



國家同步輻射研究中心
National Synchrotron Radiation Research Center

Photoemission Spectroscopy (I)

Cheiron School 2013

September 30, 2013 SPring-8, Japan

Ku-Ding Tsuei

tsuei@nsrrc.org.tw

National Synchrotron Radiation Research Center

NSRRC

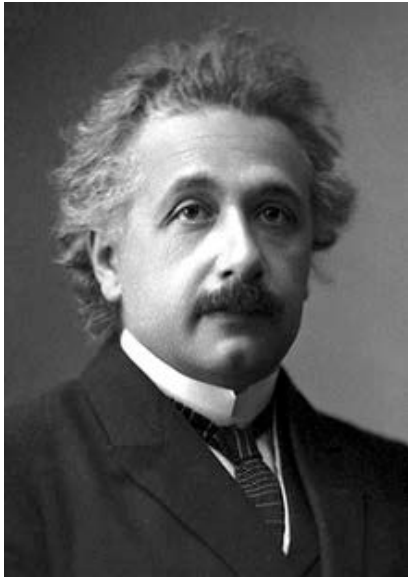


Outline

1. What is photoemission spectroscopy?
2. Fundamental aspects of photoemission.
3. Examples.
4. Increase bulk sensitivity: HAXPES.
5. Challenging future directions.

Reference books:

1. "Photoelectron Spectroscopy" 3rd Ed. by S. Hufner, Springer-Verlag 2003
2. "Angle-Resolved Photoemission: Theory and Current Applications", S. D. Kevan, ed., Amsterdam; Elsevier 1992
3. "Very High Resolution Photoelectron Spectroscopy" Ed. by S. Hufner, Springer 2007



In 1905 Albert Einstein proposed the concept of light quanta (**photons**) to explain the **photoelectric effect**, which was pivotal in establishing the **quantum theory** in physics

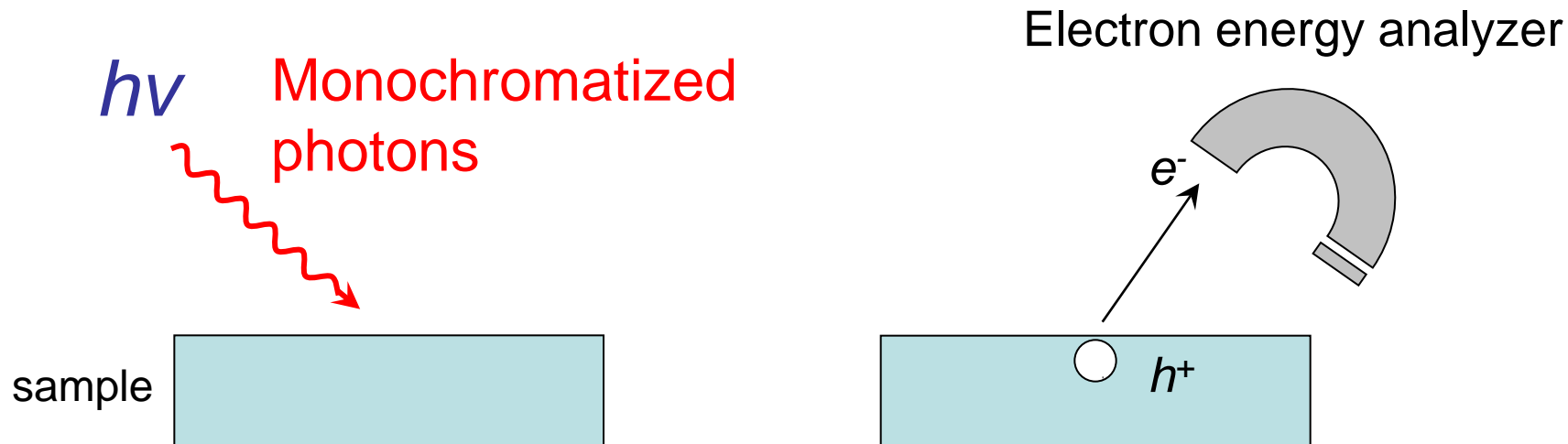
In 1921 he was awarded the **Nobel Prize in Physics** “for his services to theoretical physics, and especially for his **discovery of the law of the photoelectric effect**”



Since the late 1940's Kai Siegbahn has been working on the **Electron Spectroscopy for Chemical Analysis (ESCA)** also termed the X-ray Photoelectron Spectroscopy (**XPS**)

In 1981 he was awarded the **Nobel Prize in Physics** “for his contribution to the development of **high-resolution electron spectroscopy**”

What is photoemission spectroscopy? (photoelectron spectroscopy) (PES)



Initial state: ground (neutral) state

Final state: hole (excited) state

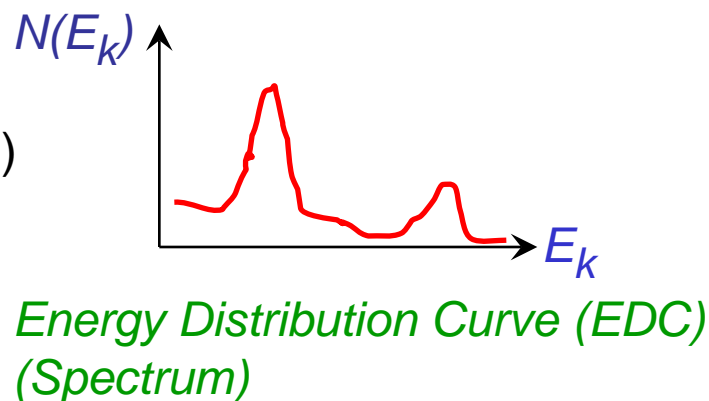
Conservation of energy

$$E_k = h\nu + E_i - E_f \quad (\text{most general expression})$$

E_k : photoelectron kinetic energy

$E_i(N)$: total initial state system energy

$E_f(N-1)$: total final state system energy



What are the samples and probed states?

Atoms

atomic orbitals (states)

Molecules

molecular orbitals

core level states (atomic like)

Nanoparticles

valence bands/states

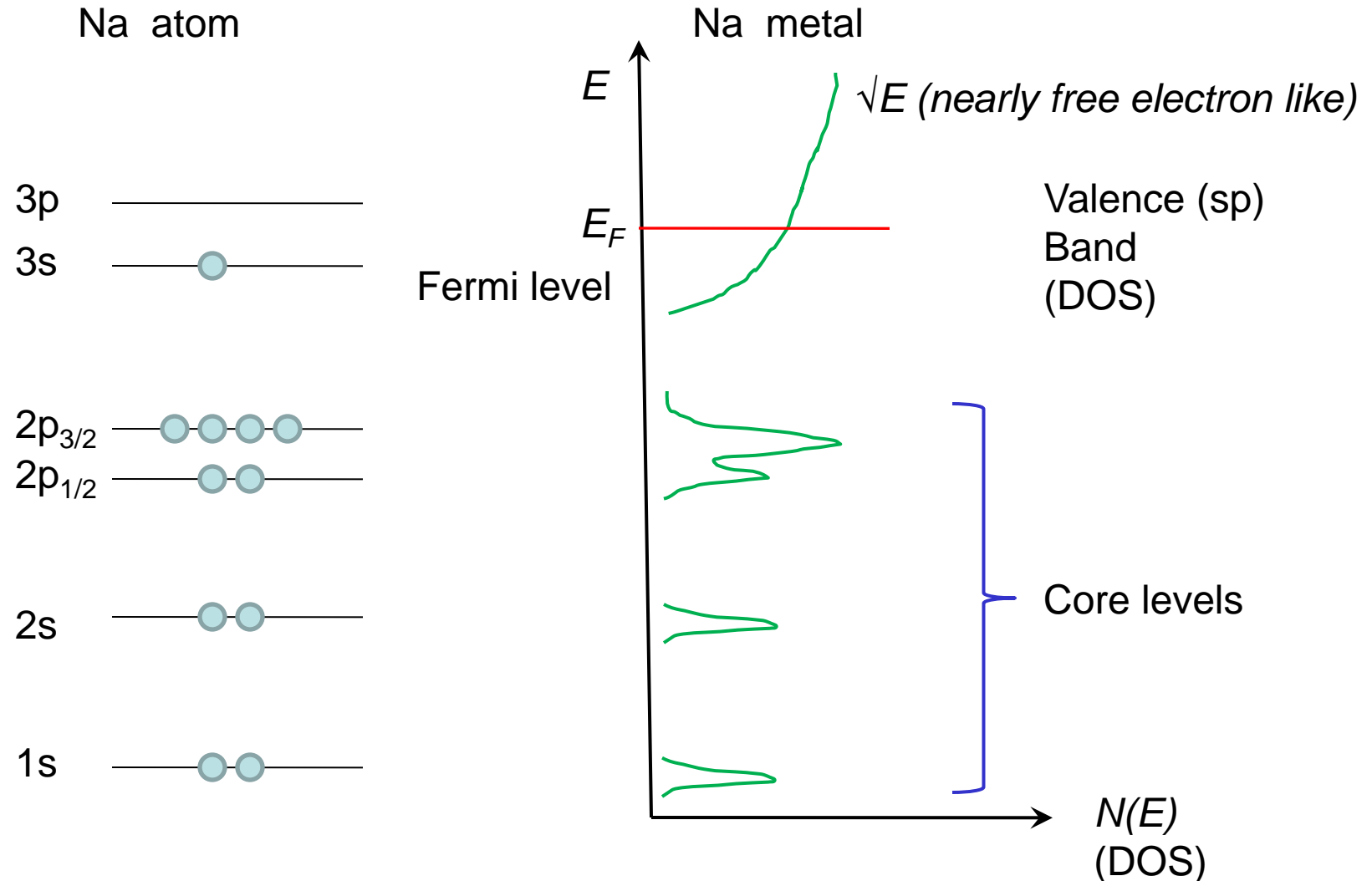
core level states (atomic like)

Solids

valence bands

core level states (atomic like)

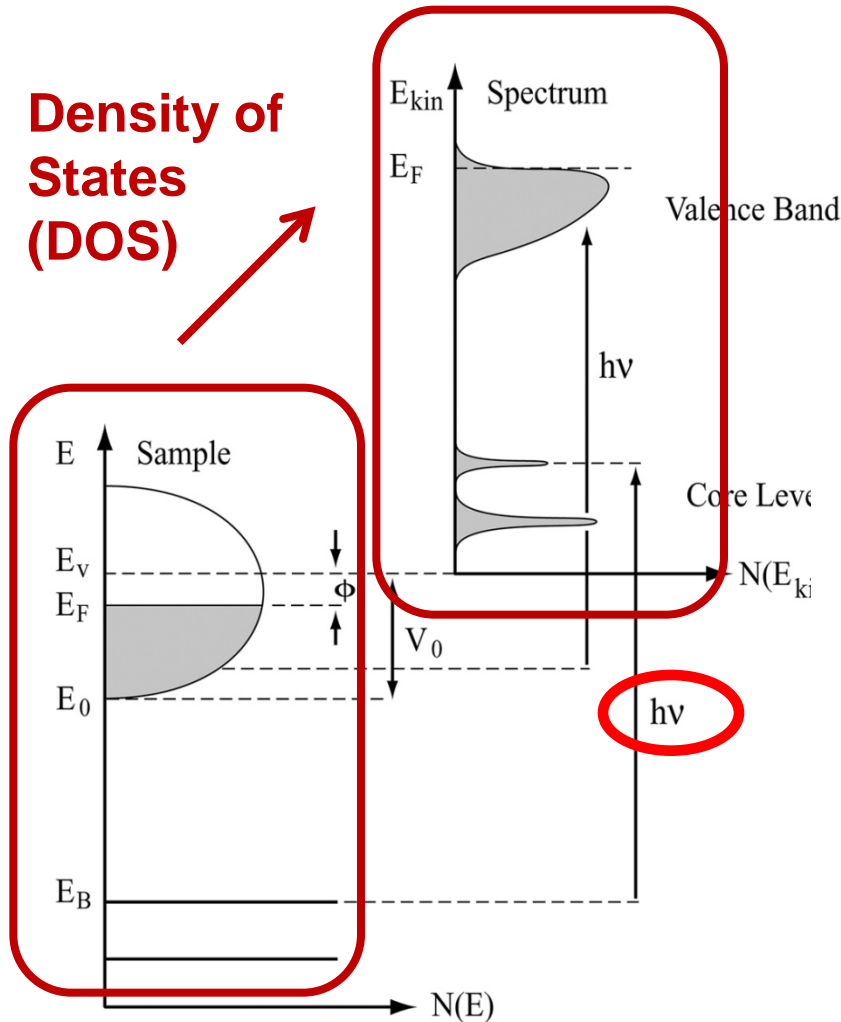
Single particle description of energy levels (Density of States) (most convenient in PE)



Energetics in PES

Conservation of energy

Density of States (DOS)



Hufner, Damascelli

$$E_k = h\nu - E_B - \phi$$

E_V : vacuum (energy) level

E_F : Fermi (energy) level

$\phi = E_V - E_F$: work function

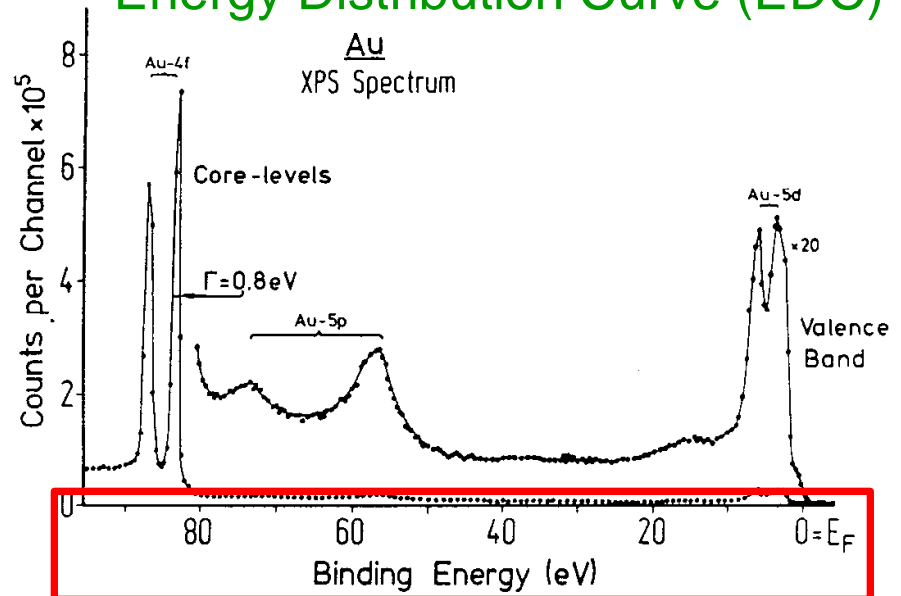
E_0 : bottom of valence band

$V_0 = E_V - E_0$: inner potential

E_k^{max} marks E_F in spectra

E_B measured relative to $E_F = 0$

Energy Distribution Curve (EDC)



Hufner

Light sources and terminology

Ultraviolet Photoemission Spectroscopy (UPS)

UV He lamp (21.2 eV, 40.8 eV)

valence band PE, direct electronic state info

X-ray Photoemission Spectroscopy (XPS) (Electron Spectroscopy for Chemical Analysis) (ESCA)

x-ray gun (Al: 1486.6 eV, Mg: 1253.6 eV)

core level PE, indirect electronic state info
chemical analysis

Synchrotron radiation:

continuous tunable wavelength

valence band: <100 eV, maybe up to several keV

core level: 80-1000 eV, maybe up to several keV
depending on core level binding energies

Inelastic Electron Mean Free Path (IMFP)

$$I(d) = I_0 e^{-d/\lambda(E)}$$

$\lambda(E)$: IMFP depending on KINETIC ENERGY inside solid or relative to E_F

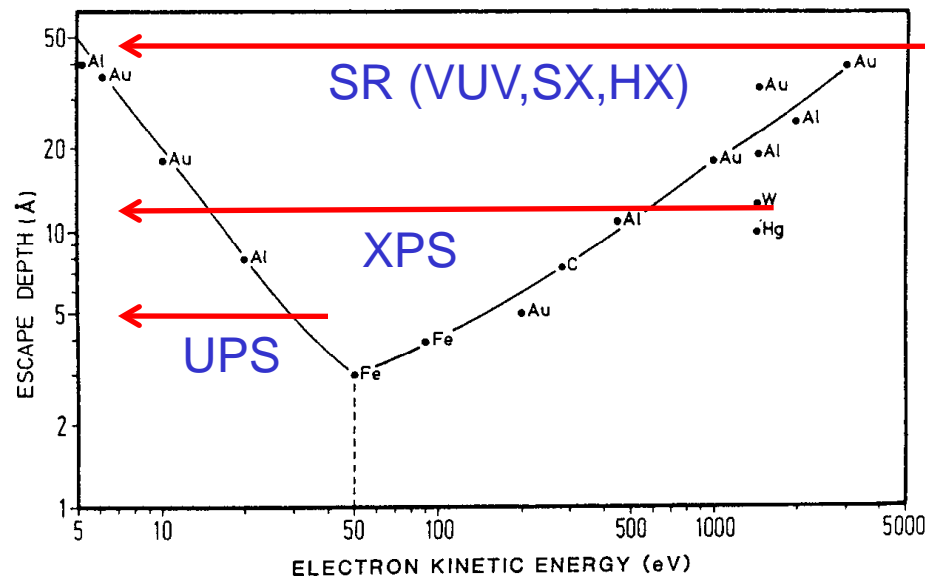


Fig.1.9. Electron escape depth as a function of their kinetic energy for various metals. The data indicate a universal curve with a minimum of $2 \div 5$ Å for kinetic energies of $50 \div 100$ eV. The scatter of the data is evident from the values obtained at $E_{\text{kin}} = 1480$ eV

Hufner

Minimum due to electron-electron scattering, mainly plasmons

PE is a surface sensitive technique! (requires UHV)

High energy photoemission: several keV to increase bulk sensitivity

Table 1-1. Electron binding energies, in electron volts, for the elements in their natural forms.

Element	K 1s	L ₁ 2s	L ₂ 2p _{1/2}	L ₃ 2p _{3/2}	M ₁ 3s	M ₂ 3p _{1/2}	M ₃ 3p _{3/2}	M ₄ 3d _{3/2}	M ₅ 3d _{5/2}	N ₁ 4s	N ₂ 4p _{1/2}	N ₃ 4p _{3/2}
1 H	13.6											
2 He	24.6*											
3 Li	54.7*											
4 Be	111.5*											
5 B	188*											
6 C	284.2*											
7 N	409.9*	37.3*										
8 O	543.1*	41.6*										
9 F	696.7*											
10 Ne	870.2*	48.5*	21.7*	21.6*								
11 Na	1070.8†	63.5†	30.65	30.81								
12 Mg	1303.0†	88.7	49.78	49.50								
13 Al	1559.6	117.8	72.95	72.55								
14 Si	1839	149.7*b	99.82	99.42								
15 P	2145.5	189*	136*	135*								
16 S	2472	230.9	163.6*	162.5*								
17 Cl	2822.4	270*	202*	200*								
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*					
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*					
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†					
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†					
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†					
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†					
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†					
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*			
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†			
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2			
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*			
34 Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*			
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*			
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3 *
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†	38.9†	21.3	20.1†
39 Y	17038	2373	2156	2080	392.0*b	310.6*	298.8*	157.7†	155.8†	43.8*	24.4*	23.1*
40 Zr	17998	2532	2307	2223	430.3†	343.5†	329.8†	181.1†	178.8†	50.6†	28.5†	27.1†
41 Nb	18986	2698	2465	2371	466.6†	376.1†	360.6†	205.0†	202.3†	56.4†	32.6†	30.8†
42 Mo	20000	2866	2625	2520	506.3†	411.6†	394.0†	231.1†	227.9†	63.2†	37.6†	35.5†
43 Tc	21044	3043	2793	2677	544*	447.6	417.7	257.6	253.9*	69.5*	42.3*	39.9*
44 Ru	22117	3224	2967	2838	586.1*	483.5†	461.4†	284.2†	280.0†	75.0†	46.3†	43.2†
45 Rh	23220	3412	3146	3004	628.1†	521.3†	496.5†	311.9†	307.2†	81.4*b	50.5†	47.3†
46 Pd	24350	3604	3330	3173	671.6†	559.9†	532.3†	340.5†	335.2†	87.1*b	55.7†a	50.9†
47 Ag	25514	3806	3524	3351	719.0†	603.8†	573.0†	374.0†	368.3	97.0†	63.7†	58.3†

Core level binding energies are characteristic of each orbital of each element

Finger prints

Core level BE independent of photon energy used

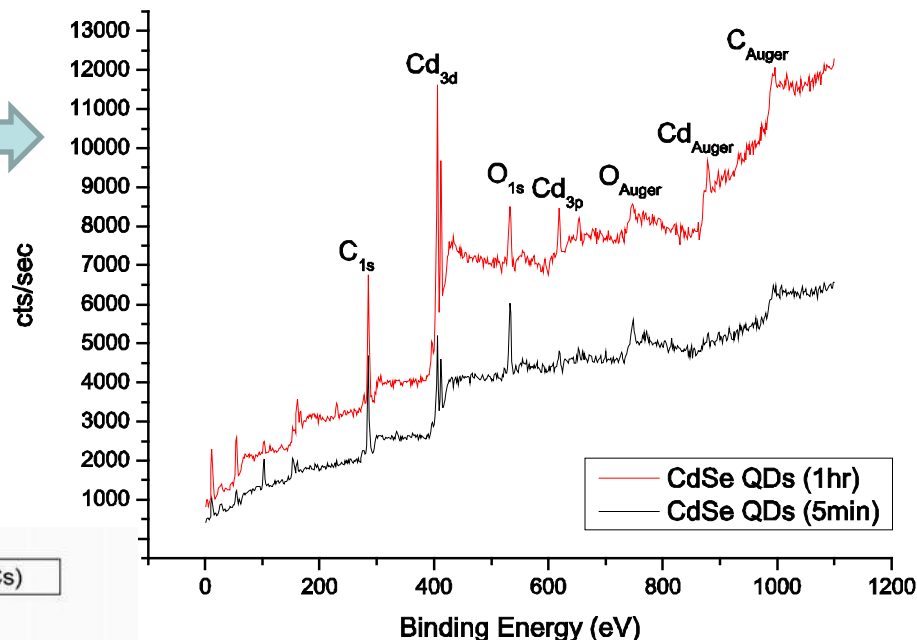
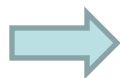
X-Ray Data Booklet

<http://xdb.lbl.gov/>

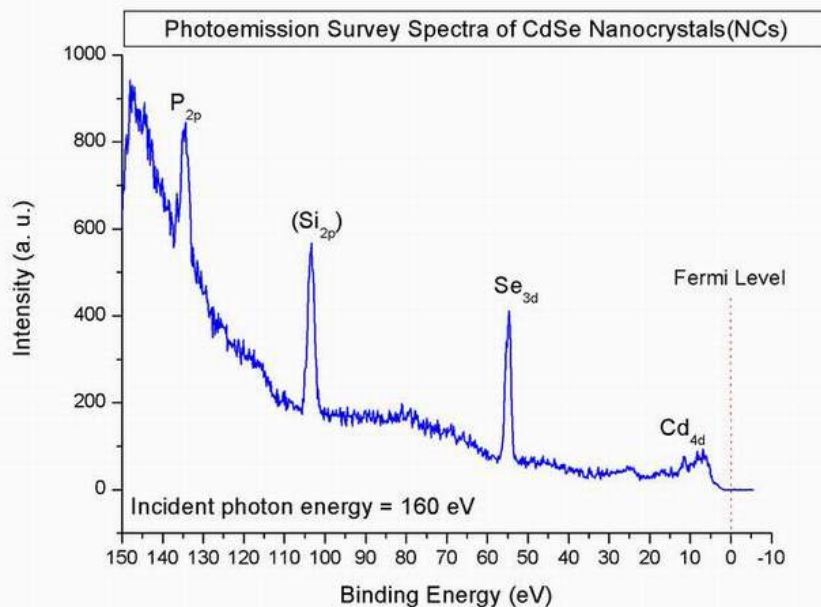
Core level photoemission: chemical analysis of elements

ESCA (XPS)

$h\nu = \text{Mg } K\alpha = 1253.6 \text{ eV}$

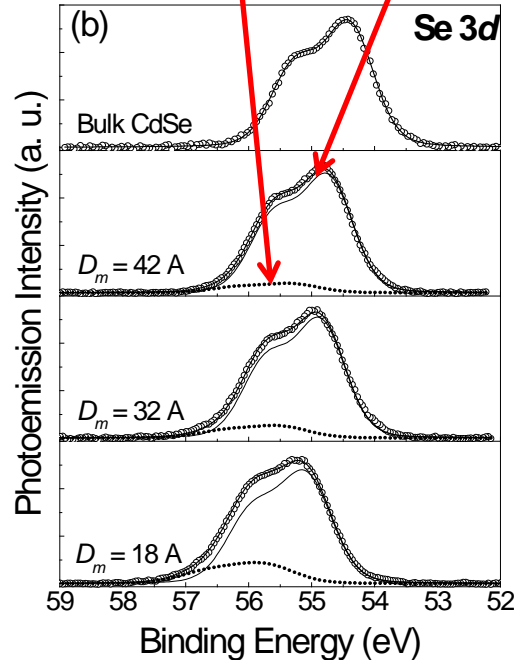
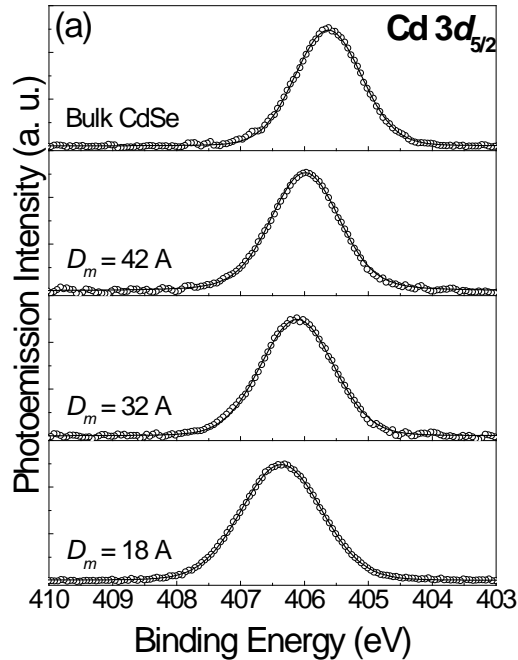


Synchrotron $h\nu = 160 \text{ eV}$



Different photon energy \rightarrow
different relative cross section
for various core levels \rightarrow
Relative intensity changes
with photon energy

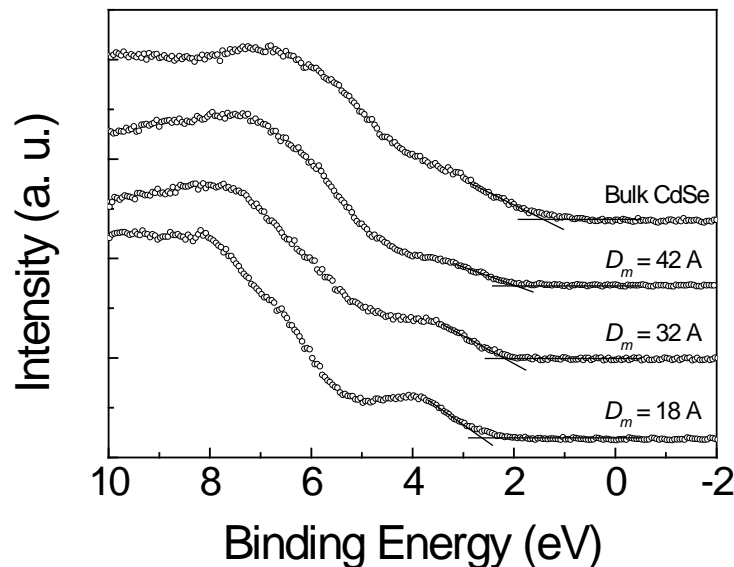
surface component bulk component



Surface core level shift
(chemical and/or
environmental)

A case study of IMFP
applied to PE of CdSe
nano particles with
tunable SR

How to choose photon
energies for valence
and different core levels
with the max surface
sensitivity?



Actual choices:

Cd $3d_{5/2}$: 480 eV

Se $3d$: 120 eV

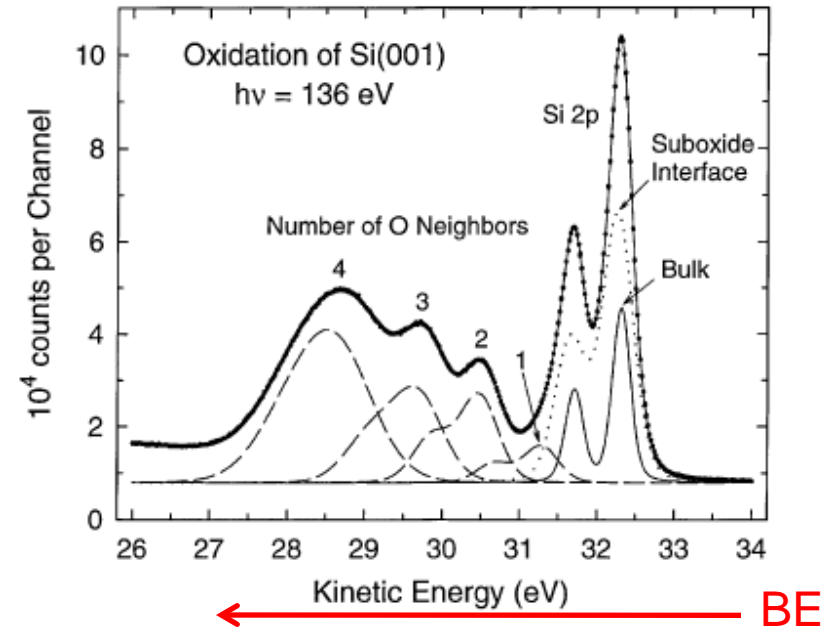
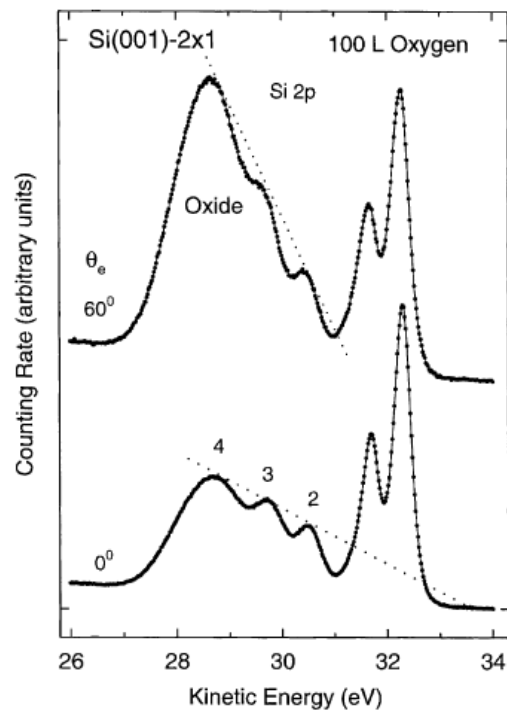
Valence band: 50 eV

$E_k \sim 45\text{-}74 \text{ eV}$, most surface sensitive

Wu, PRB 2007 NSRRC

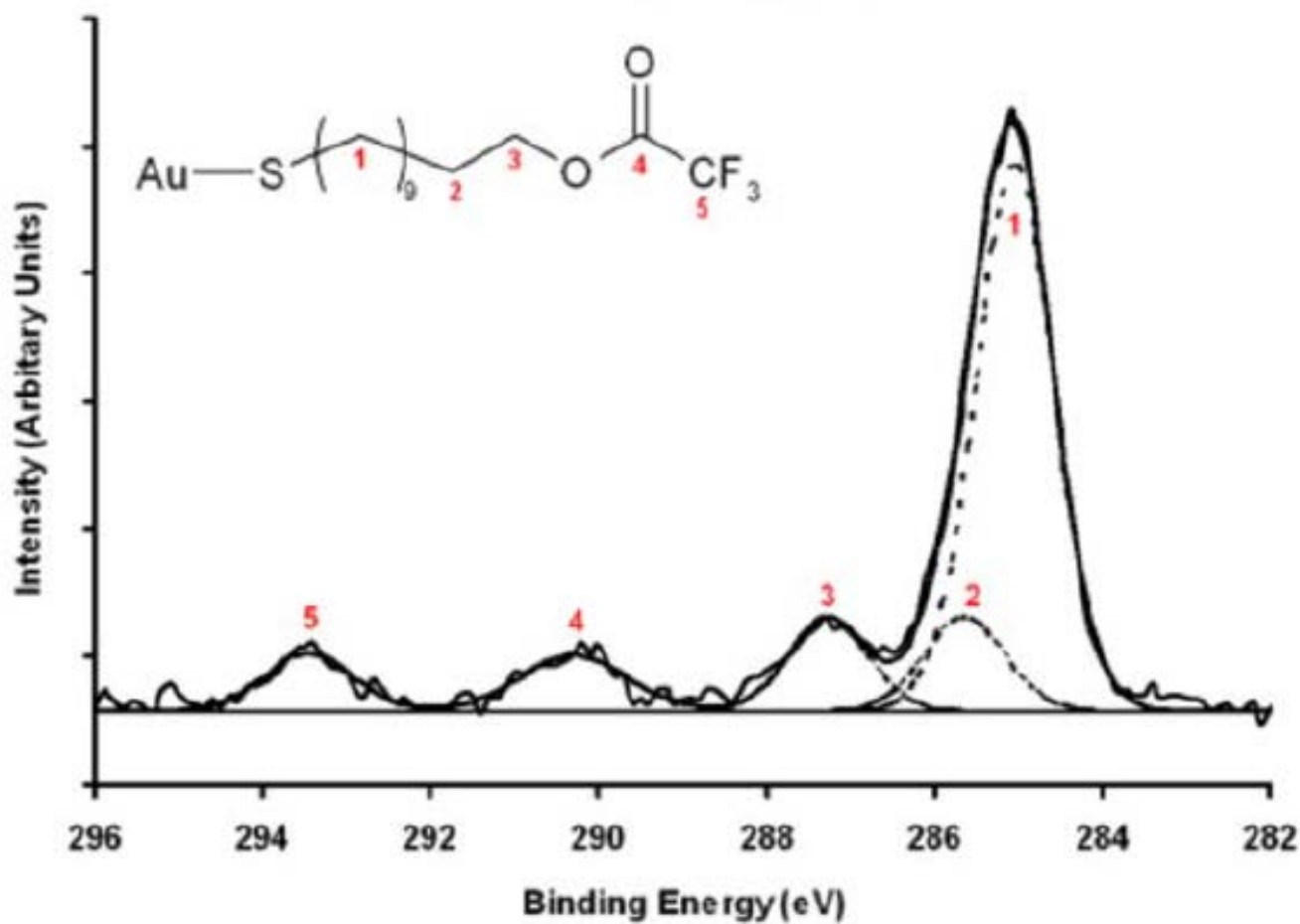
Core level photoemission: chemical shift

higher oxidation state
=> higher BE



higher emission angle
→ more surface sensitive
(IMFP) Pi, SS 2001 NSRRC

Chemical Analysis of C1s core levels



Auger Electron Spectroscopy

Core electron ionized by
photons or high energy
electrons
Non-radiative core hole decay
→ Auger electron emission
Radiative decay
→ Fluorescent x-ray emission

Comparison between PES
and AES

PES: constant BE, E_k shift
with changing photon energy

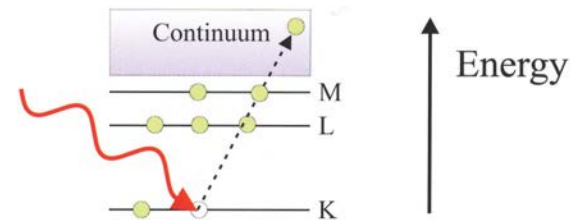
AES: constant E_k , apparent
BE shift with changing photon
energy

(synchrotron)

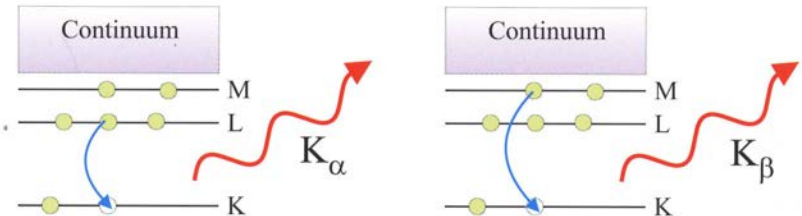
<http://xdb.lbl.gov/>

[Handbook of XPS](#)

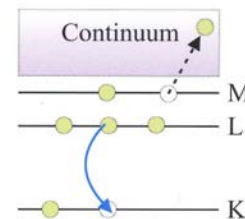
(a) Photoelectric absorption



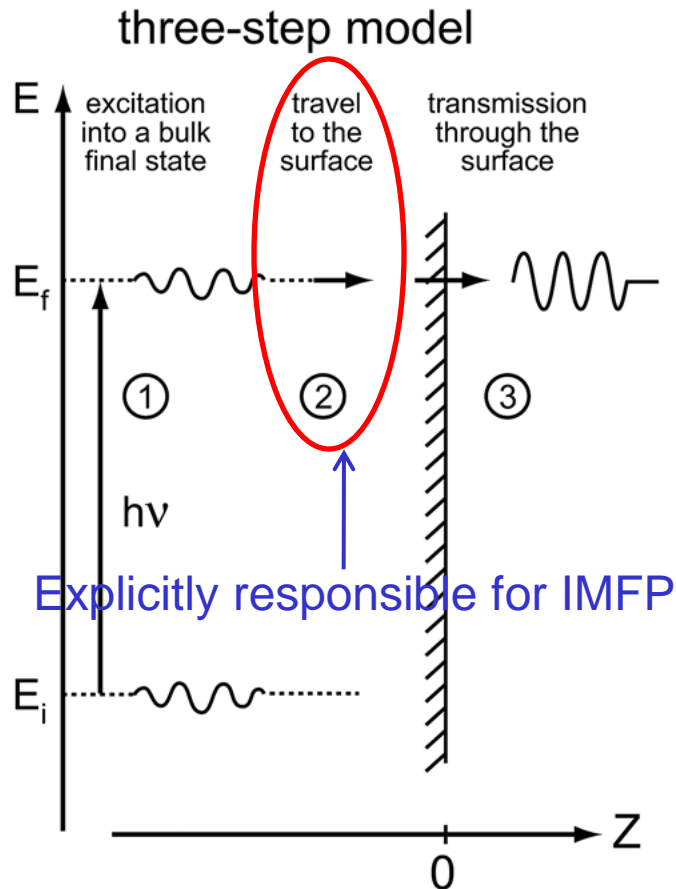
(b) Fluorescent X-ray emission



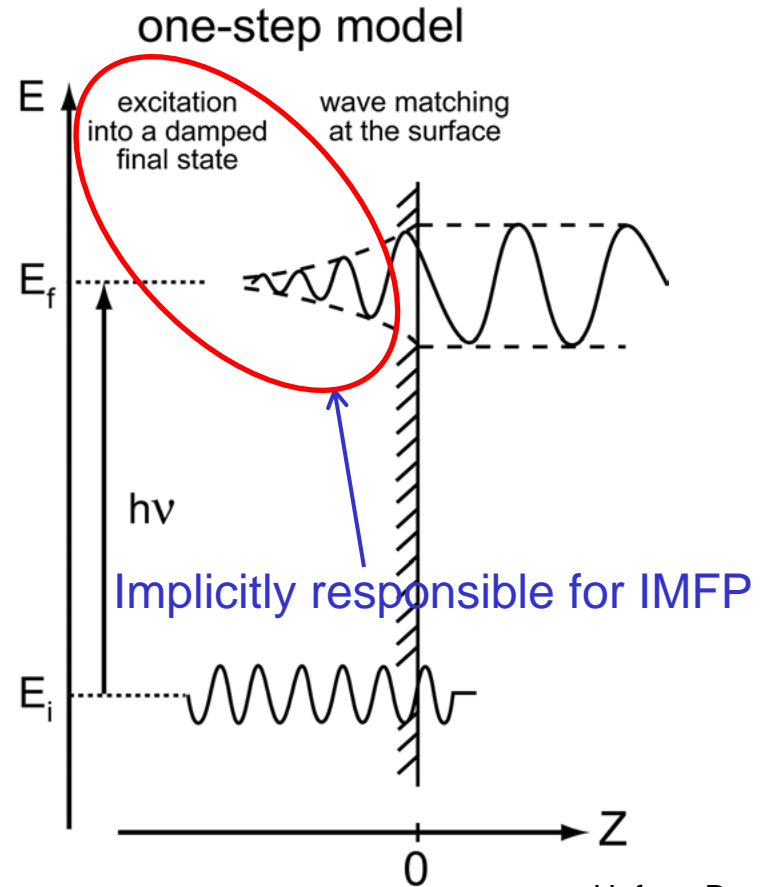
(c) Auger electron emission



Photoemission Process



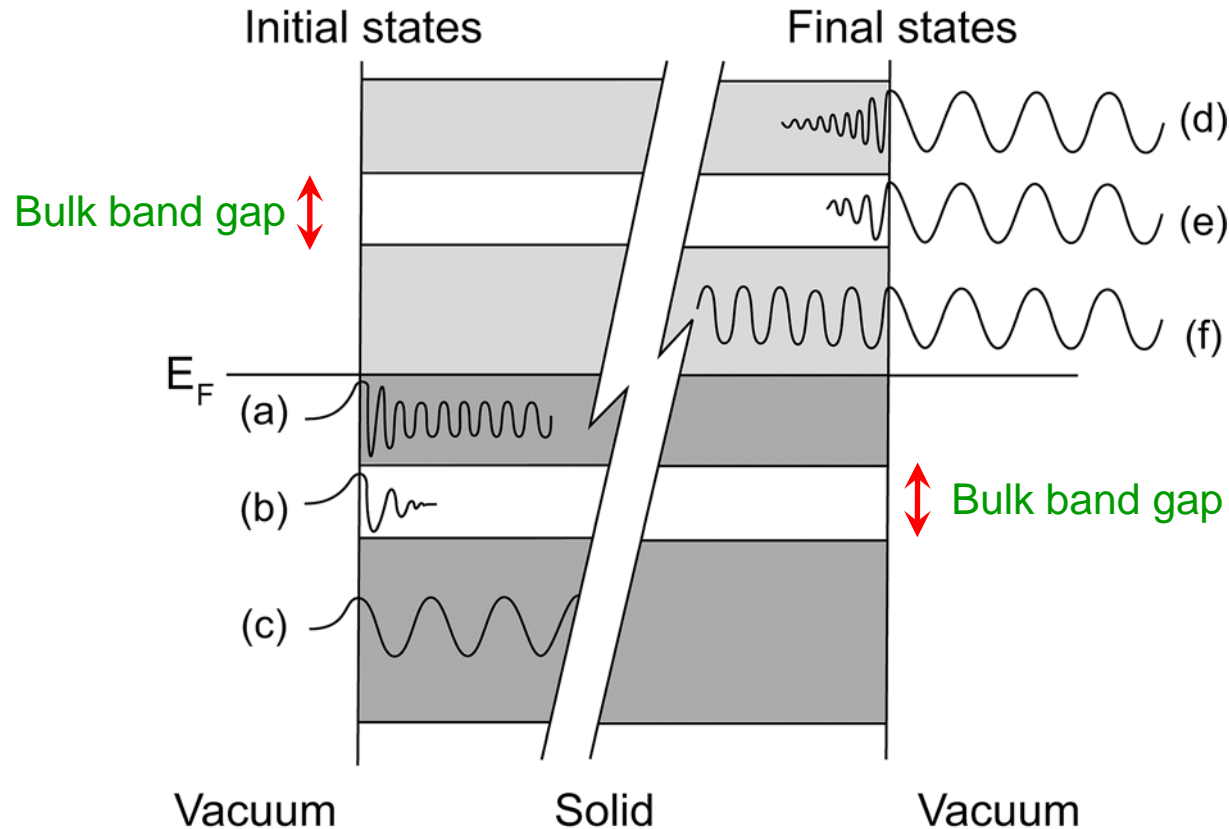
Conceptually intuitive,
Simple calculation works



Hufner, Damascelli

Rigorous,
requires sophisticated calculation

Schematic wave functions of initial and final states (valence band initial states)

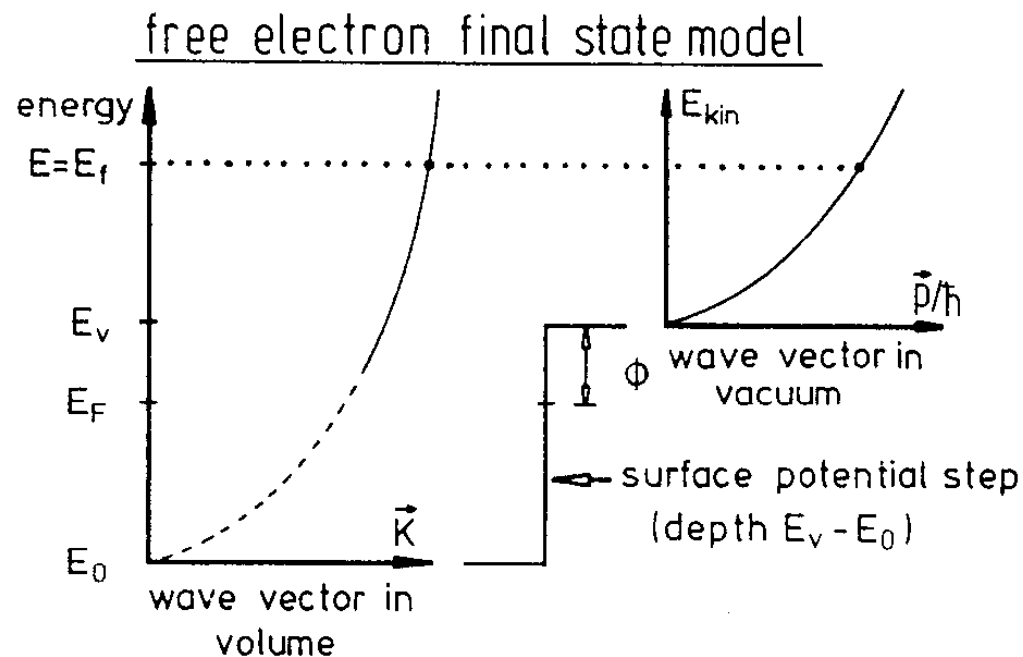


- (a) Surface resonance
- (b) Surface state
- (c) Bulk Bloch state

- (d) Surface resonance
- (e) in-gap evanescent state
- (f) Bulk Bloch final state

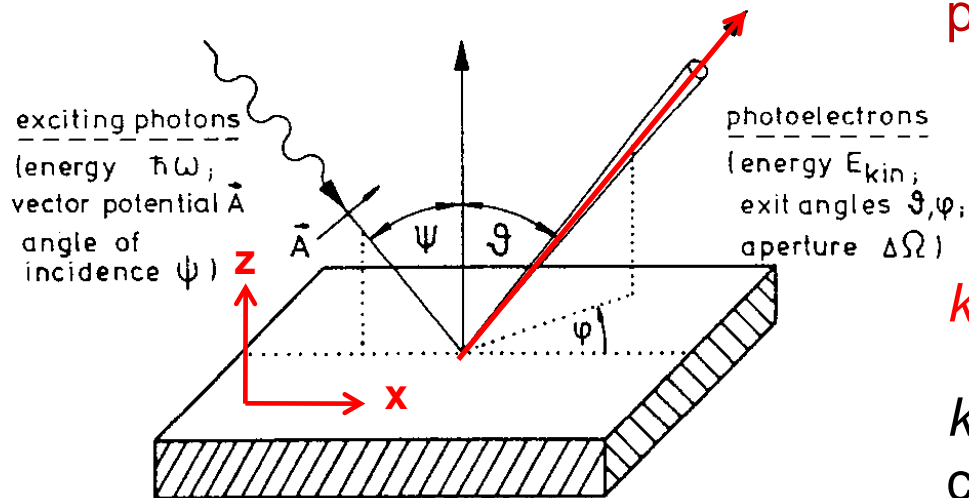
Electron kinetic energy inside and outside of solids

Inner potential: $E_v - E_0$



Concept of inner potential is used to deduce 3D band structure from PE data assuming free electron like final state inside solids

Angle-resolved photoemission (ARPES)



Conservation of linear momentum
parallel to the surface

$$k_{\parallel} = \sqrt{\frac{2m}{\hbar^2} E_k} \cdot \sin \theta$$

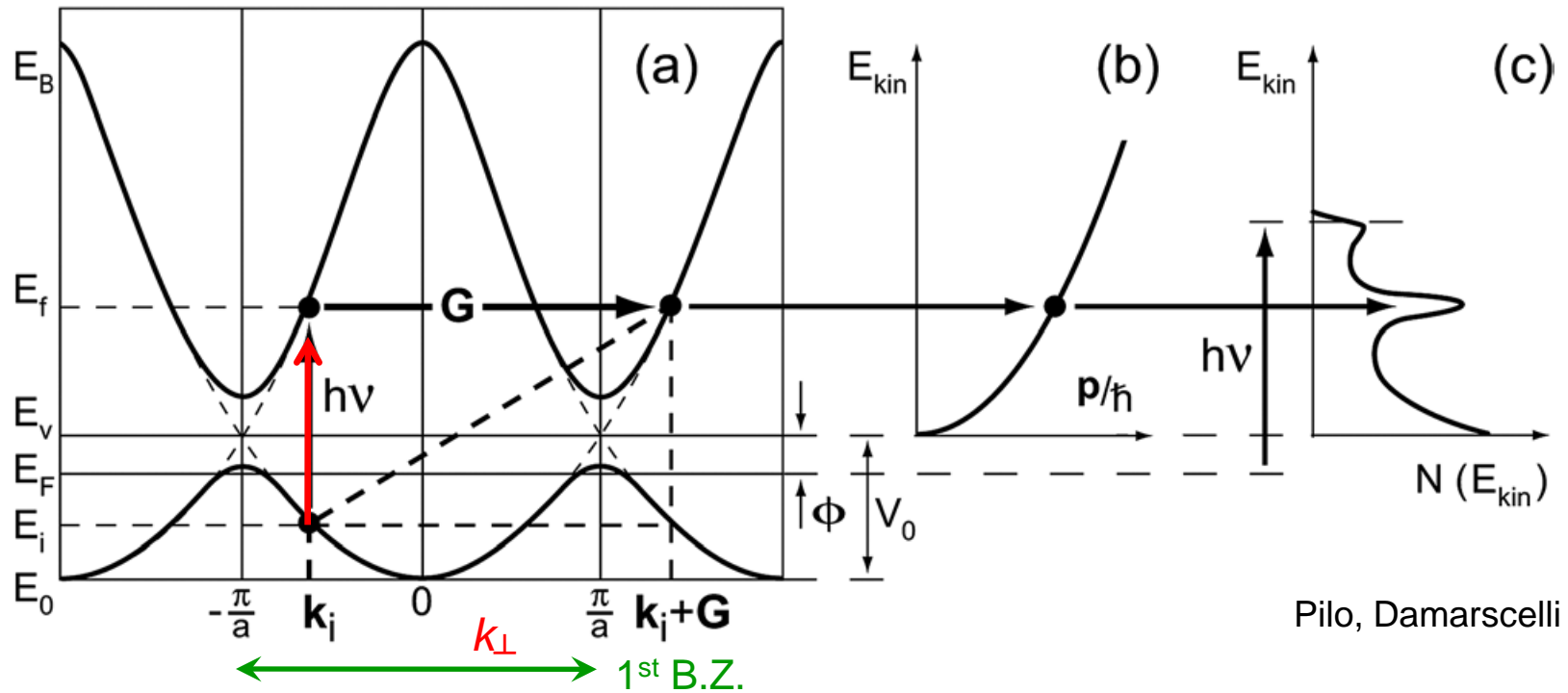
$$k_{\parallel}(\text{inside solid}) = k_{\parallel}(\text{outside in vacuum})$$

k_{\perp} is not conserved, obtained by
changing photon energy

Electron emission angle θ with respect to the crystalline
surface normal and symmetry planes is also measured

⇒ Electronic band dispersion $E(\mathbf{k}_{\parallel}, k_{\perp})$
inside (ordered) crystalline solids

Band Mapping (3D) $E(k_{\perp}, k_{\parallel}=0)$



Pilo, Damarscelli

Vertical transition (using visible, uv and soft x-rays) at normal emission

For hard x-ray photon momentum cannot be neglected

Using different $h\nu$ at normal emission to map out $E(k_{\perp})$

Bulk band structure and Fermi surfaces

Fermi surfaces:

Electron pockets and hole pockets

Related to

Hall coefficient

Electric conductivity

Magnetic susceptibility

Cu

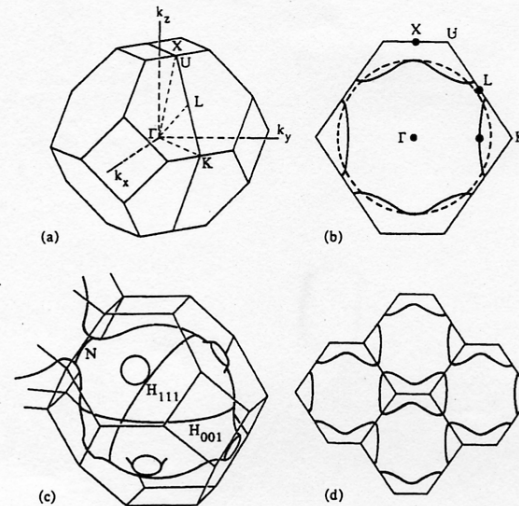


Fig. 10-15 Various aspects of the Fermi surface of Cu. (a) The Brillouin zone of an fcc lattice with some special points labeled. (b) A (110) section of the Brillouin zone. See the text for the meaning of the internal curves. (c) The proposed Fermi surface of Cu. (d) The extended zone picture of a (110) section of the Fermi surface showing the dog bone orbits.

Gap below $E_F (=0)$ at L-point

(nearly free electron like) sp -band

Small dispersion d -band
more localized state

Large dispersion sp -band
extended state

Dispersion of a band can tell how localized or extended a state is in a solid

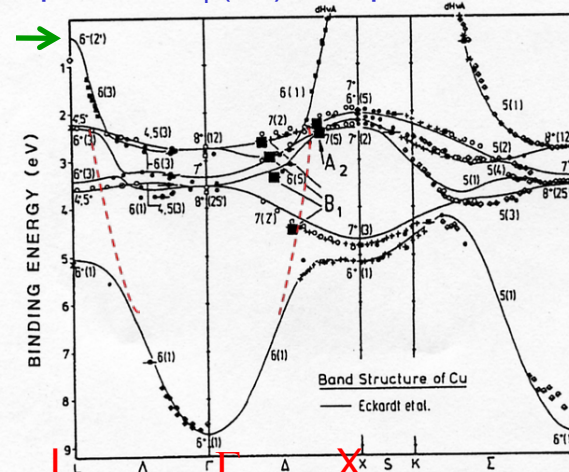
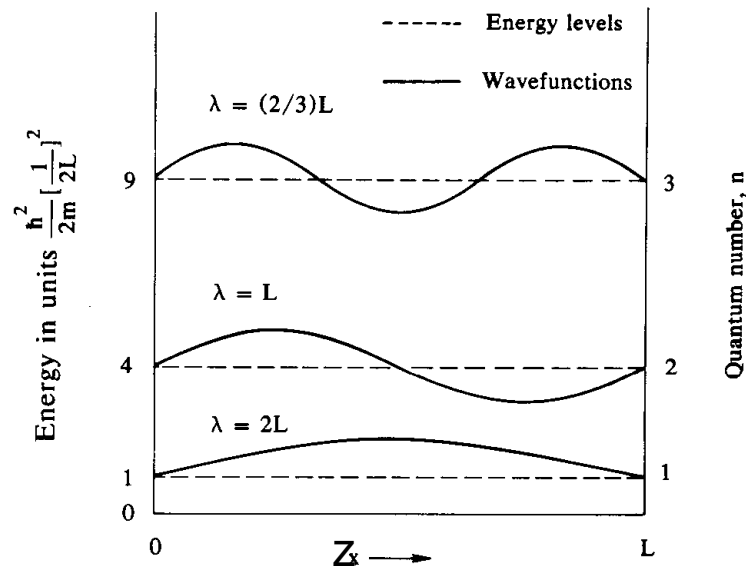


Fig.7.17. Occupied part of the band structure of Cu [7.39] with data points from various sources and a theoretical result [7.53]. Also shown (squares) are the two A_2 points and the four B_1 points from Fig.7.16

(111) ← → (001)

Hufner

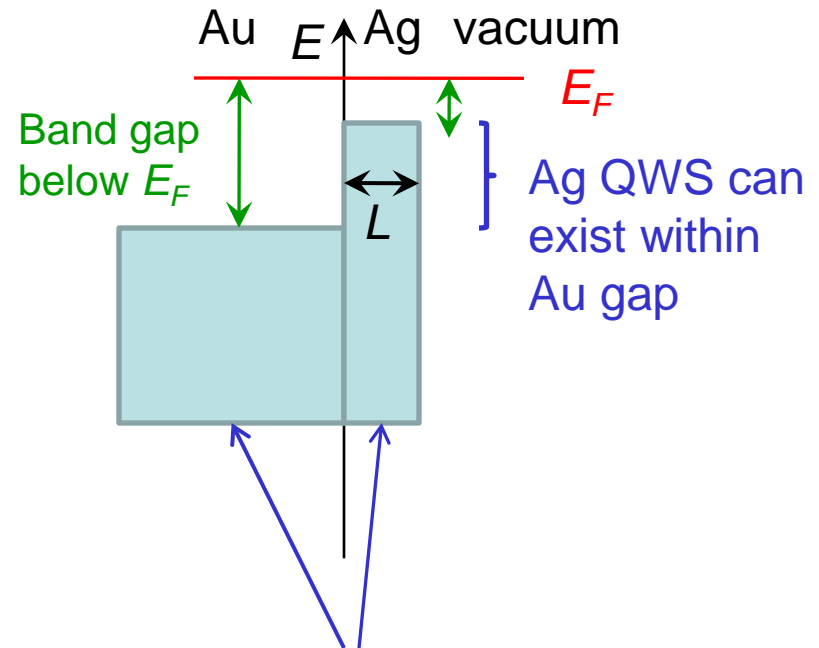
Quantum well states: manifestation of particle in a box in real materials



Quantized discretely along z-direction
Energy levels depend on film thickness L

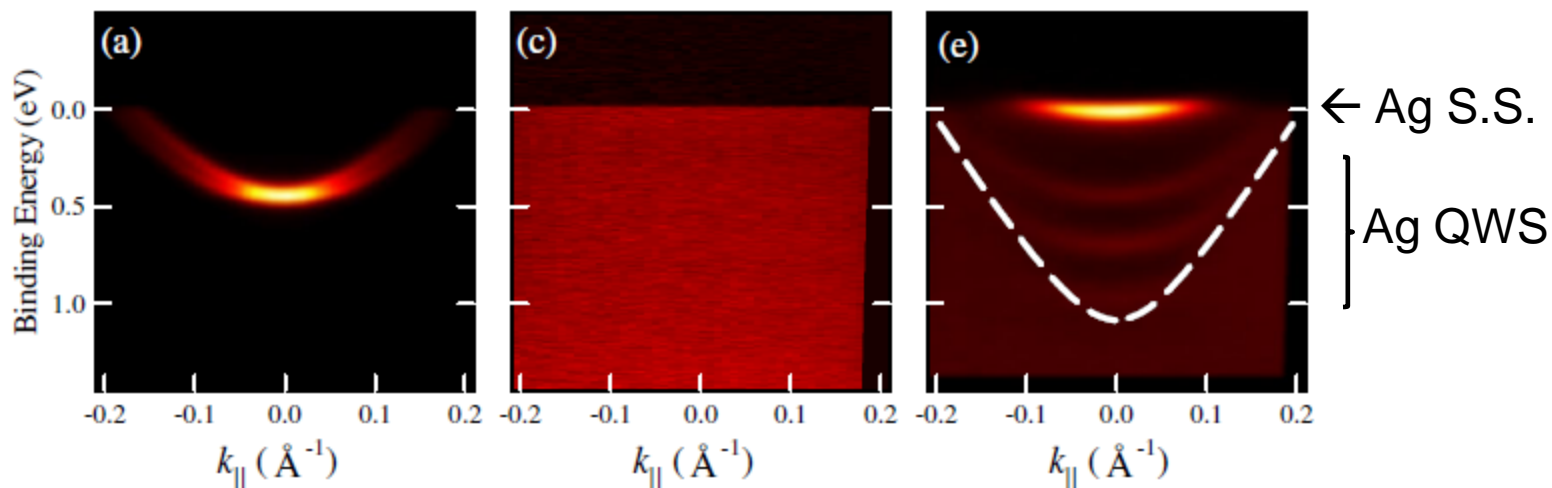
Nearly free electron like in xy-plane

Ag(111) thin films expitaxially grown on Au(111) substrate

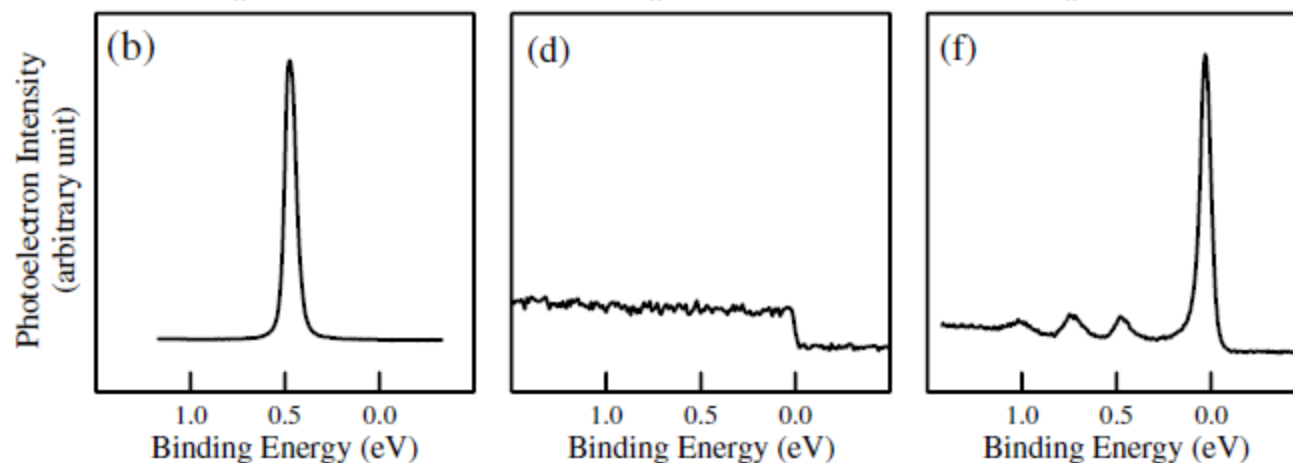


Bulk projected bands along ΓL
of Au and Ag, respectively

2D
Int.
plots



$k_{\parallel} = 0$
EDCs

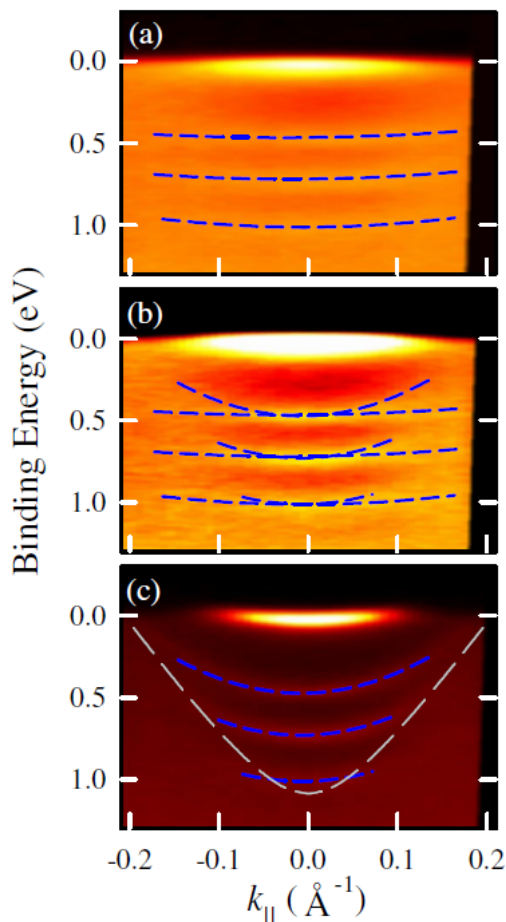


Luh et al.
PRL 2008
NSRRC
BL21B1

Clean Au(111)
surface state

Deposit 22 ML Ag
at 37 K
disordered form

Anneal to 258 K
Atomically flat
22 ML thin film

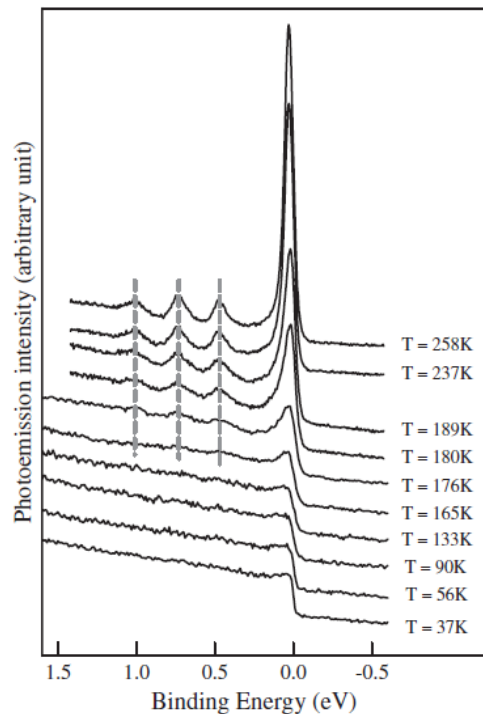


Anneal to 180 K
QWS appear
minimal flat
dispersion
Small localized
domains within
xy-plane

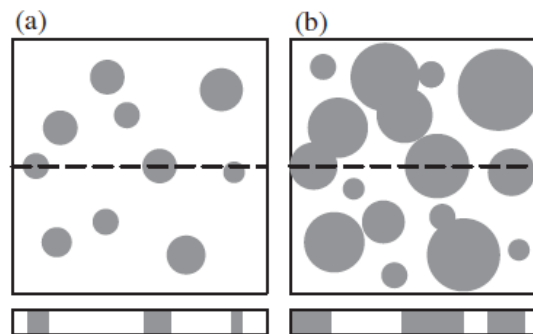
Anneal to 189 K
Coexistence of
two kinds of
dispersion

Anneal to 258 K
Well developed
dispersion
Large, good
crystalline
domains
in xy-plane

Proposed growth model



Same QWS energies →
Same crystalline film
thickness along z
even though lateral
crystalline domains
grow from small to
large



Annealing Temp →

One-particle spectral function near E_F measured by ARPES with many-particle correction (quasi-particle)

$$A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{[\omega - \varepsilon_k - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}$$

ε_k : single particle energy without many-particle correction

$\omega = 0$: E_F

Self energy correction due to interaction with phonons, plasmons and electrons, etc.

$$\Sigma(k, \omega) = \Sigma'(k, \omega) + i\Sigma''(k, \omega)$$

Real part: shift observed peak energy from single particle energy

Imaginary part: peak FWHM = $2 \Sigma''$

Many-Body Effects in Angle-Resolved Photoemission: Quasiparticle Energy and Lifetime of a Mo(110) Surface State

T. Valla,¹ A. V. Fedorov,¹ P. D. Johnson,¹ and S. L. Hulbert²

¹*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000*

²*National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973-5000*

(Received 28 January 1999)

In a high-resolution photoemission study of a Mo(110) surface state various contributions to the measured width and energy of the quasiparticle peak are investigated. Electron-phonon coupling, electron-electron interactions, and scattering from defects are all identified mechanisms responsible for the finite lifetime of a valence photohole. The electron-phonon induced mass enhancement and rapid change of the photohole lifetime near the Fermi level are observed for the first time.

Peak position

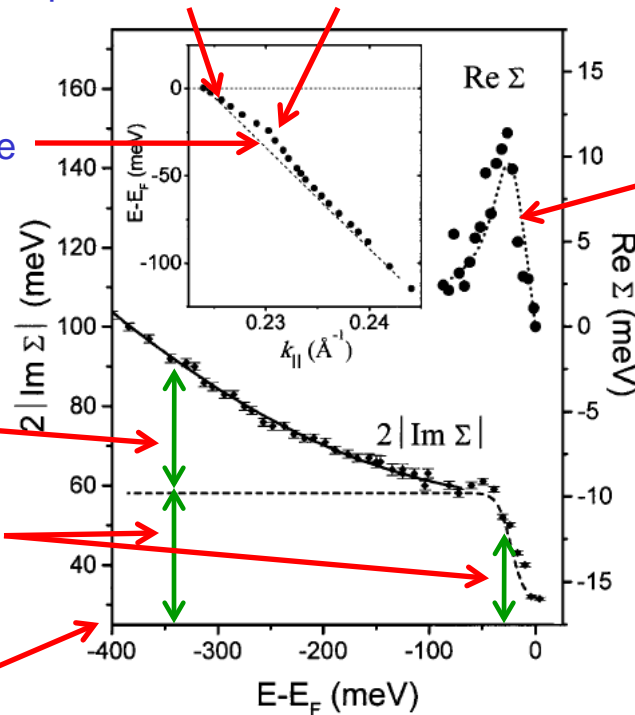
Kink ~25 meV due to electron-phonon scattering

Featureless
single particle
dispersion
curve

Width due to
electron-electron
scattering $\sim \omega^2$

Width due to
electron-phonon
scattering

Const bkg width
due to impurities



Peak position – single particle curve

$$\text{Total } W = W_{e-e} + W_{e-ph} + W_{im}$$

ARPES for valence band PE uses primarily VUV light because of

1. Better absolute photon energy resolution for most BLs designed as nearly const $\Delta E/E$.

2. Better photoionization cross section at low photon energy.

3. Better momentum resolution for a given angular resolution.

$$\Delta k_{\parallel} (1/\text{\AA}) = 0.5123 \sqrt{E_k(\text{eV})} \cos(\theta) \Delta\theta$$

SX ARPES has been tried for increasing bulk sensitivity, more free electron like final states and reduced matrix element effects. The increasing bulk sensitivity will be discussed.

NSRRC U9 BL21B1 BL and high resolution photoemission end station

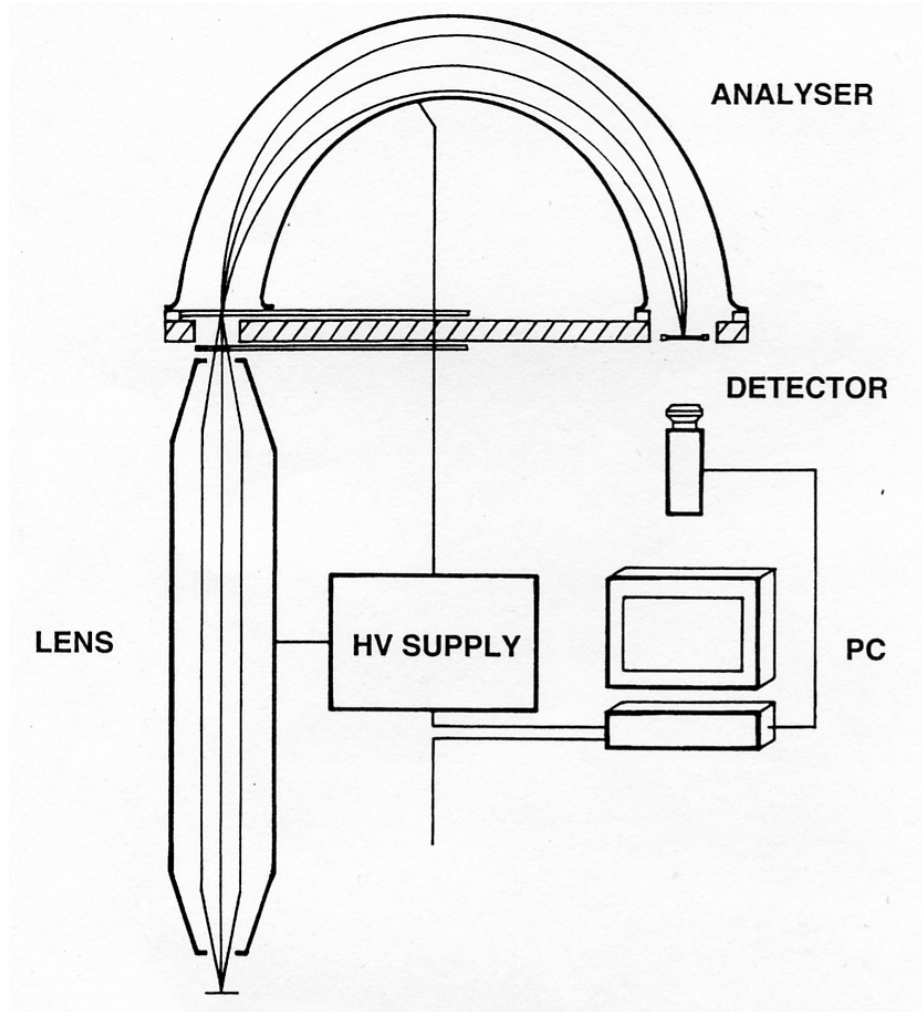


U9
undulator

CGM

Scienta
SES 200
analyzer

Hemispherical electron energy analyzer



R1 : radius of inner sphere
R2 : radius of outer sphere
 $R_o = (R1 + R2) / 2$: mean radius
and along electron path
V1: inner potential
V2: outer potential
Ep: pass energy = electron
kinetic energy along mean
radius

Comments on photoelectron IMFP

Valence band PE using VUV and SX has IMFP near minimum, very surface sensitive. It is great to probe surface electronic structure such as surface states and surface resonances.

Many **strongly correlated systems** have electronic structure sensitive to coordination, thus **surface contains different electronic structure from that of deeper bulk**. Great surface sensitivity posts a serious problem to probe true bulk properties.

Buried interface is mostly undetectable by PE using VUV/SX photons because IMFP is too small compared to thickness of outermost thin layer.

Need larger IMFP by using higher energy photons to enhance bulk sensitivity.

Drive to go to even higher photon energies into hard x-ray regime

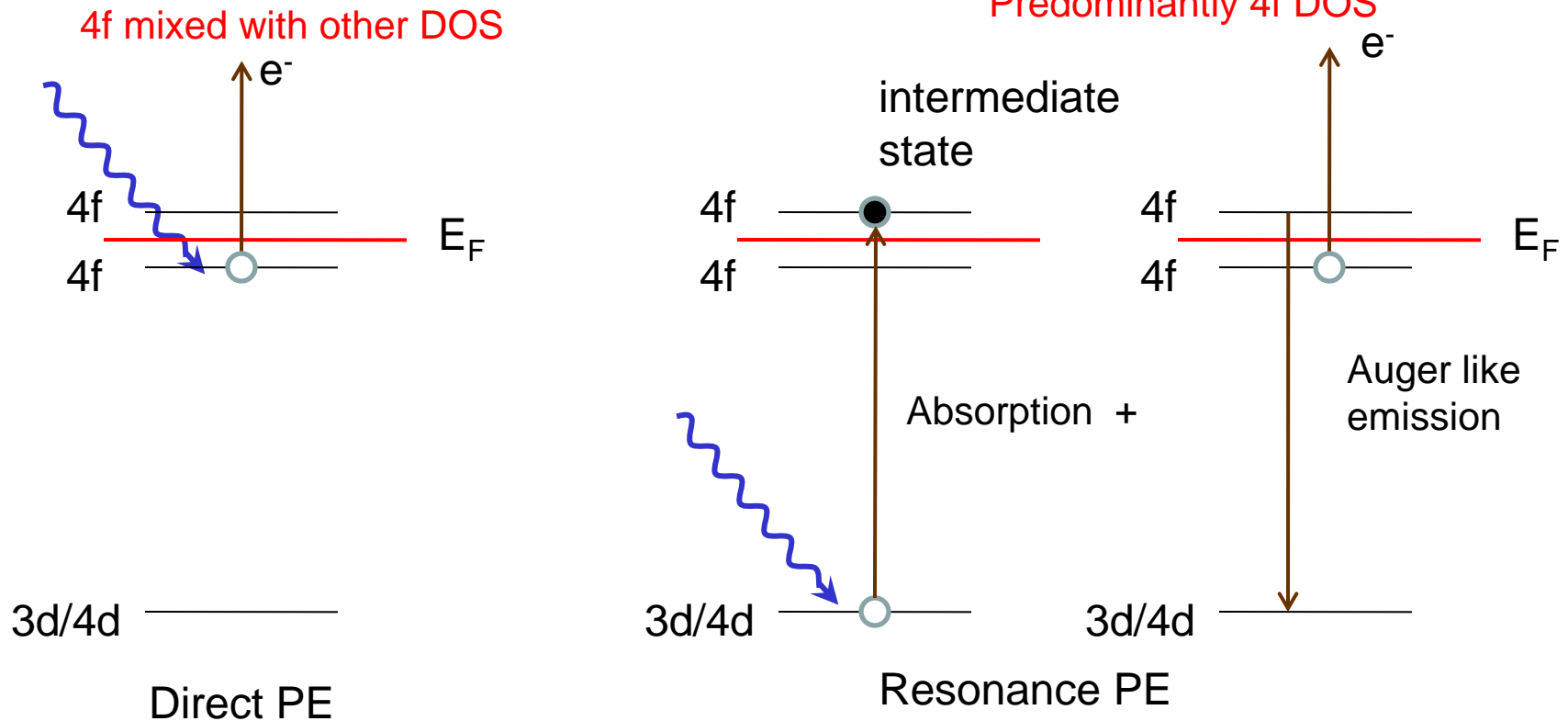
HARd X-ray PhotoEmission Spectroscopy (HAXPES)

HAXPES not only reach even closer to true bulk properties of strongly correlated systems, but also becomes capable of probing interface electronic structure, Very difficult using conventional VUV/SX.

Resonance photoemission (near-edge absorption followed by Auger like electron emission)

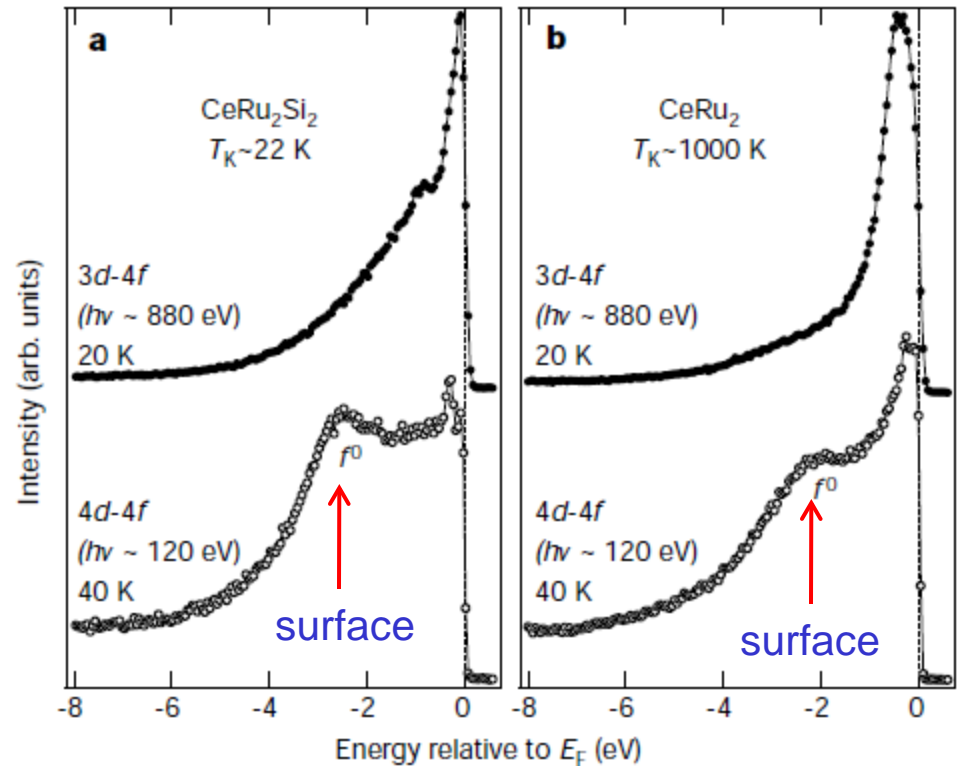
e.g. $\text{Ce}^{3+} (4f^1)$

Intensity enhanced by absorption
Predominantly 4f DOS



Probing bulk states of correlated electron systems by high-resolution resonance photoemission

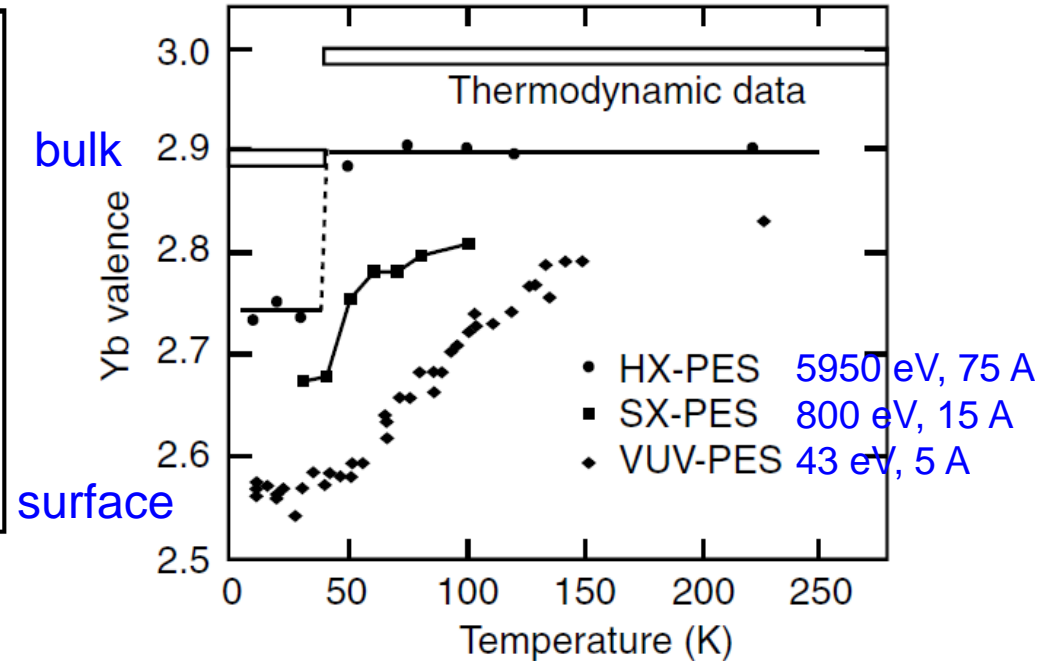
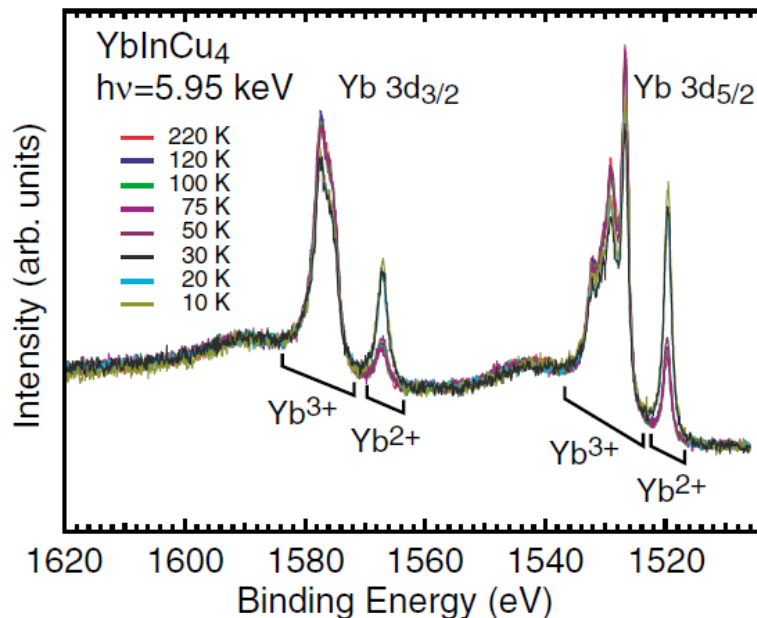
A. Sekiyama^{*}, T. Iwasaki^{*}, K. Matsuda^{*}, Y. Saitoh[†], Y. Ōnuki[‡] & S. Suga^{*}



By using Ce $3d \rightarrow 4f$ Res. PE near 880 eV surface 4f component becomes greatly reduced compared to $4d \rightarrow 4f$ Res. PE near 120 eV, the resulting spectra are closer to true bulk 4f DOS.

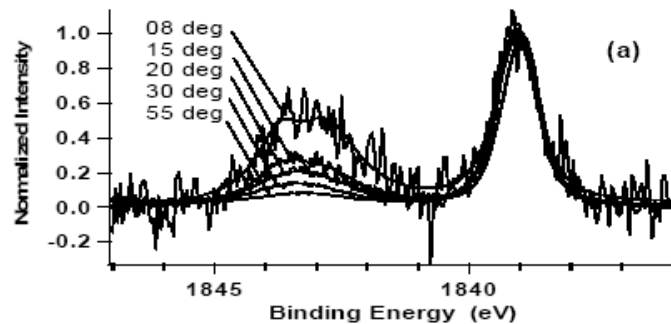
Valence Transition of YbInCu₄ Observed in Hard X-Ray Photoemission Spectra

Hitoshi Sato,^{1,*} Kenya Shimada,¹ Masashi Arita,¹ Koichi Hiraoka,² Kenichi Kojima,³ Yukiharu Takeda,^{1,†}
Kunta Yoshikawa,⁴ Masahiro Sawada,¹ Masashi Nakatake,¹ Hirofumi Namatame,¹ Masaki Taniguchi,^{1,4}
Yasutaka Takata,⁵ Eiji Ikenaga,⁶ Shik Shin,^{5,7} Keisuke Kobayashi,⁶ Kenji Tamasaku,⁸ Yoshinori Nishino,⁸ Daigo Miwa,⁸
Makina Yabashi,⁶ and Tetsuya Ishikawa⁸

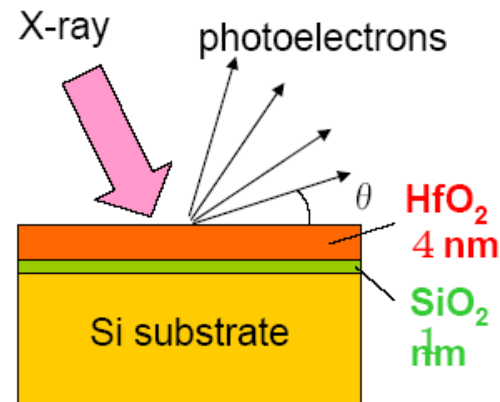
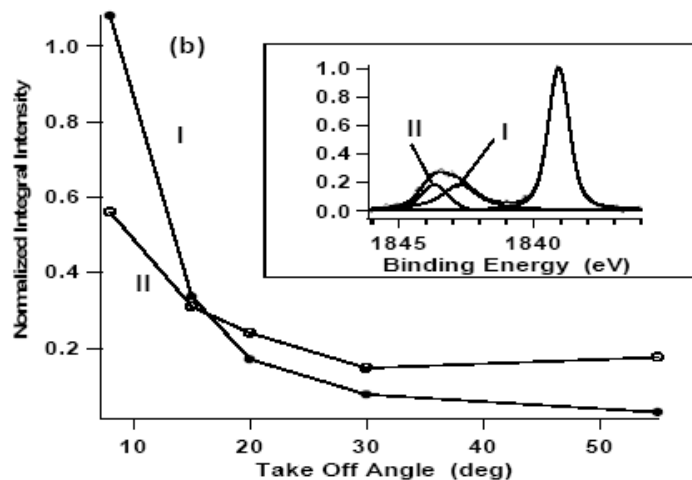


Bulk sensitive HAXPES can determine sharp first order valence band transition

HAXPES example: Hard x-ray photoemission on Si-high k insulator buried interface



Kobayashi, APL 2003 **SP**ring-8



Annealed sample
HfSix formation

$$h\nu = 6 \text{ keV}, \Delta E \sim 0.24 \text{ eV}$$

Take-off angle dependence => non-destructive depth profile

Can probe buried interface at 35 nm ! (achievable only by hard x-ray PE)

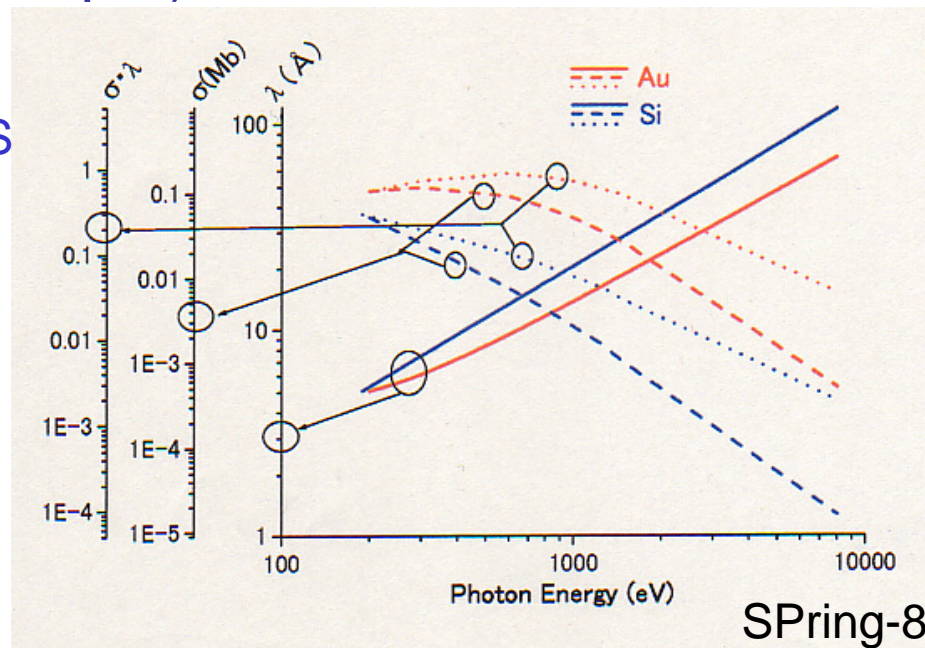
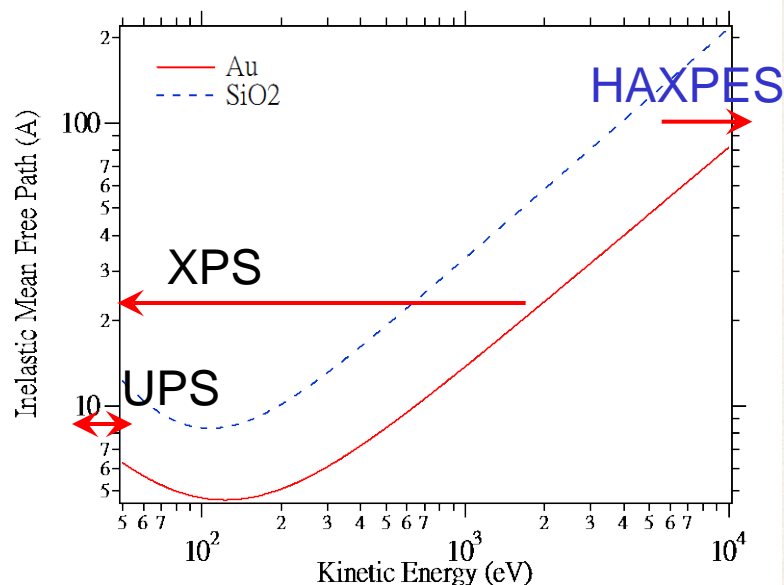
NSRRC HAXPES project at SPring-8

World wide efforts on SR based HAXPES

- * **SPring-8** BL29XU (RIKEN, HAXPES end station can move in, pioneer in HAXPES)
- * **SPring-8** BL15XU (National Institute Materials Science (NIMS) WEBRAM, fixed installation)
- * **SPring-8** BL19LXU (RIKEN long undulator BL, HAXPES end station can move in)
- * **SPring-8** BL46XU (JASRI Engineering Science Research, fixed installation)
- * **SPring-8** BL47XU (JASRI HXPES, fixed installation)
- * **SPring-8 BL12XU-SL (NSRRC, fixed installation) unique with dual analyzers**
- * **ESRF** ID16 (mainly for IXS, used by VOLPE)
- * **ESRF** ID32 (fixed installation, shared with XRD)
- * **ESRF** BM32 SpLine (fixed installation, PXD/XAS/SRD/HAXPES+SXRD)
- * **BESSY II** KMC-1 BM (HIKE and XUV diffraction, fixed installation)
- * **NSLS** X24A BM (fixed installation)
- * **DESY** BW2 Wiggler (fixed installation)
- * **DLS** I09 (Surface and Interface Analysis (SISA))
- * **SOLEIL** Galaxies (under construction, RIXS and HAXPES)
- * **CLS** SXRMB BM (wide range 1.7-10 keV)
- * **APS** (?)

Why Hard X-rays?

Electron IMFP (probing depth) and Cross section



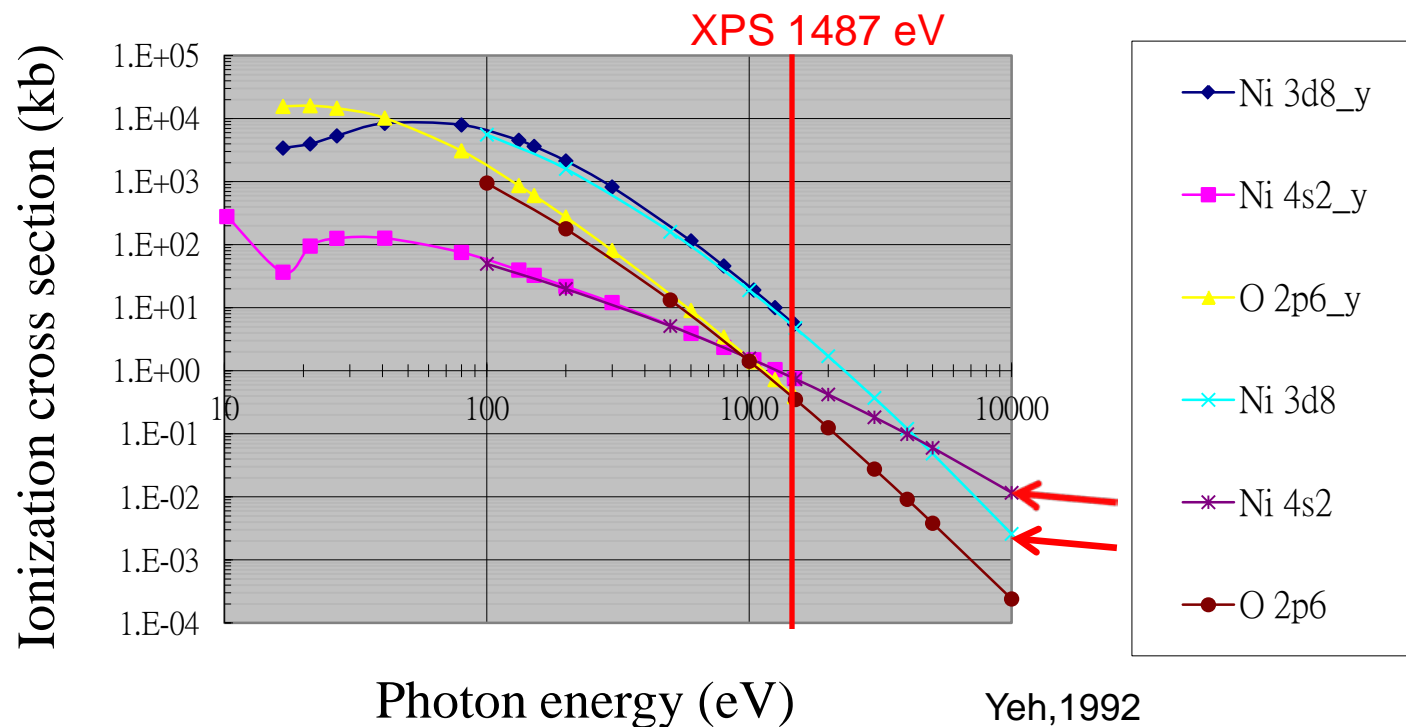
Higher E_k for deeper probing depth or more bulk sensitivity, for strongly correlated systems and interface properties

Photoemission signal ($\sigma \cdot \lambda$) decreases rapidly > 1 keV

Need photon source of higher flux/brightness (modern SR), efficient BL design and good electron analyzers

HAXPES is a low count rate, photon hungry experiment!
(except at a grazing incident angle)

A serious issue on going to hard x-rays



Cross sections of 3d TM s-orbitals go down more slowly than d-orbitals which are the needed information on 3d TM strongly correlated electron systems. Hard x-ray PE spectra could be dominated by contribution from less desired s-orbitals

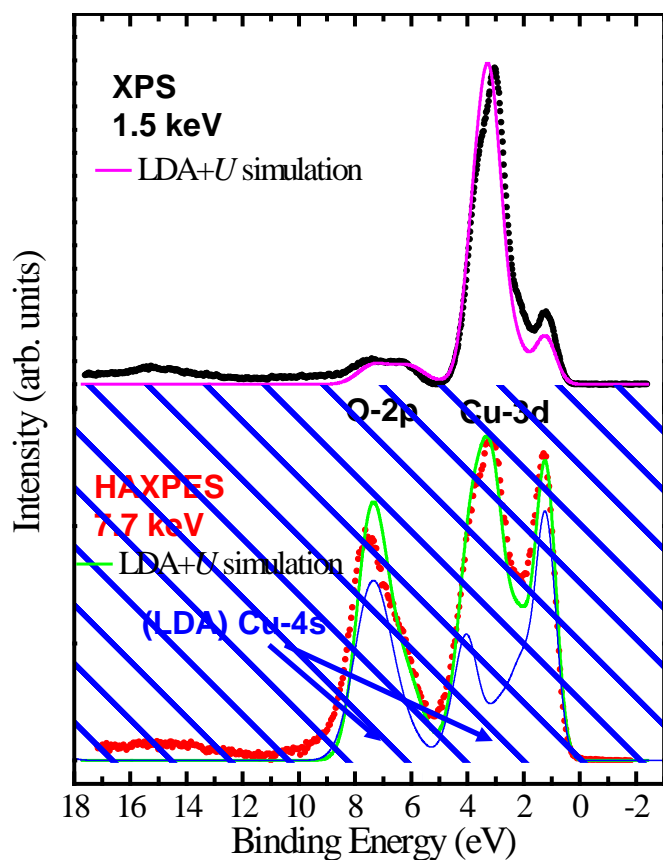
How to cope with this problem?

Unexpected lineshapes in HAXPES compared to XPS

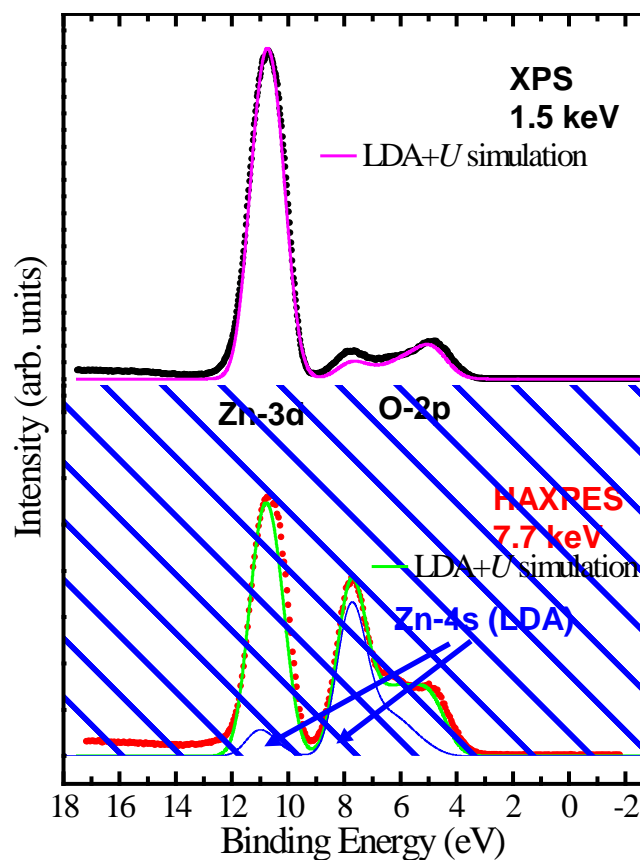
Valence band of simple oxides – e.g. Cu_2O and ZnO

band-insulators, no electron-correlation effects – LDA should do ($+U_{dd}+U_{pp}$)

Cu_2O – valence band



ZnO – valence band



Tjeng et al.

HAXPES: TM-4s overwhelms TM-3d and O-2p

Polarization dependent cross sections in HAXPES

How to suppress the 4s spectral weight?

- photo-ionization cross-section depends on e⁻ emission direction and light polarization
- make use of β -asymmetry parameter

$$\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi} [1 + \beta P_2(\cos \theta) + \dots]$$

β -parameters @ $h\nu = 5-10$ keV

Cu 3d 0.48 - 0.32

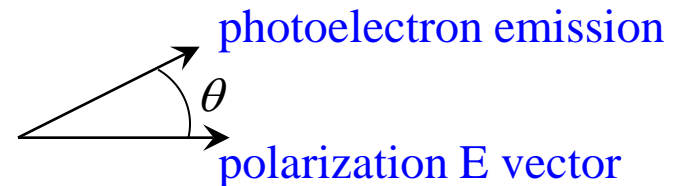
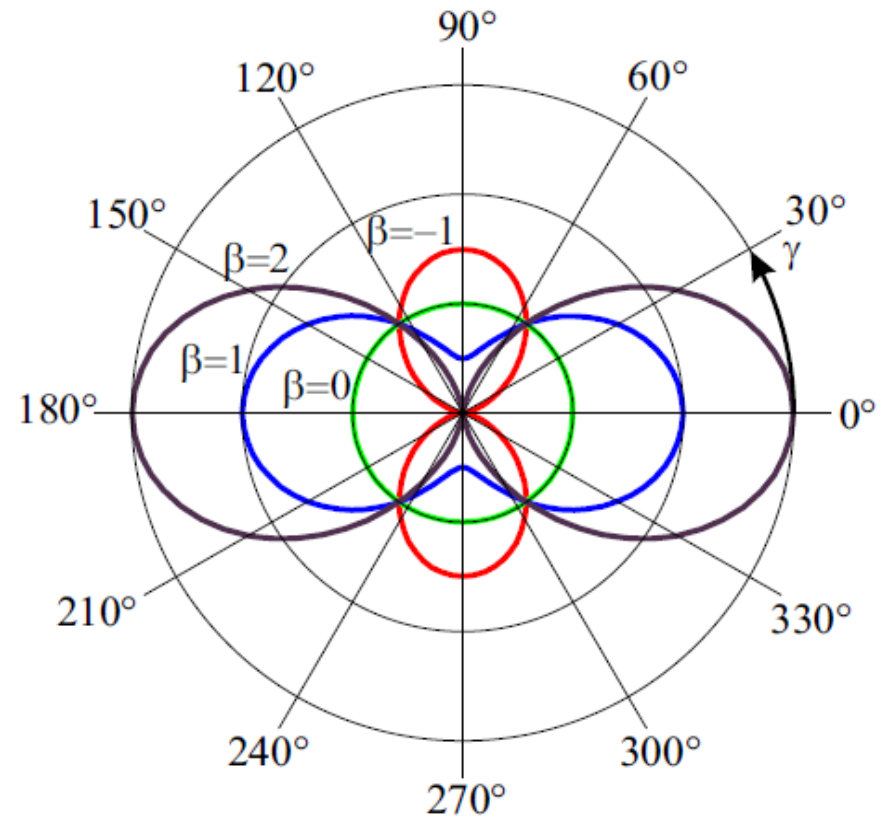
Cu 4s 1.985

Zn 3d 0.50 - 0.33

Zn 4s 1.987 - 1.986

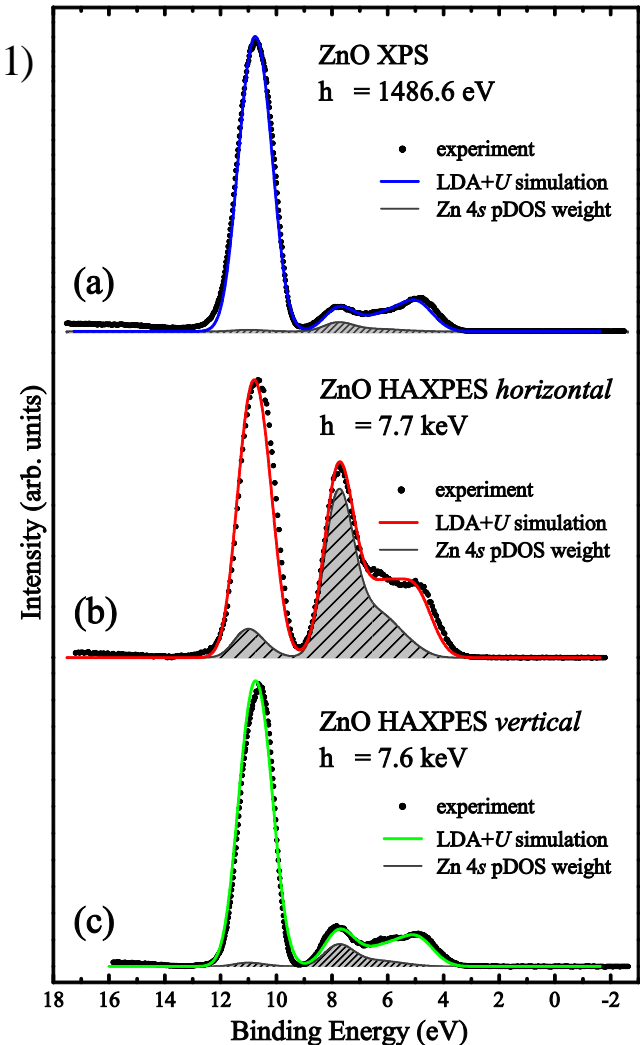
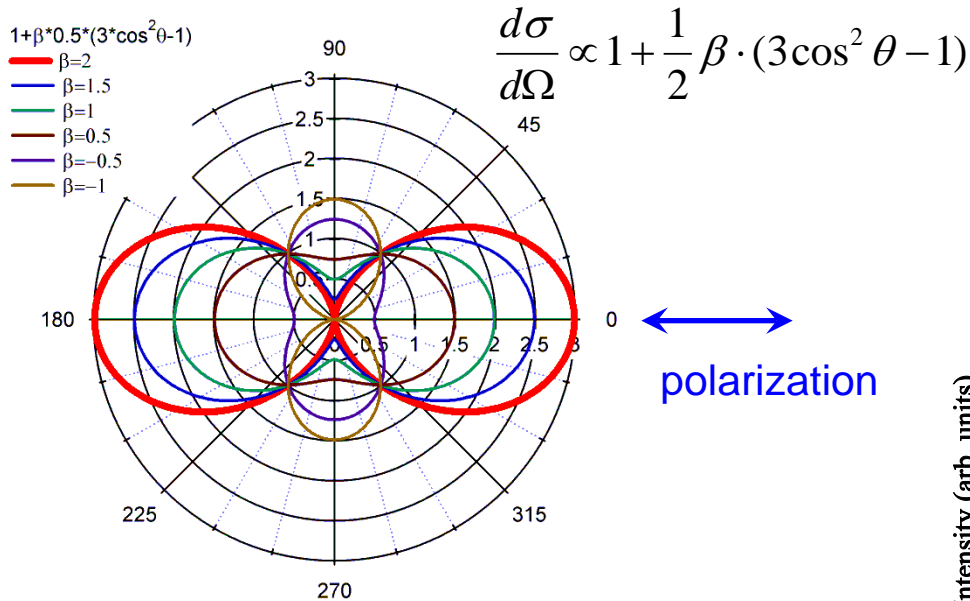
In general: s orbitals have $\beta \approx 2$:

- intensity is *enhanced* for e⁻ emission \parallel E-vector
- intensity *vanishes* for e⁻ emission \perp E-vector



→ choose suitable experimental geometry !

HAXPES Commissioning: Horizontal vs Vertical geometries



horizontal
 $\theta=0^\circ$

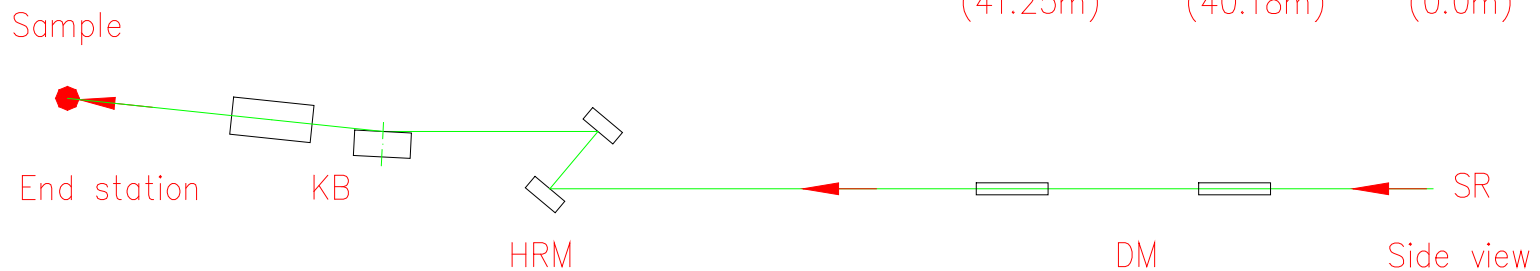
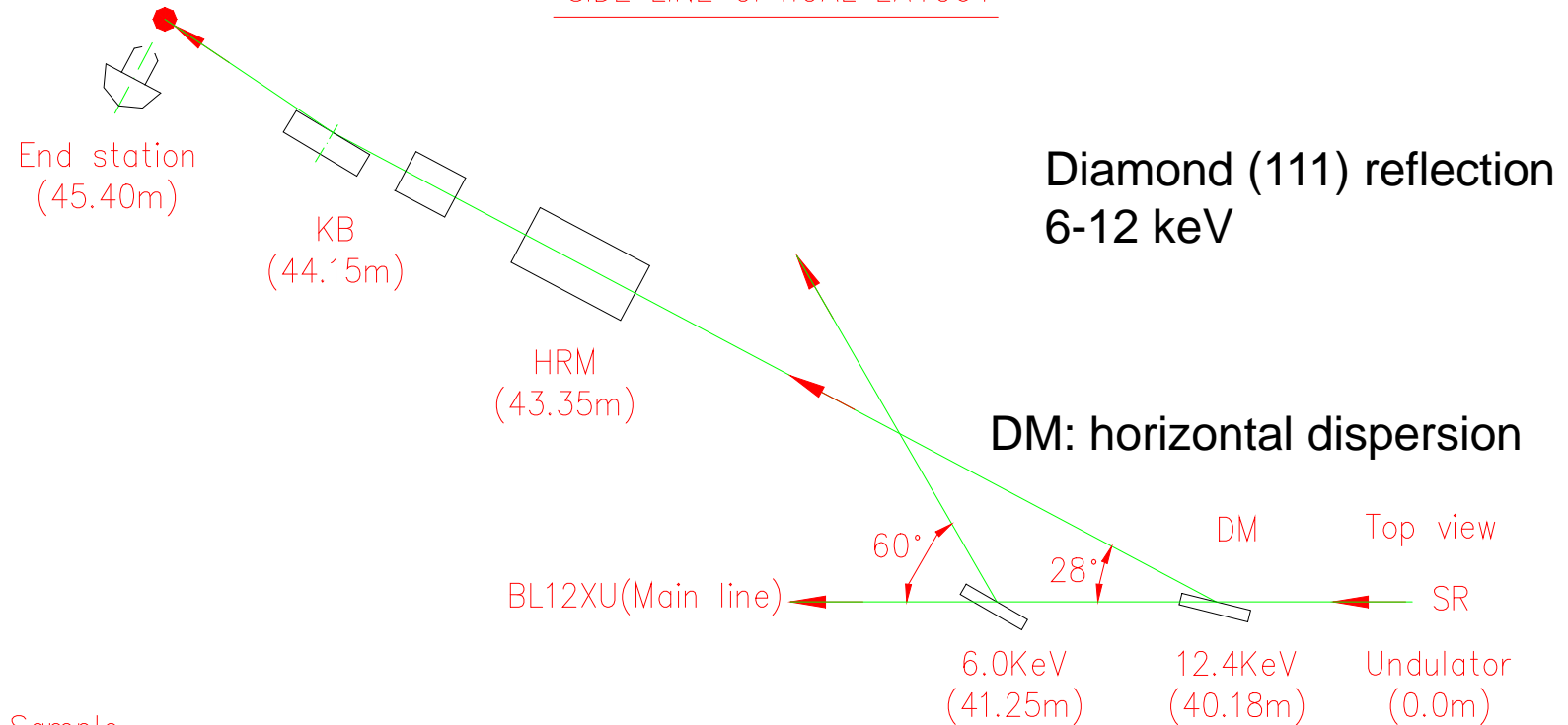
vertical
 $\theta=90^\circ$

Tjeng
et al.

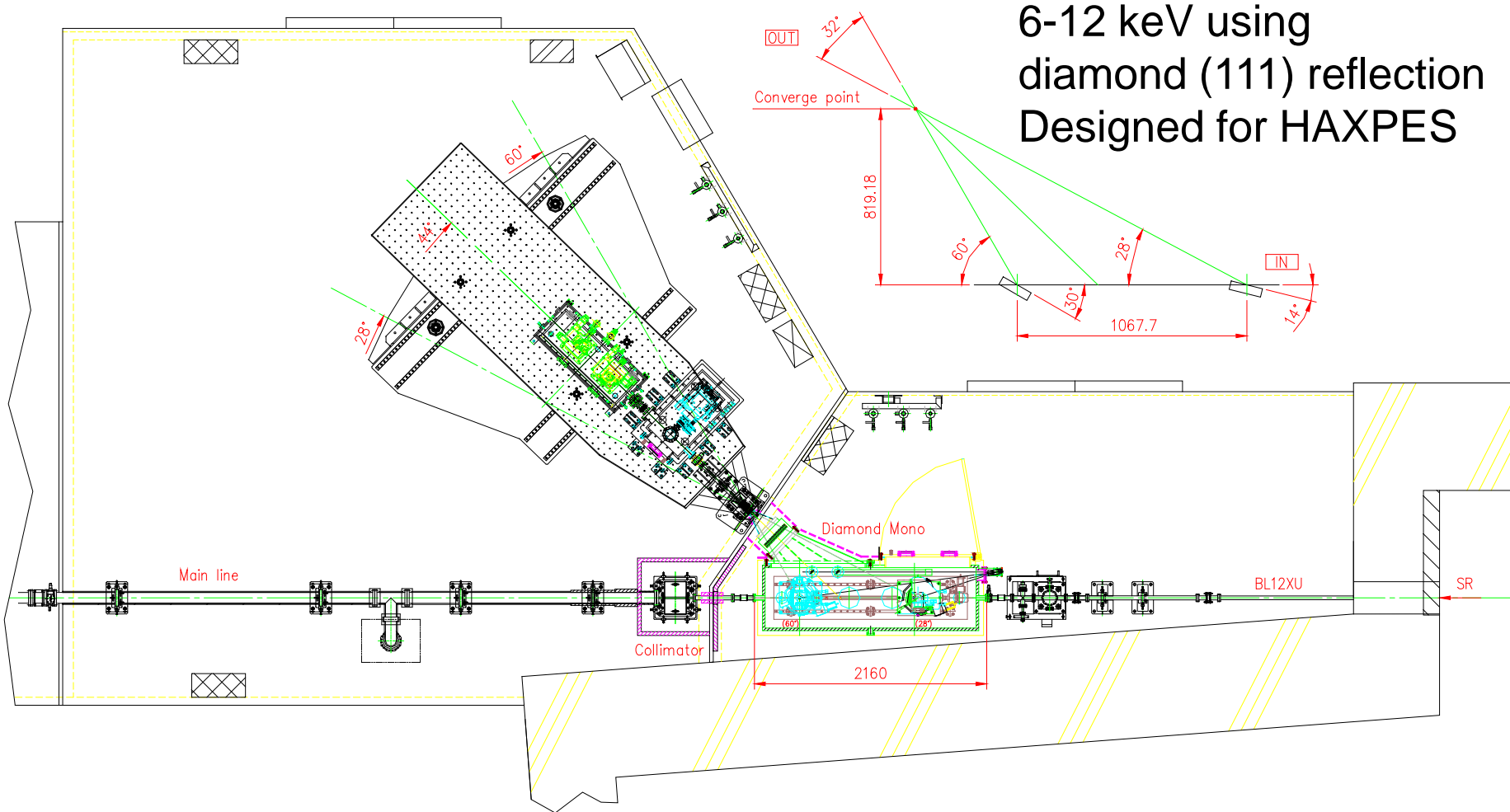
Zn 4s has relatively larger cross section than 3d at 7.6 keV compared to 1.486 keV, enhanced in horizontal geometry at 7.6 keV, while suppressed in vertical geometry

Optical design concept

SIDE LINE OPTICAL LAYOUT

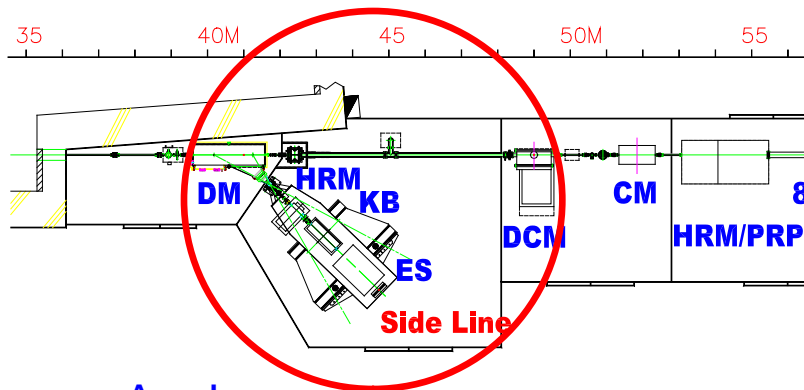


HRM: vertical dispersion

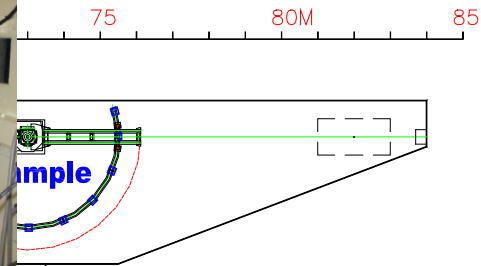
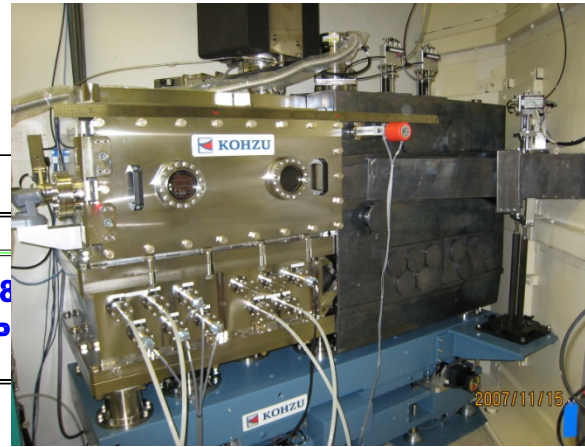


Layout of the side beamline of BL12XU

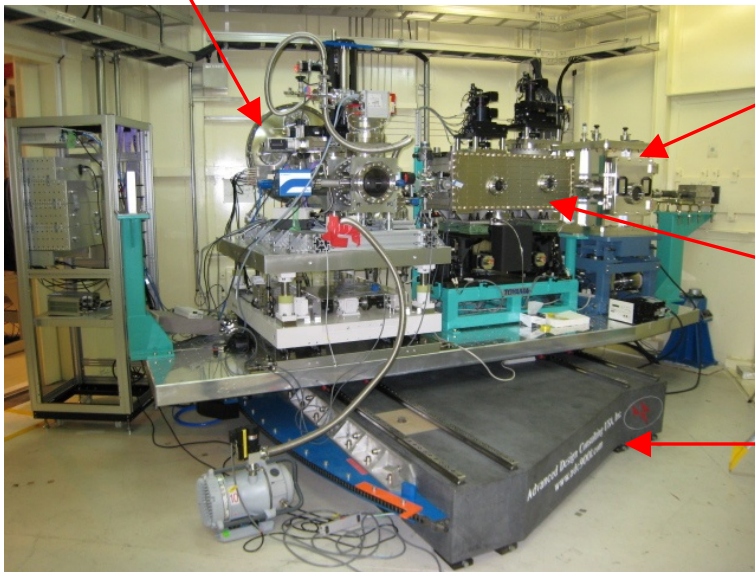
BL12XU Sideline



Diamond Mono.



Analyzer

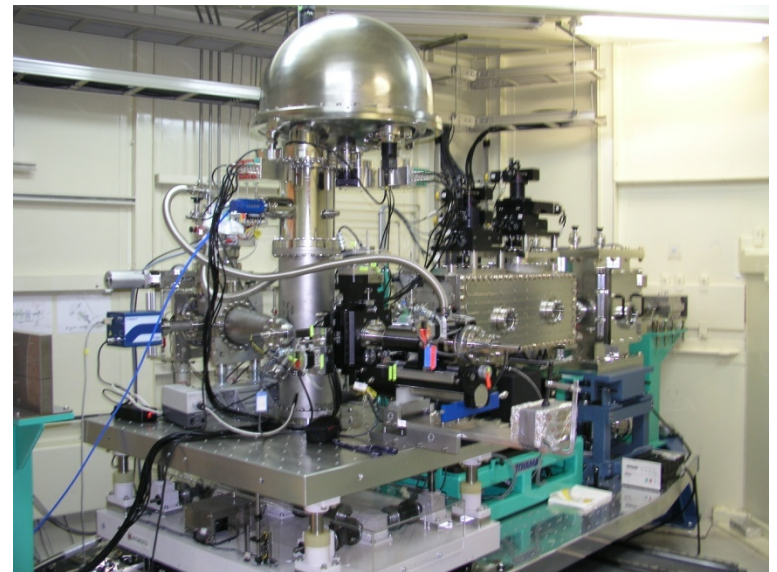


HRM

KB

Platform

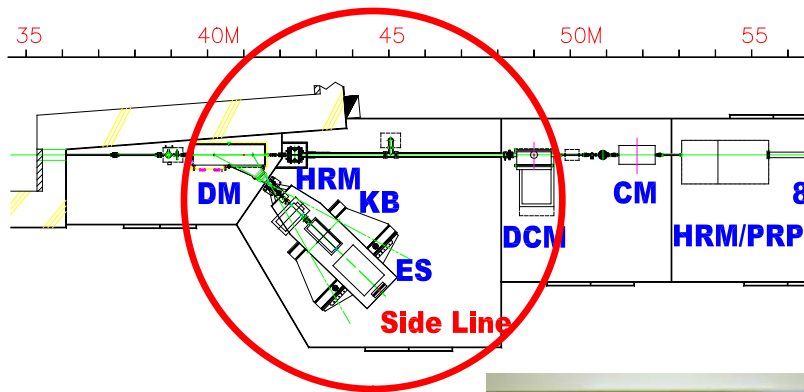
Horizontal geometry



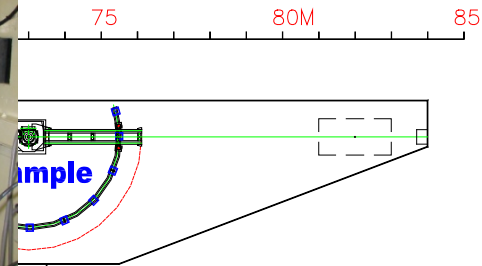
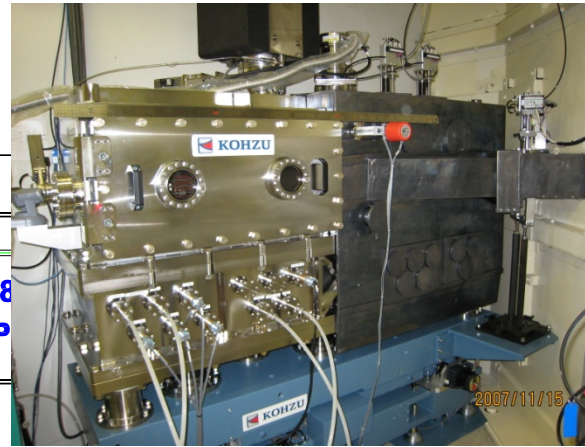
Vertical geometry

For selecting different orbital symmetries in valence band

BL12XU Sideline

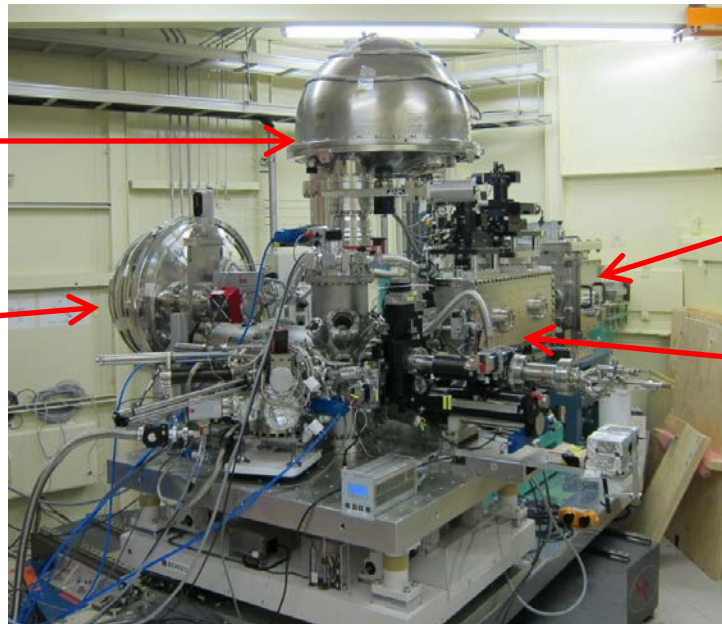


Diamond Mono.



MBS-A1HE
Analyzer
(**Vertical**)

MBS-A1HE
Analyzer
(**Horizontal**)



High Resolution
Mono. (HRM)

KB focus mirrors

New end station installed in January, 2013

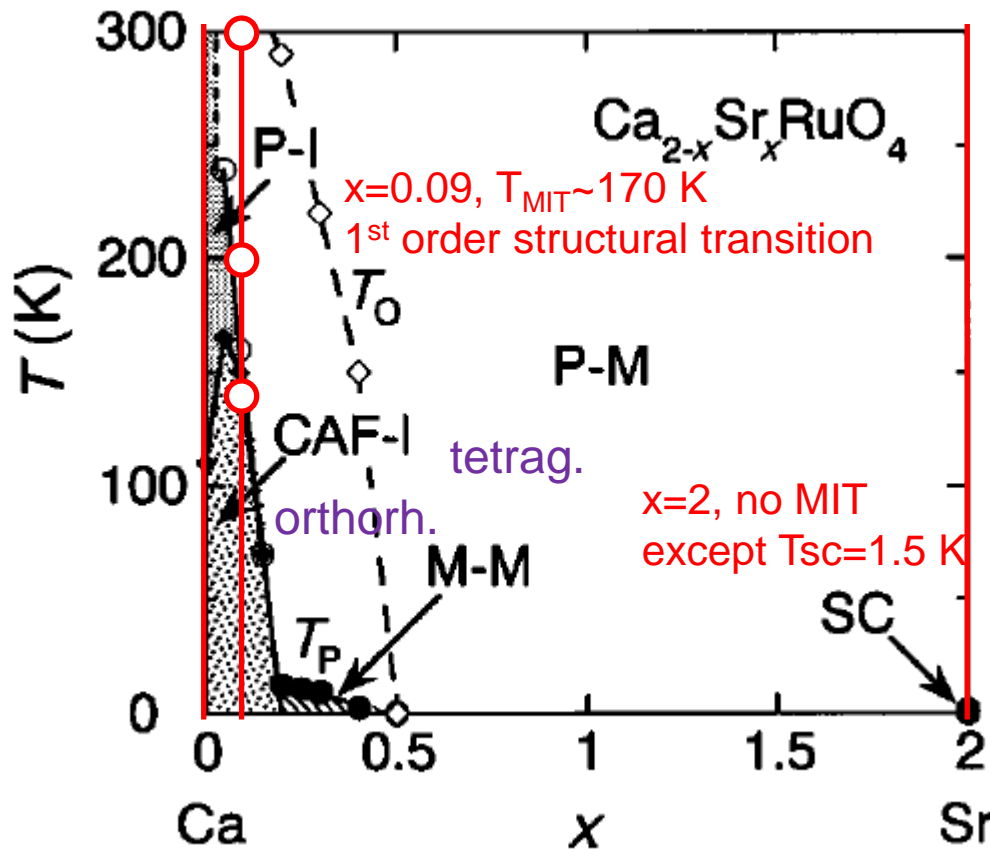
Example 1: Metal-Insulator Transition of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ (vertical geometry)

There is a rich phase diagram of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ regarding their structure, transport and magnetic properties as Sr doping and temperature are varied. Ru is a 4d element. Despite its larger wavefunction than 3d TM, structure distortion induced large Ru-O bond distance and Ru-O-Ru bond angle can result in strong correlation effect, particularly Metal-Insulator Transition (MIT).

Phase diagram

$x=0$, $T_{MIT} \sim 360$ K

1st order structural transition



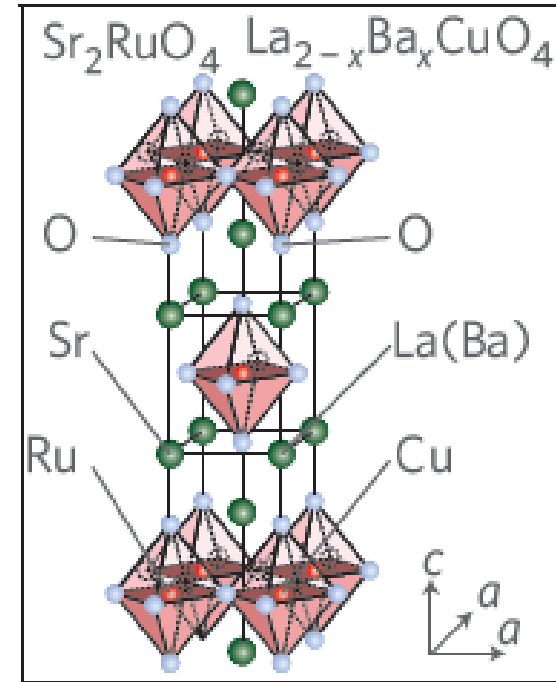
SC: superconductor

P-M: paramagnetic metal

P-I: paramagnetic insulator

CAF-I: canted antiferromagnetic insulator

M-M: AF correlated metal



Sr_2RuO_4 : tetragonal, elongated perovskite

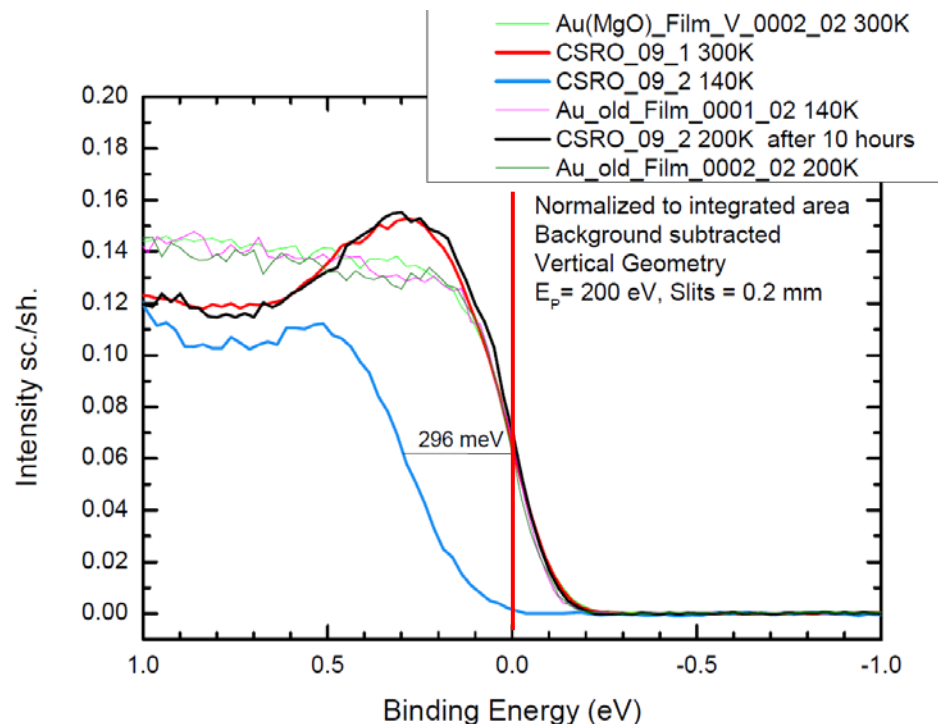
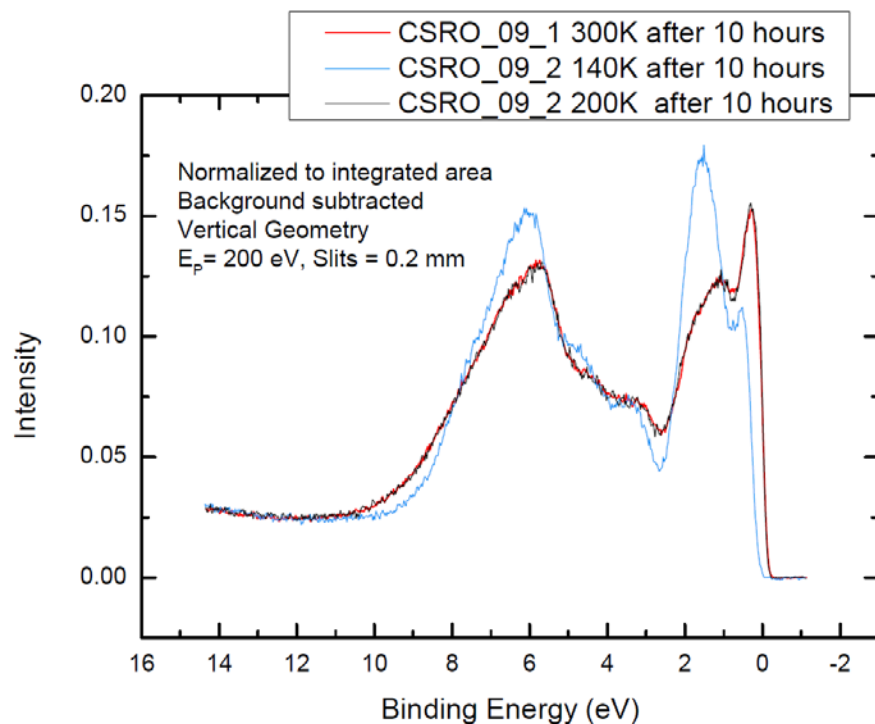
Complex structural distortion with replacement of Sr by Ca
 Ca_2RuO_4 : orthorhombic

Nakatsuji & Maeno, PRB 62, 6458 (2000)

Friedt & Maeno et al. PRB 63, 174432 (2001)

Metal Insulator Transition (MIT) of $\text{Ca}_{1.91}\text{Sr}_{0.09}\text{RuO}_4$

300 K \rightarrow 140 K \rightarrow 200 K ($T_{\text{MIT}} \sim 160$ K)



- * Dramatic PE spectral change across MIT due to 1st order phase transition
- * Gap opening about 300 meV near E_F
- * Reversible

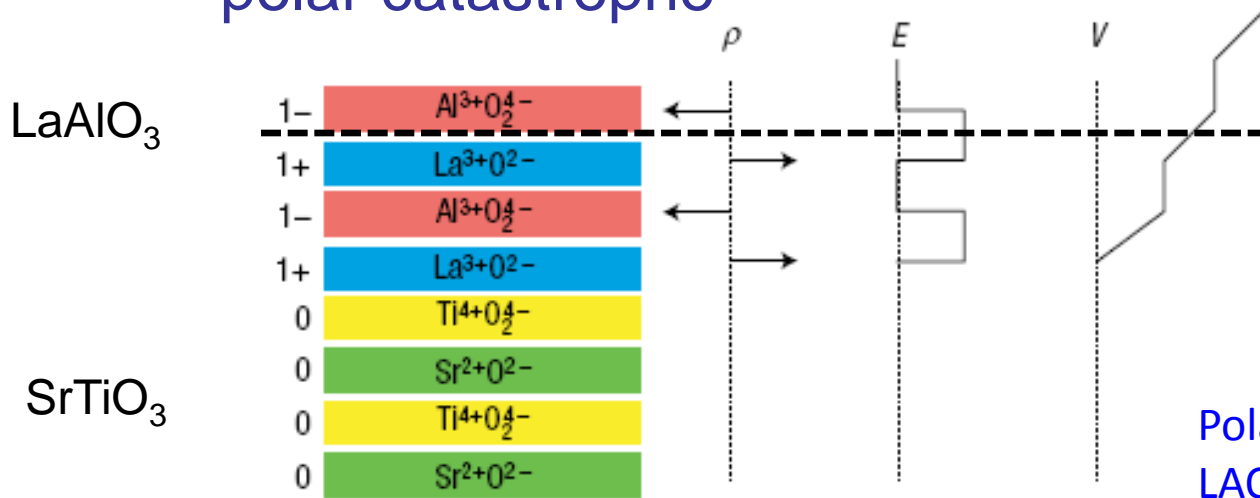
Example 2: Interface of LAO/STO (horizontal geometry)

Interface of two large gap band insulators

LaAlO_3 and SrTiO_3 becomes metallic-like.

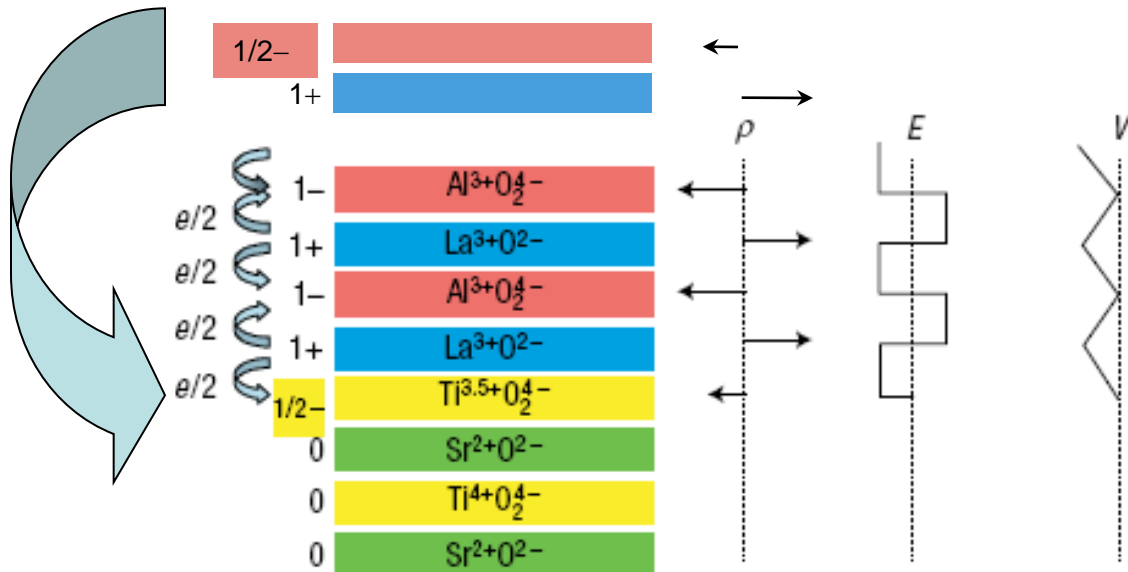
Evidence of charge transfer from LAO to
STO is observed but the amount is less than
prediction of a simplest model.

polar catastrophe



Polarity discontinuity between LAO and STO plays a crucial role.

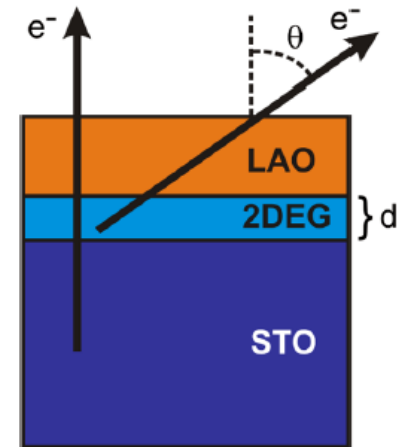
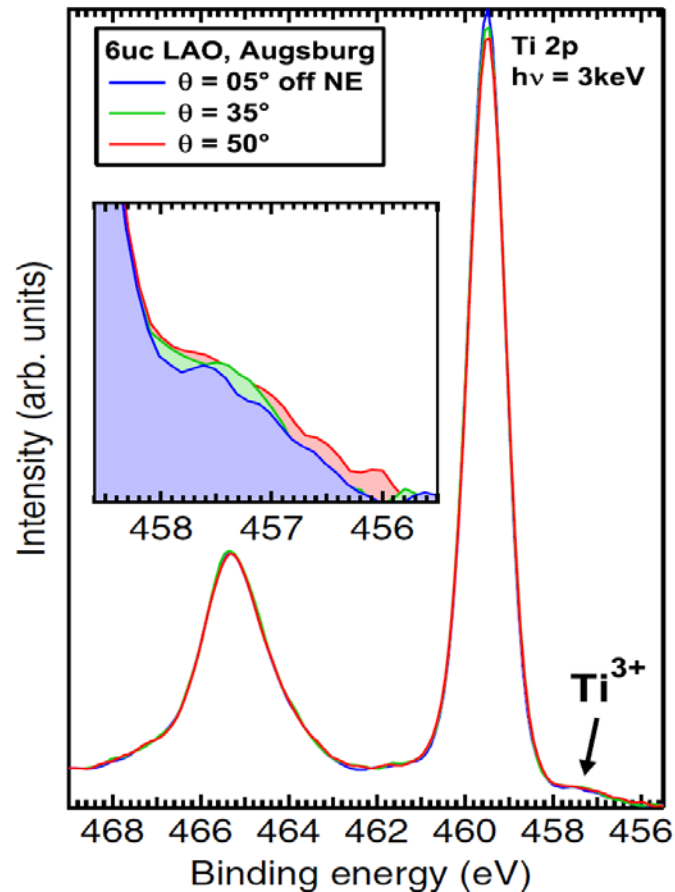
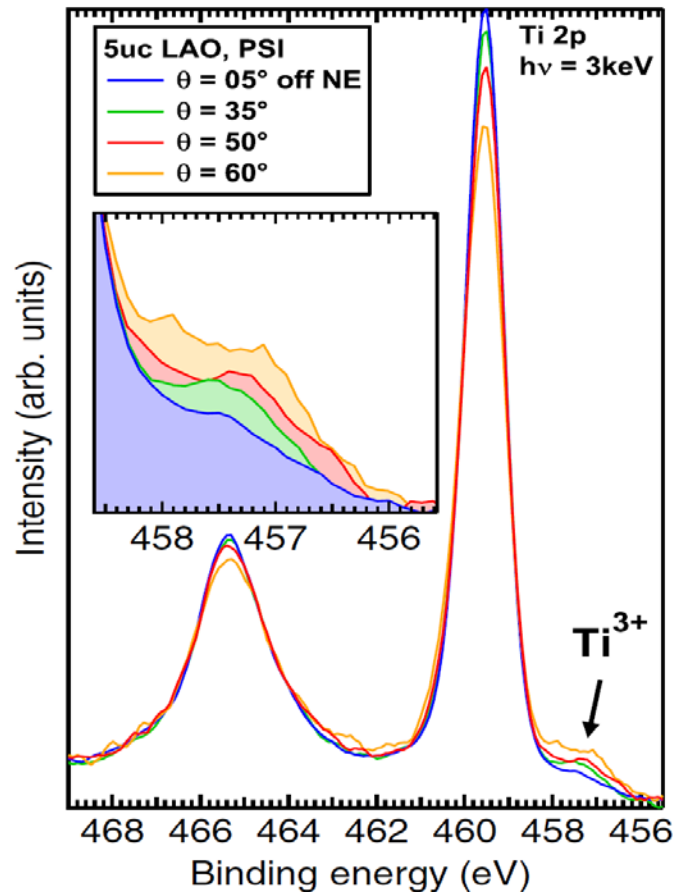
Electronic reconstruction



Charge transfer balances the polar discontinuity and leads to conducting behavior of the interface.

$1/2 e$ transferred Nakagawa et al., Nature Mater. 5, 204 (2006)

Hard X-ray Photoemission Spectroscopy (HAXPES)



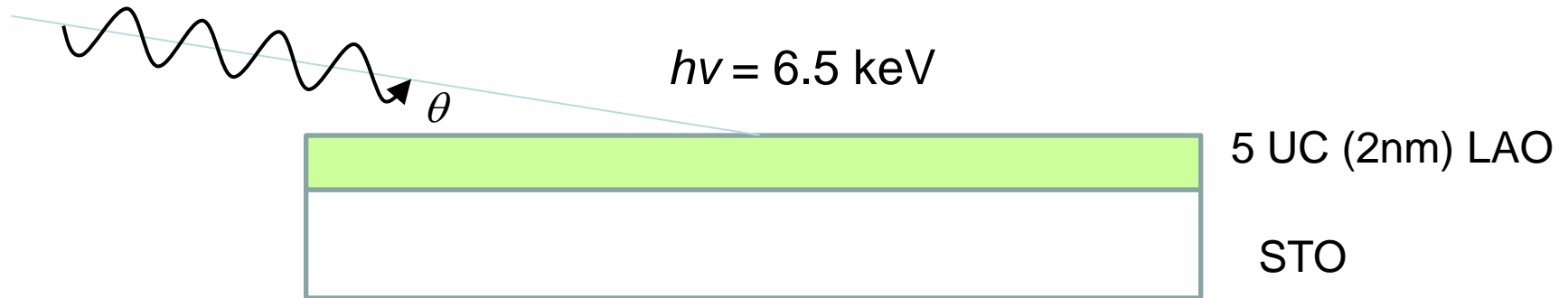
Sing et al.,
PRL 102,
176805 (2009)

$h\nu = 3\text{ keV}$

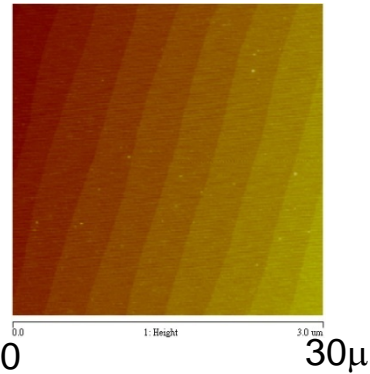
- ⇒ Conducting interface due to electronic reconstruction
- ⇒ 2DEG confined to only ~ 1 or at most a few u.c. thick
- total Ti³⁺ density < 0.28 e /2D u.c. for 5 u.c. LAO (<0.5 e); sample dependent

Our approach:

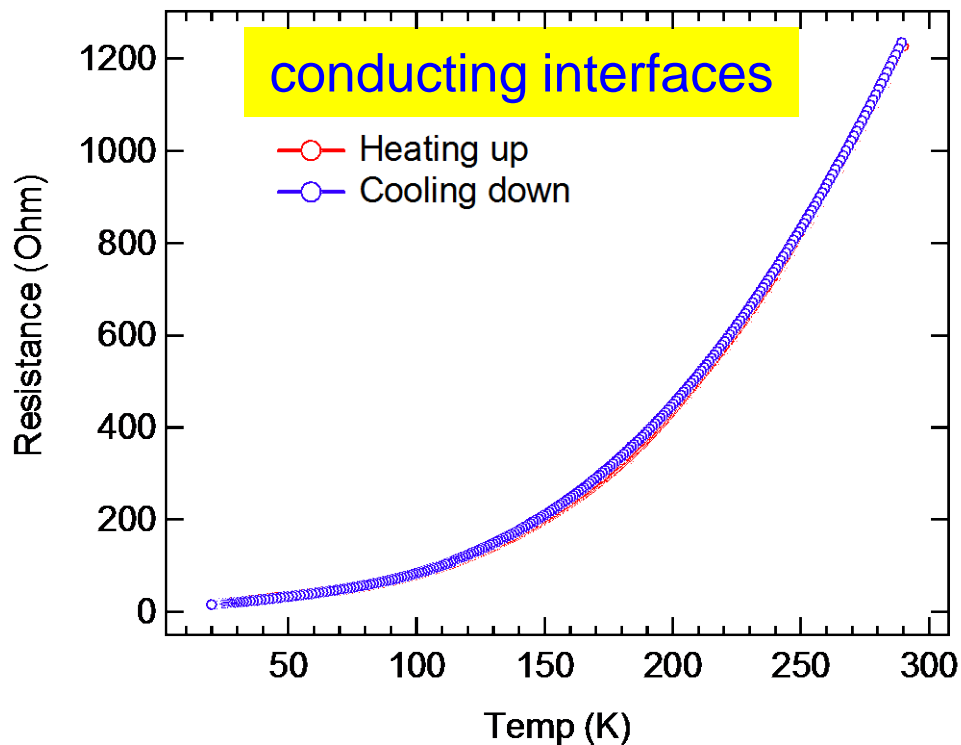
- * grazing incidence near total external reflection to enhance photon field near the surface and interface region for better detection of Ti^{3+} near the interface
- * higher photon energy (6.5 keV) to increase probing depth



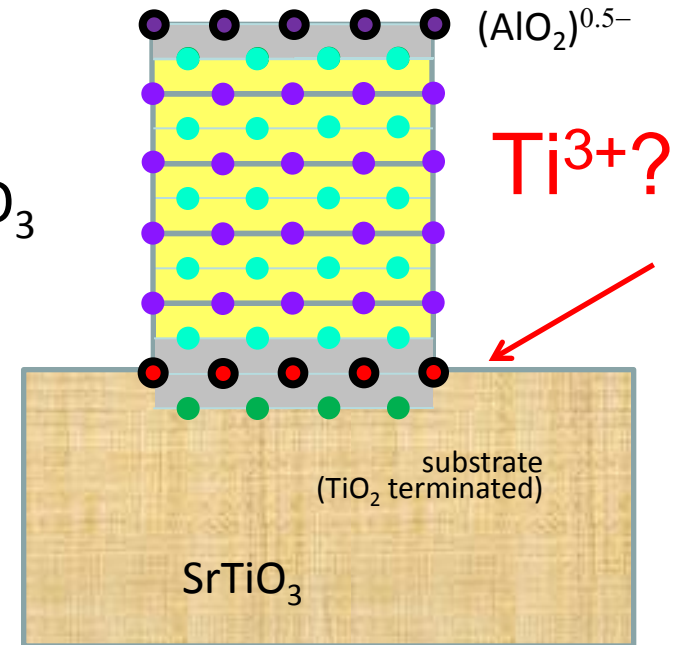
LaAlO₃/SrTiO₃ (001)

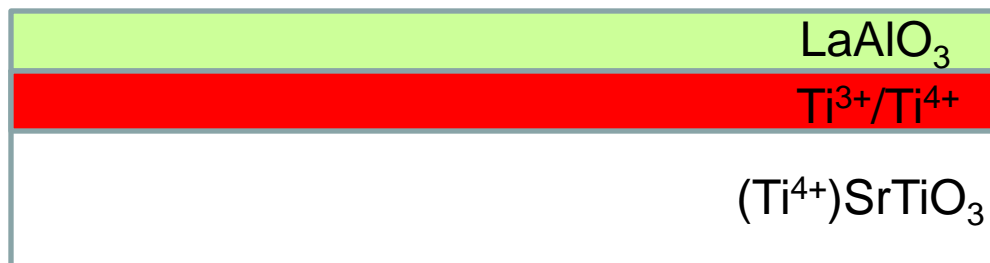


grown with PLD, 10^{-5} torr O₂, 850 C
annealed at 100 mtorr of O₂

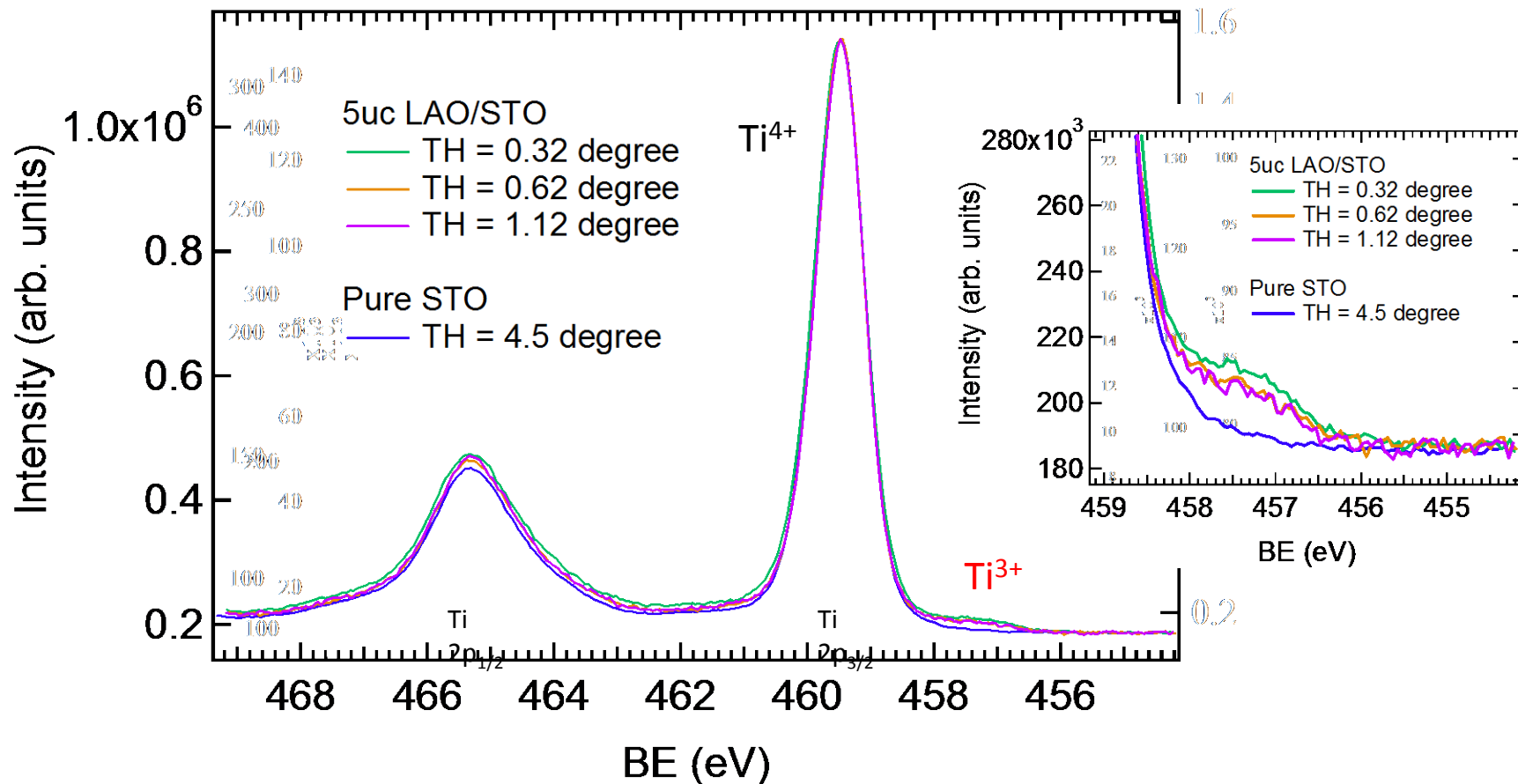


5 u.c.
LaAlO₃

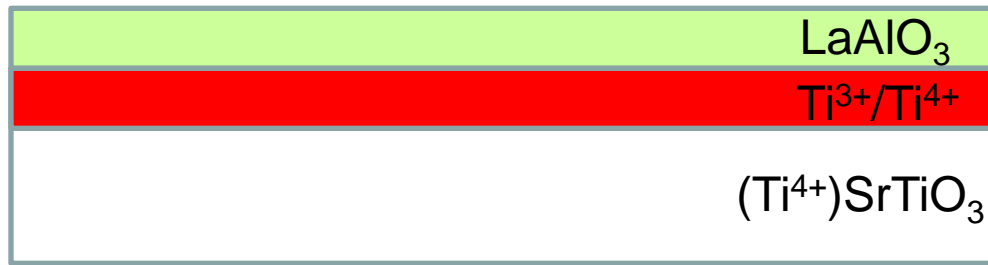




d_1
 d_2 (2DEG)

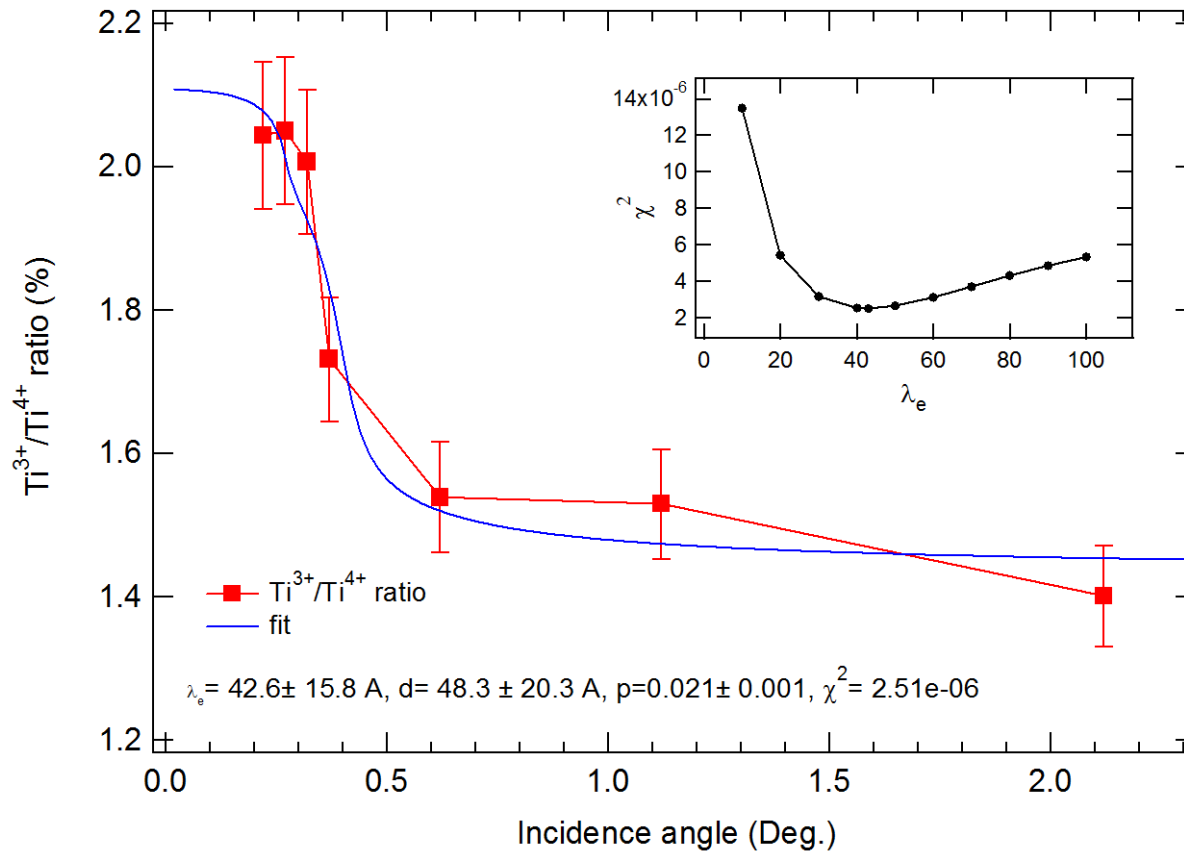


Measure intensity ratio Ti³⁺/Ti⁴⁺ as a function of incident angle



d_1

d_2 (2DEG)



$d_2 = 48.3 \pm 20.3 \text{ \AA}$
~ 12 u.c.

$\alpha = 0.021$
(Ti³⁺/Ti⁴⁺ in d_2)

Total carriers
~ 0.24 e / 2D u.c.

Consistent with
electronic
reconstruction but
only half the amount
O vacancies?

Chu et al., Appl. Phys. Lett. 99, 262101 (2011)

Challenging future directions of Photoemission Spectroscopy

1. ARPES at submicron to tens of nanometer scale,
using Schwatzchild optics or zone plates.
Need brighter light sources.
2. Time-resolved PES.
Pump-probe: dynamics.
Need efficient detection and brighter sources.
lasers or laser+SR.

Thanks for your attention