Photoemission Spectroscopy

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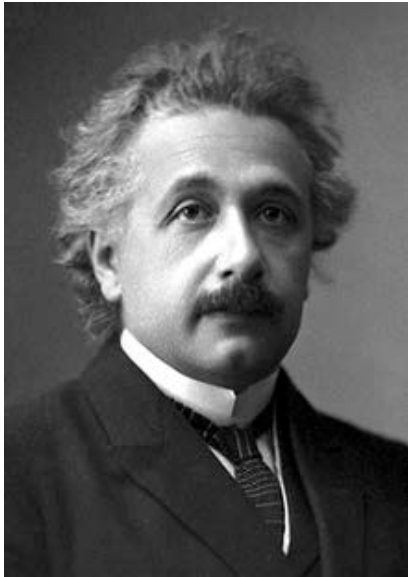
In 1905 Albert Einstein proposed the concept of light quanta (photons) to explain the photoelectric effect, which was pivotal in establishing the quantum theory in physics

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)

$h\nu$ **Monochromatized photons**

Electron energy analyzer

e^-

sample

h^+
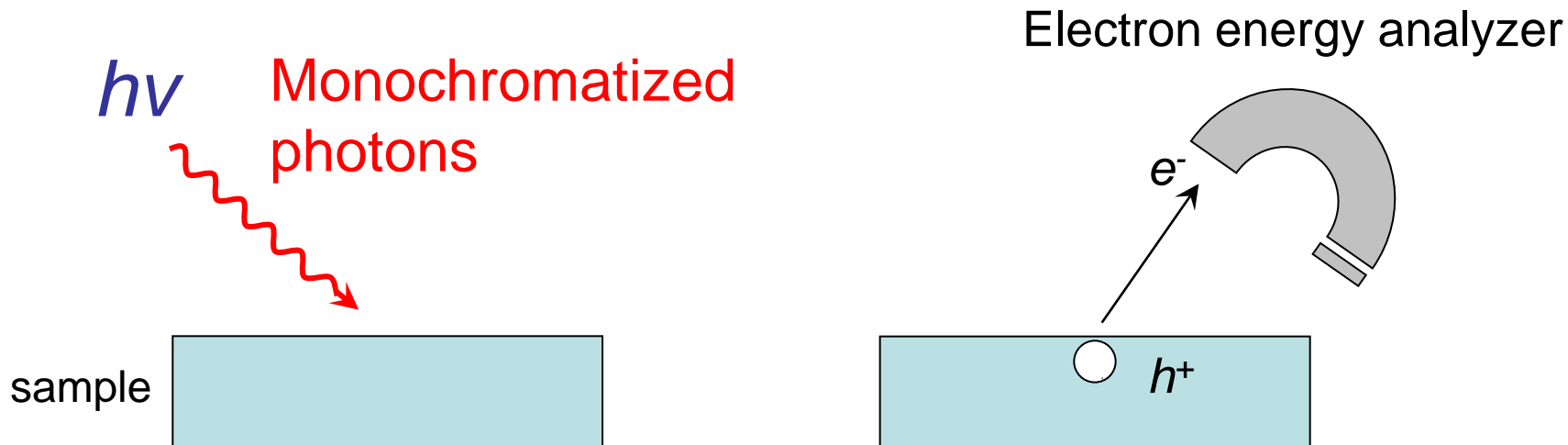
Initial state: ground (neutral) state

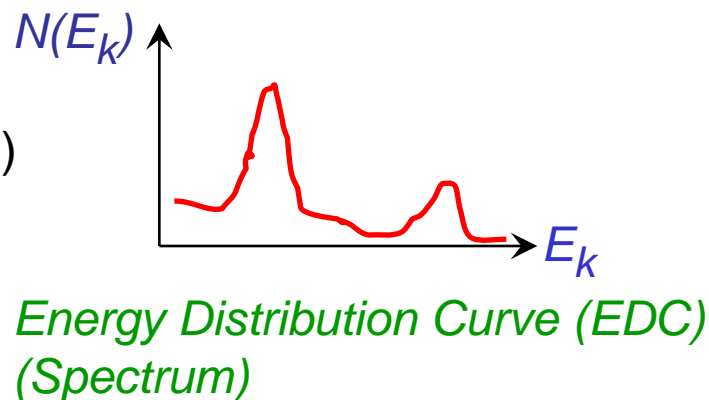Final state: hole (excited) state

Conservation of energy

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

E_k : photoelectron kinetic energy
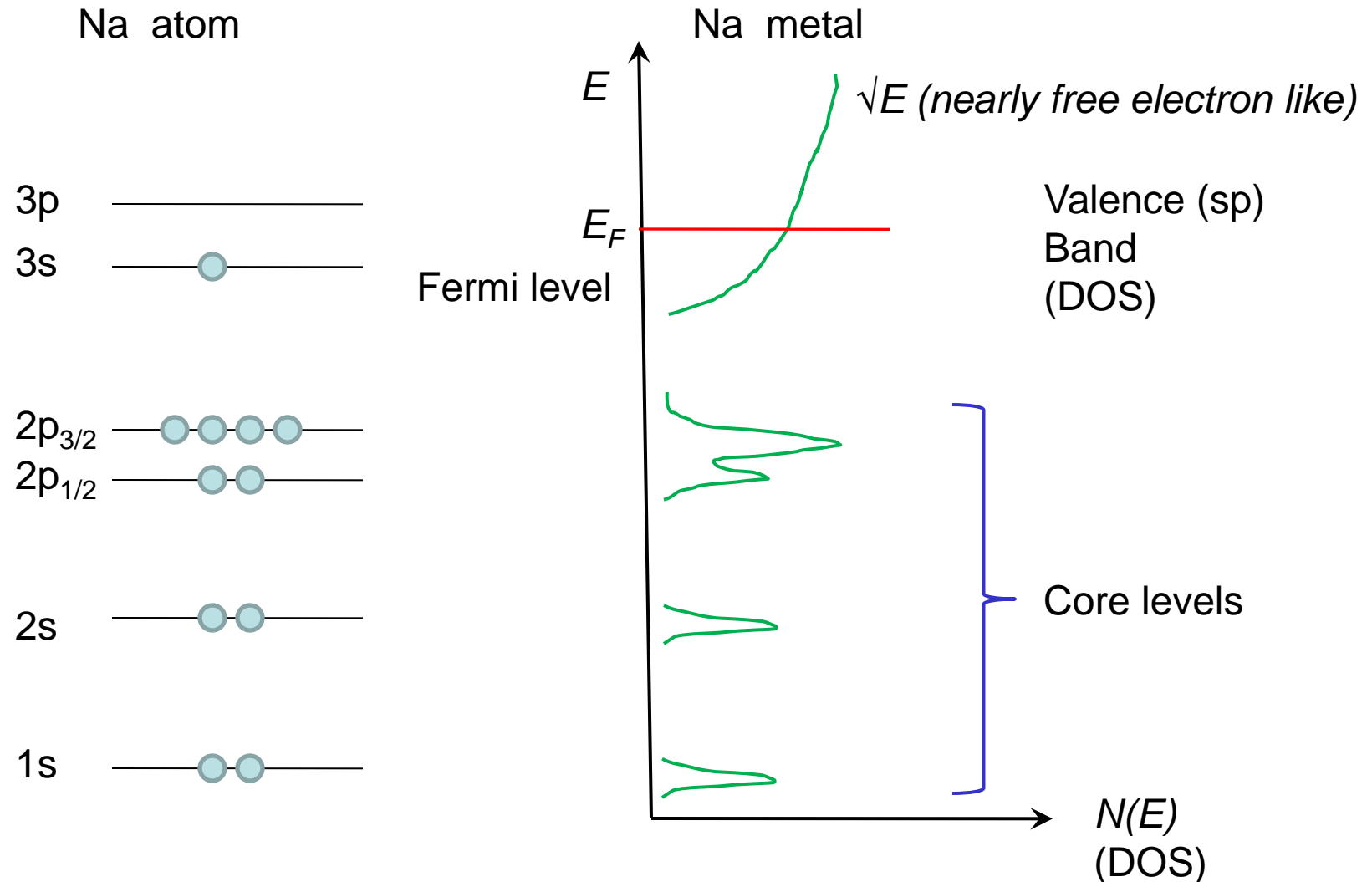E_i (N) : total initial state system energy
E_f (N-1): total final state system energy

$N(E_k)$

E_k

Energy Distribution Curve (EDC) (Spectrum)

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)

Na atom

Na metal

E

$\sqrt{E}$ (nearly free electron like)

3p

3s

E_F

Fermi level

Valence (sp)
Band
(DOS)

$2p_{3/2}$

$2p_{1/2}$

2s

Core levels

1s

$N(E)$
(DOS)

Energetics in PES

Conservation of energy

Density of States (DOS)
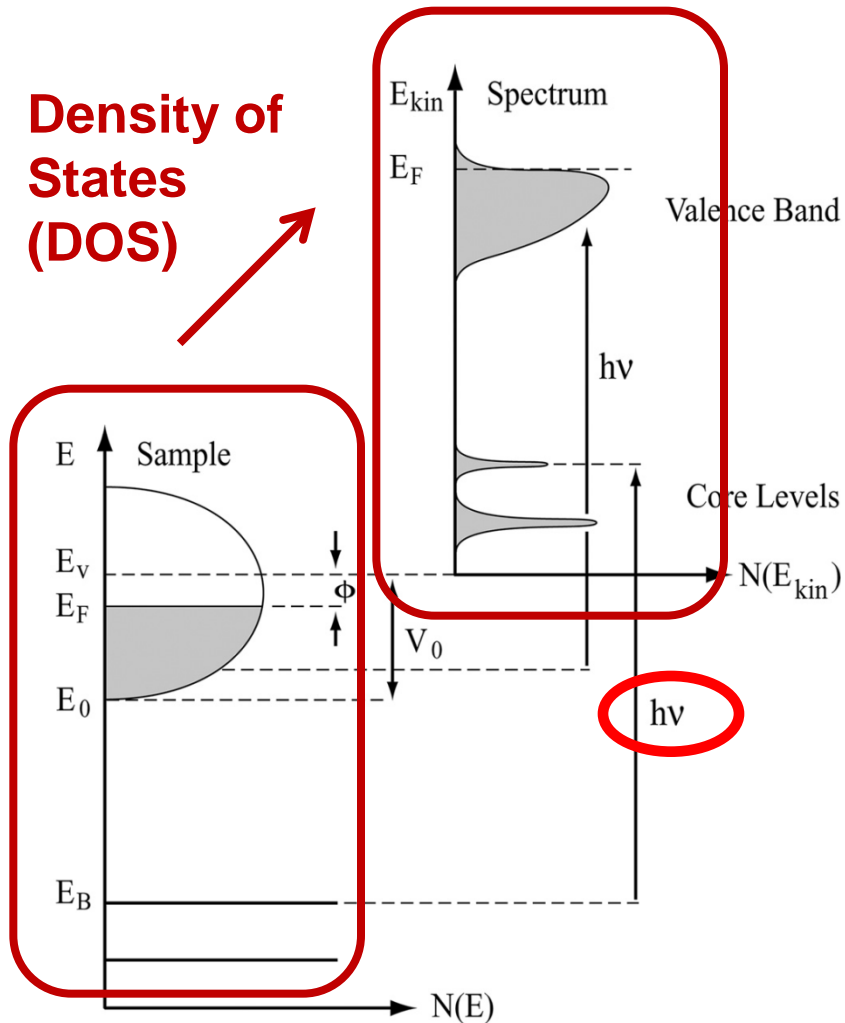
Hufner, Damascelli

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

E_v : vacuum (energy) level

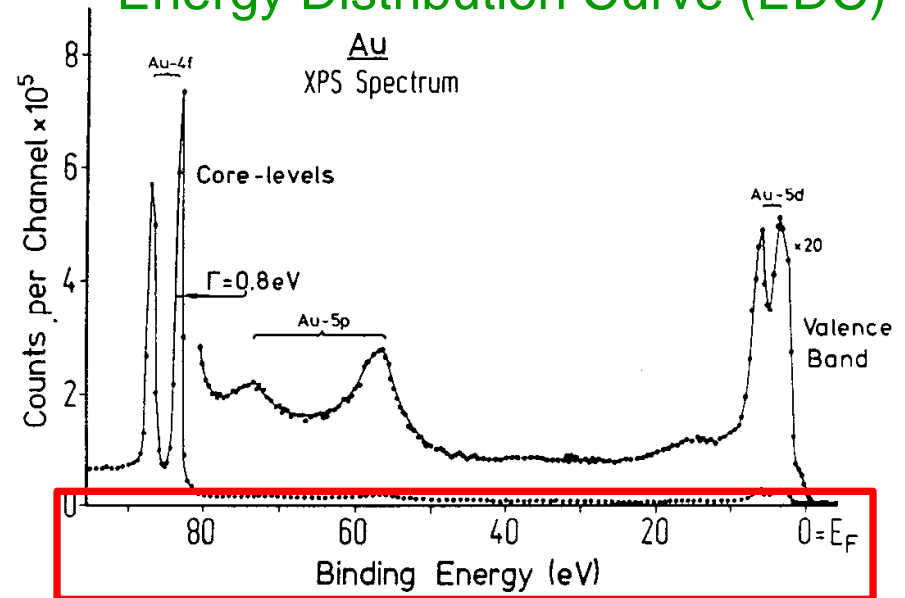E_F : Fermi (energy) level

$\phi = E_v - E_F$: 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)

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

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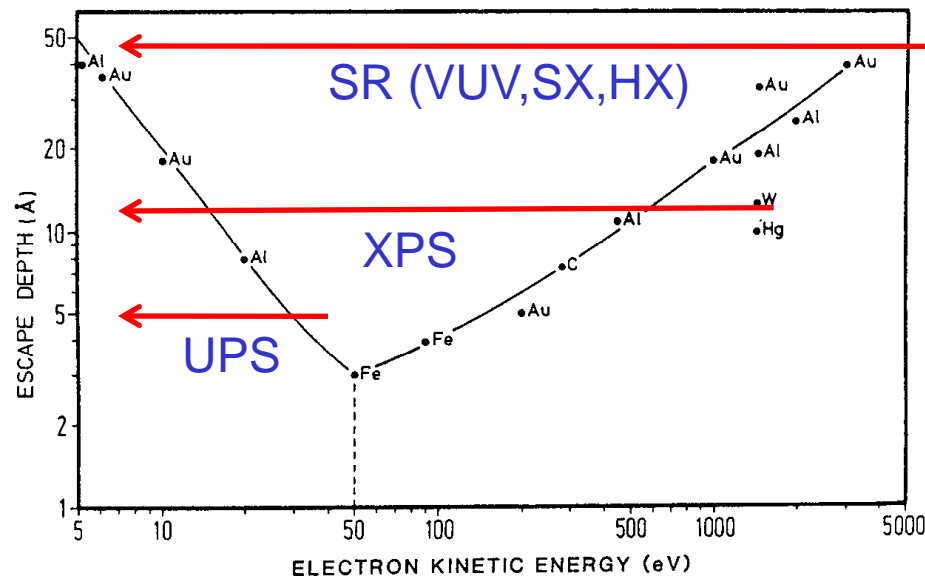

SR (VUV,SX,HX)

Universal curve

XPS

UPS

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÷5 Å for kinetic energies of 50÷100 eV. The scatter of the data is evident from the values obtained at E_{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

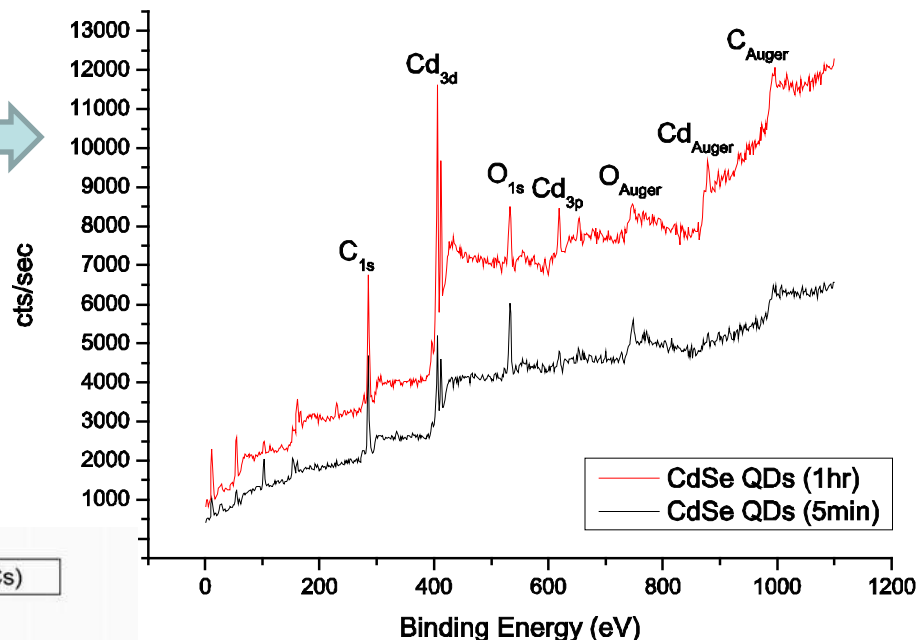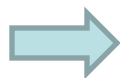Finger prints

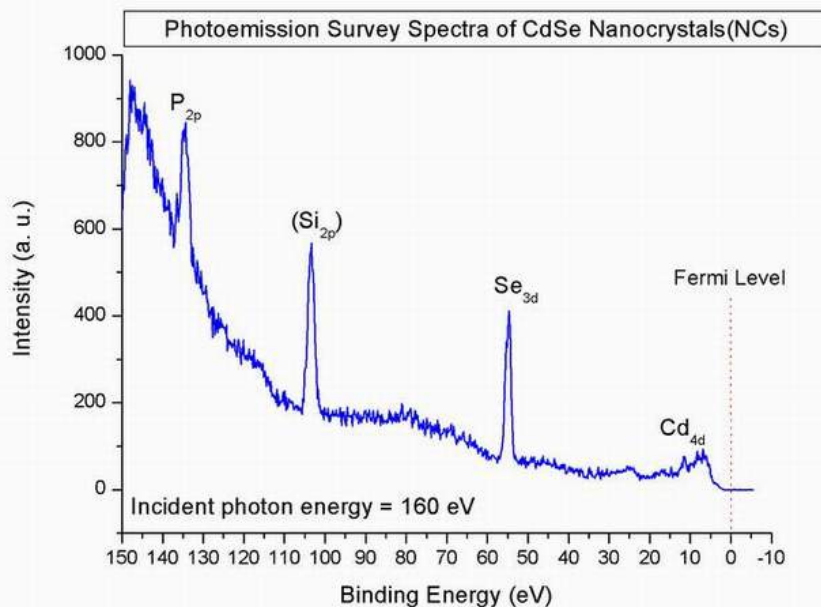Core level BE independent of photon energy used

X-Ray Data Booklet

http://xdb.lbl.gov/

Core level photoemission: chemical analysis of elements
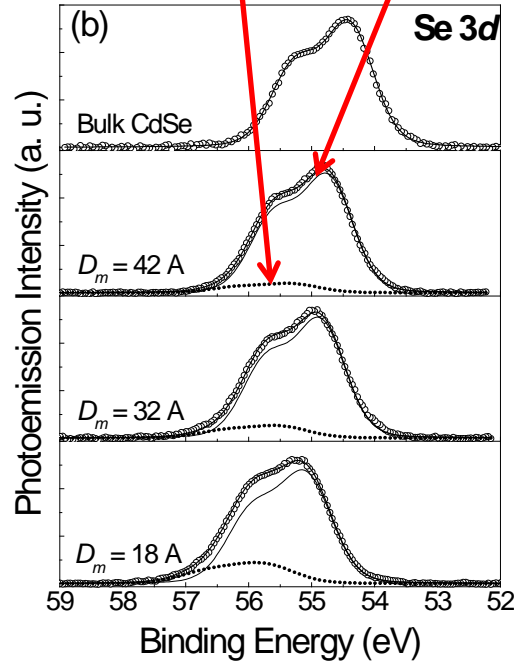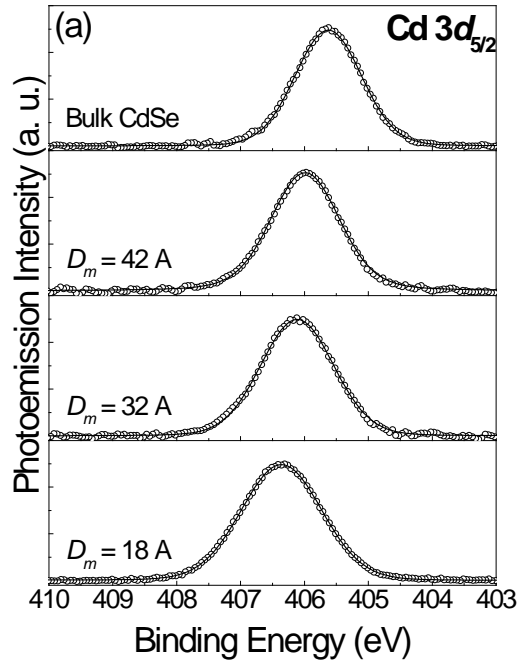
ESCA (XPS)
$hv = \text{Mg } K\alpha = 1253.6 \text{ eV}$

Synchrotron $hv = 160 \text{ eV}$

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

PJW, NSRRC

surface component   bulk component

(a)   Cd 3d$_{5/2}$

Bulk CdSe

D_m = 42 A

D_m = 32 A

D_m = 18 A

Photoemission Intensity (a. u.)

Binding Energy (eV)

(b)   Se 3d

Bulk CdSe

D_m = 42 A

D_m = 32 A

D_m = 18 A

Photoemission Intensity (a. u.)

Binding Energy (eV)

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?

Bulk CdSe

D_m = 42 A

D_m = 32 A

D_m = 18 A

Intensity (a. u.)

Binding Energy (eV)
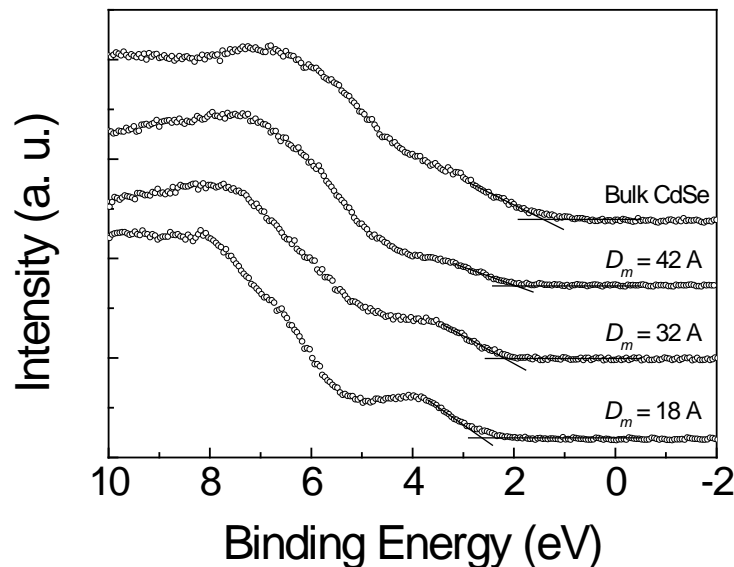
Actual choices:
Cd 3d$_{5/2}$:   480 eV
Se 3d: 120 eV
Valence band: 50 eV

E_k ~ 45-74 eV, most surface sensitive

Wu, PRB 2007 NSRRC

Core level photoemission: chemical shift

higher oxidation state
=> higher BE

Oxidation of Si(001)
hν = 136 eV

Si 2p

Suboxide Interface

Number of O Neighbors

4 3 2 1

Bulk

10^4 counts per Channel

Kinetic Energy (eV)

BE

Si(001)-2x1   100 L Oxygen

Si 2p

Oxide

θ_e

60^0

4 3 2

0^0

Counting Rate (arbitrary units)

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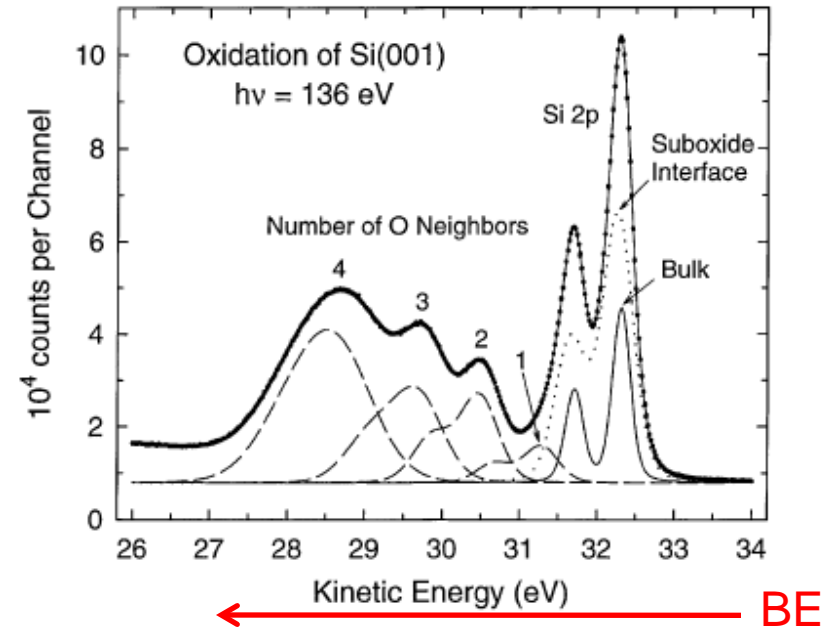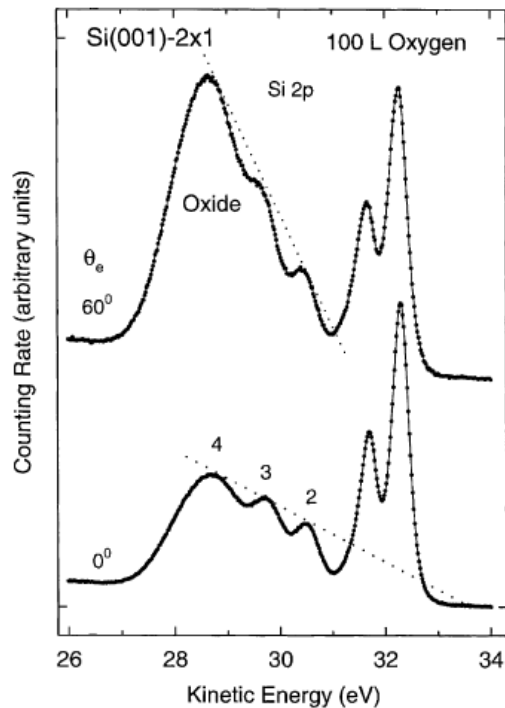
higher emission angle
→ more surface sensitive
(IMFP)   Pi, SS 2001 NSRRC

Chemical Analysis of C1s core levels
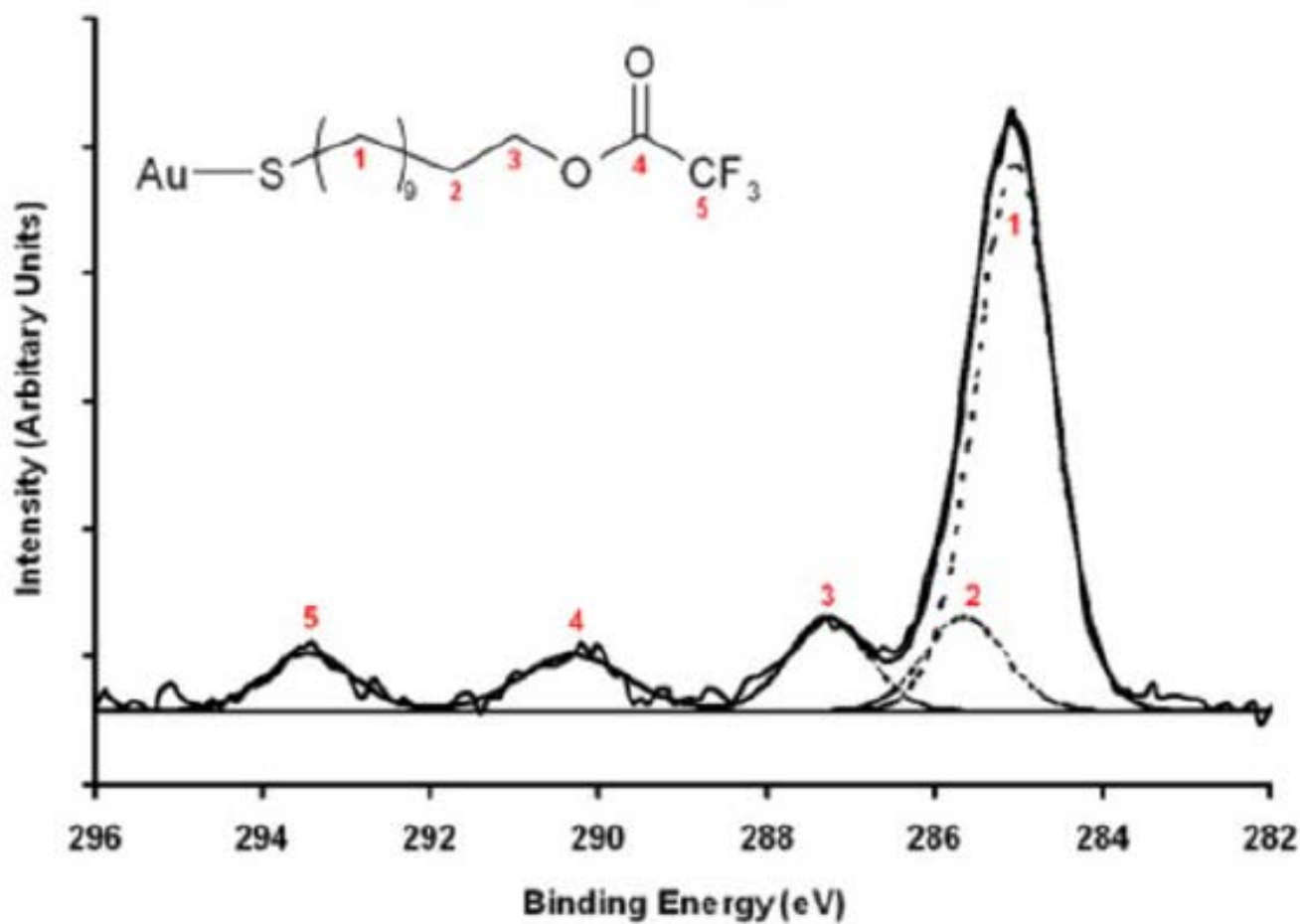
Auger Electron Spectroscopy

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, Ek shift with changing photon energy
AES: constant Ek, apparent BE shift with changing photon energy
(synchrotron)

http://xdb.lbl.gov/

Handbook of XPS

(a) Photoelectric absorption
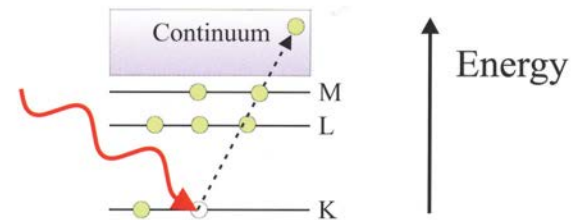
(b) Fluorescent X-ray emission
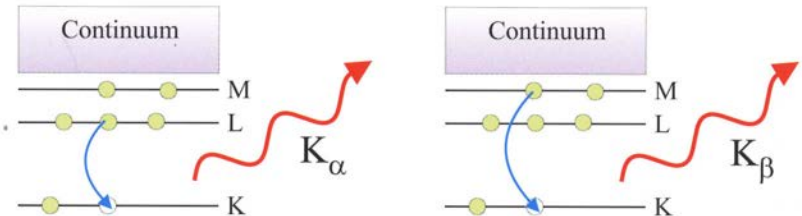
(c) Auger electron emission
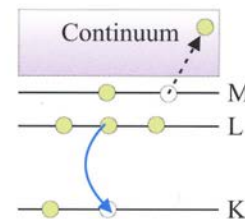
Photoemission Process
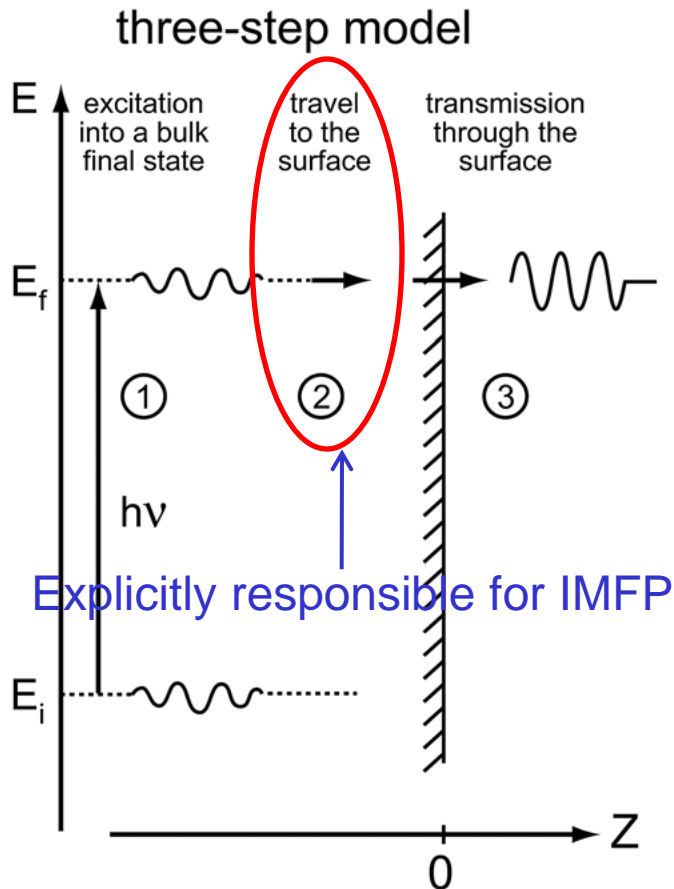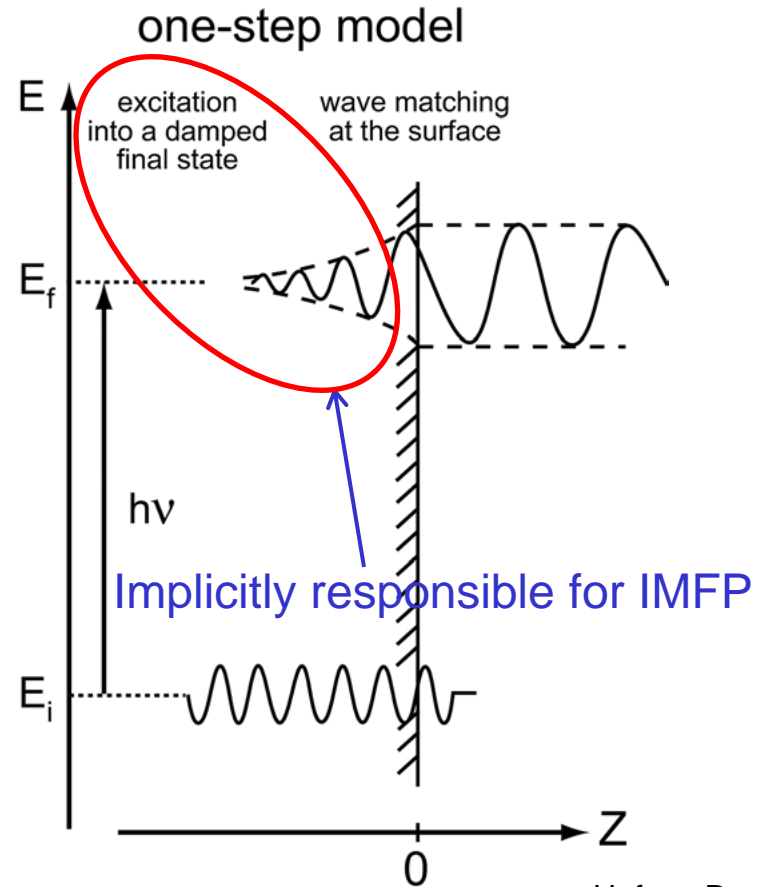
Hufner, Damascelli

Schematic wave functions of initial and final states
(valence band initial states)
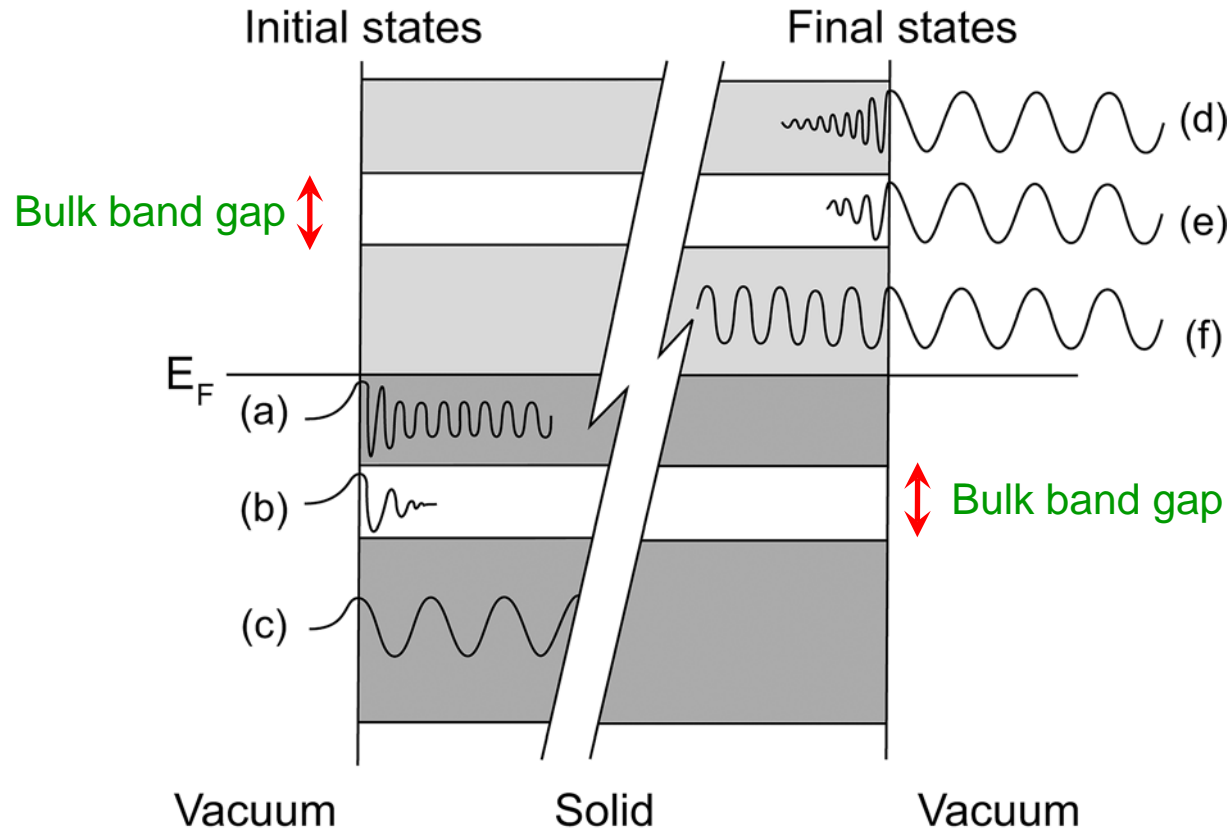
(a) Surface resonance
(b) Surface state
(c) Bulk Bloch state
(d) Surface resonance
(e) in-gap evanescent state
(f) Bulk Bloch final state

Electron kinetic energy inside and outside of solids

Inner potential: $E_V - E_0$

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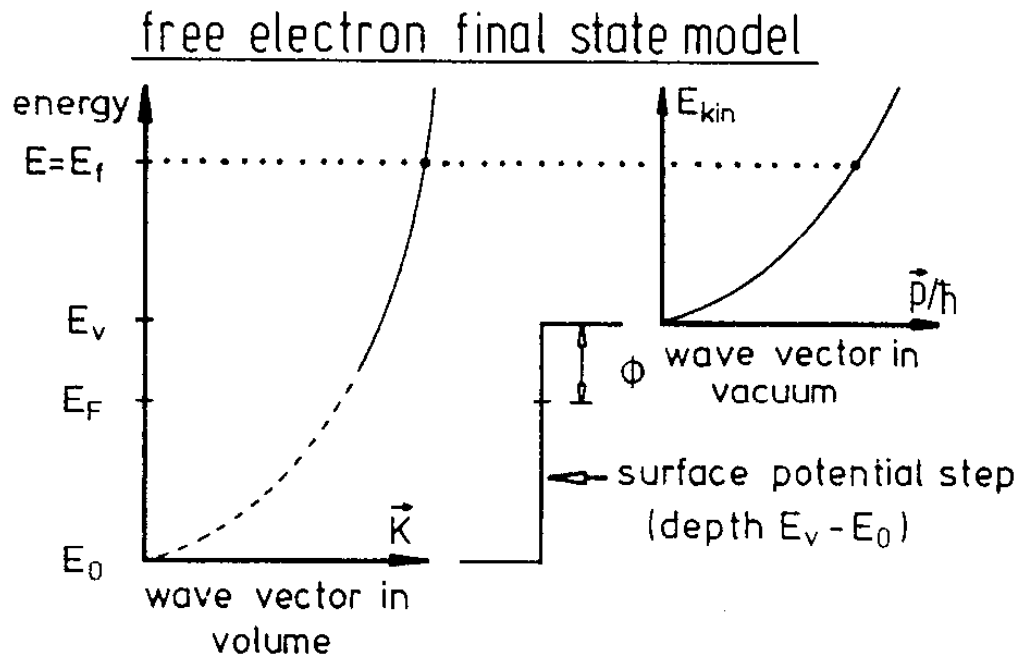
Concept of inner potential is used to deduce 3D band structure from PE data assuming free electron like final state inside solids

Angle-resolved photoemission (ARPES)

exciting photons
(energy ℏω;
vector potential $\vec{A}$
angle of
incidence ψ)

photoelectrons
(energy E_{kin};
exit angles ϑ,φ;
aperture ΔΩ)
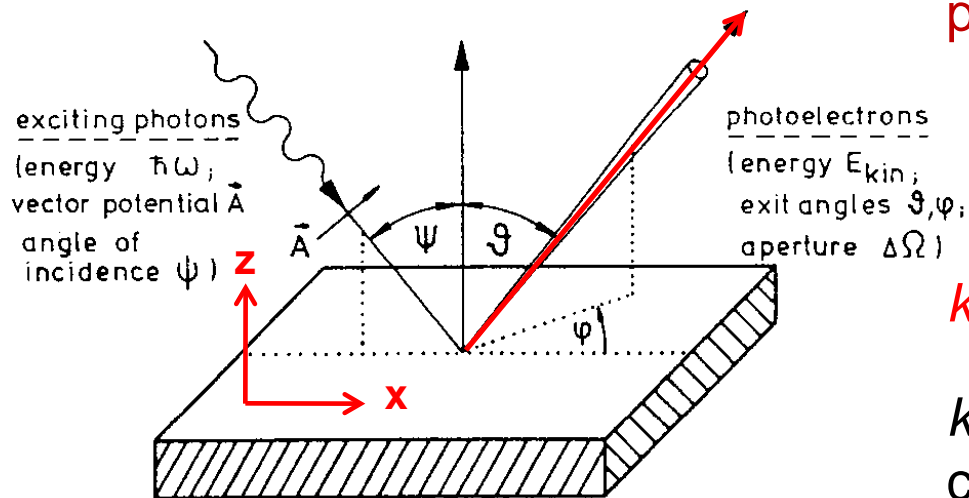
xz plane: crystal symmetry plane

Conservation of linear momentum parallel to the surface

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

$k_\parallel$(inside solid) = $k_\parallel$(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

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

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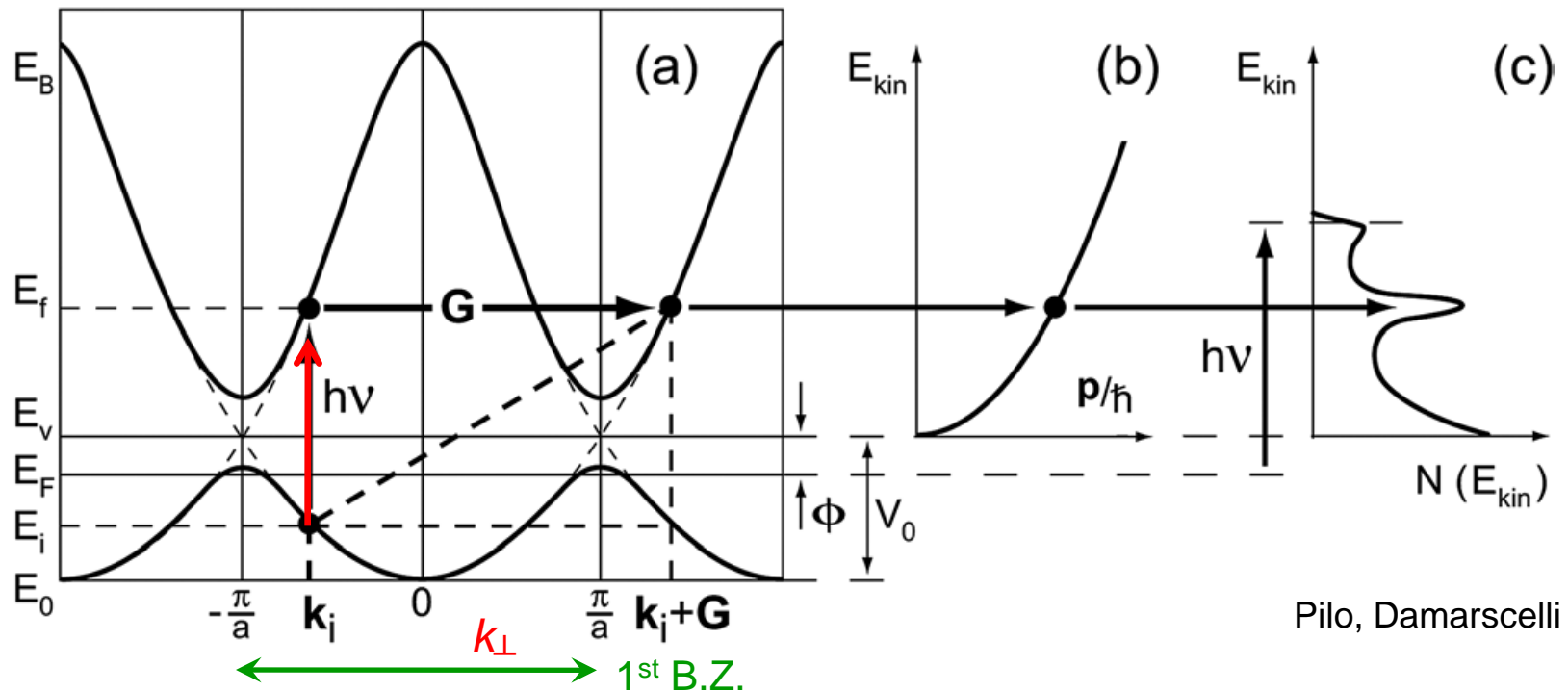
Pilo, Damarscelli

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

(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

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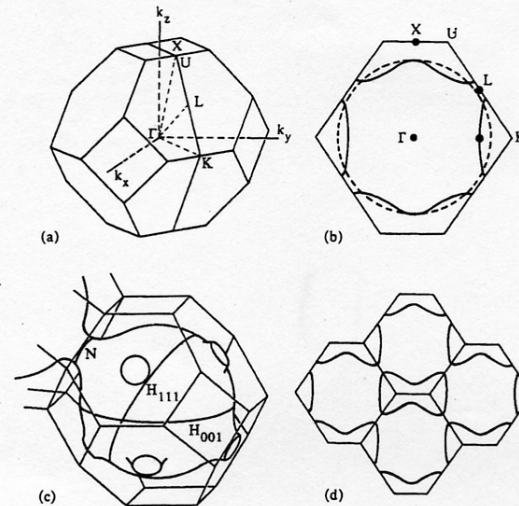
Fig. 10-15 Various aspects of the Fermi surface of Cu. (a) The Brillouin zone of an fcc lattice with some special points labeled. (b) A (110) section of the Brillouin zone. See the text for the meaning of the internal curves. (c) The proposed Fermi surface of Cu. (d) The extended zone picture of a (110)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

Gap below E_F(=0) at L-point

Band Structure of Cu
— Eckardt et al.

BINDING ENERGY (eV)

L   Γ   X

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

Ag(111) thin films expitaxially grown on Au(111) substrate
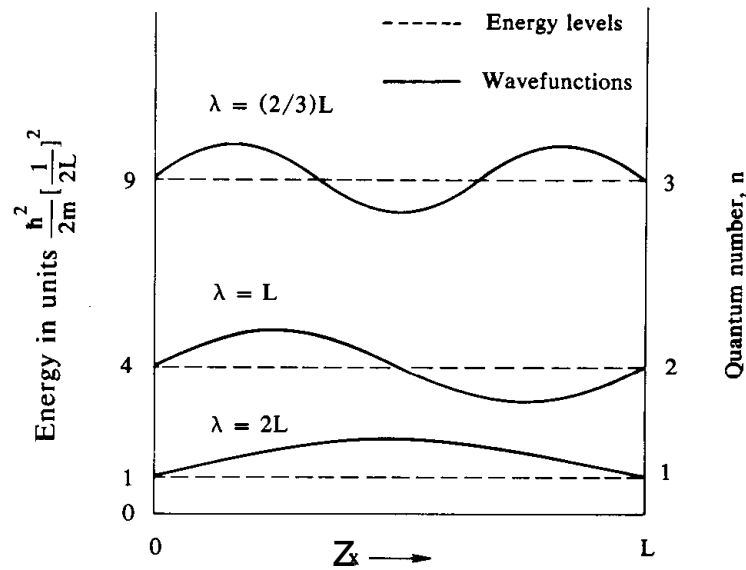
Quantized discretely along z-direction
Energy levels depend on film thickness L

Nearly free electron like in xy-plane

Band gap below E_F

Ag QWS can exist within Au gap
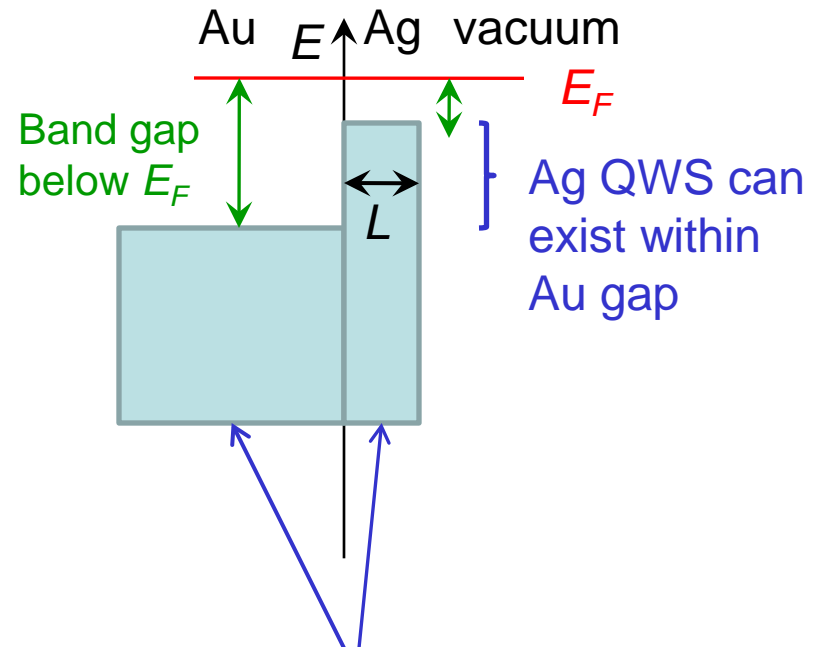
Bulk projected bands along ΓL of Au and Ag, respectively

2D
Int.
plots

$k_{\parallel} = 0$
EDCs

(a)

Binding Energy (eV)

0.0

0.5

1.0

-0.2   -0.1   0.0   0.1   0.2

$k_{\parallel}$ (Å^{-1})

(c)

-0.2   -0.1   0.0   0.1   0.2

$k_{\parallel}$ (Å^{-1})

(e)

← Ag S.S.

Ag QWS

-0.2   -0.1   0.0   0.1   0.2

$k_{\parallel}$ (Å^{-1})

(b)

Photoelectron Intensity
(arbitrary unit)

1.0   0.5   0.0

Binding Energy (eV)

(d)

1.0   0.5   0.0

Binding Energy (eV)

(f)

1.0   0.5   0.0

Binding Energy (eV)
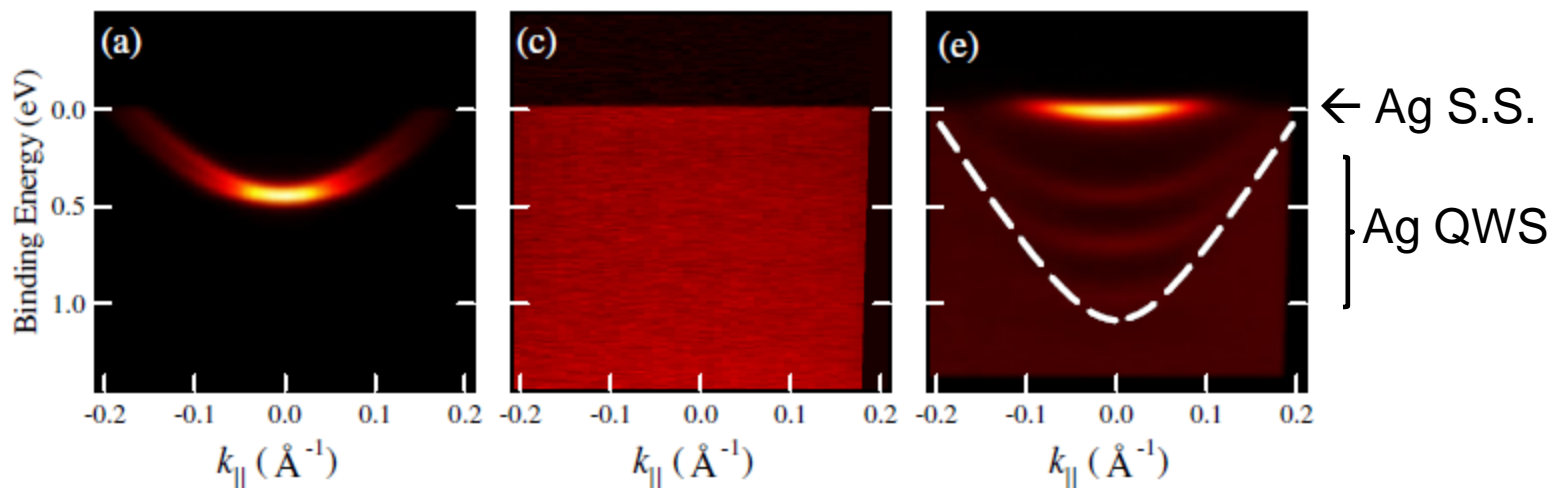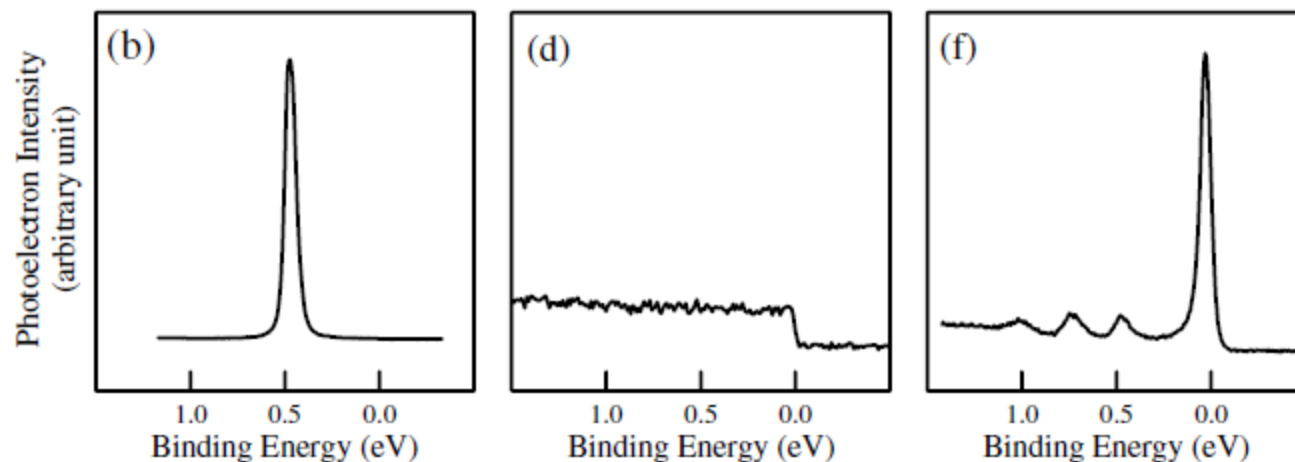
Luh et al.
PRL 2008
NSRRC
BL21B1

Clean Au(111)
surface state

Deposit 22 ML Ag
at 37 K
disordered form

Anneal to 258 K
Atomically flat
22 ML thin film
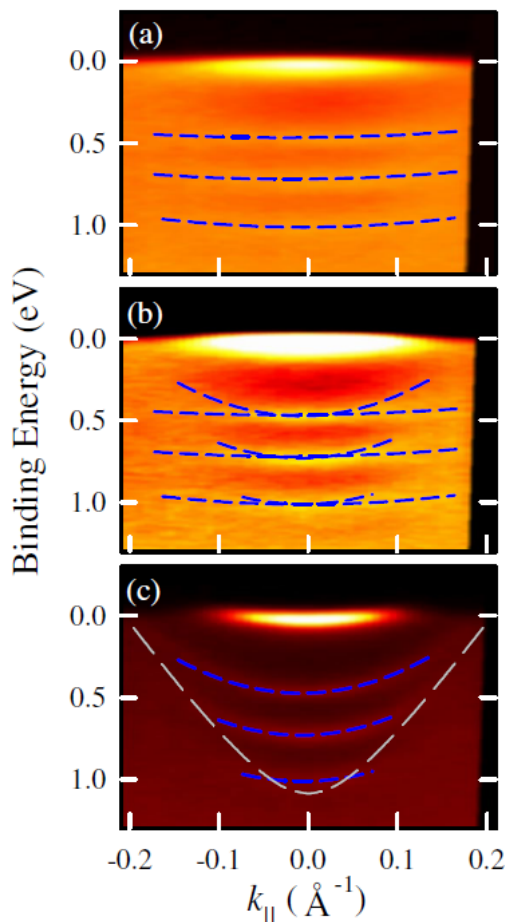
Anneal to 180 K
QWS appear
minimal flat
dispersion
Small localized
domains within
xy-plane

Anneal to 189 K
Coexistence of
two kinds of
dispersion

Anneal to 258 K
Well developed
dispersion
Large, good
crystalline
domains
in xy-plane
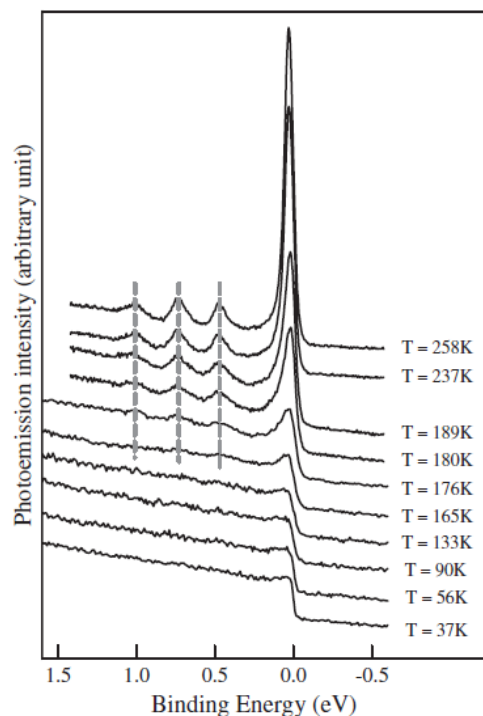
Same QWS energies → Same crystalline film thickness along z even though lateral crystalline domains grow from small to large

Proposed growth model
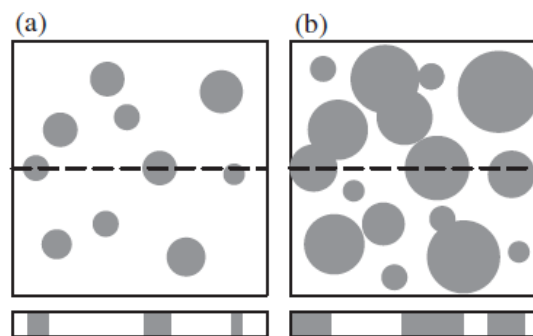
Annealing Temp →

Surface state of topological insulators

Insulating bulk but with conductive surface by strongly dispersive surface states

Bi_2Se_3 single crystal surface

Electron occupation in a surface band can be determined by k_F:

$2*\pi*k_F^2/$(2D B.Z. area)

2 : spin
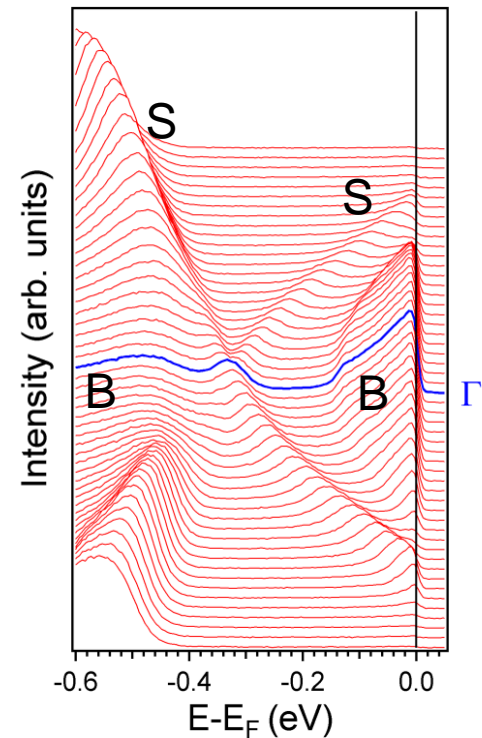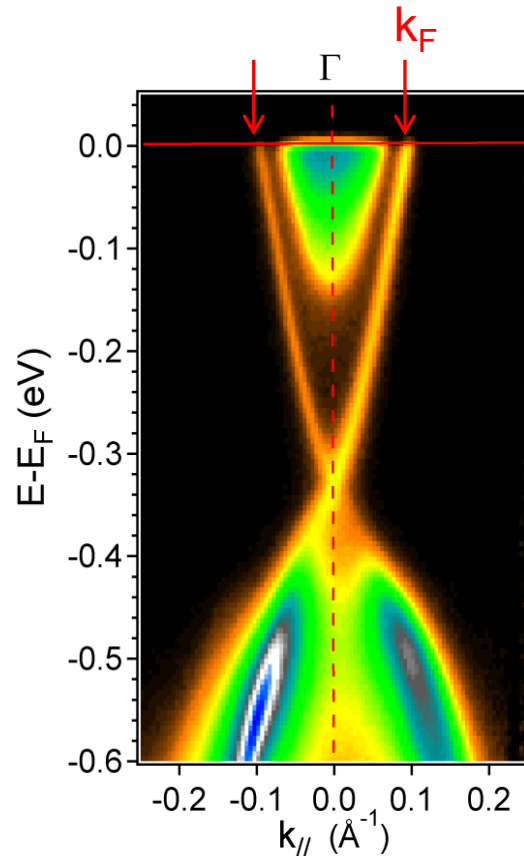
Luo et al., Adv. Optical Mater. 1, 804 (2013)
Luo et al., Nano Lett. 13, 5797 (2013)

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 Σ''

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. Hulbert[2]

[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

Peak position – single particle curve

Width due to electron-electron scattering ~ ω^2

Width due to electron-phonon scattering

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

Const bkg width due to impurities

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. Larger photoionization cross section at low photon energies.
3. Better momentum resolution for a given angular resolution.
 $\Delta k_{||}(1/\text{Å}) = 0.5123 \sqrt{(E_k(eV))} \cos(\theta) \Delta\theta$

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.

TLS U90 undulator beamline & ARPES end station

2 white light branches

ARPES End station

2 spectroscopy branches
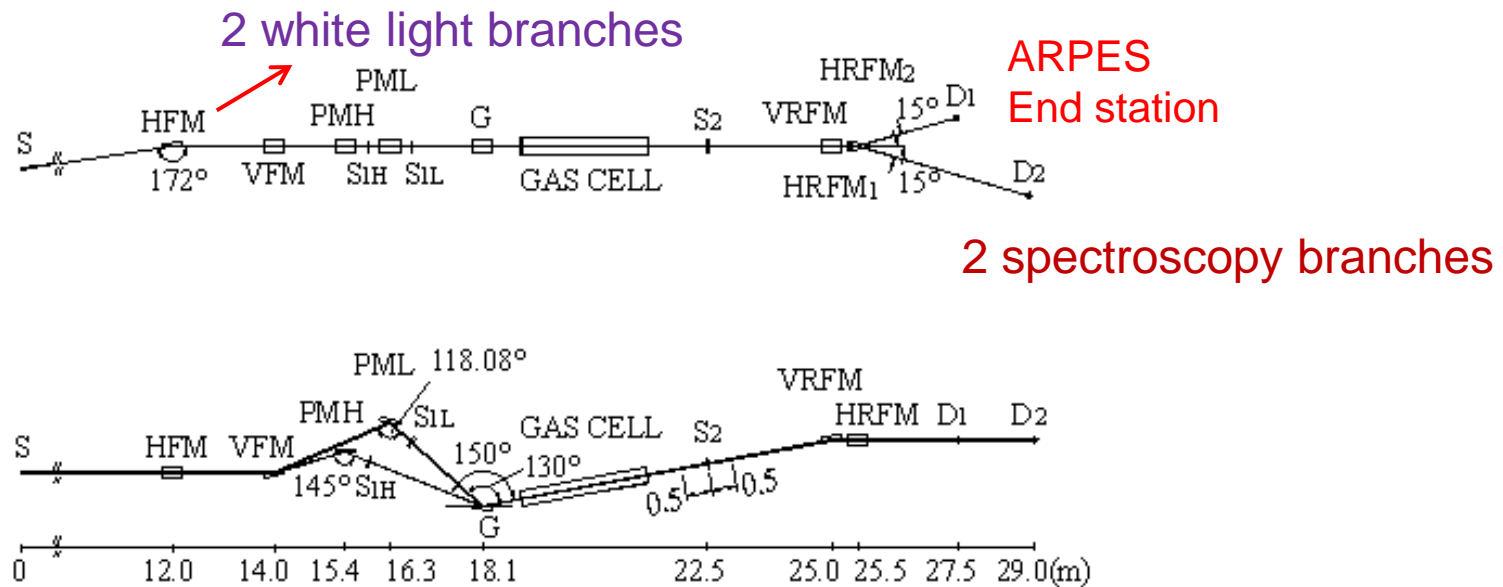
U90 plane undulator w/ 90 mm period and 4.5 m long
CGM spectroscopy BL: 6 ~ 120 eV
Best ΔE ~ 0.15 meV @ 16 eV, R.P. ~ 100,000; for gas phase
Beam spot size at sample: ~200 (H) x 80 (V) um^2

Current status of ARPES end station

Preparation chamber
Load-lock system
R4000
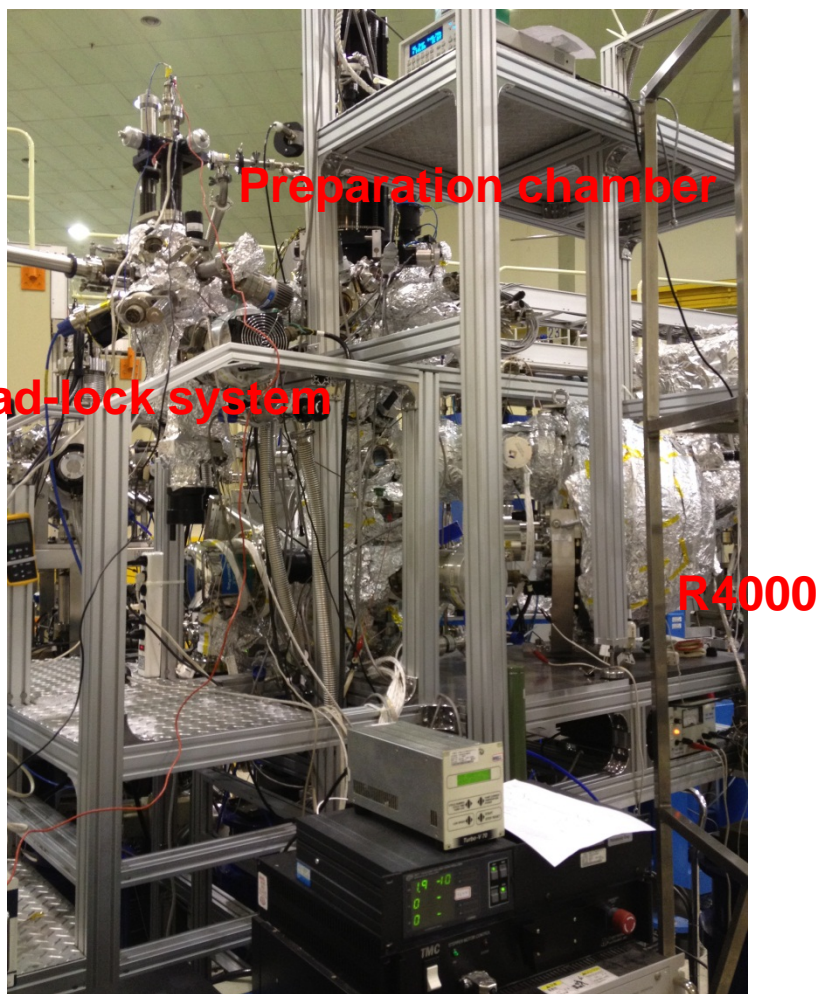
Electron energy analyzer: Scienta R4000
   with $\pm$ 15° collecting angle

Overall energy resolution:
   < 7 meV at 64 eV and 5 meV at 22 eV

6-axis motorized manipulator, < 10 K
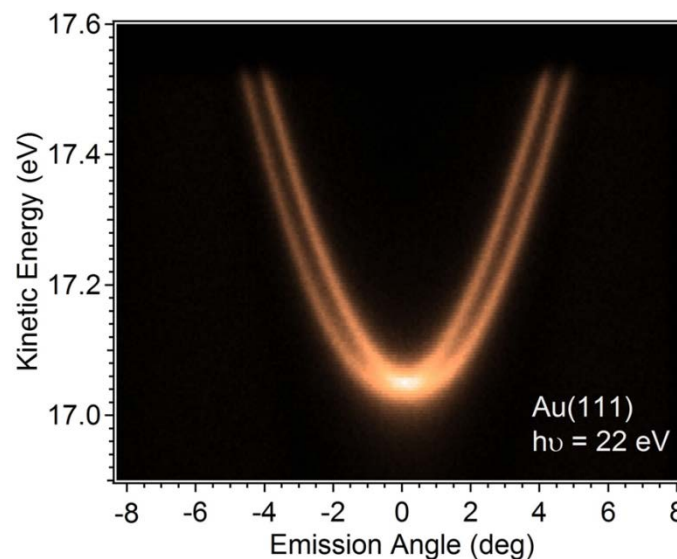
Au(111) Surface State data taken in 3 minutes

Hemispherical electron energy analyzer
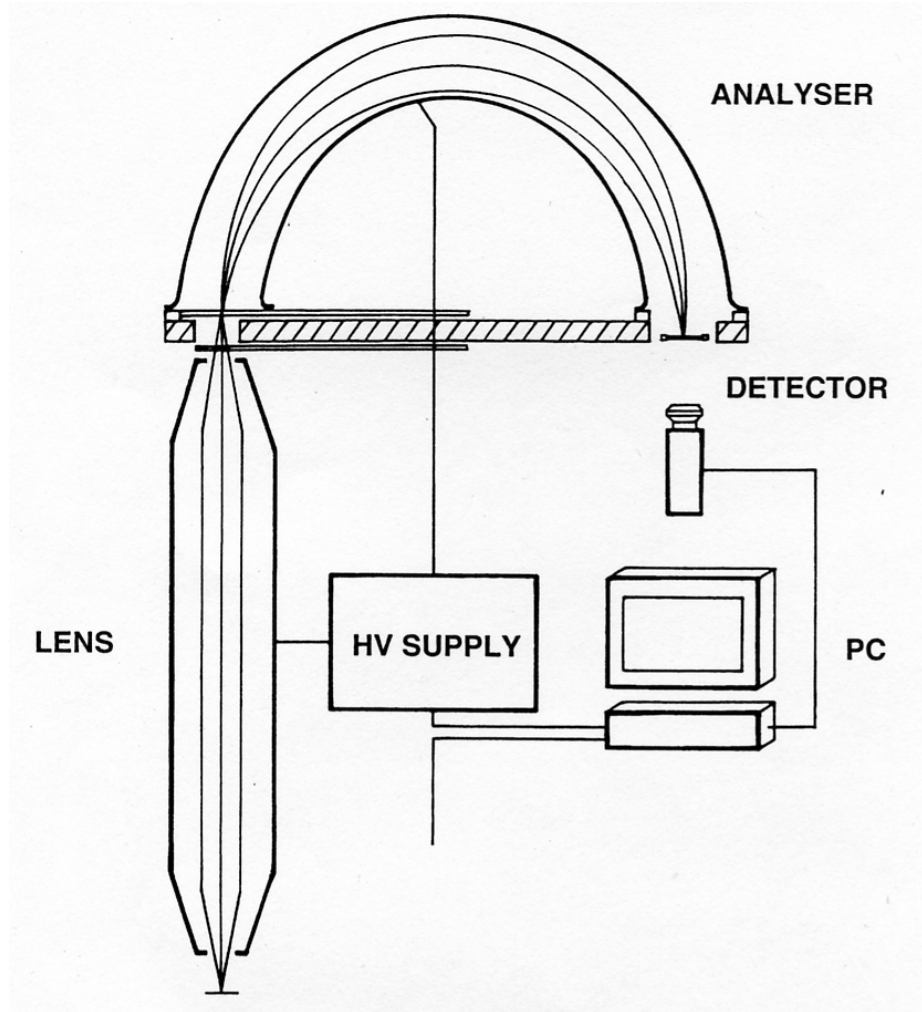
R1 : radius of inner sphere
R2 : radius of outer sphere
R0=(R1+R2)/2 : mean radius and along electron path
V1: inner potential
V2: outer potential
Ep: pass energy = electron kinetic energy along mean radius

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. Ce^{3+} ($4f^1$)

4f mixed with other DOS

Intensity enhanced by absorption
Predominantly 4f DOS

e⁻

4f

4f

E_F

intermediate state

4f

4f

Absorption +

e⁻

4f

4f

E_F

Auger like emission

3d/4d

3d/4d

3d/4d

Direct PE

Resonance PE

2000
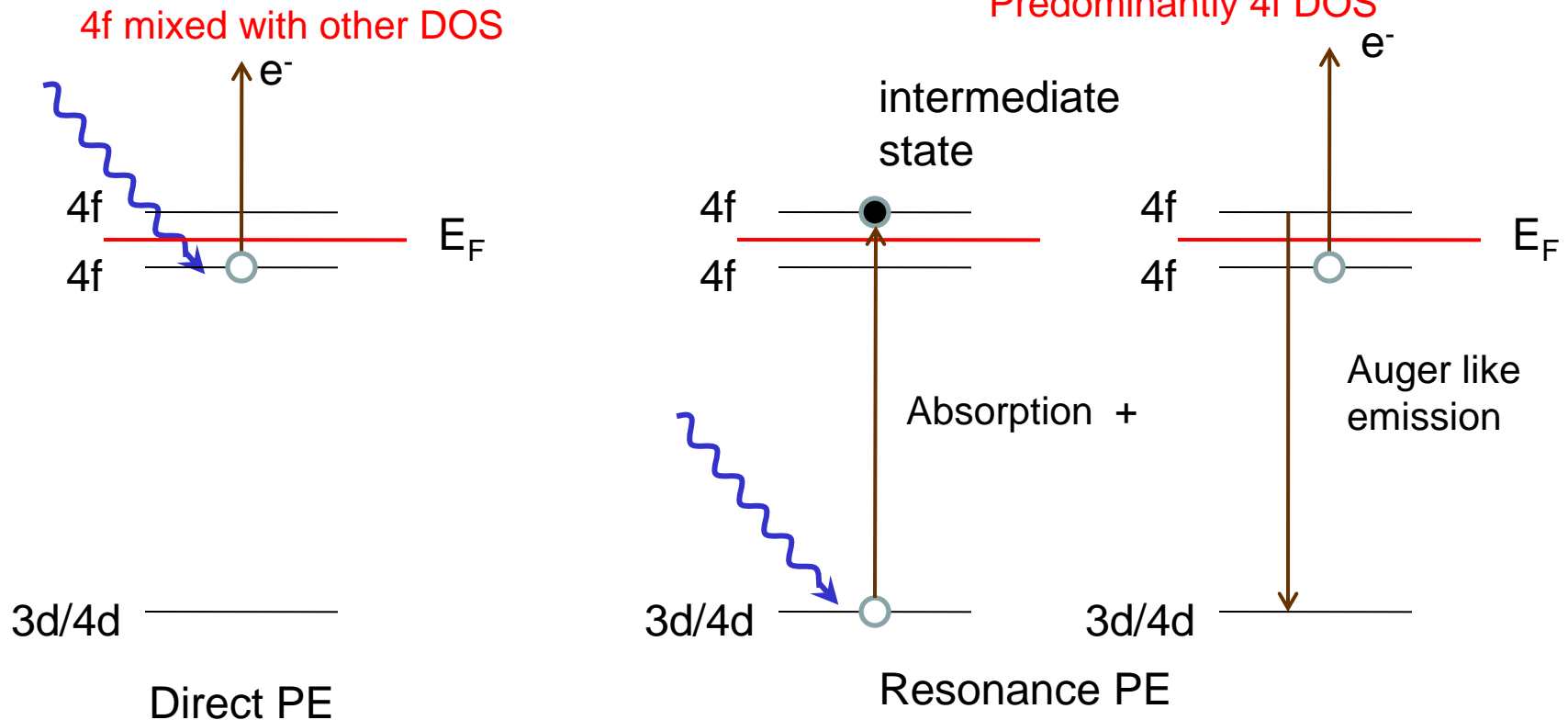
Probing bulk states of correlated electron systems by high-resolution resonance photoemission

A. Sekiyama*, T. Iwasaki*, K. Matsuda*, Y. Saitoh†, Y. Ônuki‡ & S. Suga*
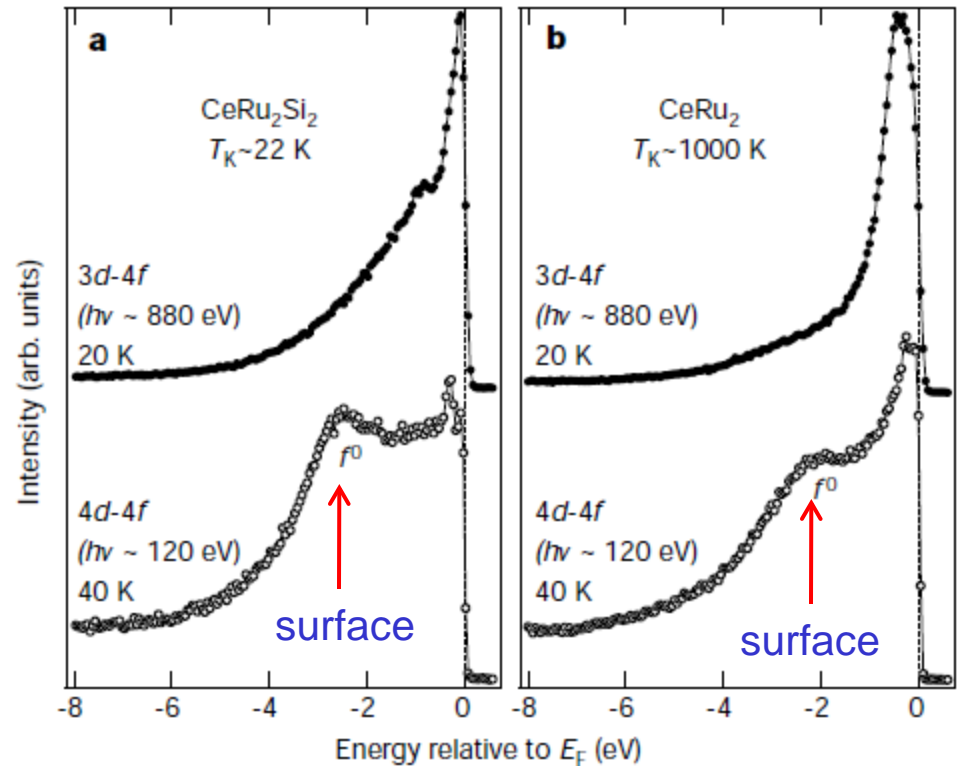
By using Ce 3d → 4f Res. PE near 880 eV surface 4f component becomes greatly reduced compared to 4d → 4f Res. PE near 120 eV, the resulting spectra are closer to true bulk 4f DOS.

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 Ishikawa[8]
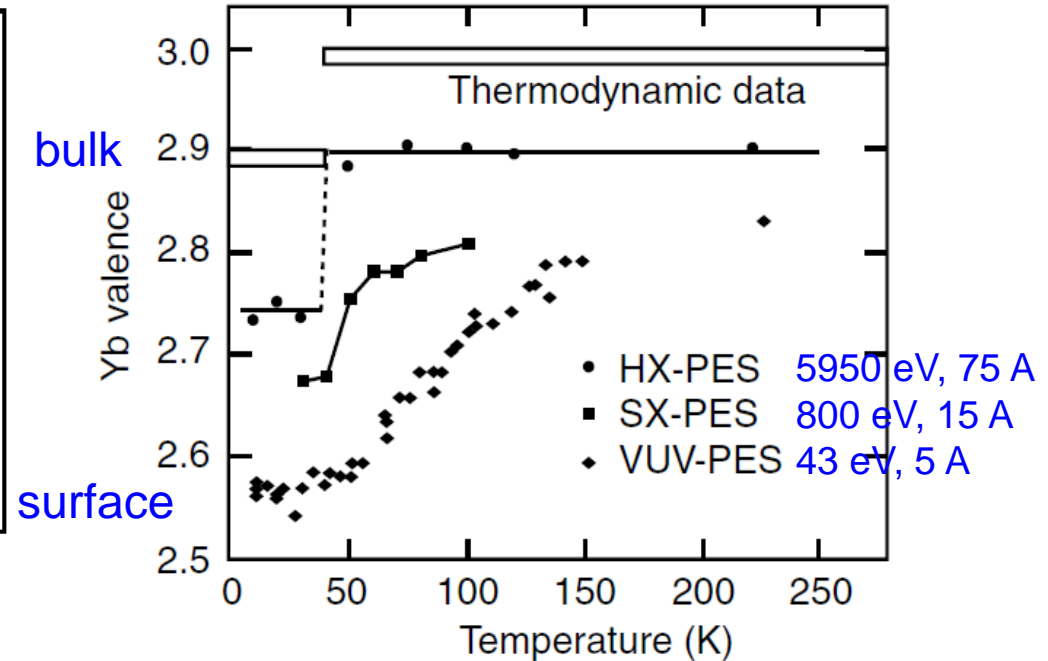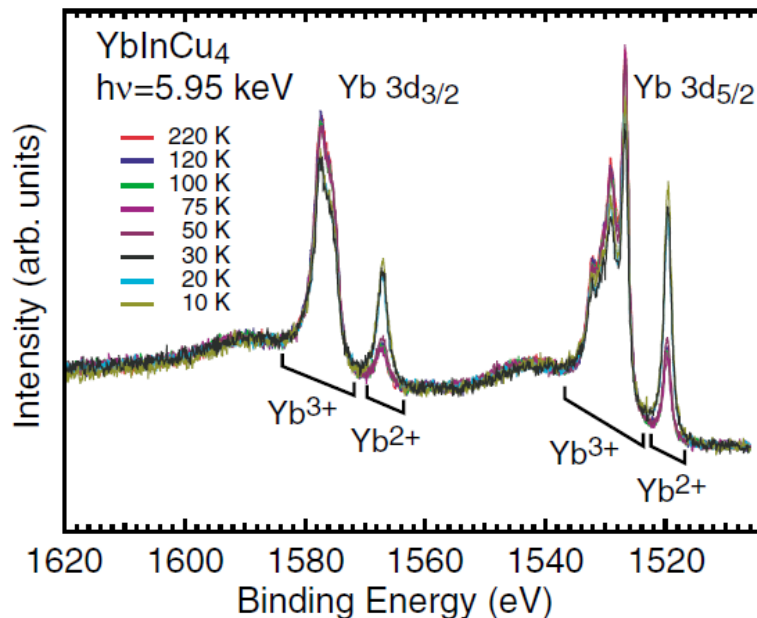
Bulk sensitive HAXPES can determine sharp first order valence band transition

HAXPES example: Hard x-ray photoemission on Si-high k insulator buried interface
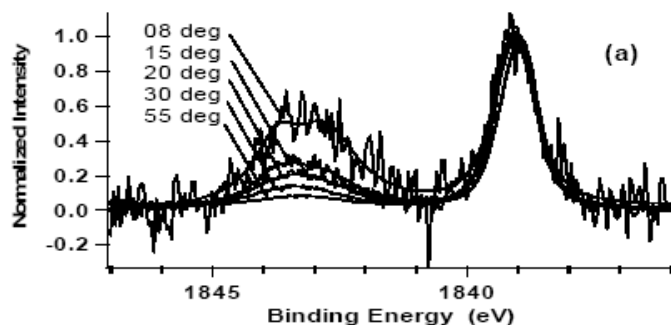
Kobayashi, APL 2003 SPring-8
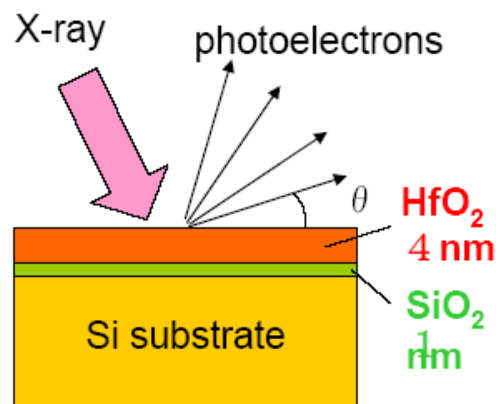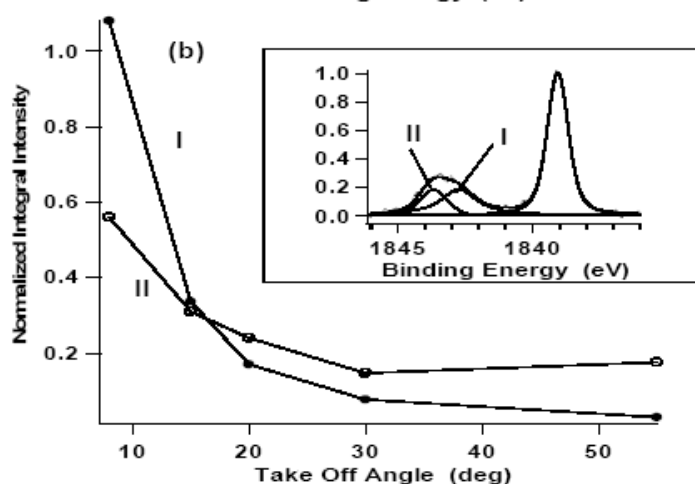
Annealed sample
HfSix formation

hv = 6 keV, ΔE ~ 0.24 eV

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

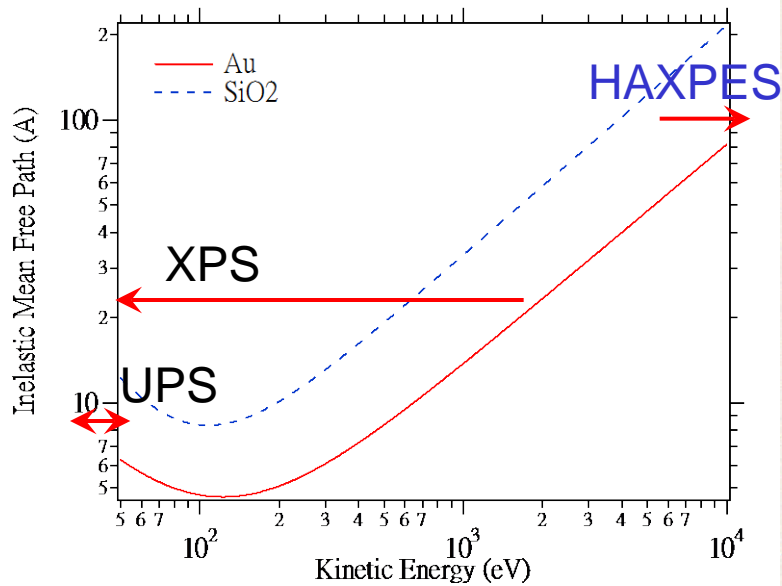Can probe buried interface at 35 nm ! (achievable only by hard x-ray PE)

NSRRC HAXPES project at SPring-8 (in collaboration with the Max Planck Institute for Chemical Physics of Solids (MPI-CPfS) in Dresden, Germany)

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 Reseach, 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 (RIXS and HAXPES)
* **CLS** SXRMB BM (wide range 1.7-10 keV)
* **APS** (?)

Why Hard X-rays?

Electron IMFP (probing depth) and Cross section

HAXPES

XPS

UPS

Inelastic Mean Free Path (A) vs Kinetic Energy (eV)
— Au
--- SiO2

σ·λ   σ(Mb)   λ (Å)
--- Au
··· Si

SPring-8
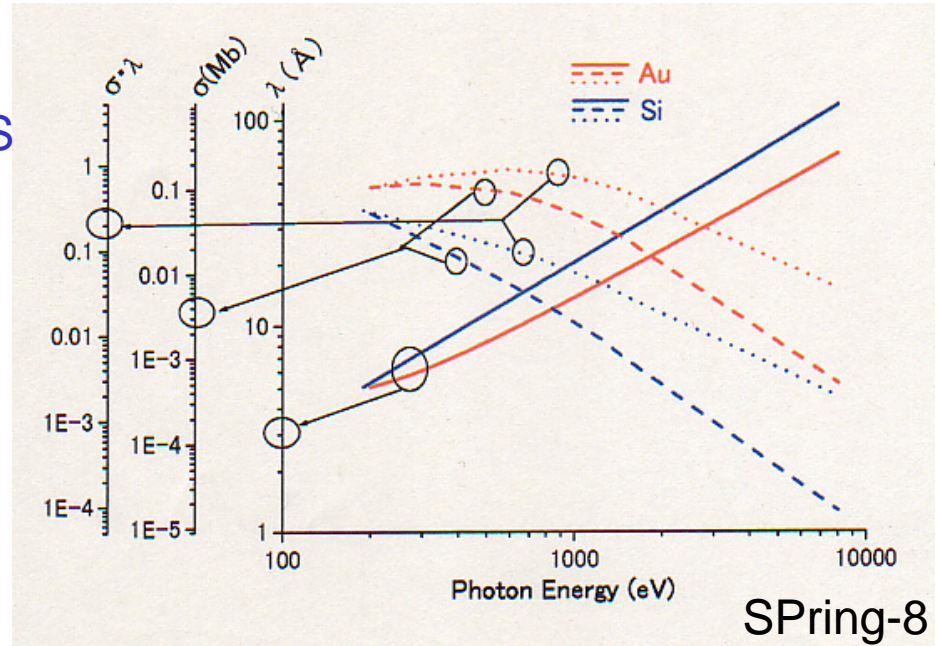
Higher Ek for deeper probing depth or more bulk sensitivity, for strongly correlated systems and interface properties

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

Yeh,1992
Trzhaskovskaya et al., ADNDT 2001,2006
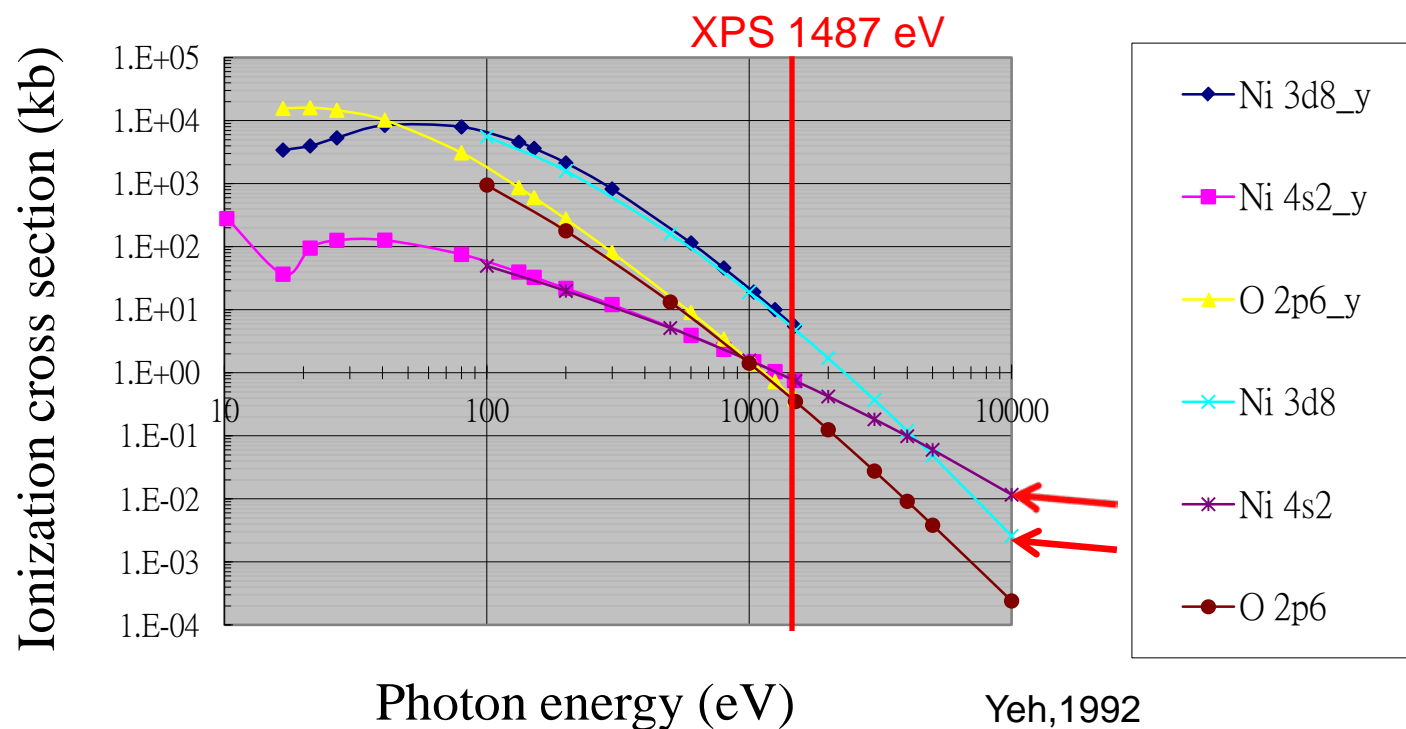
Cross sections of 3d TM s-orbitals go down more slowly than d-orbitals which are the needed information on 3d TM strongly correlated electron systems. Hard x-ray PE spectra could be dominated by contribution from less desired s-orbitals

How to cope with this problem?

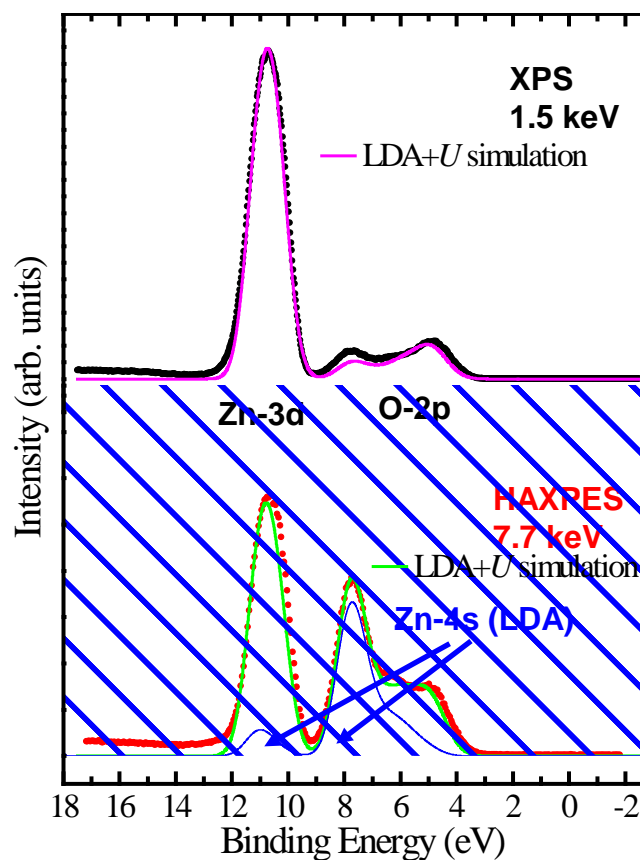# Unexpected lineshapes in HAXPES compared to XPS

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
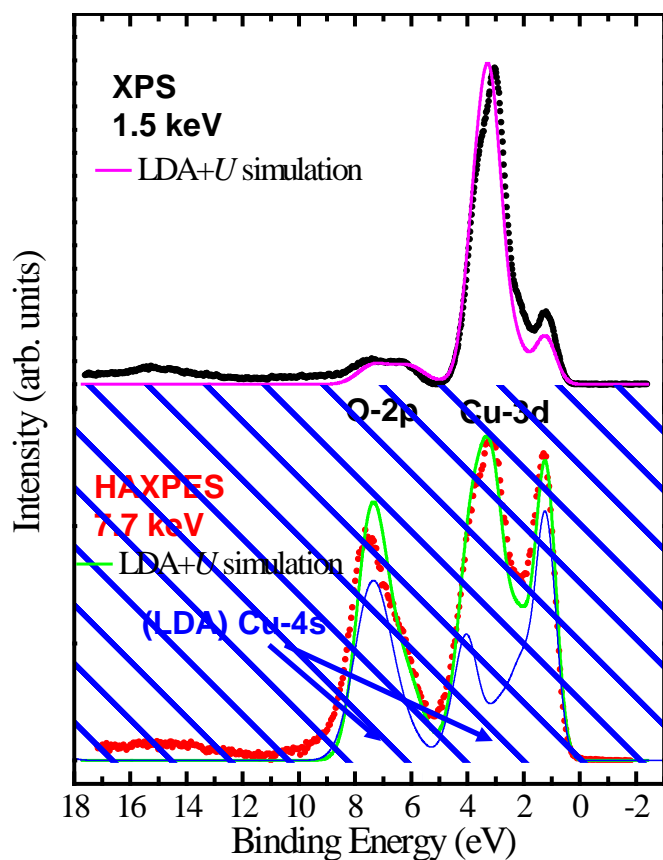
ZnO – valence band

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

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

β-parameters @ h*v* = 5-10 keV

Cu 3*d* 0.48 - 0.32
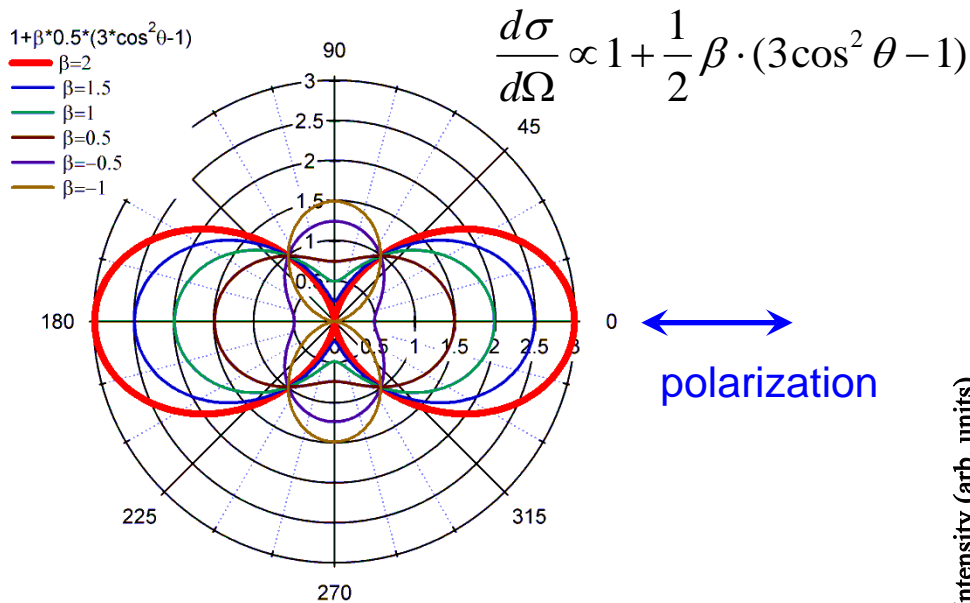Cu 4*s* 1.985

Zn 3*d* 0.50 - 0.33
Zn 4*s* 1.987 - 1.986

In general: s orbitals have β ≈ 2:
- intensity is *enhanced* for e⁻ emission ∥ *E*-vector
- intensity *vanishes* for e⁻ emission ⊥ *E*-vector
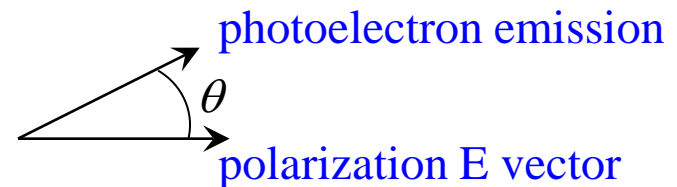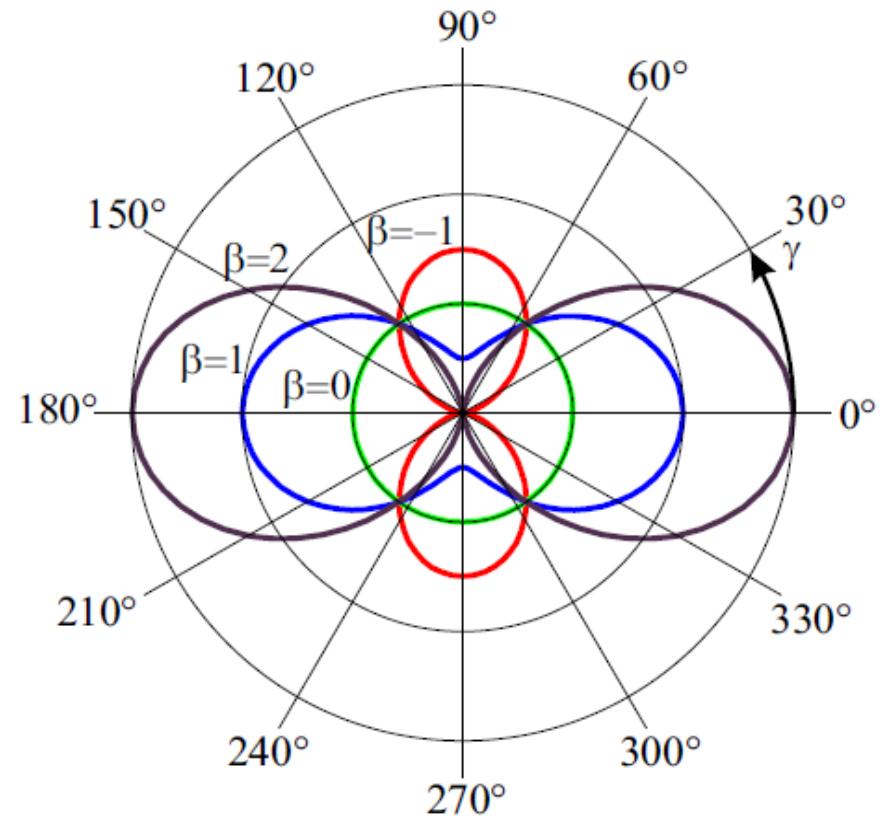
→ **choose suitable experimental geometry !**

photoelectron emission

θ

polarization E vector

HAXPES Commissioning: Horizontal vs Vertical geometries

$$\frac{d\sigma}{d\Omega} \propto 1 + \frac{1}{2}\beta \cdot (3\cos^2\theta - 1)$$

$1 + \beta*0.5*(3*\cos^2\theta - 1)$
- $\beta = 2$
- $\beta = 1.5$
- $\beta = 1$
- $\beta = 0.5$
- $\beta = -0.5$
- $\beta = -1$

polarization

θ: angle between electron emission and polarization vector

β: electron emission asymmetry parameter

$\beta \sim 2$ for s-orbitals, strong emission near $\theta = 0^o$ (horiz.) while suppressed near $\theta = 90^o$ (vertical); can be used to distinguish

s-orbital, important in chemical bonding, and

d-orbital, important in strongly correlated systems

(a) ZnO XPS
h = 1486.6 eV
- experiment
- LDA+U simulation
- Zn 4s pDOS weight

(b) ZnO HAXPES *horizontal*
h = 7.7 keV
- experiment
- LDA+U simulation
- Zn 4s pDOS weight

horizontal
$\theta = 0^o$

(c) ZnO HAXPES *vertical*
h = 7.6 keV
- experiment
- LDA+U simulation
- Zn 4s pDOS weight

vertical
$\theta = 90^o$

Intensity (arb. units)

Binding Energy (eV)

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

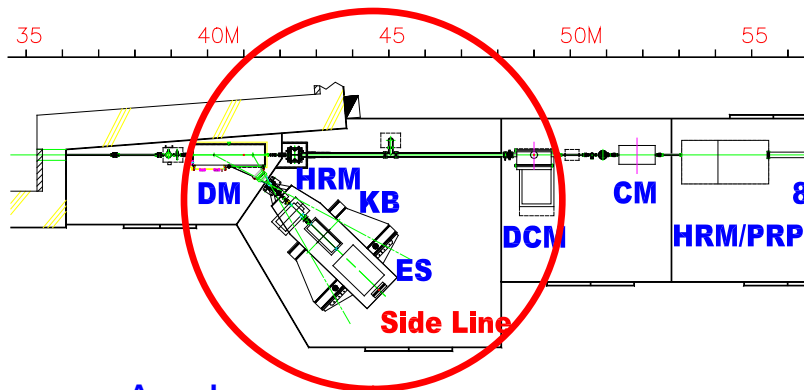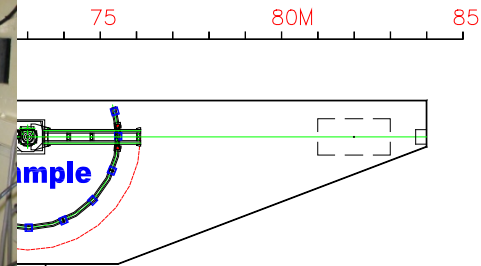# Optical design concept

SIDE LINE OPTICAL LAYOUT

Diamond (111) reflection
6-12 keV

DM: horizontal dispersion
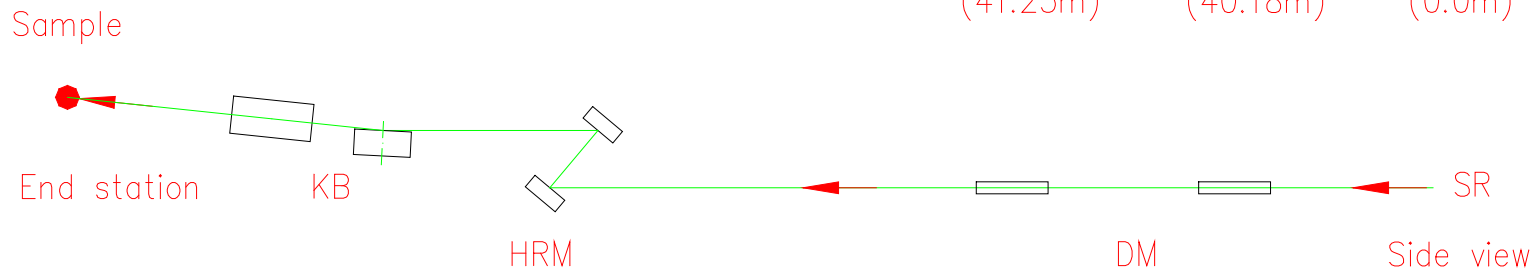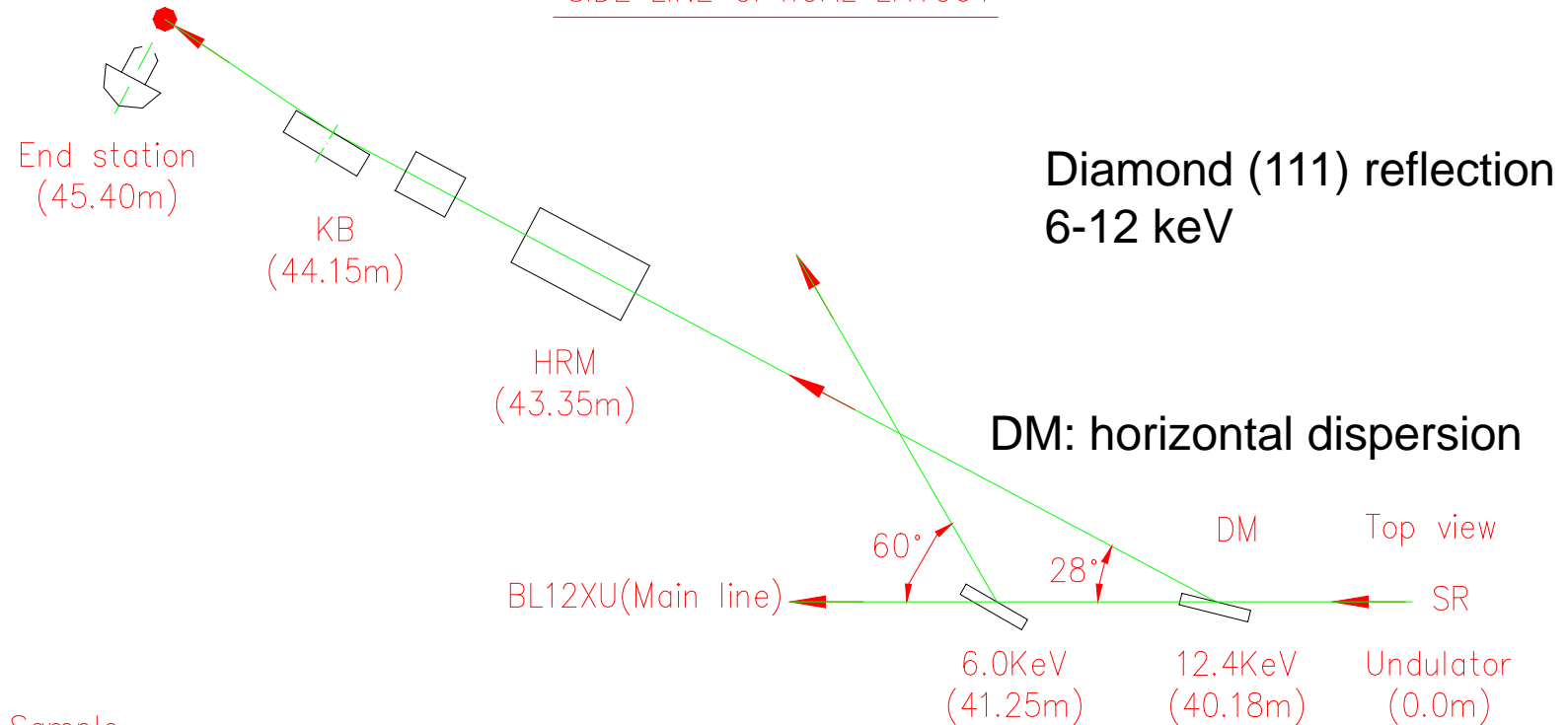
HRM: vertical dispersion
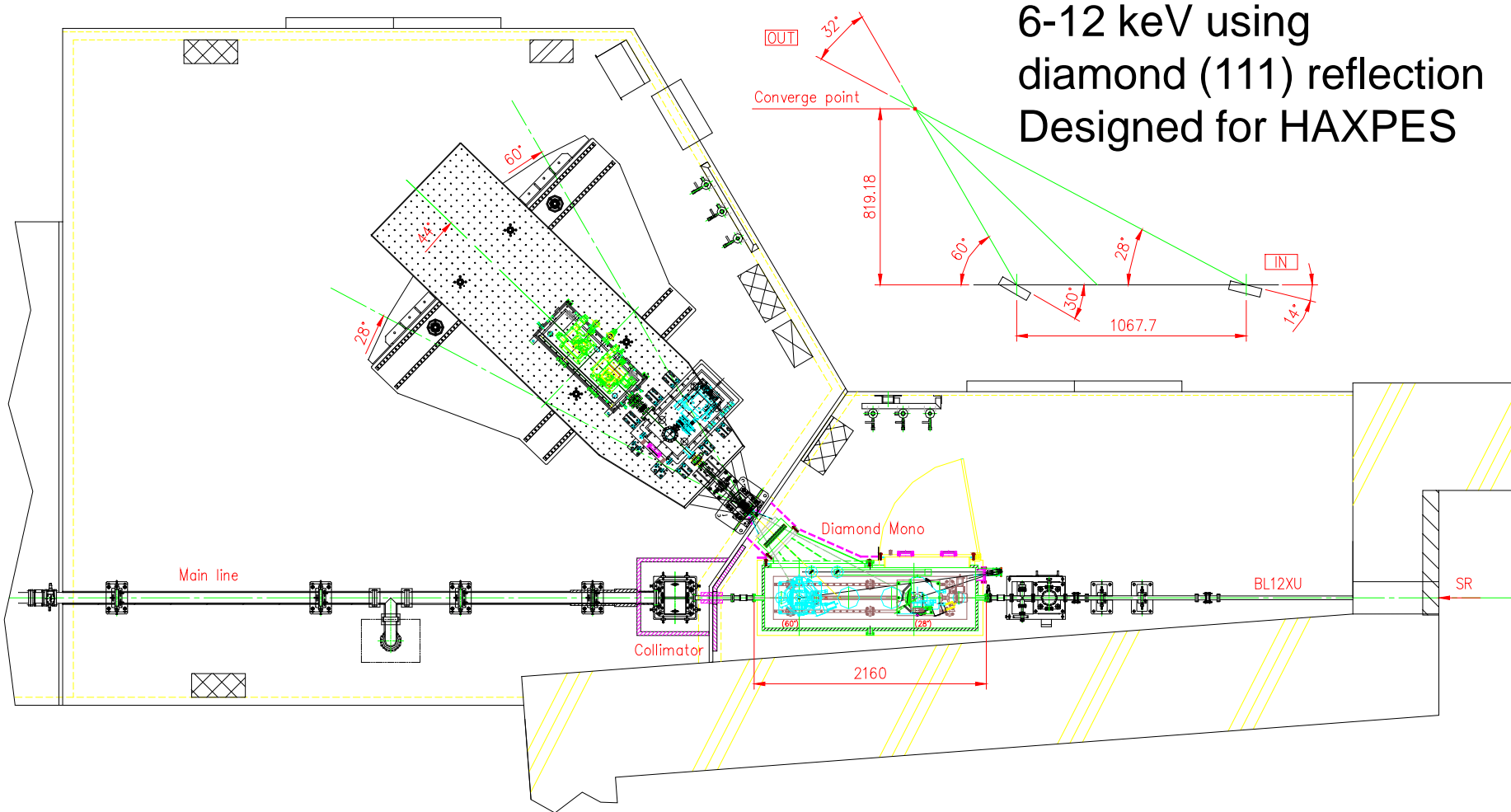
6-12 keV using diamond (111) reflection
Designed for HAXPES

OUT

32°

Converge point

819.18

60°

28°

30°

14°

IN

1067.7

60°

44°

28°

Main line

Collimator

Diamond Mono

(60°)

(28°)

2160

BL12XU

SR

Layout of the side beamline of BL12XU

BL12XU Sideline

Diamond Mono.

35   40M   45   50M   55   75   80M   85

DM   HRM   KB   DCM   CM   HRM/PRP   8   Sample

ES
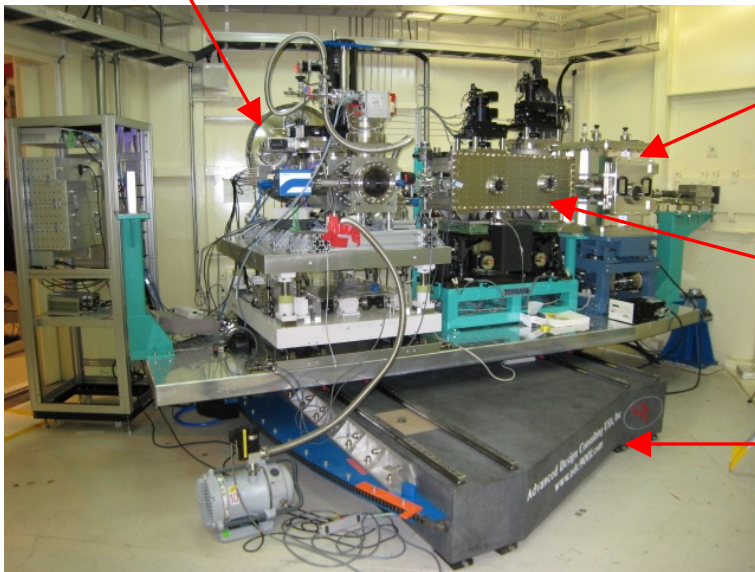
Side Line

Analyzer

HRM

KB

Platform
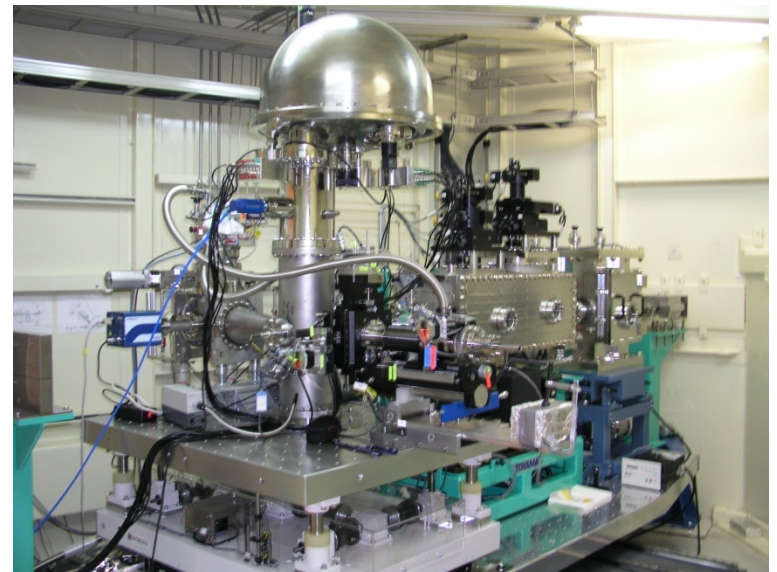
Horizontal geometry   **Vertical geometry**

For selecting different orbital symmetries in valence band

BL12XU Sideline

Diamond Mono.

35 40M 45 50M 55 75 80M 85

DM HRM KB

DCM CM

ES

HRM/PRP

Side Line

KOHZU

KOHZU

2007/11/15
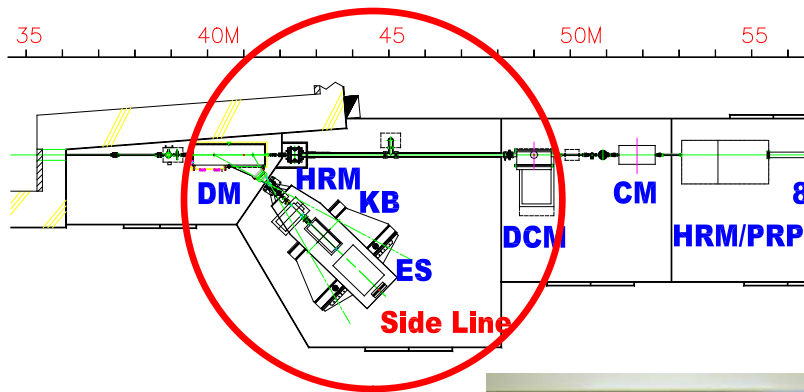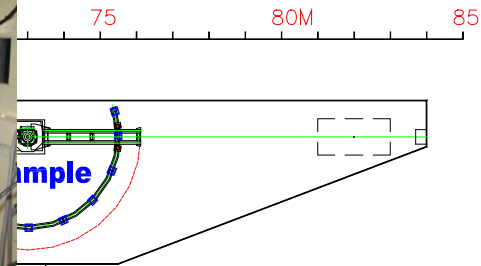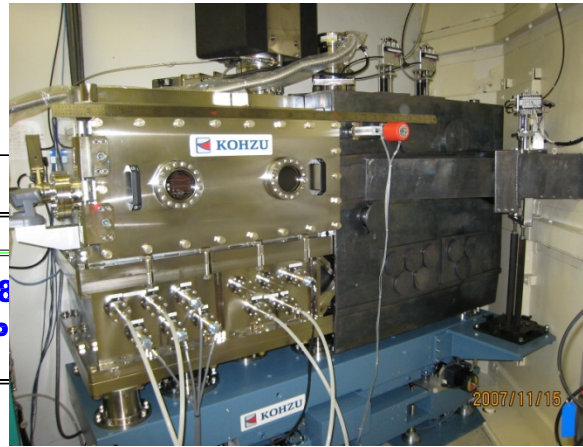
ample

MBS-A1HE
Analyzer
(**Vertical**)

MBS-A1HE
Analyzer
(**Horizontal**)
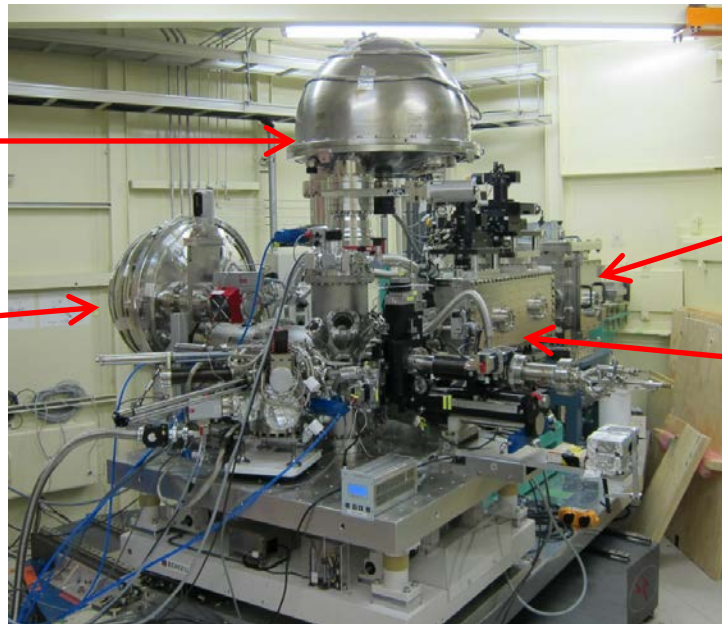
High Resolution
Mono. (HRM)

KB focus mirrors

New end station installed in January, 2013

Example 1: Metal-Insulator Transition of $Ca_{2-x}Sr_xRuO_4$ (vertical geometry)

There is a rich phase diagram of $Ca_{2-x}Sr_xRuO_4$ regarding their structure, transport and magnetic properties as Sr doping and temperature are varied.
Ru is a 4d element. Despite its larger wave function 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} ~ 360 K
1sr order structural transition

x=0.09, T_{MIT}~170 K
1st order structural transition

$Ca_{2-x}Sr_xRuO_4$

P-I

T_O

P-M

CAF-I

tetrag.

orthorh.

x=2, no MIT
except Tsc=1.5 K

M-M

T_P

SC

Sr_2RuO_4 $La_{2-x}Ba_xCuO_4$

O — — O

Sr   La(Ba)

Ru   Cu
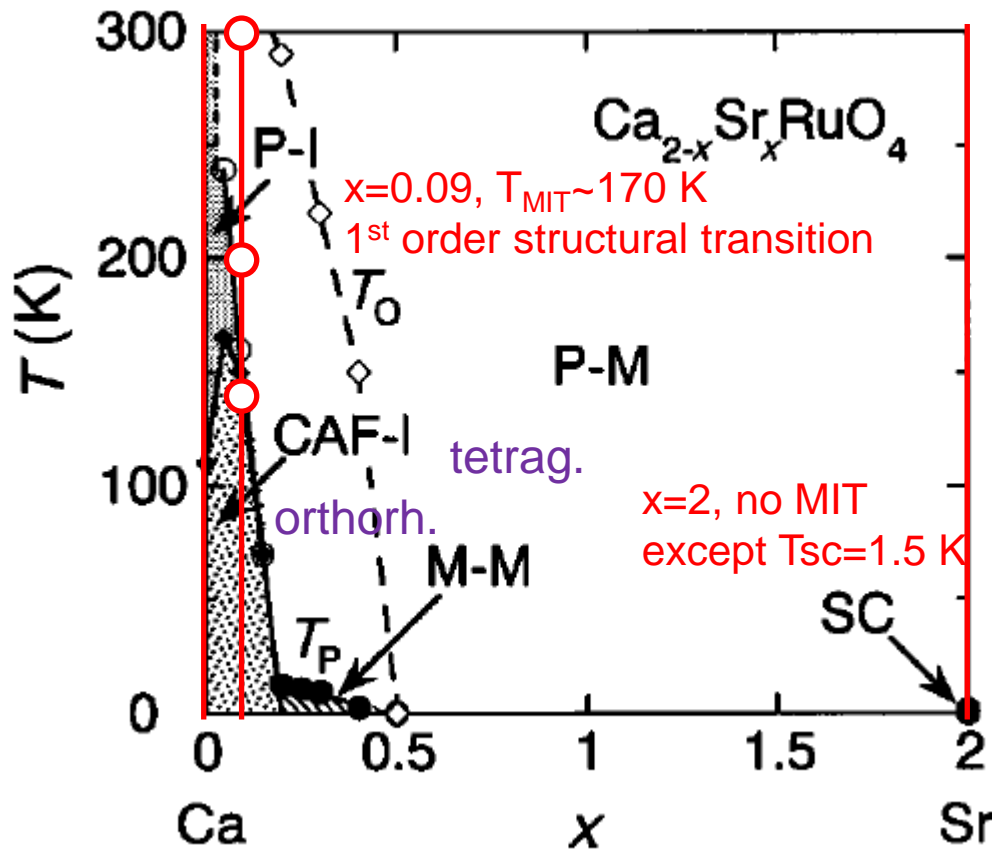
SC: superconductor
P-M: paramagnetic metal
P-I: paramagnetic insulator
CAF-I: canted antiferromagnetic
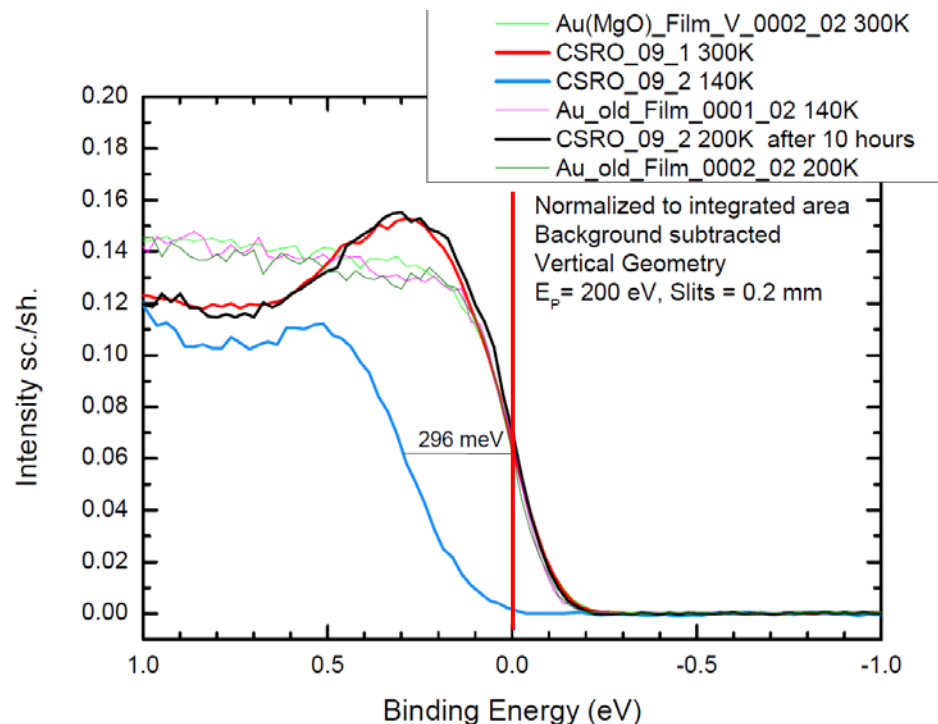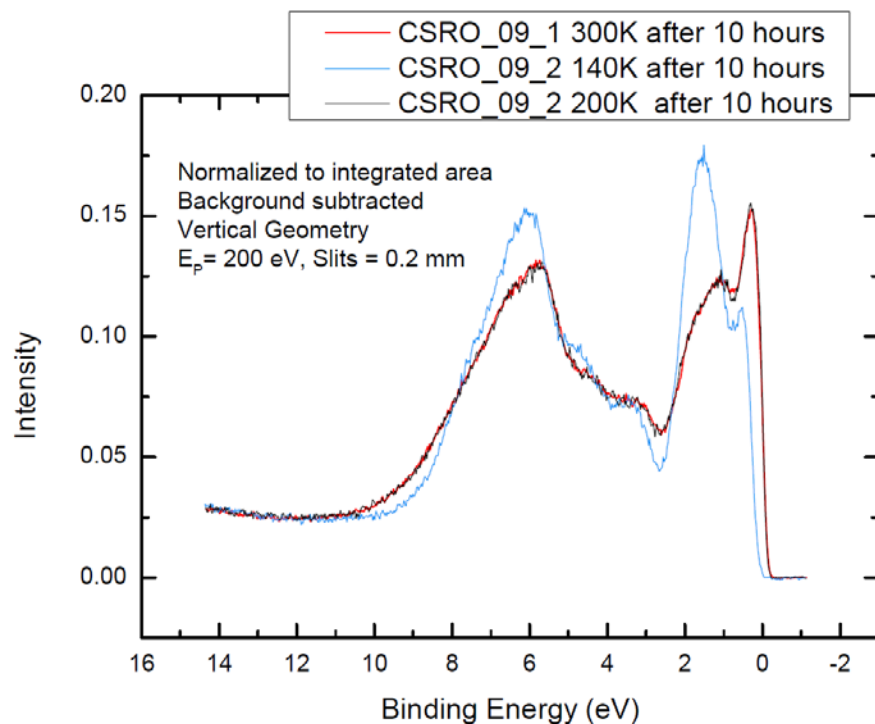   insulator
M-M: AF correlated metal
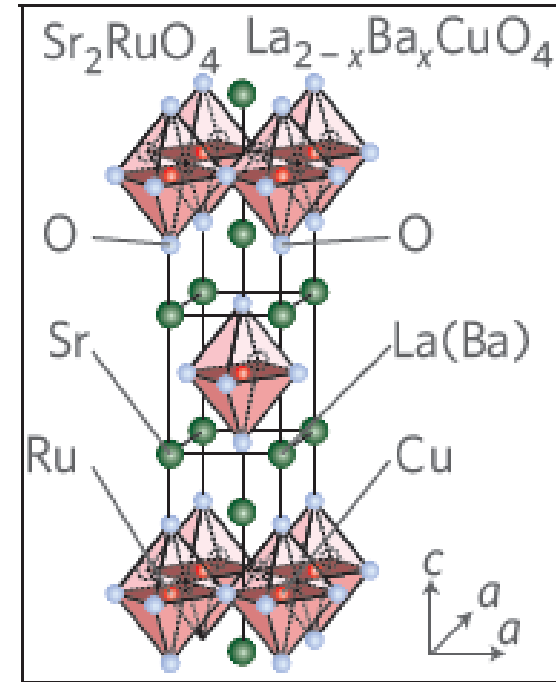
Sr_2RuO_4: tetragonal, elongated
    perovskite
Complex structural distortion
    with replacement of Sr by Ca
Ca_2RuO_4: orthorhombic

Nakatsuji & Maeno, PRB 62, 6458 (2000)
Friedt & Maeno et al. PRB 63, 174432 (2001)

Metal Insulator Transition (MIT) of $Ca_{1.91}Sr_{0.09}RuO_4$

300 K → 140 K → 200 K (T_{MIT} ~ 160 K)

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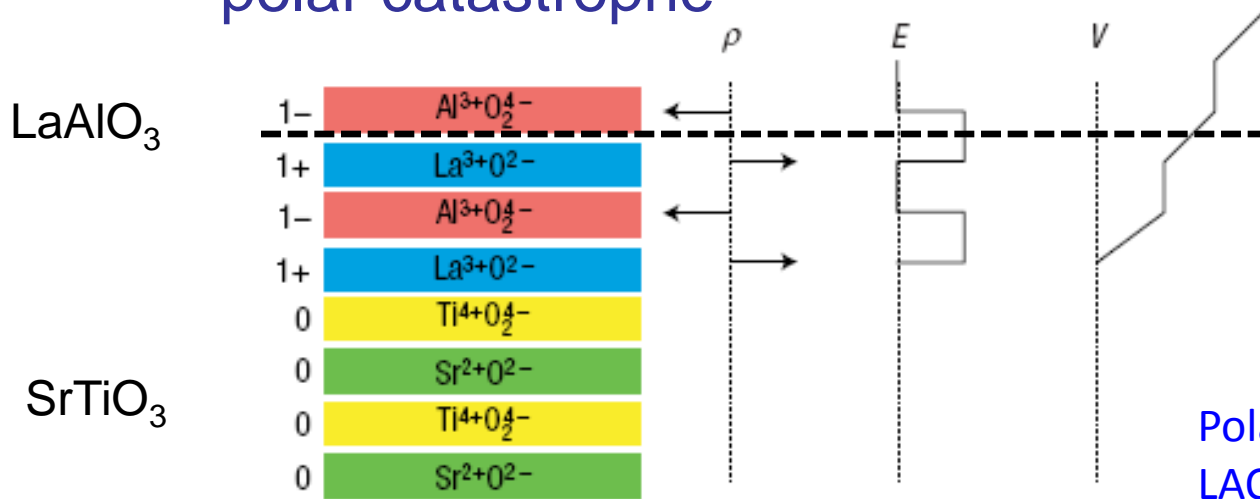* Reversible

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

Interface of two large gap band insulators
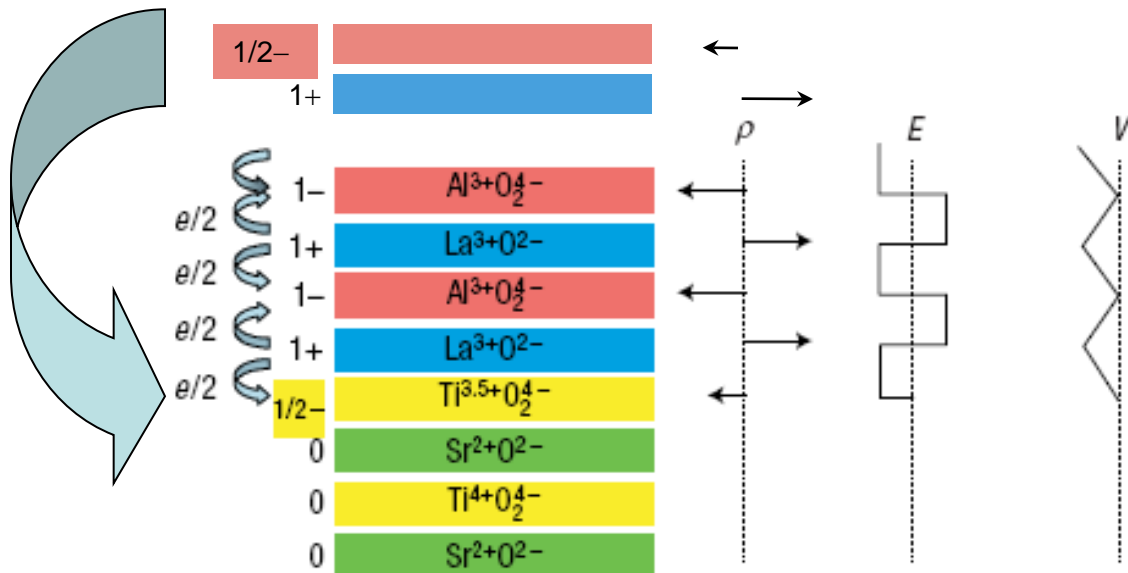 LaAlO$_3$ and SrTiO$_3$ becomes metallic-like.
Evidence of charge transfer from LAO to
  STO is observed but the amount is less than
  prediction of a simplest model.

polar catastrophe

LaAlO$_3$

SrTiO$_3$

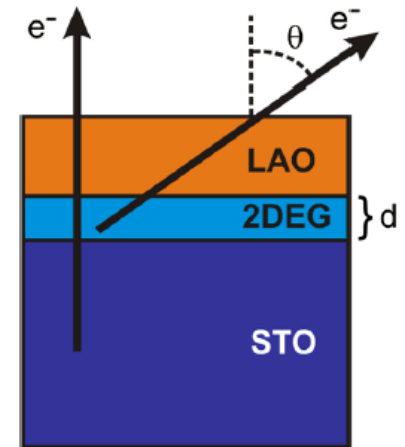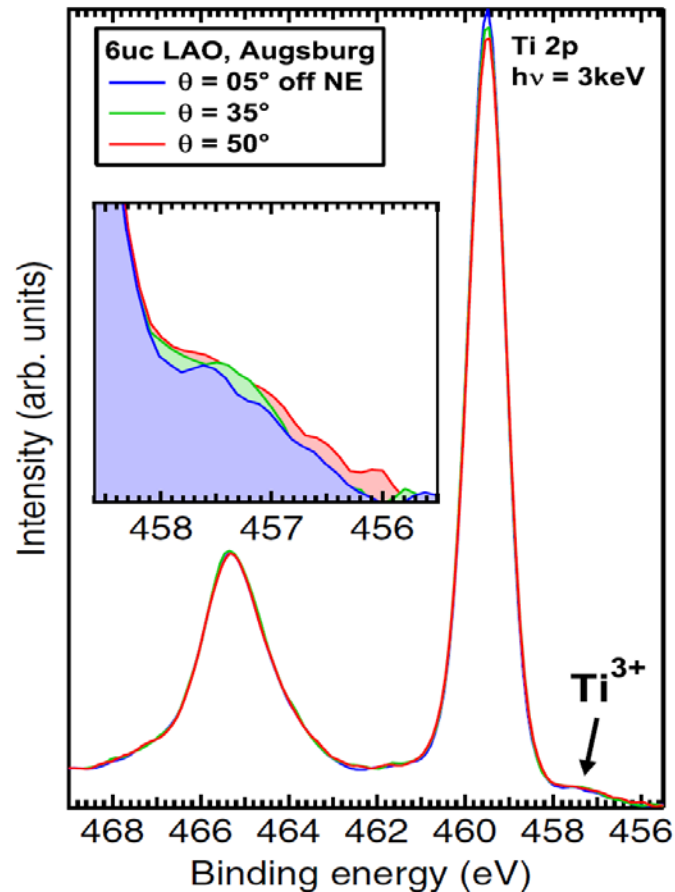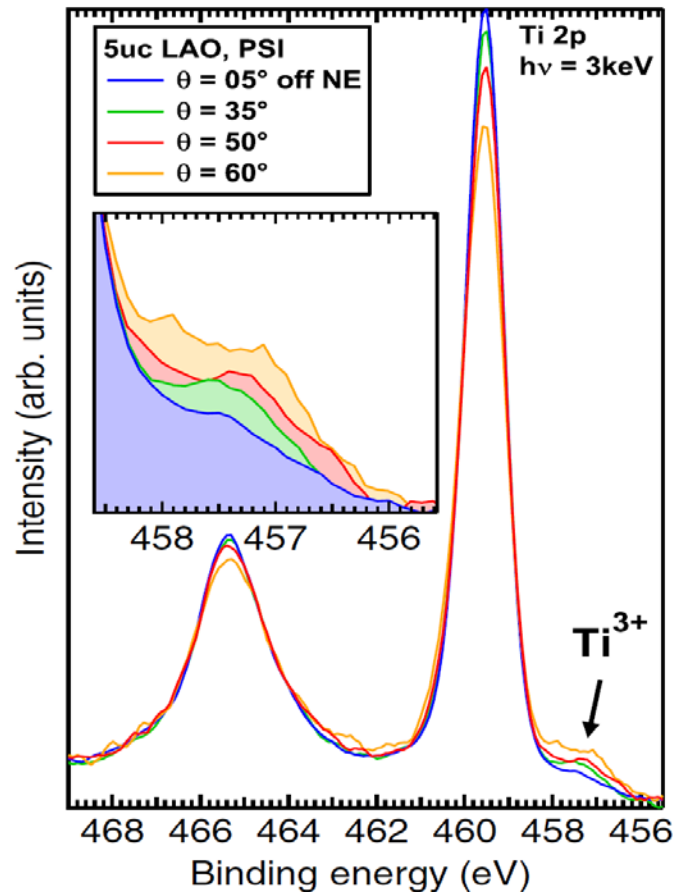Polarity discontinuity between LAO and STO plays a crucial role.

Electronic reconstruction

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

½ e transferred   Nakagawa et al., Nature Mater. 5, 204 (2006)

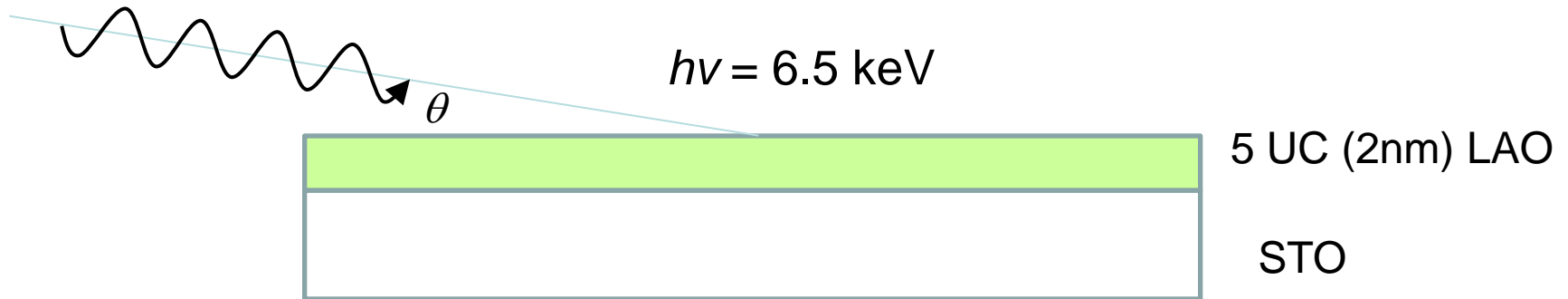# Hard X-ray Photoemission Spectroscopy (HAXPES)
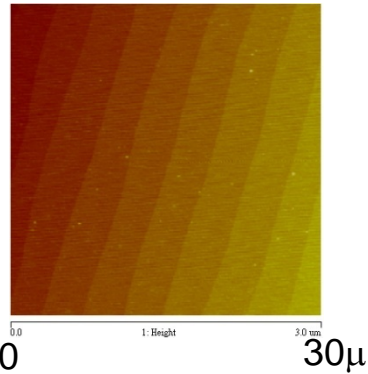

Sing et al.,
PRL 102,
176805 (2009)

$hv = 3$ keV

$\Rightarrow$ Conducting interface due to electronic reconstruction
$\Rightarrow$ 2DEG confined to only ~ 1 or at most a few u.c. thick
   total Ti^{3+} density < 0.28 e /2D u.c. for 5 u.c. LAO (<0.5 e); sample dependent
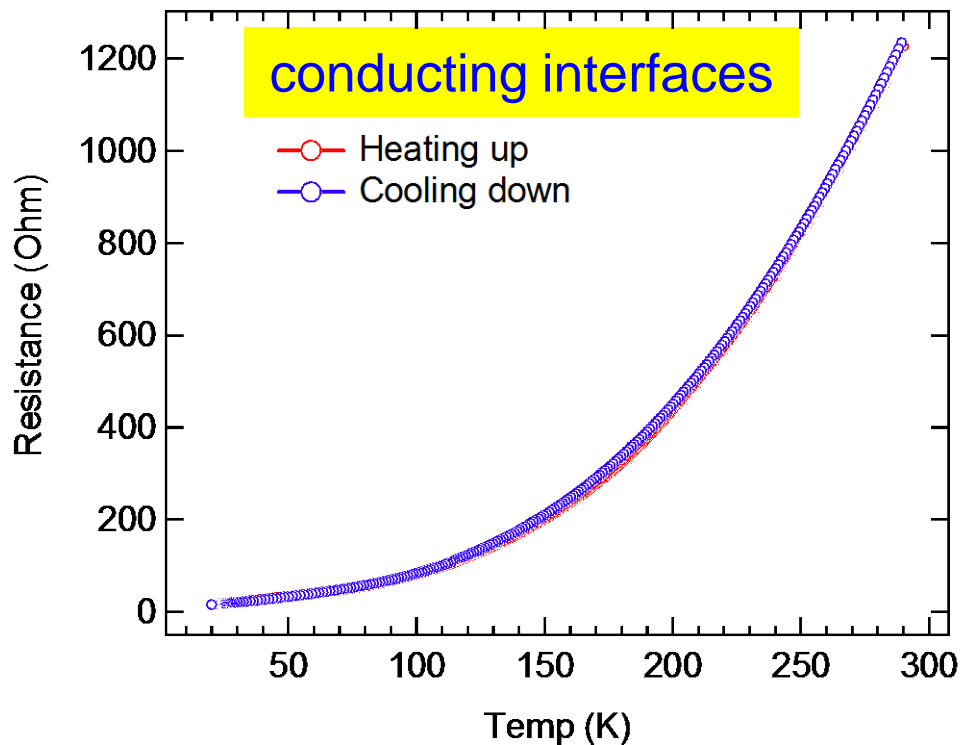
Our approach:

* 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

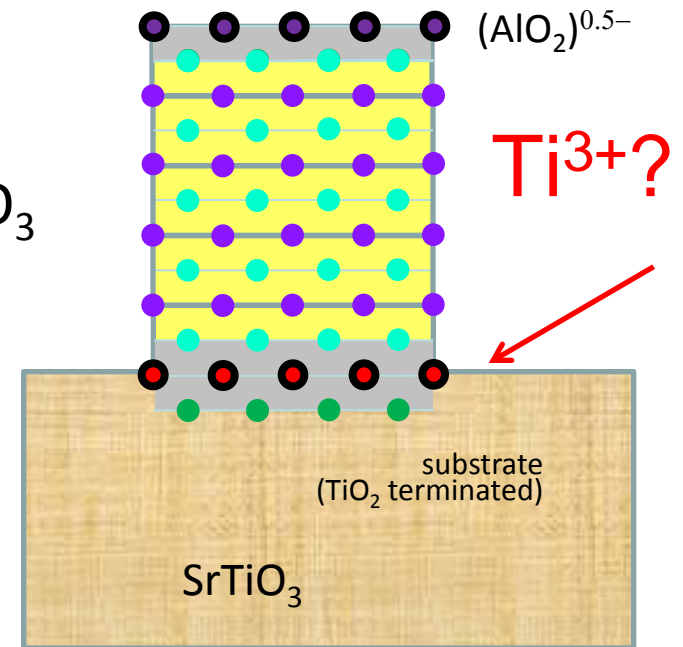* higher photon energy (6.5 keV) to increase probing depth

$h\nu = 6.5$ keV
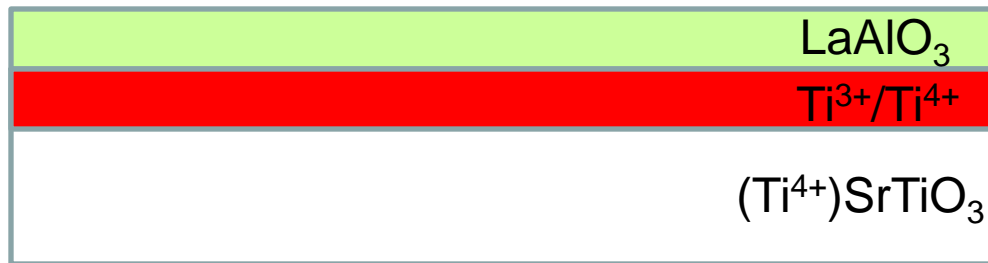
θ

5 UC (2nm) LAO

STO

LaAlO$_3$/SrTiO$_3$ (001)

0   1: Height   30μ

grown with PLD, 10^{-5} torr O$_2$, 850 C
annealed at 100 mtorr of O$_2$

5 u.c.
LaAlO$_3$

(AlO$_2$)$^{0.5-}$

Ti^{3+}?

substrate
(TiO$_2$ terminated)

SrTiO$_3$

conducting interfaces

— Heating up
— Cooling down
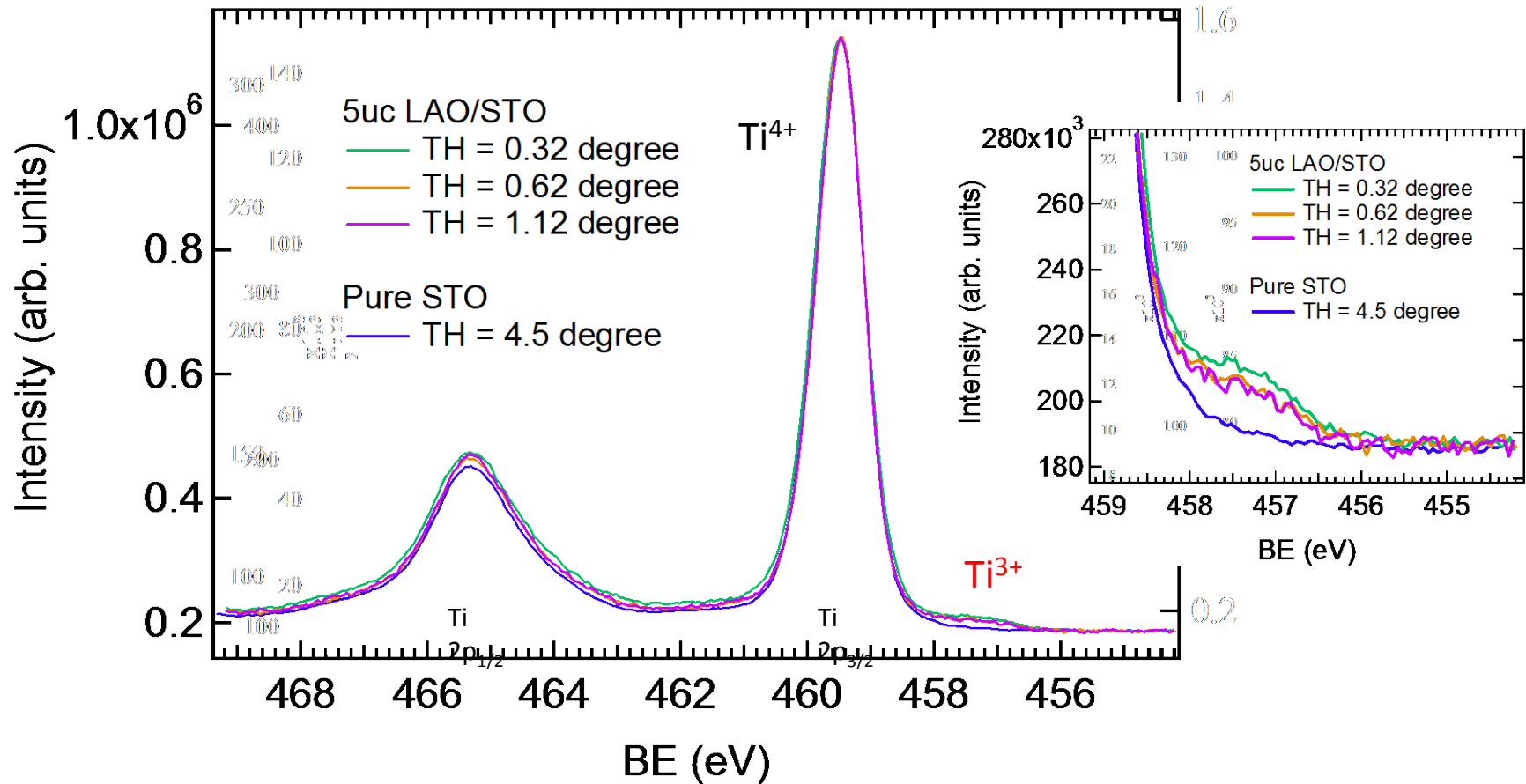
Measure intensity ratio Ti^{3+}/Ti^{4+} as a function of incident angle

LaAlO$_3$ — d_1

Ti^{3+}/Ti^{4+} — d_2 (2DEG)

(Ti^{4+})SrTiO$_3$
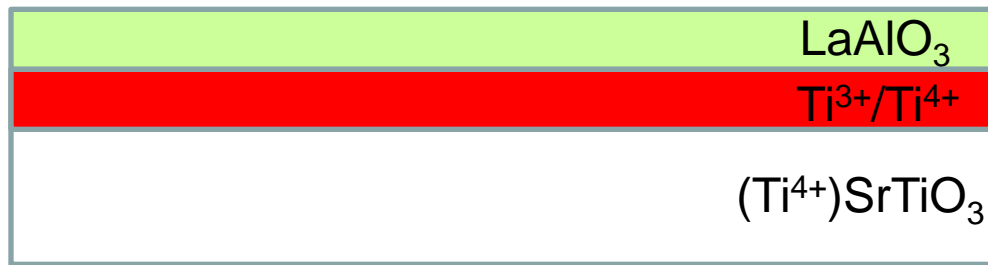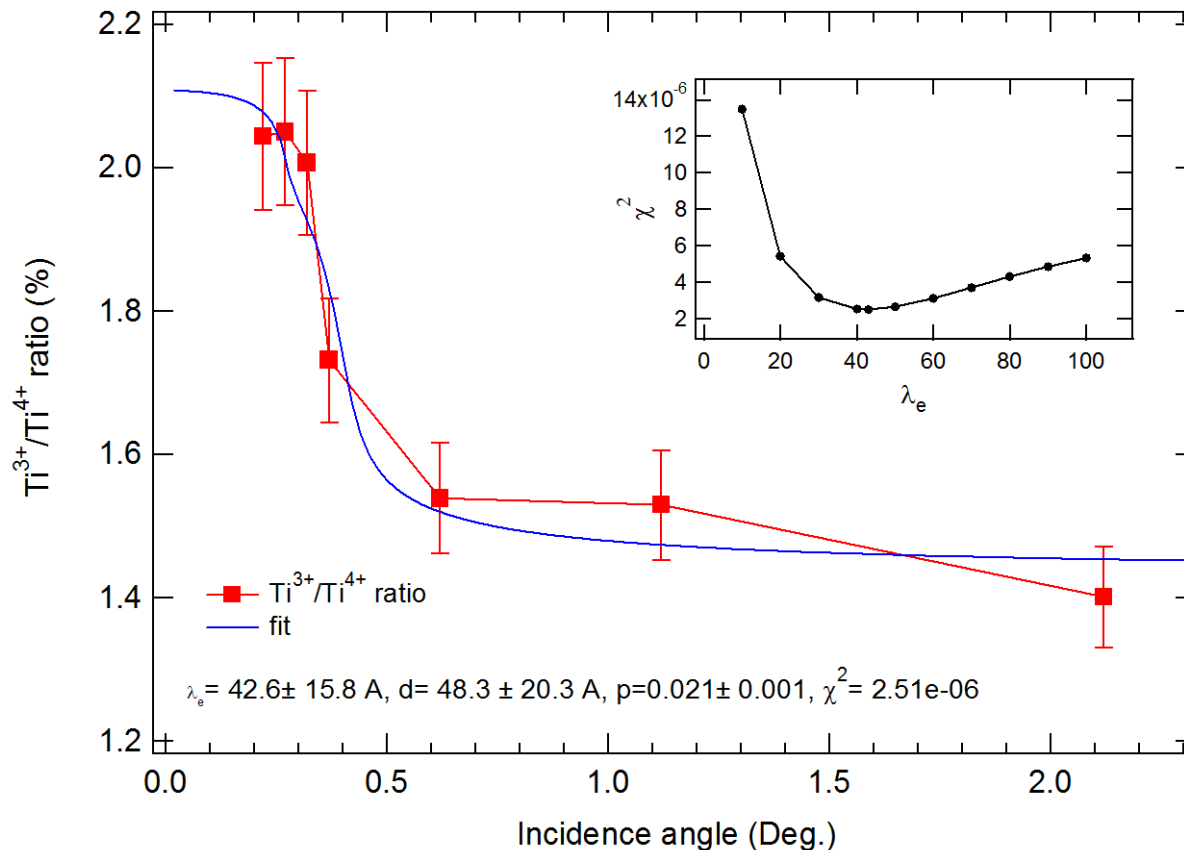
d_2 = 48.3 $\pm$ 20.3 A
~ 12 u.c.

α = 0.021
(Ti^{3+}/T^{4+} in d_2)

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

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

λ_e = 42.6 $\pm$ 15.8 A, d= 48.3 $\pm$ 20.3 A, p=0.021 $\pm$ 0.001, χ^2 = 2.51e-06

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 Fresnel 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