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

Photoemission (I) Spectroscopy

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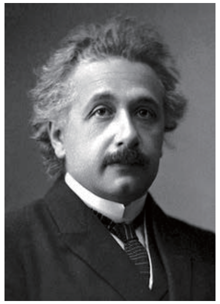
Outline

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



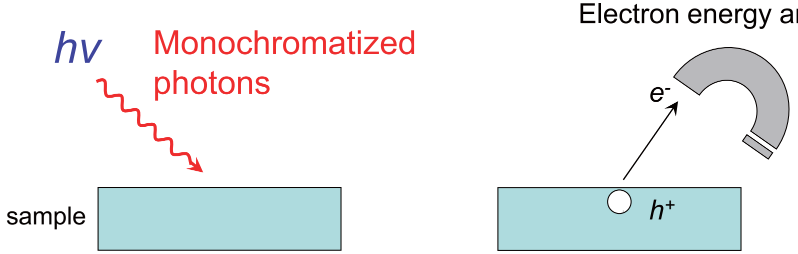
In 1905 Albert Einstein proposed the concept of light quanta (photons) to explain the photoelectric effect, which was pivotal in establishing the quantum theory in physics

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)

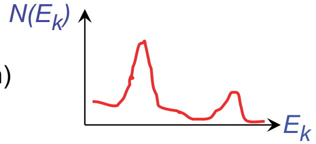


Initial state: ground (neutral) state   Final state: hole (excited) state

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
$E_f(N\text{-}1)$: total final state system energy

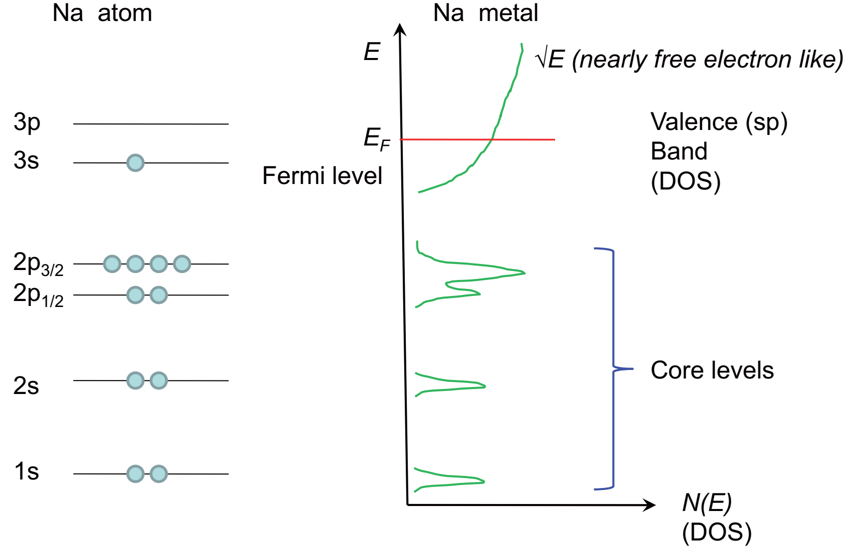


Energy Distribution Curve (EDC) (Spectrum)

What are the samples and probed states?

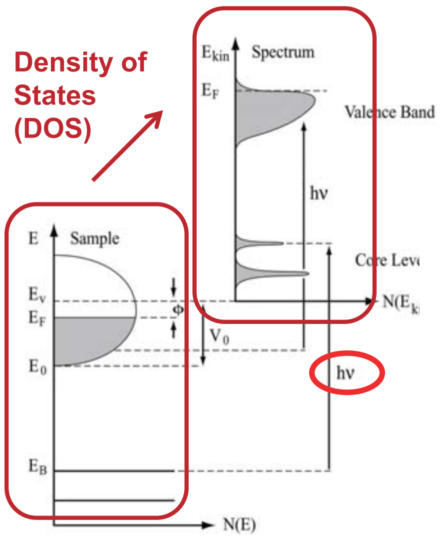
Atoms	atomic orbitals (states)
Molecules	molecular orbitals
	core level states (atomic like)
Nanoprticles	valence bands/states
	core level states (atomic like)
Solids	valence bands
	core level states (atomic like)

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



Energetics in PES

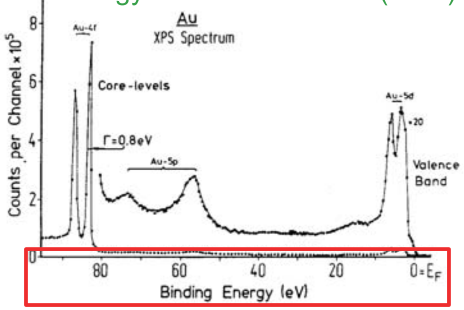
Conservation of energy



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

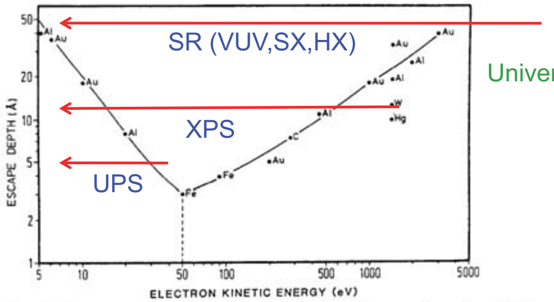


Fig.1.9. Electron escape depth as a function of their kinetic energy for various metals. The data indicate a universal curve with a minimum of 2÷5 Å for kinetic energies of 50÷100 eV. The scatter of the data is evident from the values obtained at E_{kin} = 1480 eV

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

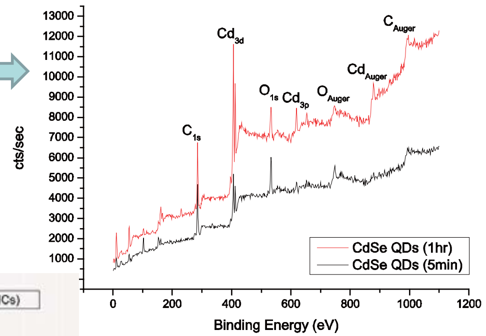
Core level BE independent of photon energy used

X-Ray Data Booklet

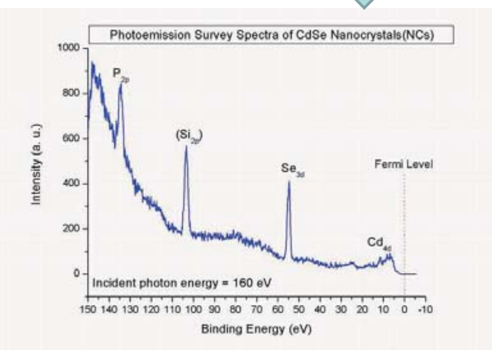
http://xdb.lbl.gov/

Core level photoemission: chemical analysis of elements

ESCA (XPS)
$h\nu$ = Mg $K\alpha$ = 1253.6 eV

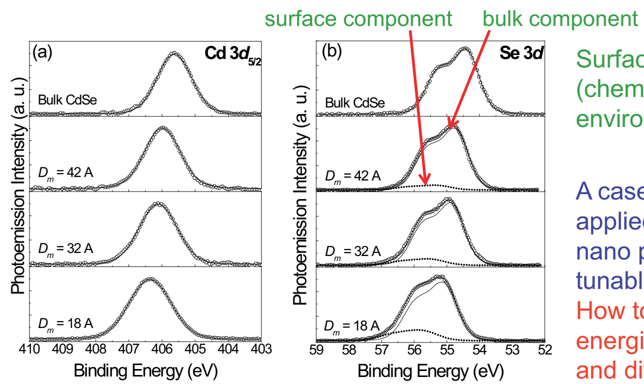


Synchrotron $h\nu$ = 160 eV



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

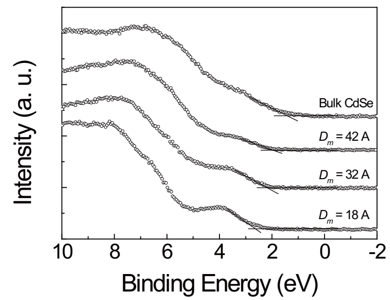
PJW, NSRRC



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:

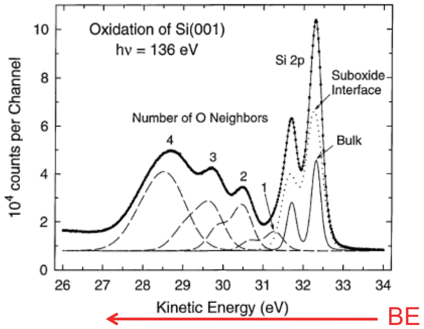
Cd $3d_{5/2}$:	480 eV
Se 3d:	120 eV
Valence band:	50 eV

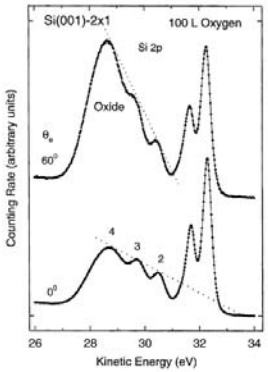
E_k ~ 45-74 eV, most surface sensitive

Wu, PRB 2007 NSRRC

Core level photoemission: chemical shift

higher oxidation state
=> higher BE

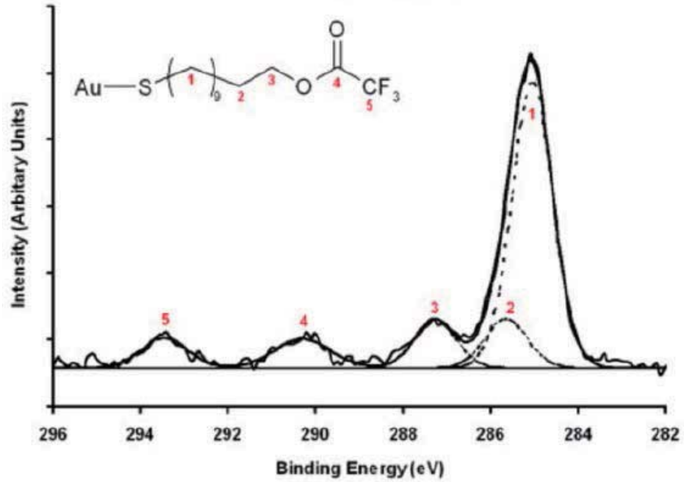




higher emission angle
→ more surface sensitive
(IMFP)

Pi, SS 2001 NSRRC

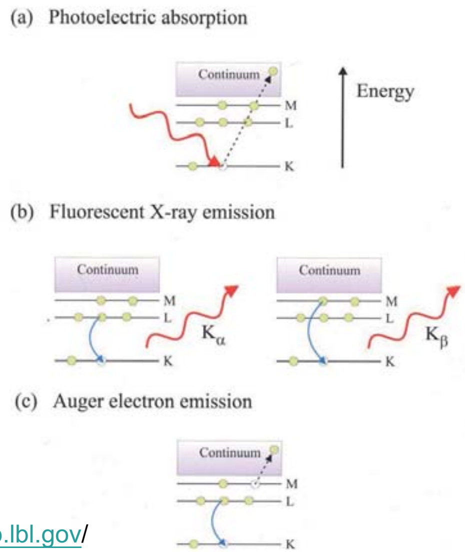
Chemical Analysis of C1s core levels



http://surfaceanalysis.group.shef.ac.uk

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

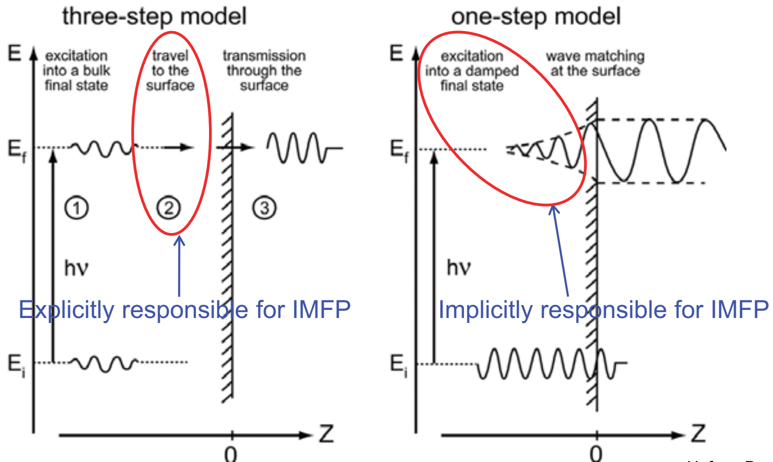


Comparison between PES and AES
PES: constant BE, Ek shift with changing photon energy
AES: constant Ek, apparent BE shift with changing photon energy
(synchrotron)

http://xdb.lbl.gov/

Handbook of XPS

Photoemission Process

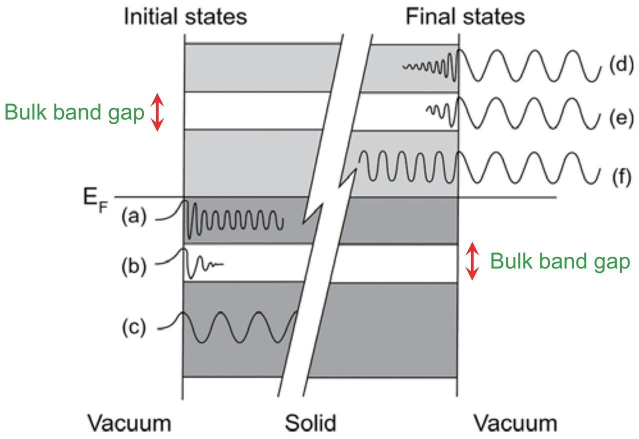


Hufner, Damascelli

Conceptually intuitive,
Simple calculation works

Rigorous,
requires sophisticated calculation

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

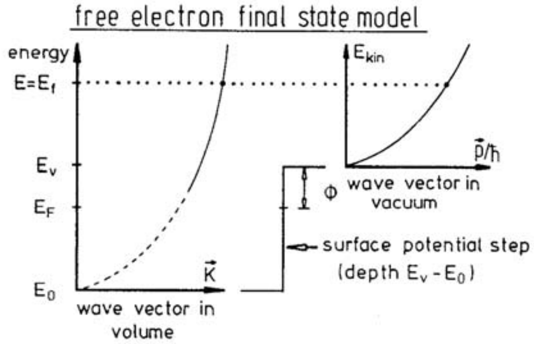


(a) Surface resonance
(b) Surface state
(c) Bulk Bloch state

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

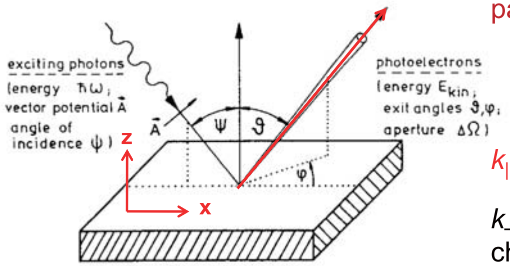
Electron kinetic energy inside and outside of solids

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 (ARPES)



xz plane: crystal symmetry plane

Conservation of linear momentum parallel to the surface

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

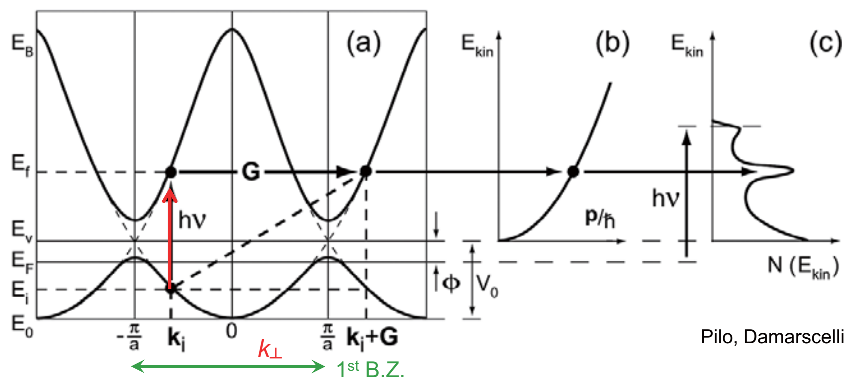
$k_{\parallel}$(inside solid) = $k_{\parallel}$(outside in vacuum)

$k_{\perp}$ 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) $E(k_{\perp}, k_{\parallel}=0)$



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

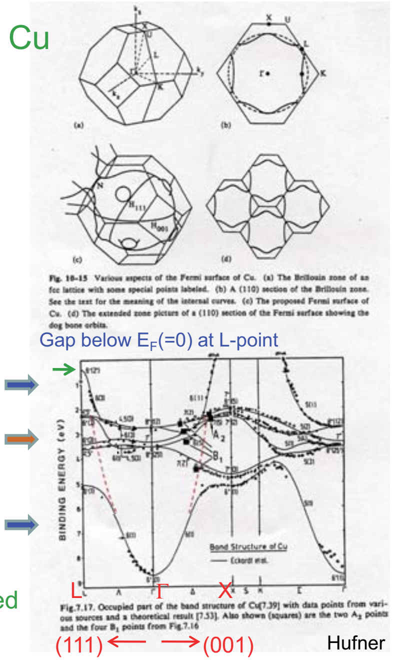
(nearly free electron like) *sp*-band

Small dispersion *d*-band
more localized state

Large dispersion *sp*-band
extended state

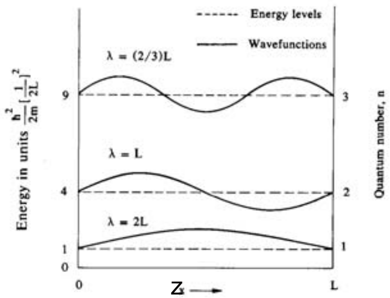
Dispersion of a band can tell how localized or extended a state is in a solid

Cu



Hufner

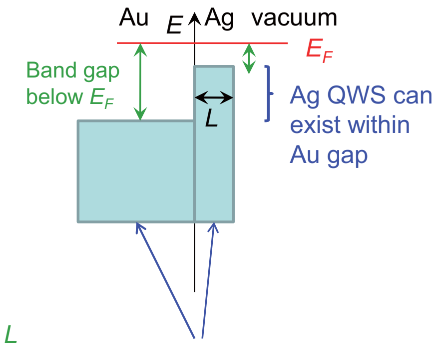
Quantum well states: manifestation of particle in a box in real materials



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

Nearly free electron like in xy-plane

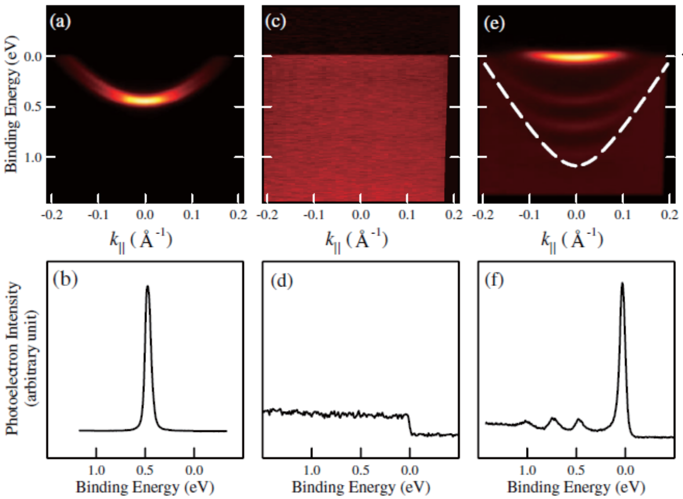
Ag(111) thin films expitaxially grown on Au(111) substrate



Bulk projected bands along ΓL of Au and Ag, respectively

2D Int. plots

$k_{||} = 0$ EDCs

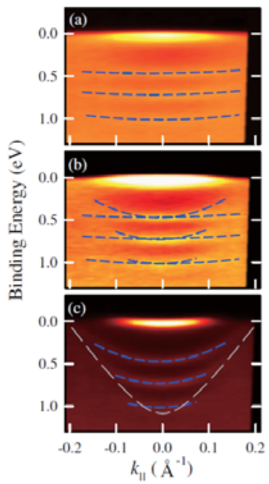


Clean Au(111) surface state

Deposit 22 ML Ag at 37 K disordered form

Anneal to 258 K Atomically flat 22 ML thin film

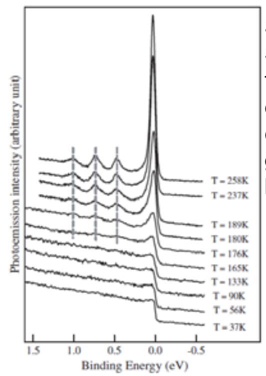
Luh et al.
PRL 2008
NSRRC
BL21B1



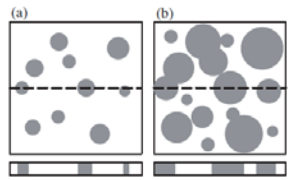
Anneal to 180 K
QWS appear
minimal flat dispersion
Small localized domains within xy-plane

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"

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

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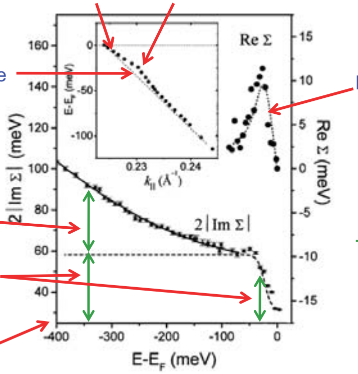
(Received 28 January 1999)

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.



ARPES for valence band PE uses primarily VUV light because of
1. Better absolute photon energy resolution for most BLs designed as nearly const ΔE/E.
2. Better photoionization cross section at low photon energy.
3. Better momentum resolution for a given angular resolution.
   $\Delta k_{||}(1/Å) = 0.5123 \sqrt{E_k(eV)} \cos(\theta)\, \Delta\theta$

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.

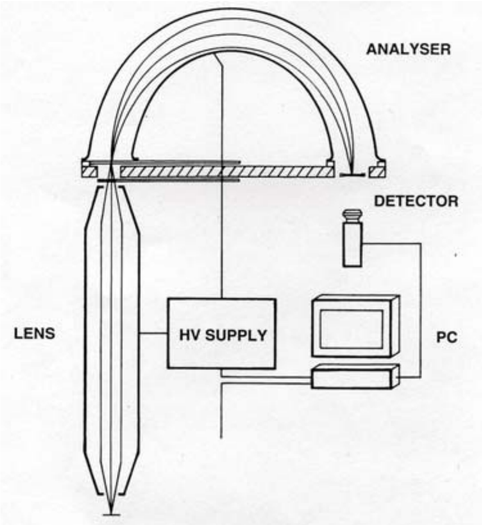
NSRRC U9 BL21B1 BL and high resolution photoemission end station

U9 undulator

CGM

Scienta SES 200 analyzer

Hemispherical electron energy analyzer



R1 : radius of inner sphere
R2 : radius of outer sphere
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

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.

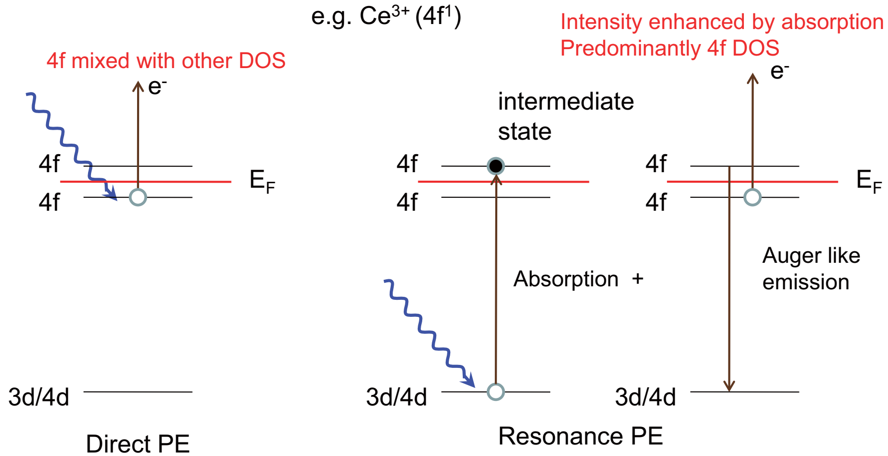
Need larger IMFP by using higher energy photons to enhance bulk sensitivity.

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)



letters to nature 2000

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

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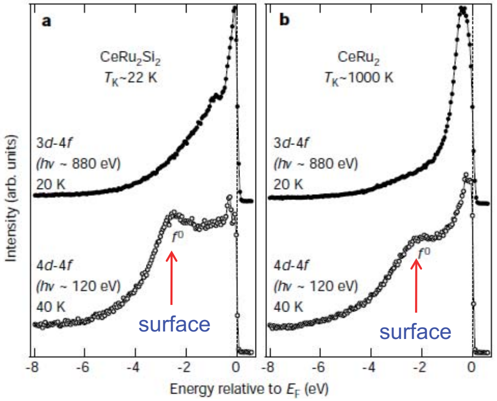

By using Ce 3d → 4f Res. PE near 880 eV surface 4f component becomes greatly reduced compared to 4d → 4f Res. PE near 120 eV, the resulting spectra are closer to true bulk 4f DOS.

PRL 93, 246404 (2004) PHYSICAL REVIEW LETTERS week ending 10 DECEMBER 2004

Valence Transition of $YbInCu_4$ Observed in Hard X-Ray Photoemission Spectra

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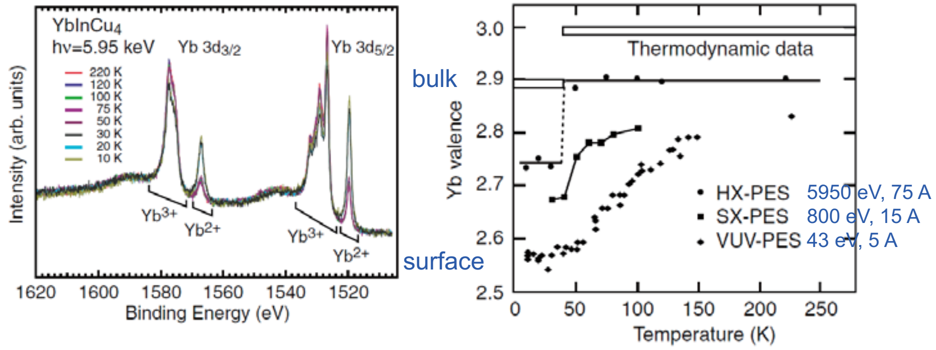
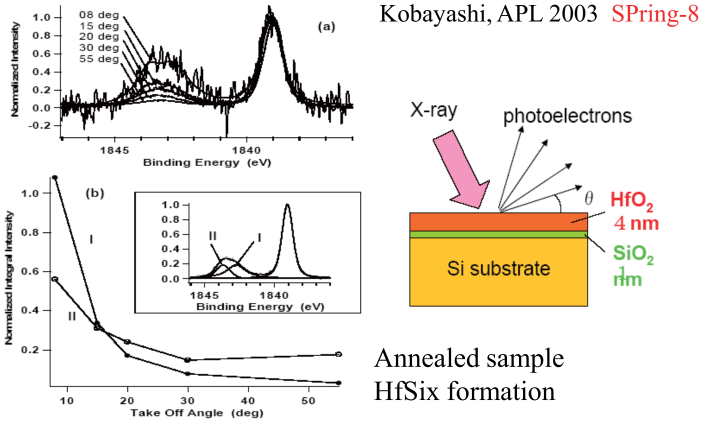


Bulk sensitive HAXPES can determine sharp first order valence band transition

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)

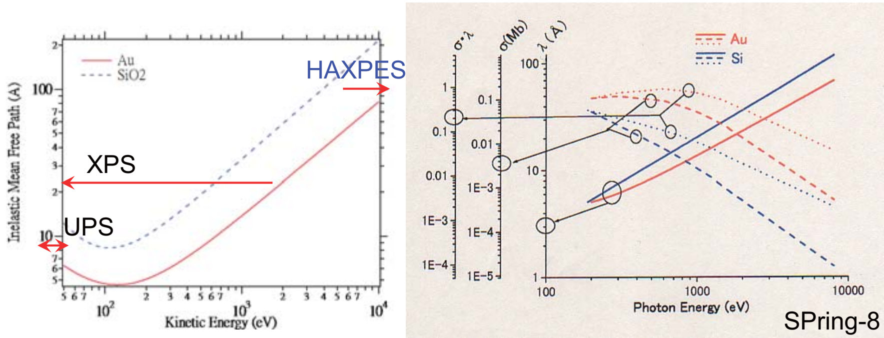
NSRRC HAXPES project at SPring-8

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

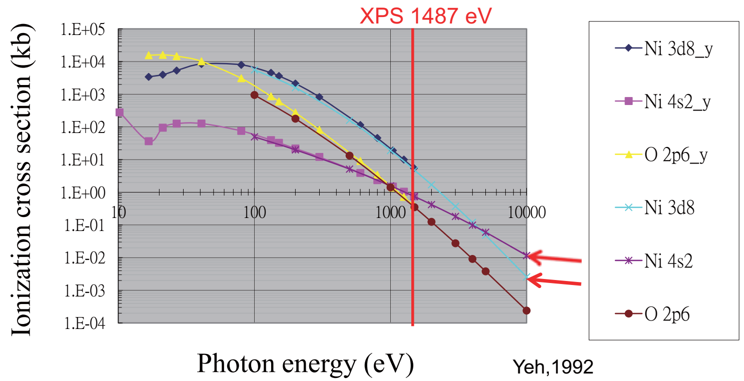
Photoemission signal ($\sigma \cdot \lambda$) decreases rapidly > 1 keV

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

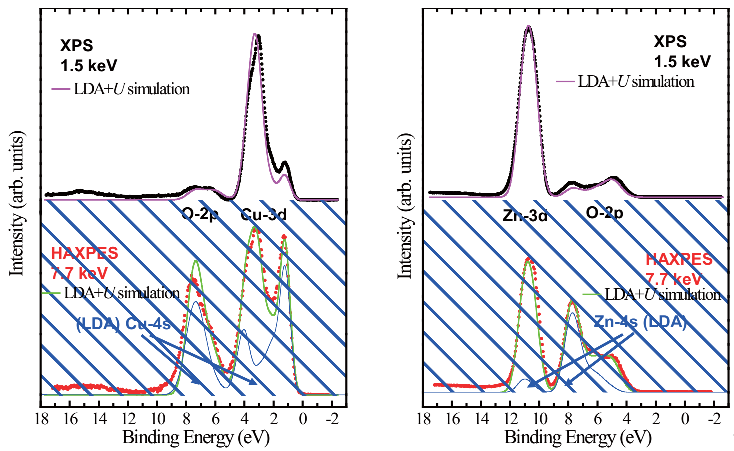
How to cope with this problem?

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-$2p$

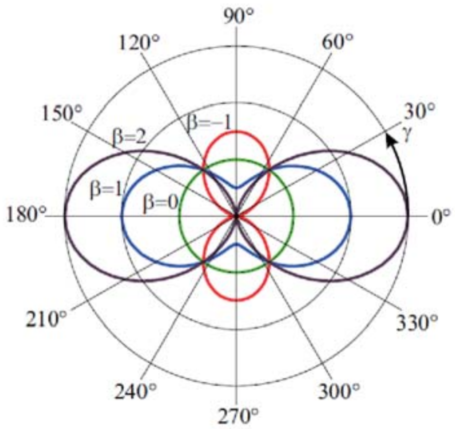
Polarization dependent cross sections in HAXPES

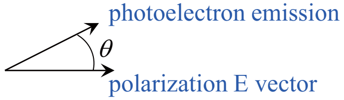
How to suppress the *4s* spectral weight?
- photo-ionization cross-section depends on e^- emission direction and light polarization
- make use of β-asymmetry parameter

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

β-parameters @ hν= 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

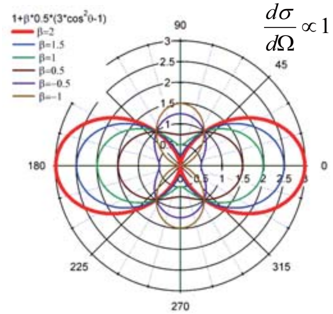




In general: s orbitals have β ≈ 2:
- intensity is *enhanced* for e^- emission || *E*-vector
- intensity *vanishes* for e^- emission ⊥ *E*-vector

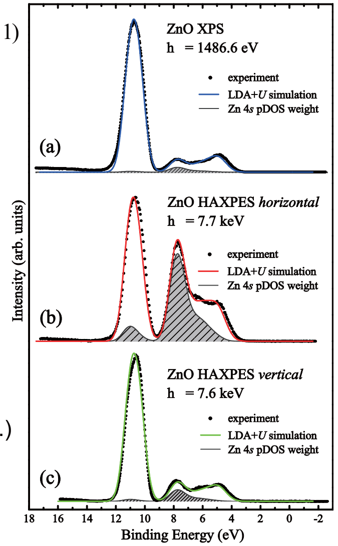
→ choose suitable experimental geometry !

HAXPES Commissioning: Horizontal vs Vertical geometries



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

polarization



horizontal
θ=0°

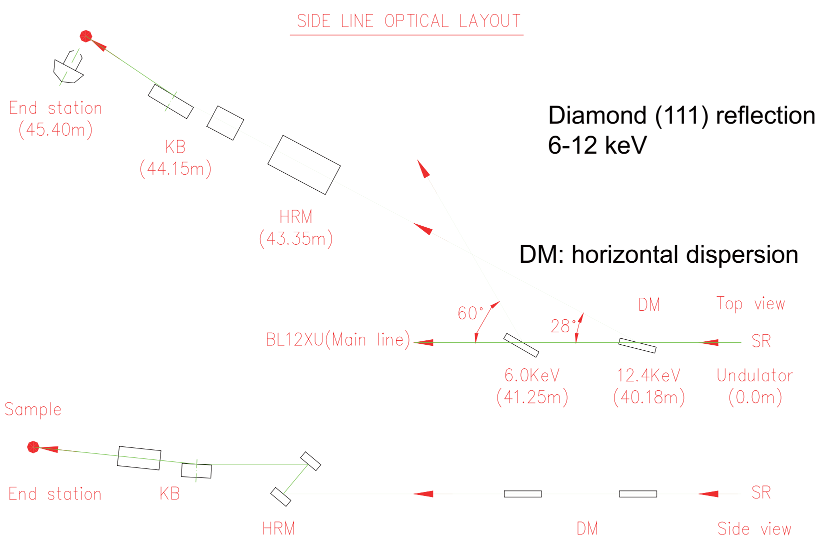
vertical
θ=90°

Tjeng et al.

θ: angle between electron emission and polarization vector
β: electron emission asymmetry parameter
β~2 for s-orbitals, strong emission near θ=0° (horiz.) while suppressed near θ=90° (vertical);
can be used to distinguish
s-orbital, important in chemical bonding, and
d-orbital, important in strongly correlated systems

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

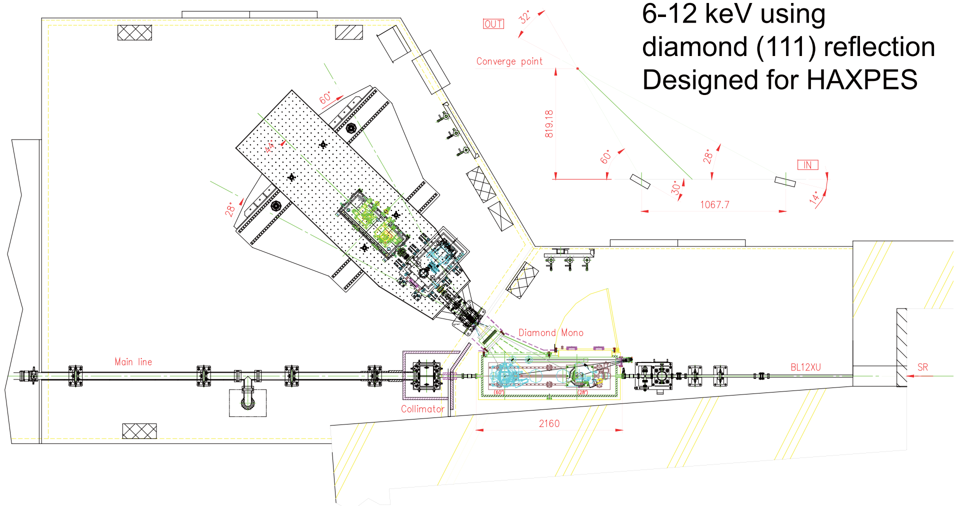
Optical design concept



Diamond (111) reflection
6-12 keV

DM: horizontal dispersion

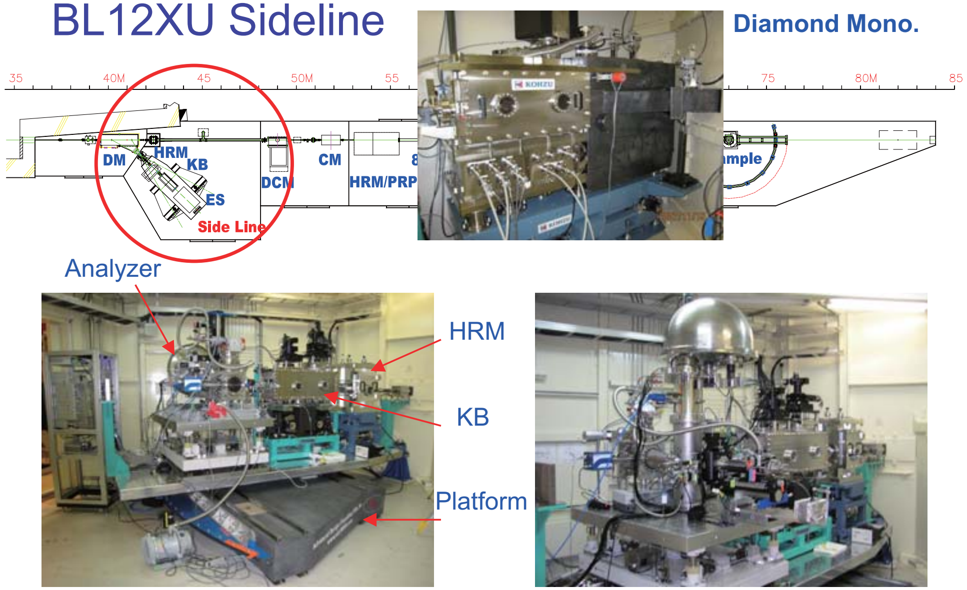
HRM: vertical dispersion



6-12 keV using
diamond (111) reflection
Designed for HAXPES

Layout of the side beamline of BL12XU

BL12XU Sideline



Horizontal geometry **Vertical geometry**

For selecting different orbital symmetries in valence band

HAXPES Example 1:
NiO at RT and high temp.

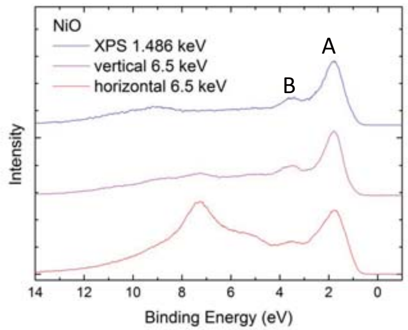
Interpretation of XPS valence spectra of NiO against argument of surface effect

First ionization (photohole final) valence state identified as Ni^{2+} low spin state

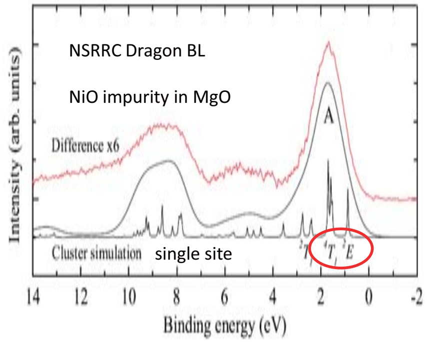
Indication of non-local screening in valence band of bulk NiO compared to impurity NiO

Peaks splitting due to non-local screening in valence and Ni 2p core level diminishes as temp. approaches T_N=523 K

NiO: a prototypical strongly correlated electron system



Peak B is a true bulk feature



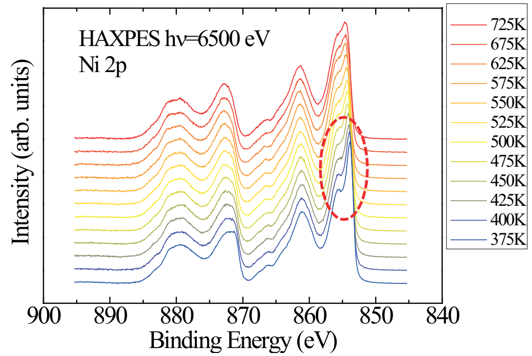
Peak B is absent in single NiO_6 cluster

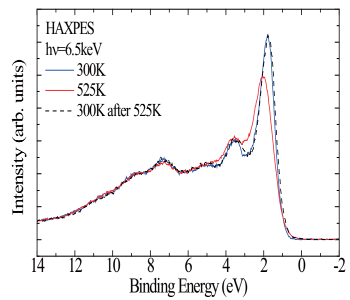
Implications:

1. First ionization state is ^2E (compensated spin, (photo)hole in the mixed state made of e_g (d^7) and O $2p_\sigma$ (d^8L) (ZR-doublet), instead of $^4T_1$ (atomic-like Hund's rule high spin, d^7, quasi-core) as previously suggested.
2. Peak B due to non-local (neighboring sites) effect.

NiO above Neel temperature at 523 K

How important is long range AF ordering?





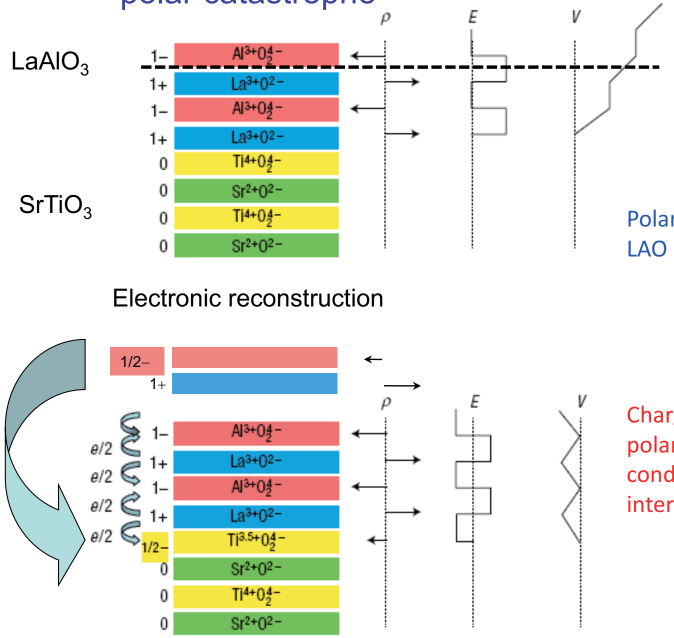
- Ni $2p_{3/2}$ splitting due to non-local screening mechanism (Veenendaal and Sawartzky PRL1993)
- Splitting goes smaller with increasing temp.
- Valence band doublet structure also changes w/ temp.

(Why need bulk sensitive HAXPES? Because O decomposes leaving surf. at high T)

HAXPES Example 2:
Interface of LAO/STO

Interface of two 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 simplest model

polar catastrophe

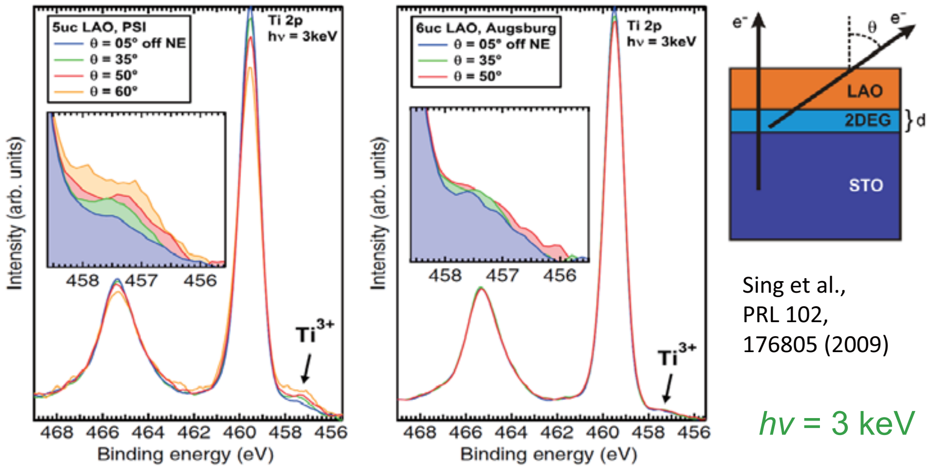


Polarity discontinuity between LAO and STO plays a crucial role.

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)

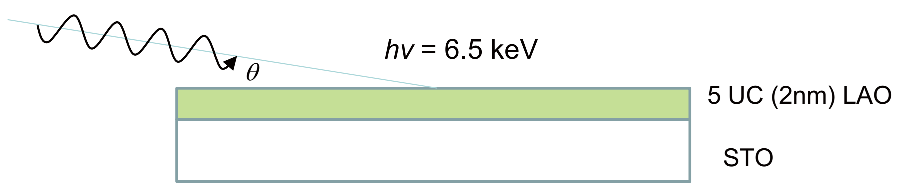
$h\nu$ = 3 keV

⇒ 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

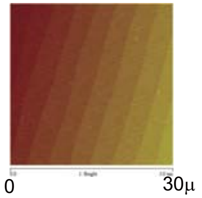
Our approach:

* 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

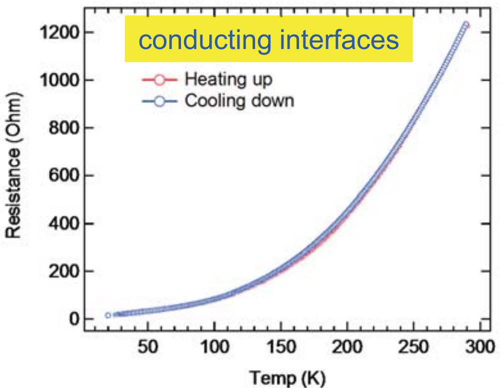
* higher photon energy (6.5 keV) to increase probing depth

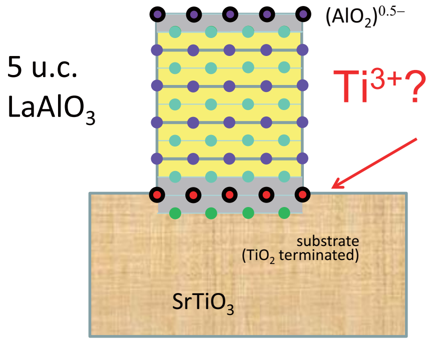


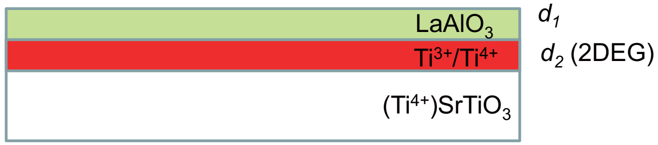
$LaAlO_3/SrTiO_3$ (001)

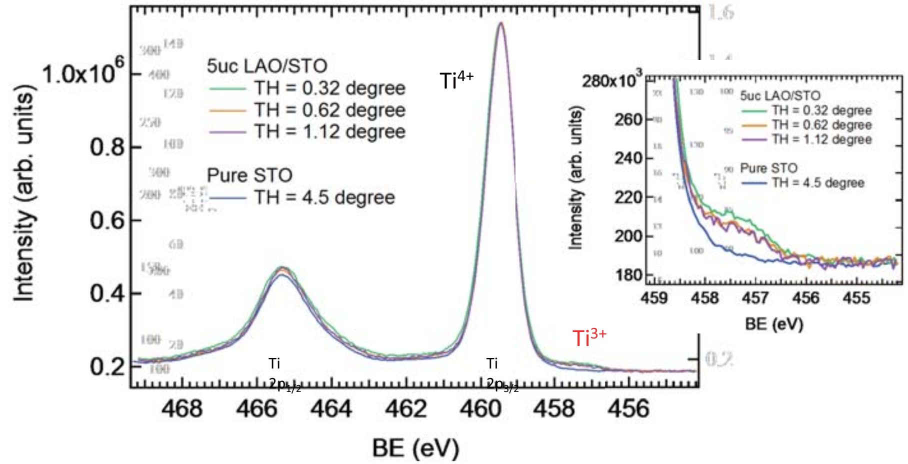


grown with PLD, 10^{-5} torr O_2, 850 C
annealed at 100 mtorr of O_2

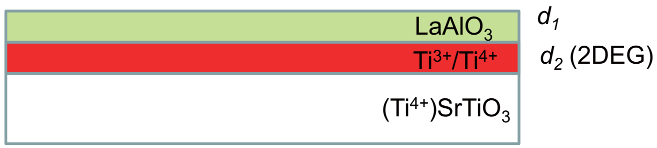


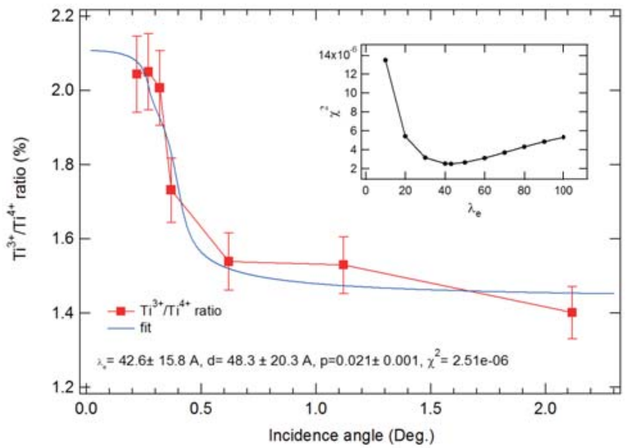






Measure intensity ratio Ti^{3+}/Ti^{4+} as a function of incident angle





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

d_2 = 48.3 ± 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?

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