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

Photoemission (I) Spectroscopy

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National Synchrotron Radiation Research Center

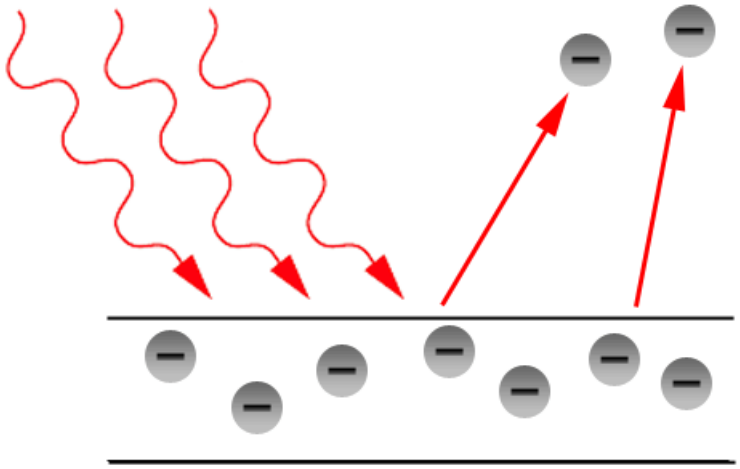
Outline

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

General 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

What is photoemission?

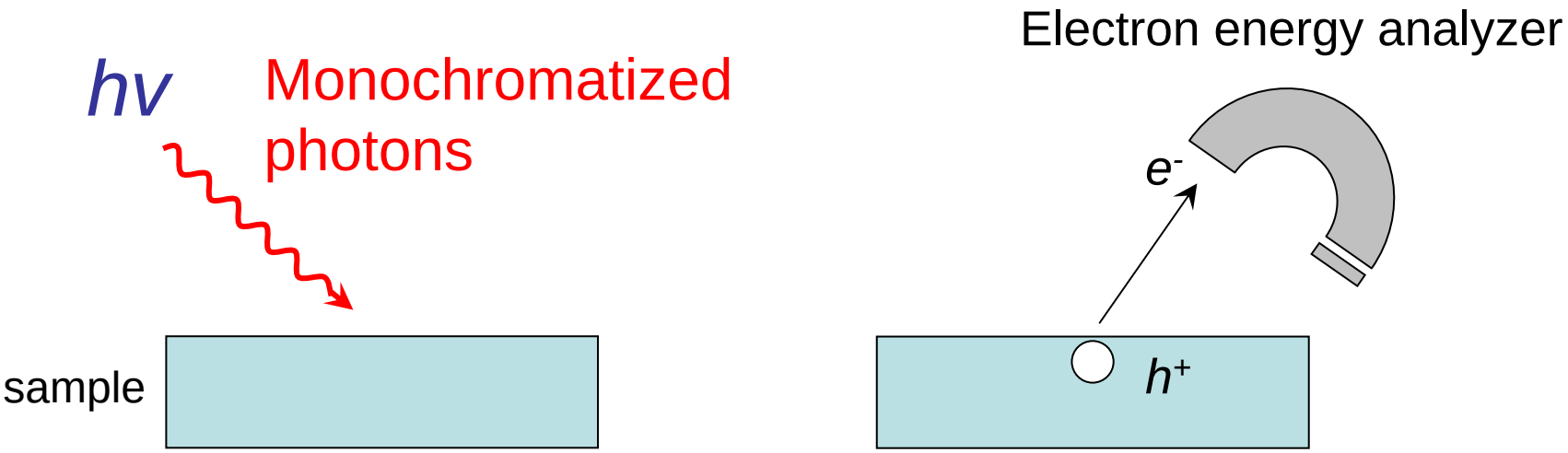


Photon in –> electron out (emission)

What are the samples and probed states?

Atoms	atomic orbitals (states)
Molecules	molecular orbitals
	core level states (atomic like)
Nanoprticles	valence bands/states
	core level states (atomic like)
Solids	valence bands
	core level states (atomic like)

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



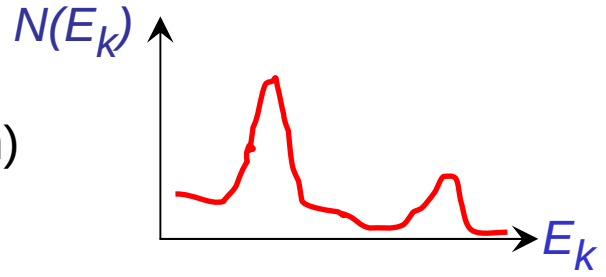
Initial state: ground (neutral) state

Final state: hole (excited) state

Conservation of energy

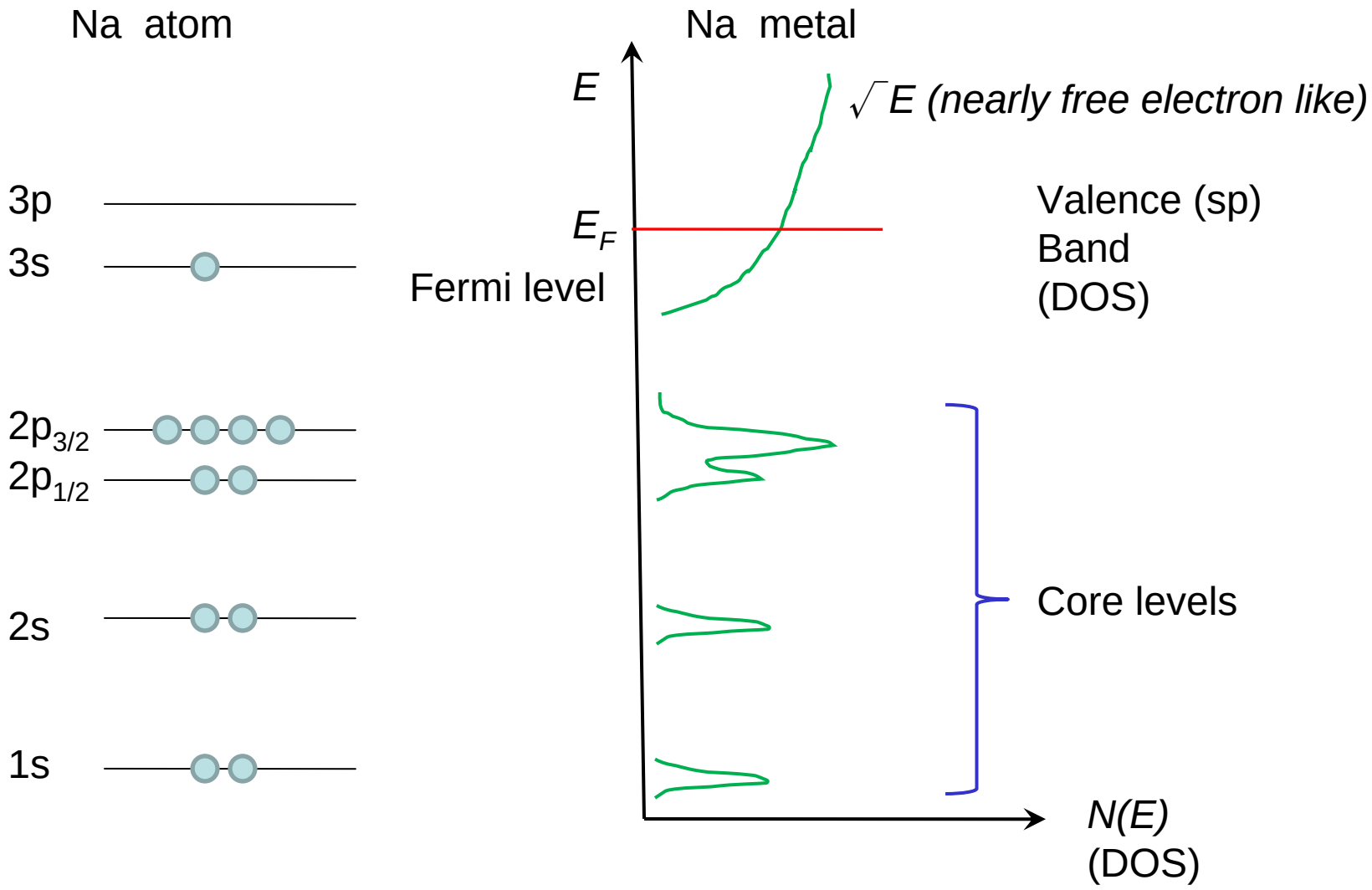
$E_k = h\nu + E_i - E_f$ (most general expression)

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

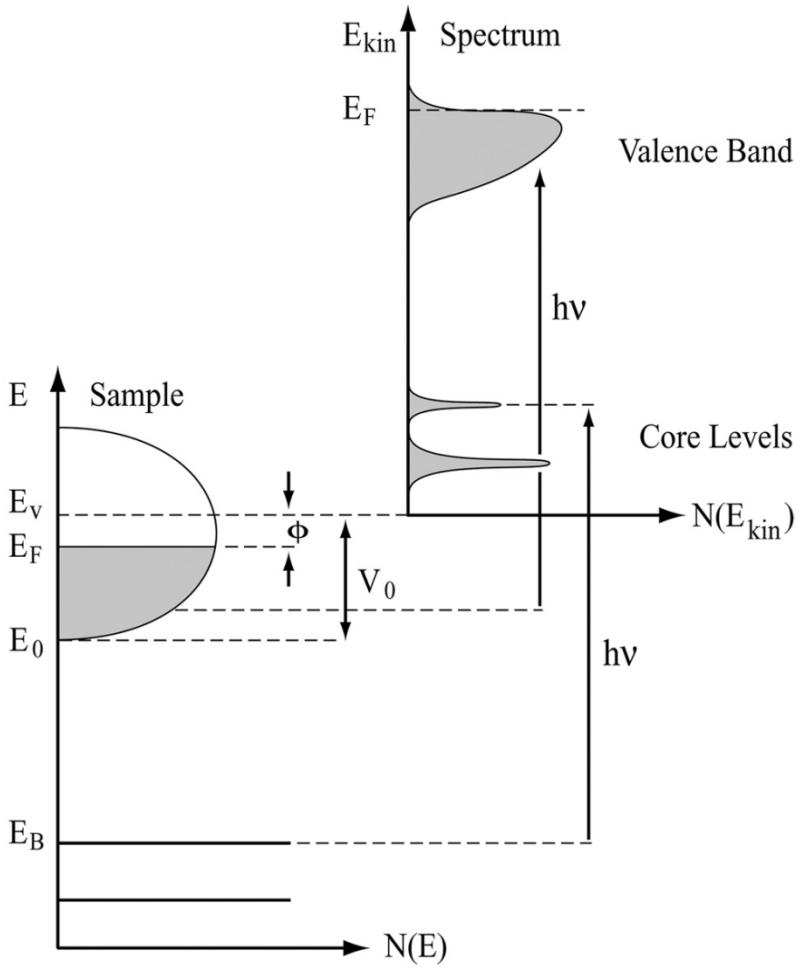


Energy Distribution Curve (EDC) (Spectrum)

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



Energetics in PES



Hufner, Damascelli

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

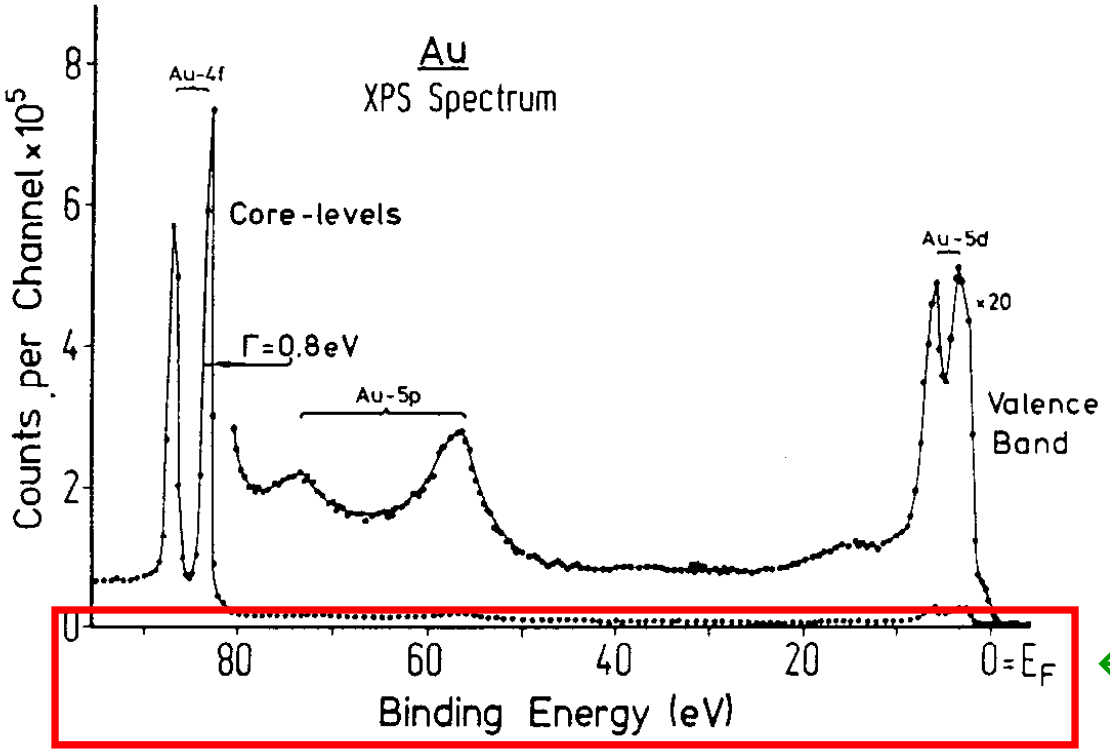
Conservation of energy

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 $E_F = 0$

Usually fixed photon energy
scanning not needed

An XPS Energy Distribution Curve (EDC)



← Most spectra expressed this way

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

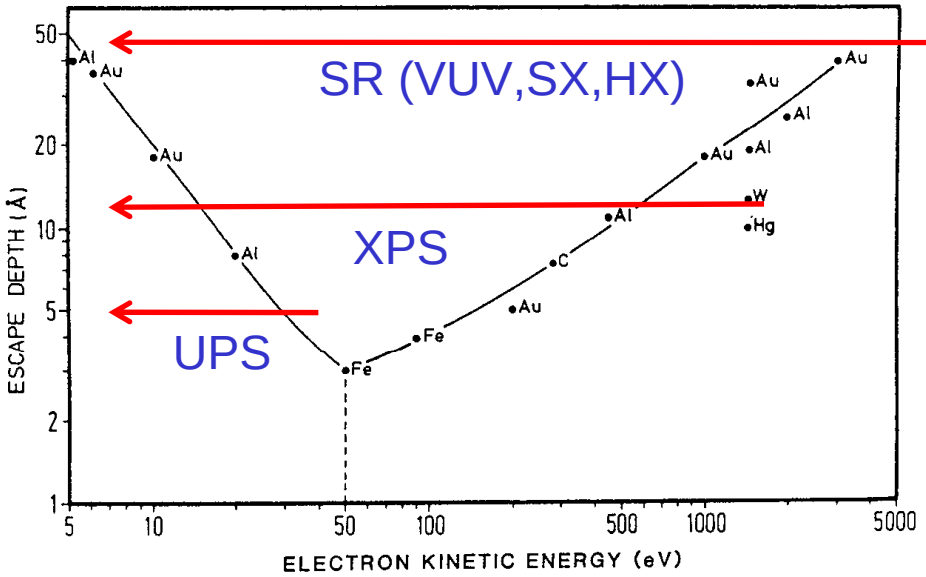
Synchrotron radiation:

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 relative to E_F



Univeral curve

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†

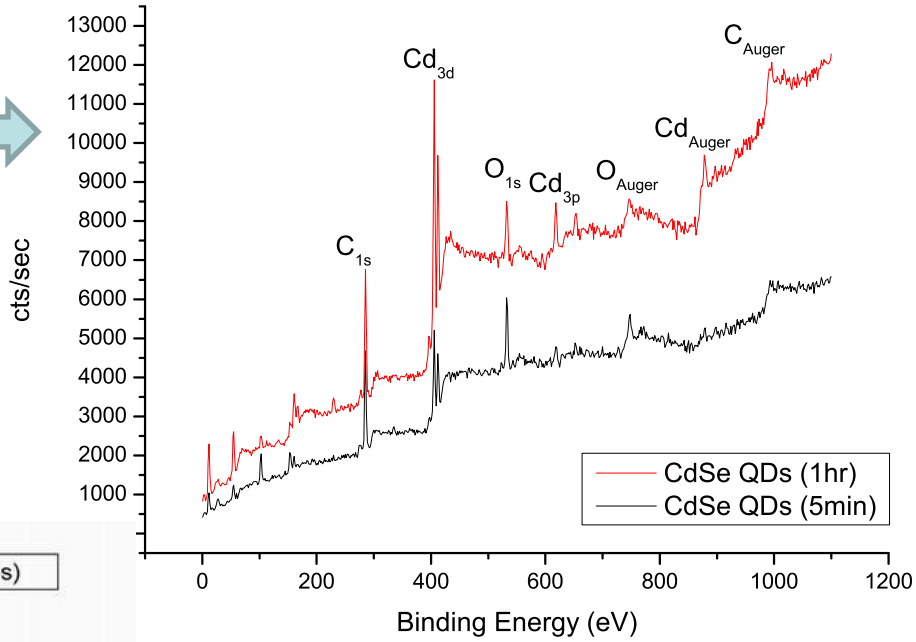
Core level binding energies are characteristic of each orbital of each element

Finger prints

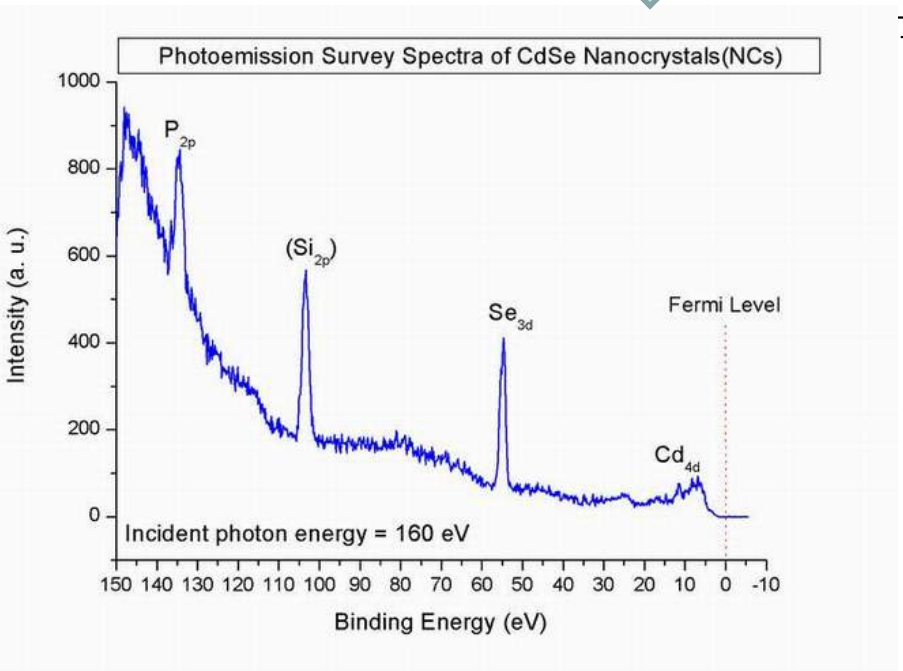
Core level BE independent of photon energy used

Core level photoemission: chemical analysis of elements

ESCA (XPS)
hv = Mg *Kα* = 1253.6 eV

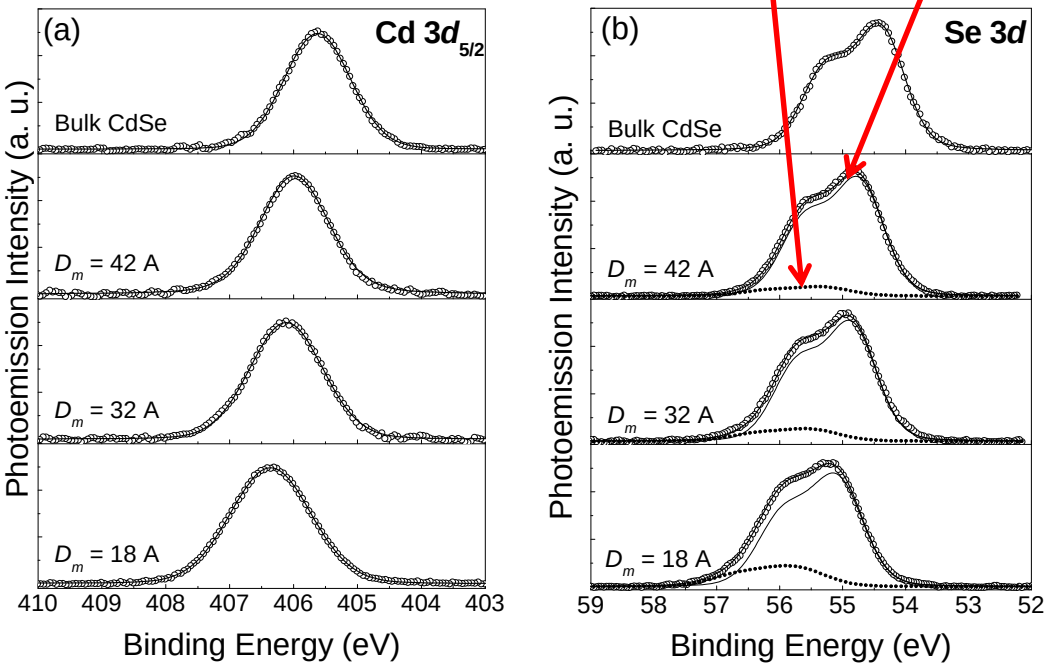


Synchrotron *hv* = 160 eV



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

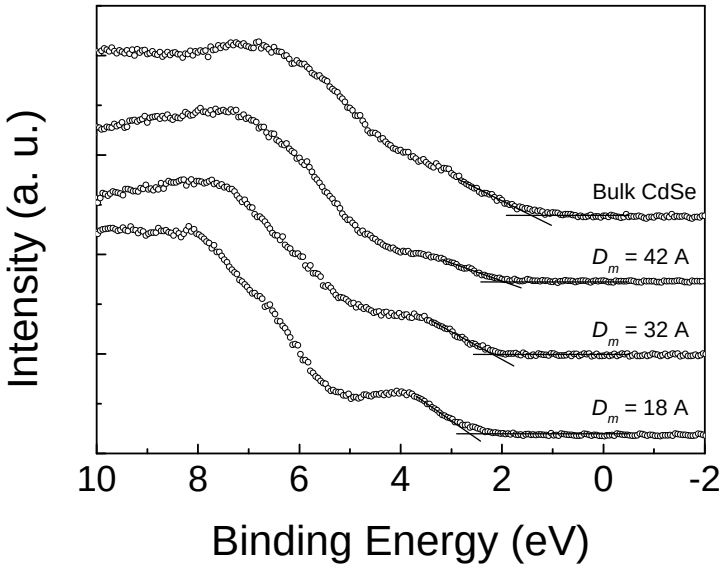
PJW, NSRRC



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:

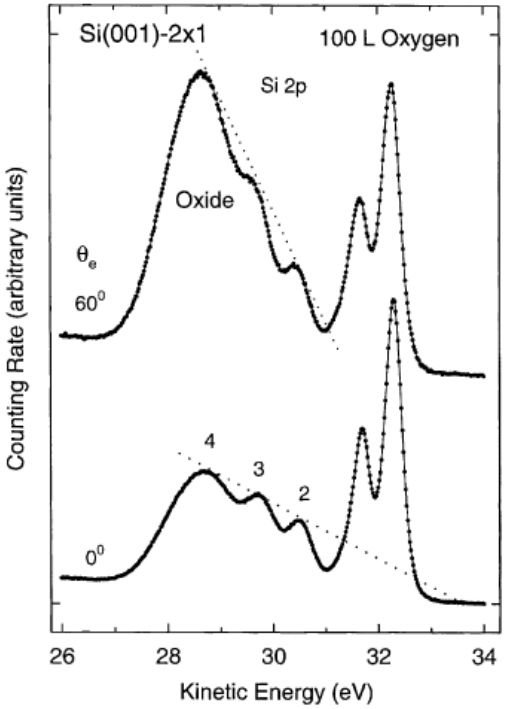
Cd $3d_{5/2}$:	480 eV
Se 3d:	120 eV
Valence band:	50 eV

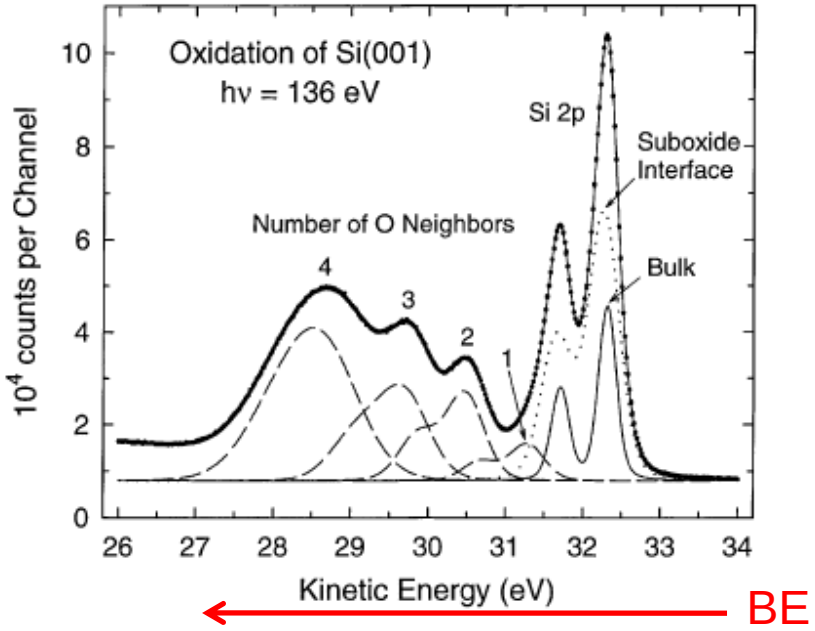
E_k ~ 45-74 eV, most surface sensitive

Wu, PRB 2007 NSRRC

Core level photoemission: chemical shift

higher oxidation state
=> higher BE





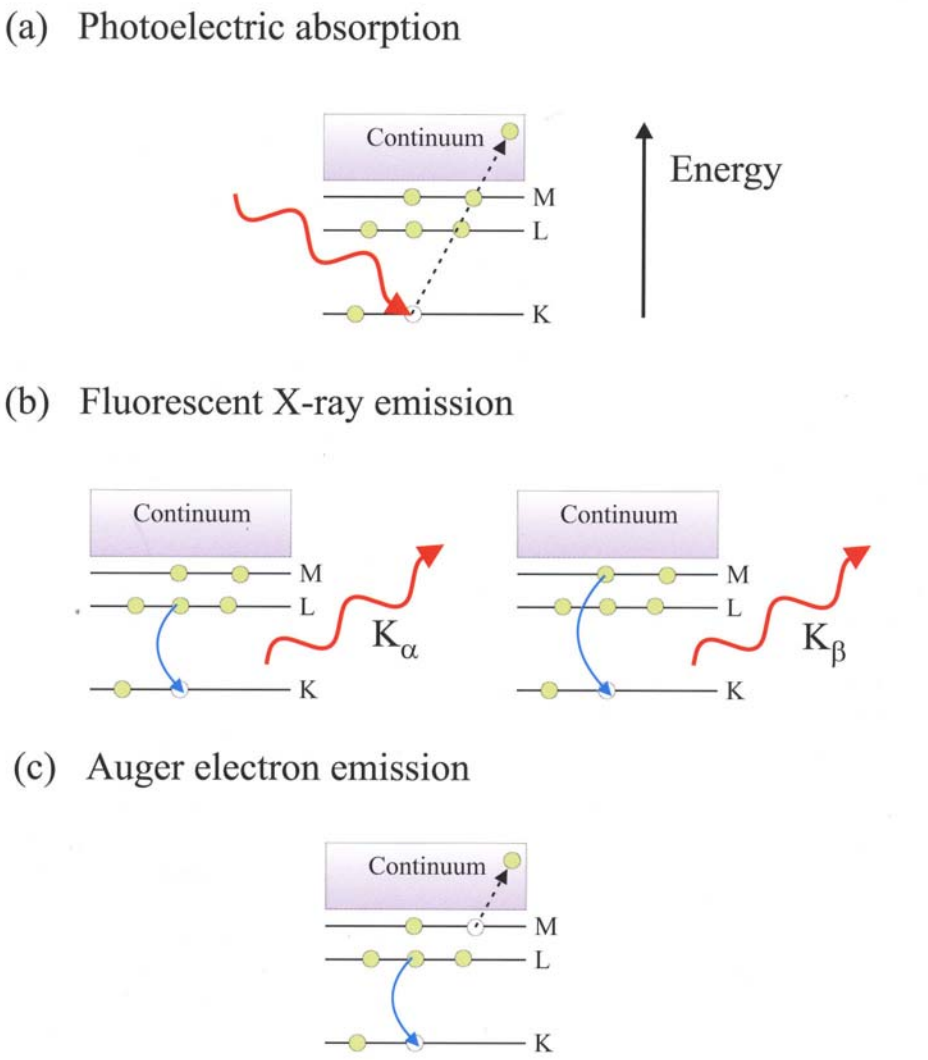
higher emission angle
→ more surface sensitive
(IMFP)

Pi, SS 2001 NSRRC

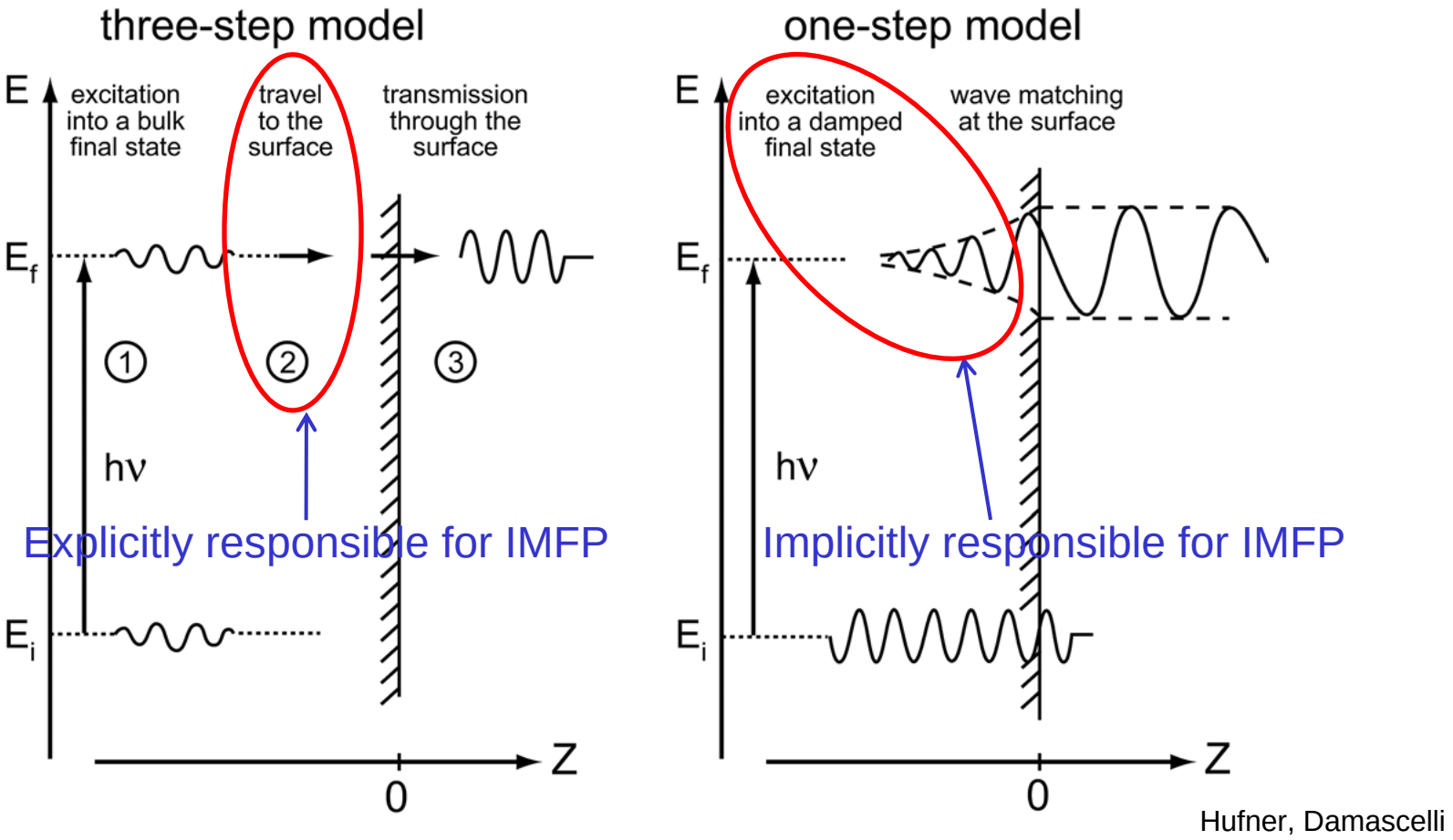
Auger Electron Spectroscopy

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)



Photoemission Process

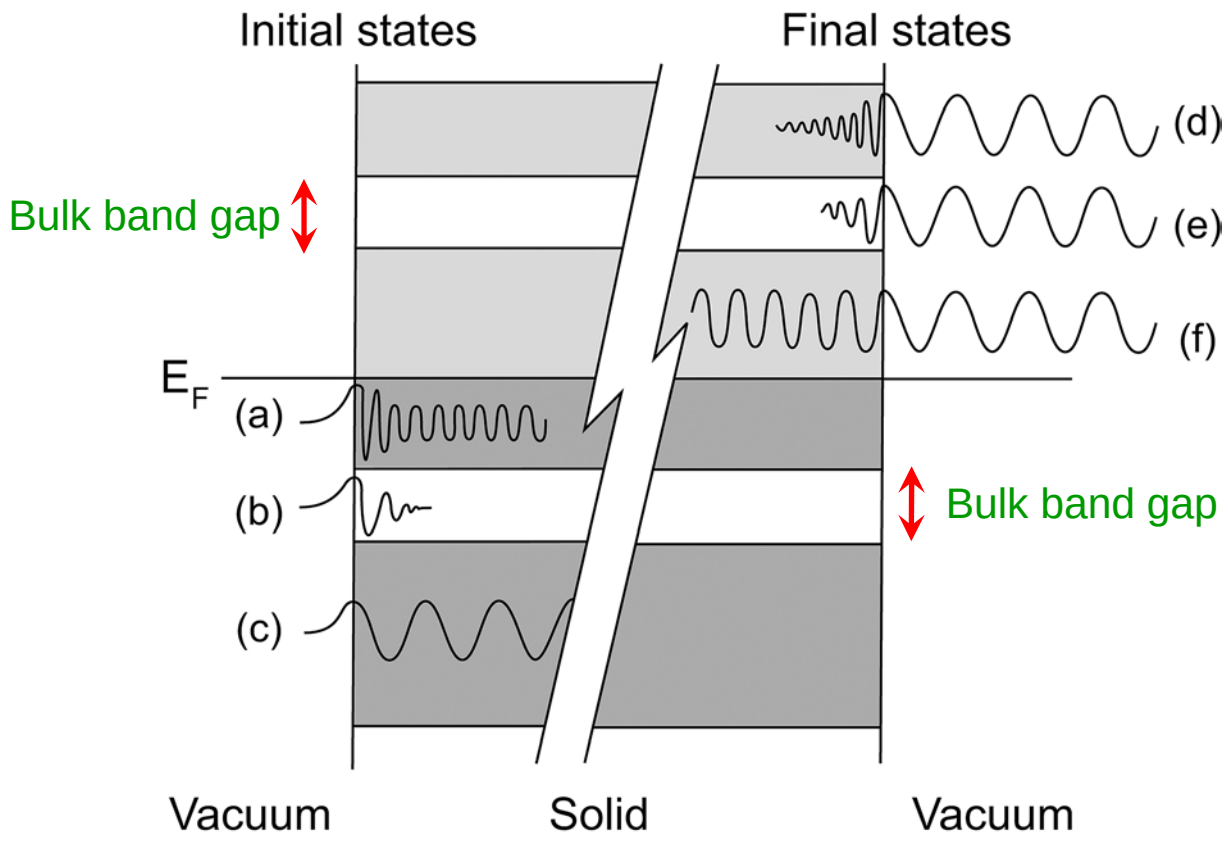


Hufner, Damascelli

Conceptually intuitive,
Simple calculation works

Rigorous,
requires sophisticated calculation

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

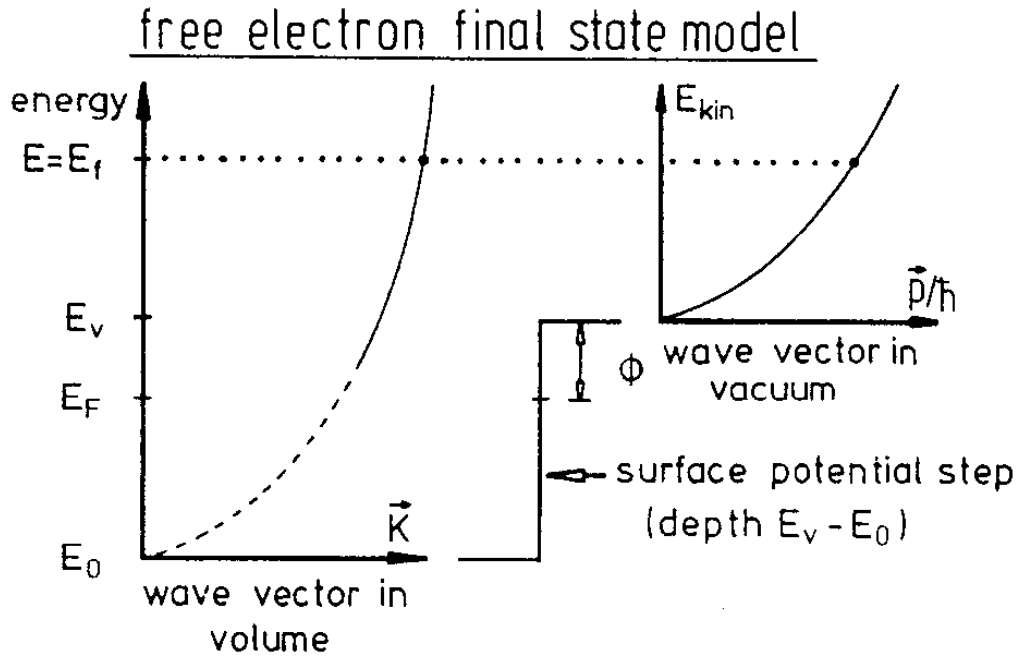


(a) Surface resonance
(b) Surface state
(c) Bulk Bloch state

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

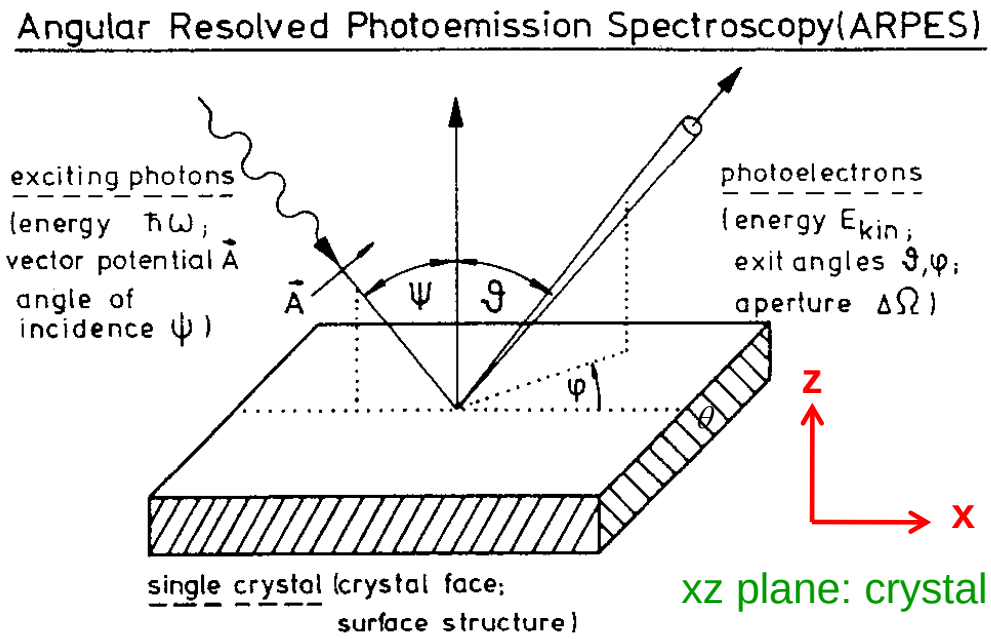
Electron kinetic energy inside and outside of solids

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 Spectroscopy (ARPES)

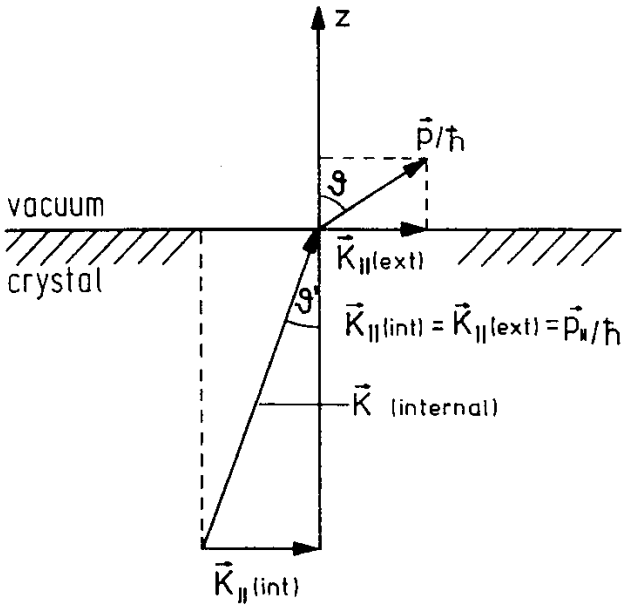


xz plane: crystal symmetry plane

Electron emission angle: Θ

Photon incident angle: ϕ, *s*- and *p*-polarization

Conservation of linear momentum parallel to the surface



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

$$k_{//}(\text{Å}^{-1}) = 0.5123\sqrt{E_k(eV)} \cdot \sin\theta$$

$k_{||}$(inside) = $k_{||}$(outside)

Conservation of liner momentum

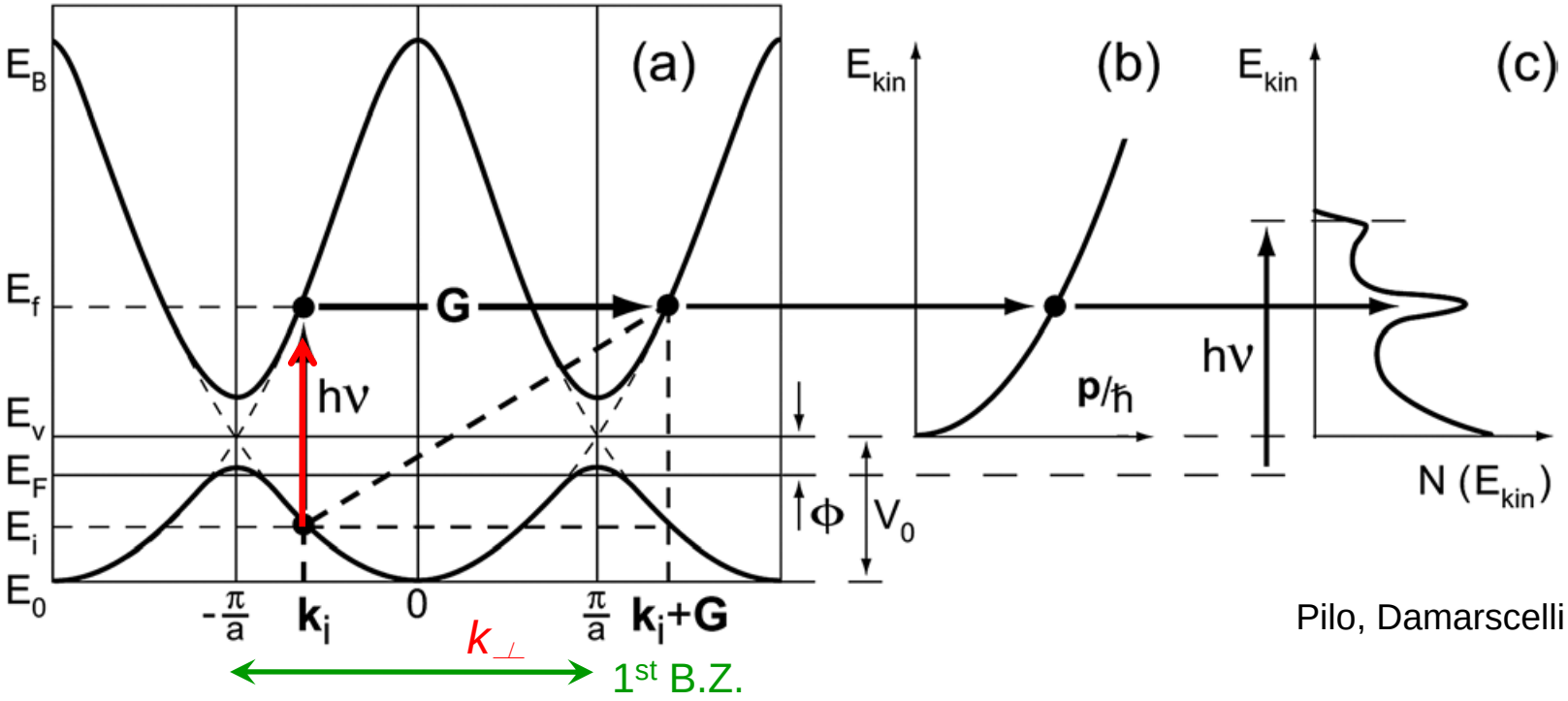
Important for 3D and 2D band mapping

$k_{\perp}$ (inside) $\neq$ $k_{\perp}$ (outside) because of inner potential

Ultimately to deduce band dispersion $E(k_{\perp})$ or $E(k_{\perp},k_{||})$

Normal emission: θ = 0, or $k_{||}$ = 0, most used detection geometry

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 *hv* at normal emission to map out $E(k_\perp)$

Bulk band structure and Fermi surfaces

Cu

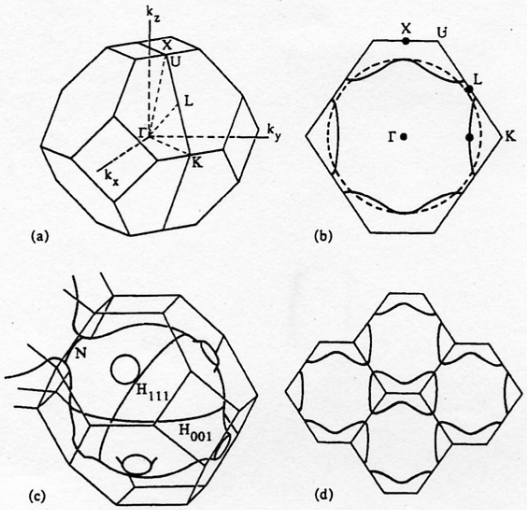


Fig. 10–15 Various aspects of the Fermi surface of Cu. (a) The Brillouin zone of an fcc lattice with some special points labeled. (b) A (110) section of the Brillouin zone. See the text for the meaning of the internal curves. (c) The proposed Fermi surface of Cu. (d) The extended zone picture of a (110)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

Fermi surfaces:

Electron pockets and hole pockets
Related to
Hall coefficient
Electric conductivity
Magnetic susceptibility

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

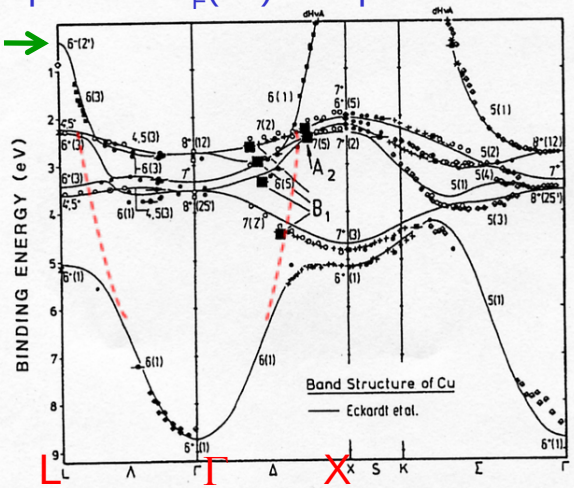


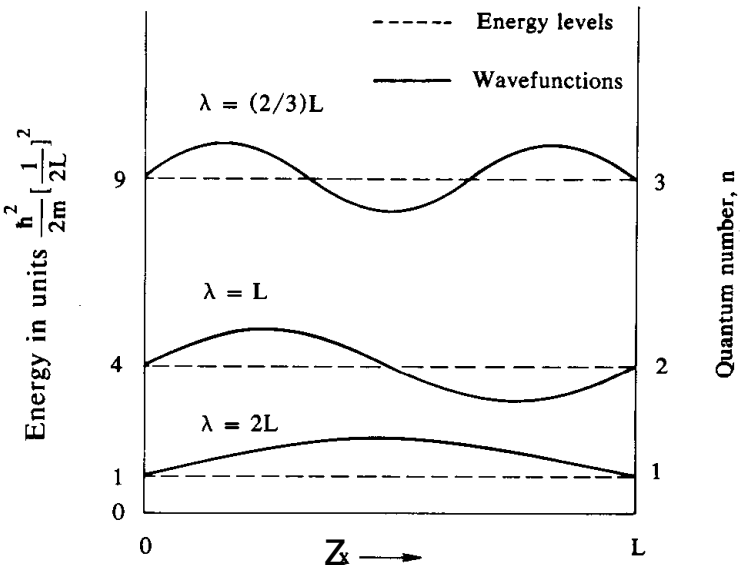
Fig.7.17. Occupied part of the band structure of Cu[7.39] with data points from various sources and a theoretical result [7.53]. Also shown (squares) are the two A_2 points and the four B_1 points from Fig.7.16

(111) ← → (001)

Hufner

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

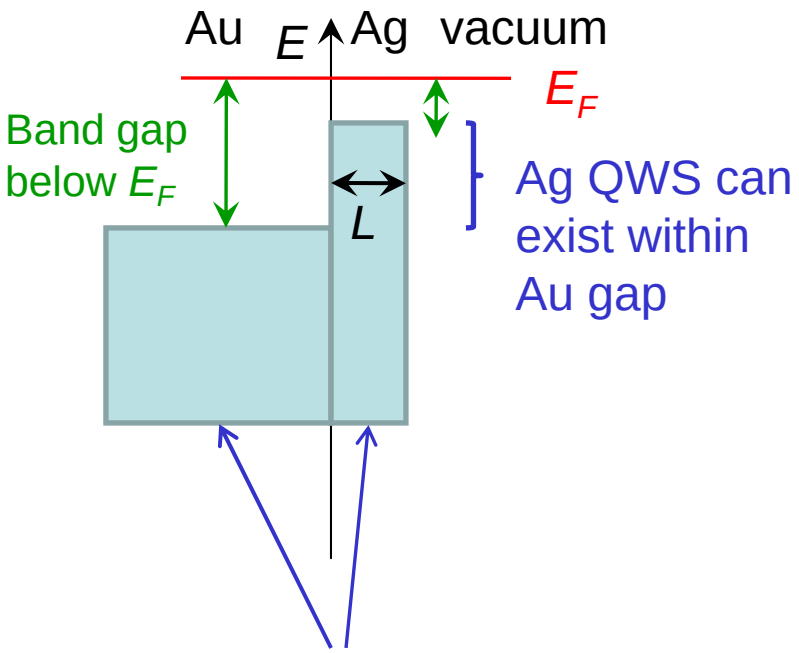
Quantum well states: manifestation of particle in a box in real materials



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

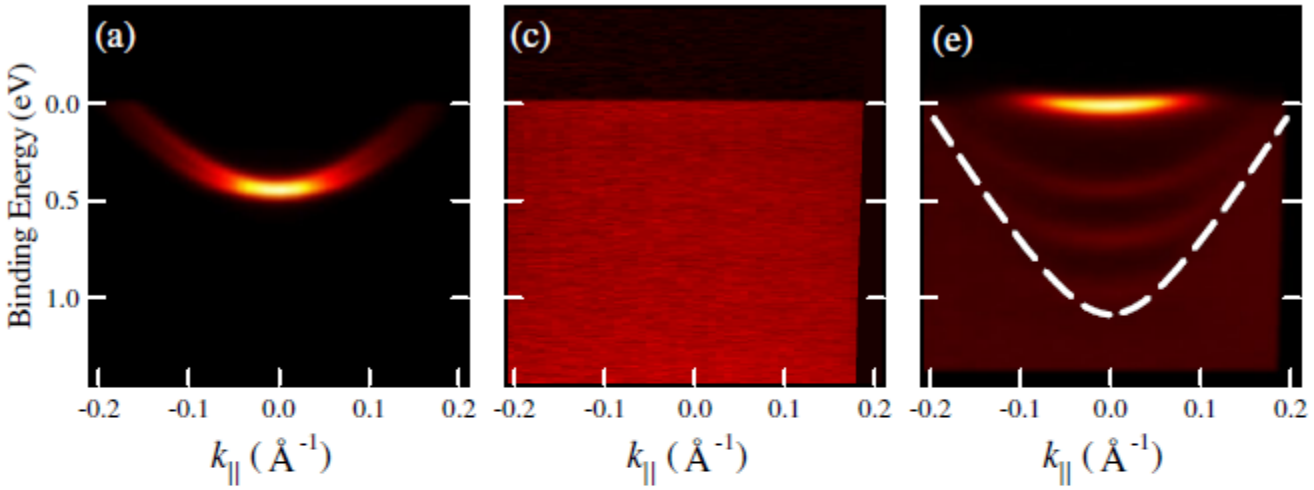
Nearly free electron like in xy-plane

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



Bulk projected bands along ΓL of Au and Ag, respectively

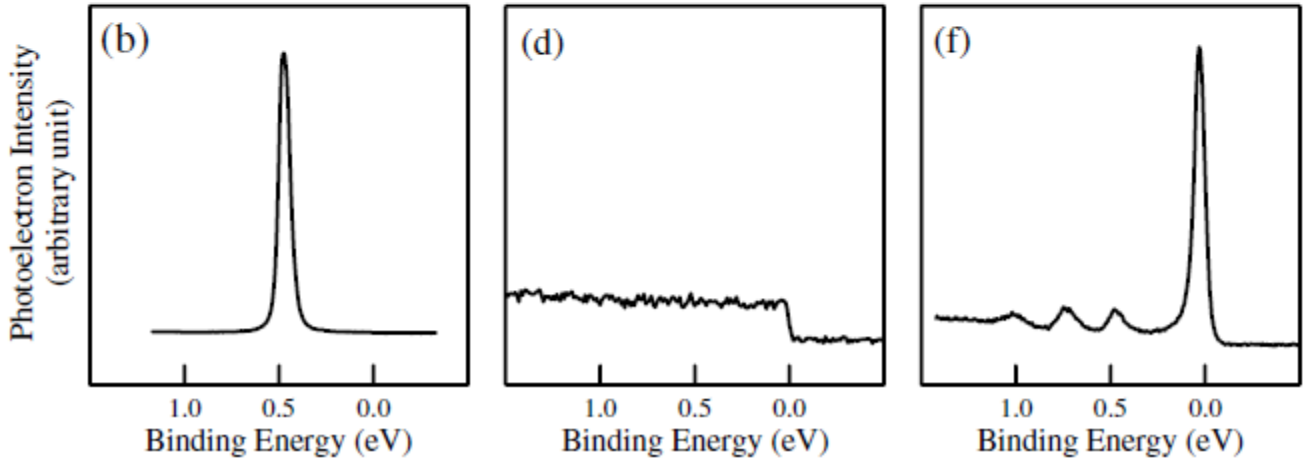
2D Int. plots



← Ag S.S.

Ag QWS

$k_{||}$ = 0 EDCs

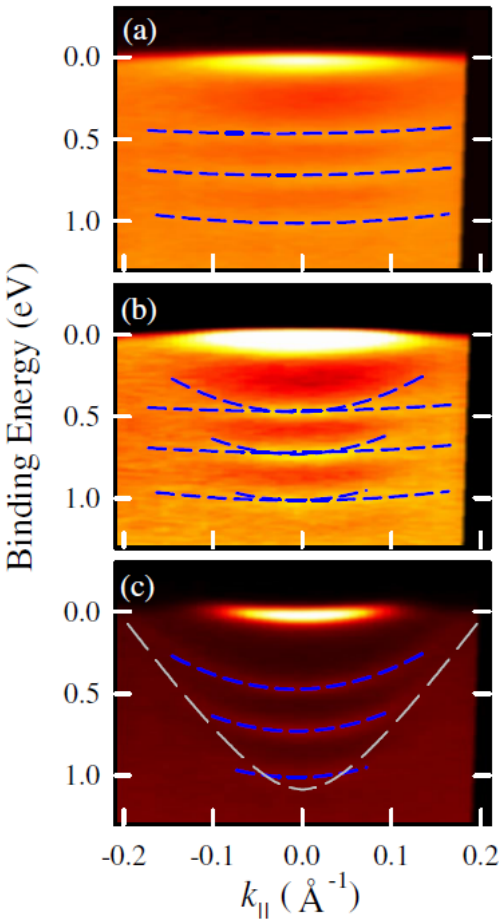


Luh et al. PRL 2008 NSRRC BL21B1

Clean Au(111) surface state

Deposit 22 ML Ag at 37 K disordered form

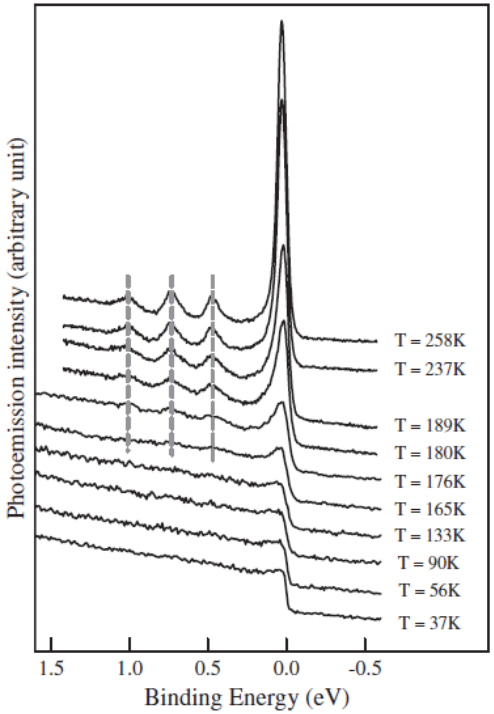
Anneal to 258 K Atomically flat 22 ML thin film



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

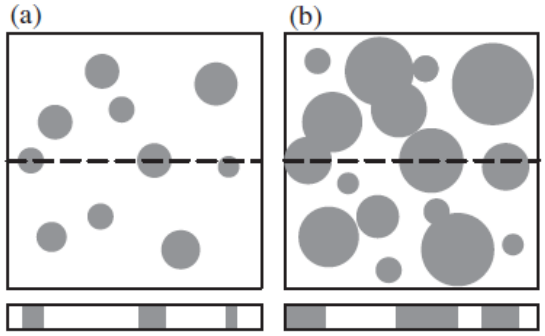
Anneal to 189 K
Coexistence of two kinds of dispersion

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



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

Proposed growth model



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 Σ”

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

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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

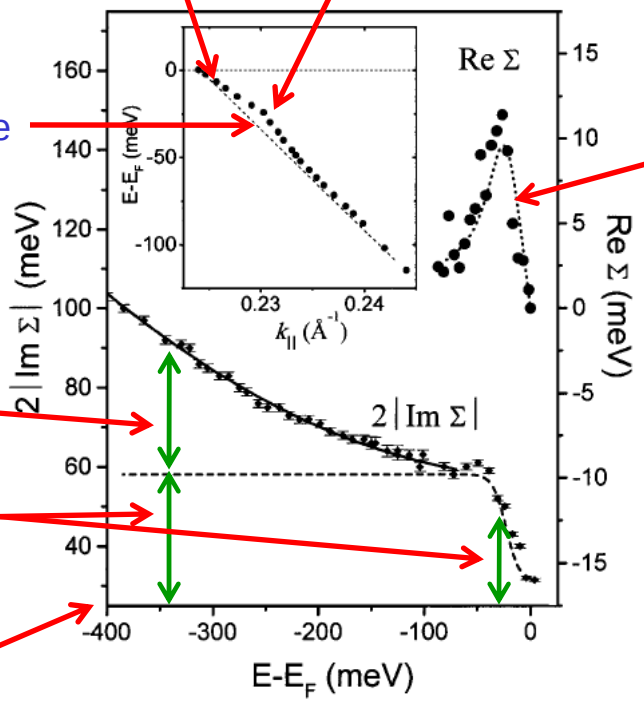
Featureless single particle dispersion curve

Peak position – single particle curve

Width due to electron-electron scattering ~ ω^2

Width due to electron-phonon scattering

Const bkg width due to impurities



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

Photoemission cross section in single particle approximation (1st step in 3-step model, inside bulk)

$$\frac{d\sigma}{d\Omega} \propto \sum \left| \left\langle \Psi_f \left| A \cdot p \right| \Psi_i \right\rangle \right|^2 \cdot \delta\left(E_f - E_i - h\nu\right)$$

$$M_{fi} = \left\langle \Psi_f \left| A(r) \cdot p \right| \Psi_i \right\rangle \cong A(0) \cdot \left\langle \Psi_f \left| p \right| \Psi_i \right\rangle \propto A(0) \cdot \left\langle \Psi_f \left| r \right| \Psi_i \right\rangle$$

dipole approximation

A : polarization vector

Ψ_i : initial state (orbital) wave function (1s, 2p, valence states etc.)
contain orbital symmetry information

Ψ_f : final state (orbital) wave function ~ exp($i\boldsymbol{k}\cdot\boldsymbol{r}$) for high kinetic energy photoelectrons, no orbital symmetry retains (non-resonance photoemission)

(orbital symmetry in final state is important in near edge absorption measurements (XAS) and in intermediate state in resonance photoemission)

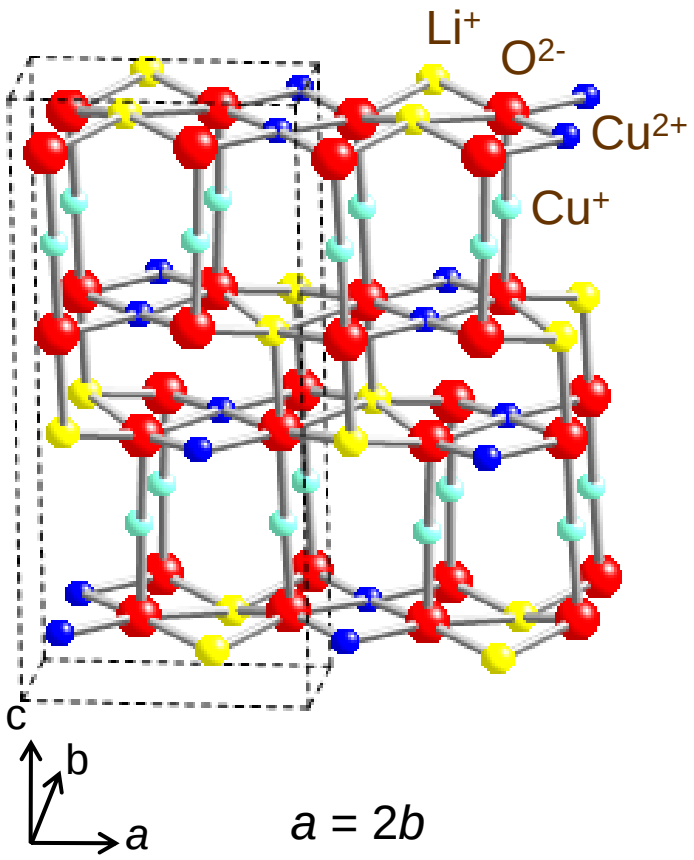
Dipole transition rule: $\Delta l = \pm 1$

Symmetry selection rule for initial (valence) state governed by matrix element

e.g. suppose $A(0) = Ax$, $\langle e^{ikz} \mid x \mid \psi_i(x) \rangle = 0$ if $\psi_i(-x) = +\psi_i(x)$

Important for crystalline samples

Symmetry of states in ARPES determined by selection rule example: LiCu2O2



$Cu^{2+}O^{2-}_2$ chains along b-axis built by edge sharing $Cu^{2+}O^{2-}_4$ plaquettes

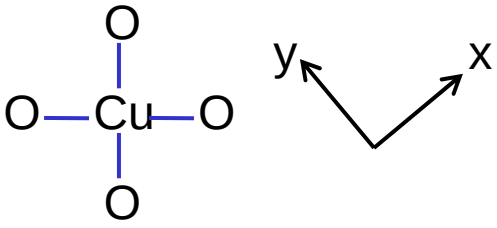
Cu^{2+} : $3d^9$ → spin-1/2

Quasi-1D spin-1/2 chain

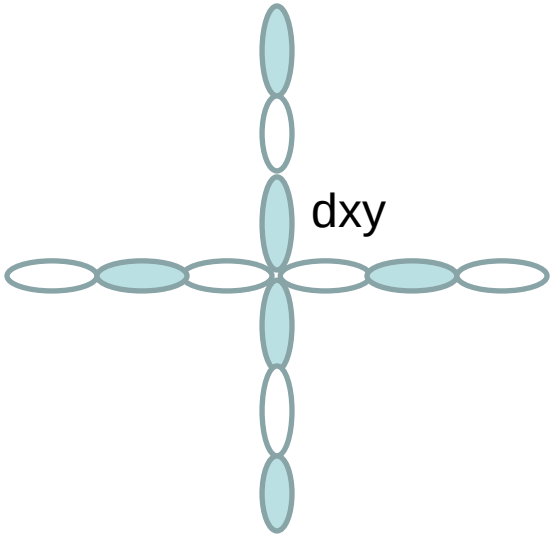
Coexistence of spin-spiral long range order with ferroelectricity → multiferronic

Ideal spin-1/2 1D chain system will have spin-charge separation of photo-hole decay
Does it happen on LiCu2O2?
Must be checked by ARPES
(not discussed further)

Will focus on symmetry of states determined by ARPES with polarization

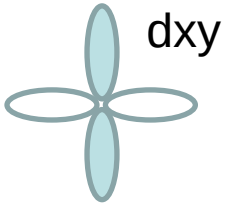


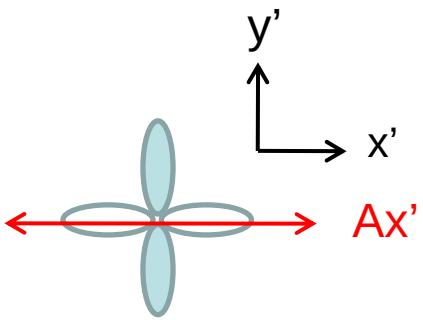
Basic building unit: CuO4 planar plaquette



Highest energy state:
Cu 3dxy and O 2p antibonding (AB) state

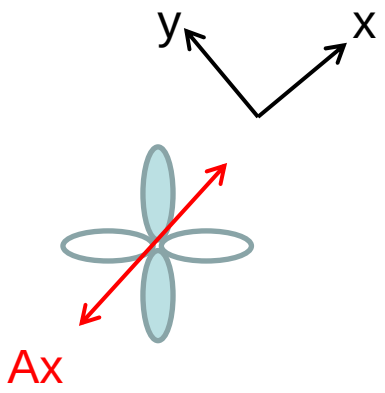
Still keeps dxy symmetry





Normal emission |f> = exp(ikz) even to all symmetry op
[i> even to y’z-plane, Ax’ odd to y’z-plane
<f| Ax’ |i> = <+| - | +> = 0, forbidden

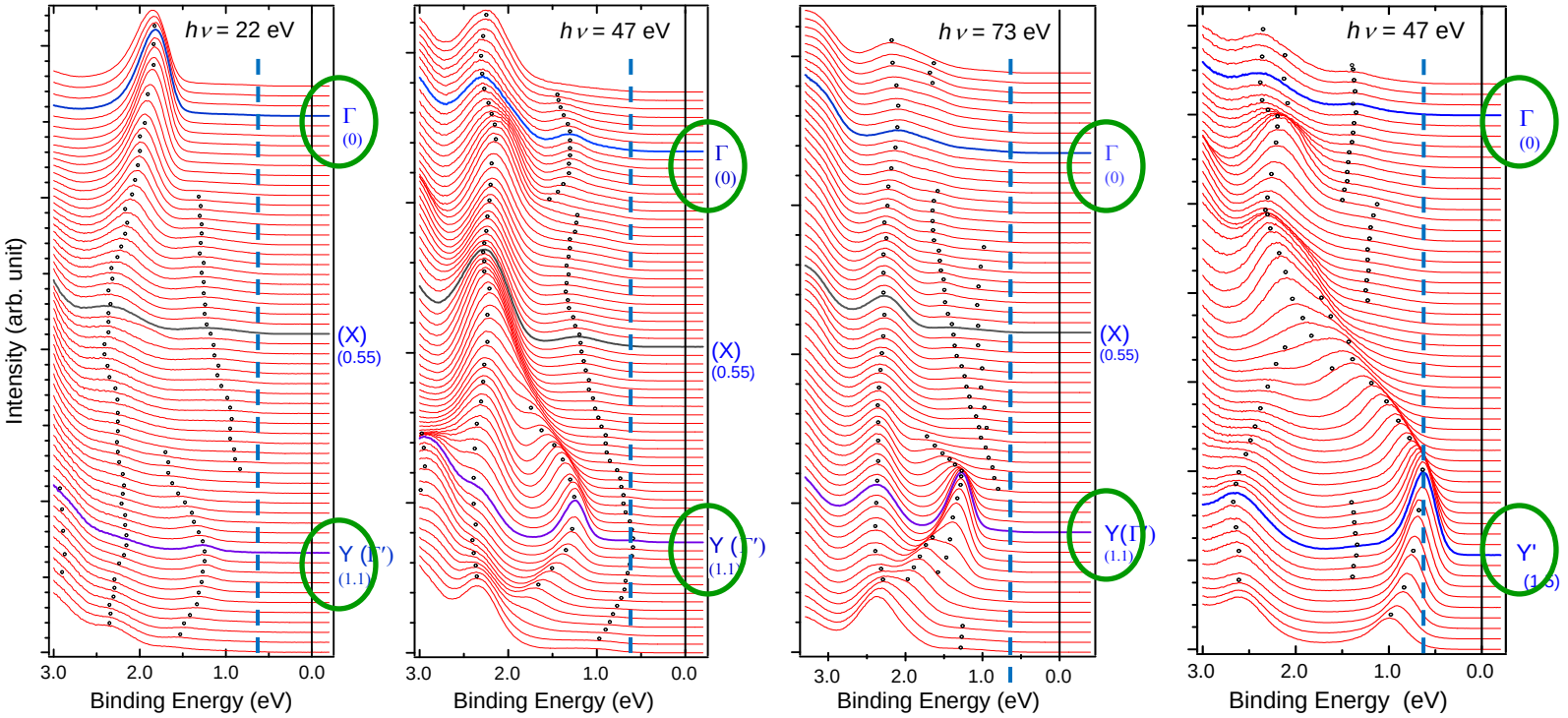
Off-normal emission [f> = exp(ikz+kx’) even to x’z-plane
|i> even to x’z-plane, Ax’ even to x’z-plane
<f| Ax’ |i> = <+| + | +> != 0, allowed

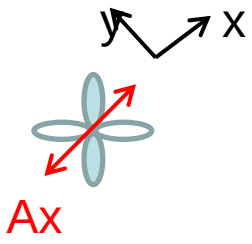


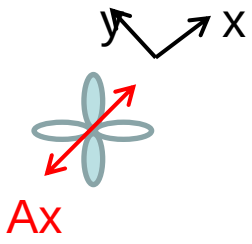
Normal emission [f> = exp(ikz) even to all symmetry op
[i> odd to xz-plane, Ax even to xz-plane
<f| Ax |i> = <+| + |-> = 0, forbidden

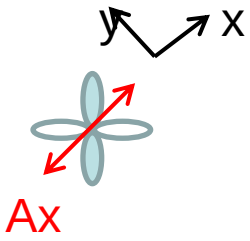
Off-normal emission |f> = exp(ikz+ikx) even to xz-plane
|i> odd to xz-plane, Ax even to xz-plane
<f| Ax |i> = <+| + |-> = 0, forbidden

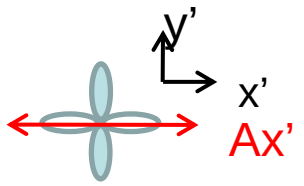
Focus on B.E. = 0.7 eV peak at Y’











The highest energy peak at 0.7 eV has dxy symmetry!

ARPES for valence band PE uses primarily VUV light because

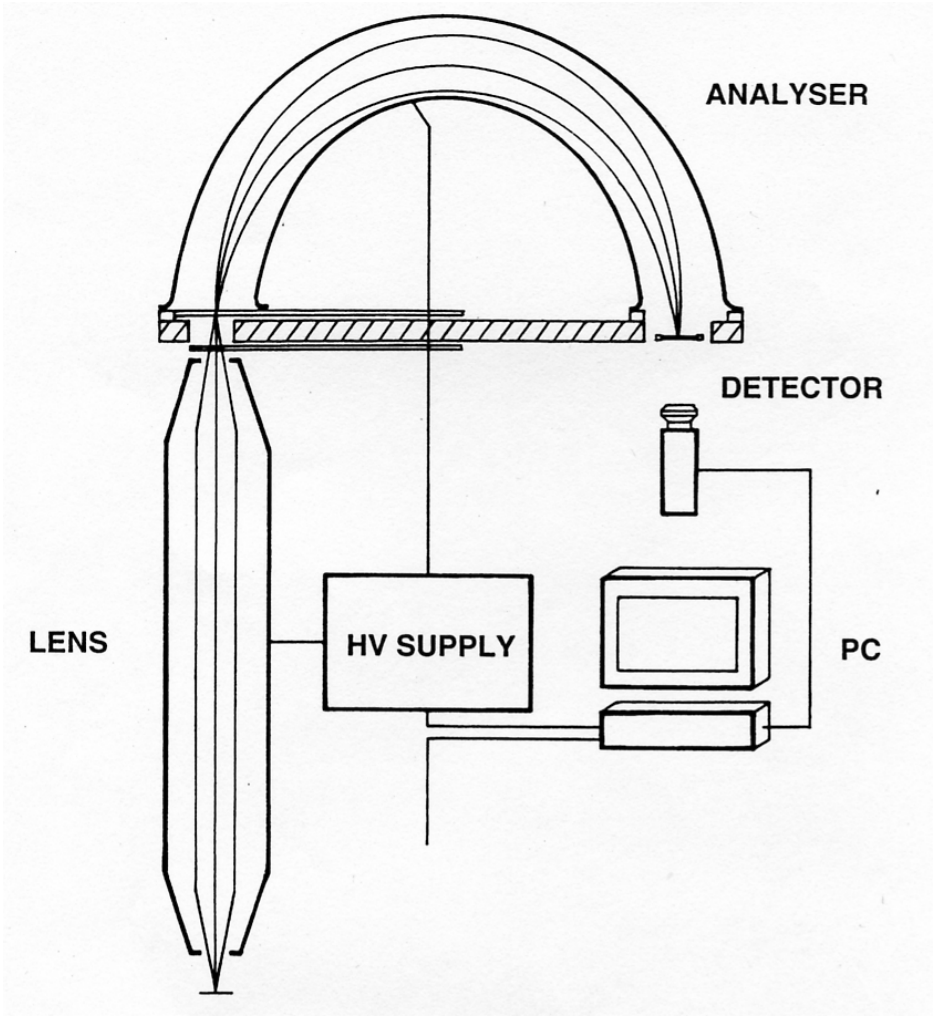
1. Better absolute photon energy resolution for most BLs designed as const $\Delta E/E$.
2. Better photoionization cross section at low photon energy.
3. Better momentum resolution for a given angular resolution.

$$\Delta k_{||} = 0.5123 \sqrt{(Ek)} \cos(\theta) \Delta\theta$$

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

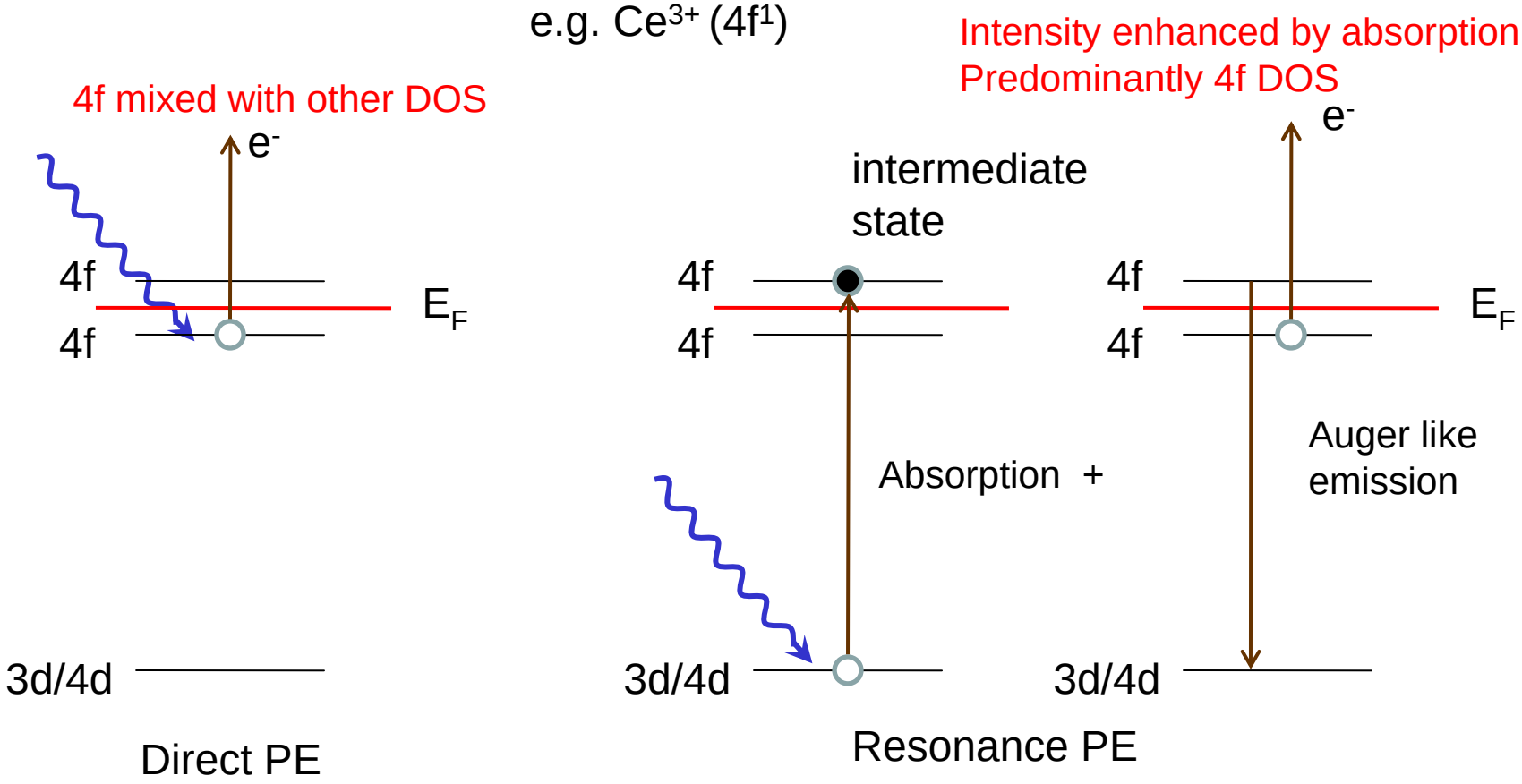
Hemispherical electron energy analyzer



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

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

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



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.

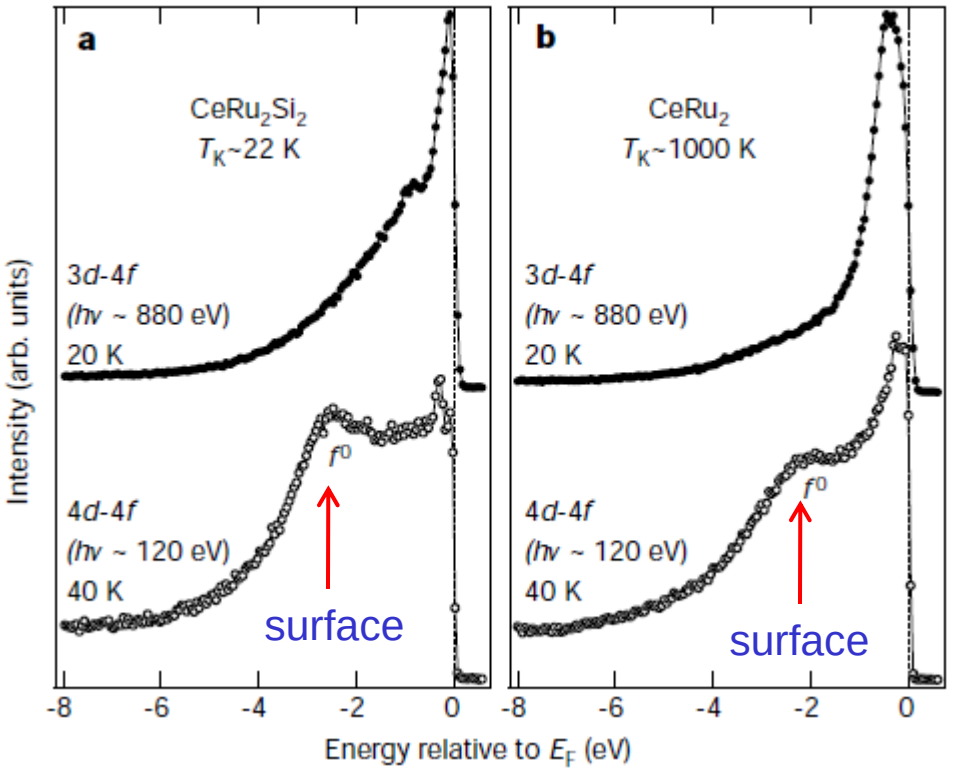
Need larger IMFP by using higher energy photons to enhance bulk sensitivity.

letters to nature

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*



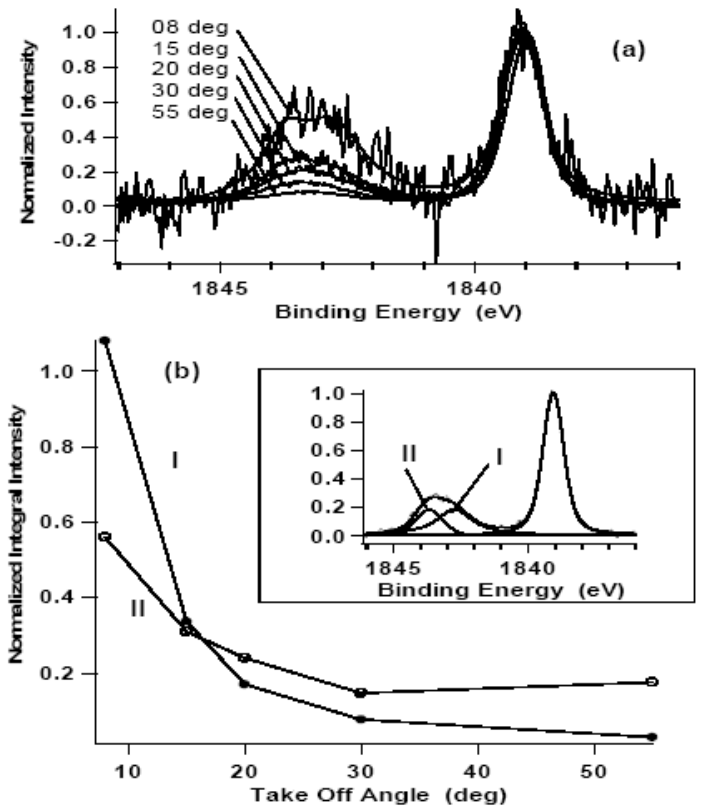
By using Ce 3d → 4f Res. PE near 880 eV surface 4f component becomes greatly reduced compared to 4d → 4f Res. PE near 120 eV, the resulting spectra are closer to true bulk 4f DOS.

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

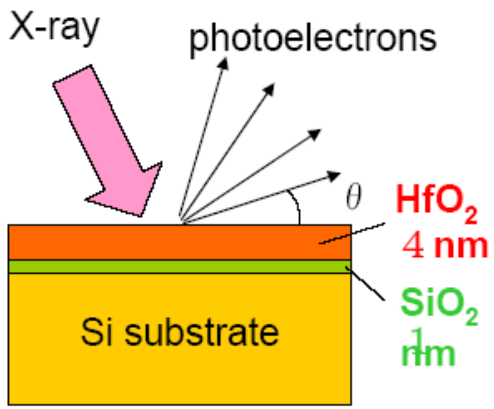
HArd X-ray PhotoEmission Spectroscopy (HAXPES)

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.

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

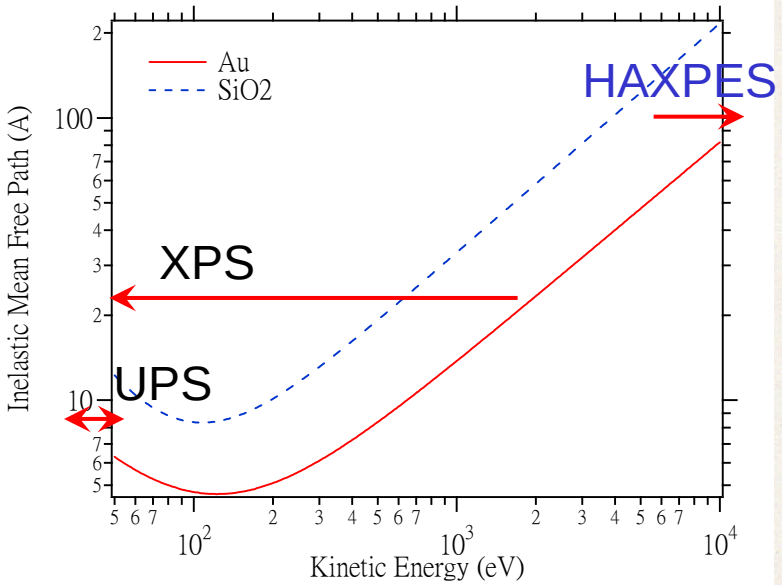
Take-off angle dependence => non-destructive depth profile

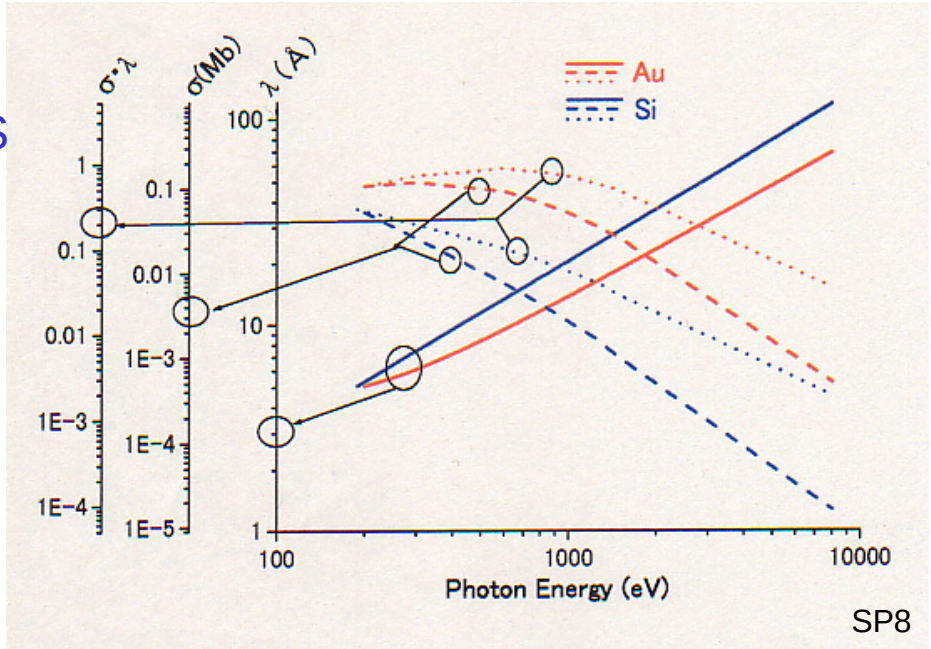
Can probe buried interface at 35 nm ! (achievable only by hard x-ray PE)

NSRRC HAXPES project at SPring-8

Why Hard X-rays?

Electron IMFP (probing depth) and Cross section





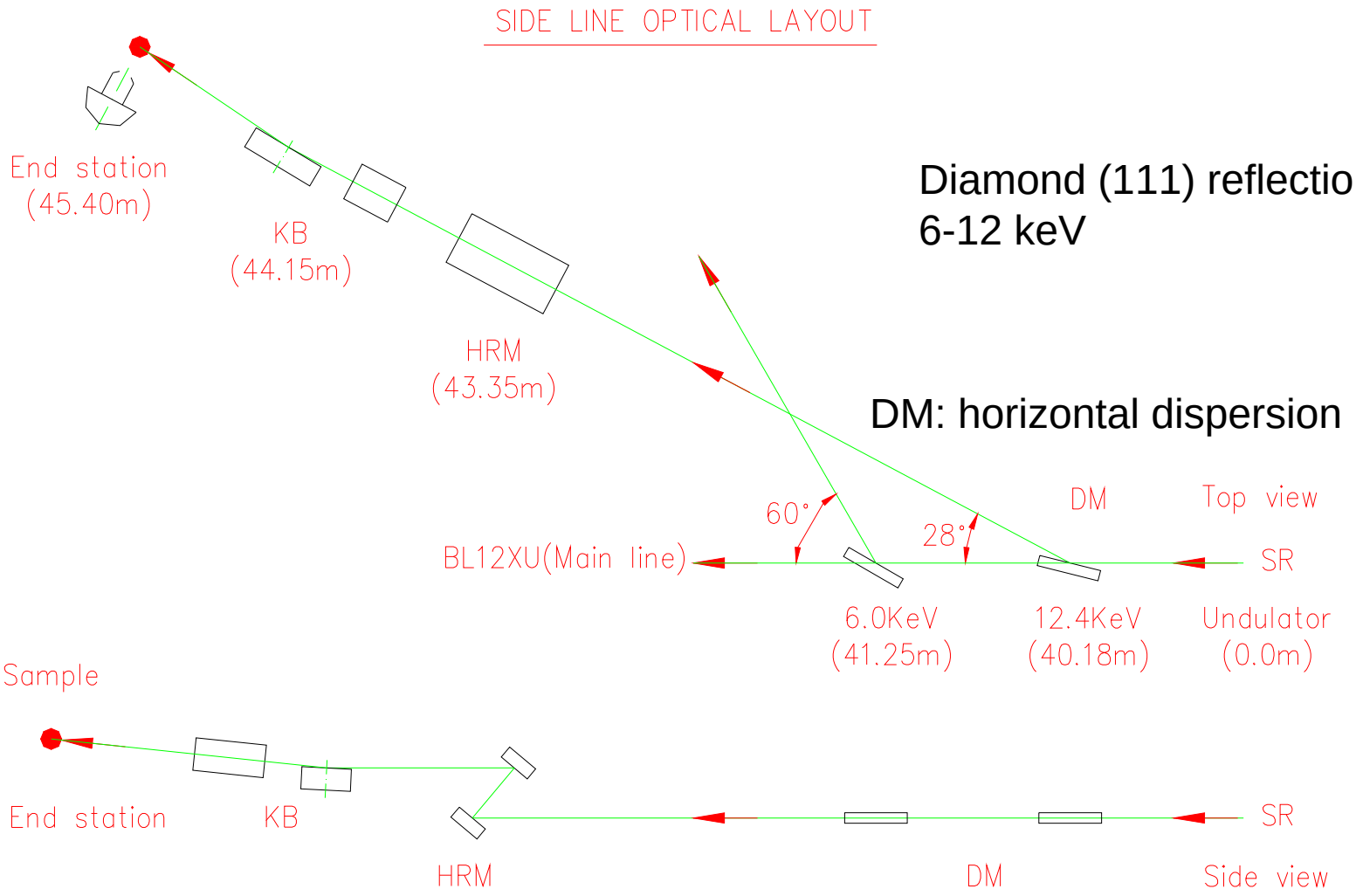
Higher Ek for deeper probing depth or more bulk sensitivity, for strongly correlated systems and interface properties

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!

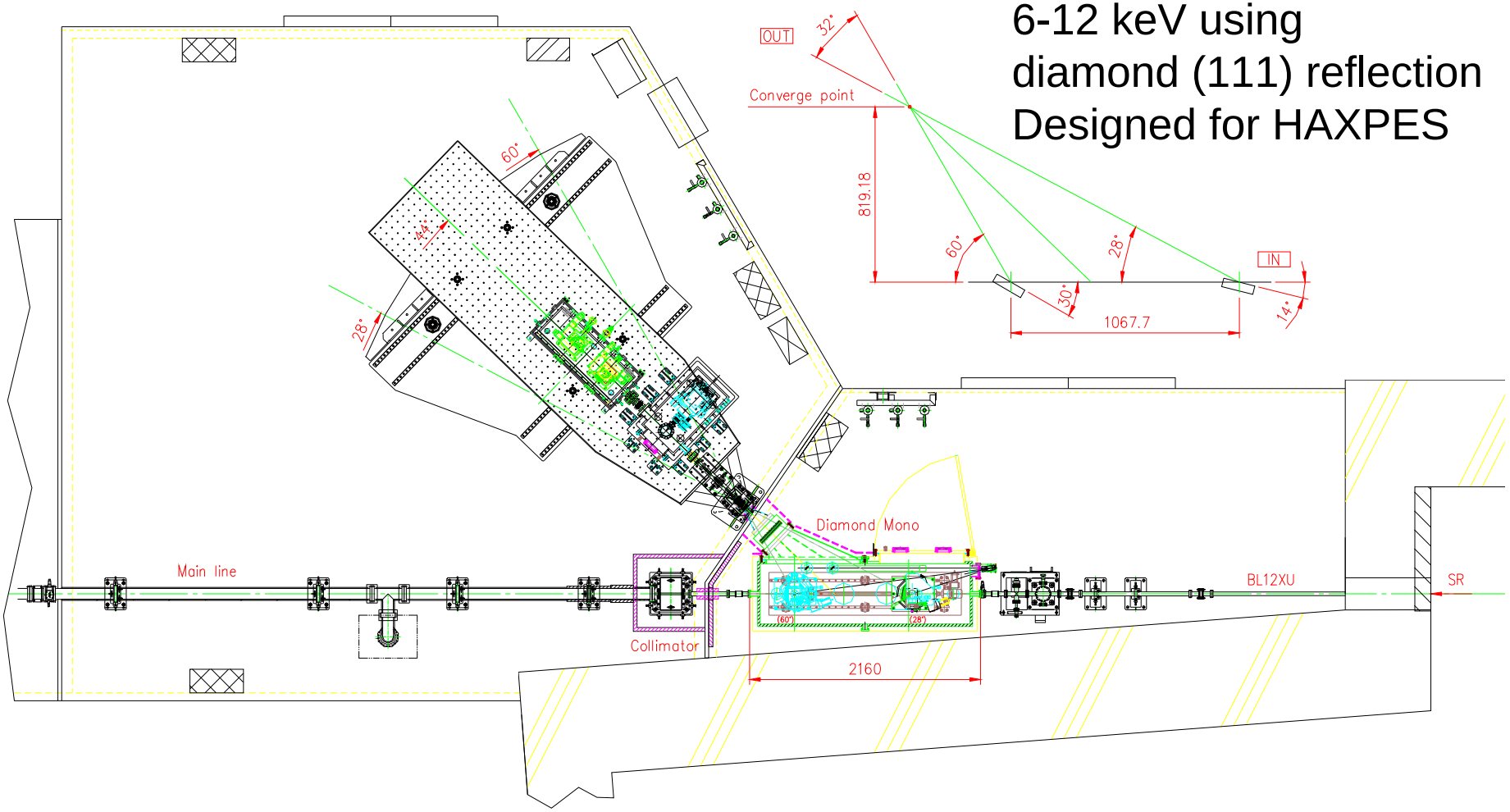
Optical design concept



Diamond (111) reflection
6-12 keV

DM: horizontal dispersion

HRM: vertical dispersion

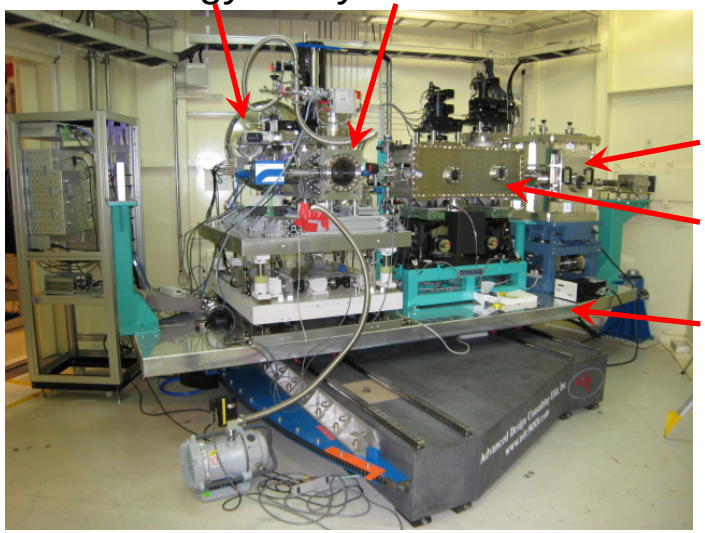


Layout of the side beamline of BL12XU

Diamond monochromator: installed Aug. 3, 2007

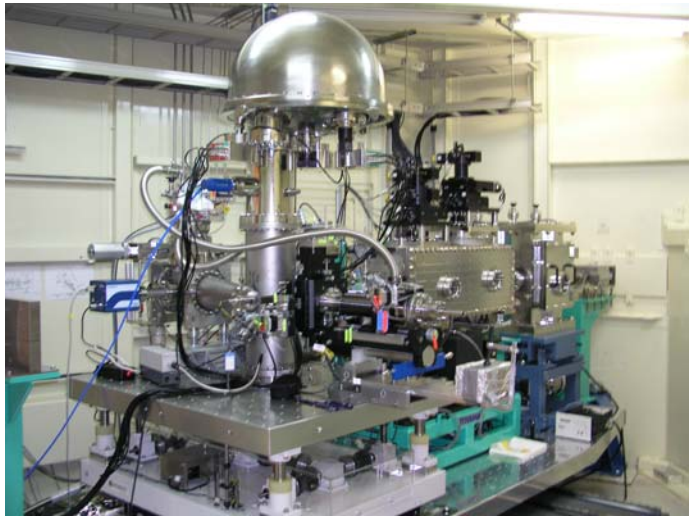
Commission of SPring-8 BL12XU SL HAXPES end station

MBS energy analyzer End station



Horizontal setup

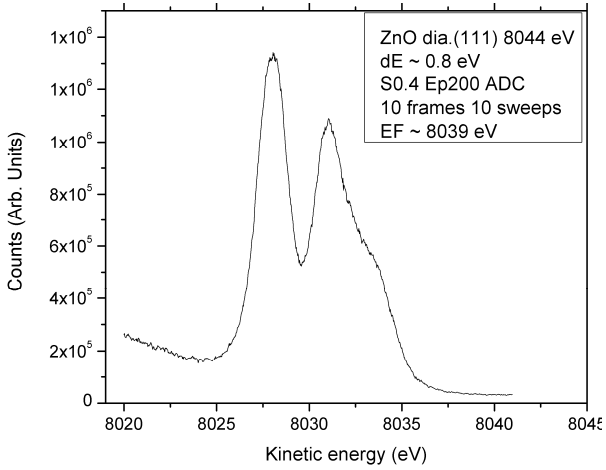
High Res. Mono.
KB focus mirrors
Rotational platform



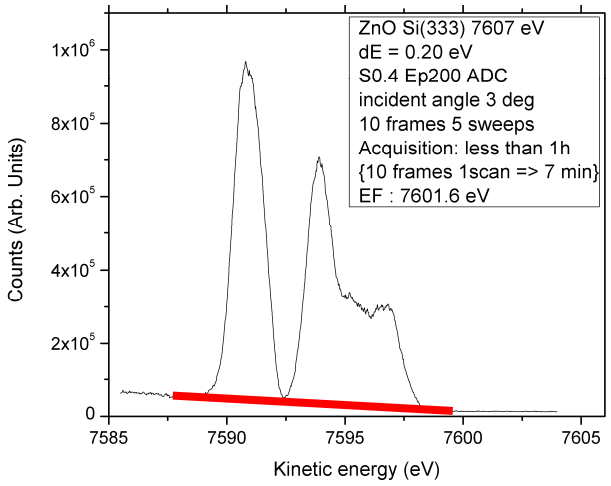
Vertical setup

KB Focus at sample
Aft HRM Si(333)
7.6 keV
38x38 microns

In collaboration with Cologne U of Germany



Low resolution w/o HRM
8 keV



Medium resolution
Si(333) HRM, 7.6 keV

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