulk" or buried layer quantitative analysis, but be careful of photoelectron diffraction effects

Pardini, Offi, Panaccione, CF

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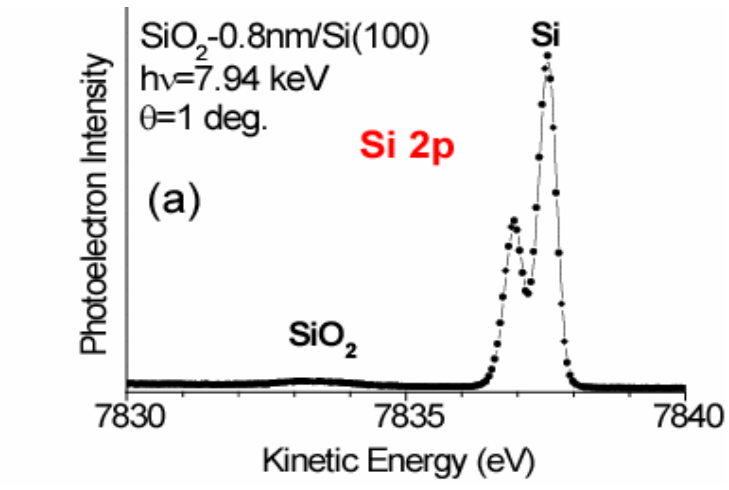
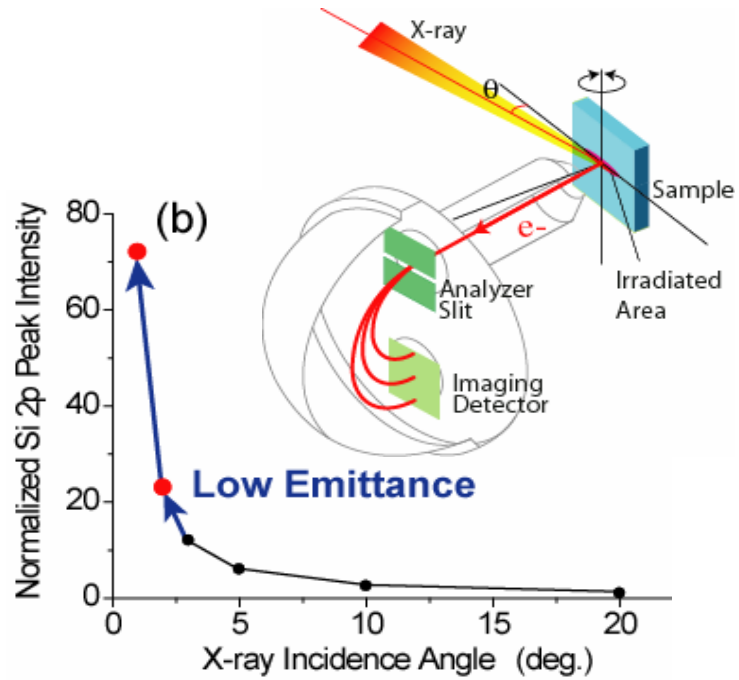
Minusses

Effect of Grazing Incidence of X-rays





Takata et al.

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•Easier interpretation of ARXPS data → surface and bulk information

Minusses

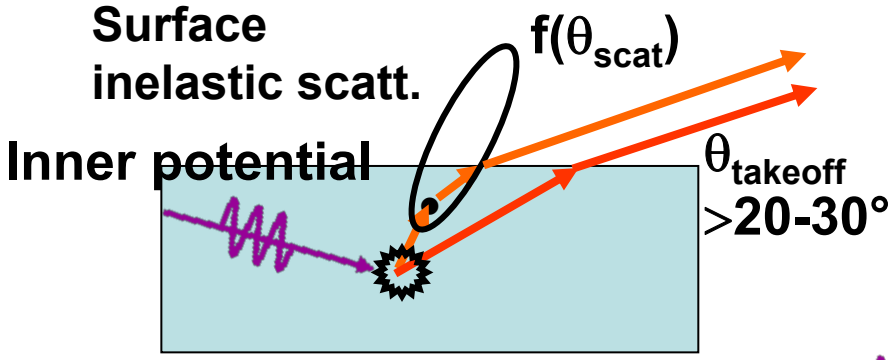
Varying surface sensitivity for lower electron takeoff angles—ARXPS & ARHXPS

Simplest interpretation:

Average emission depth = $\Lambda_{inelastic} \sin\theta_{takeoff}$

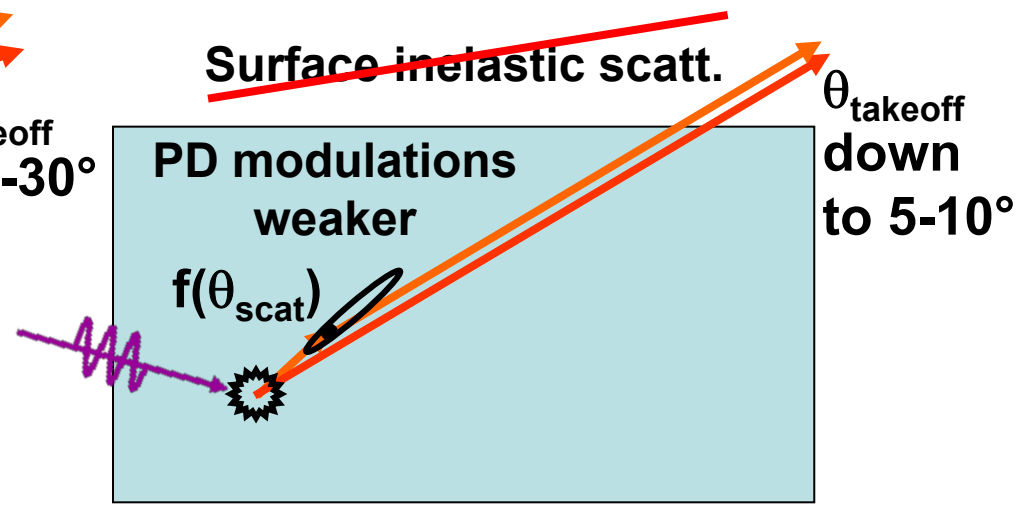
How valid?

$E_{kin} \approx$ 500-1000 eV



E.g.: A. Jablonski and C. J. Powell, J. Vac. Sci. Tech. A 21, 274 (2003):
→ Mean Emission Depth (MED) more relevant than $\Lambda_{inelastic}$

$E_{kin} \approx$ 10,000 eV



Approx. constant analyzer transmission

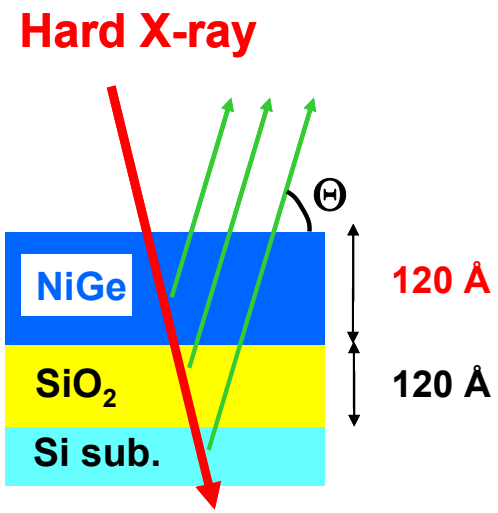
Simpler analysis

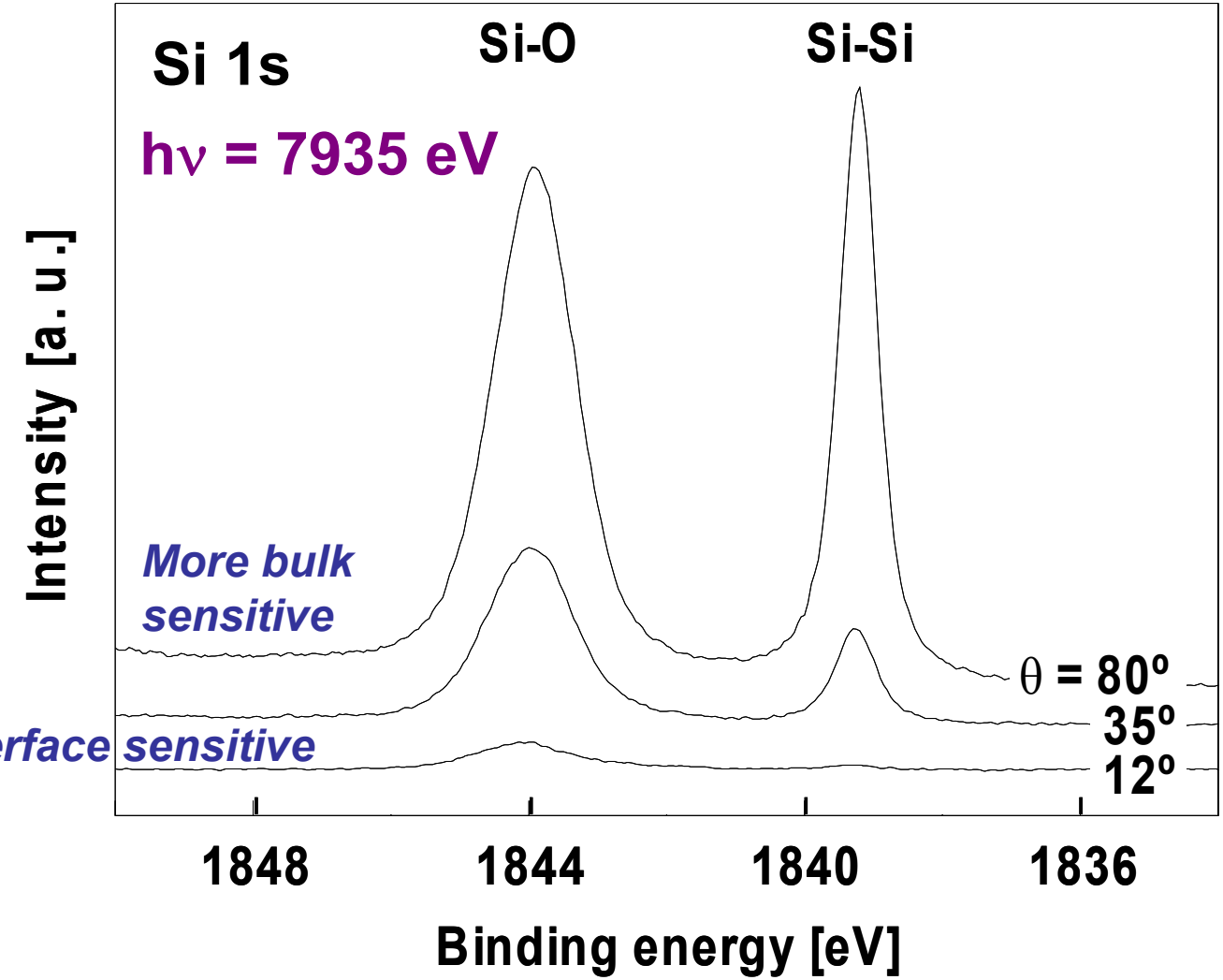
Cleaner bulk & surface distinction

C.S.F., Nucl. Inst. & Meth. A 547, 24 (2005)

Kover, Werner, Drube, et al., Surf. & Int. Anal. 38, 569 (2006)

ARHXPS for Si 1s photoelectron spectra from NiGe(12-nm)/SiO_2(12-nm)/Si(100)



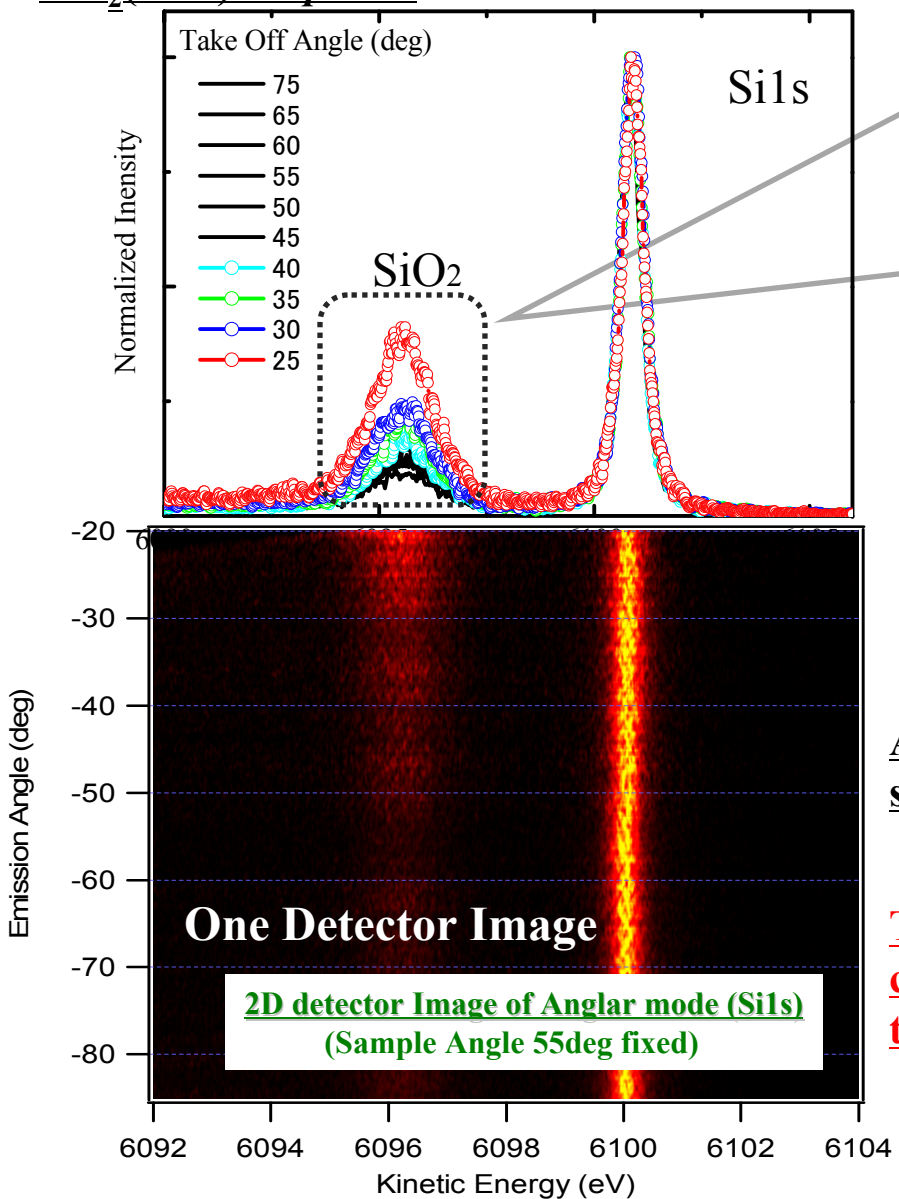


Unpublished data courtesy of H. Kondo, Nagoya University

Angle-Resolved Hard X-ray Photoemission Spectroscopy

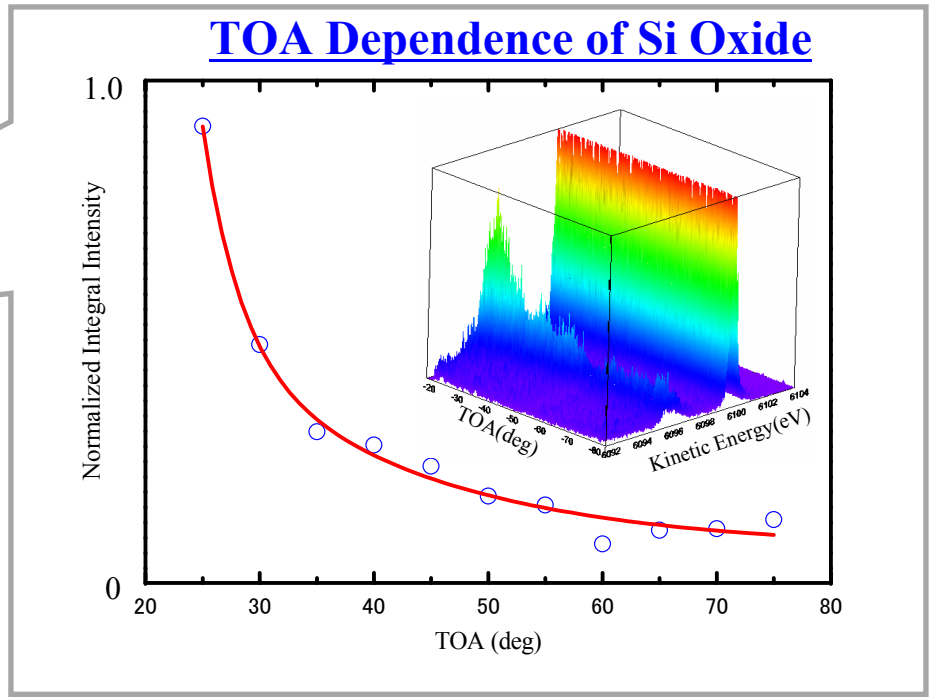
(Evaluation of Depth Probing)

SiO_2(4nm)/Si *spectra*



TOA dependence of Si1s from SiO_2
Normalized by substrate Si1s intensity

Photon Energy=7.94KeV
Pass Energy=200eV
Slit:=C 0.5



An oxide component increase is confirmed at the surface !

The emitted electron angle and depth information can be acquired without changing the angle of the sample.

10 min acquisition

Ikenaga

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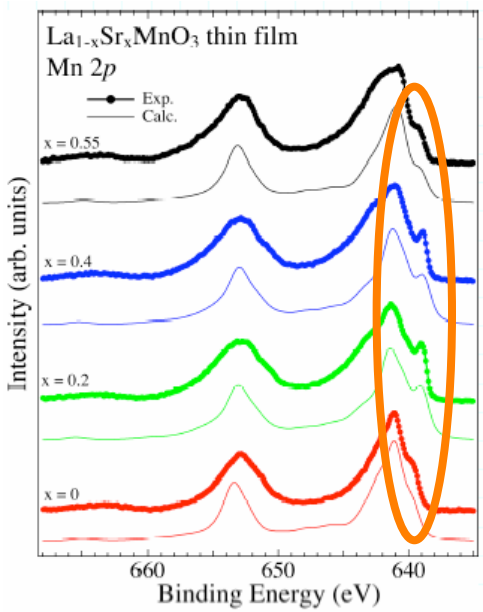
•New "bulk fingerprint" screening effects seen in both core and valence spectra

Minusses

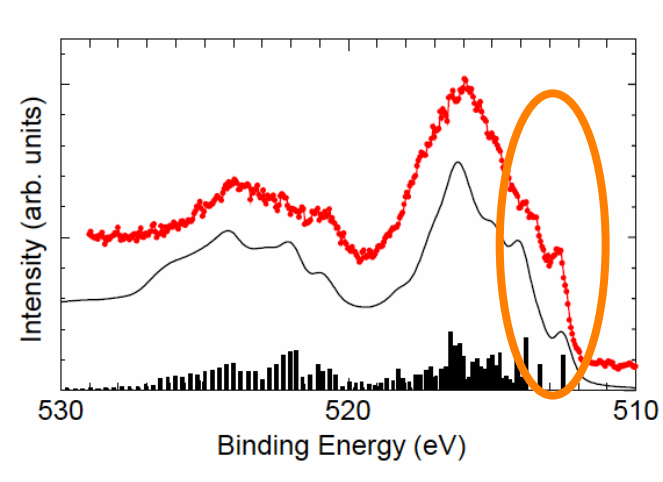
Introduction

$La_{1-x}Sr_xMnO_3$



Horiba *et al.*,
PRL **93** 236401 (2004)

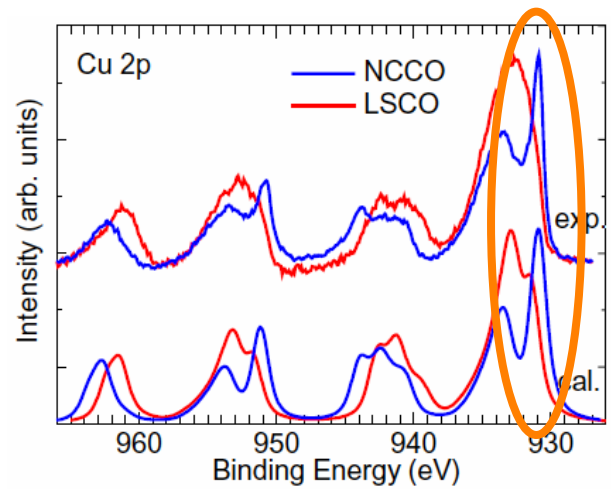
$V_{1.98}Cr_{0.02}O_3$



Taguchi *et al.*,
PRB **71** 155102 (2005)

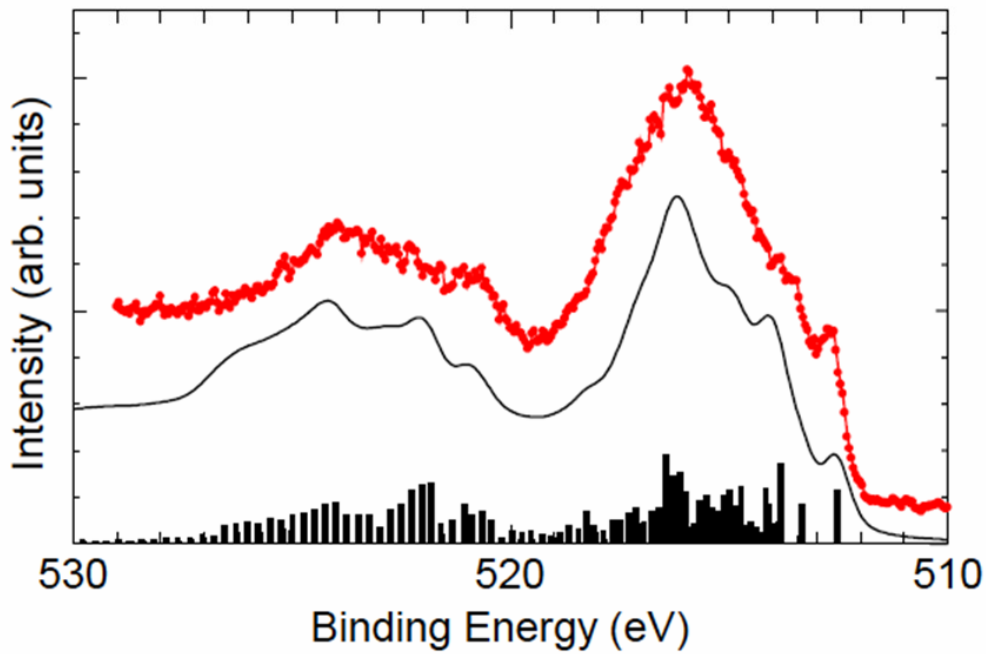
Kamakura *et al.*,
EPL 68 557 (2004)

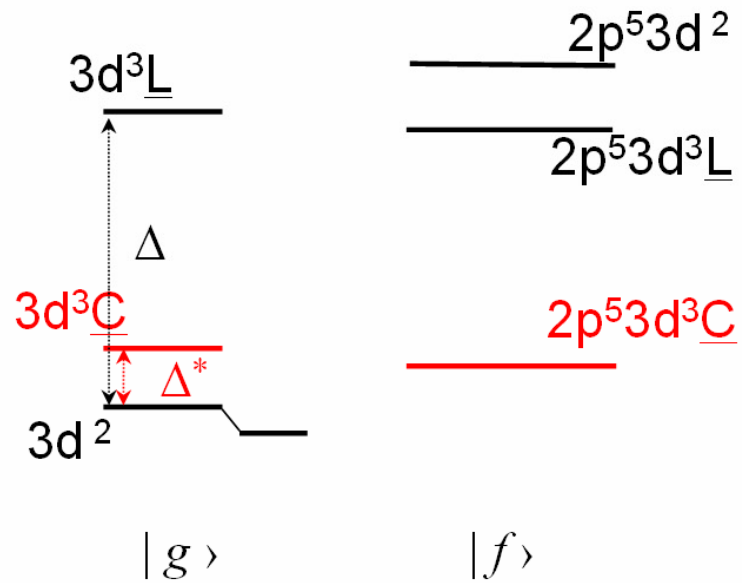
High T_c cuprates



Taguchi *et al.*,
PRL **95** 177002 (2005)

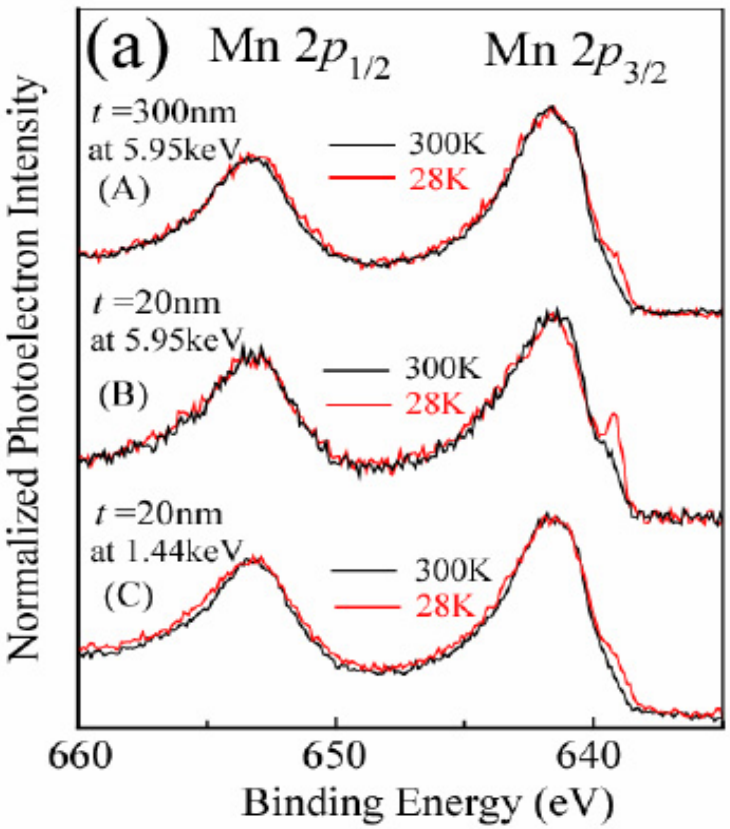
Calculation vs. Experiment

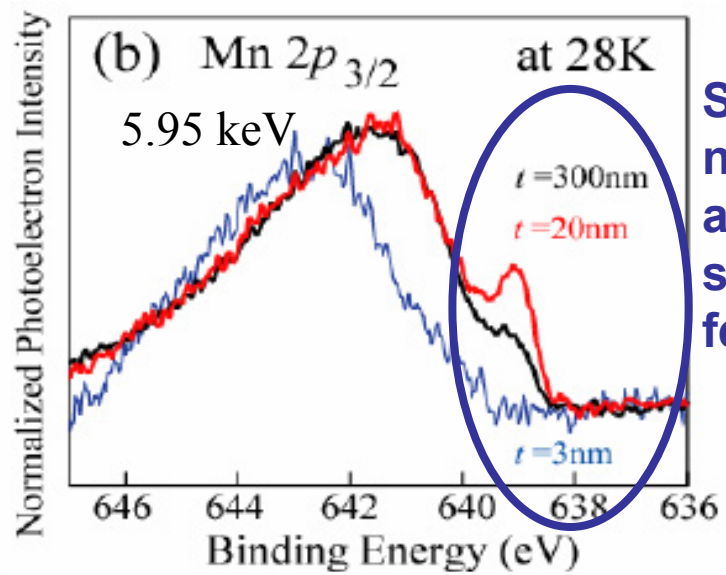




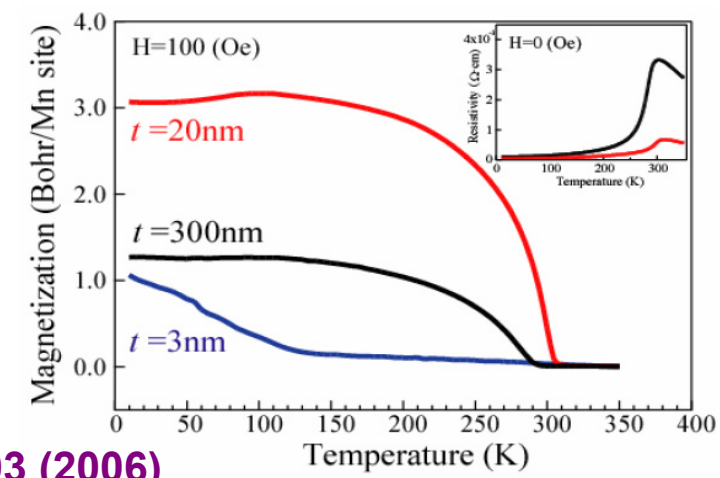
Taguchi *et al.*
PRB **71**, 155102 (2005)

Electronic Structure of Strained Manganite Thin Films with Room Temperature Ferromagnetism Investigated by Hard X-ray Photoemission Spectroscopy: $La_{0.85}Ba_{0.15}MnO_3$



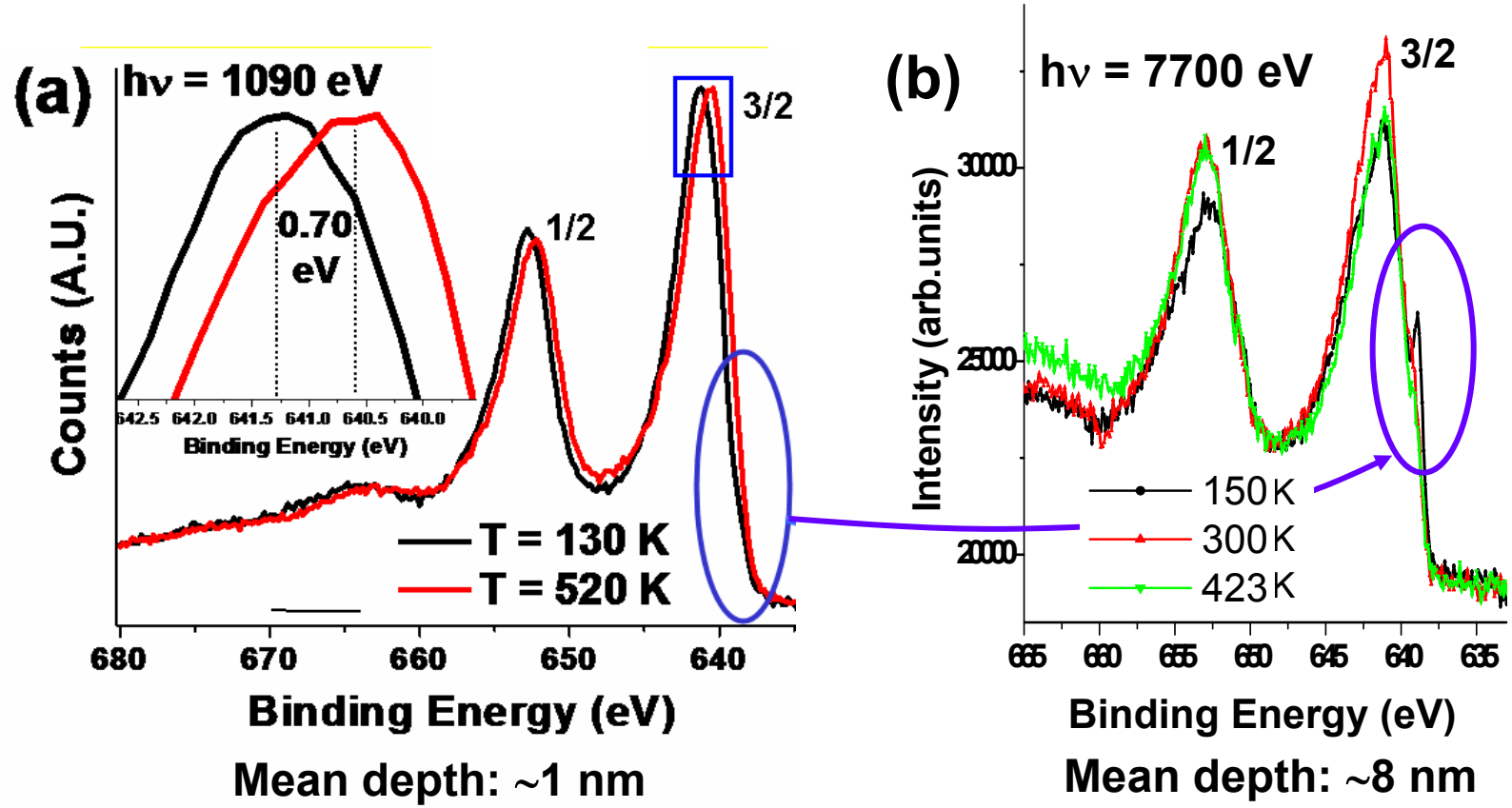


Strain/Magnetism-associated screening feature



Tanaka et al., Spring8, Phys. Rev. B 73, 094403 (2006)

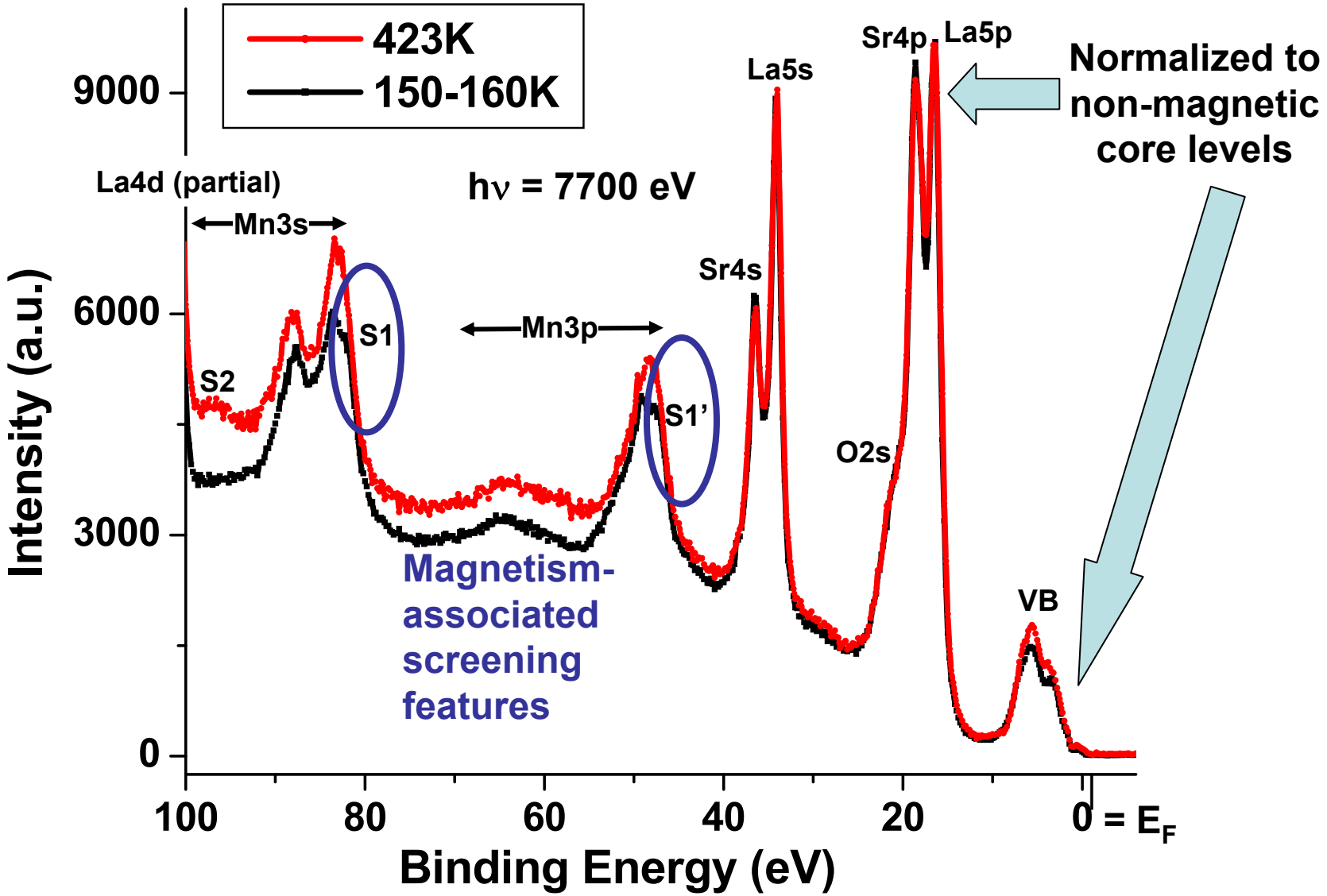
Mn magnetic moment change: bulk or surface effect?
Compare soft and hard x-ray data
Temperature dependence of Mn2p spectra: $La_{0.7}Sr_{0.3}MnO_3$



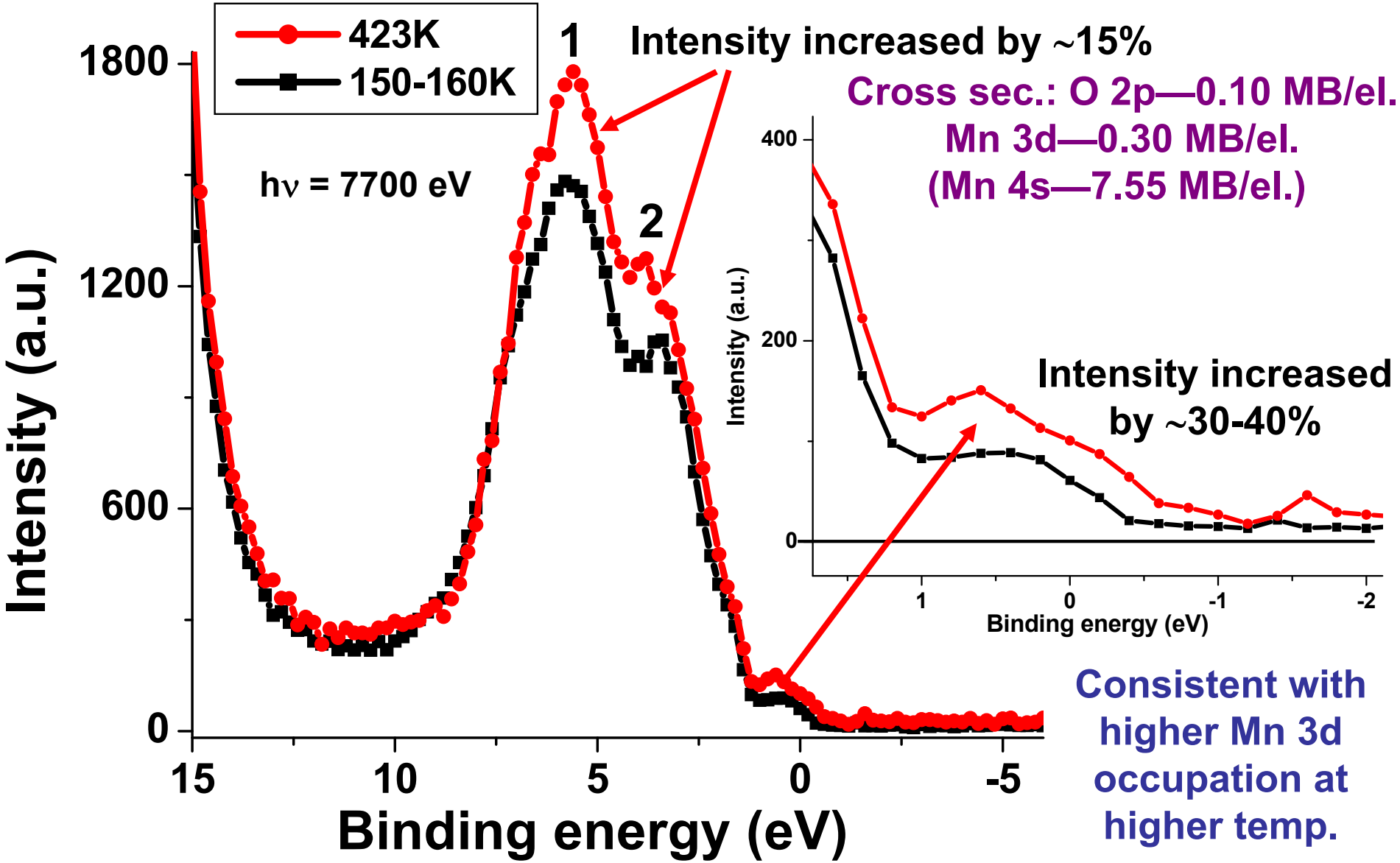
→Suggests bulk electronic structure not reached until ca. 8 nm depth

Offi, Mannella et al., Phys. Rev B 77, 174422 (2008)

Presence of "bulk" magnetism-associated screening features on on both Mn 3s and 3p features



Derivation of density-of-states information from core-normalized HXPS valence-band spectra



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•3d "bulk" band mapping ARPES capability with cryocooling—How high in energy?

-And/Or-

•Direct DOS info. at higher energies and temperatures

Minusses

•Intensity calculations must allow for photon wave vector, other non-dipole effects

•Phonon effects reduce capability for ARPES at higher energies/temperatures

Hard X-Ray Angle-Resolved and Standing-Wave Photoemission

Julich Research Center

The Advanced Light Source

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technische universität dortmund

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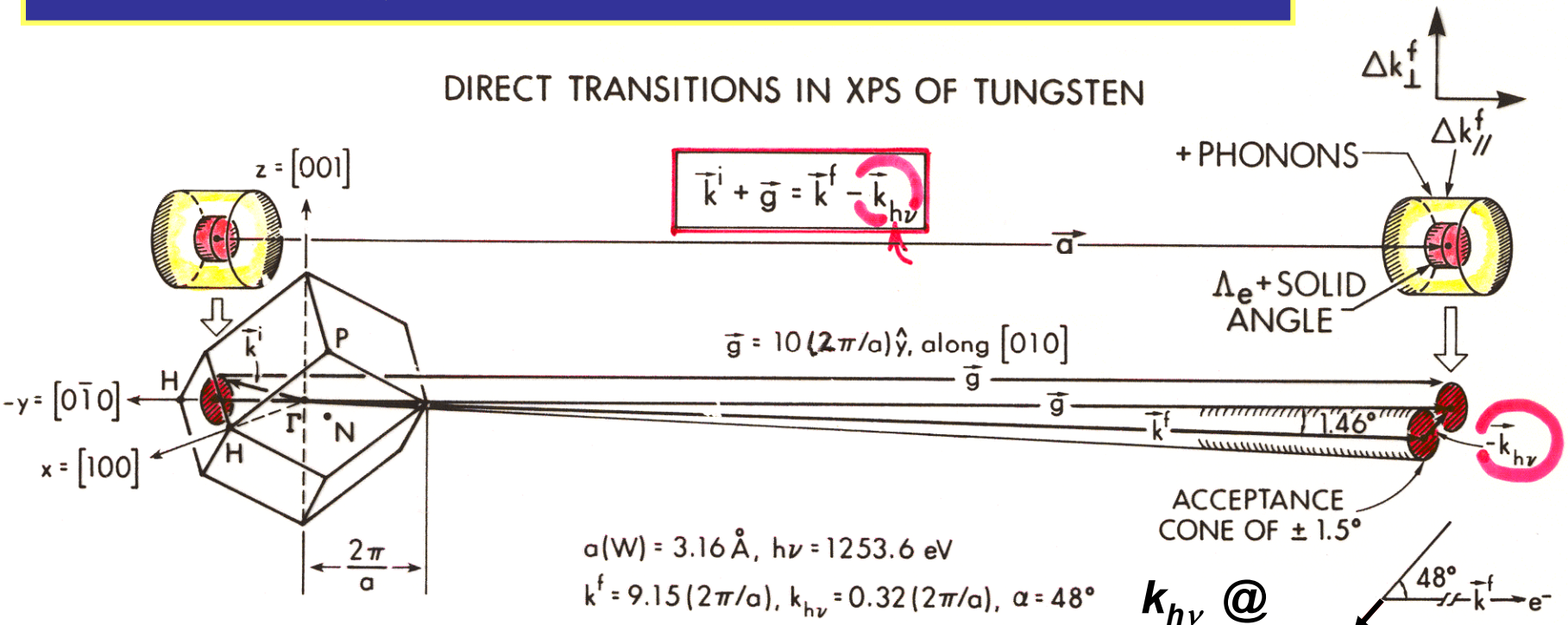
[4]Physics Dept., Tech. Univ. of Dortmund, Germany
[5]Advanced Light Source, Lawrence Berkeley National Laboratory,
[6]RIKEN, Low Temperature Physics Lab., Saitama, Japan
[7]Dept. of Applied Physics, Stanford University
[8]NIMS, SPring8
[9]BESSY, Berlin, Germany
[10]Research Center Jűlich, Germany
[11]Applied Materials Inc.

Valence-Band Photoemission at High Energy-- What & Where is the "XPS Limit"?:



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

$k_{h\nu}$ @ 10,000 eV

Additional effects at higher energies:

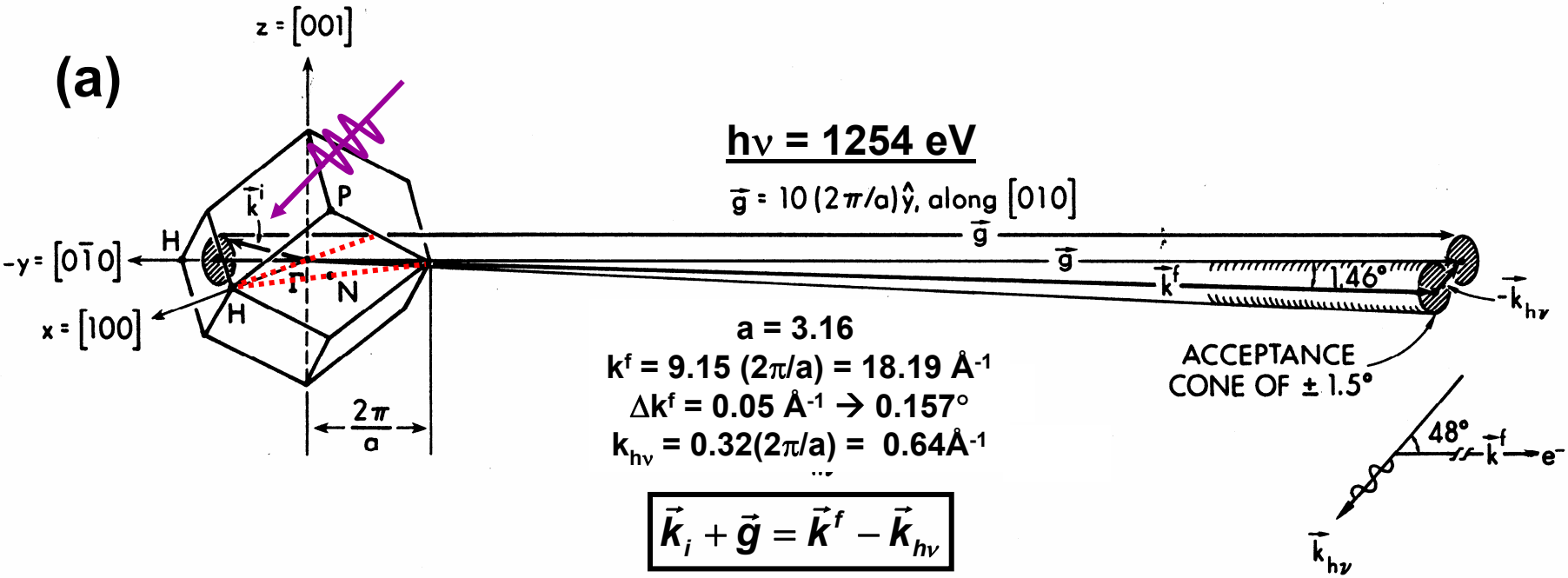
- **non-dipole--the photon momentum**
- **angular acceptance→B.Z. averaging**
- **lattice recoil, phonon creation→more B.Z. averaging, ~Debye-Waller factor =** $W(T) \approx \exp[-(k^f)^2 \langle u^2(T)\rangle]$

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

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

Hussain et al., Phys. Rev. B 22, 3750 ('80)

(a)



hν = 1254 eV

$\vec{g} = 10(2\pi/a)\hat{y}$, along [010]

a = 3.16

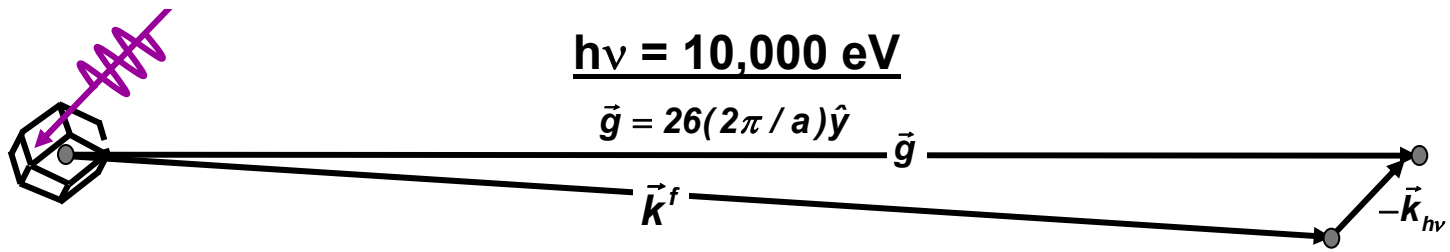
$k^f = 9.15\ (2\pi/a) = 18.19\ Å^{-1}$

$\Delta k^f = 0.05\ Å^{-1} \rightarrow 0.157°$

$k_{h\nu} = 0.32(2\pi/a) = 0.64 Å^{-1}$

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

(b)



hν = 10,000 eV

$\vec{g} = 26(2\pi/a)\hat{y}$

$k^f = 25.80\ (2\pi/a) = 51.29\ Å^{-1}$

$\Delta k^f = 0.05\ Å^{-1} \rightarrow 0.055°$

$k_{h\nu} = 2.54(2\pi/a) = 5.05\ Å^{-1}$

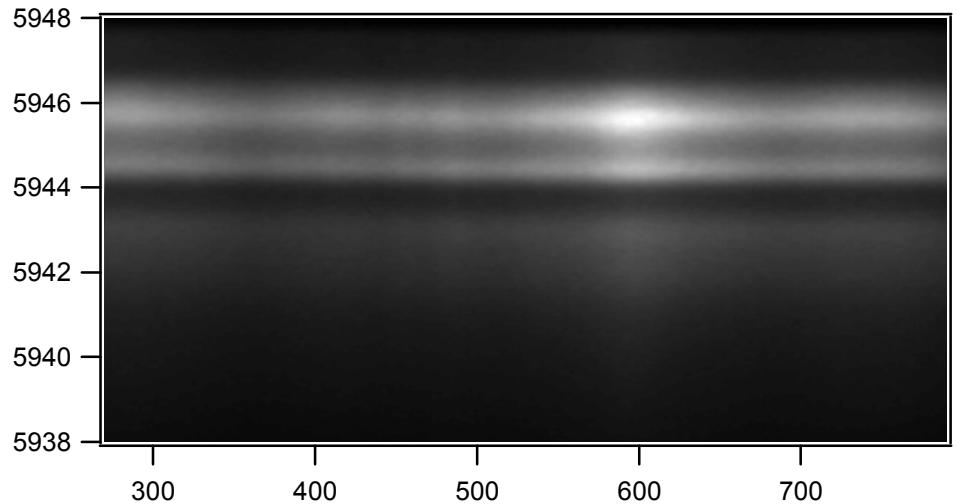
ACCEPTANCE
CONE OF ±0.53°

But angular resolutions of 0.02° with an acceptance ±2° may be possible!
B. Wannberg

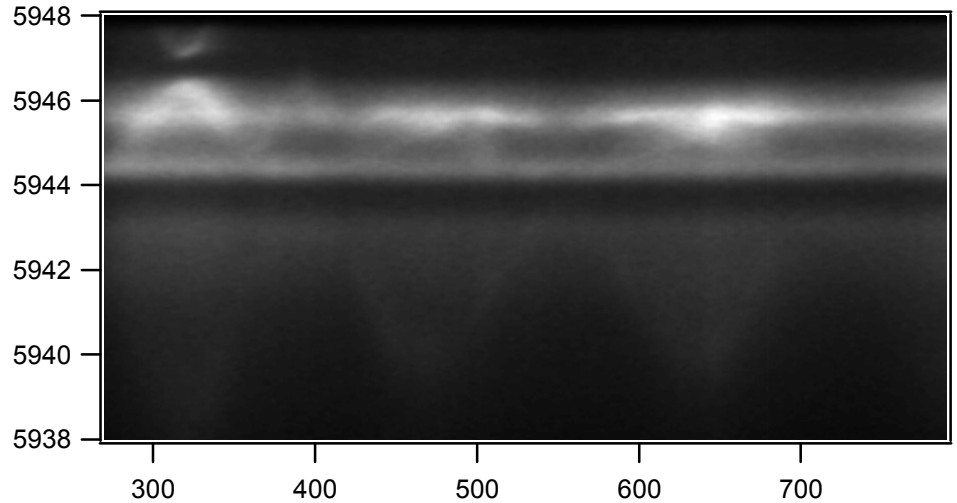
W(110)-Raw data, Temperature Dependence 5954 eV

39 channels = 1 deg

Room temperature: W(T) ≈ 0.10 Density of states ("XPS limit") + x-ray photoelectron diffraction* (Winkelmann poster)



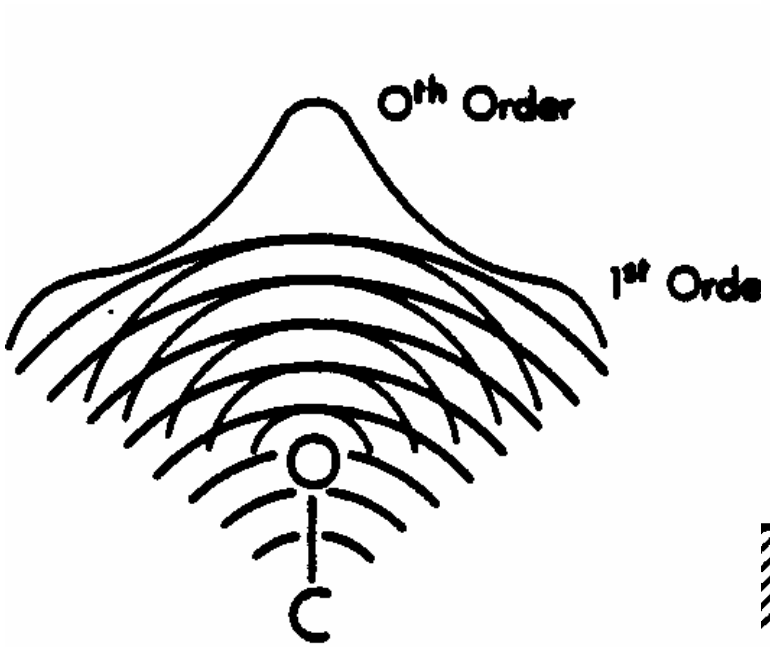
30 K: Mix of bands HX-ARPES and DOS+XPD

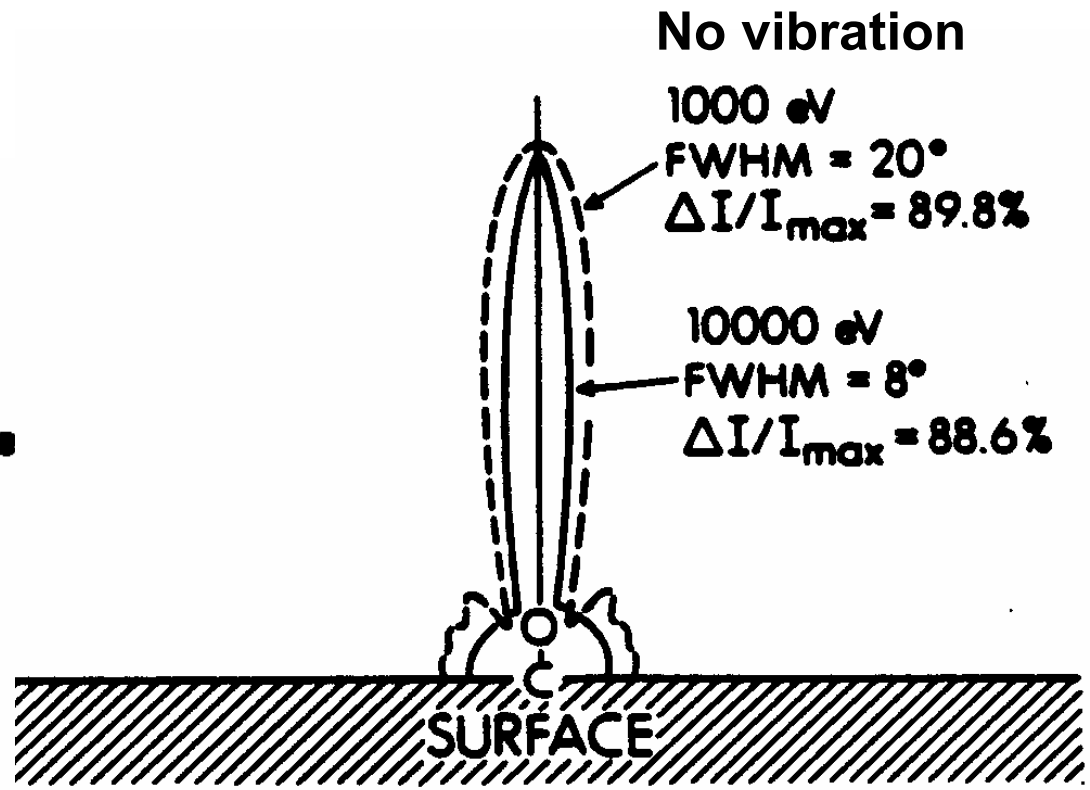


*Osterwalder et al. PRL 64, 2683 (1990)
Herman et al., PRL 68, 1204 (1992)
Zampieri et al., PRB 54, 14703 (1996)

Ueda, Kobayashi, et al., SPring8

Photoelectron diffraction with hard x-ray excitation: 1000 eV→10,000 eV, the first theoretical study





Qualitative expectations:

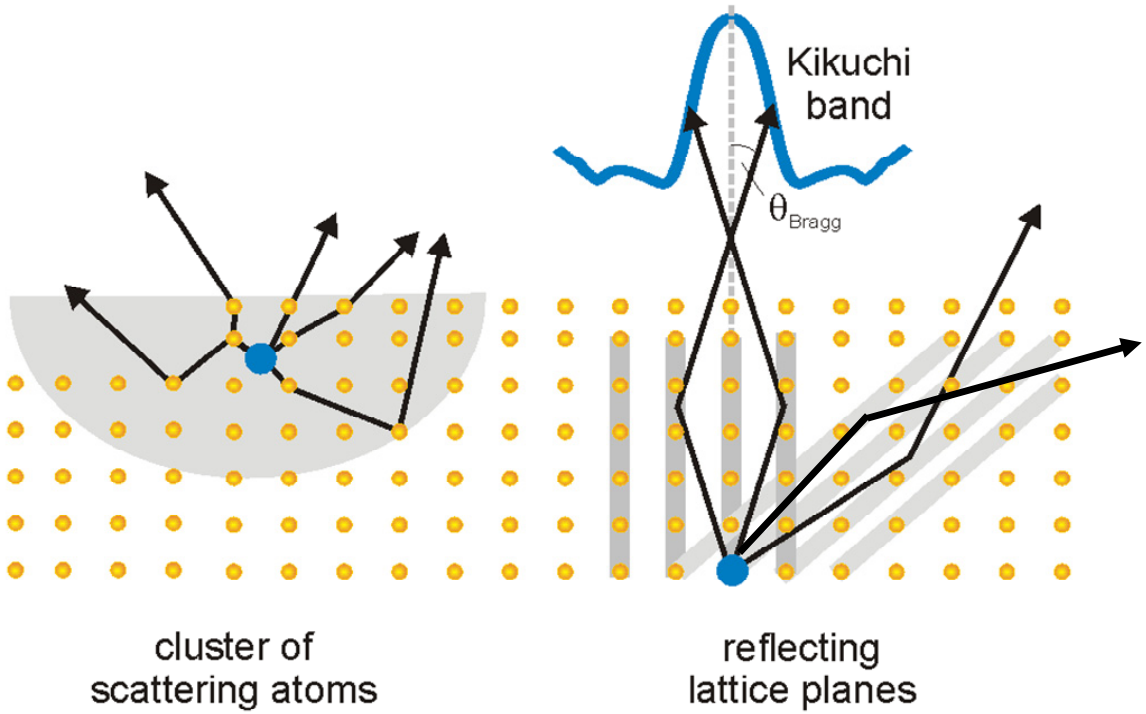
Forward scattering peak strengths f(0) ~ constant

Overall scattering cross section $\sigma = \int f d\Omega$ decreases

K.A. Thompson and C.F.
J. Elect. Spect. 33, 29 ('84)

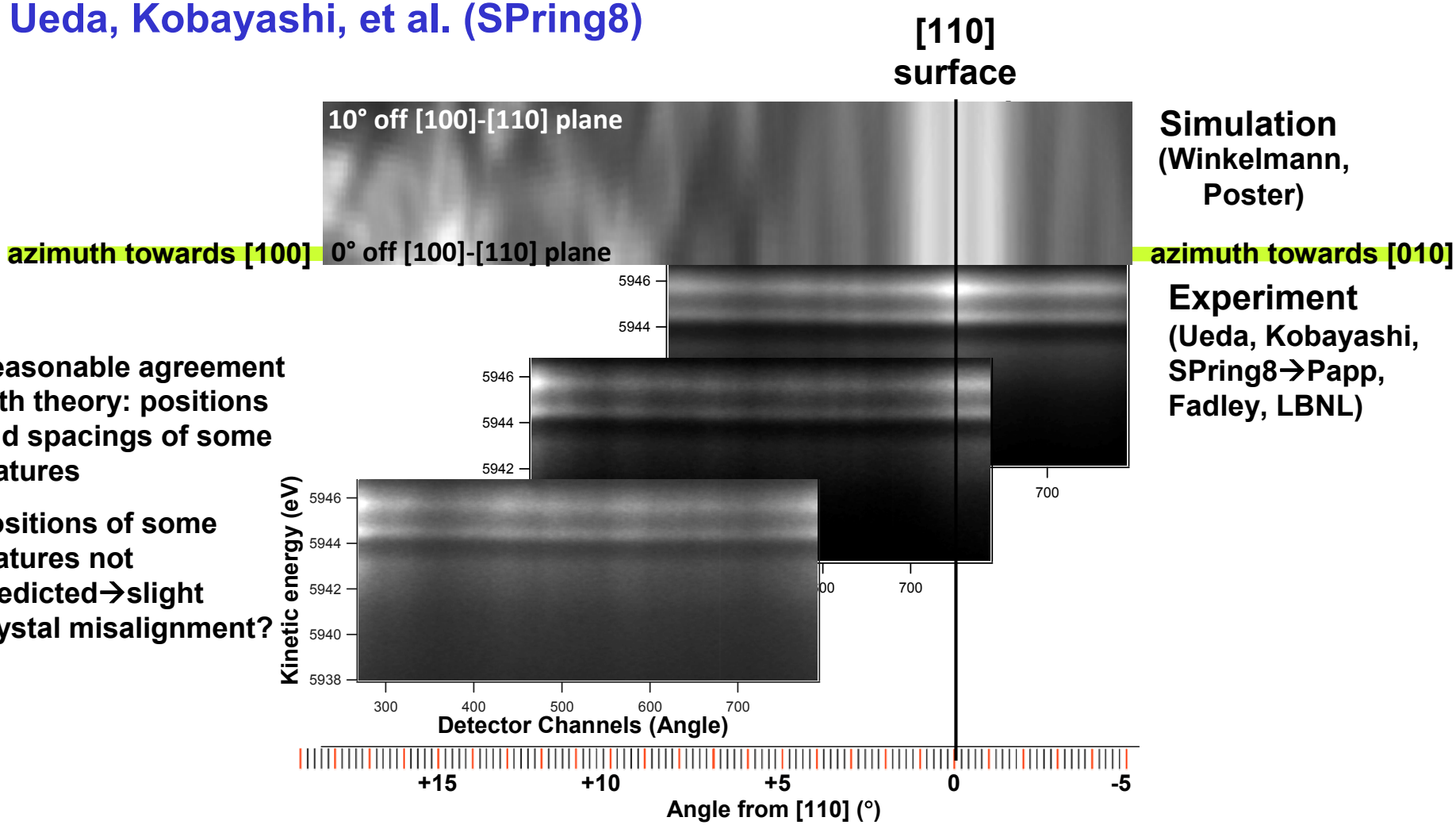
PHOTOELECTRON DIFFRACTION

The scattering of photoelectrons from localized sources can be described in real space (multiple scattering cluster) and reciprocal space (dynamical theory of electron diffraction)



A. Winkelmann, J. Garcia de Abajo, C.F.,
B. New Journal of Physics 10 (2008) 113002
(poster in HAXPES09)

W(110) Valence-Band HXPD from W(110) at 6kV, 300K by Ueda, Kobayashi, et al. (SPring8)



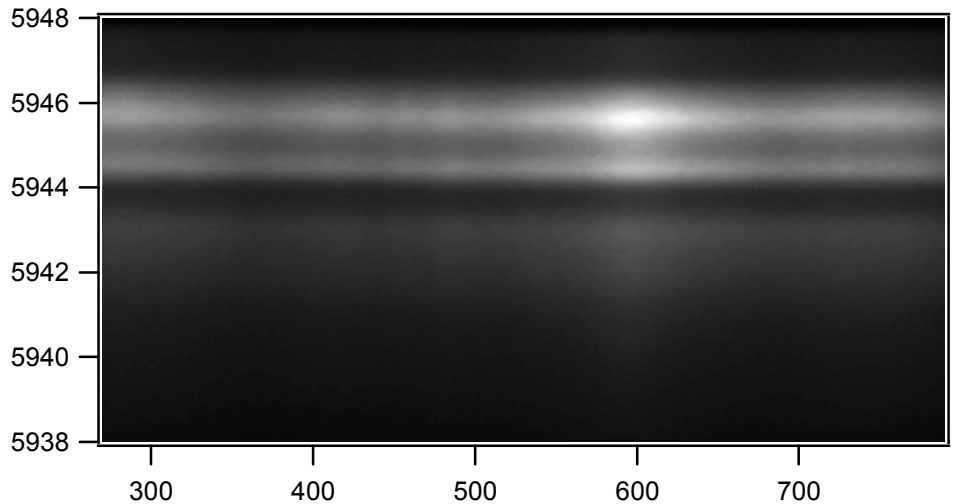
Reasonable agreement with theory: positions and spacings of some features

Positions of some features not predicted→slight crystal misalignment?

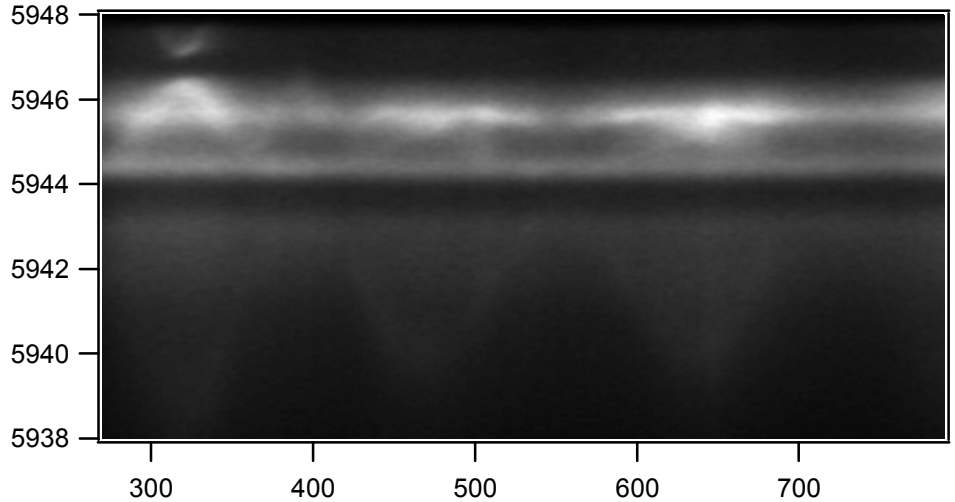
W(110)-Raw data, Temperature Dependence 5954 eV

39 channels = 1 deg

Room temperature:
W(T) ≈ 0.10
Density of states ("XPS limit") + x-ray photoelectron diffraction (Winkelmann poster)



30 K:
W(T) ≈ 0.45
Mix of bands
HX-ARPES and DOS+XPD



Ueda, Kobayashi, et al., SPring8

Hard X-Ray ARPES: W(110), hν = 5945 eV
SPring8, BL15XU, Ueda et al.

The free-electron picture:

$(2\pi / a) = 1.988\ A^{-1}$

$h\nu = 5945$ eV

$|\vec{k}_f| = 0.512E_{kin}^{0.5}(eV) = 39.48\ A^{-1} = 19.85\ (2\pi / a)$

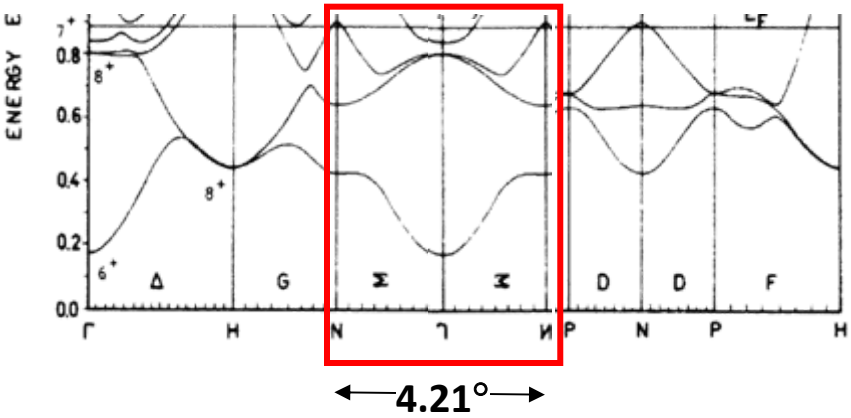
$|\vec{k}_{h\nu}| = 0.000507(h\nu(eV)) = 3.01\ A^{-1} = 1.51\ (2\pi / a)$

$|\vec{k}_f - \vec{k}_{h\nu}| = \left[39.48^2 + 3.01^2\right] = 39.59\ A^{-1} = 19.91\ (2\pi / a) - - > 14.08\ [1.414((2\pi / a)]$

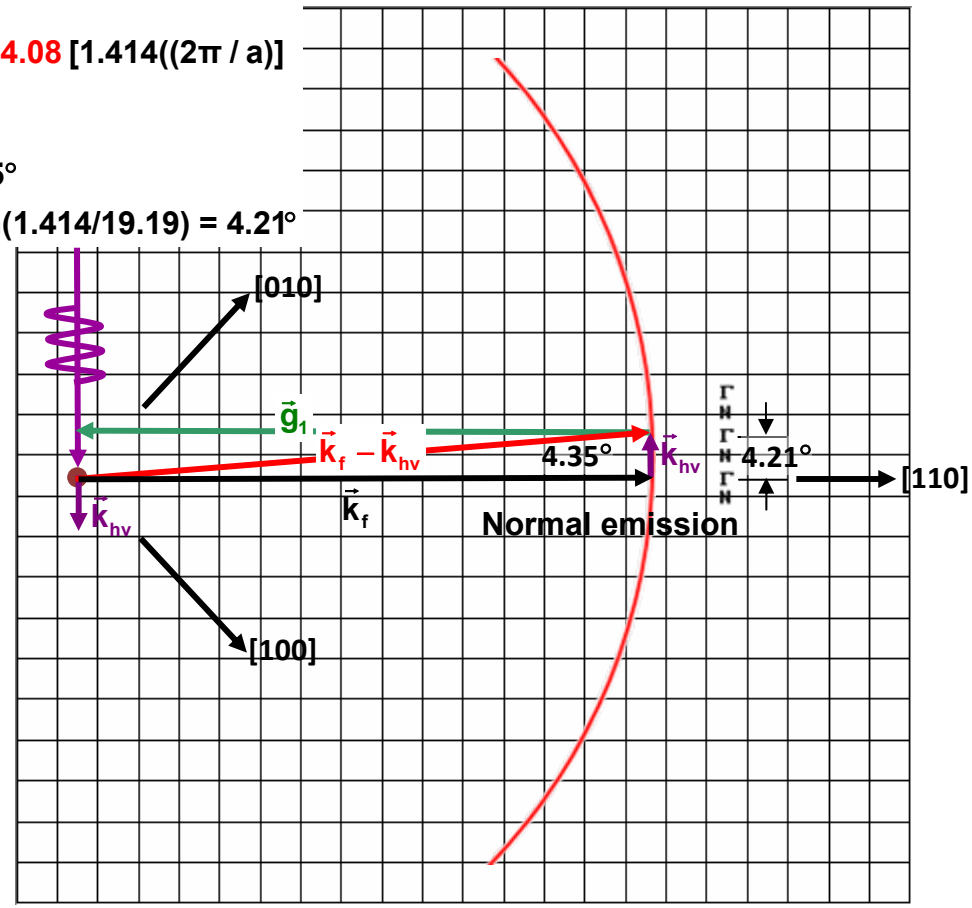
$|\vec{g}_1| = 14.00\ [1.414((2\pi / a)]$

Angular deflection due to $\vec{k}_{h\nu}$ is : $\arctan(3.01 / 39.48) = 4.35°$

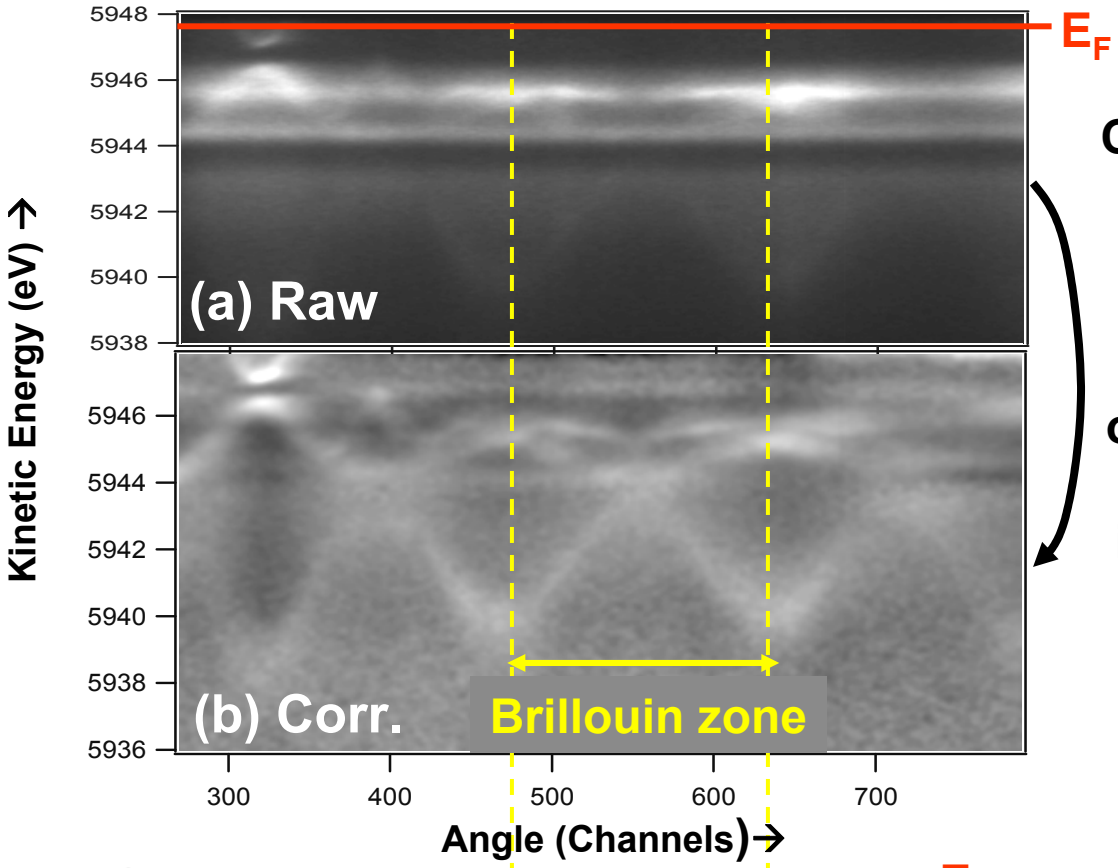
$\Gamma - N - \Gamma$ is $1.414(2\pi / a)$, so angular range of this is $\arctan(1.414/19.19) = 4.21°$



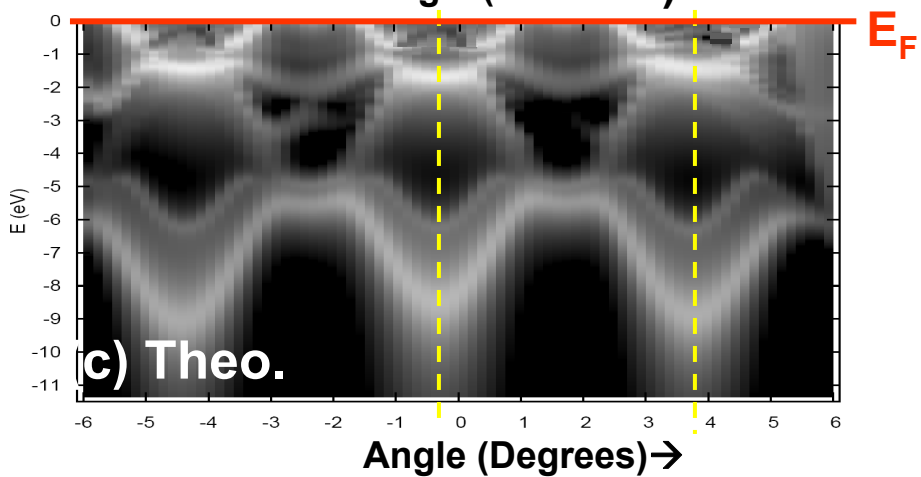
W extended zone-[110]-[100] plane



W(110), hν = 5,954 eV, T = 30K: Comparison to one-step theory, matrix elements

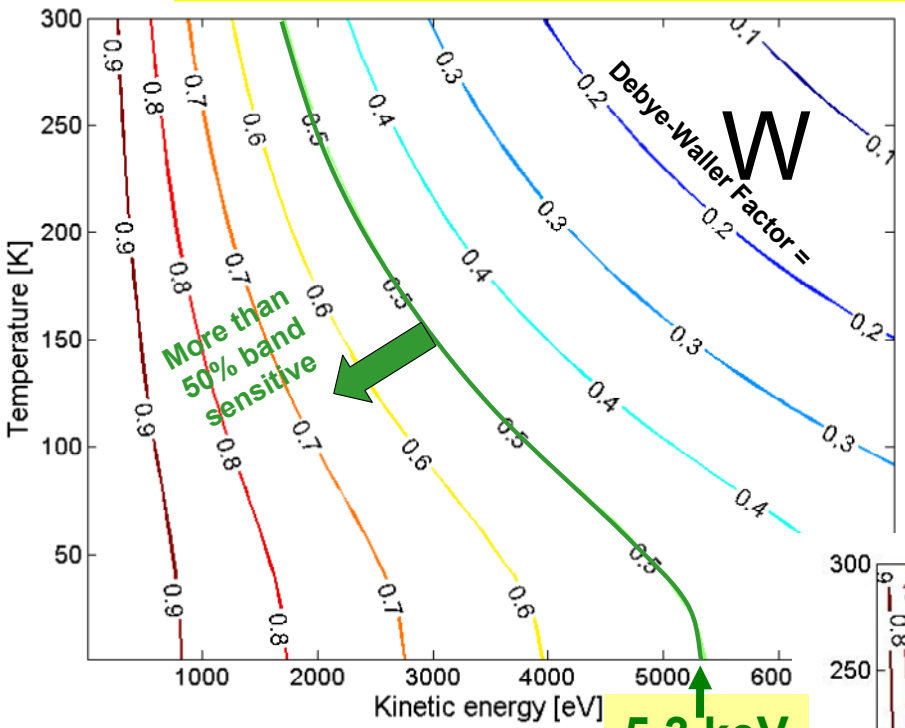


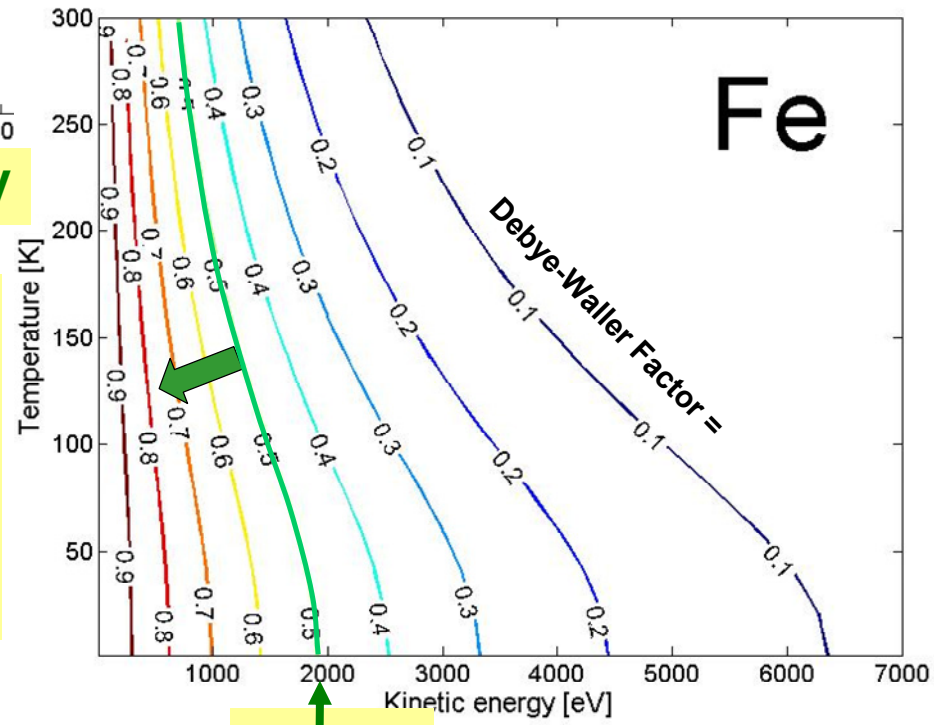
Corrected for phonon-induced density-of-states-like intensity



Expt.-Ueda, Kobayashi, SPring8
Data analysis-Papp, Gray, Plucinski, C.F.
Theory-Minar, Braun, Ebert

Approximate recoil-free fraction→fraction DTs





W an optimal case, but for 37 elements*, ~1-3 keV OK, maybe higher with better DOS correction procedures and theory of phonons in ARPES

Plucinski

Hard x-ray photoemission—plusses and minusses

•Plusses

•More bulk sensitive spectra → a versatile tool for any new material, multilayer nanostructure

•Inelastic background less important & Augers more widely spread, less overlap

•Easier quantitative analysis via core spectra, but intensity drops for non-grazing incidence

•Less radiation damage?

•Easier interpretation of ARXPS data → surface and bulk information

•New "bulk fingerprint" effects seen in both core and valence spectra

•3d "bulk" band mapping ARPES capability with cryocooling—How high in energy?

-And/Or-

•Direct DOS info. at highest energies and temperatures

Minusses

•Recoil energy limits resolution, esp. for lighter elements, complex systematics, depending on local bond distances/phonon frequencies→Doppler spectroscopy?

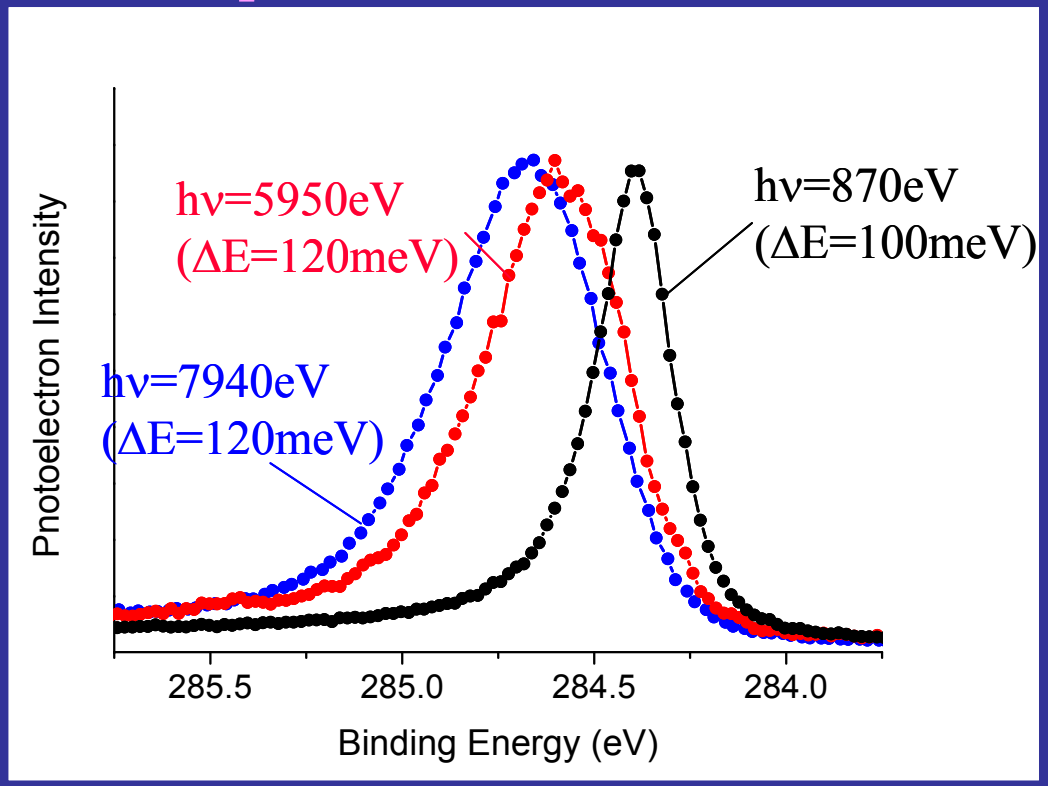
•Intensity calculations must allow for photon wave vector, other non-dipole effects

•Phonon effects reduce capability for ARPES at higher energies/temperatures

Recoil effects in PES: C 1s core level spectra of graphite

Y. Takata et al., PRB 75, 233404 (2007)

KE dependence at normal emission



$$E_{recoil} \approx (m_e/M_{atom})E_{kin}$$

With increase of hν (KE)

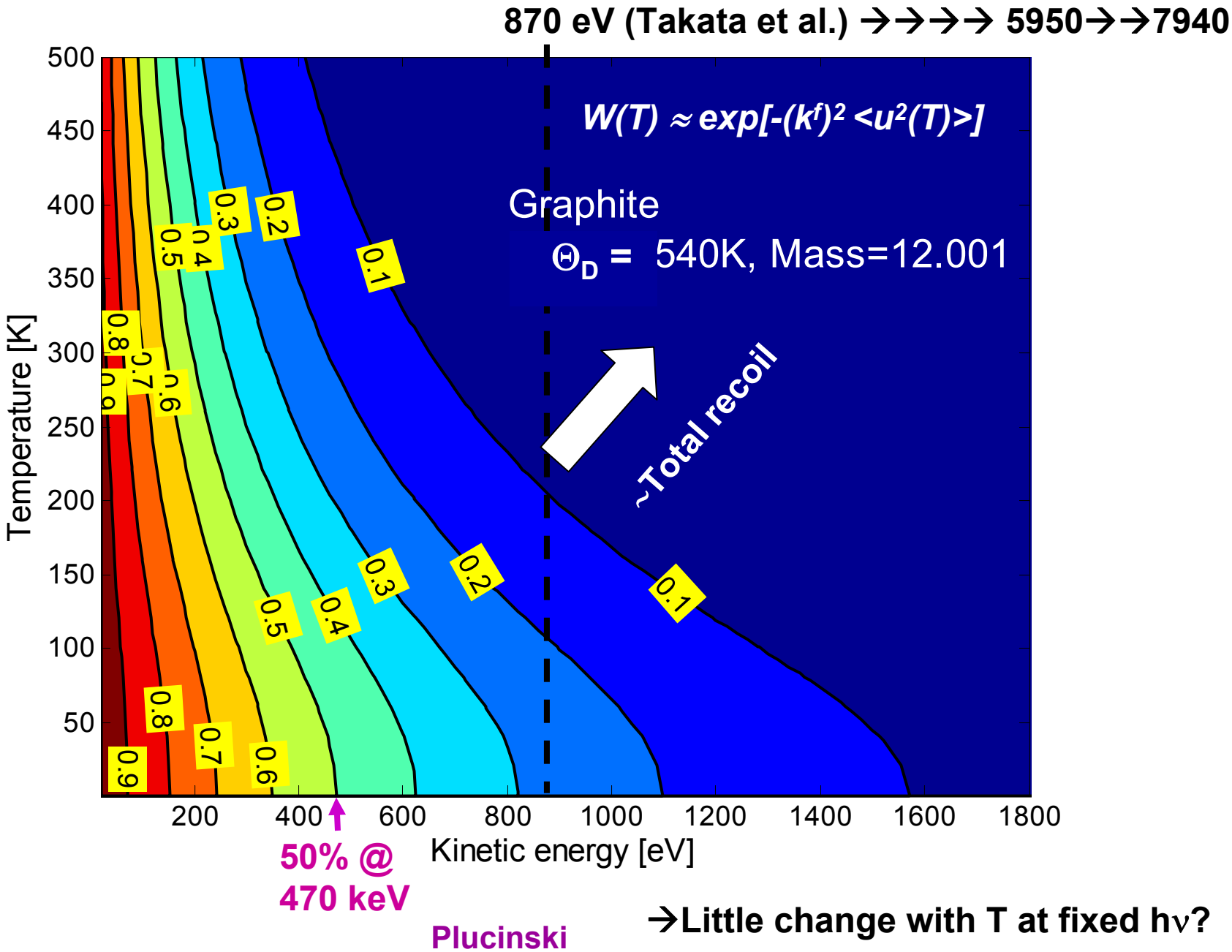
- ☆increase of BE
- ★KE loss
- ★asymmetric broadening

- ★ not observed in Au
- ★ not due to semimetallic character
- ★ not due to bulk vs surface

but

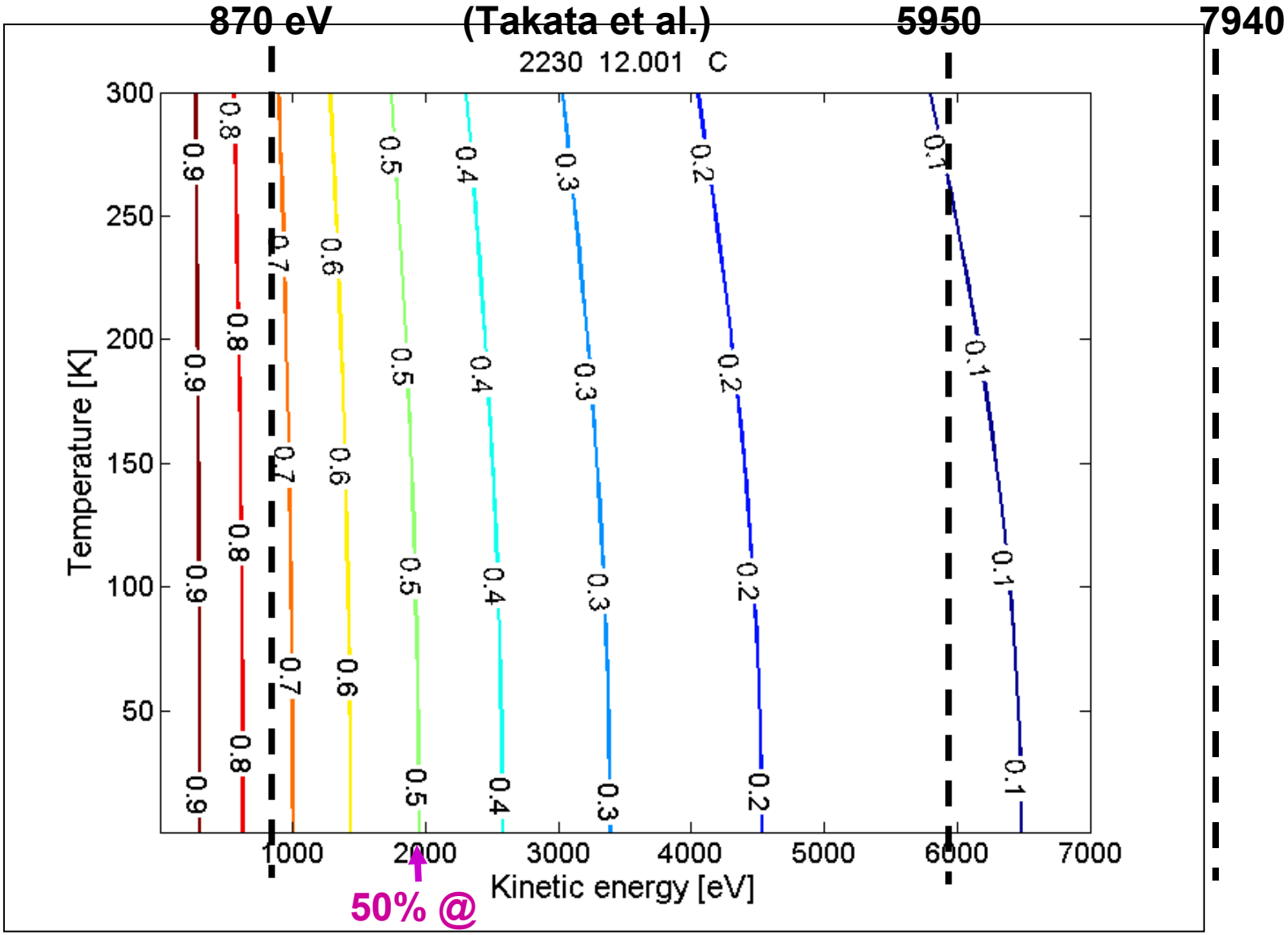
- ★ due to recoil effect !
  - light element
  - high energy photoelectron

Approximate recoil-free fraction = Debye-Waller factor--Graphite



→Little change with T at fixed hν?

Approximate recoil-free fraction = Debye-Waller factor--Diamond



Plucinski

→Also little change with T?

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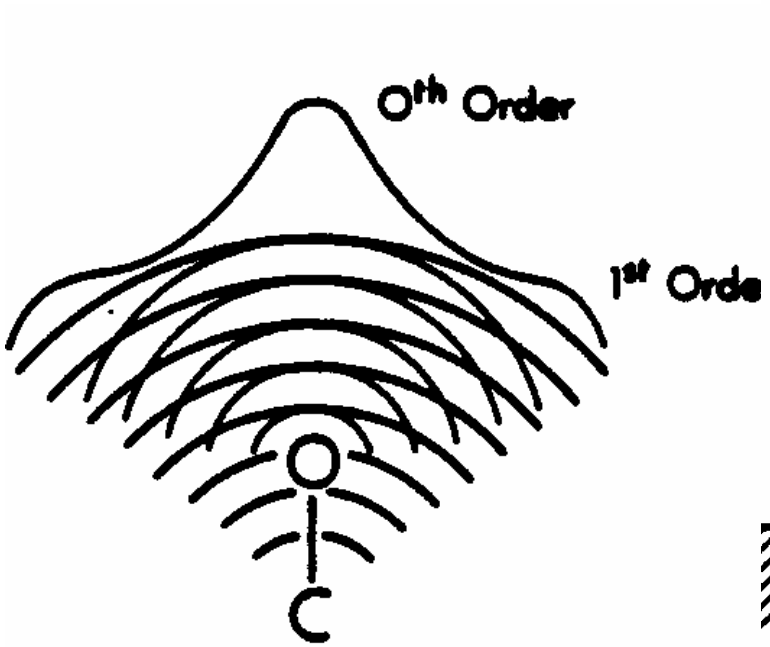
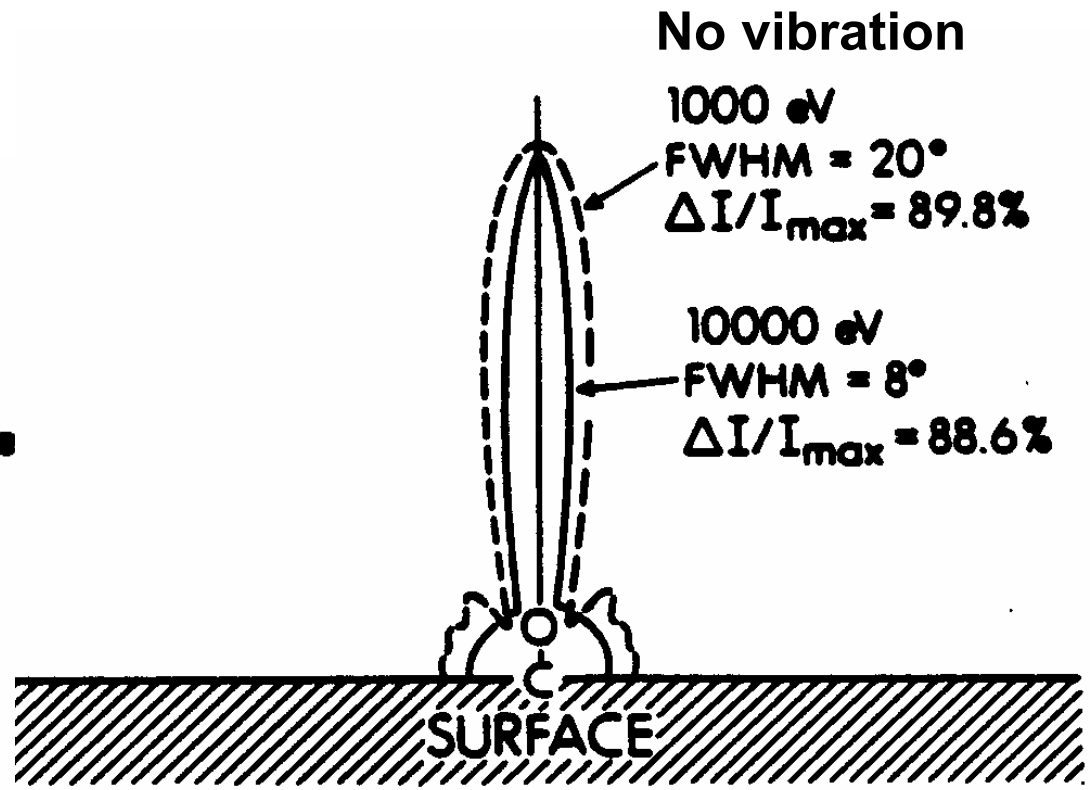
Photoelectron diffraction with hard x-ray excitation: 1000 eV→10,000 eV, the first theoretical study





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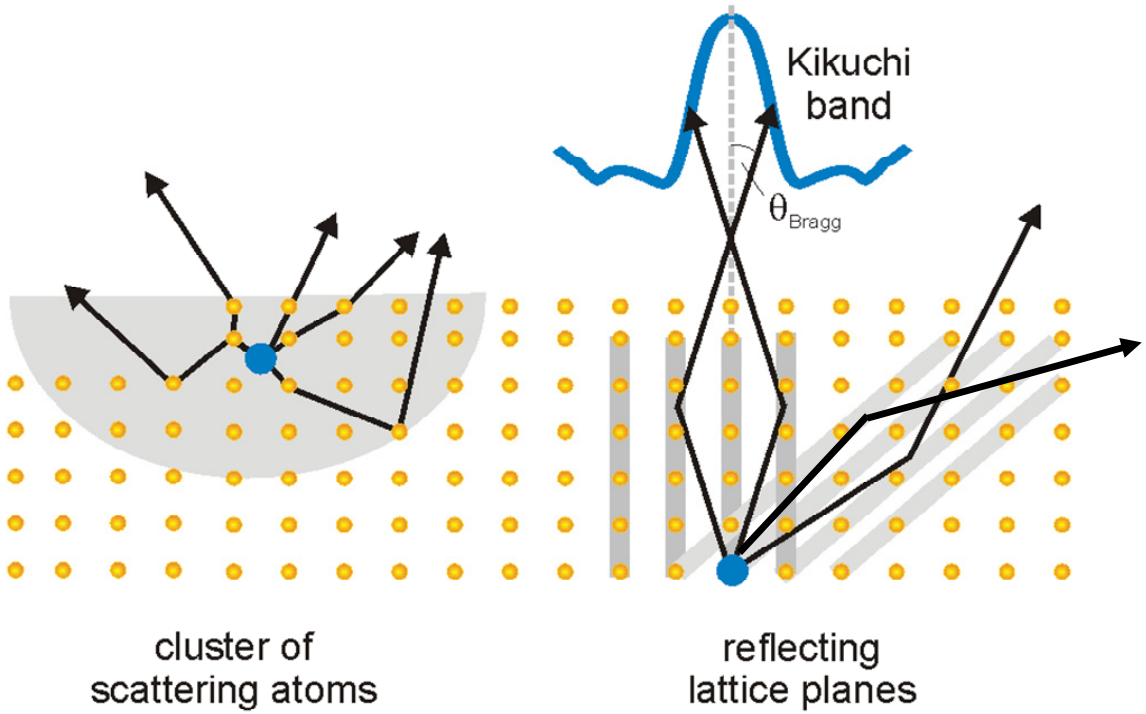
K.A. Thompson and C.F.
J. Elect. Spect. 33, 29 ('84)

PHOTOELECTRON DIFFRACTION

The scattering of photoelectrons from localized sources can be described in real space (multiple scattering cluster) and reciprocal space (dynamical theory of electron diffraction)

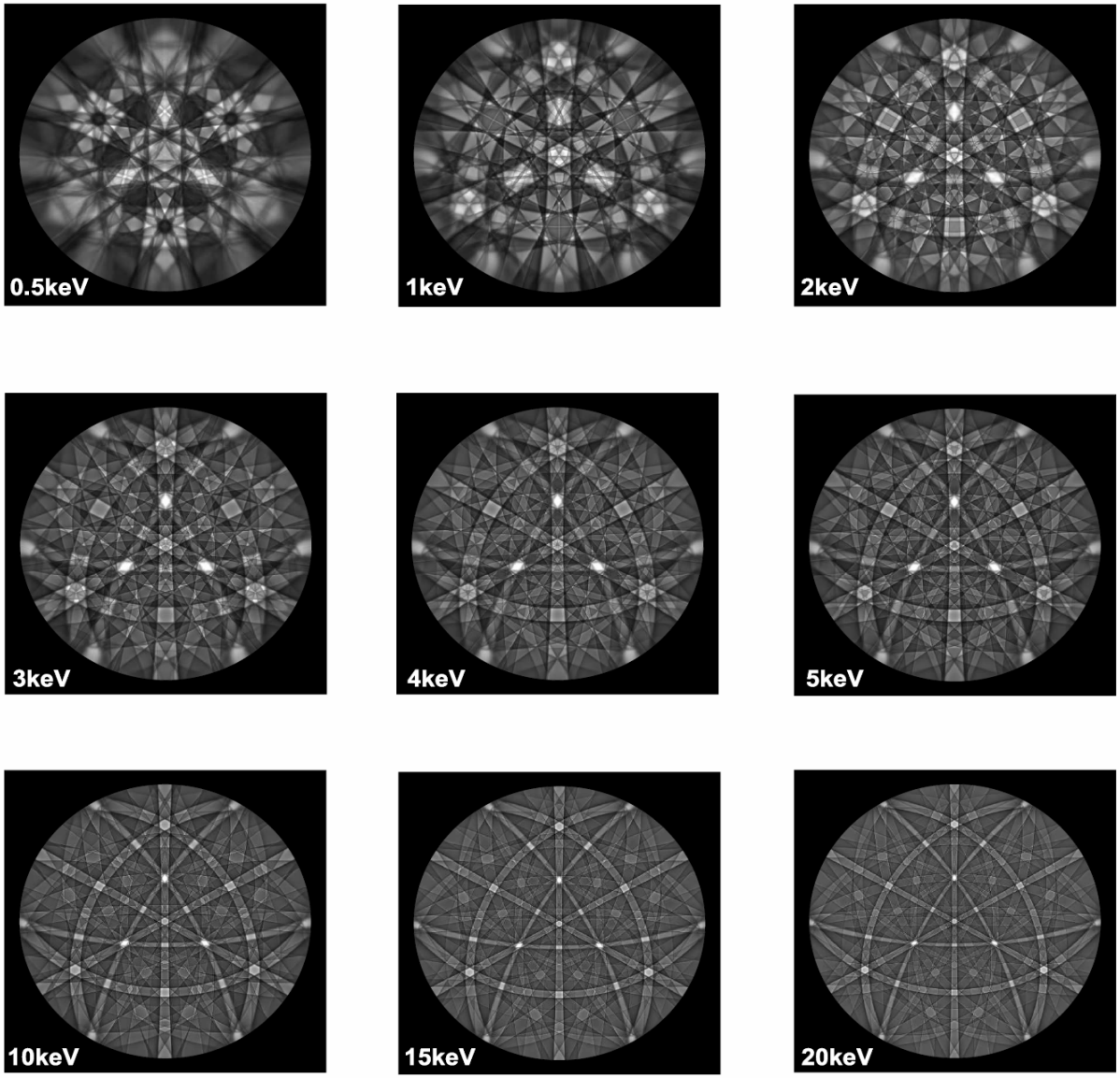


Soft x-ray excitation

Hard x-ray excitation

A. Winkelmann et al, New J. Phys 10 (2008) 113002

XPD from Soft to Hard X-ray:
What can be expected from 0.5 to 20 keV?

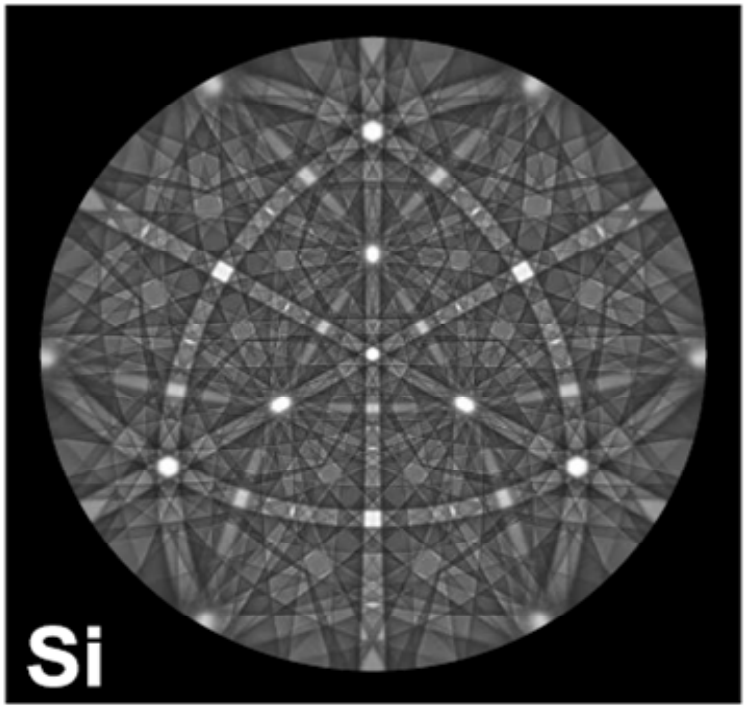


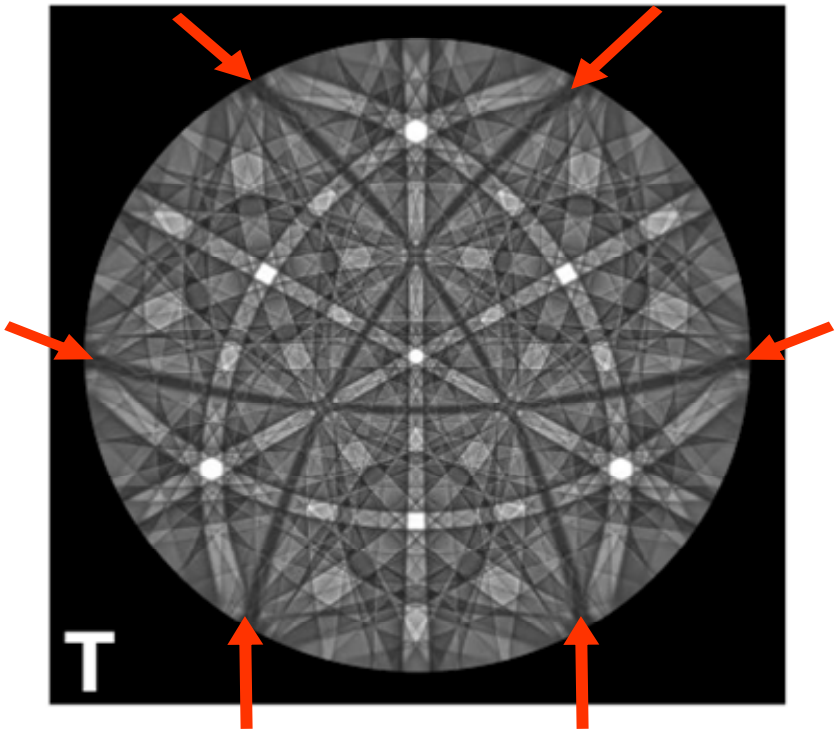
C(111)

A. Winkelmann et al, NJP 10 (2008) 113002

Hard x-ray photoelectron diffraction--Theory: Sensitivity to lattice distortions and atomic site type?

Si(111)-6 keV: Impurity atom on lattice site (Si) vs. tetrahedral interstitial (T)



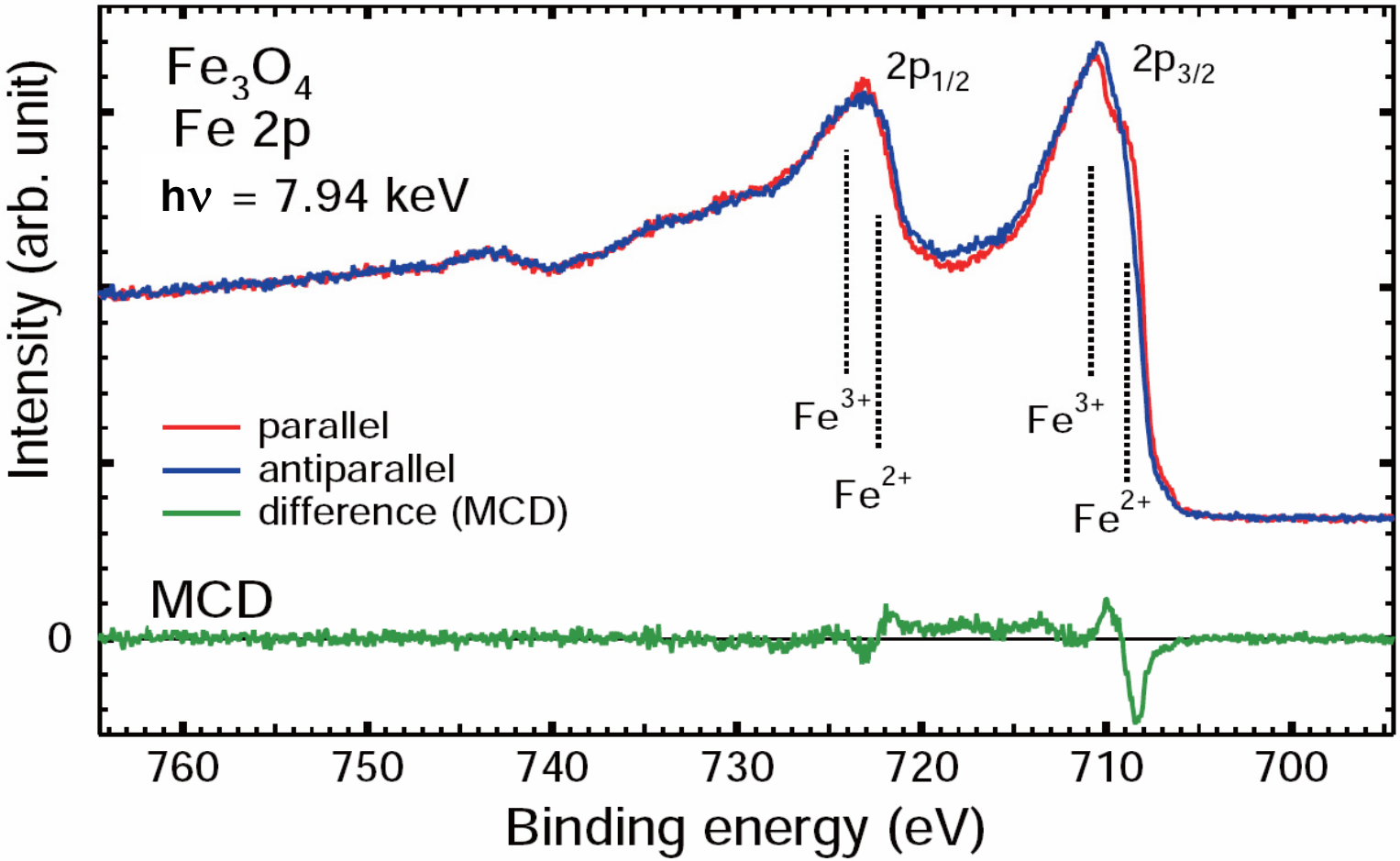


A. Winkelman, J. Garcia de Abajo, MPI Halle, CF, New Journal of Physics 10 (2008) 113002

Missing Kikuchi bands-->"forbidden reflections"

→Added option: Standing waves for x-rays in plus XPD→ standing waves for electrons out?

Some first MCD data with hard x-ray excitation



S. Ueda et al., Appl. Phys. Exp. 1 (2008) 077003
SPring8-BL15XU

→ **Combine with HXPD to yield site-specific magnetization?**

Hard x-ray photoemission—plusses and minusses

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•More bulk sensitive spectra → a versatile tool for any new material, multilayer nanostructure

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•Easier quantitative analysis via core spectra, but intensity drops for non-grazing incidence

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•New "bulk fingerprint" effects seen in both core and valence spectra

•3d "bulk" band mapping ARPES capability with cryocooling—How high in energy?

-And/Or-

•Direct DOS info. at highest energies and temperatures

•Hard x-ray photoelectron diffraction promising: dopants, lattice distortions

• Strong reflectivity and standing wave effects for depth-resolved properties

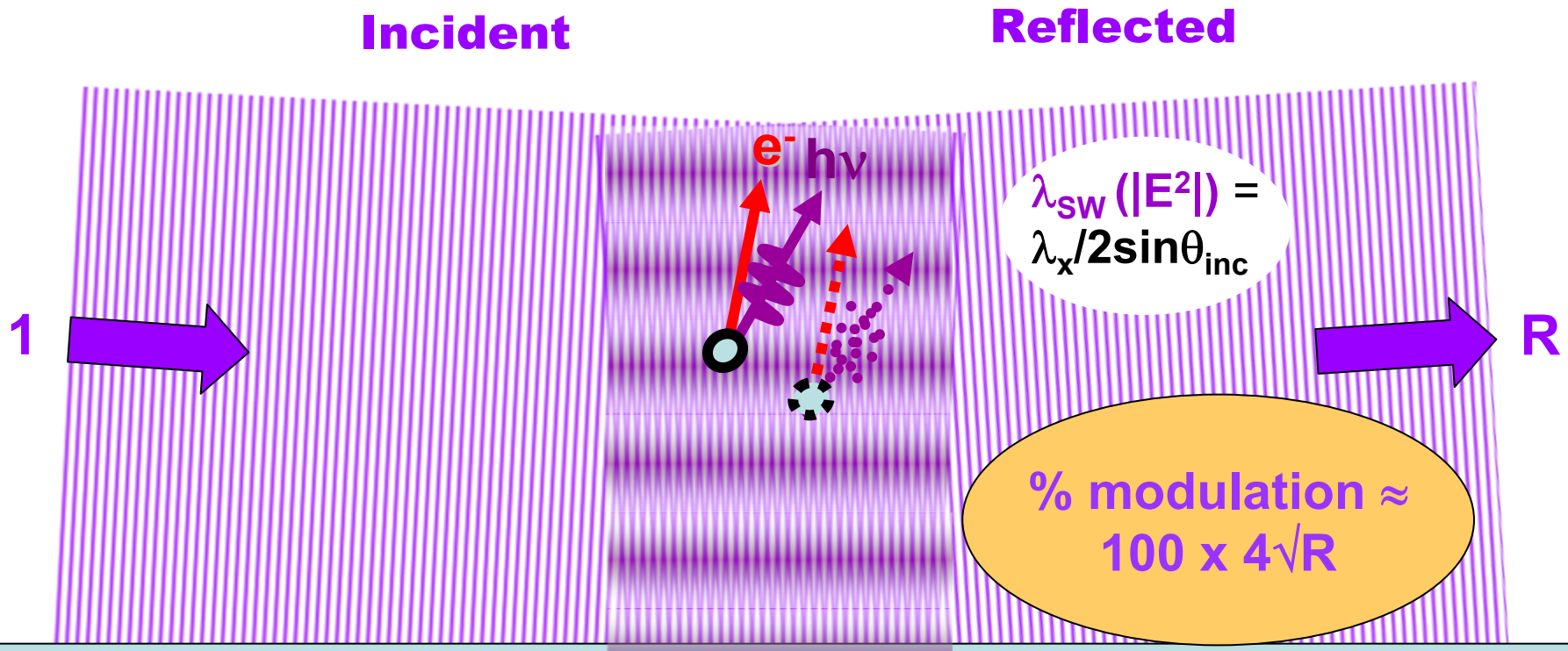
Minusses

•Recoil energy limits resolution, esp. for lighter elements, complex systematics, depending on local bond distances/phonon frequencies→Doppler spectroscopy?

•Intensity calculations must allow for photon wave vector, other non-dipole effects

•Phonon effects reduce capability for ARPES at higher energies/temperatures

Standing wave formation in reflection from a surface, or single-crystal Bragg planes[+], or a multilayer mirror



- ***Rocking curve:***

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

XMCD—Kim, Kortright, PRL 86, 1347 (2001)

- ***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

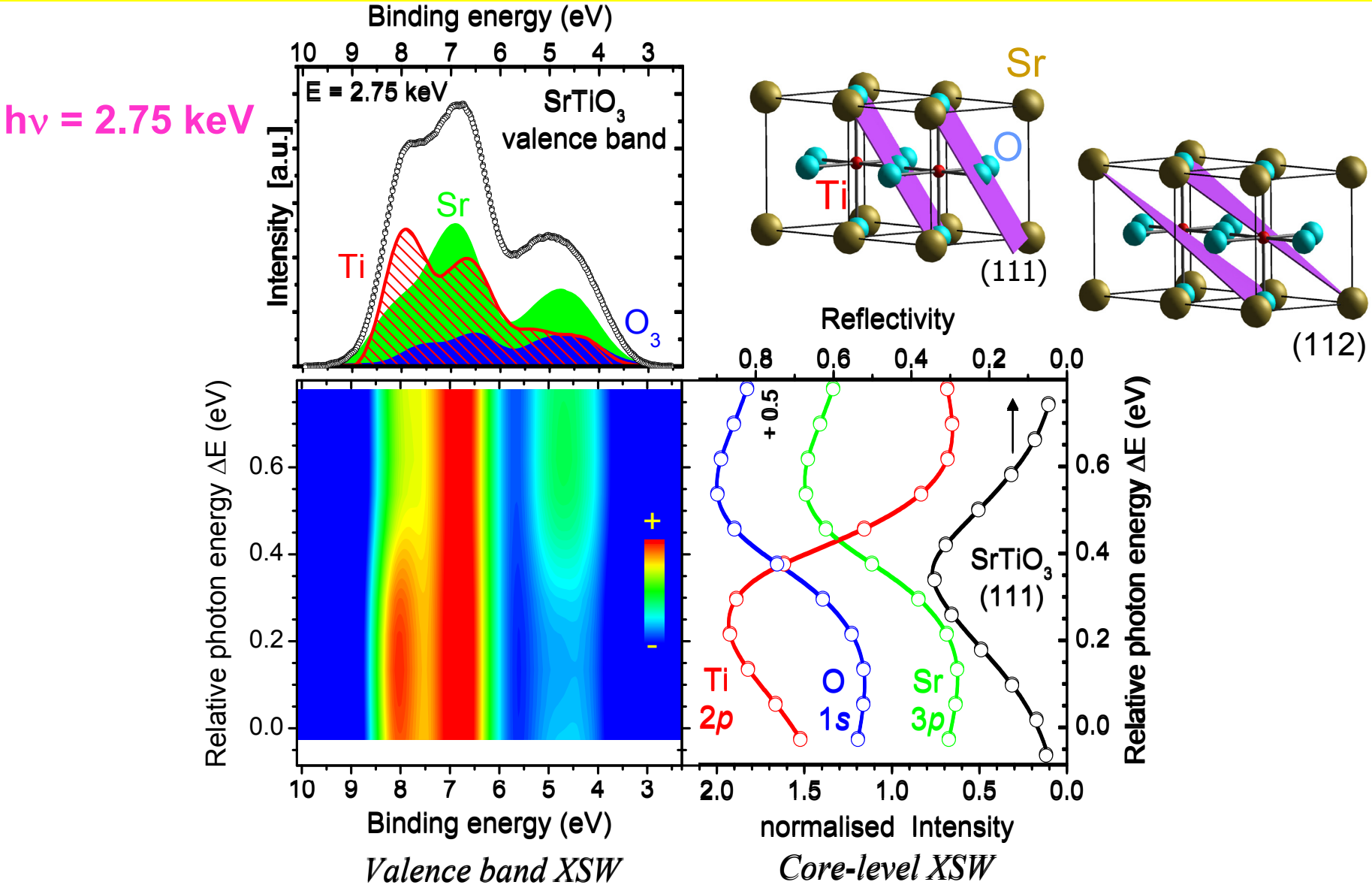
- ***Phase scan with wedge-shaped sample ("Swedge" method):***

[+]Standing waves via Bragg reflection of hard x-rays: Batterman, Phys. Rev A 133, 759 (1964)

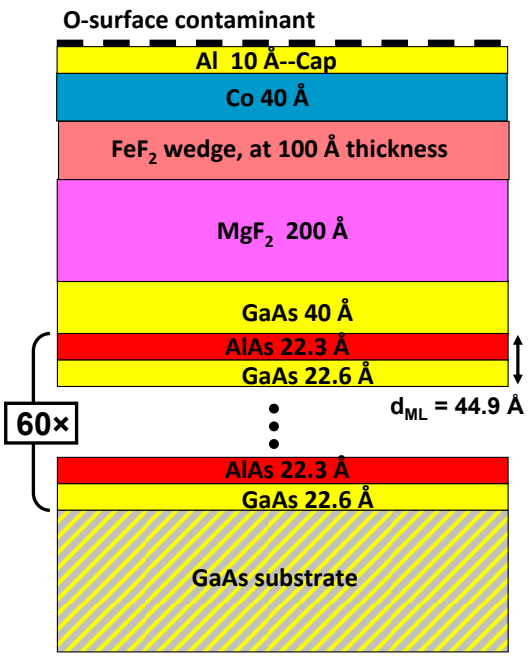
Site-specific valence electronic structure of SrTiO3

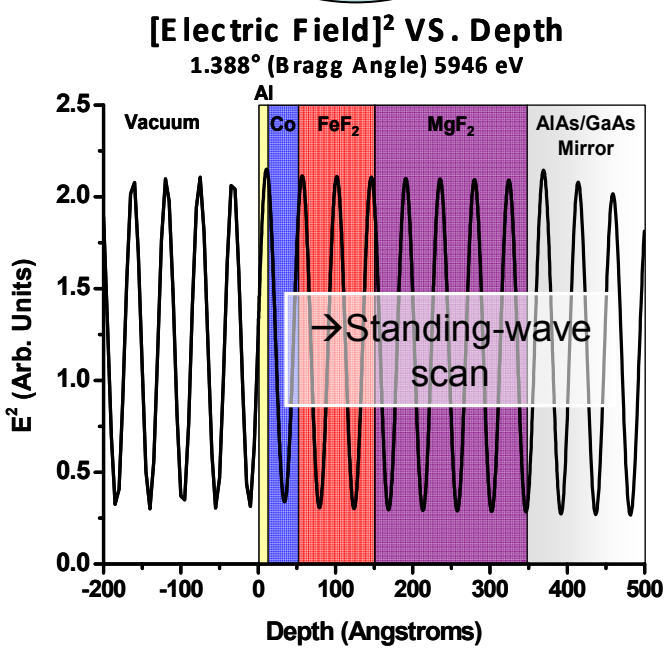
S. Thieß, T.-L. Lee, F. Bottin, B. Cowie and J. Zegenhagen

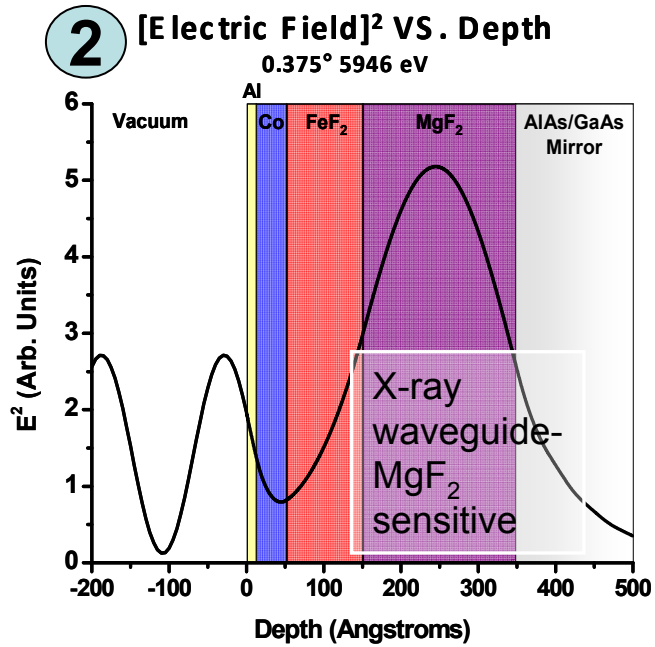
ESRF Highnlights- 2005, pa. 79

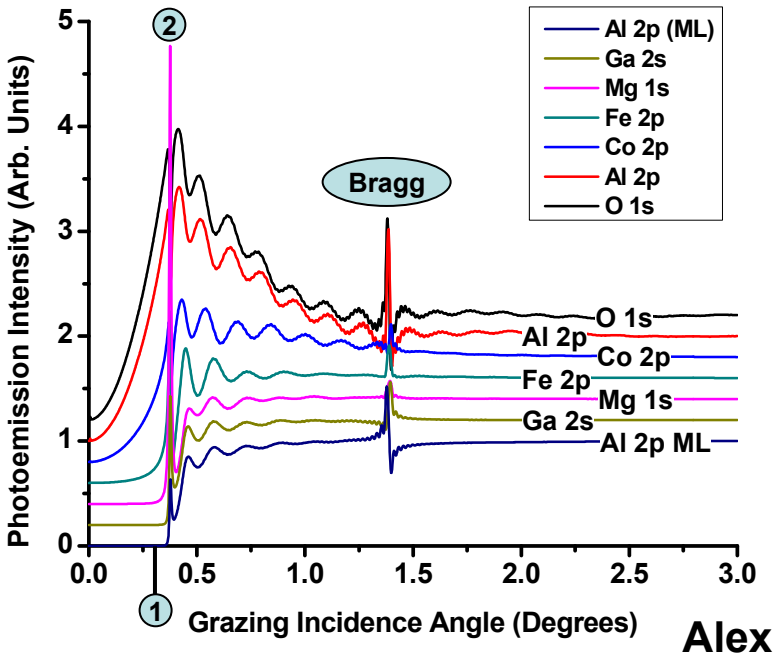


X-ray optical calculations- 6 keV

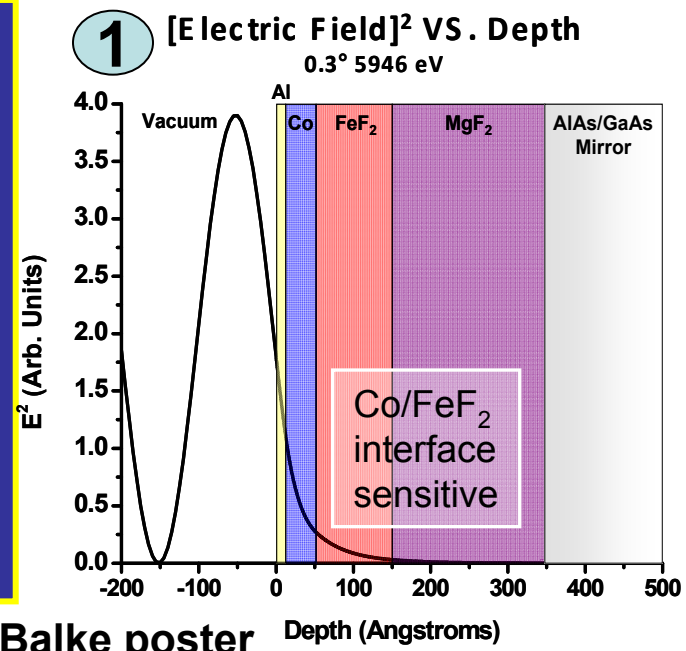






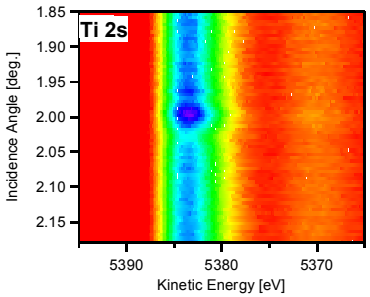


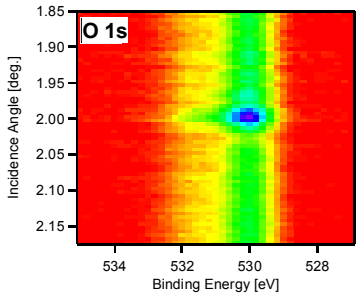
Exchange-bias Co/FeF_2: Calculated intensities and E^2 vs Incidence Angle @ 5946 eV

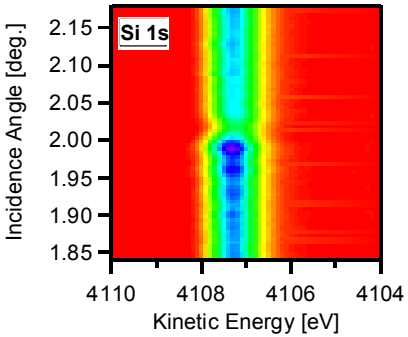


Alex Gray-LBNL, UCD →Balke poster

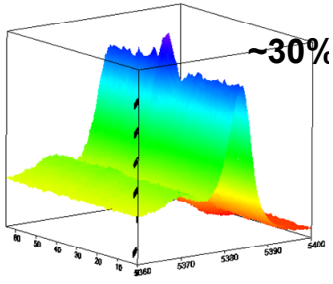
Rocking curves for 90 Å TiN/[Si/Mo multilayer-30 Å period]



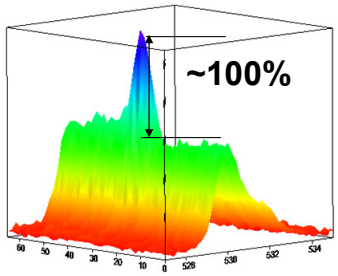




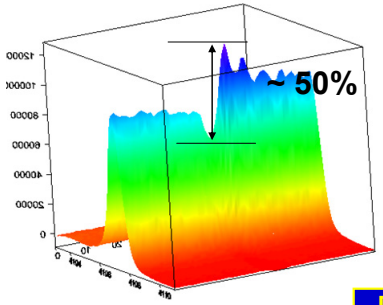
Ti 2s



O 1s—Surface oxide

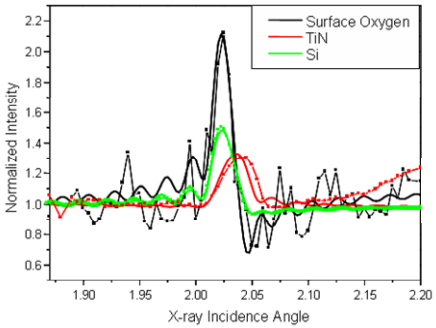


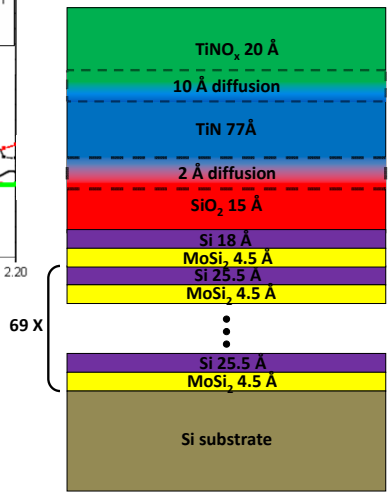
Si 1s



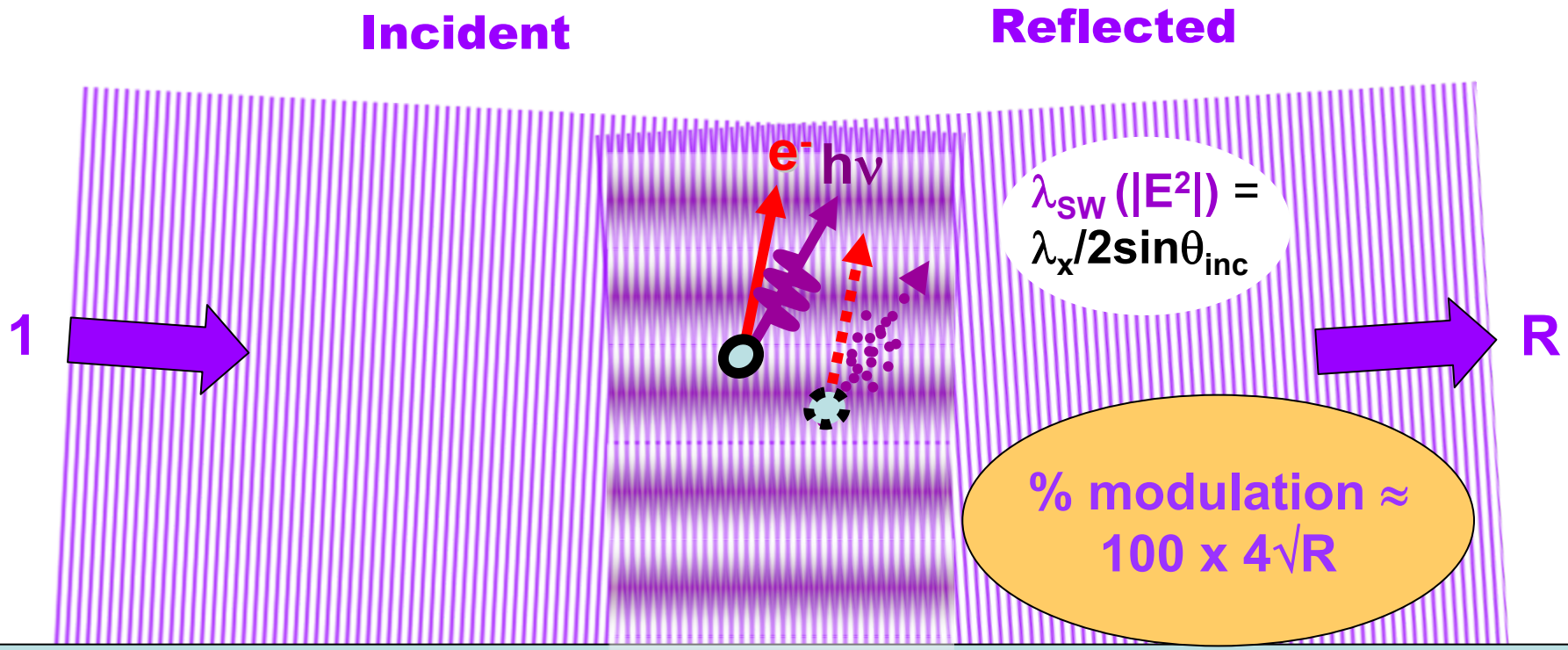
Depth-resolved composition from simulations of the rocking curves

Rocking curve for a TiN/Si interface 5.9 keV





Standing wave formation in reflection from a surface, or single-crystal Bragg planes[+], or a multilayer mirror



- ***Rocking curve:***

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

- ***Energy scan:***

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

XMCD—Kim, Kortright, PRL 86, 1347 (2001)

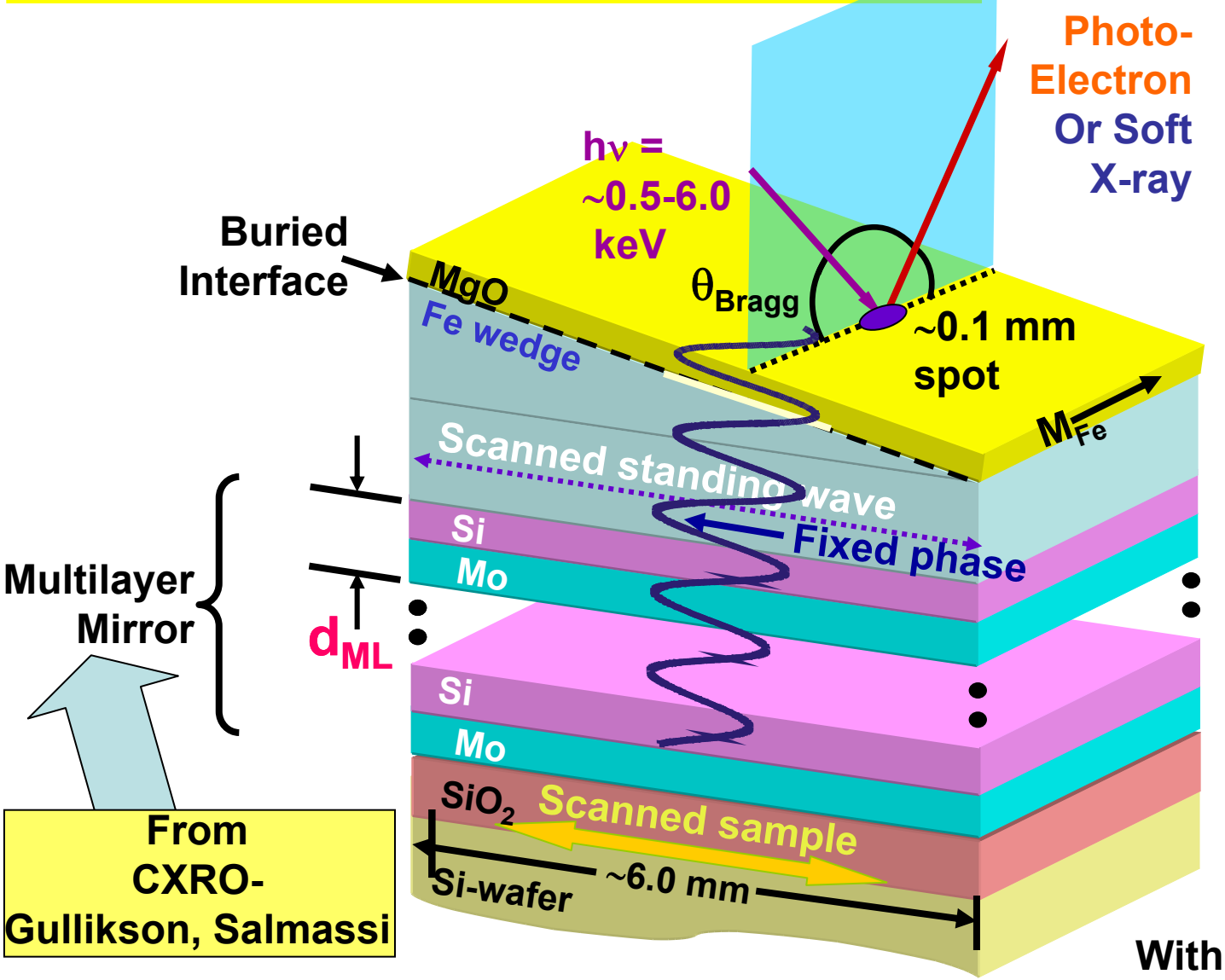
with: f = coherent fraction of atoms, P = phase of coherent-atom position

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

[+]Standing waves via Bragg reflection of hard x-rays: Batterman, Phys. Rev A 133, 759 (1964)

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

The MgO/Fe MTJ interface



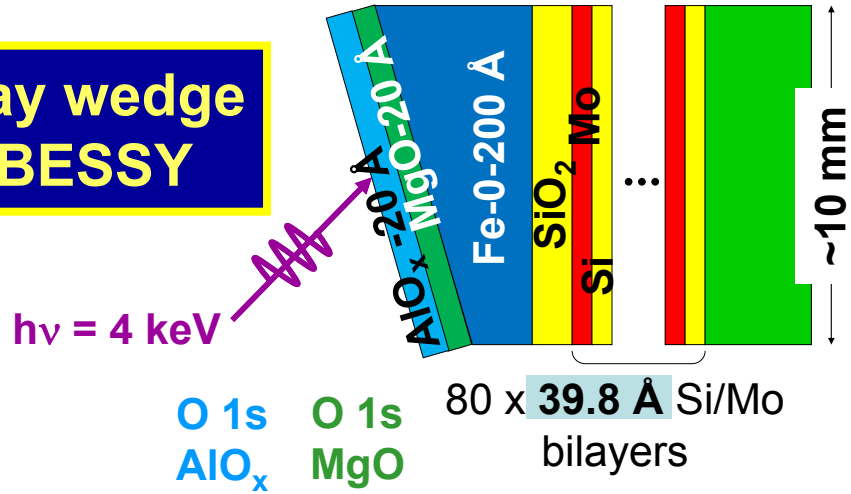
$\lambda_{SW}(|E^2|) = \lambda_x/2\sin\theta_{inc} \approx d_{ML}$

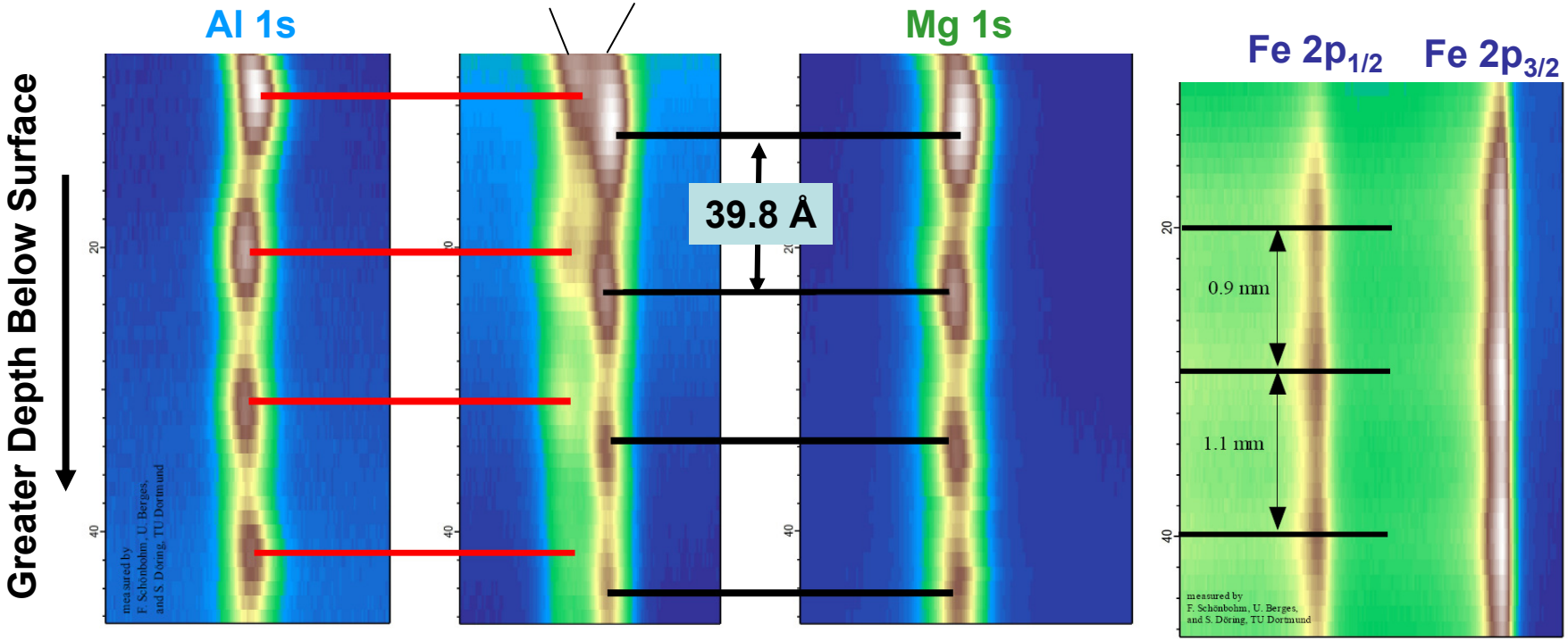
1st order Bragg: $\lambda_x = 2d_{ML}\sin\theta_{Bragg}$

From CXRO-Gullikson, Salmassi

With Kortright, Fischer

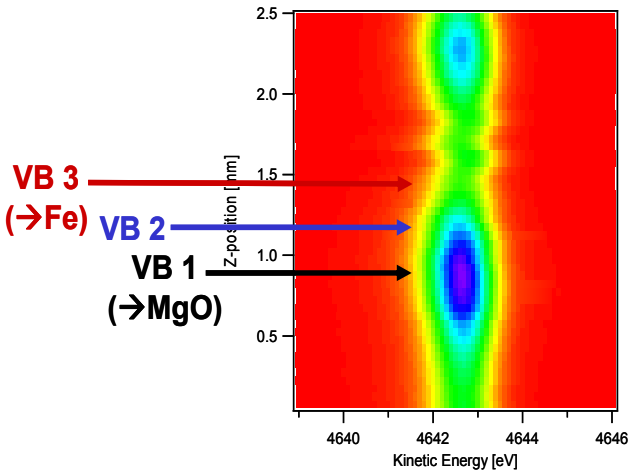
Hard x-ray wedge scans-BESSY





F. Schonbohm, U.Berges, S.Döring, M. Gorgoi, C. Westphal,
D. Buergler, C. Schneider, C. Papp, B. Balke, C.F...

MgO/Fe depth dependent densities of states info. at 0.9 keV and 5.9 keV



Papp, Balke, Ueda, Kobayashi et al., SPring8, BLXU15

Fe cross sections @ 1 keV

3 D 3/2	3 D 5/2	4 S 1/2
3.8858E+03	5.7077E+03	1.4494E+03

9.592/6 e⁻ = 1.598/e-

1.4494/2 e⁻ = 0.7247/e-

O cross sections @ 1 keV

2 P 1/2	2 P 3/2
3.5731E+02	7.0783E+02

1.065/6 e⁻ = 0.1775/e-

Fe cross sections @ 6 keV

3 D 3/2	3 D 5/2	4 S 1/2
3.7147E+00	5.3354E+00	3.3508E+01

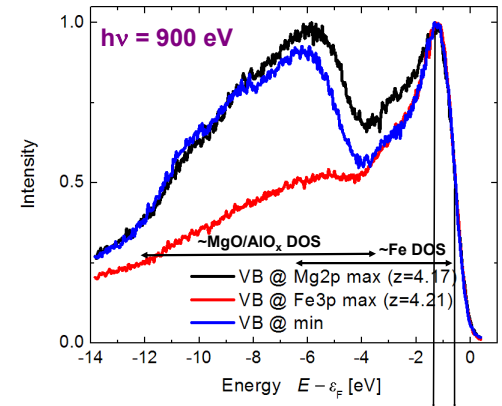
9.0501/6 e⁻ = 1.508/e-

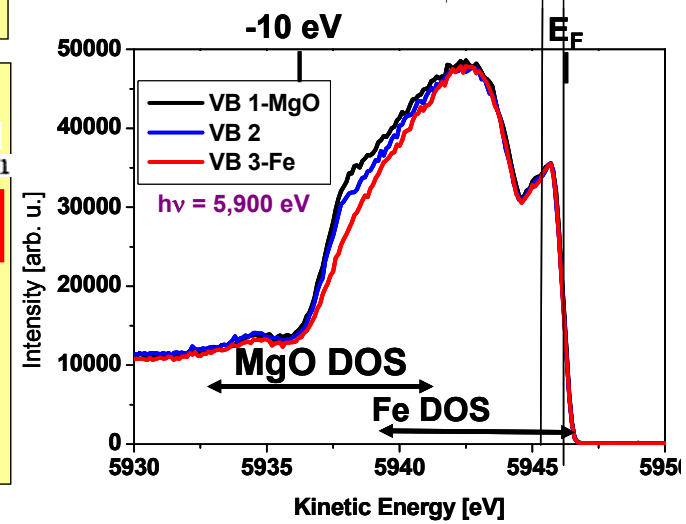
33.508/2 e⁻ = 16.754/e-

O cross sections @ 6 keV

2 P 1/2	2 P 3/2
4.2796E-01	8.4088E-01

1.270/6 e⁻ = 0.21/e-





Hard x-ray photoemission—plusses and minusses

•Plusses

•More bulk sensitive spectra → a versatile tool for any new material, multilayer nanostructure

•Inelastic background less important & Augers more widely spread, less overlap

•Easier quantitative analysis via core spectra, but intensity drops for non-grazing incidence

•Less radiation damage?

•Easier interpretation of ARXPS data → surface and bulk information

•New "bulk fingerprint" effects seen in both core and valence spectra

•3d "bulk" band mapping ARPES capability with cryocooling—How high in energy?
-And/Or-
•Direct DOS info. at highest energies and temperatures

• Strong reflectivity and standing wave effects for depth-resolved properties

•Hard x-ray photoelectron diffraction promising: dopants, lattice distortions

Minusses

•Cross sections low, need special undulatorbeamline/spectrometer combinations—several solutions→1 micron, and 10 meV

•Resolution not as good as VUV/SX, but 50 meV, maybe lower, good enough

•Recoil energy limits resolution, esp. for lighter elements, complex systematics, depending on local bond distances/phonon frequencies→Doppler spectroscopy?

•High *n,* low-ℓ cross section components
•strongly favored, but they can be more involved in conductivity

•Intensity calculations must allow for photon wave vector, other non-dipole effects

•Phonon effects reduce capability for ARPES at higher energies/temperatures

•Resonant measurements more difficult, but depends on monochromator design→ being done (Drube)

Hard x-ray photoemission—applications areas

- High-k dielectrics, advanced semiconductor structures and materials→reactions at buried interfaces, stack profiles, band alignment

  (Conti, Drube, Garfunkel, Hughes, Herrera-Gomez, Lysaght, Yanagi, Zaima)

- Energy conversion devices: Photovoltaic cells, Fuel-cell electrodes, Li-ion batteries→interfaces and depth-resolved chemical states

  (Lysaght, Shikano, Zaima)

- Magnetic/spintronic multilayers→ interfaces, MCD, standing waves, spin resolution?,

  (Felser, Gorgoi, Papp/Balke, Ryan, Ueda, Zegenhagen)

- Strongly correlated, novel materials→surface vs bulk electronic structure in high TC, heavy Fermions, manganites, Heuslers

  (Chainani, Drube, Felser, Panaccione, Sawatzky, Suga, Taguchi, Tjeng…)

- Oxides, oxide interfaces, 2DEG, superconductivity, "Mottronics",…

  (Claessen, Panaccione, Rumaiz, Sawatzky, Tjeng, Zegenhagen)

- Catalysis, environmental, polymer science→depth distributions, high-pressure studies

  (Bluhm, Bare, Mitchell)

- Lanthanide/Actinide systems→surface vs bulk electronic structure

  (Joyce)

- Atomic, molecular, cluster studies→non-dipole effects, recoil, many-electron, vibrational, rotational excitation

  (Lindle, Rosenberg, Simon)

HAXPES/HXPS is already a well-established technique for materials, nanostructure, nanomaterial, and device characterization!

Hard x-ray photoemission—instrumentation

- Beamlines, spectrometers, microscopes—various new directions
  (Browning, Cai, Cholewa, Dierker, Drube, Hu, Ikenaga, Lee, Simon, Stefani; Focus, MBS, VG Scienta, SPECS)
- Detectors? OK, but ~20th century: need individual pixel counting at up to GHz integrated rates, 1D→2D with spin-the holy grail
  (Cholewa, instrument vendors)

Hard x-ray photoemission—basic effects and theory

- Inelastic mean free paths, effects of elastic scattering, peak fitting and analysis of ARXPS
  (Herrera-Gomez, Powell, Zaima,…)
- Cross sections, asymmetry parameters, non-dipole effects
  (Lindle, Yoshikawa, Zegenhagen,…)
- Anderson impurity model for core/valence levels
  (Chainani, Sawatzky, Suga, Taguchi,…)
- One-step ARPES theory with matrix elements, relativistic effects, spin resol.
  (Ebert, Rehr)
- Phonons! In recoil, in ARPES (UPS-band limit→XPS-DOS limit), in inelastic scattering→more development needed
  (Ebert, Kayanuma, Papp, Suga, Takata)