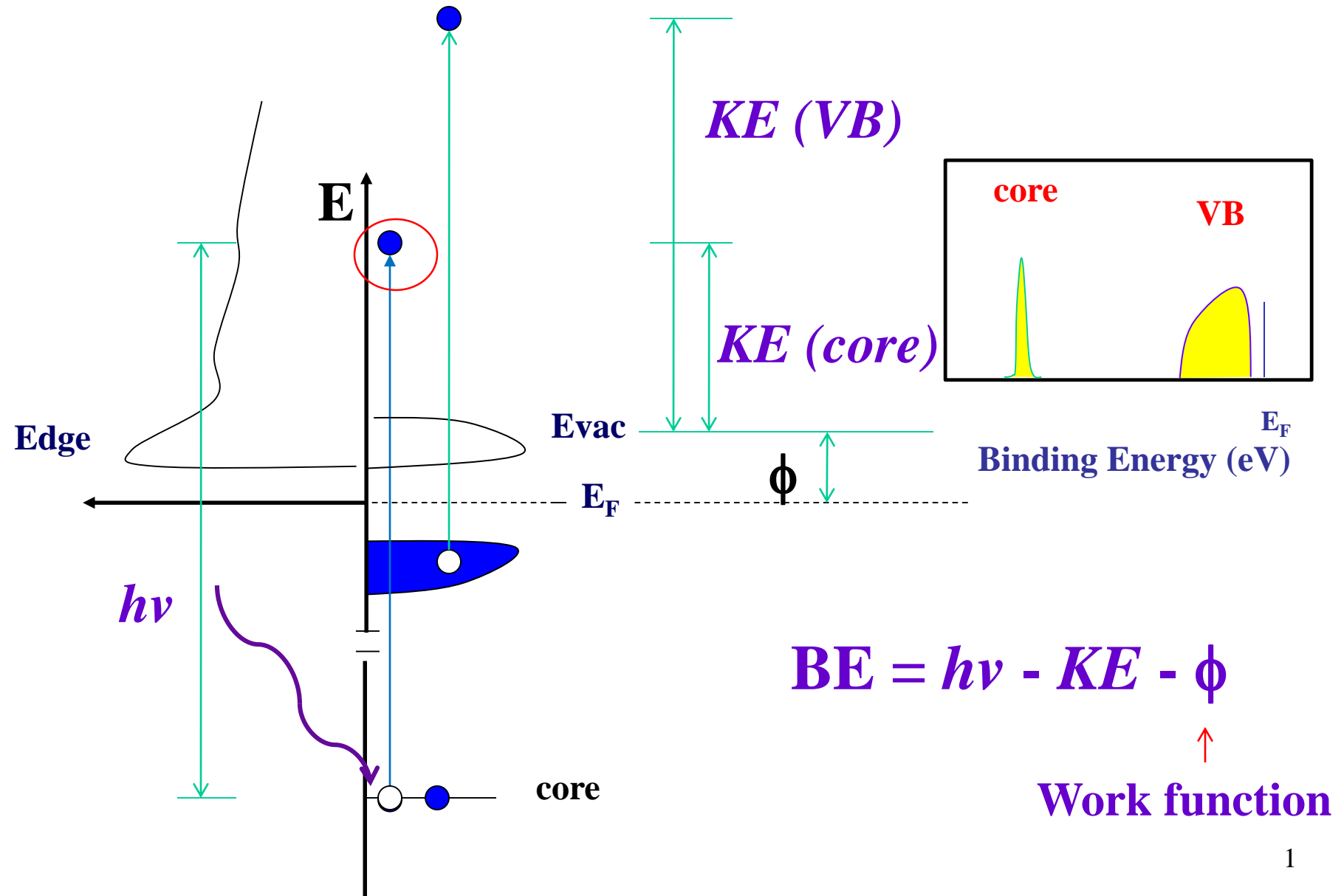


# XAS and XPS



# Photoelectron spectroscopy

- **Photoelectron spectroscopy:** photons (at a fixed energy) in, electrons out technique - core and valence electrons are ejected if the photon energy is greater than the binding energy of the electrons. **Photoelectric effect, KE of electrons are studied.**
- The kinetic energy (and sometimes the momentum) of the photoelectrons are analysed (photoelectron spectrum exhibits peaks which are *chemically sensitive*)
- Information about the electronic structure (**atomic and molecular orbitals, and bands**) of the specimen can be obtained.

# Photoemission and X-ray Absorption

- XAS measures the absorption coefficient across the threshold of the absorption edge of a core level and the **absorption coefficient is the sum of all ionization channels.**
- Photoemission measures the kinetic energy of the photoelectrons ejected from all levels (binding energy) accessible at a given photon energy.  
**(partial cross sections)**
- They both are *element* and *chemical specific* since they both monitor the change of the threshold of core levels, which are element specific

# Photoelectron spectroscopy

- ESCA: Electron spectroscopy for chemical analysis
- XPS: X-ray photoelectron spectroscopy
- UPS: Ultraviolet photoelectron spectroscopy
- PES: Photoemission spectroscopy
- Physical process:  
photoelectric effect

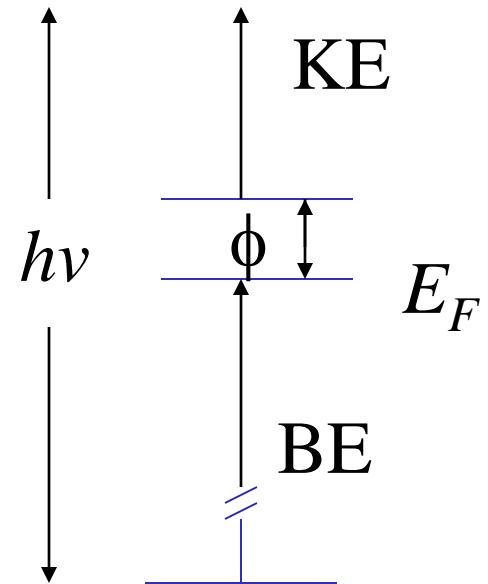
(Einstein)

$$\text{KE} = h\nu - \text{BE} - \phi$$

↑ Kinetic energy

↑ Binding energy

↑ Work function



# What is PES/XPS measuring ?

- PES probes the **electron** energy states of matter
  - i) electrons with discrete energy – atomic orbital
  - ii) shallowly bound electrons – molecular orbitals
  - iii) closely spaced energy states – energy bands in solids
    - i) – Core level
    - ii) and iii) – Valence band

# What is in a peak in a PES/XPS spectrum

- **Single particle approximation**

The energy of the photoelectron is to a good approximation independent of the movement of the other electrons – yields a *single peak (spin-orbit doublets)* in the PES spectrum.

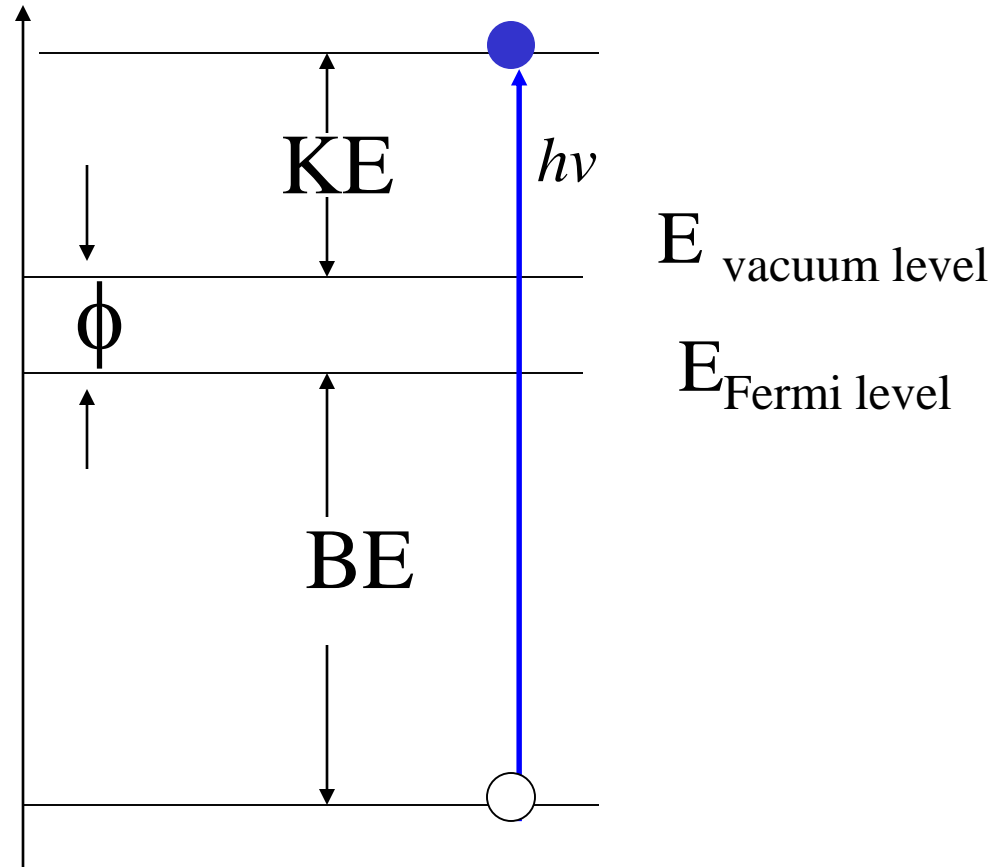
- **Manybody effects**

The energy of the photoelectron depends on the presence of other electrons which get excited simultaneously yielding *satellite peaks* (shake-up, shake-off, shake-down) or even the complete disappearance of the single particle peak.

# Photoelectric effect

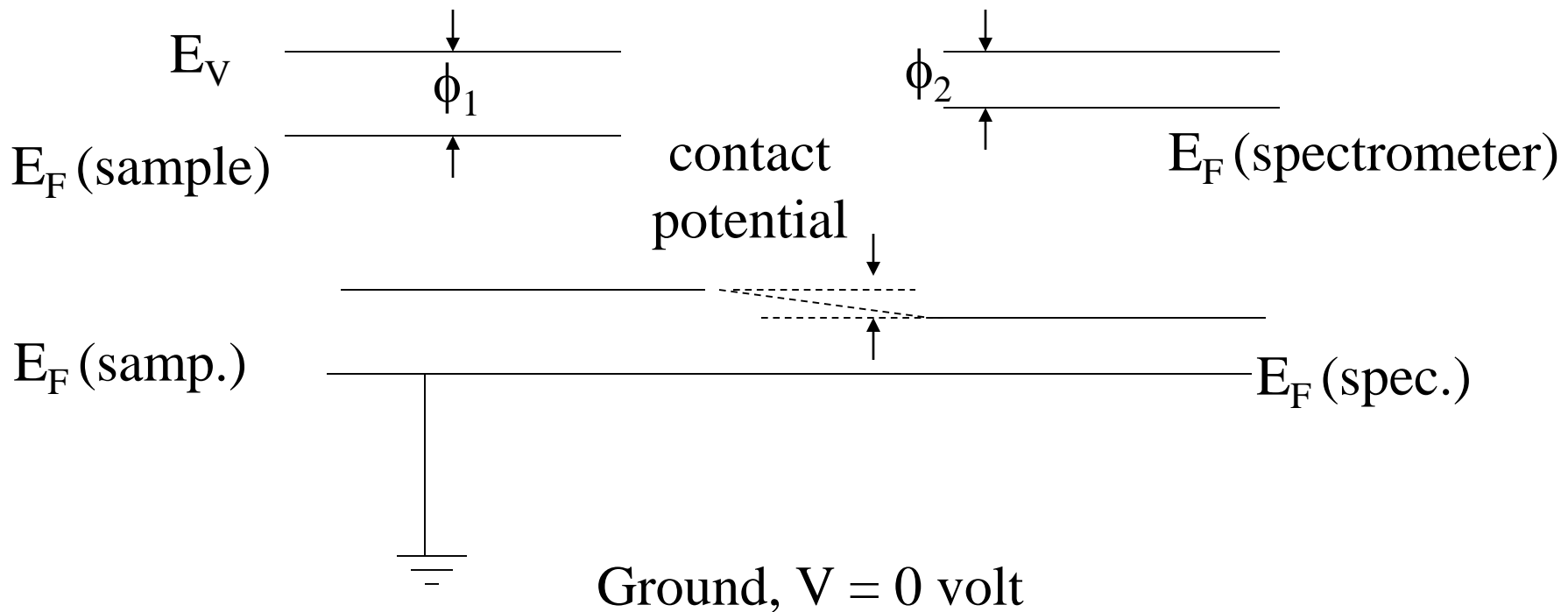
$$KE = h\nu - BE - \phi$$

Work function



# Experimental considerations

- Let's consider a metallic sample whose Fermi level equalizes with the Fermi level of the spectrometer upon contact at  $V = 0$  Volt



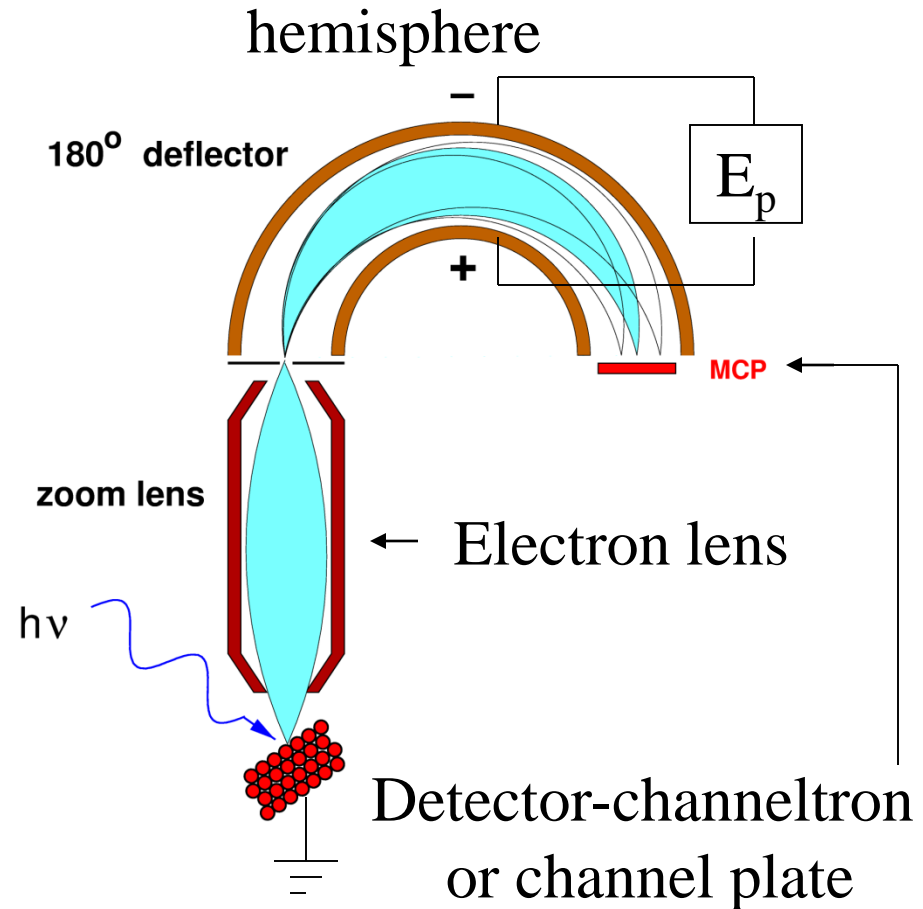


# Experimental consideration (cont')

- KE is relative to the Fermi level of the spectrometer at  $V = 0$  volt
- KE is retarded to the pass energy  $E_p$  of the electron energy analyzer such that

$$KE = E_p + V_R$$

Pass energy  $\uparrow$   
Retarding potential  $\uparrow$   
Scanning  $V \rightarrow$



Spectrometer resolution,  
 $E_p$ : 2, 5, 10, 20, 50, 100 V etc.

# XPS peak notation: $nl_j$

$n$ : principle quantum #,  $n = 1, 2, \dots$   
 $l$ : notation of orbital quantum #;  
 s for  $l = 0$ , p for  $l = 1$ , d for  $l = 2$   
 $j$ : spin orbit coupling;  $j = l + s, l - s$

$2p^6 + hv \rightarrow 2p^5 + e$   $2p^1$  hole;

$l = 1, s = 1/2$ ;

$j$ : 2 possible values

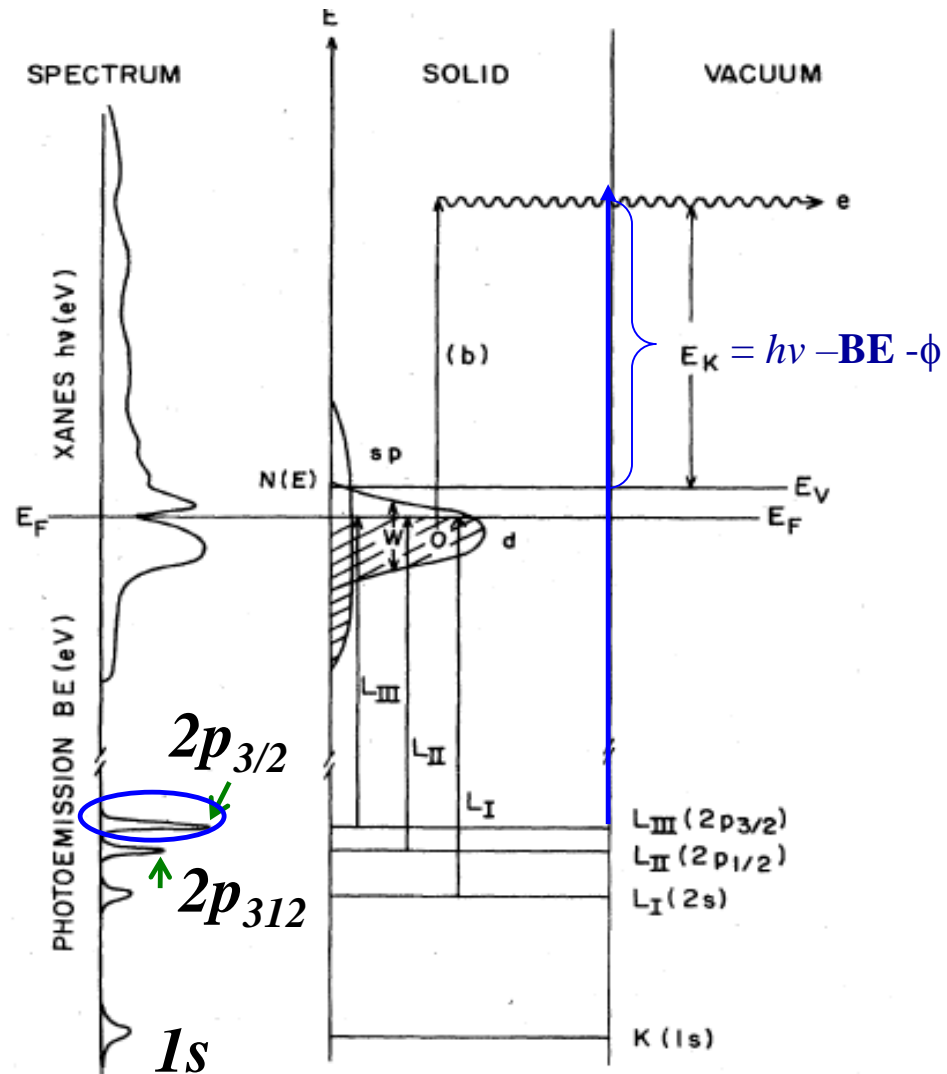
$j = 1 + s = 1 + 1/2 = 3/2$

$j = 1 - s = 1 - 1/2 = 1/2$

Multiplicity:  $2j + 1$

$I(2p_{3/2})/I(2p_{1/2}) = 4/2 = 2/1$

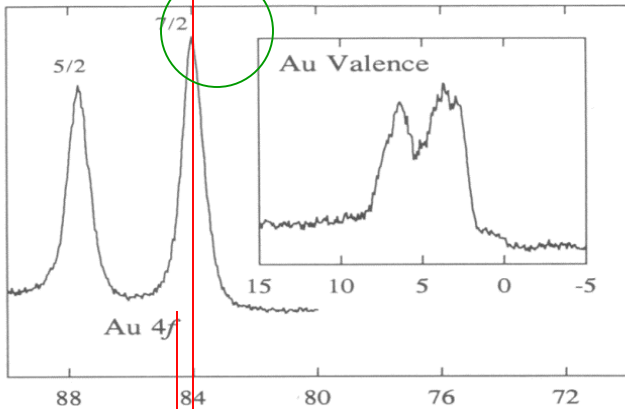
$1s^2 \rightarrow 1s^1 + e$



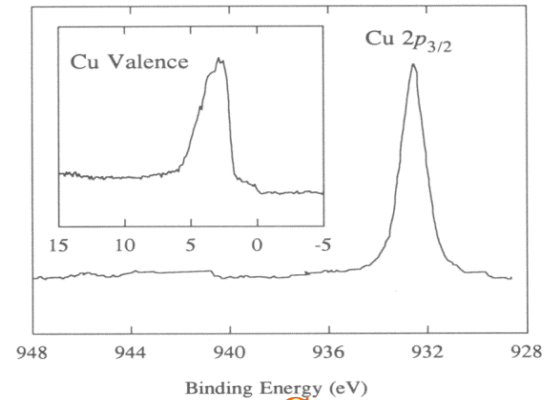
# What does an XPS spectrum of the core level and Valence Band look like?



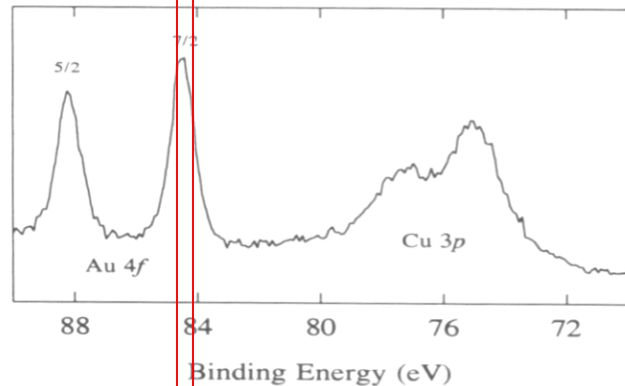
$$n = 4, l = 3, s = 1/2; j = 7/2, 5/2$$



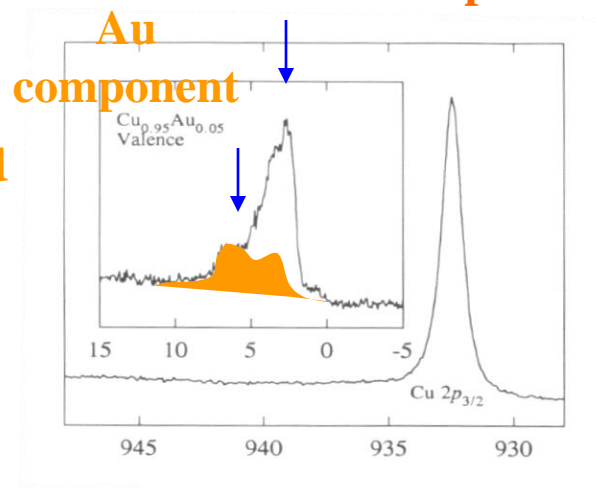
**Au**



**Cu**



**5% Au  
in Cu**



**Cu component**

**Au  
component**



Chemical shift → charge redistribution upon alloying

# Typical photon source for photoelectron spectroscopy

## XPS

- Al  $K_{\alpha 1}$ ,  $K_{\alpha 2}$ : 1486.3 eV, 1486.7 eV
- Mg  $K_{\alpha 1}$ ,  $K_{\alpha 2}$ : 1253.4 eV 1253.7 eV

## UPS

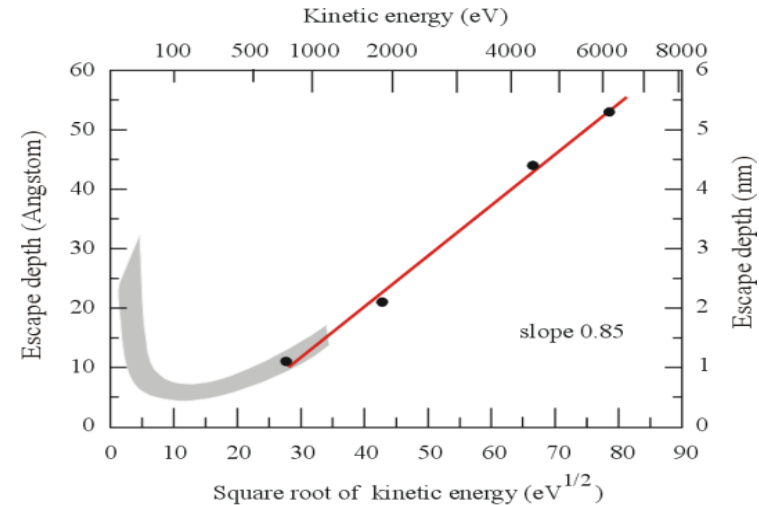
- He (I) 21.2 eV
- He (II) 40.8 eV

## Synchrotron radiation

- 5 -10000 eV

# XPS with tunable photon energy

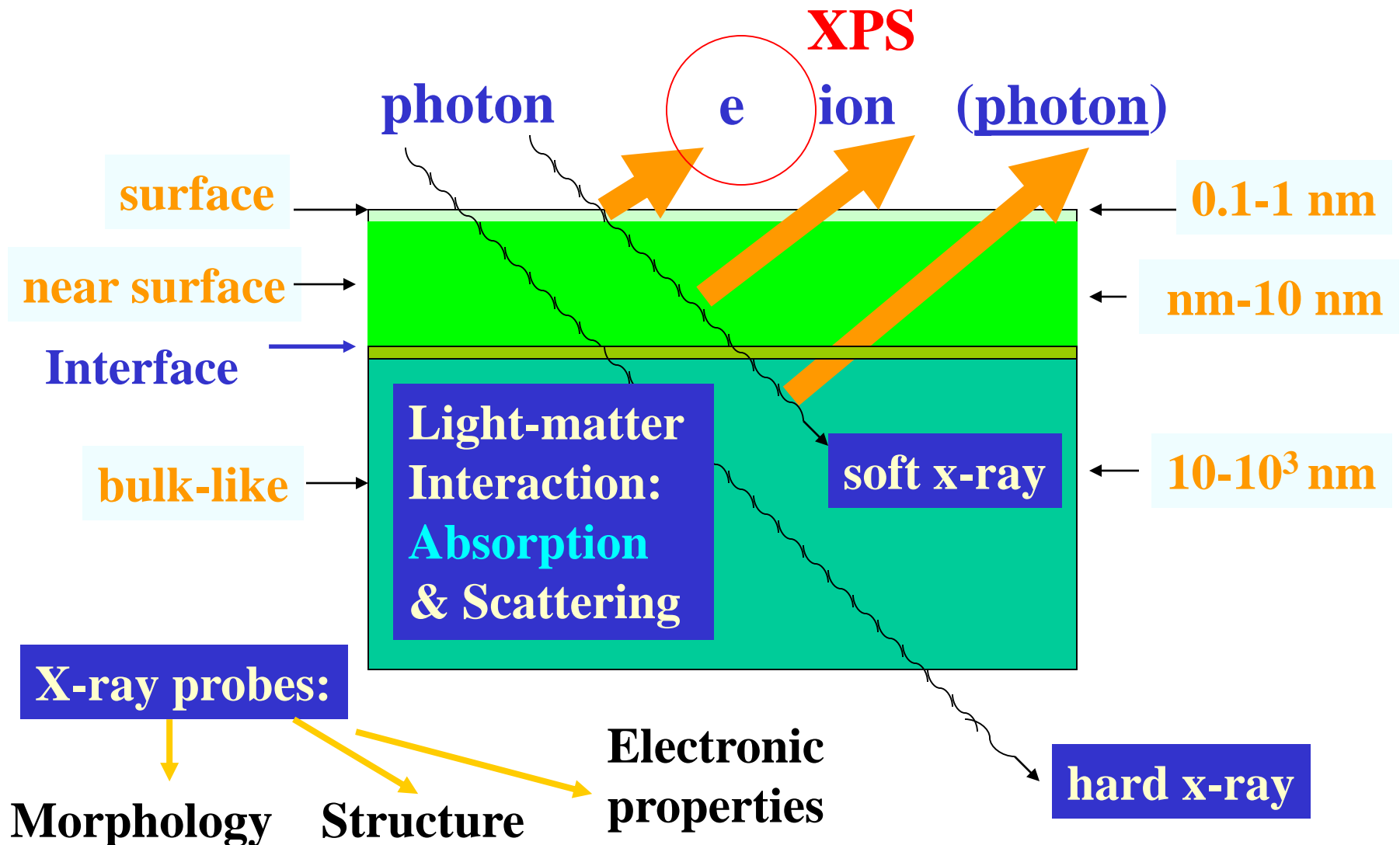
- **Surface sensitivity varies with  $h\nu$  (hence e- KE)**  
→ e.g. Si surface core level shifts



- **The photoionization cross section (**intensity**) changes as a function of photon energy.**

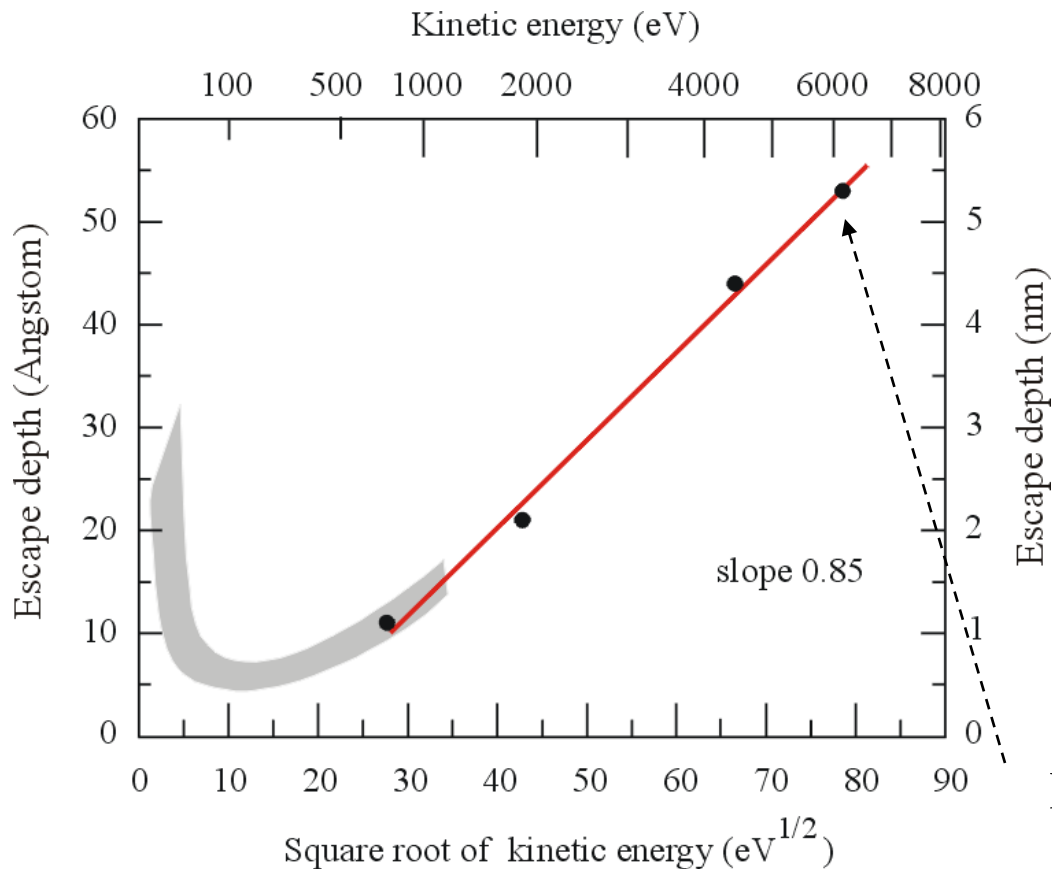
**Cross section with a Cooper minimum can enhance element sensitivity: e.g. Cs on Ru(0001)**  
→

# Probing matters with light



# Surface sensitivity in photoemission

**Electron Escape Depth:** Distance a photoelectron can travel in a solid without losing its energy (chemical identity),  $1/e$

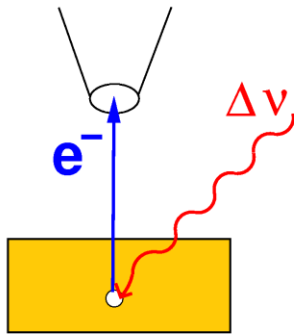


Recent measurements of the **electron escape depth** in comparison with the universal escape depth curve as known up to now (shaded curve). Measurements at ID32, ESRF (European Synchrotron Radiation Facility (J. Zegenhagen)

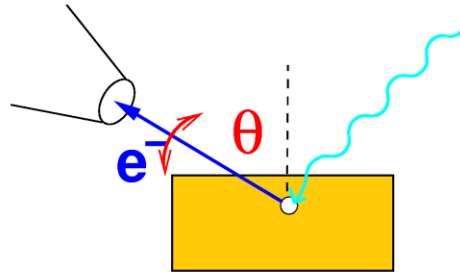
Electron with 6400 eV KE  
Can only be done with SR

Escape depth is sometimes known as Inelastic Mean Free Path (IMFP)

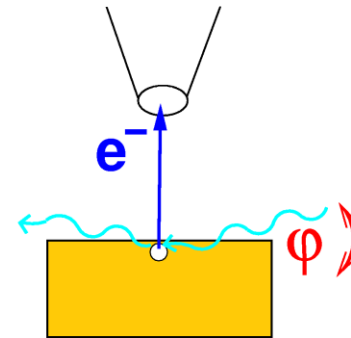
# Probing depth variation



Normal  
emission:  
bulk sensitive

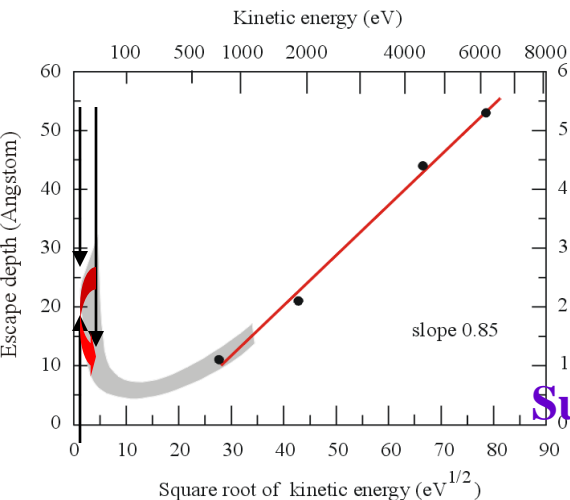


Glancing  
emission:  
surface sensitive

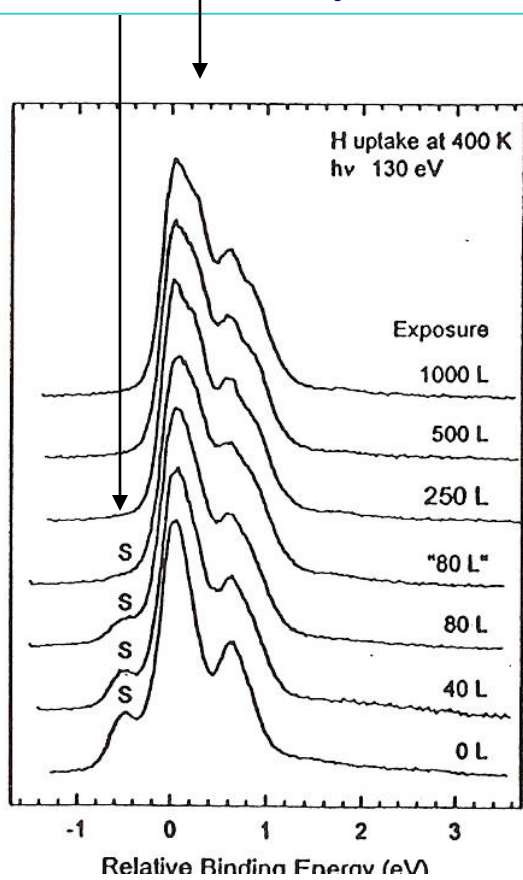
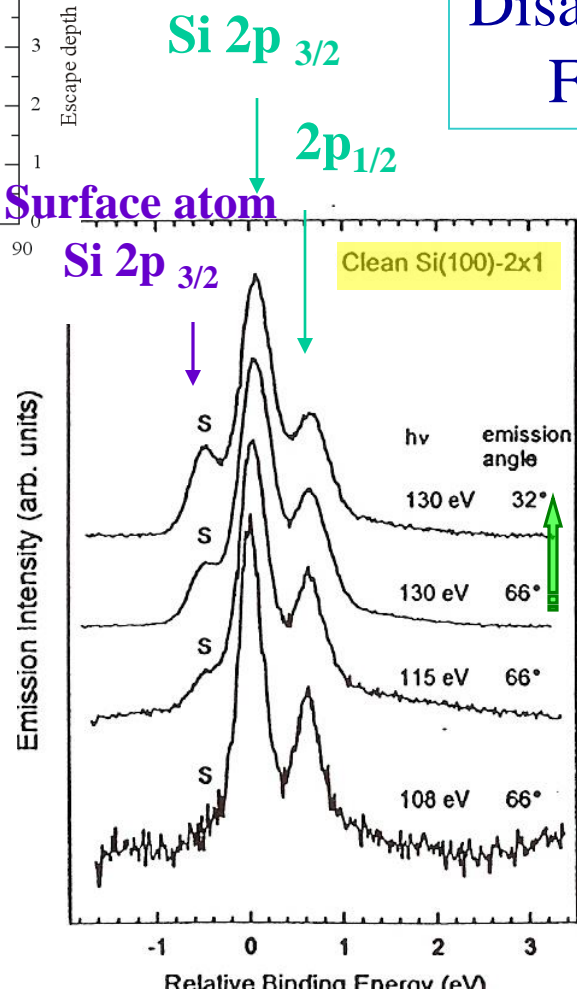


Glancing incident,  
normal emission:  
surface sensitive





Disappearance of surface state  
Formation of hydride states



$KE = (hv - 99.5 - 4)eV$

$h\nu$	KE	↑ surface sensitivity
108	4.5	
115	11.5	
130	26.5	

Si XPS BE( $2p_{3/2}$ ) ~ 99.5 eV

# Peak width and corehole lifetime

## Lifetime of a core hole

The **lifetime** of the core hole contributes as a **broadening** to the photoelectron peak. In the absence of any other contributions the width at half maximum of the peak is related to the lifetime according to the **uncertainty principle**

$$\Delta E \cdot \Delta t \geq \hbar/2\pi$$

where  $\Delta E$  and  $\Delta t$  are the uncertainty in energy and time in the alternative expression;  $\hbar = h/2\pi$ ,  $h$  is the Planck constant,  $h = 6.63 \times 10^{-34}$  J s,

$$(1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}; 1 \text{ J} = 6.24 \times 10^{18} \text{ eV})$$

**The linewidth (uncertainty in energy) is related to the corehole lifetime (uncertainty in time)**

$$\Gamma \cdot \tau \geq \hbar/2\pi$$

$$\Gamma(\text{eV}) = (6.63 \times 10^{-34} \times 6.24 \times 10^{18}) / [2 \times 3.1416 \tau \text{ (sec)}]^2$$
$$= 1.43 \times 10^{-16} / \tau(\text{sec})$$

$$\Gamma(\text{eV}) = 1.43 \times 10^{-16} / \tau \text{ (sec)}$$

**Example:** A femto sec. ( $10^{-15}$  s) corehole lifetime ( typical) will contribute to a lifetime broadening of 0.143 eV to the PES peak. Other contributions come from instrumentation, photon and electron analyzer ( $\Delta E = \sqrt{\Delta E_{core}^2 + \Delta E_{instru.}^2}$ )

# The differential cross section (intensity): a semi-classical view

- The Hamiltonian of a bound electron, in an em field radiation,  $A = |A_0|e^{ikr}$  (photon) is

$$H = \frac{p^2}{2m} + \frac{e^2}{2mc^2} A^2 + V(r) - \frac{e}{mc} A \cdot p$$

Hamiltonian for the unperturbed

Hamiltonian system for the photoelectric interaction

$H'$

a good Approx.

$\propto (\vec{\epsilon} \cdot \vec{r})$

$A(\epsilon)$  is the vector potential corresponding to the e-m field (photon).

## The differential cross section is

$$\frac{d\sigma_\nu}{d\Omega} = 4\pi^2 \alpha h\nu \left| \langle \mathbf{f} | \vec{A} \cdot \vec{p} | \mathbf{i} \rangle \right|^2$$

$\alpha = \frac{e^2}{\hbar c}$  is the fine structure constant

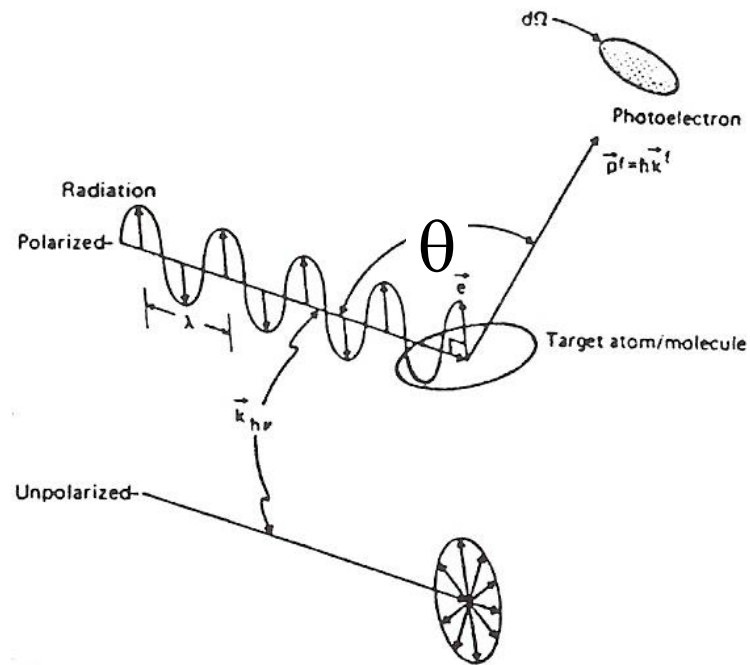
$\Omega$ : solid angle;  $h\nu$ : photon energy

$\frac{d\sigma_\nu}{d\Omega} \Rightarrow$  photoelectron peak intensity

# Angular dependence of the photoemission process: The Yang's Theorem [C.N. Yang, Phys. Rev. 74, 764 (1948)]

$$\frac{d\sigma_{\nu}}{d\Omega} = 4\pi^2 \alpha h\nu |\langle f | \vec{A} \cdot \vec{p} | i \rangle|^2$$

The differential cross section illustrated for polarized and unpolarized light.



## For linear polarized radiation

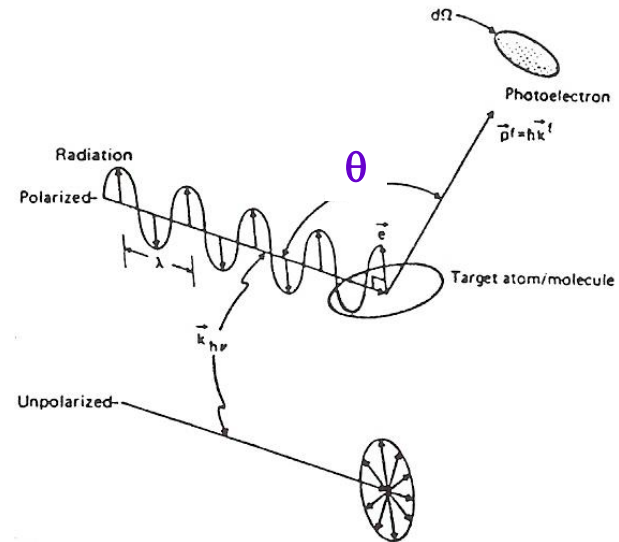
$$\frac{d\sigma_v}{d\Omega} = \frac{\sigma_v}{4\pi} [1 + \beta P_2(\cos\theta)] = \frac{\sigma_v}{4\pi} \left[ 1 + \frac{\beta}{2} (3\cos^2\theta - 1) \right]$$

$\beta$ : asymmetric parameter

varies from -1 to 2;

$P_2(\cos\theta) = 2(3\cos^2\theta - 1)$ ,

$\theta$ : angle between light and angle of detection

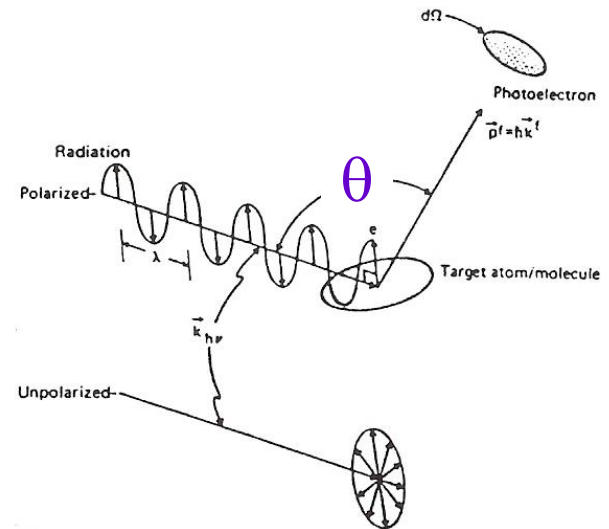


Experimentally, angular average means that the analyzer has to collect as large a solid angle as possible! In most solid experiments the angular dependence is neglected. Fortunately for random samples (powder, polycrystalline) this is usually o.k. (not always valid for single crystals).

## For unpolarized light

$$\frac{d\sigma_v}{d\Omega} = \frac{\sigma_v}{4\pi} \left[ 1 - \frac{\beta}{2} P_2(\cos\theta) \right]$$

$\frac{d\sigma_v}{d\Omega}$  has an angular dependence except when  $P_2(\cos\theta) = 0$  or  $\theta = 54.73^\circ$  (magic angle).



**Exercise:** Show that the magic angle is indeed  $54.73^\circ$ . Gas phase experiments are often conducted at this angle

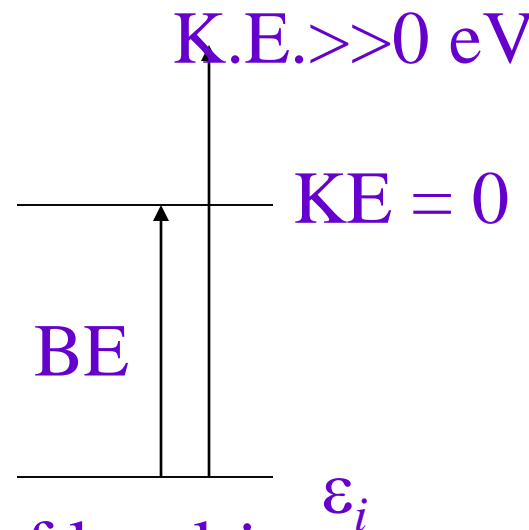


# Binding energy and Koopmans theorem (what is BE really measuring? details)

If the kinetic energy of the photoelectron is large, then the photon electron, can be assumed to leave the system faster than the rest of the electrons in the system can respond to the core-hole (**Sudden Approximation**).

In a free atom (gas phase), Koopmans theorem is equivalent to the following expression

$$E_v$$



$$\mathbf{BE} = -\epsilon_i$$

Binding Energy  
A +ve value

one electron energy of level  $i$   
Hartree-Fock approximation

**Rigorously speaking, BE is the difference in the total energy between the initial and the final state!**

$$BE = E_f^{\text{exact}}(N-1) - E_i^{\text{exact}}(N)$$

$$BE = E_f^{\text{HF}}(N-1) + E_f^{\text{C}} - [E_i^{\text{HF}}(N) + E_i^{\text{C}}]$$

$$BE = [E_f^{\text{HF}}(N-1) - E_i^{\text{HF}}(N)] + (E_f^{\text{C}} - E_i^{\text{C}})$$

The first term is the one electron energy -  $\varepsilon_i$  and the second term is the difference in **Correlation energy,  $\Delta C$** , and is always positive.

If the atom is allowed to relax (response of all the electrons to the core), we have to include

**the Relaxation energy,  $\Delta R$**  (always *-ve*)

**A realistic description of the binding energy is**

$$BE = -\varepsilon_i + \Delta C + \Delta R$$

# In solids such as metal or semiconductor, the BE can be described as

$$\text{BE} + \phi = -\varepsilon_i + \Delta C + \Delta R$$

$\varepsilon_i$ : one electron energy, determined by chemical environment, no correlation,  $-ve$

BE: binding energy ref. to the Fermi level,  $+ve$

$\phi$ : work function (minimum energy to remove an e- from Fermi level to vacuum),  $+ve$

$\Delta C$ : difference in correlation energy ( $E_f^C - E_i^C$ ),  $+ve$

Note: correlation energy  $E^C$  ( $-ve$ ) increases in magnitude as the number of electrons increases

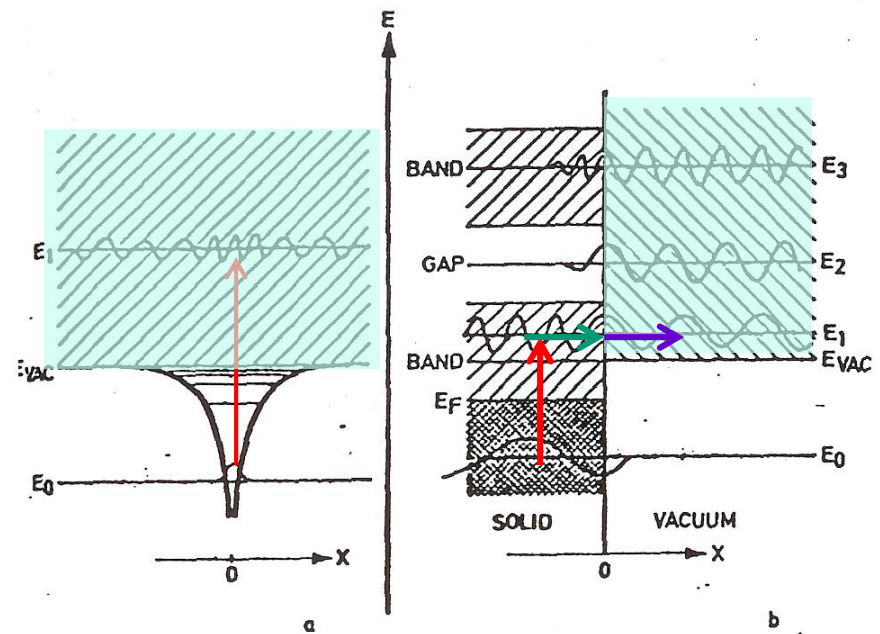
$\Delta R$ : Relaxation, it is associated with the final state, it is *always -ve*

# Transport of photoelectron from bulk to vacuum solids: the three step model

Step 1. Photoexcitation of an electron from a bound state (core or valence) of an atom in the solid to an energetic state in the solid.

Step 2. The energetic electron migrates to the surface, in the process, the electron undergoes inelastic and elastic scattering.

Step 3. The electron escapes into the vacuum



**Free atom**

**Solid**

# Theoretical photoionization cross-sections of elements

Yeh and Lindau, *At. Data & Nucl. Data* 32, 1 (1985)

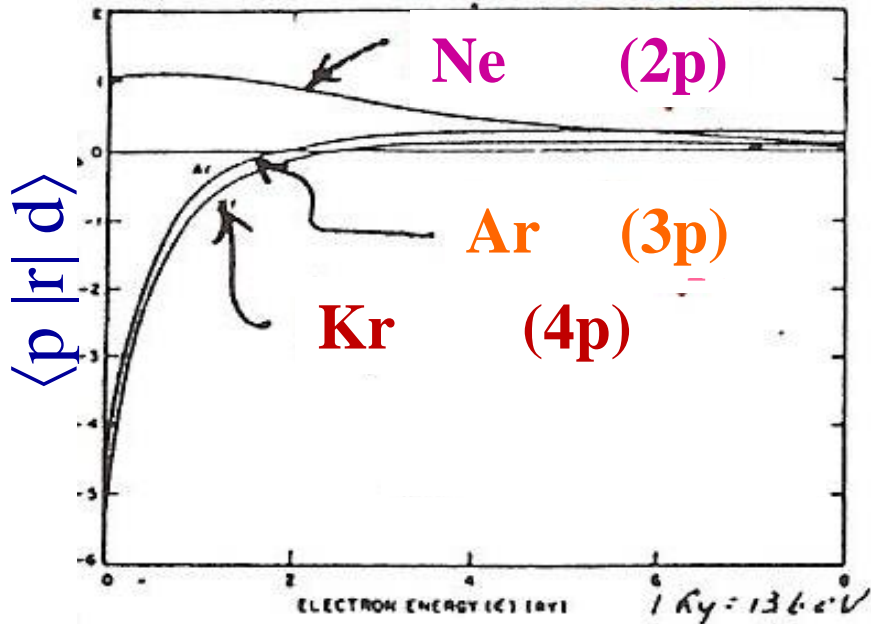
There are *photon energy dependent* cross-section minima associated with **some atomic orbitals** in the vicinity above an absorption threshold. There are called **Cooper minimum** and are associated with the initial state wavefunction ( $\psi$ ) which has a node in  $r$ .

**Cooper minimum** is widely used in the optimization of adsorbate vs. substrate signals.

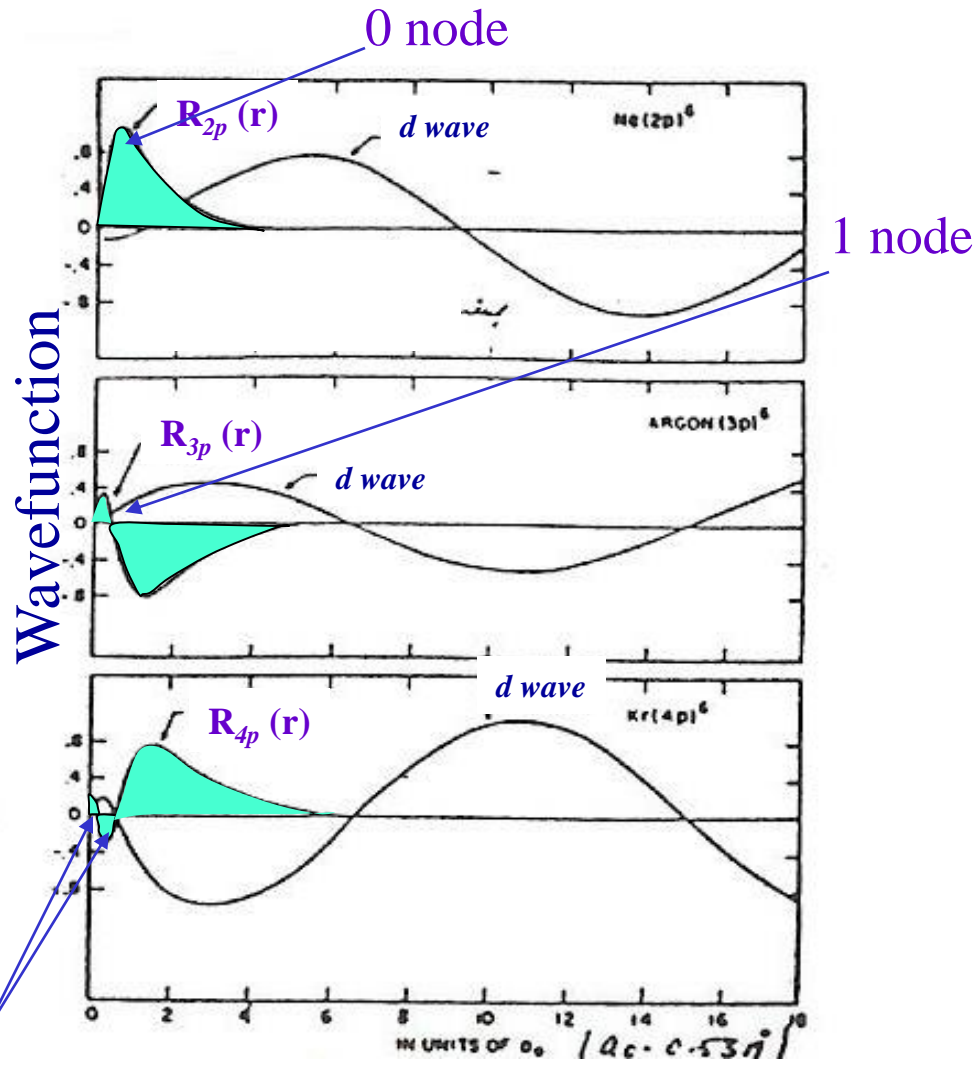
$\psi$ s that do not have a node in  $r$ : 1s, 2p, 3d, 4f etc.

$\psi$ s that have a node (changes sign) in  $r$ : 2s, 3p, 4p, 4d, 5d, etc.

# Graphical illustration of Cooper minimum



$E - E_0$



2 nodes

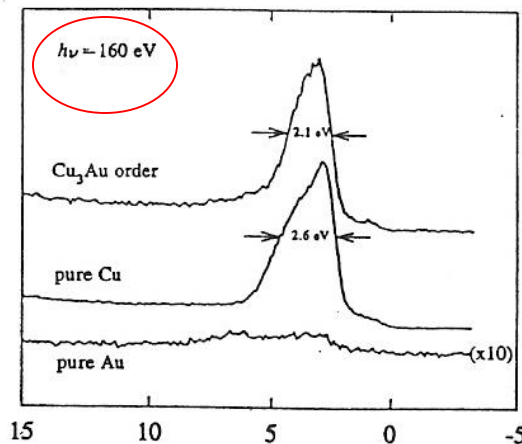
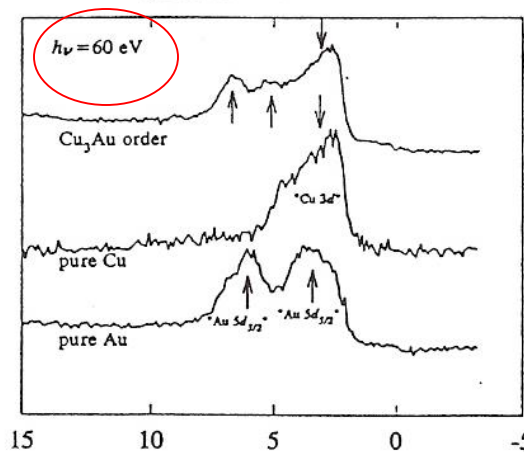
$r$

# Valence band using variable photon energies

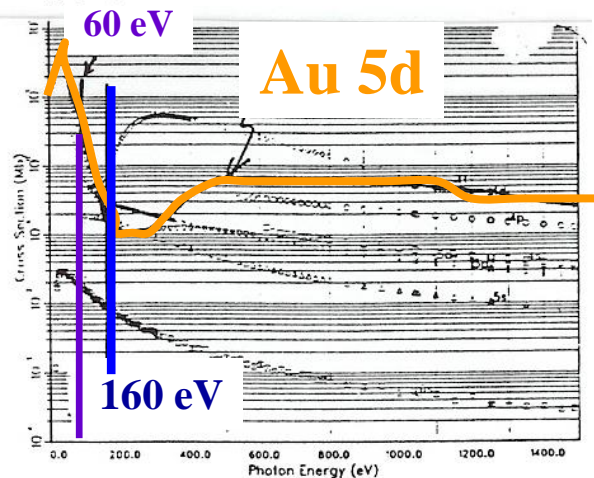
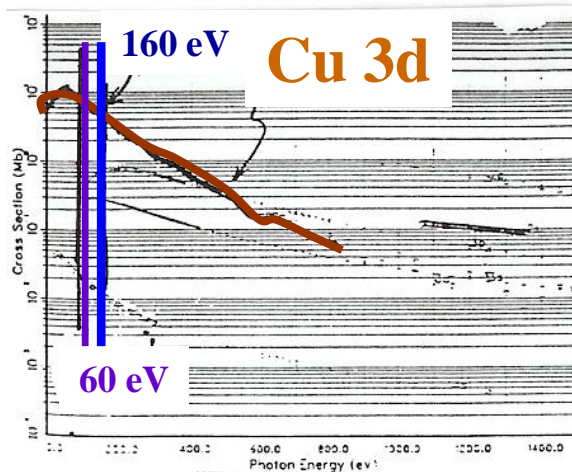
a. The interaction of d electrons in Au-Cu alloys:

The figs. below show the valence band spectra of a Au-Cu alloy.

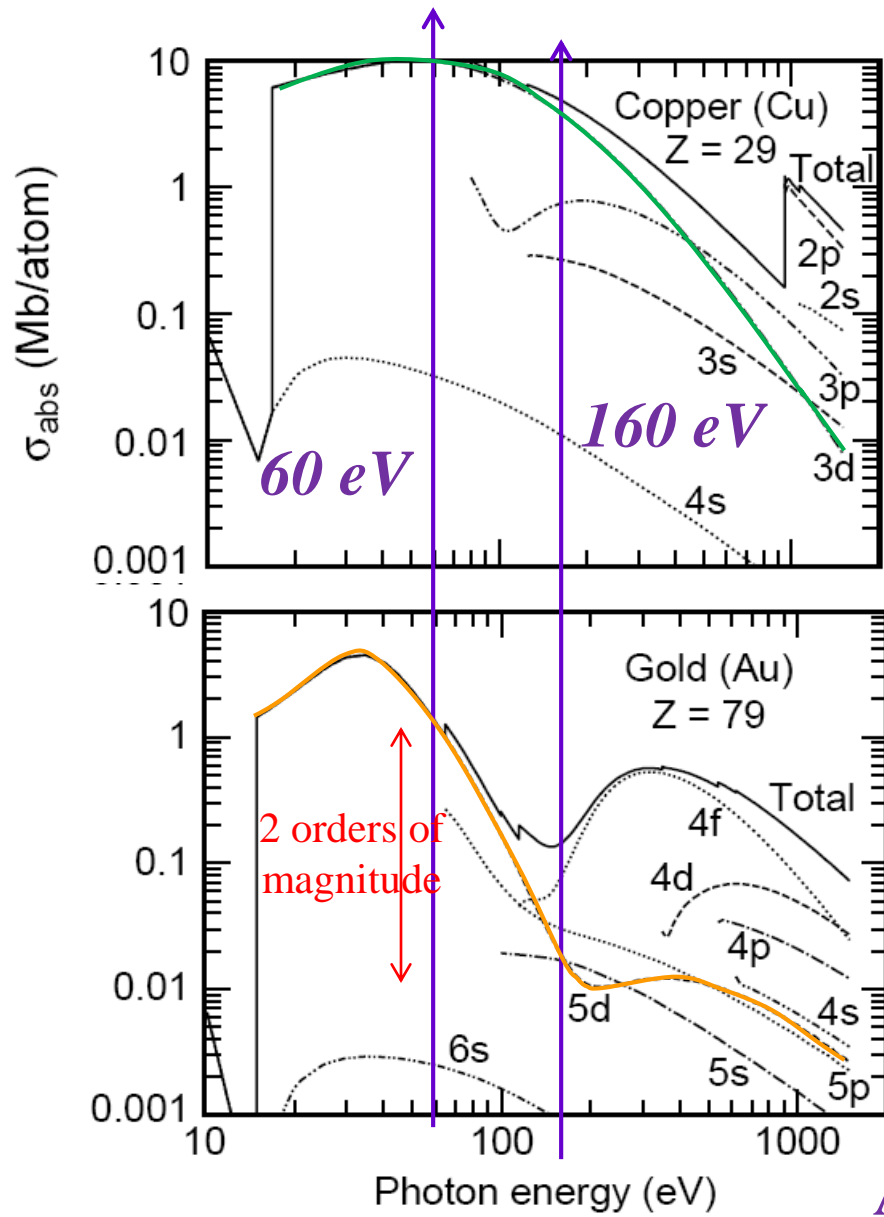
Since Au 5d and Cu 3d have different cross sections, one can reveal the Cu and Au character of the valence electrons by changing the photon energy. *Au 5d has a Cooper minimum at 160 eV*



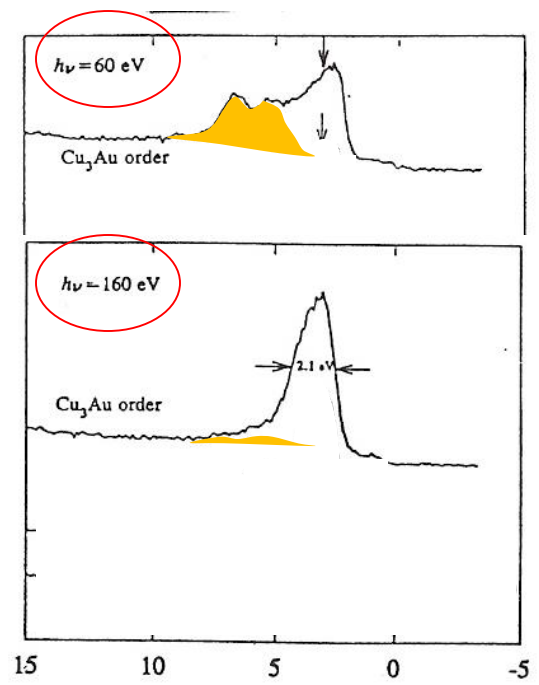
Binding Energy (eV)







Cu 3d: No Cooper minimum



Au 5d: Cooper minimum

Au signal is suppressed at 160 eV



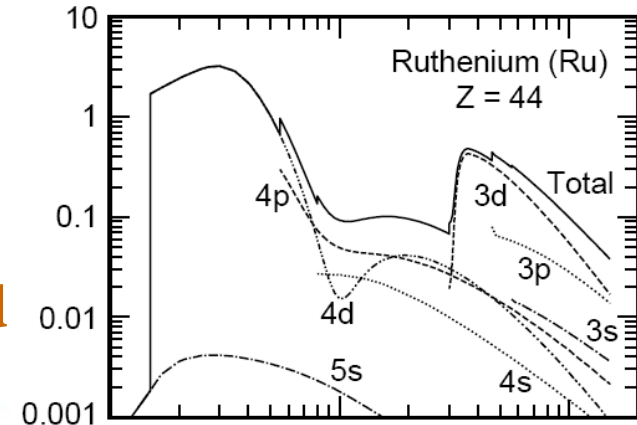
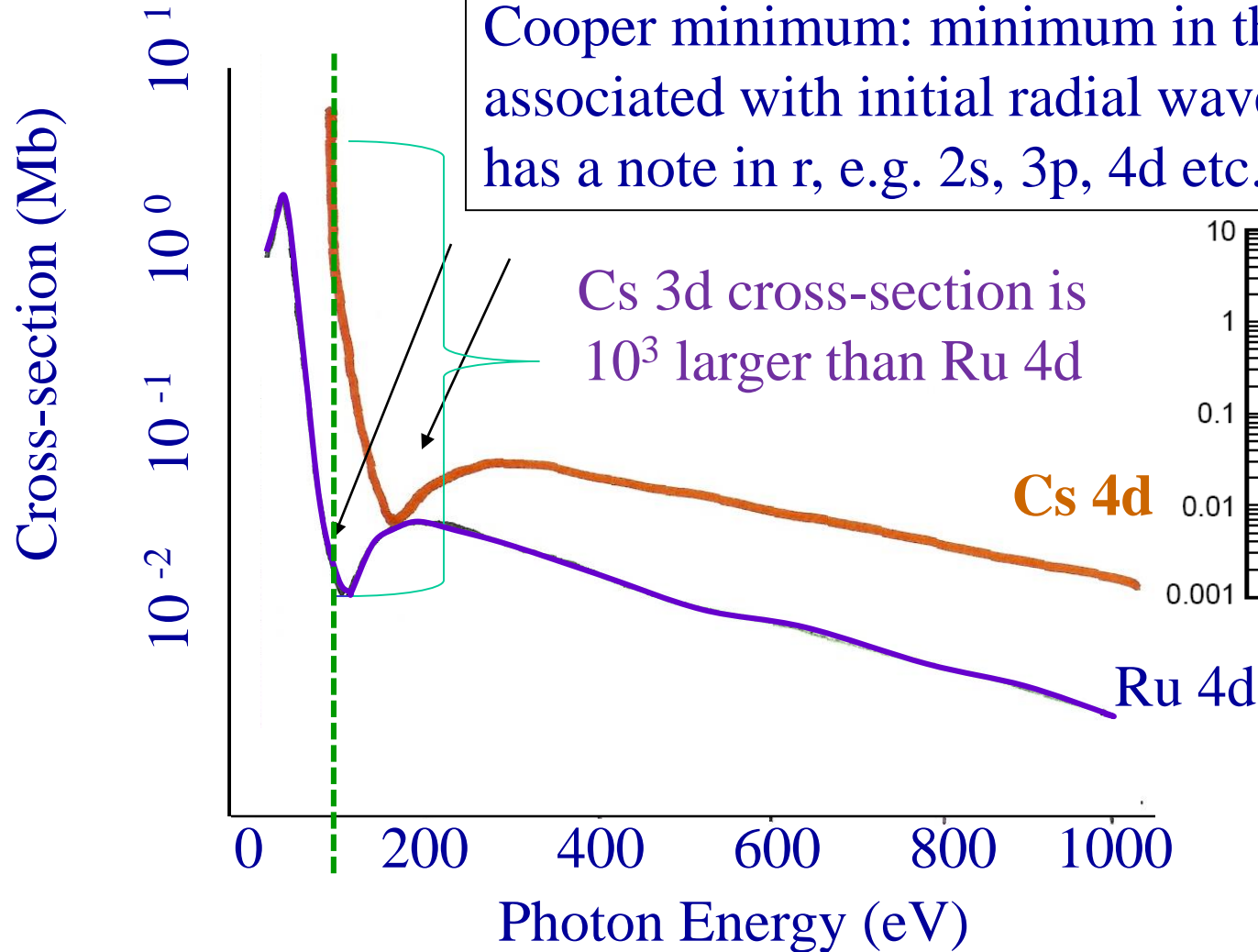
## b. Cross section optimization and electron escape depth considerations: layer-resolved spectroscopy: Cs on Ru (001)

by selecting an *appropriate* photon energy, one can reveal the identity of many **different adsorption states** with very high sensitivity.

Cs on Ru(001) is an example in that we can select a good photon energy at which the Cs 4d cross section is high and the Ru 4d cross section is minimized (**Cooper minimum**)

# Photoionization Cross Section of Cs and Ru

Yeh & Lindau At. Data & Nucl. Data, 32 (1(1985))



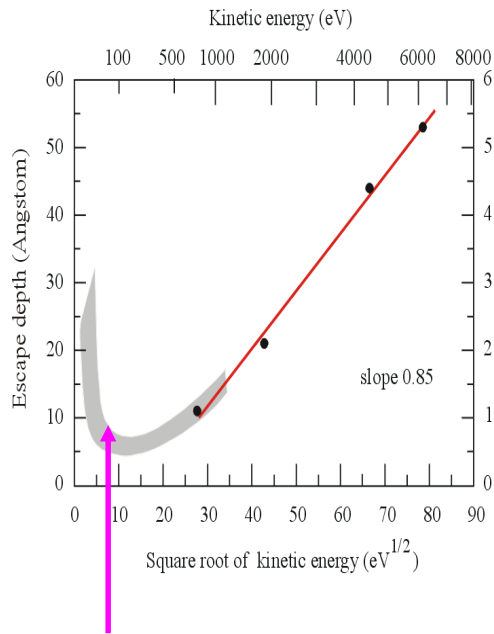
# Photoemission: Examples

**Surface core-level shifts (SCS) =  $BE_s - BE_b$ :**

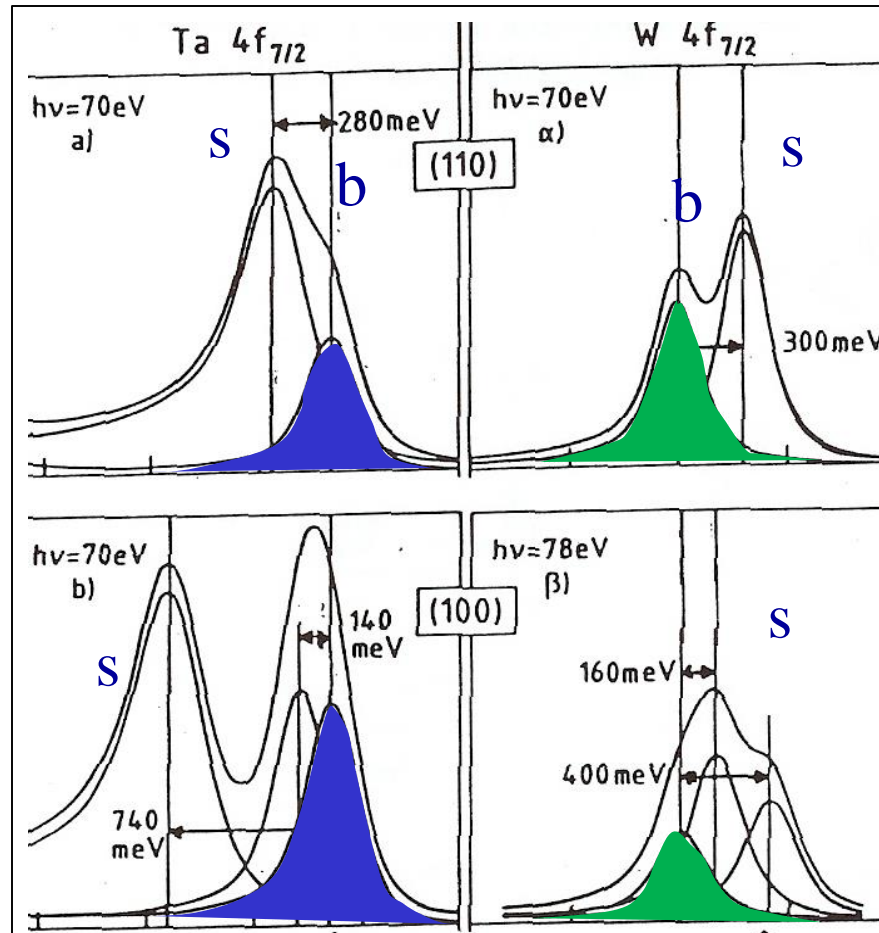
**Observation:** in metals, the core level BE of the surface atom is shifted relative to that of the bulk (surface atom has reduced coordination)

- i) SCS is + ve when the d band is less than half filled (e.g. Ta)
- ii) SCS is -ve when d band is more than half filled (e.g. Au)
- iii) SCS is also dependent on the surface structure

# 4f SCS from W and Ta



KE ~ minimum



Wertheim et al. Phys. Rev. B 30, 4343(1984)



Increasing BE

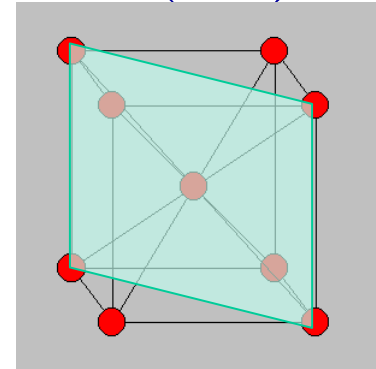
21.65 eV

31.1 eV

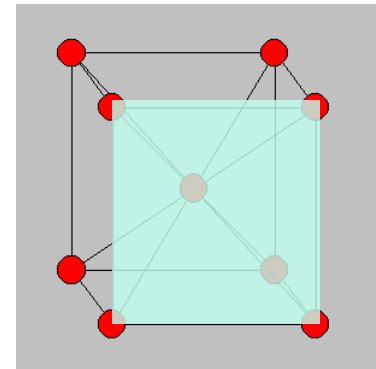
$6s^1 5d^4 6s^1 5d^5$

57-71	72	73	74	75	76	77	78	79	80
	<b>Hf</b>	<b>Ta</b>	<b>W</b>	<b>Re</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	<b>Hg</b>
	Hafnium 178.49	Tantalum 180.9479	Tungsten 183.85	Rhenium 186.207	Osmium 190.23	Iridium 192.22	Platinum 195.08	Gold 196.9665	Mercury 200.59

bcc (110)



bcc (100)



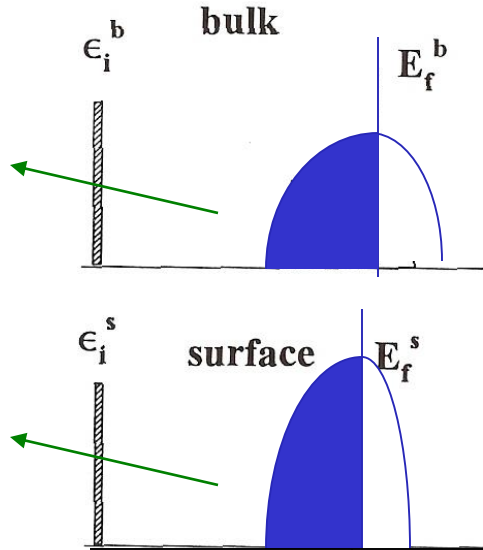
# Interpretation of SCS- the band model

## Realignment of the surface and bulk Fermi levels

[Citrin and Wertheim PRB 27, 3176 (1983)]

### d band more than half filled

Shaded area contains the same # of d electrons



- Surface d band always narrows, d count remains the same
- Surface and bulk Fermi level must equalize

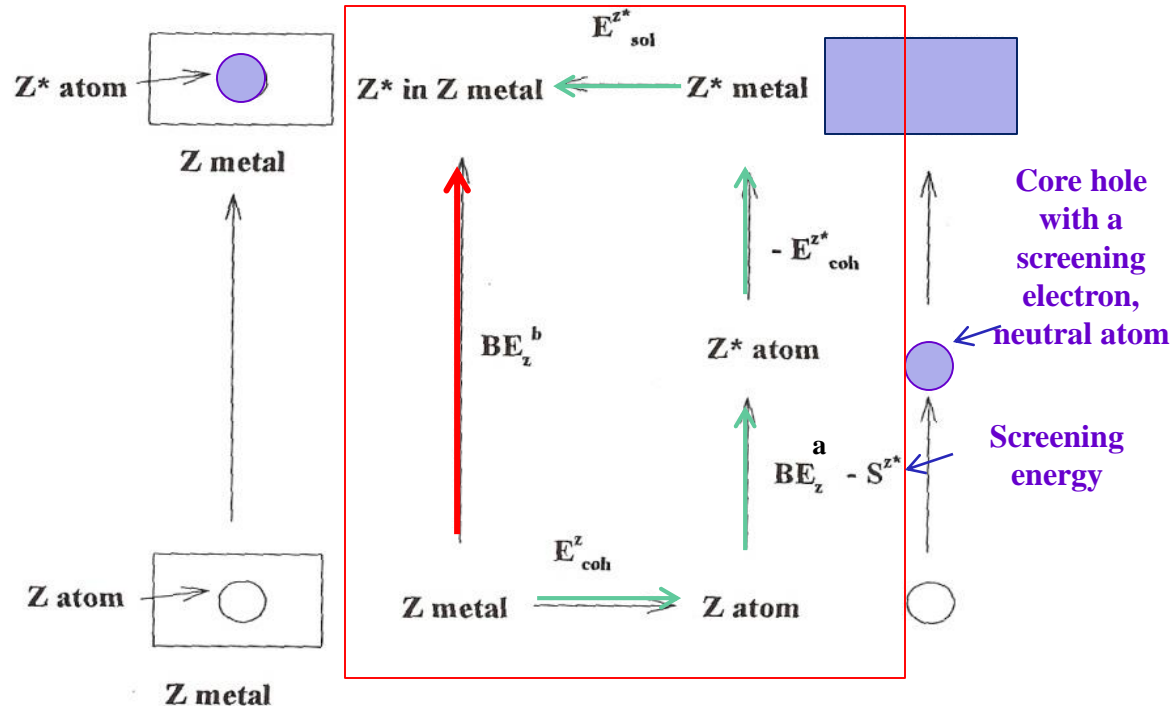
## SCS in metals based on the Band model

- **Noble metal, SCS = -ve**
- Transition metal with  $d^n$   $n > 5$ , SCS = -ve
- Transition metal with  $d^n$   $n < 5$ , SCS = +ve
- Experimentally, the trend is generally valid
- Alkali and alkaline earth metals are more difficult to predict.

# Interpretation of SCS: the JM model

Thermodynamic (JM) model: **Born-Haber cycle, equivalent core** [Johnasson & Martensson, PRB,21, 4427(1980)]

It is generally recognized that the surface cohesion energy is approx. 80% that of bulk



Note :  $Z^*$  in the metal becomes  $Z+1$ , this is the equivalent core approximation

$$SCS(\Delta BE_{s-b}) = [E^{Z+1}_{coh,b} - E^Z_{coh,b}] - [E^{Z+1}_{coh,s} - E^Z_{coh,s}]$$

e.g. : if  $Z = Na$ ,  $Z+1 = Mg$ ; etc.

# The JM Model, cont'

This model makes use of the Born-Harber cycle (equivalent core approximation,  $Z^* = Z+1$ ) and experimentally derived energies.

## Relevant parameters:

- (1) Cohesive energy,  $E_{\text{coh}}^Z$  = energy required to remove an atom (atomic #  $Z$ ) from the solid, a positive value.
- (2) The binding energy of an atom with atomic number  $Z$ ,  $BE_Z^a$
- (3) The screening energy  $S$  gained by an electron from the lattice to screening the atom  $Z$  with a core hole,  $Z^*$ .

Note:  $Z^*$  is an atom with a core hole and a neutralized charge from the surrounding,  $Z^*$  is neutral locally.

- (4) The cohesion energy of the atom  $Z^*$ ,  $E_{\text{coh}}^{Z^*}$ . (note: equivalent-core implied)
- (5) The heat of solution of dissolving  $Z^*$  atom in the  $Z$  host,  $E_{\text{sol}}^{Z^*}$



# Alignment of energy levels in metals, semiconductors and molecules:

*Fermi level,  $\epsilon_F$*  : the highest occupied electronic level (analogous to HOMO in molecules)

*Vacuum level  $E_{vac}$* : electrons with zero kinetic energy

*Intrinsic semiconductor*: no doping

*p-type* : doped with  $e^-$  acceptor, e.g. Si doped with B.

*n-type* : doped with  $e^-$  donors, e.g. Si doped with N, P

*Valence band*: occupied densities of states below the Fermi level

*Conduction band*: unoccupied densities of states above the Fermi level

*Densities of States (DOS)*: In a solid, the atom orbital in the valence region overlaps to form energy bands. The occupancy of the energy levels within the band per unit energy (energy distribution of the electrons) is the densities of states.

***Band gap:*** The energy separation between the top of the valence band and the bottom of the conduction band

***Direct band gap:*** The top and bottom of the valence band and conduction band respectively have the same  $k$  (lattice vector) value; e.g. GaAs

***Indirect band gap:*** The top and bottom of the valence band and conduction band respectively do not have the same  $k$  (lattice vector) value; e.g. Si, Ge

***Contact potential:*** when materials of different work functions are in contact, there exists a potential difference between them.

***Fermi level pinning and band banding:*** when metals and semiconductors are in contact, the Fermi level equalizes.

## Binding energy shifts in semiconductors:

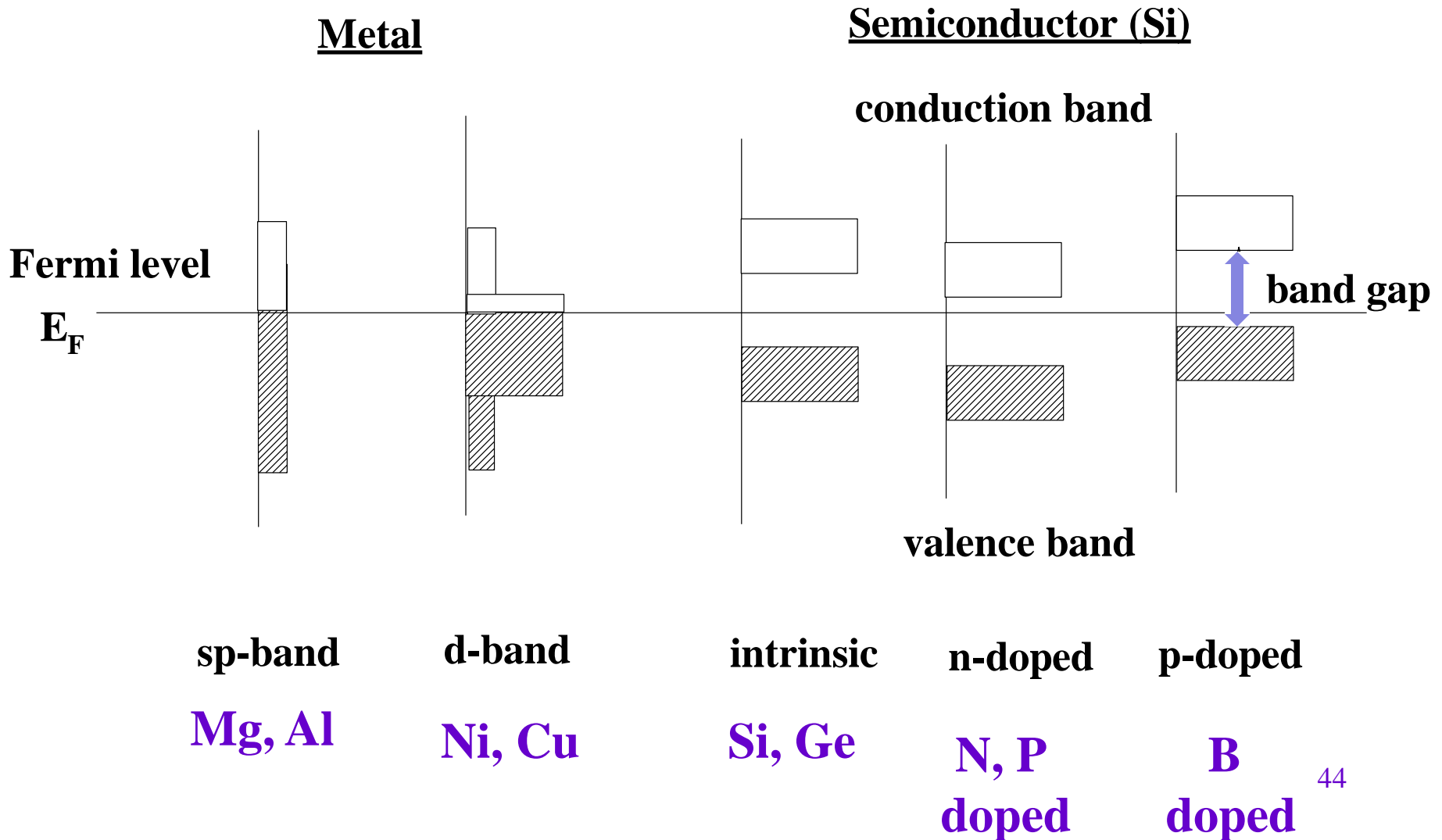
For semiconductor such as Si and Ge or InP and GaAs, there exist a band-gap between the valence band and the conduction band.

For **intrinsic semiconductor** (undoped), the Fermi level is in the mid-point of the band gap,

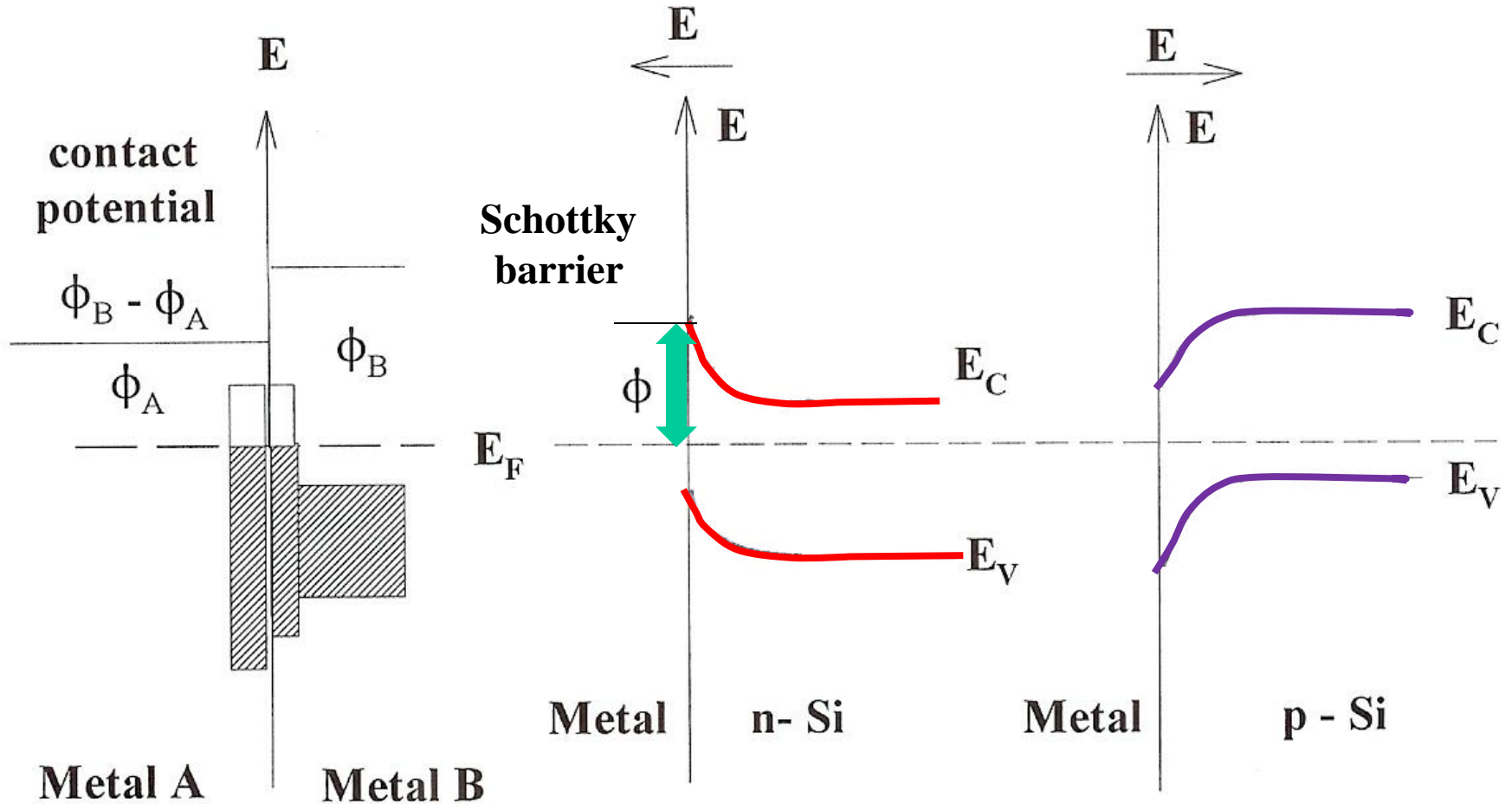
For **p-type** or **n-type** Si for example, the Fermi level moves towards, the top of the conduction band and the bottom of the valence band, respectively, resulting in large Fermi level shift, hence a large shift in the observed energy.

# Metals and semiconductors

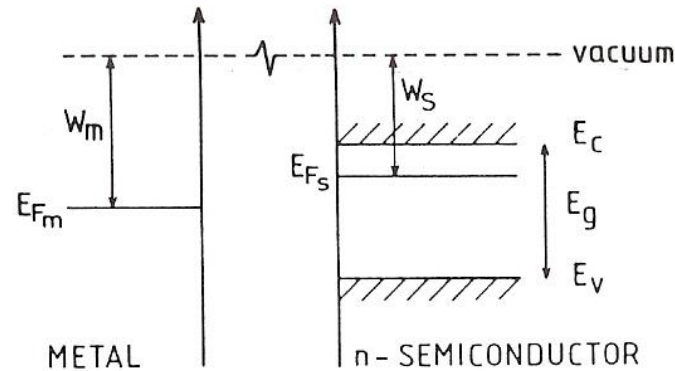
## Electron distribution



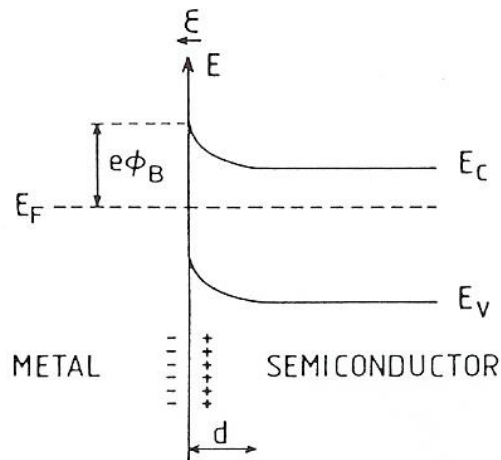
# Metals and semiconductor contacts



# Matching of energy levels at interface upon contact



**Fig. 6.3.** The band diagram of an isolated metal and an n-type semiconductor with their work functions and Fermi energies relative to the vacuum indicated. Since the semiconductor is doped with donors, its Fermi energy lies closer to the conduction band edge  $E_c$ .



**Fig. 6.4.** The equilibrium band diagram of a metal–semiconductor interface formed by the materials shown in Fig. 6.3:  $\phi_B$  is the contact potential;  $d$  is the width of the depletion layer. The direction of the electric field across the interface is also indicated.

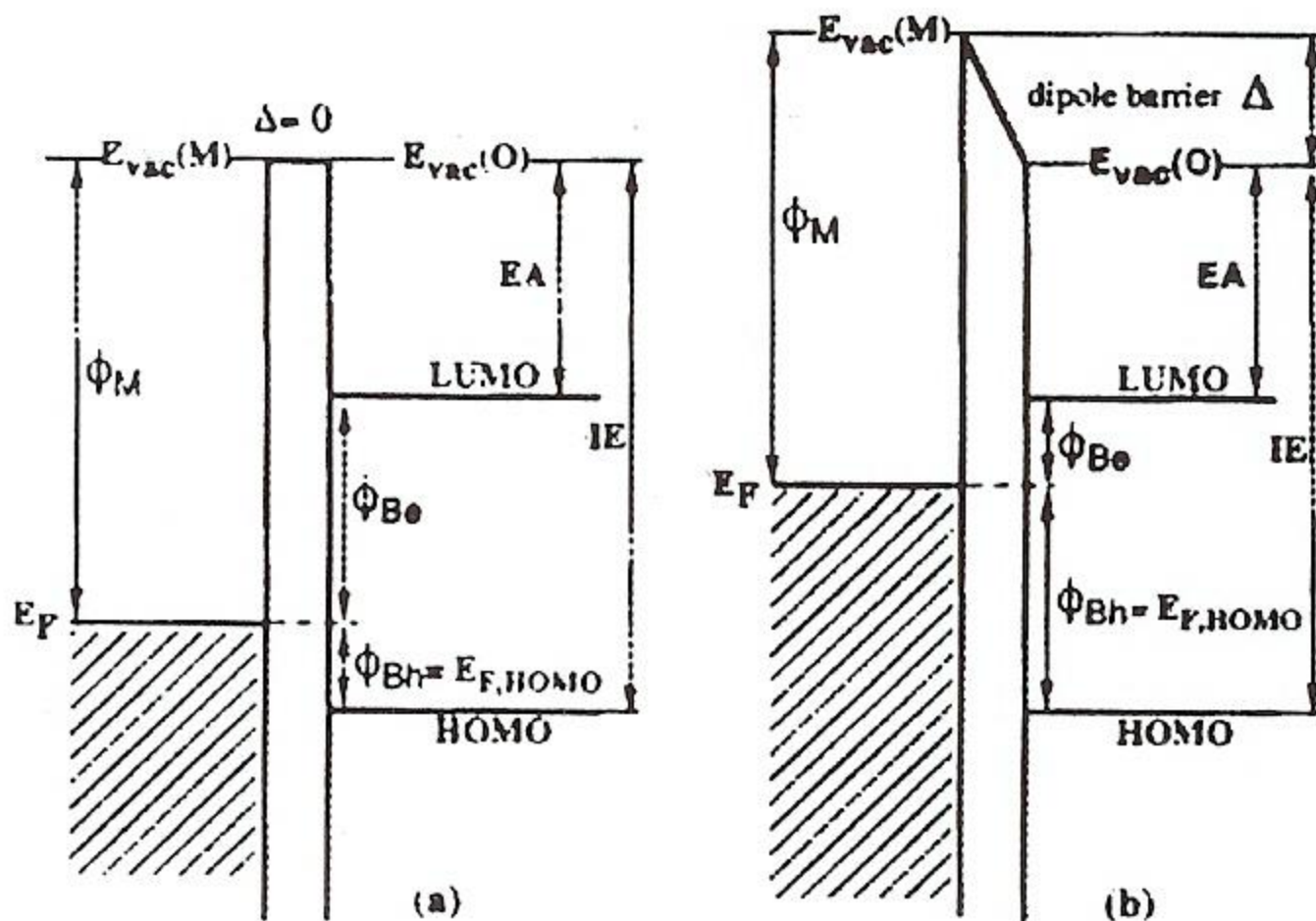
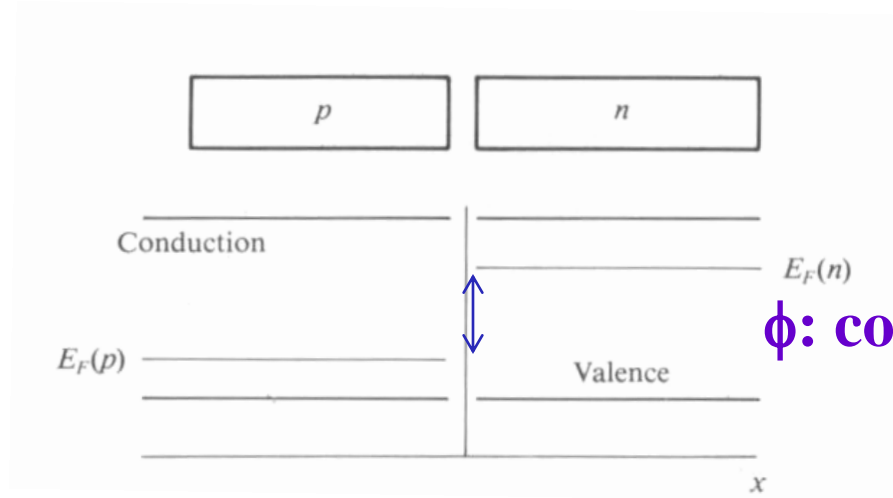


FIG. 1. Schematic of an organic-metal interface energy diagram (a) without and (b) with an interface dipole  $\Delta$ .  $\phi_{Be}$  and  $\phi_{Bh}$  are the electron and hole barriers, and  $E_{vac}(O)$  and  $E_{vac}(M)$  are the organic and metal vacuum levels, respectively.

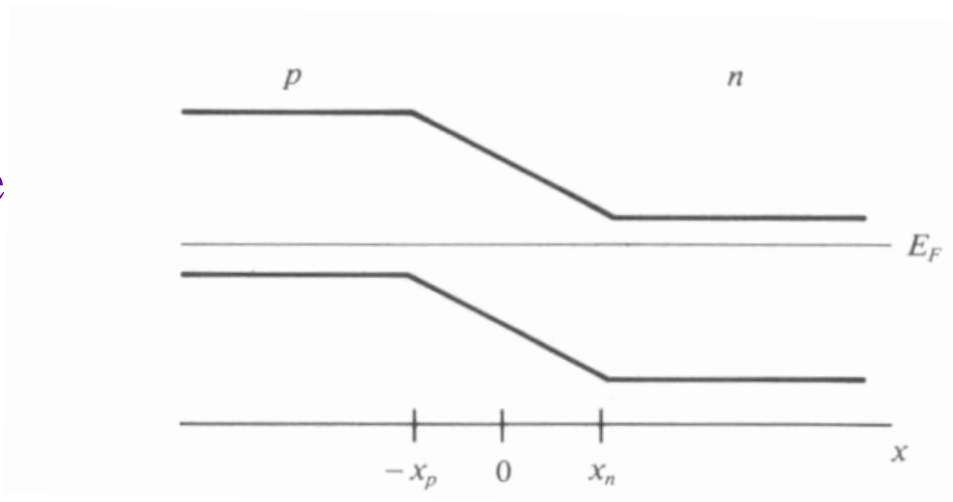
# The p - n junction

When p type and n type semiconductor are in contact, the Fermi level equalizes



$\phi$ : contact potential

At equilibrium, there is a charge depletion in the region of the interface





The BE of the Si 2p level is a constant with respect to the mid point of the band gap in pure Si. All the shift in doped silicon is given rise by Fermi level shifts

Heavily doped n and p type Si moves the Fermi level toward CB and VB respectively

Ref. Himpsel et.al. Proc.of the Enrico Fermi School on "Photoemission and absorption spectroscopy of solids and interfaces with Synchrotron Radiation". ed. by M Campagna and R. Rosei, North Holland (Amsterdam 1990).

### Absorption at The Si L<sub>2,3</sub> edge

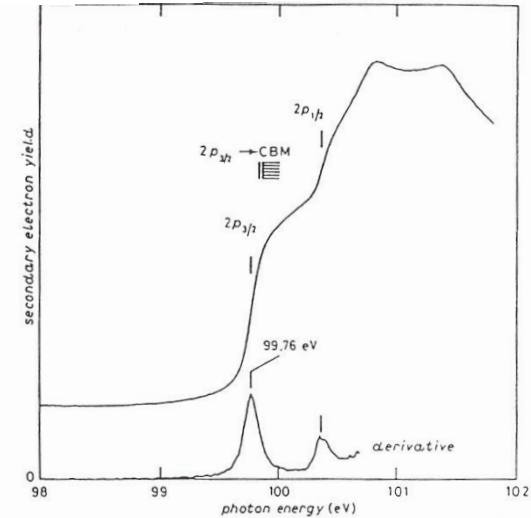


Fig. 4. - The Si2p absorption edge and its derivative. The intensity of secondary is detected, which is proportional to the absorption coefficient.

### Si 2p photoemission

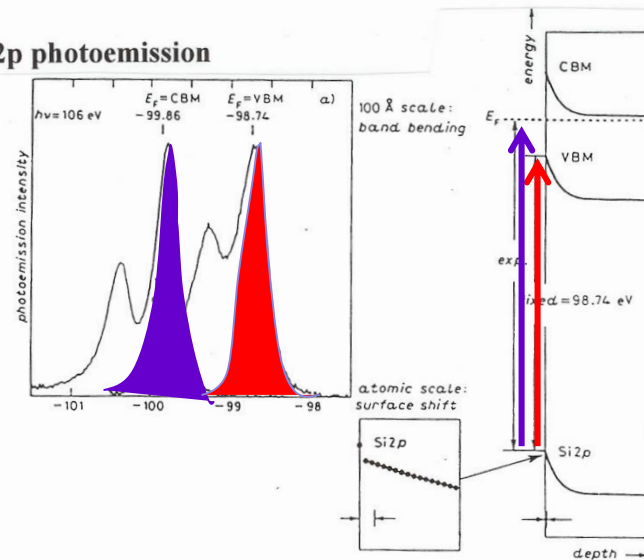
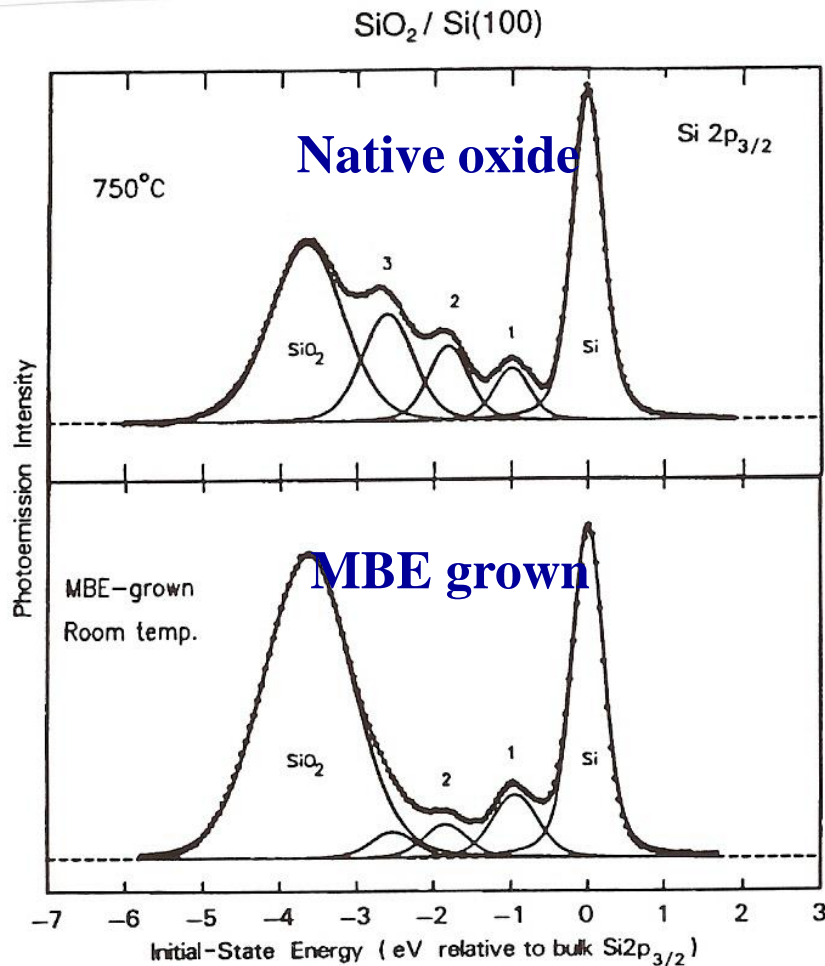


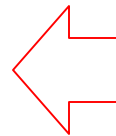
Fig. 5. - The two contributions to the Si2p core level energy from Fermi level pinning and from chemical effects at the surface. The former affects the position of the whole core level spectrum (bulk plus surface), the latter introduces extra surface core level peaks originating from the outermost Si layer. Examples for the two effects are given in fig. 6a), b).

# SCS in semiconductors overlayers



F.J. Himpsel et al. Phys. Rev. B 38 (1988)

Remove  
the 2p<sub>1/2</sub>  
component



2p<sub>3/2,1/2</sub>

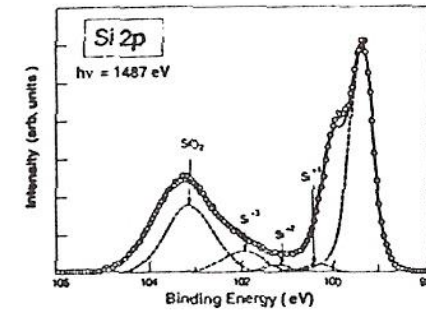


FIG. 3. XPS data taken with AlK $\alpha$  radiation at a 12.5° takeoff angle. The open circles are as-recorded data after a Shirley background subtraction. The dashed lines are 2p<sub>1/2</sub> components of deconvoluted oxide species as labelled. The solid line is the sum of all these Si peaks including their respective 2p<sub>1/2</sub> components.

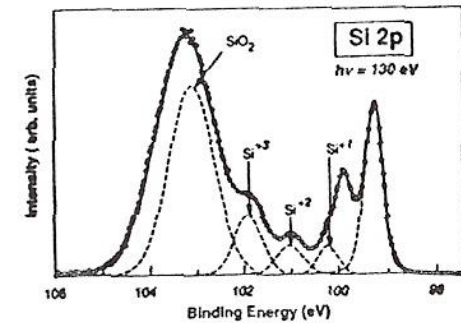
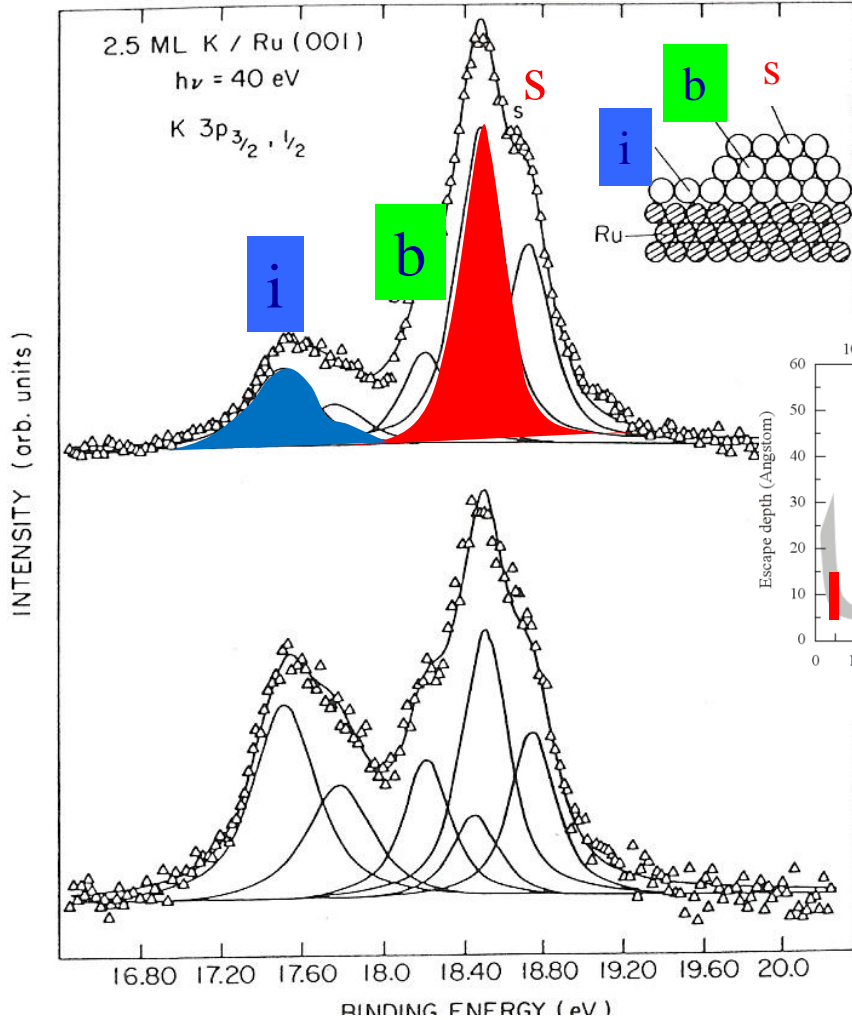


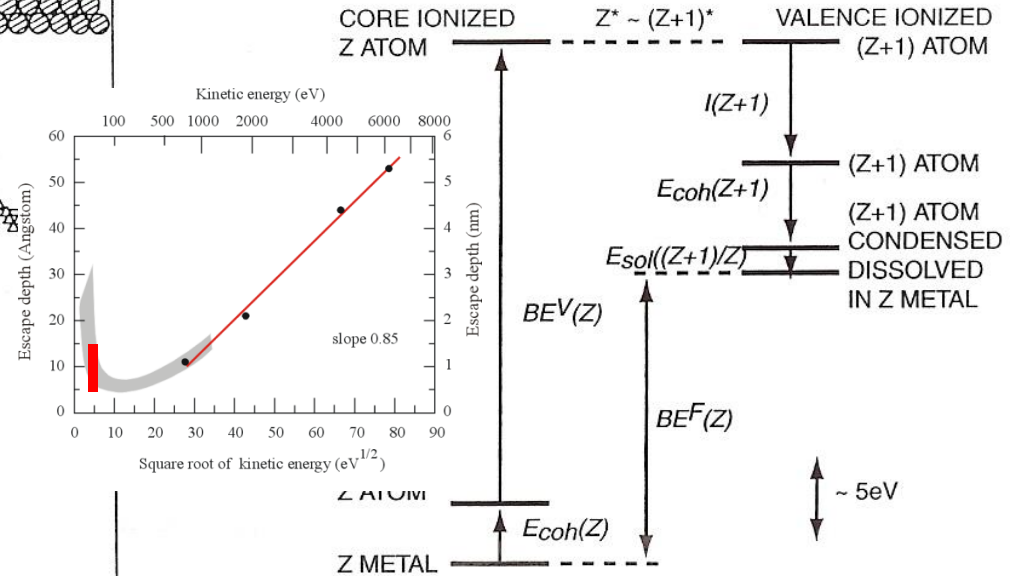
FIG. 1. PES data taken with 130 eV photons at a 54° takeoff angle. The open circles are as-recorded data after Shirley background subtraction. The dashed lines are 2p<sub>1/2</sub> components of deconvoluted oxide species as labelled. The solid line is the sum of all these Si peaks including their respective 2p<sub>1/2</sub> components.

# Photoemission: Layer-resolved spectroscopy

$$KE = 40 - BE - \phi = \sim 20 \text{ eV}$$

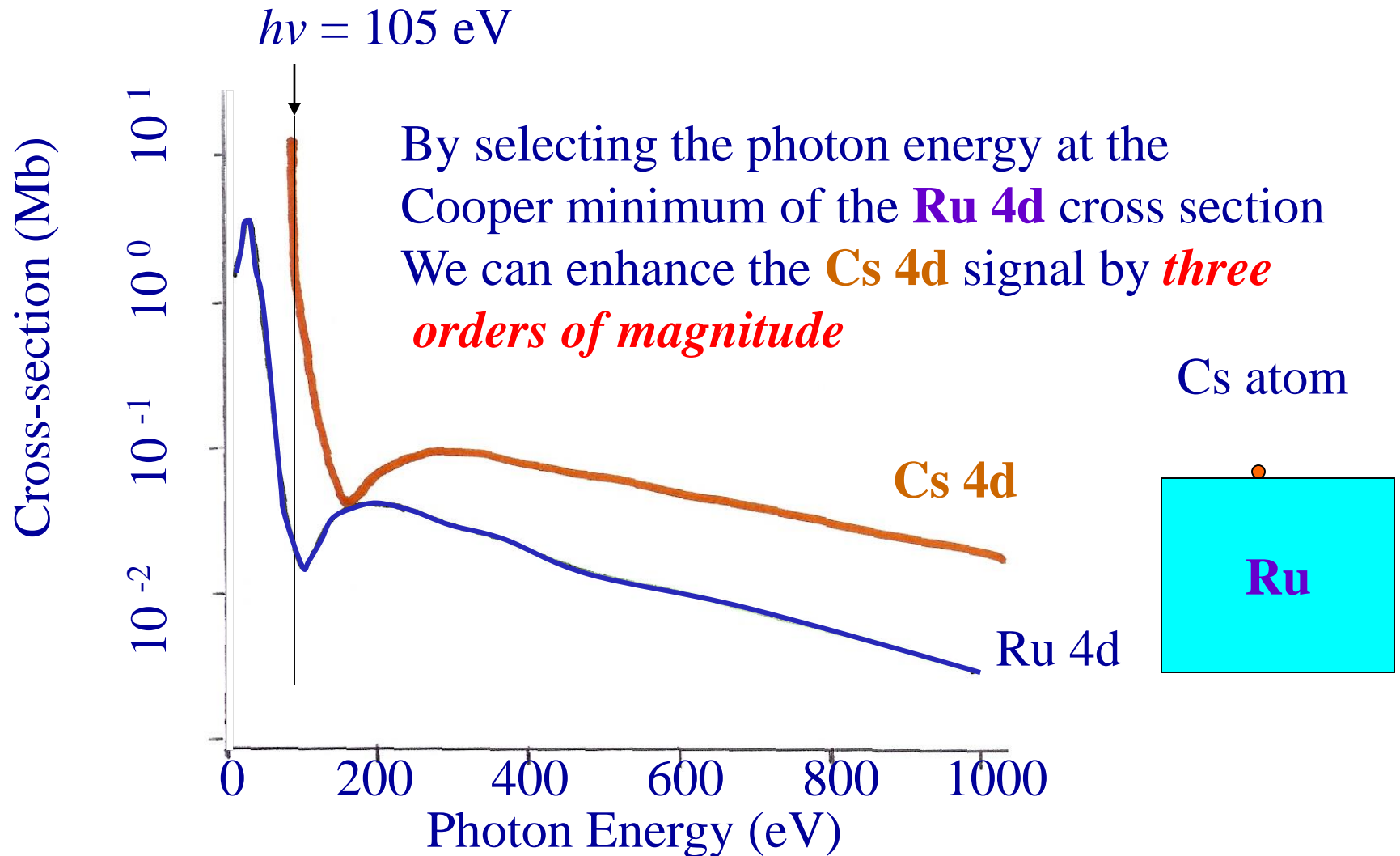


## (Z+1) EQUIVALENT CORE APPROXIMATION

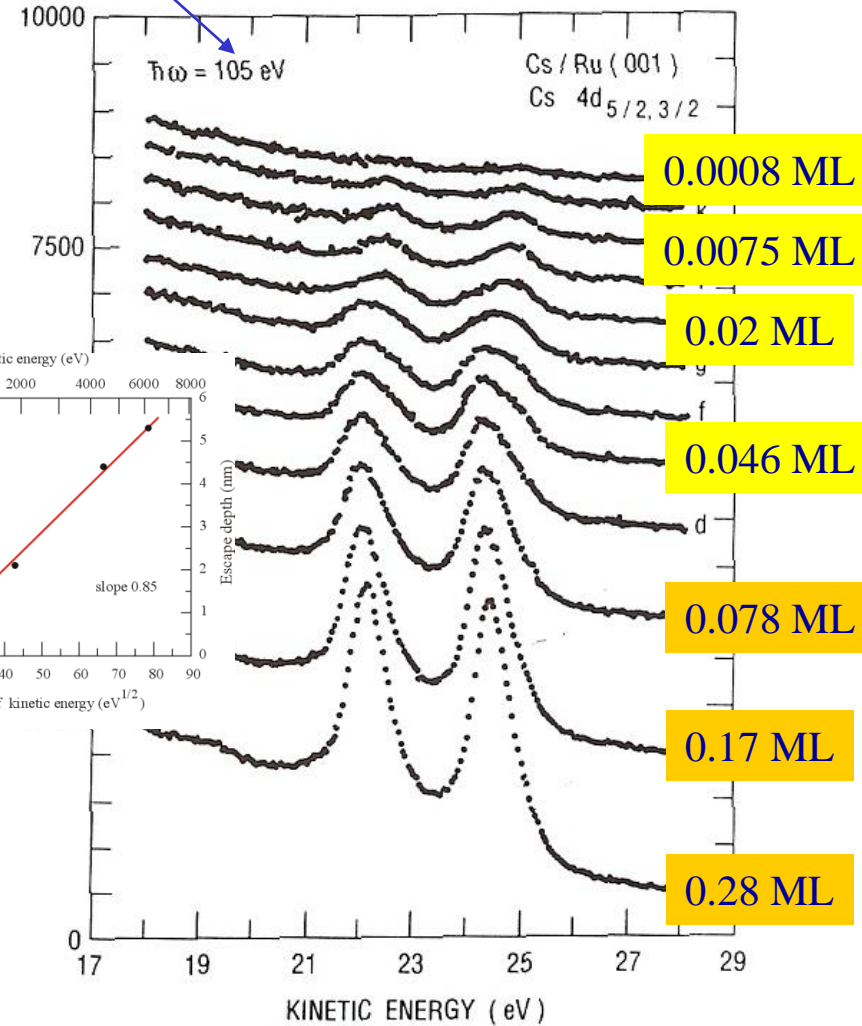
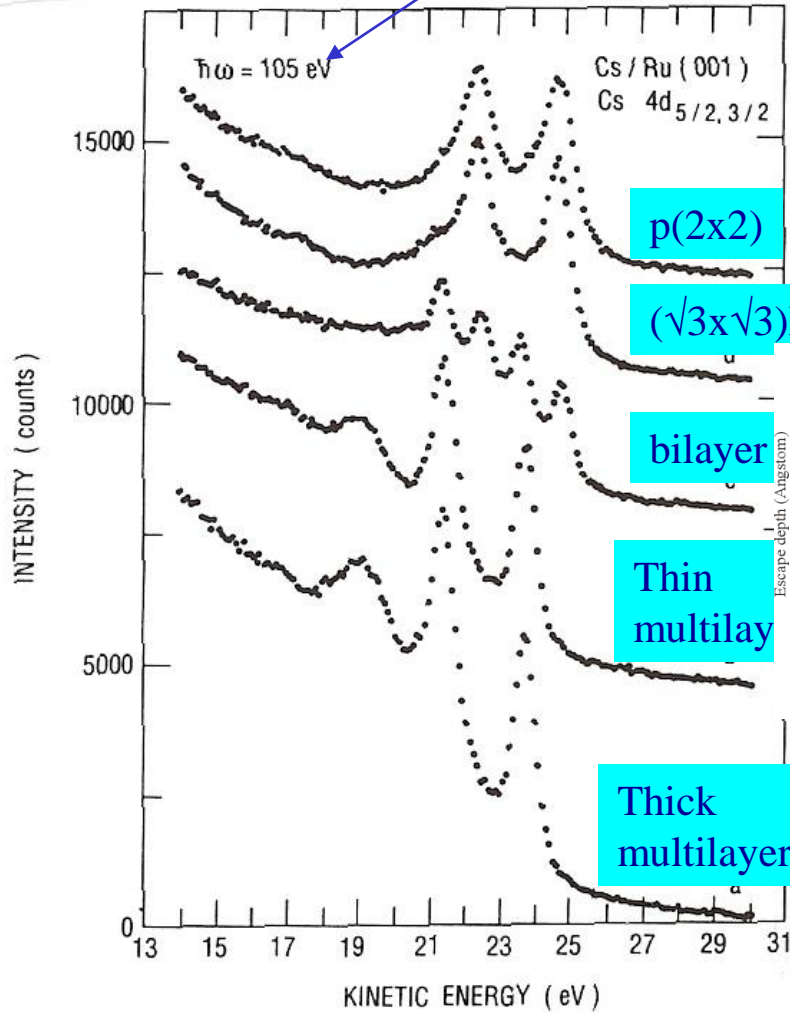


Surf. Sci. Lett. 210, L185 (1989)

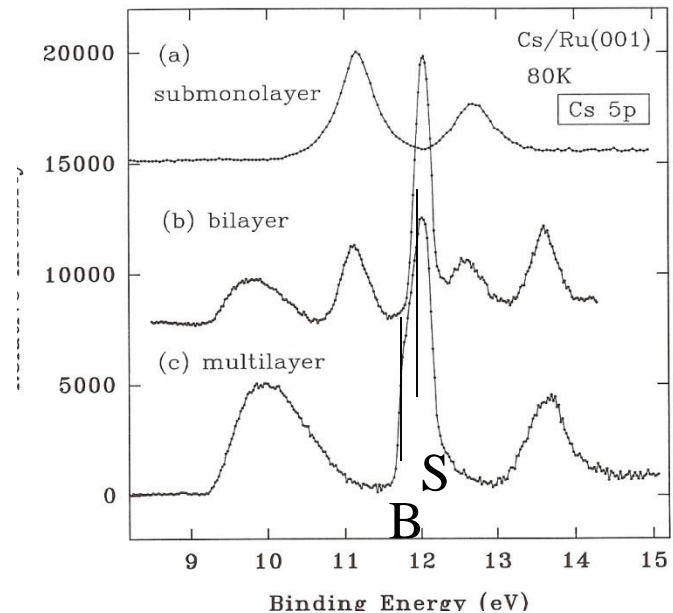
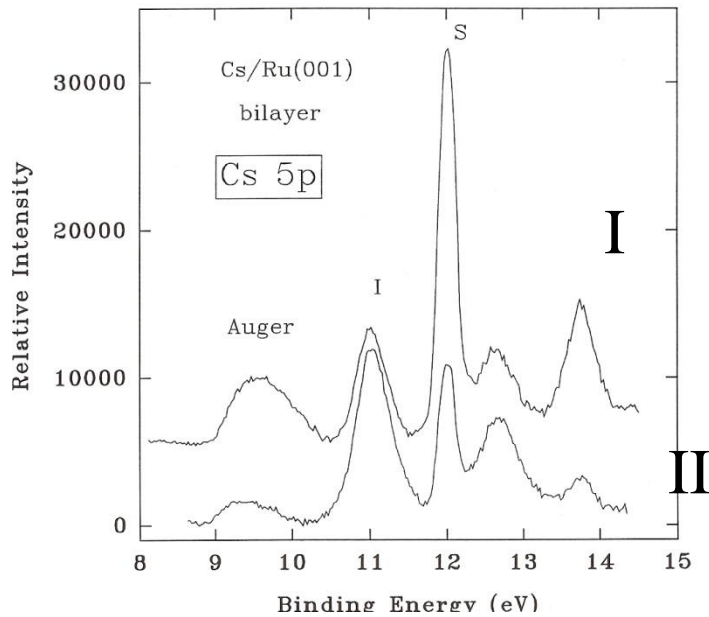
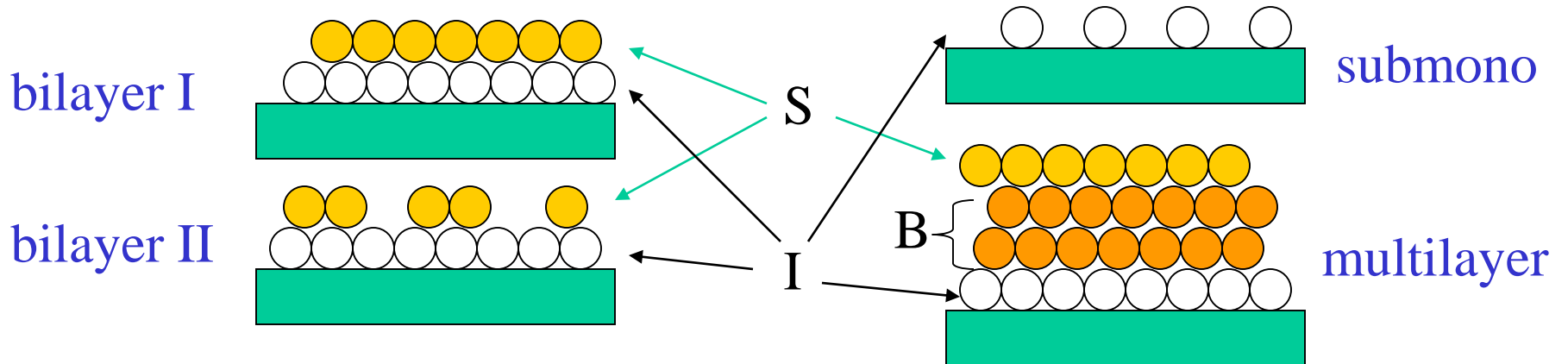
# Cs overlayers/Ru: application of the Cooper minimum



# Enhanced Cs 4d photoemission

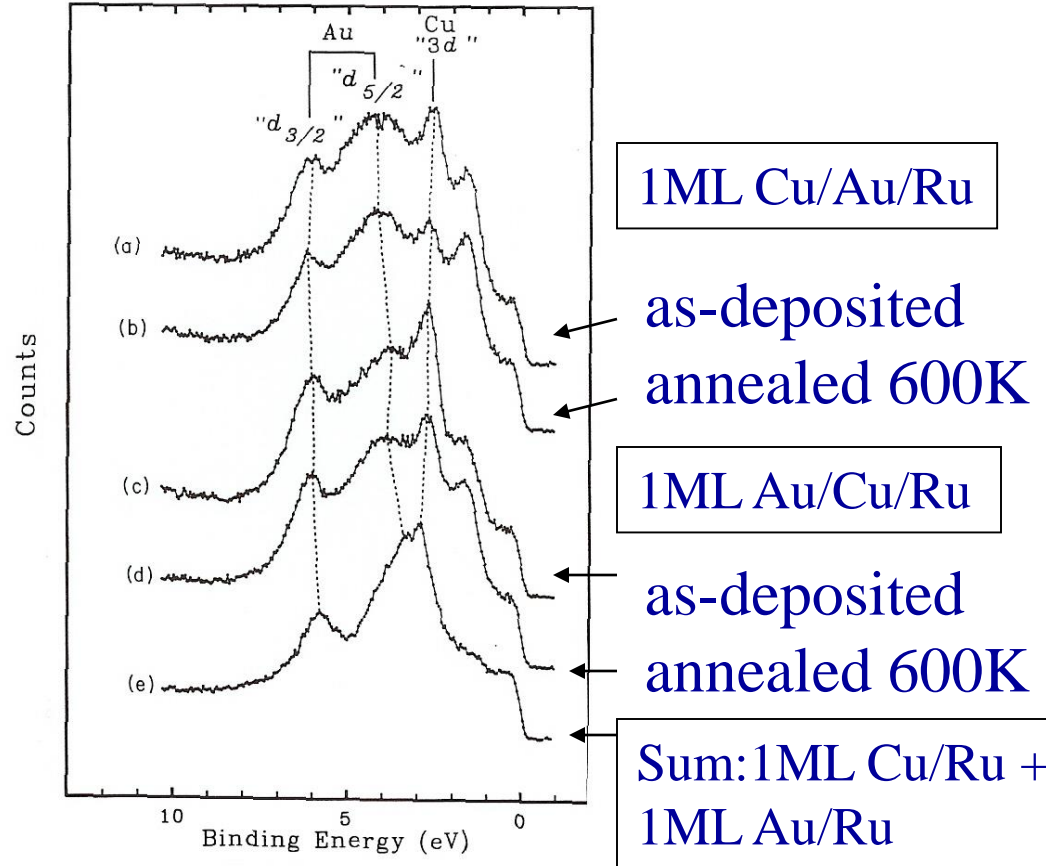
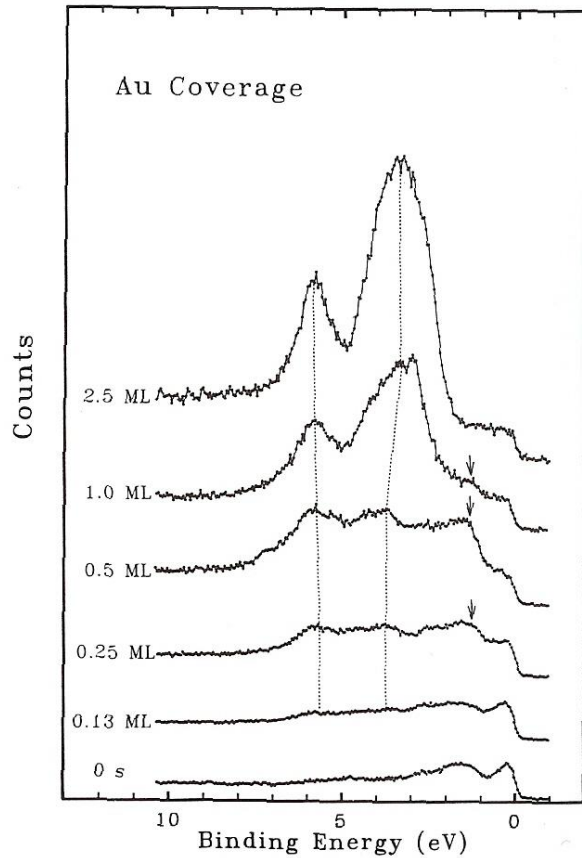


# Cs 5p photoemission of Cs/Ru(0001): Implications to charge transfer and decay dynamics



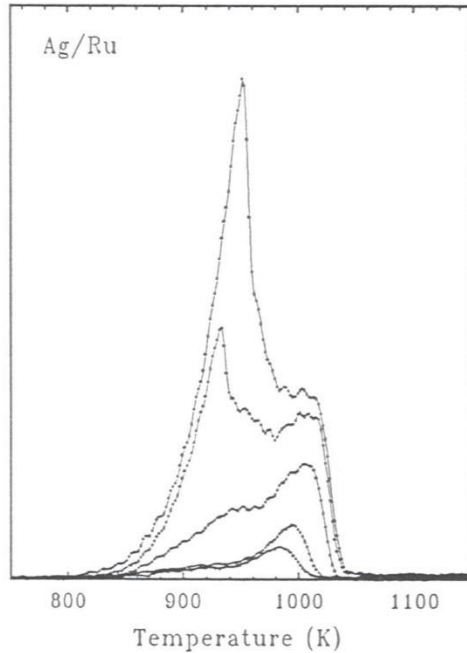


# Two-dimension alloying

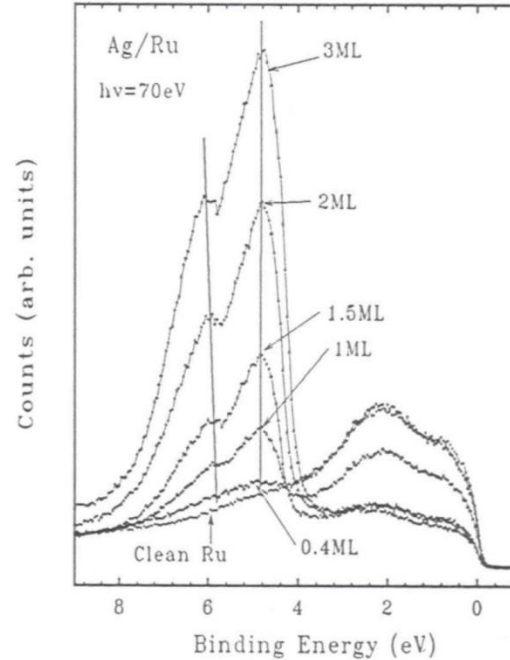


Kuhn et al. Phys. Rev. B 45, 3703(1992)

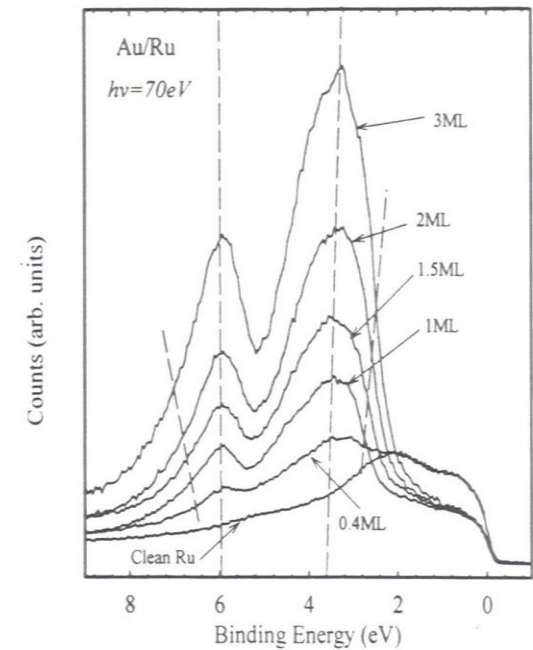
# Electronic structure of Ag and Au overlayers & 2D- alloying on Ru(0001)



TDS of Ag/Ru



VB of Ag/Ru



VB of Au/Ru

A. Bzowski et al. PRB 51,9979 (1995); PRB 59, 13379 (1999).

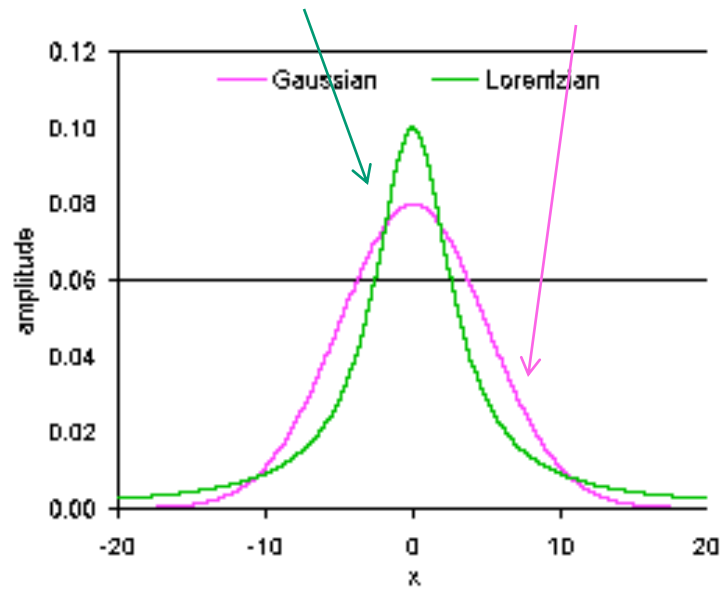


# Photoemission: Fine structures and beyond the single particle approximation

- Manybody lineshape in metallic materials
- Shake-up and shake-off
- Exchange splitting
- Vibrational/thermal broadening
- Crystal field splitting
- Plasmons
- Complete absence of a single particle peak  
(total break down of single particle approximation)

# Normal XPS line shape

$$\Gamma = \sqrt{\Delta E_{\tau}^2 + \Delta E_I^2}$$



The observed peak is normally fitted to a Voigt function which is a convolution of Gaussian and Lorentzian

[http://www.casaxps.com/help\\_manual/line\\_shapes.htm](http://www.casaxps.com/help_manual/line_shapes.htm)

# Core hole life time and widths (radiative, X-ray and Auger)

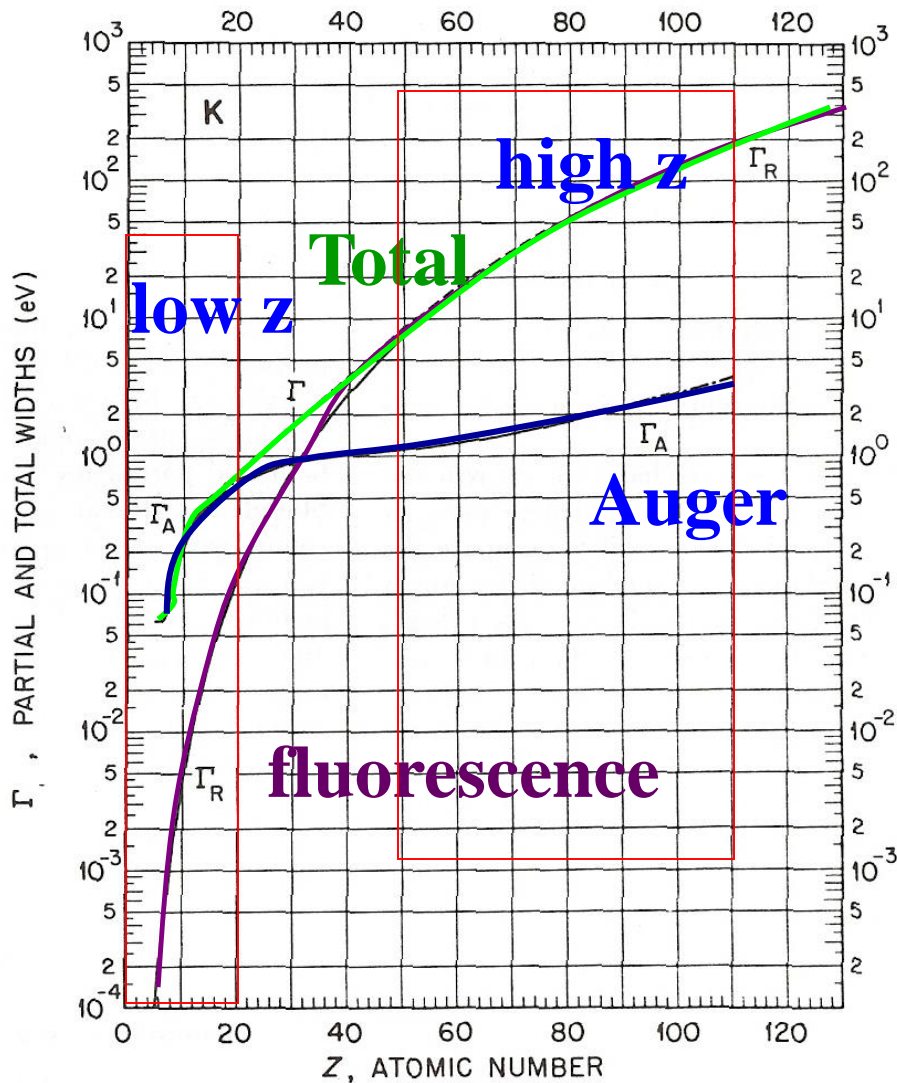


FIGURE 1. Theoretical partial and total atomic level widths for K shell.  $\Gamma_A$  = Auger width,  $\Gamma_R$  = radiative width,  $\Gamma$  = total width. Dot-dash curve represents semi-empirical  $\Gamma_A$  curve obtained from adopted  $\omega_K$  values and theoretical  $\Gamma_R$  curve:  $\omega_K \Gamma_A = (1 - \omega_K) \Gamma_R$ .

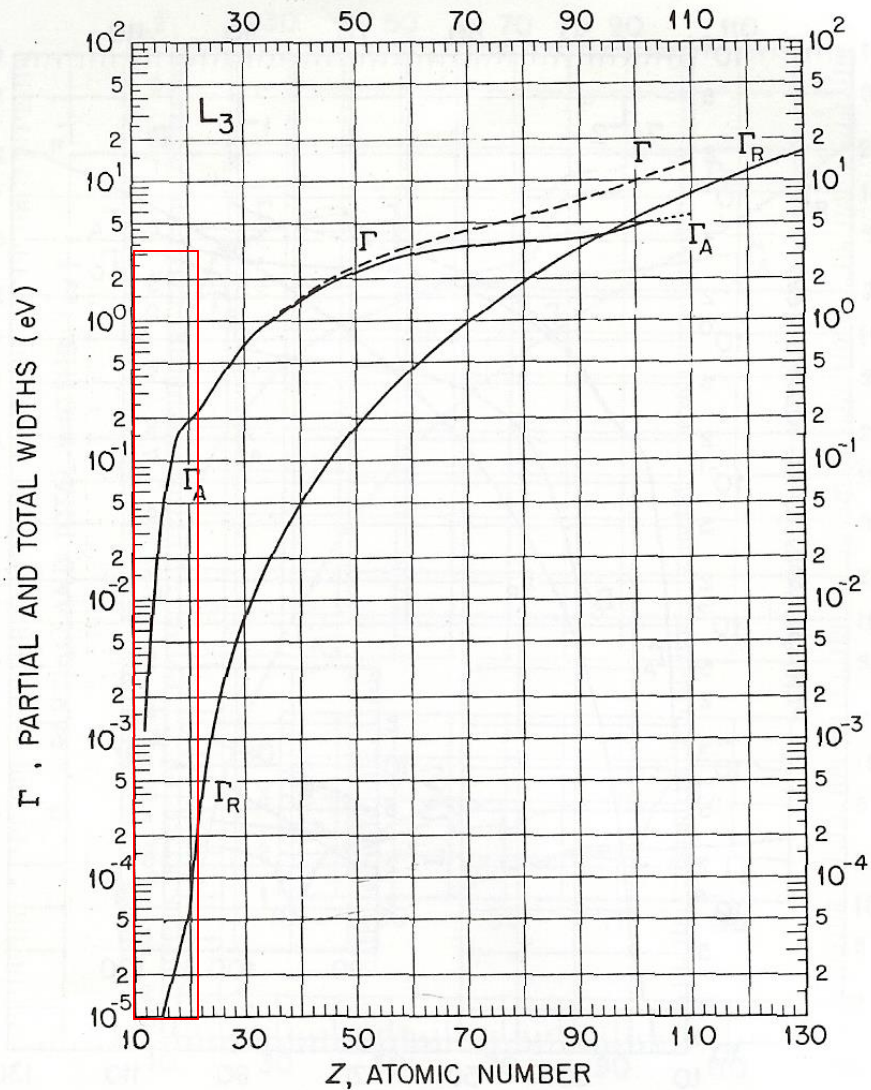


FIGURE 4. Theoretical partial and total atomic level widths for  $L_3$  subshell.  $\Gamma_A$  = Auger width,  $\Gamma_R$  = radiative width,  $\Gamma$  = total width.

# Manybody (Doniac Sunjic) line shape

Metals with a high densities of states at the Fermi level often exhibit an **asymmetric line shape** in the core level peak due to manybody effect – I.e. that the itinerant electrons gets excited simultaneously into the unoccupied band states.

$$I(E) = \frac{\cos [\pi\alpha/2 + (1 - \alpha) \tan^{-1} (E/\gamma)]}{(E^2 + \gamma^2)^{(1-\alpha)/2}}$$

where

$E$  = kinetic energy measured from the threshold of the unbroadened one-electron-transition peak

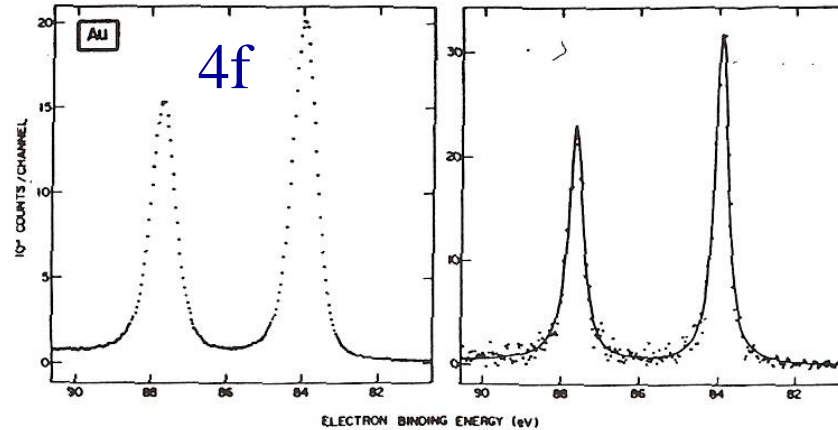
$\gamma$  = the lifetime of the core hole

$\alpha$  = an asymmetry parameter (typically 0-0.5)

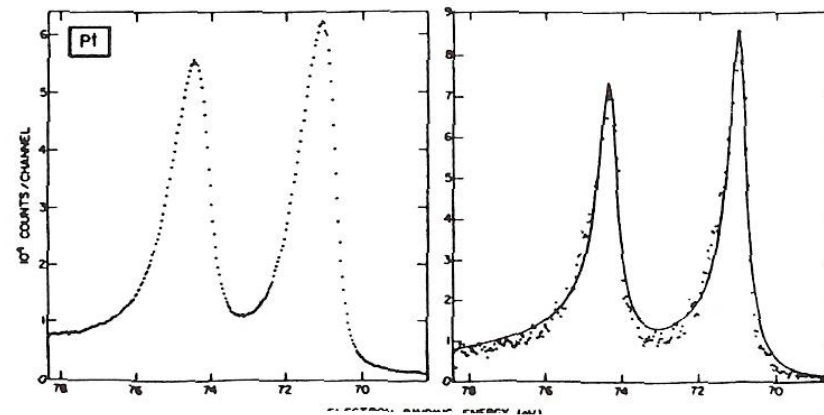
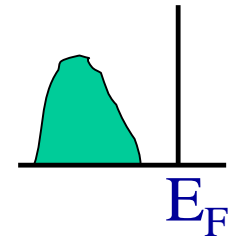
$$\alpha = 2 \sum_l (2l+1) (\delta_l/\pi)^2$$

$\delta_l$  = the phase shift of the  $l$ th partial wave for electrons at the Fermi energy scattering from the core hole.

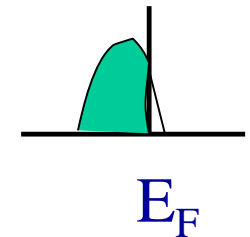
# Metallic systems with high densities of states at the Fermi level, The core level exhibits a skew shape at higher BE



Au d band



Pt d band



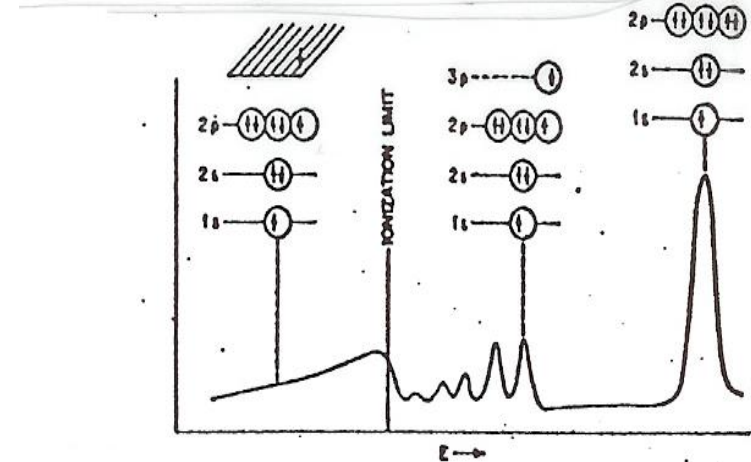
Wertheim Phys. Rev. B 25, 1987(1982)  
Doniach & Sunjic, J. Phys. C 3, 285(1970).

## Shake-up and shake-off processes

They occur in atoms, molecules as well as solids.

**Shake-up** satellites arises from simultaneous excitation of a valence electron to an unoccupied orbital. It is common and intense for compounds where the orbitals involved are in close proximity of each other.

**Shake-off** are similar excitations to the continuum. Similarly for molecules



$$\Delta J = \Delta L = \Delta S = 0; \Delta l = \Delta s = 0$$

$$P_{n,l}(\omega) = \left| \int \psi_{n,l}^* \psi_{n,l} \delta \tau \right|^2$$

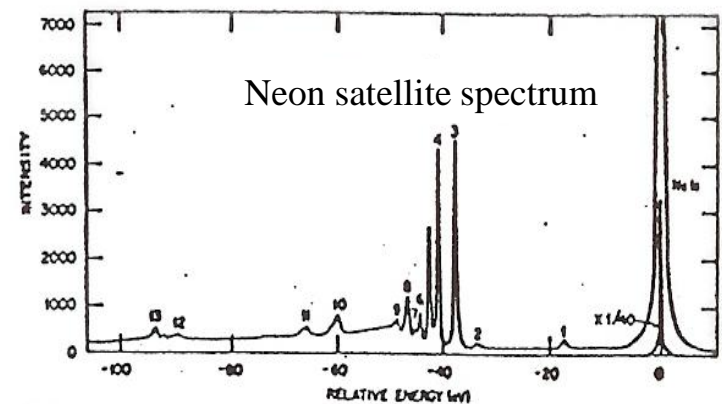
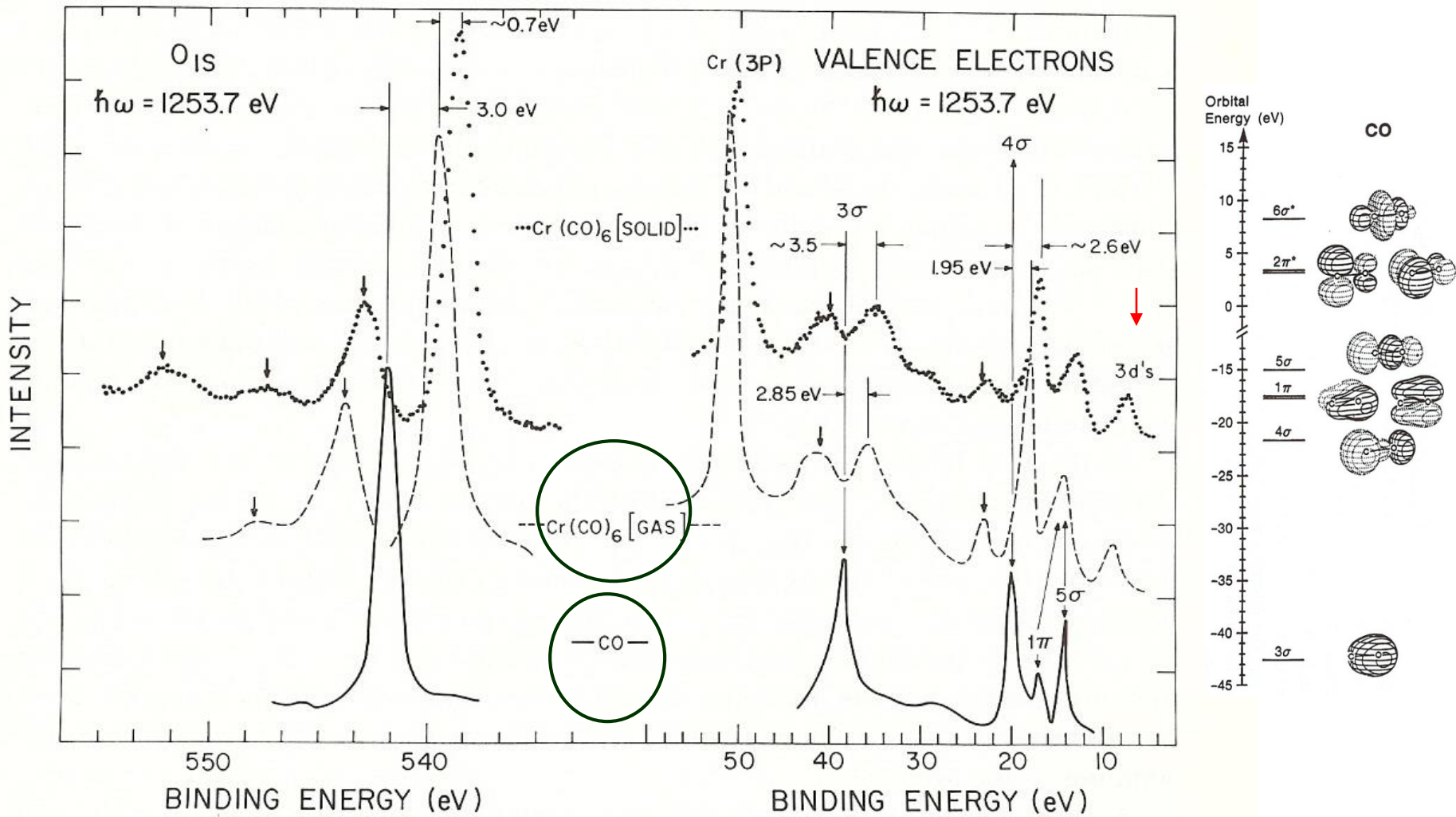


FIGURE 5.32. Shakeup and shakeoff spectrum arising from *K* shell ionization in neon. Peak 1 is due to collision losses. Remaining peaks, except 2, are from "normal" monopole transitions. Shakeoff spectrum is seen as high background gradually decreasing from about -45 eV down. (Reproduced from U. Gelius, E. Basilier, S. Sorenson, and K. Siegbahn, Univ. of Uppsala Institute of Phys. report, UUIP-817 (1973).

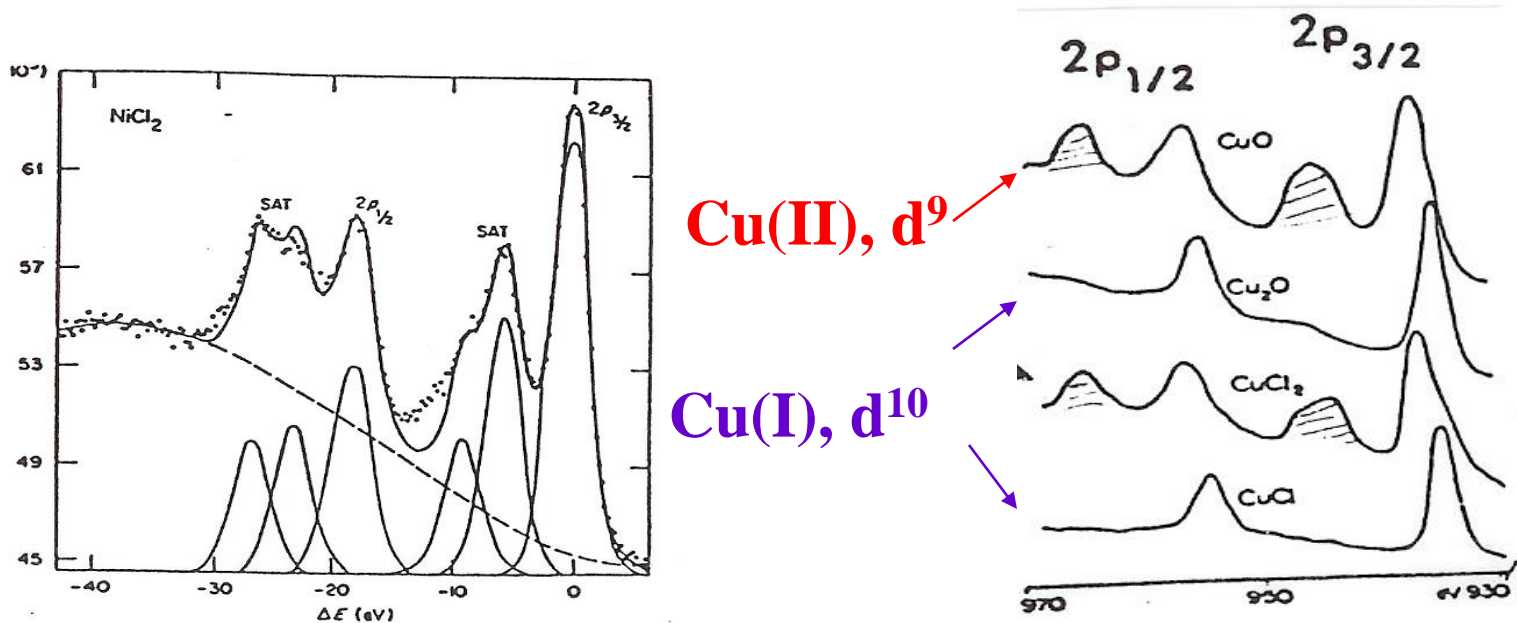


# Satellites in Metal carbonyls



E.W. Plummer, et.al. Phys. Rev. B18, 1673 (1978)

**shake-up satellites** in first row transition metal compounds where the metal has partially filled d orbitals and ligand to metal charge transfer can occur.  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are good examples. As the atom approaches a  $d^{10}$  configuration (no more d orbital is available to accommodate the electron), the satellite disappears



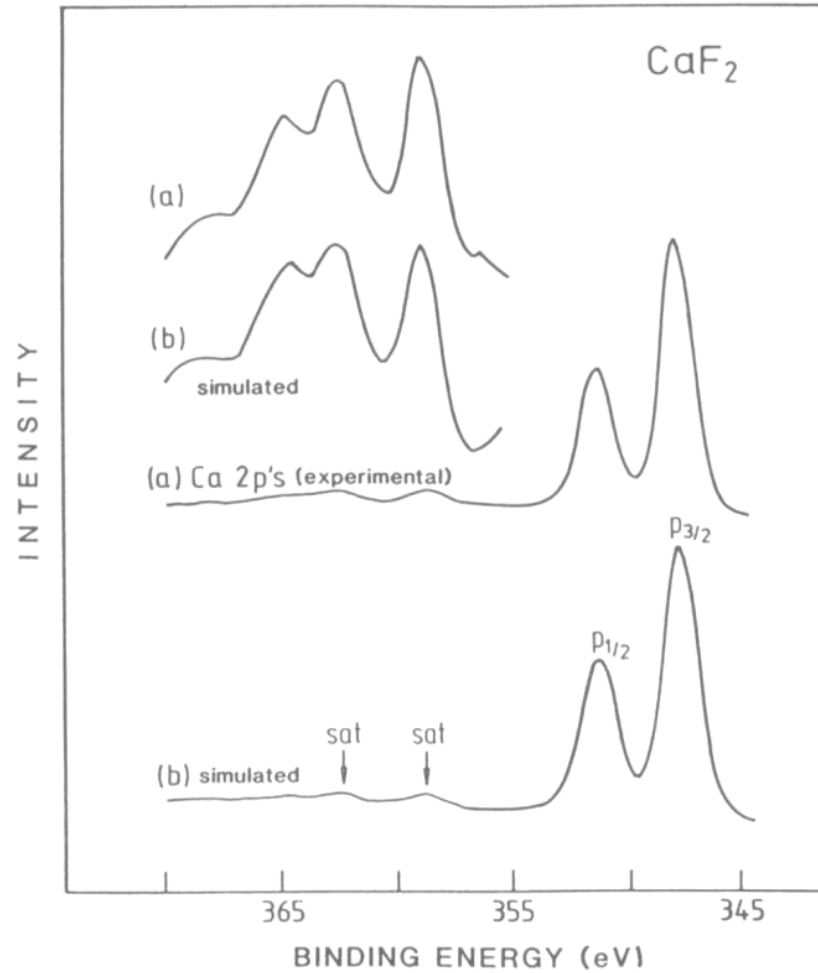
G.A. Vernon et al. Inorg. Chem.15, 278 (1976)

Wallband et al. J. Chem. Phys.69, 5405 (1975)

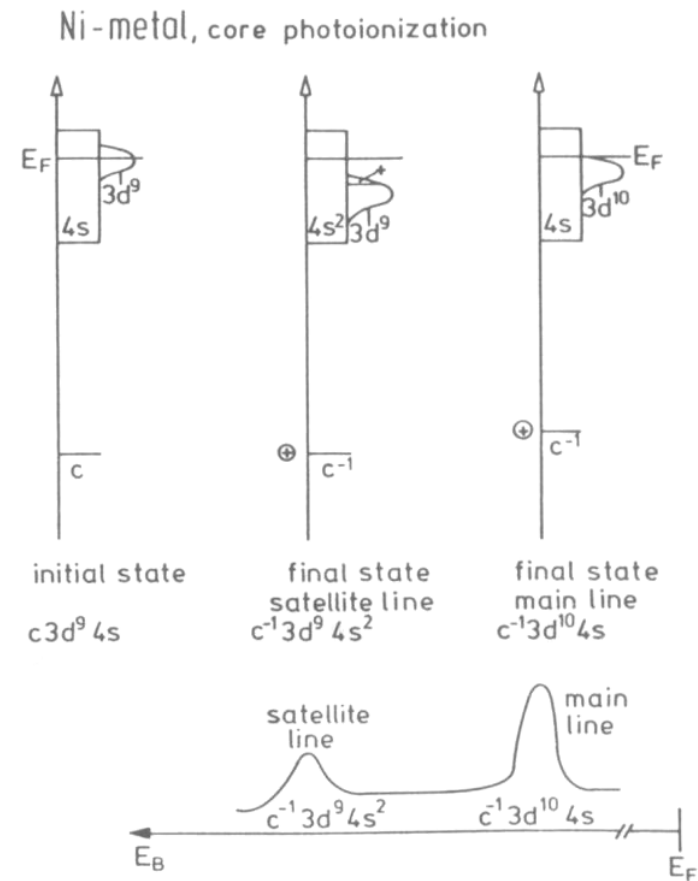
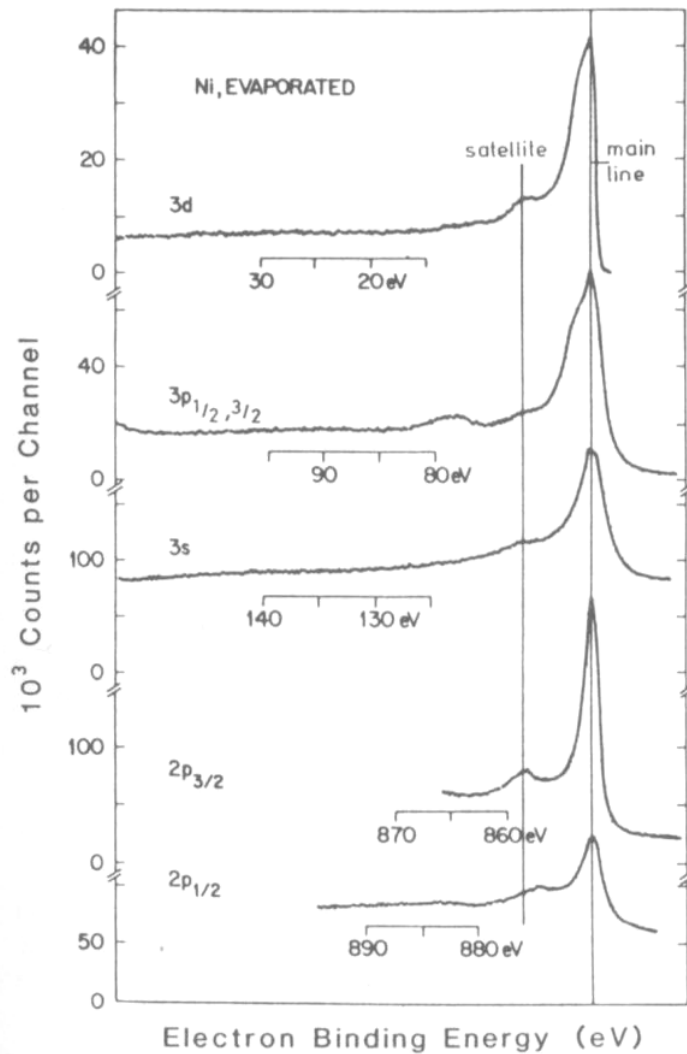
Note: Satellites can also be observed in metals; they are often weaker. The most famous one is the 6 eV satellite in Ni. These states are often dealt with as completely screened and unscreened states



# Satellite involving empty d orbitals

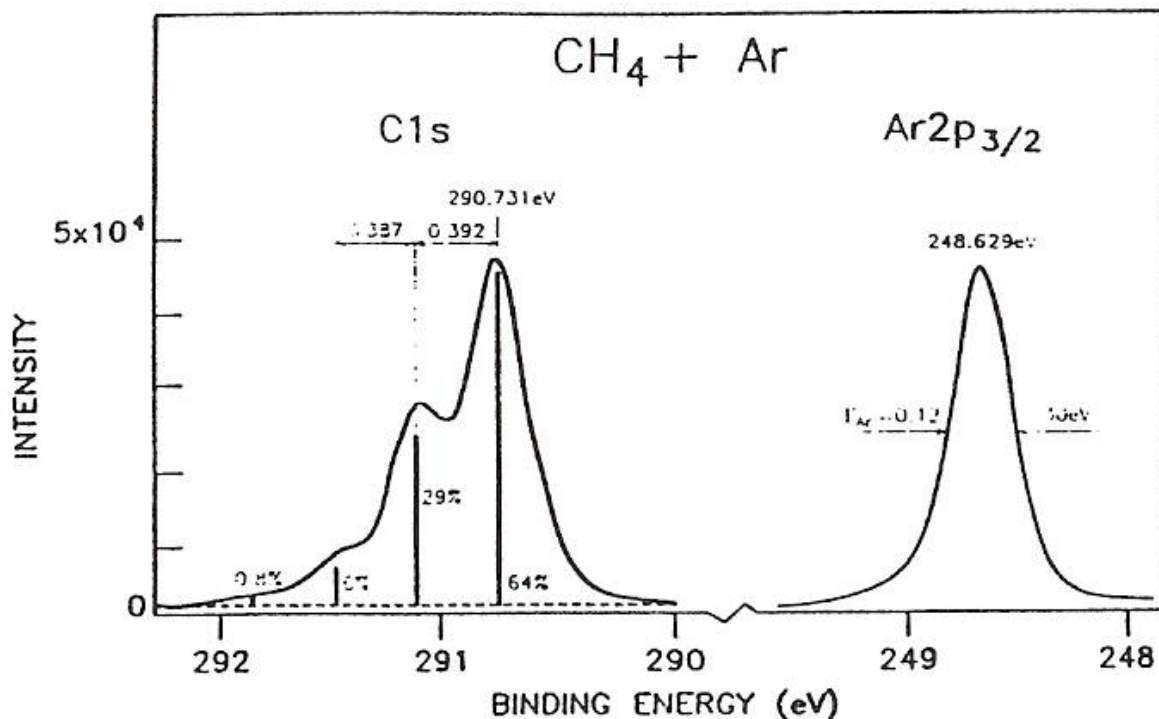


# The 6 eV satellite of Ni

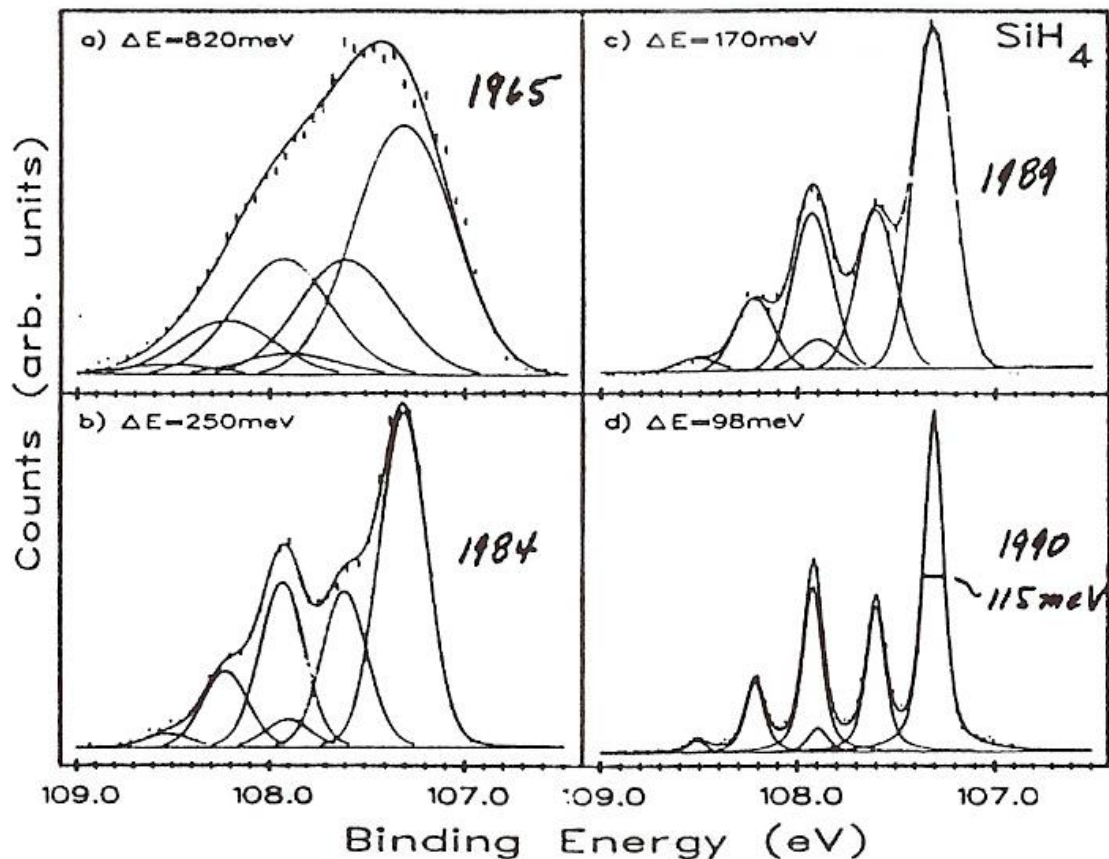


# Vibrational splitting/broadening in gas phase

Frank-Condon transitions populate more than one vibrational state of the final state of the excited molecule. The best example is  $\text{CH}_4(\text{g})$  C 1s, first resolved in 1973 by Siegbahn et.al. It was not until more recently, more vibrational structures were resolved.



The vibrational structure from **Si 2p<sub>3/2,1/2</sub>** of **SH<sub>4</sub>** (shown below) can be seen more clearly as the resolution improves through the years: J.D. Bozek et.al. Phys. Rev. Lett. 65, 2757(1990).



# Vibrational broadening in solids

Vibrational broadening in solids are primarily due to phonon broadening and it is more difficult to observe quantitatively. In general, the broadening at temperature T is treated with a Gaussian width  $\Gamma_{\text{el-phon}}$ , where

$$\Gamma_{\text{el-phon}}^2 = (C/\Theta_D) [1 + [8T/3\Theta_D]^2]^{1/2}$$

where  $\Theta_D$  is the Debye temperature and C is a parameter which depends on the electronic structure of the solid. Its contribution to the total Gaussian width may be expressed as

$$\Gamma_{\text{tG}}^2 = \Gamma_{\text{instr}}^2 + \Gamma_{\text{inh}}^2 + 8CT/3\Theta_D^2 [1 + 1/2[3\Theta_D/8T]^2 + \dots]$$

$$\Theta_D = hv_0/k \quad \text{e.g Au } 165^\circ\text{K, Ge } 366^\circ\text{K etc.}$$

Zero point energy

Boltzmann constant (kT = 0.0256 eV at 298K)

The Gaussian width can be extracted if the core hole lifetime, instrument resolution and homogeneous broadening are known. From temperature dependent measurement one can extract parameters for the lattice dynamics of the system. This kind of study has been carried out for a number of alkali metal overlayers.

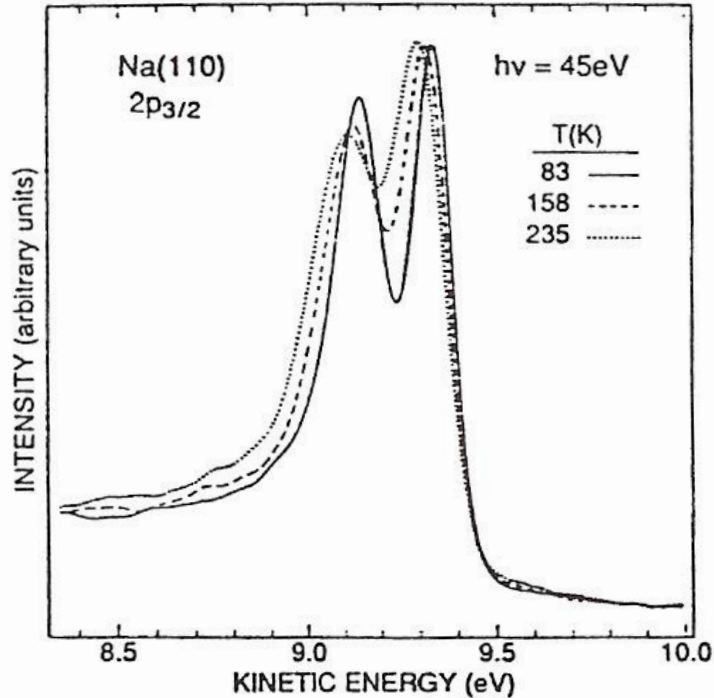


FIG. 3. Smoothed and spin-orbit-stripped  $2p_{3/2}$  data at three temperatures normalized to the height of the bulk component.

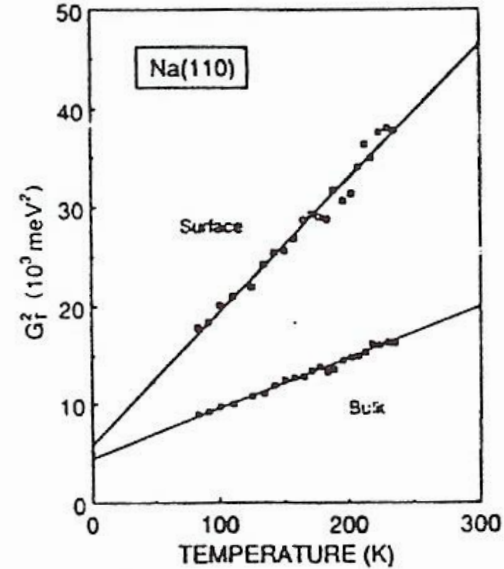
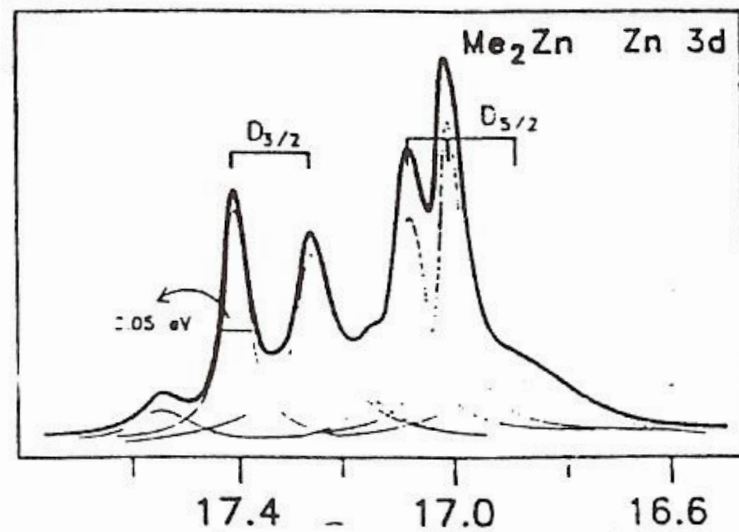
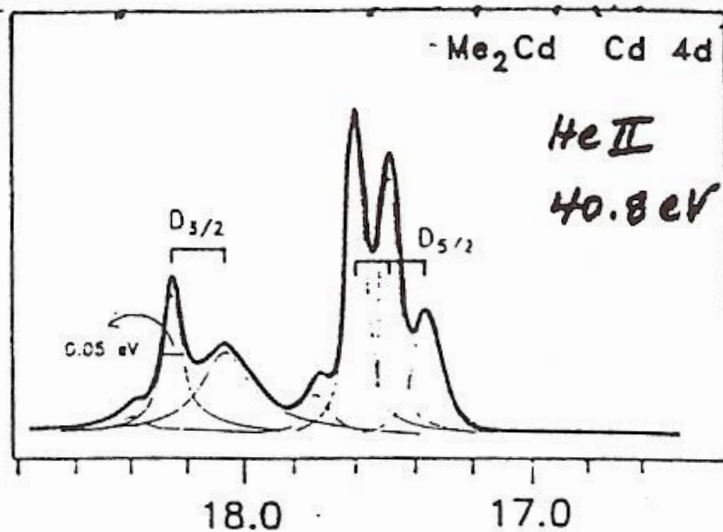


FIG. 4. Square of the total Gaussian width vs temperature for  $2p$  bulk and surface components. Note very different temperature dependence of surface line. Both least-squares-fit straight lines extrapolate to the square of the instrumental width.

# Crystal field splitting

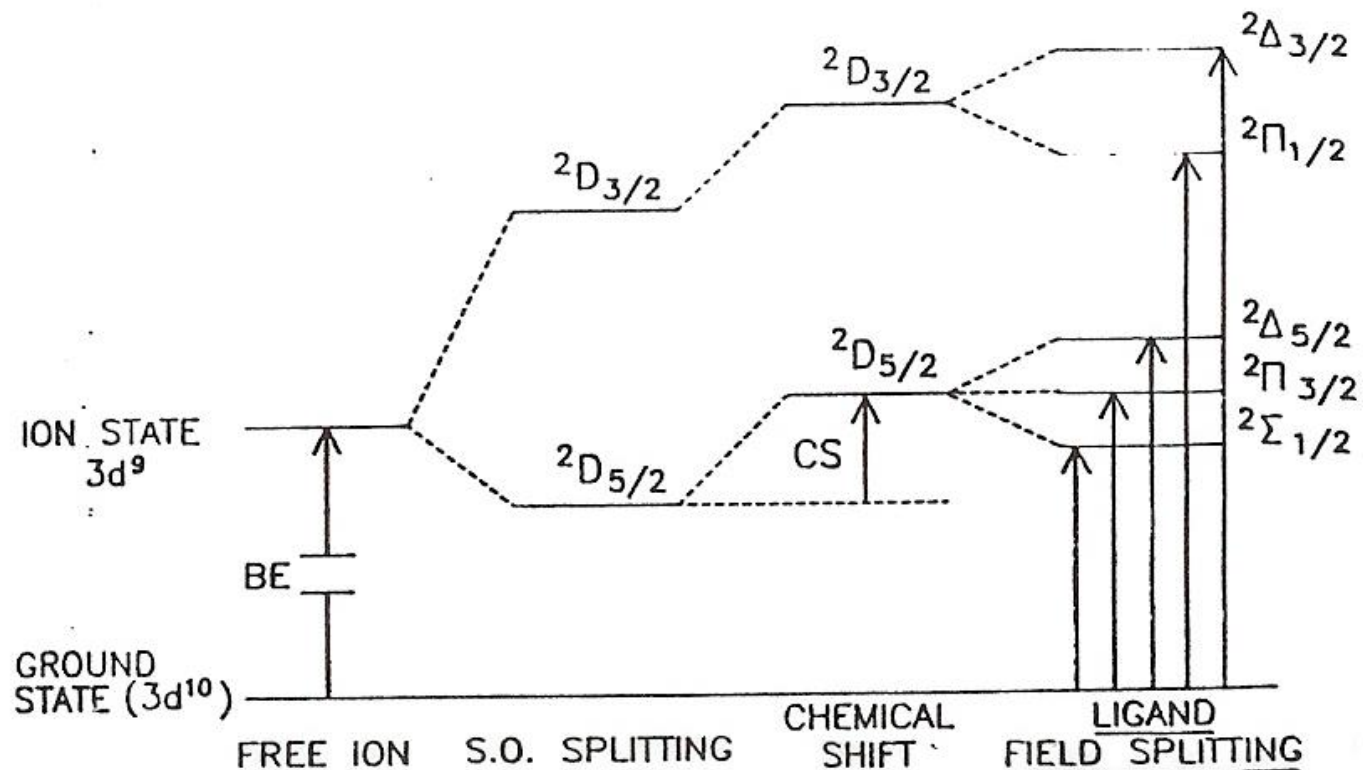
The final state in a non-cubic environment is subjected to a crystal field which splits the core level. The Hamiltonian in a linear molecule is  $H = C_2^0 [3L_z^2 - L(L + 1)]$ . For d electrons,  $H = C_2^0 [3L_z^2 - 6]$ , operating on  $d_{z^2}$ ;  $d_{xy}$ ,  $d_{yz}$ ; and  $d_{x^2-y^2}$ ,  $d_{xy}$ , one gets,  $E_0 = -6C_2^0$ ;  $E_1 = -3C_2^0$ ; and  $E_2 = +6C_2^0$ . When the 4d and 3d core of Cd and Zn respectively, ionizes, the final state is subjected to the same kind of crystal field.



BINDING ENERGY (eV)

# Crystal field splitting

CONSIDER A LINEAR  $Zn^{2+}$  ( $3d^{10}$ ) COMPLEX ( $ZnCl_2$  or  $Me_2Zn$ )



See Bancroft et.al. J. Chem. Phys. 67, 4891(1977) and  
Inorg.Chem.5, 89(1986)

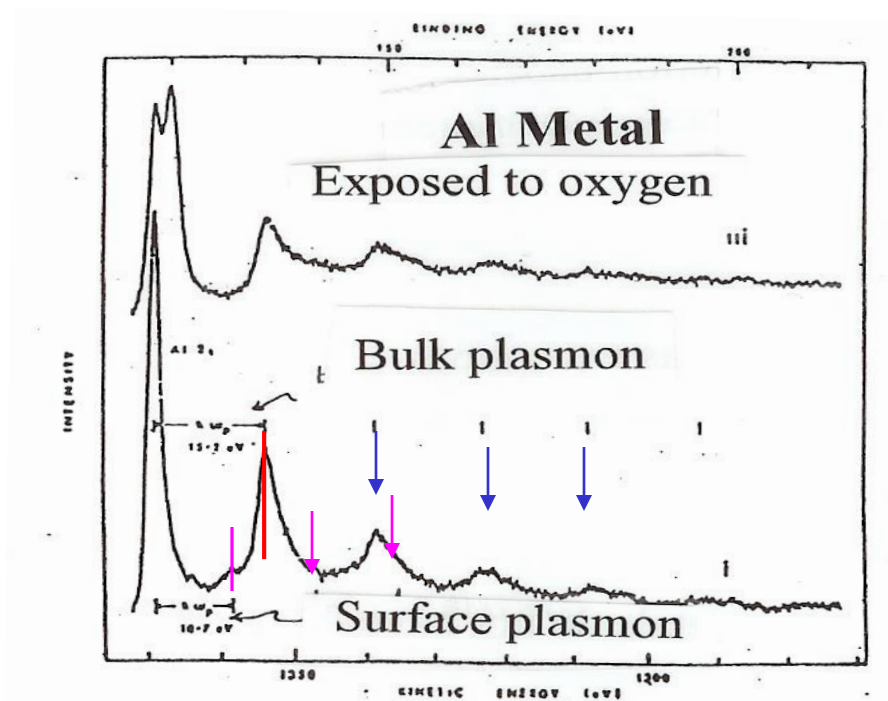


# Characteristic energy loss (plasmon)

In free-electron like metal such as alkali, alkaline and main group metals, one often observes Plasmon loss peaks (collective oscillation of itinerant electron in the metal). This process is primarily extra atomic. Both bulk and surface plasmon can be seen. Surface Plasmon can often be quenched by oxygen or any compound that quenches the free-electron-like property of the electrons in the surface. The plasmon frequency  $\omega_p$  in  $\text{rad sec}^{-1}$ , can be calculated using

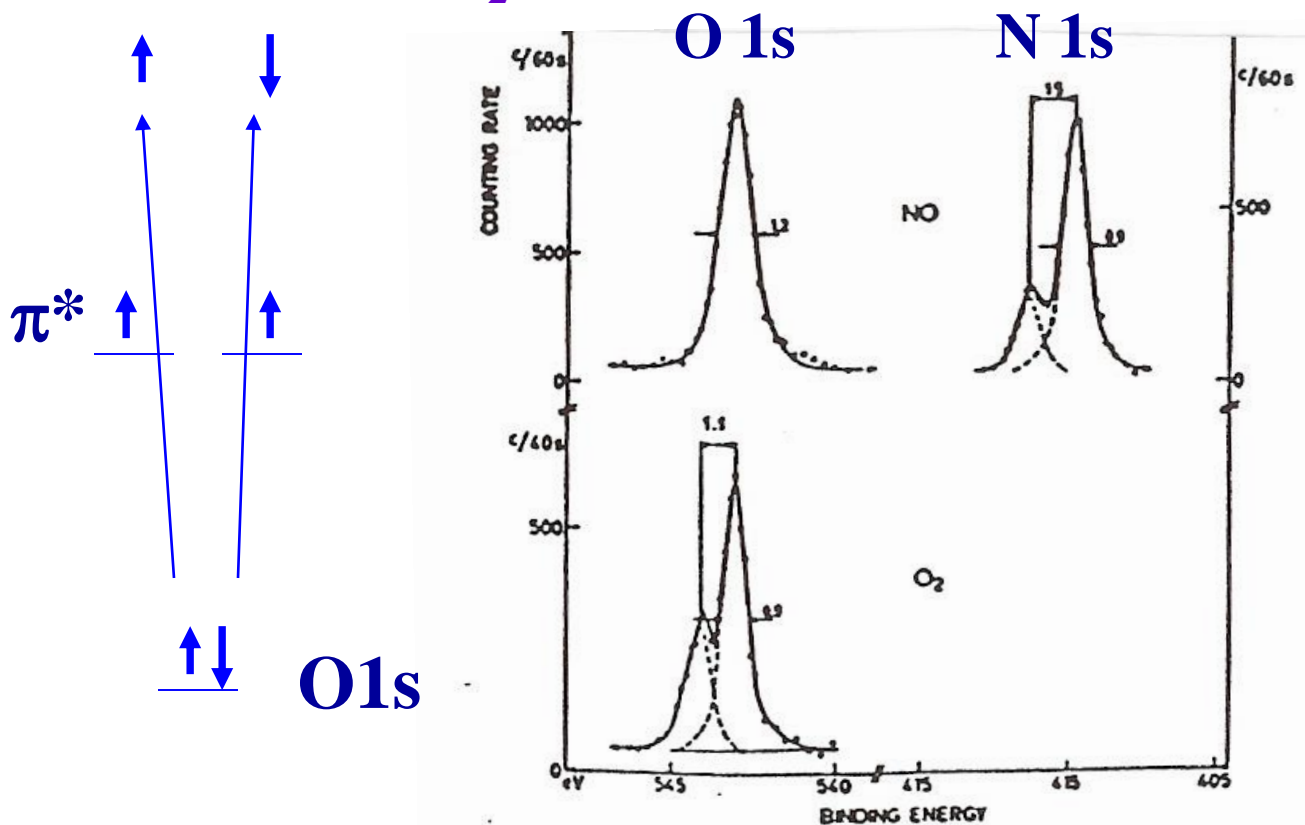
$$\omega_p = (4\pi n e^2 / m)^{1/2}$$

Where  $n$  is the density of the electron;  $n$ , number of electrons per  $\text{cm}^3$ ,  $m$  mass of the electron



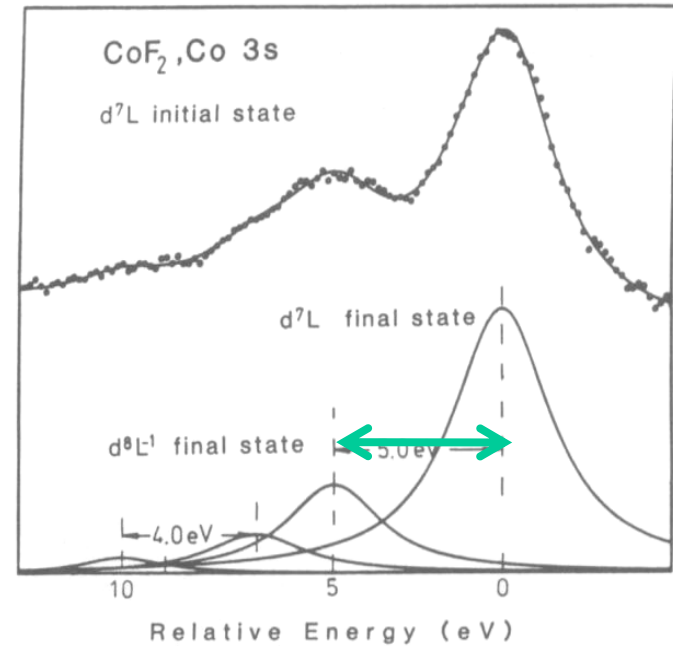
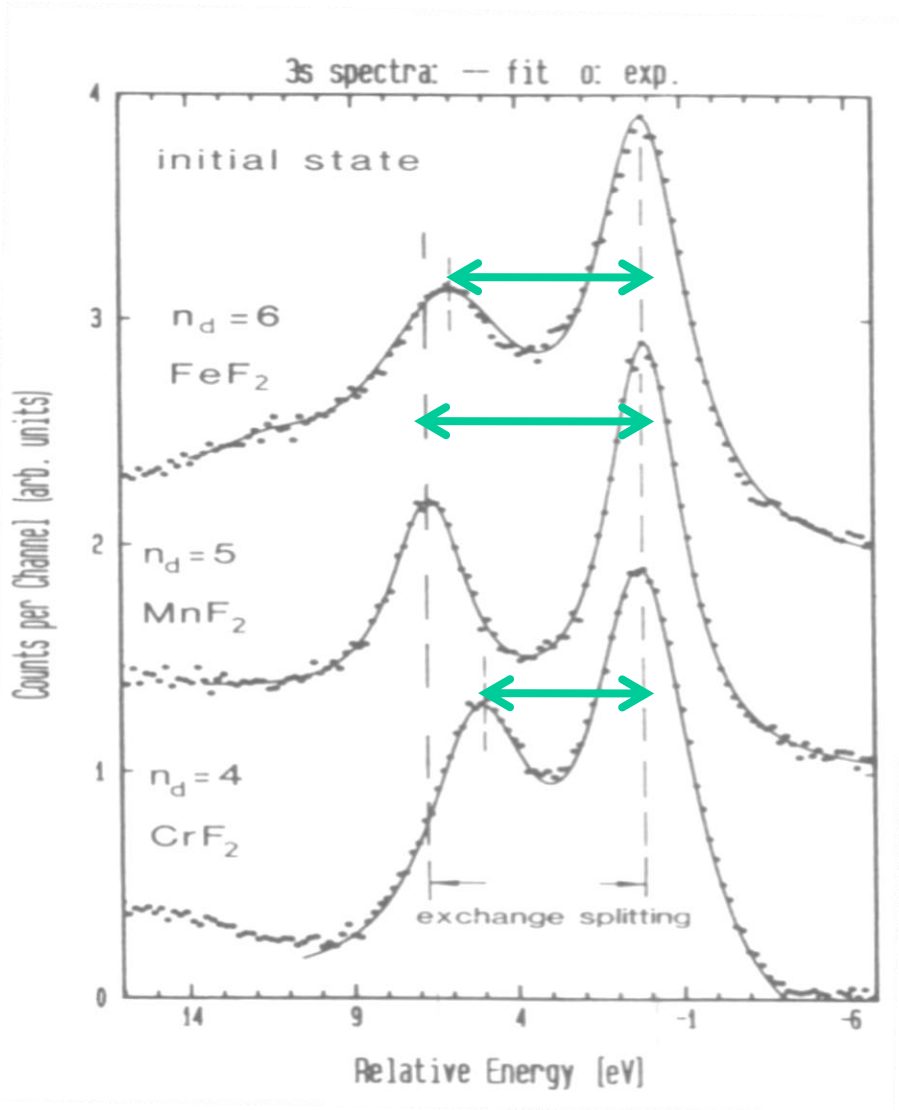
# Multiplet (exchange) splitting

When there are unpaired electrons in the valence band, there exist **exchange interaction** between the core hole and the unpaired spins. This is illustrated with the spectra of the paramagnetic  $O_2$  and NO.



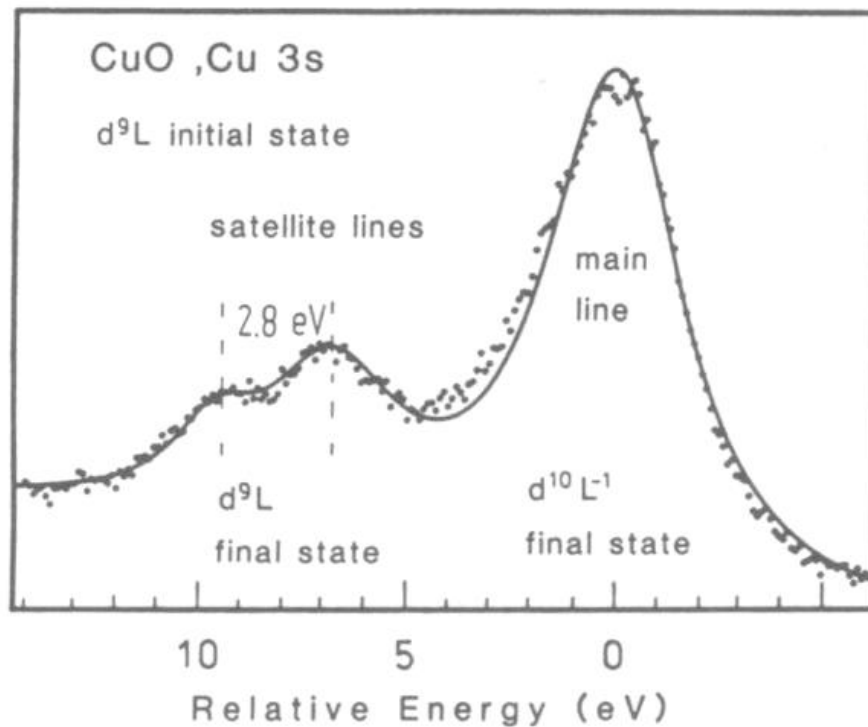
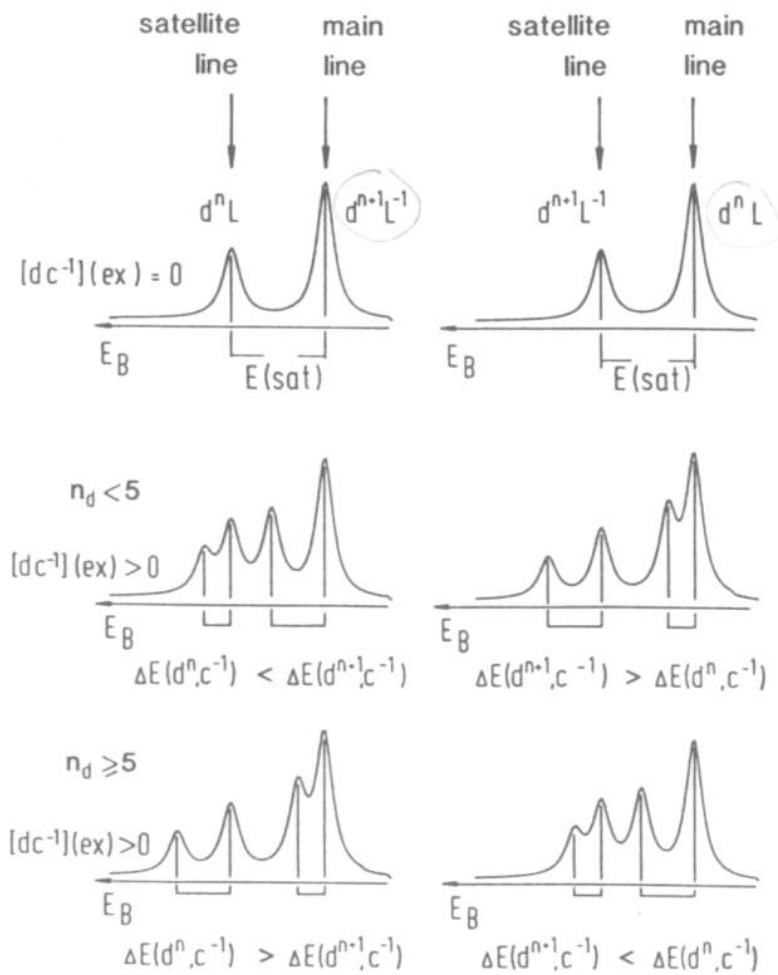
XPS spectra from the 1s core electrons of the gaseous molecules  $N_2$ ,  $O_2$  and NO. The 1s peaks from the paramagnetic molecules NO and  $O_2$  are split due to exchange interaction. Diamagnetic  $N_2$  shows no splitting. (From Siegbahn *et al.*, ref. 4.)

# Multiplet splitting & $d^n$



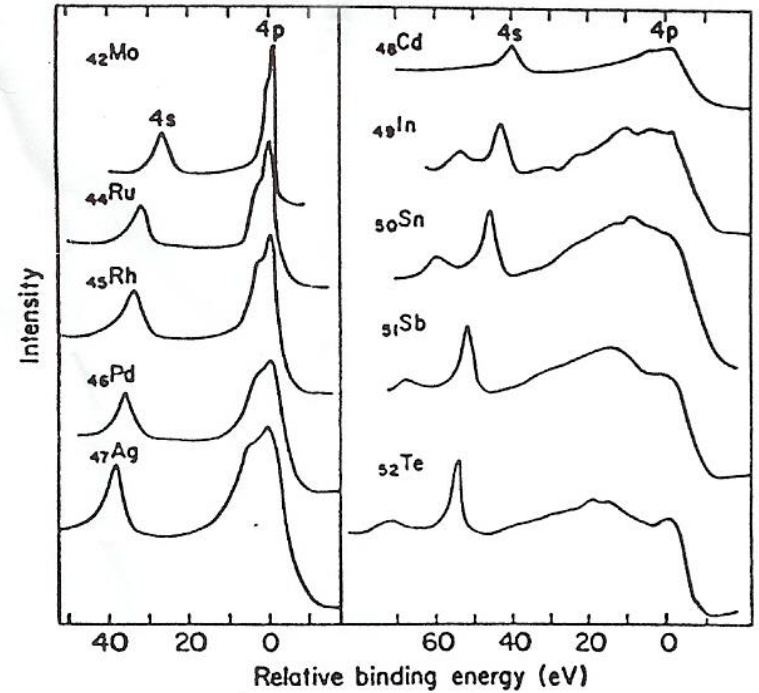
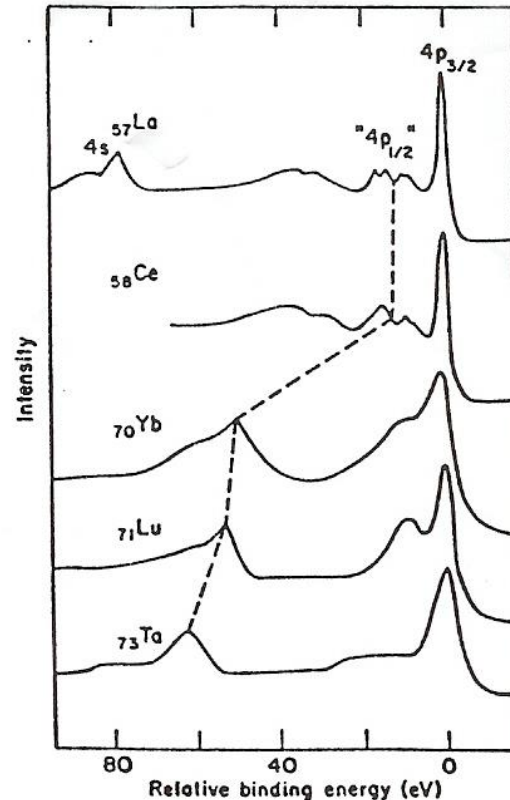
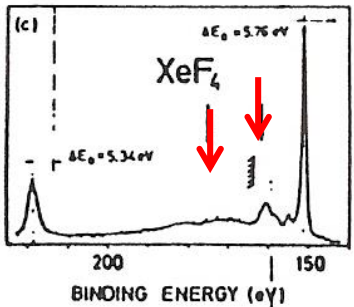
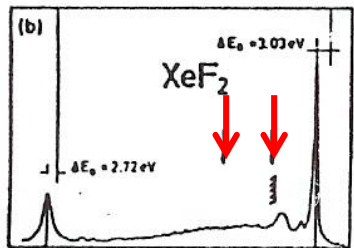
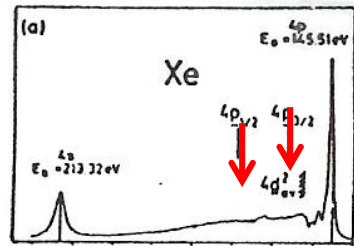
Splitting  $\propto$   
# unpaired electrons

# Multiplet splitting of L→M satellites



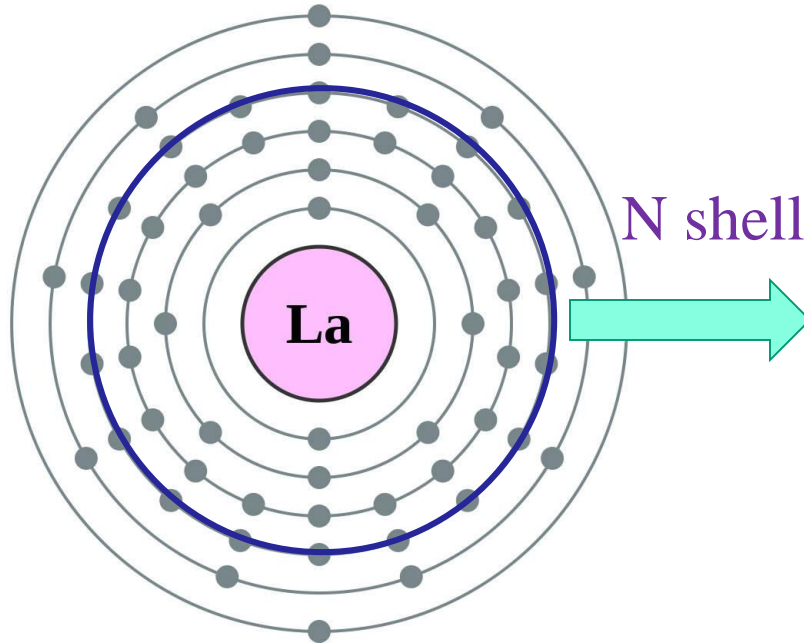
# Complete breakdown of the single-particle formalism

When the **single particle state** couples with **Coster Kronig** states it sometimes happens that the single particle state is totally wiped out. It is quite common that the **4p level** of some elements exhibits this phenomenon due to **4p, 4d<sub>av</sub><sup>2</sup>** ("\_" denotes a core hole) interaction. Lanthanides and actinides provide some of the examples.



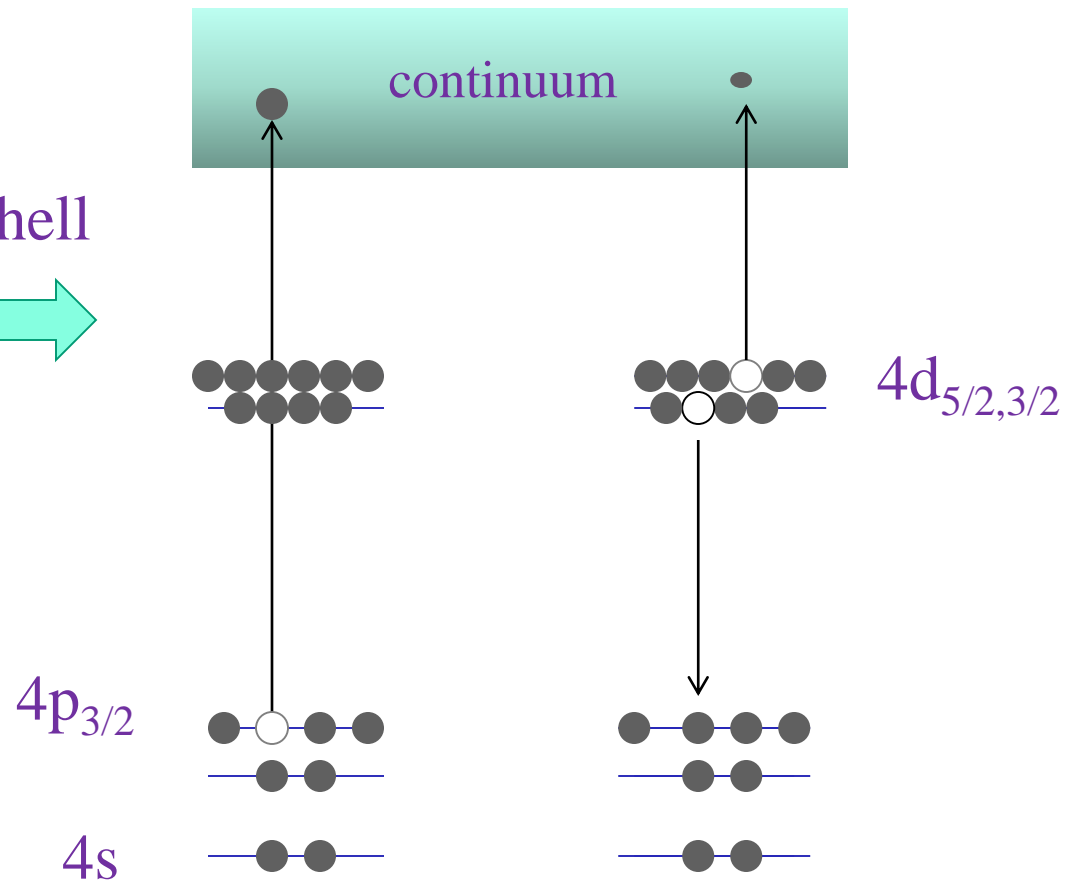
57: Lanthanum

2,8,18,18,9,2



Single particle  
final state:  $4p_{3/2} +$   
photoelectron

Manybody final  
state:  $4d^2 + \text{CK}$   
Auger



# Resonant Photoemission

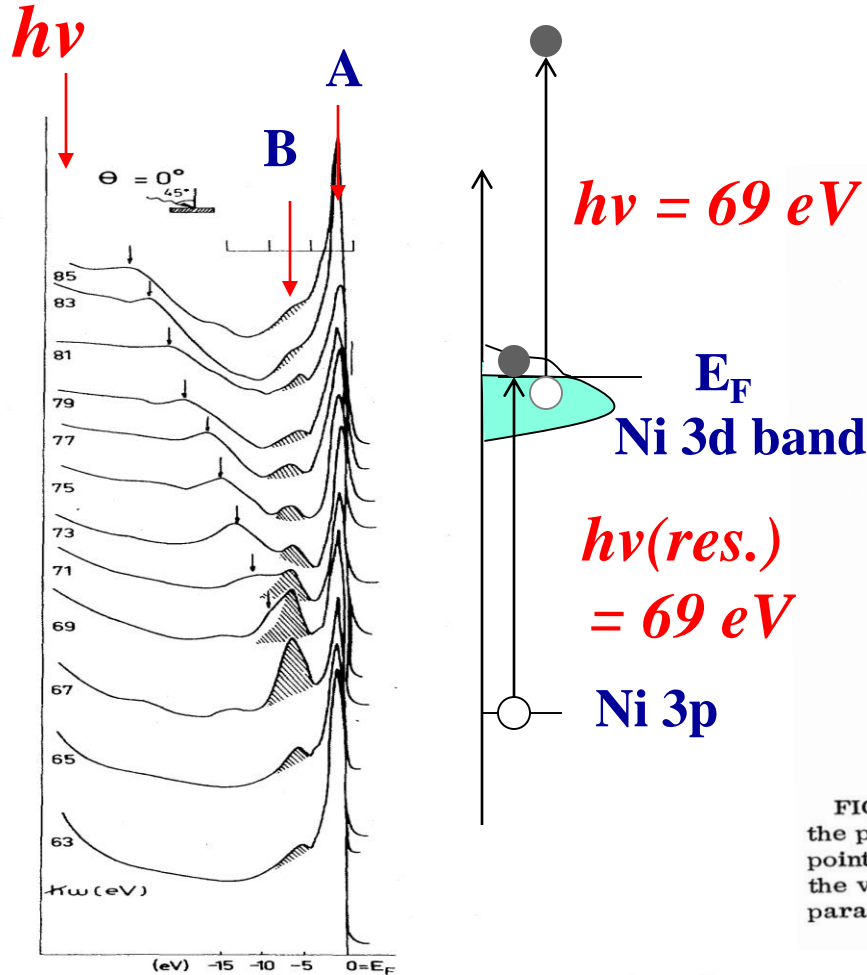


FIG. 1. Photoemission spectra of a clean Ni(100) surface for photon energy  $\hbar\omega$  between 63 and 85 eV. The peak A corresponds to the  $d$  bands; B (dashed area) is the structure located at 6 eV from the Fermi level. The arrows indicate the Auger transition.

## Intensity of B across the Ni $M_{3,2}$ edge

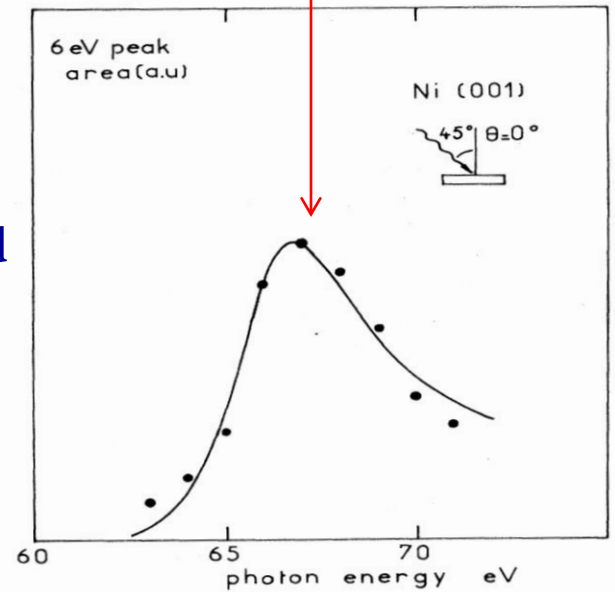
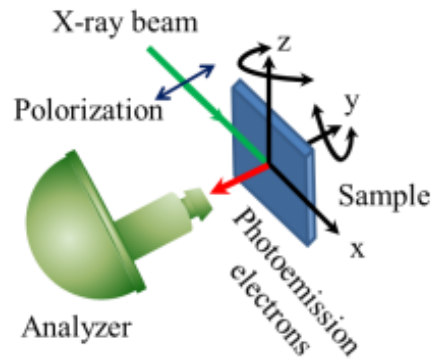
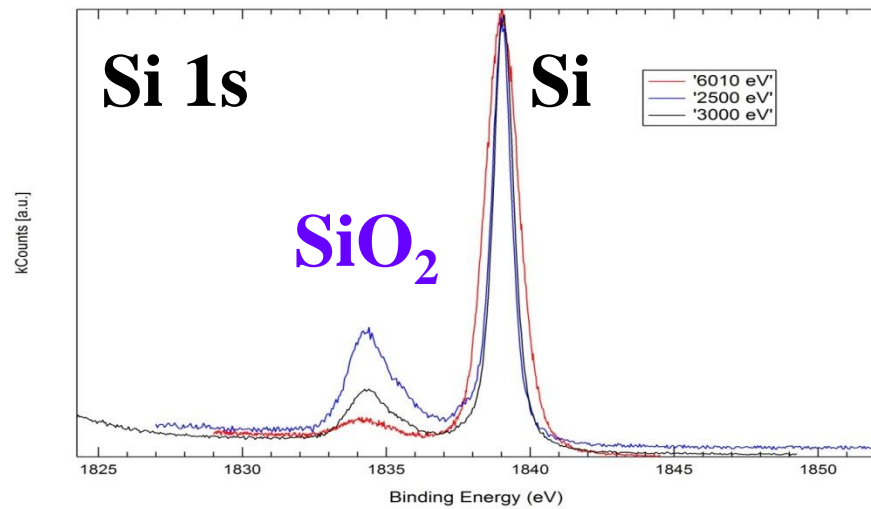
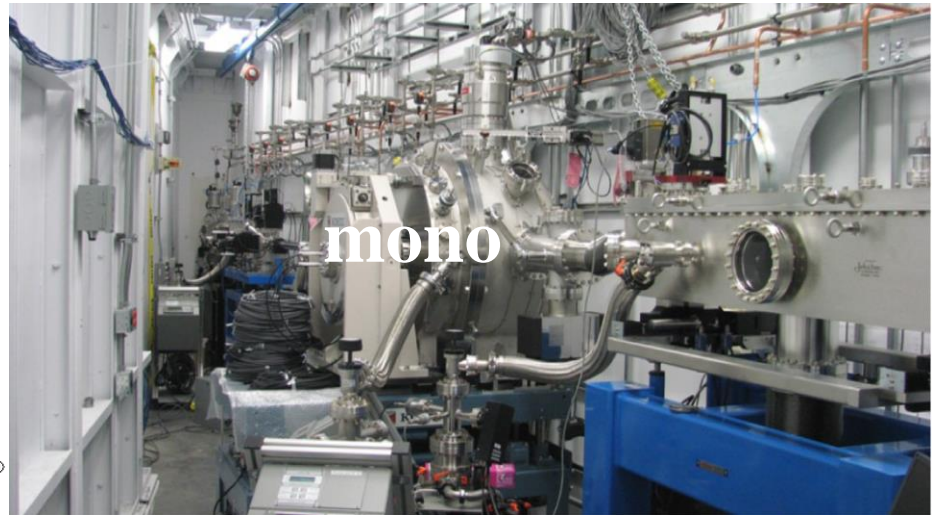
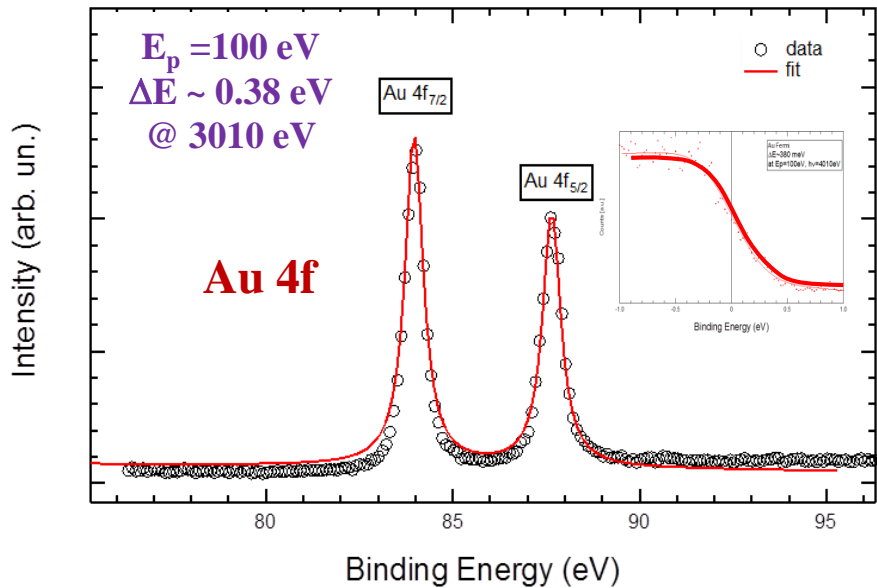


FIG. 2. Plots of the area of the B peak structure vs the photon energy in the vicinity of the  $3p$  levels. The points are experimental. The full line corresponds to the values given by Eqs. (3)–(6) with the following parameters:  $\Gamma = 2 \text{ eV}$ ,  $q = 2.5$ , and  $E_0 = 66 \text{ eV}$ .



# XPS endstation at SXRMB (CLS)





# Bulk sensitivity: SiO<sub>2</sub> thin film on SiC wafer

