The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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International Atomic Energy Agency

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School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

19 - 30 March 2012

Surface Science, Photoemission and Related Techniques
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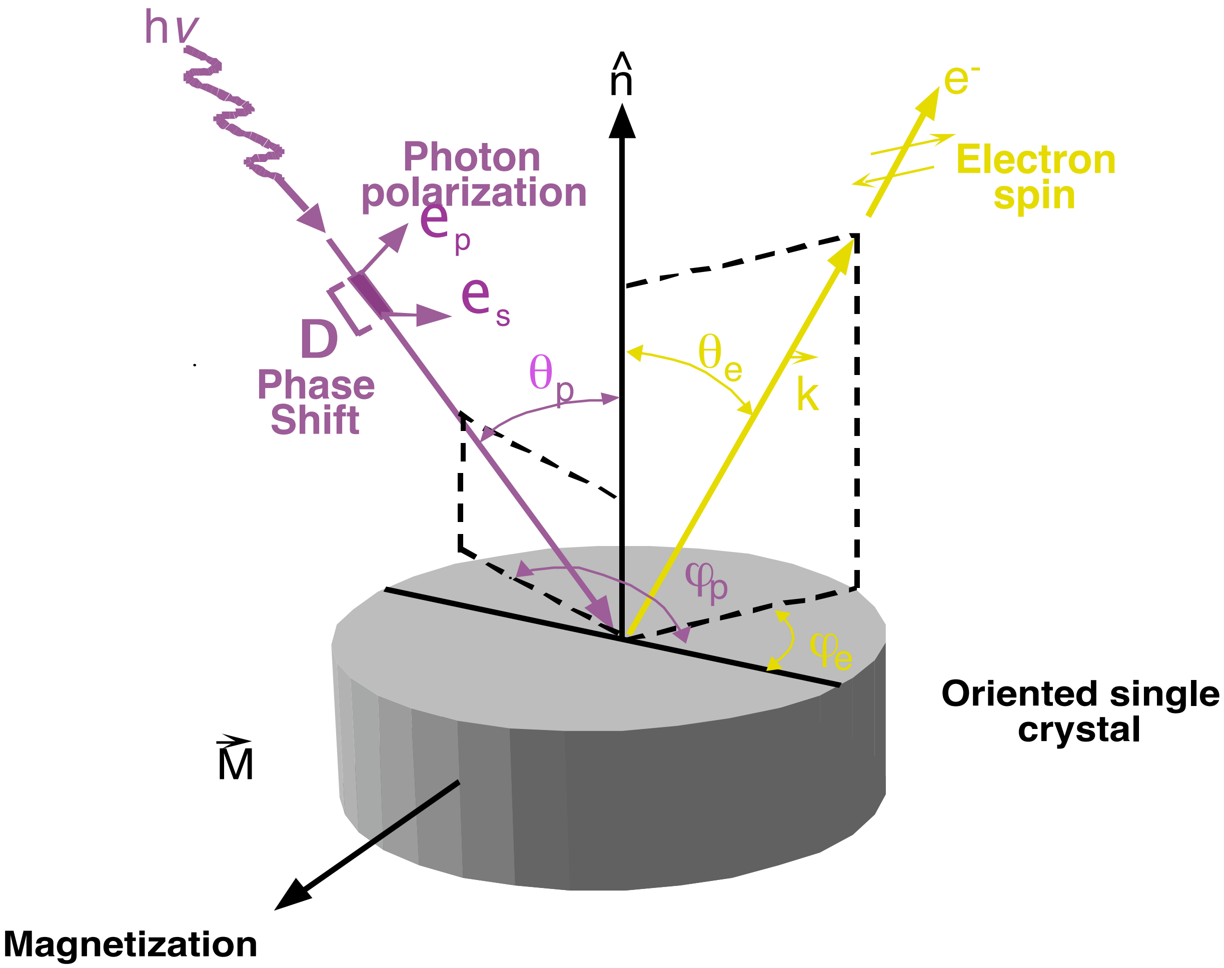
Photoemission experiment



The photoelectric effect

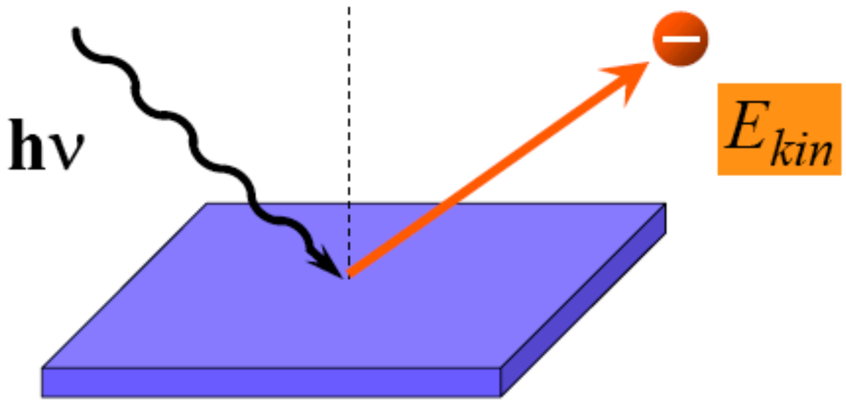
Theoretical explanation by A. Einstein (1905):
QUANTIZATION OF LIGHT

Ann. d. Phys. 17, 132 (1905):

Die kinetische Energie solcher Elektronen ist

$$\frac{R}{N}\beta\nu - P.$$

$$E_{kin}^{\max} = h\nu - \Phi$$

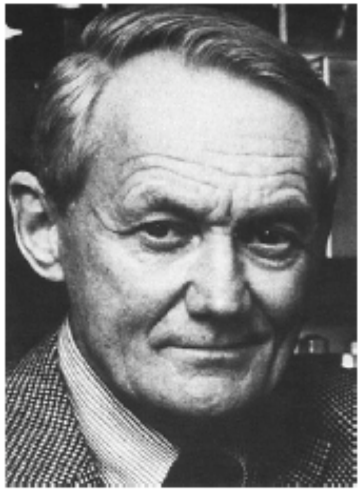


early experiments by:
- H. Hertz (1886)
- W. Hallwachs (1888)
- P. Lenard (1902)

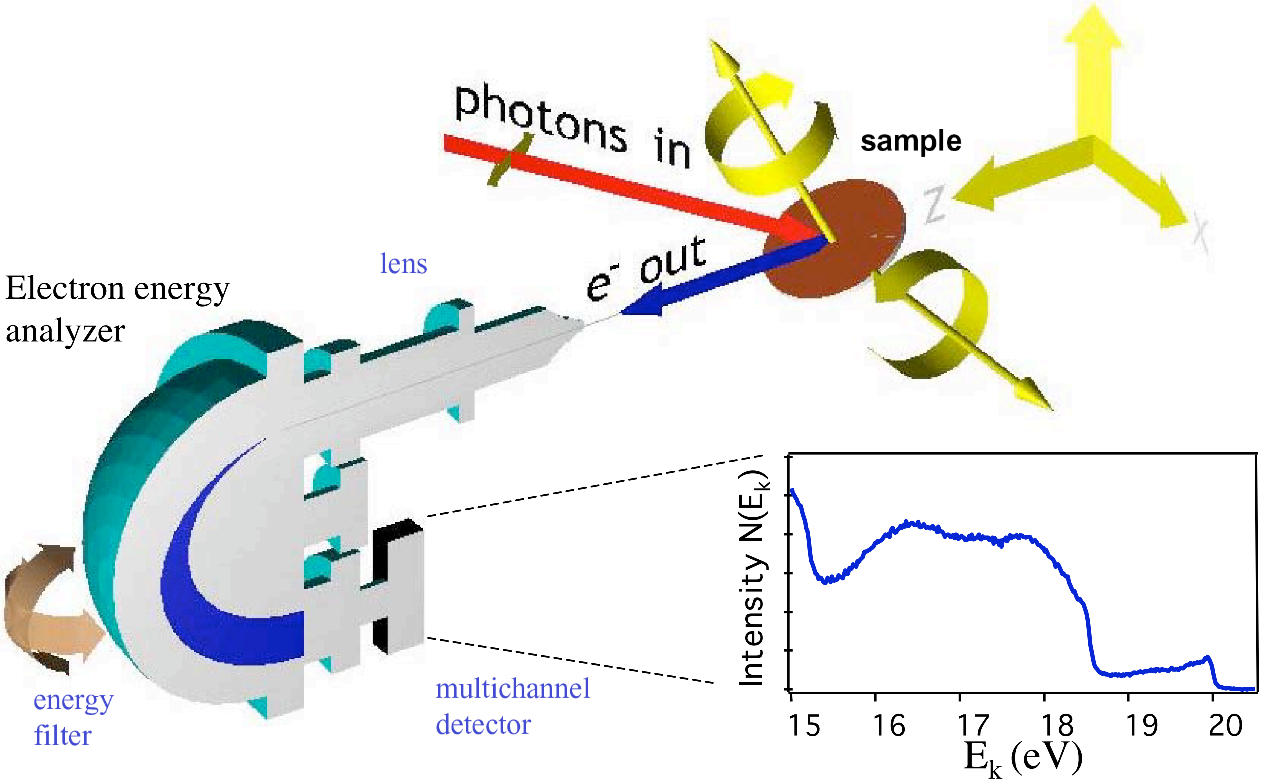
Photoelectron spectroscopy

Photoemission spectroscopy is a (photon in) - (electron out) experiment

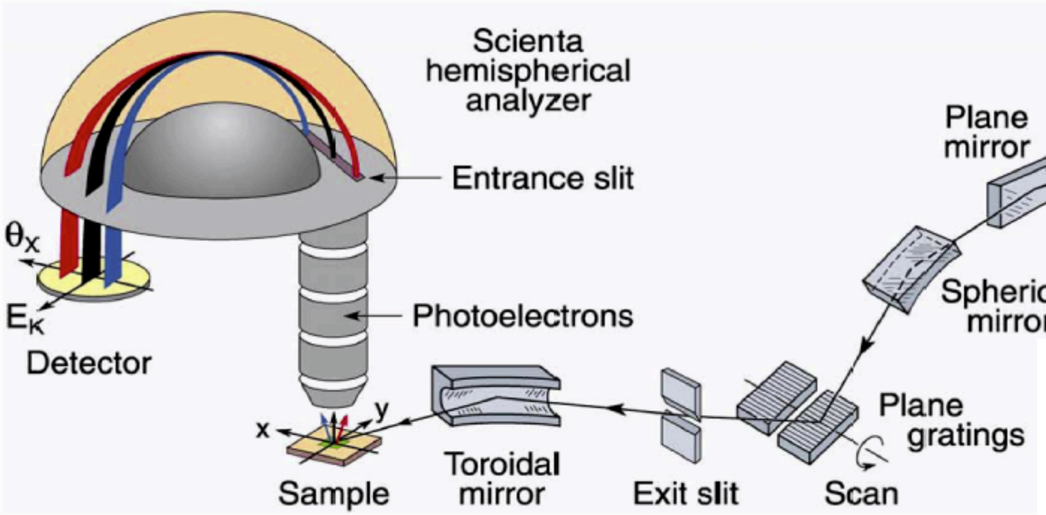
The emitted electrons may be collected over a broad (angle integrated PES) or narrow (ARPES) acceptance angle and their kinetic energy measured. The number of photoelectrons measured versus their kinetic energy, within the energy and angular windows (resolution) of the analyzer, yields a “photoemission spectrum” or “energy distribution curve” (EDC spectrum)



K.M. Siegbahn



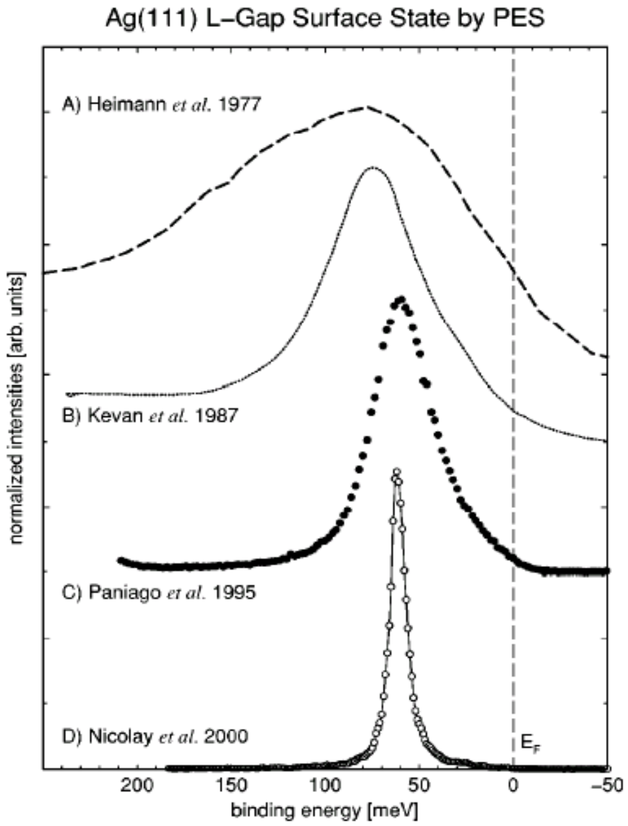
State-of-the-art



Parallel multi-angle recording

- Improved **energy resolution**
- Improved **momentum resolution**
- Improved **data-acquisition efficiency**

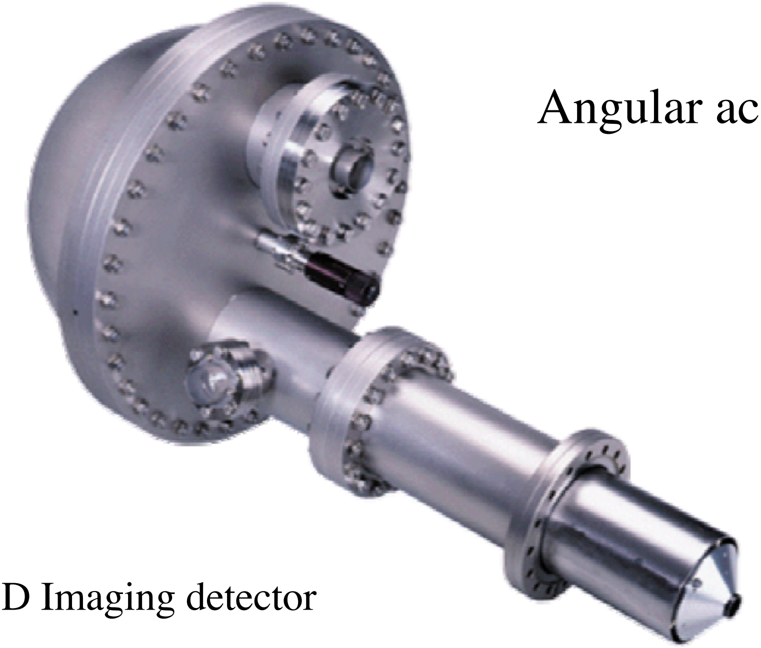
	ΔE (meV)	$\Delta\theta$
past	20-40	2°
now	2-10	0.2°



courtesy of A. Damascelli

Photoelectron detection

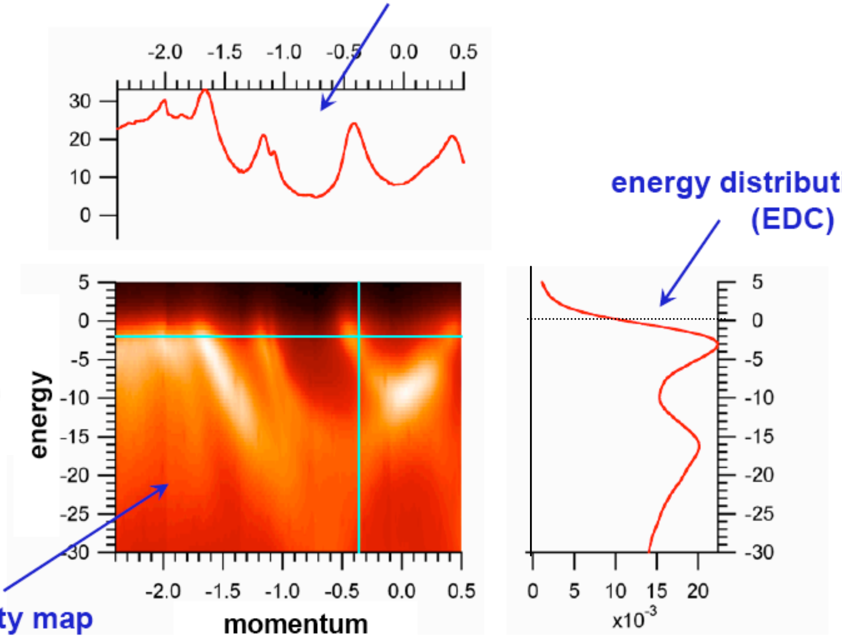
hemispherical energy analyzer



Angular acquisition max 35° at the same time

momentum distribution curve (MDC)

energy distribution curve (EDC)



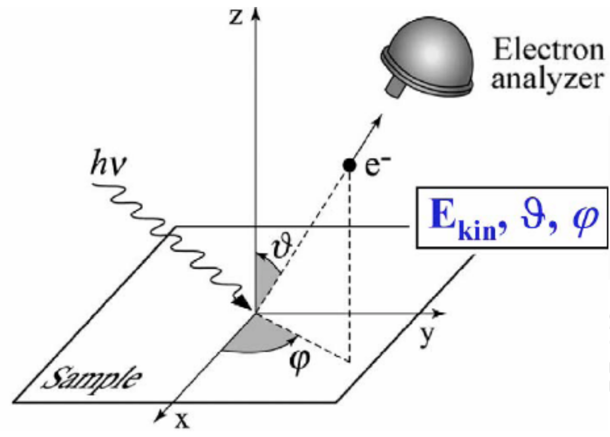
intensity map

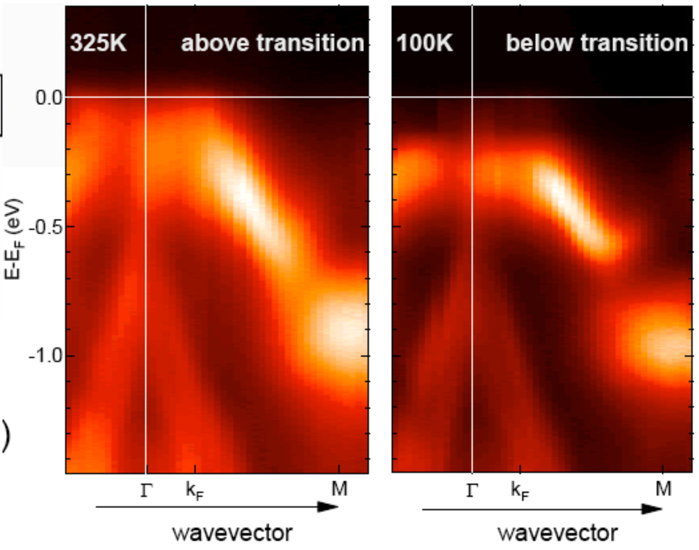
CCD Imaging detector

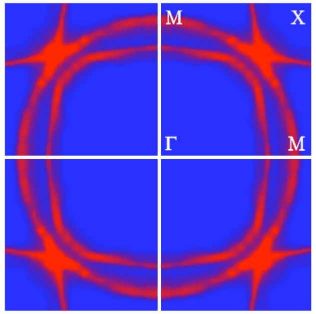
New CCD or bi-dimensional detectors: allow the possibility to acquire intensity map and fast photoemission spectra (time resolved)

What kind of information carries a photoelectron ?

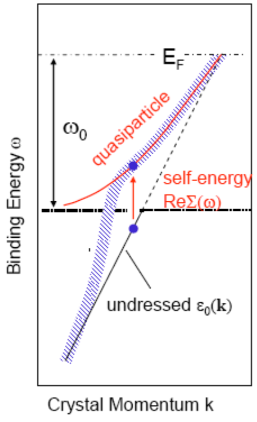
Photoemission is the most general tool for the investigation of the chemistry and of the occupied band structure of solids. Band mapping based on direct transitions has been successfully applied to numerous material.
The momentum dependence of the quasi-particle peak lineshape along the Fermi surface is a very sensitive probe of all the scattering (many body) processes.
Spin, light polarization and temperature dependences give information on magnetic behaviour, symmetries, electron-boson interactions, phase transitions … and more …







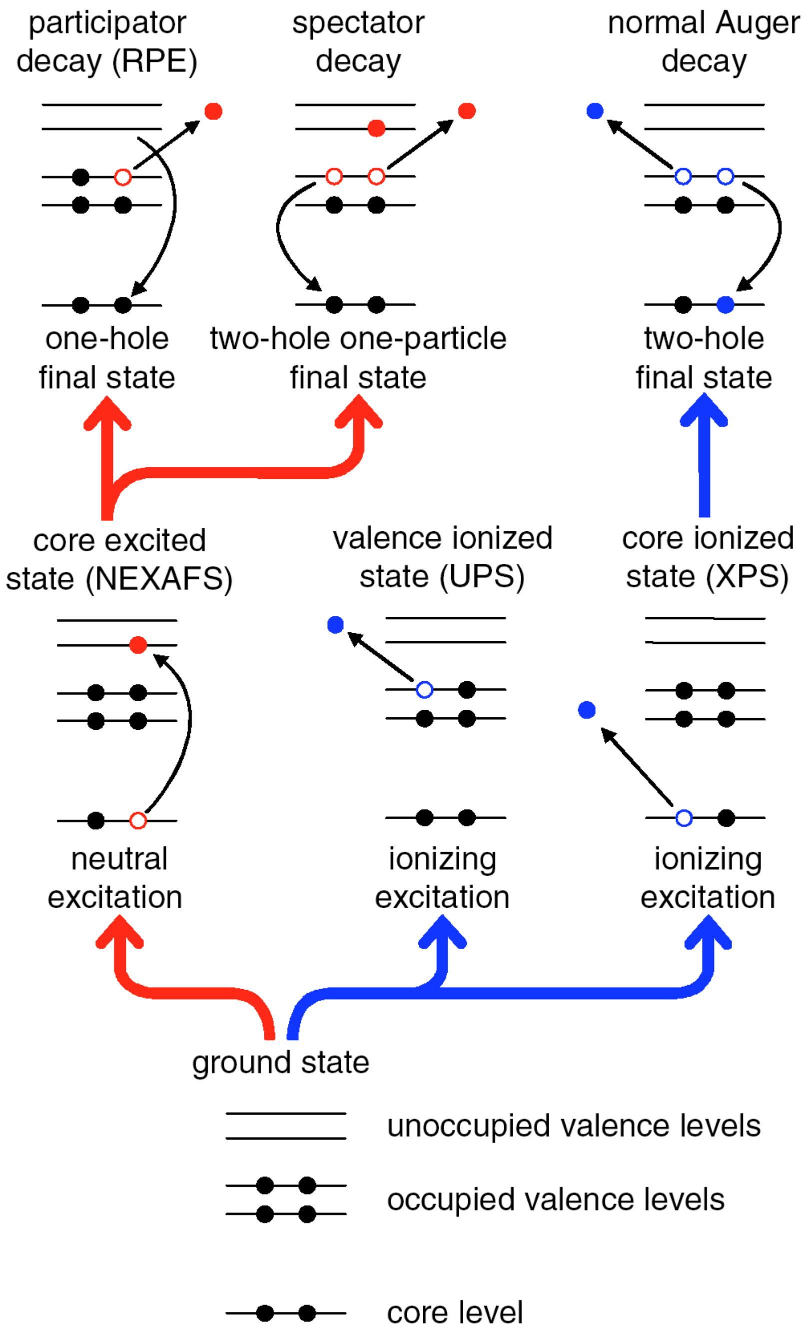
Sr_2RuO_4 cleaved at 180 K



What kind of information carries a photoelectron ?

Angle-resolved photoemission is the most general tool for the investigation of the occupied band structure of solids. Band mapping based on direct transitions has been successfully applied to numerous material.
Core level, photoelectron diffraction, fine analysis of the core lineshapes, resonant photoemission, standing waves etc… have been used to obtain many information from solid e gases…

BUT on a very ground level our physical intuition tells that the photoemission spectrum should reflect the energy and momentum distribution of electrons in the sample and the chemical environment of the emitter



participator decay (RPE)

spectator decay

normal Auger decay

one-hole final state

two-hole one-particle final state

two-hole final state

core excited state (NEXAFS)

valence ionized state (UPS)

core ionized state (XPS)

neutral excitation

ionizing excitation

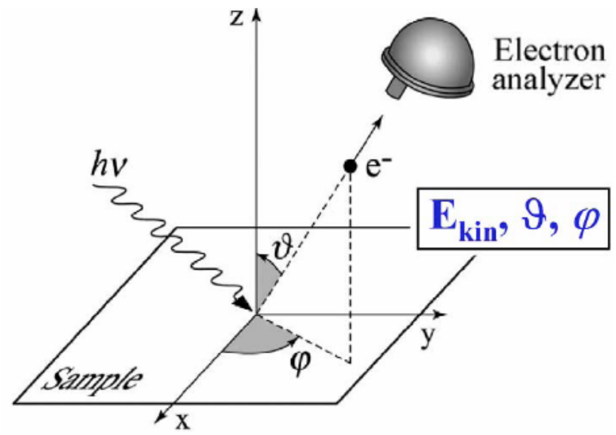
ionizing excitation

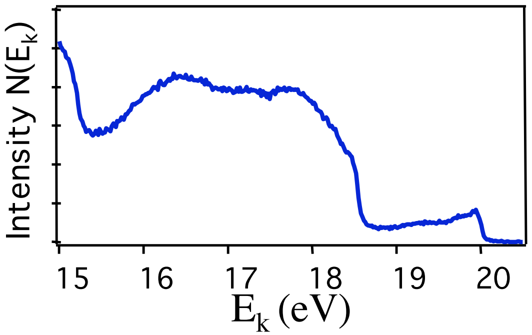
ground state

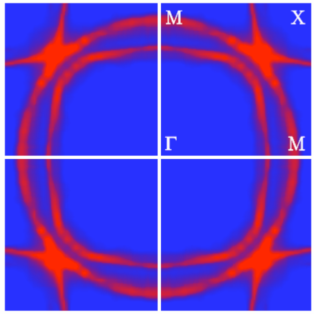
unoccupied valence levels

occupied valence levels

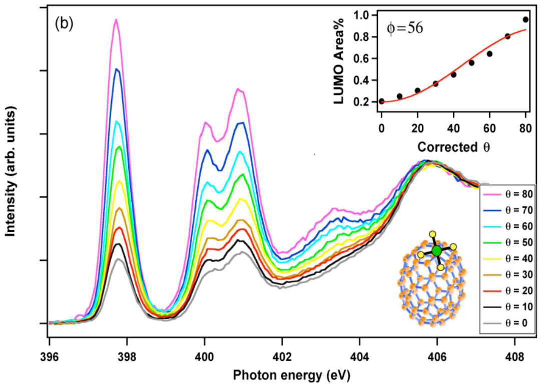
core level

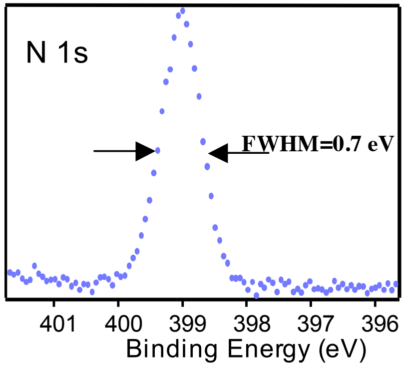






Sr_2RuO_4 cleaved at 180 K





Fermi-Dirac distribution and the Fermi-level

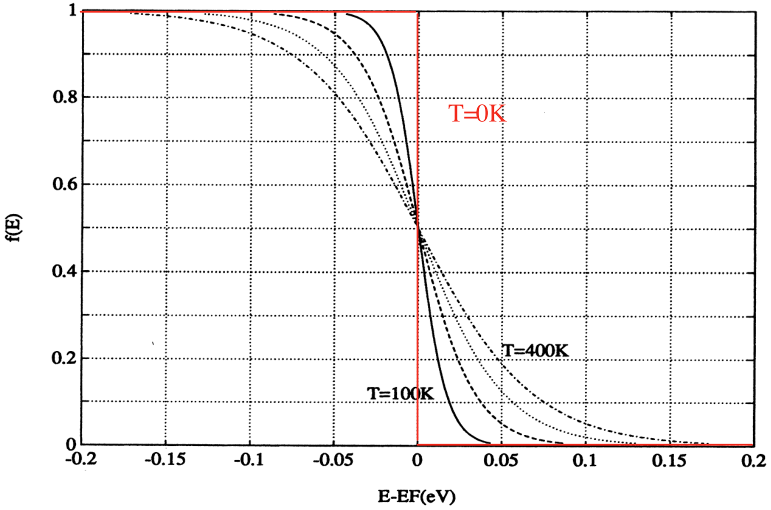
The Density of States (DOS) tells us how many states exist at a given energy E. The Fermi function $f(E)$ specifies how many of the existing states at the energy E will be filled with electrons. The function $f(E)$ specifies, under equilibrium conditions, the probability that an available state at an energy E will be occupied by an electron. It is a probability distribution function.

$$\boxed{f(E) = \frac{1}{1 + e^{(E - E_F)/kT}}}$$

E_F = Fermi energy or Fermi level

k = Boltzmann constant = 1.38×10^{-23} J/K = 8.6×10^{-5} eV/K

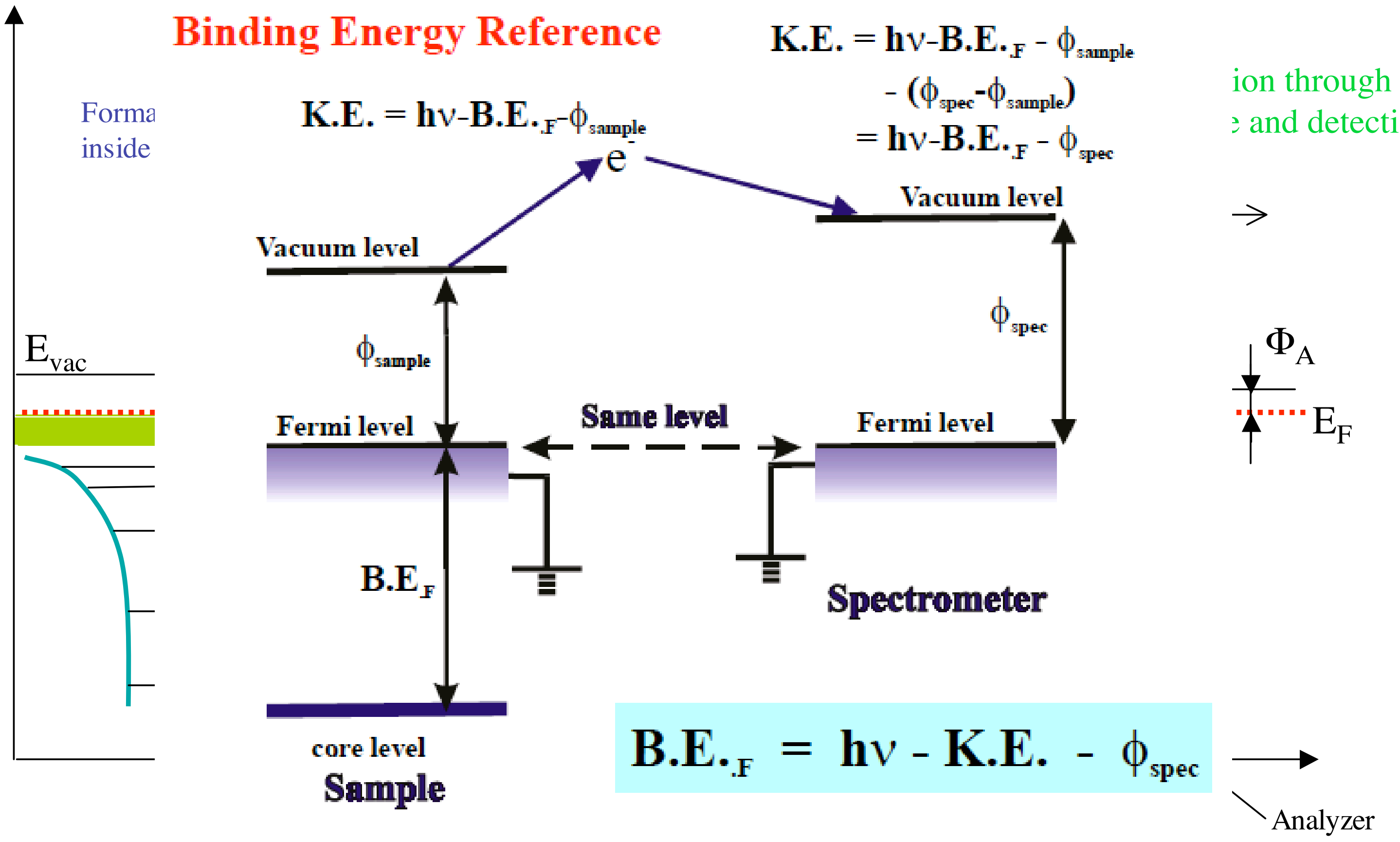
T = absolute temperature in K



An approximate (but useful) model: Three-step model

Energy conservation: $E_k = h\nu - |E_B| - \phi_A$

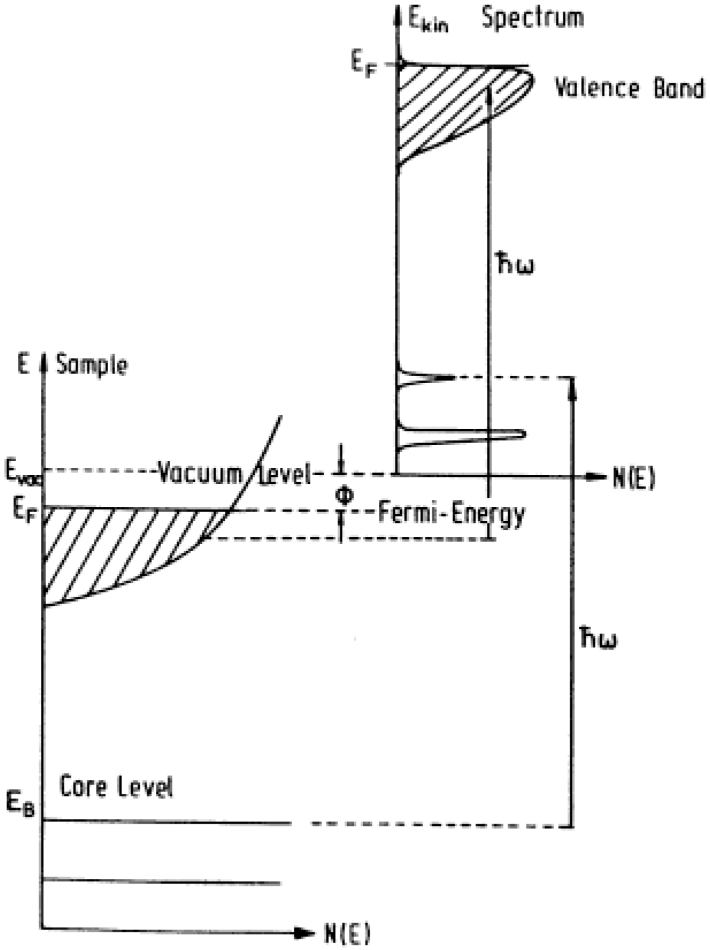
Note: when sample and analyzer are in electrical contact, the electron kinetic energy does not depend on the sample work function. The Fermi level position depends exclusively on the analyzer work function and therefore it is an absolute reference, valid also for insulators, which obviously do not exhibit a metallic Fermi edge.



$$\text{B.E.}_{,F} = h\nu - \text{K.E.} - \phi_{spec}$$

1

Photoexcitation process



Energy conservation

$$E_{kin} = \hbar\omega - \Phi - |E_B|$$

Measured Kinetic Energy

Measureed Photon Energy

Measured Work Function

Electron Binding Energy

1

Photoexcitation process: Momentum conservation

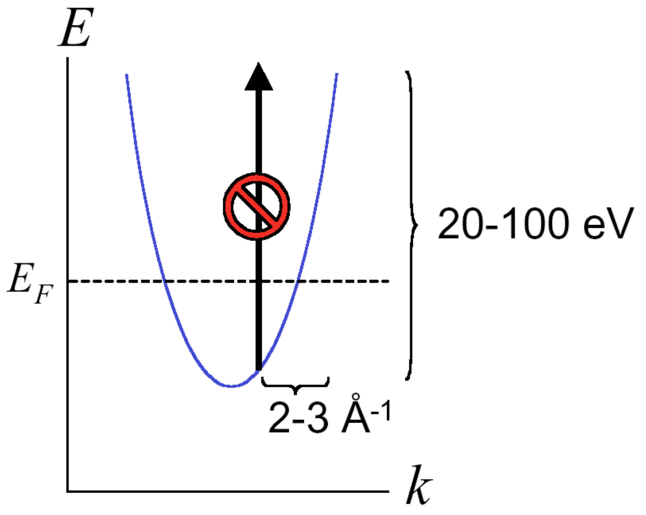
Photon Momentum $p = \hbar \mathrm{q} = h/\lambda$

Photon Energy $E = h\nu = hc/\lambda$

Typical photon wavenumber

$$\mathrm{q} = 2\pi \frac{E}{hc} = 2\pi \frac{E\ [\mathrm{eV}]}{12400\ [\mathrm{eV\text{ - }Å}]}$$

$$= .01 \text{ to } .05\ \text{Å}^{-1} \quad (\text{for } E = 20 \text{ to } 100 \text{ eV})$$



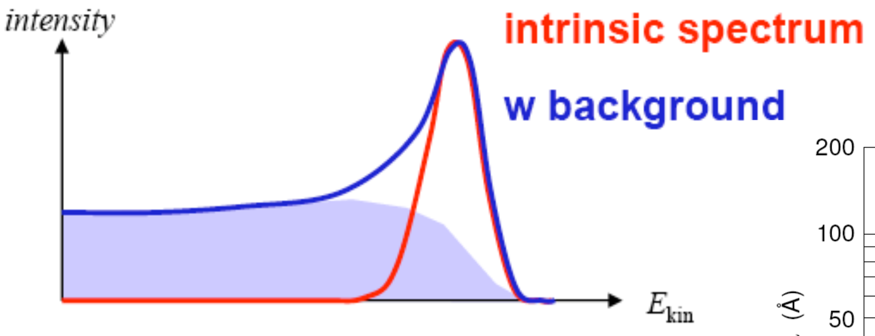
- **The photons impart very little momentum in the photoemission process, i.e. vertical transitions**

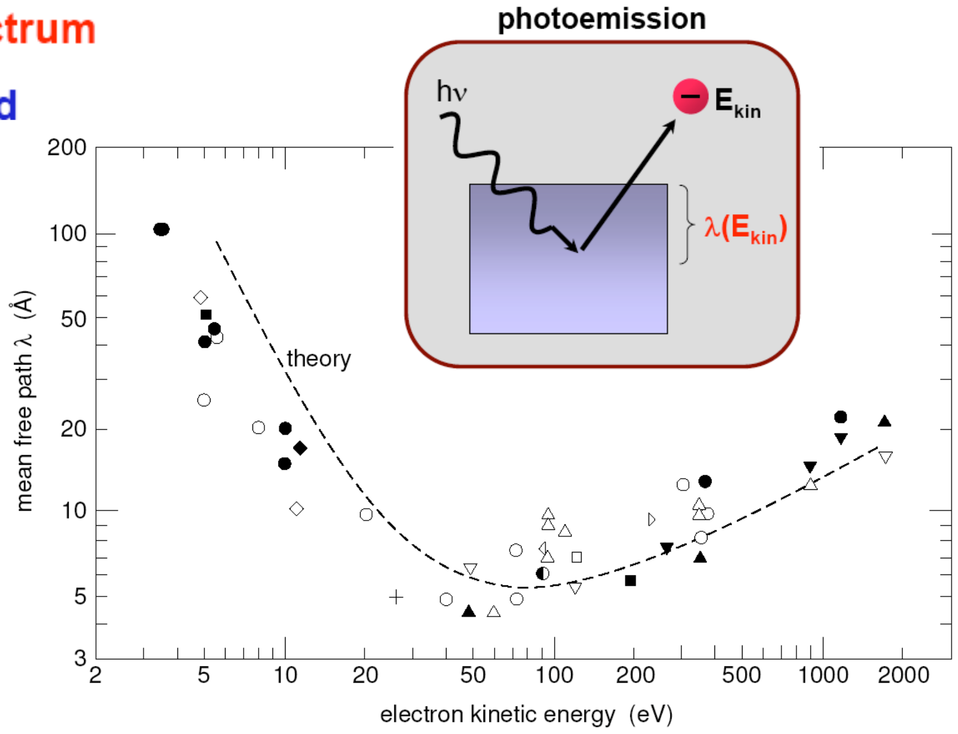
- **Therefore photon-stimulated transitions are not allowed for free electrons (energy and momentum conservation laws cannot be satisfied at the same time).**

2 Transport to the surface

Inelastic scattering of the hot-electrons (electron-electron, electron-phonon, impurities etc…) produces a loss of electrons and a loss of energy

- **Valence band measurements are sensitive to only within the first few atomic layers of the material**
- **Spectral peaks have a “loss tail” towards lower kinetic energies**



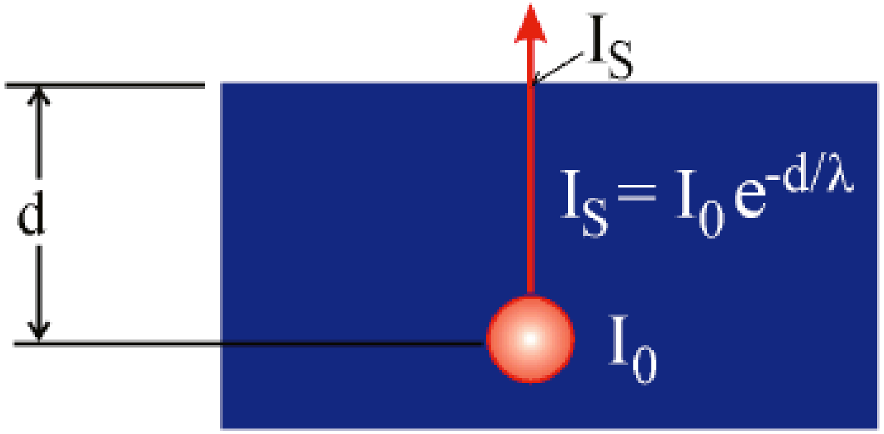


XPS Sampling Depth

λ_i = inelastic mean free path of an electron in a solid

For an electron of intensity I_o emitted at a depth d below The surface, the intensity is attenuated according to the Beer-Lambert law. So, the intensity I_s of the same electron as it reaches the surface is

$$I_s = I_o\, e^{-d/\lambda}$$



With a path length of one λ 63% of all electrons are scattered

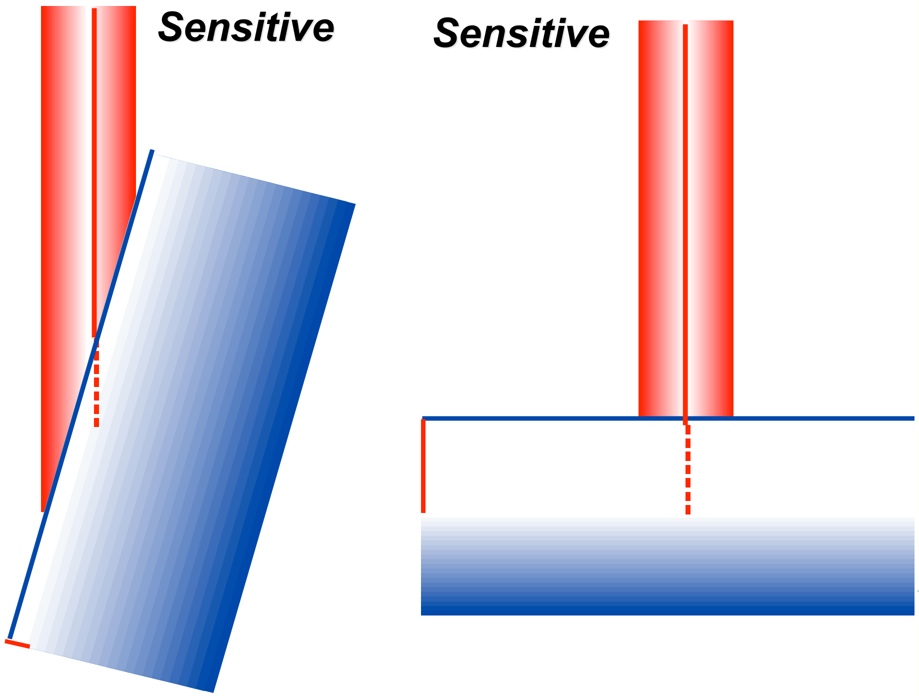
Sampling Depth

- Sampling Depth is defined as the depth from which 95% of all photoelectrons are scattered by the time they reach the surface (3λ)

- Most λ's are in the range of 1 – 3.5 nm for AlKα radiation

- So the sampling depth (3λ) for XPS under these conditions is 3-10 nm

Angle-resolved XPS

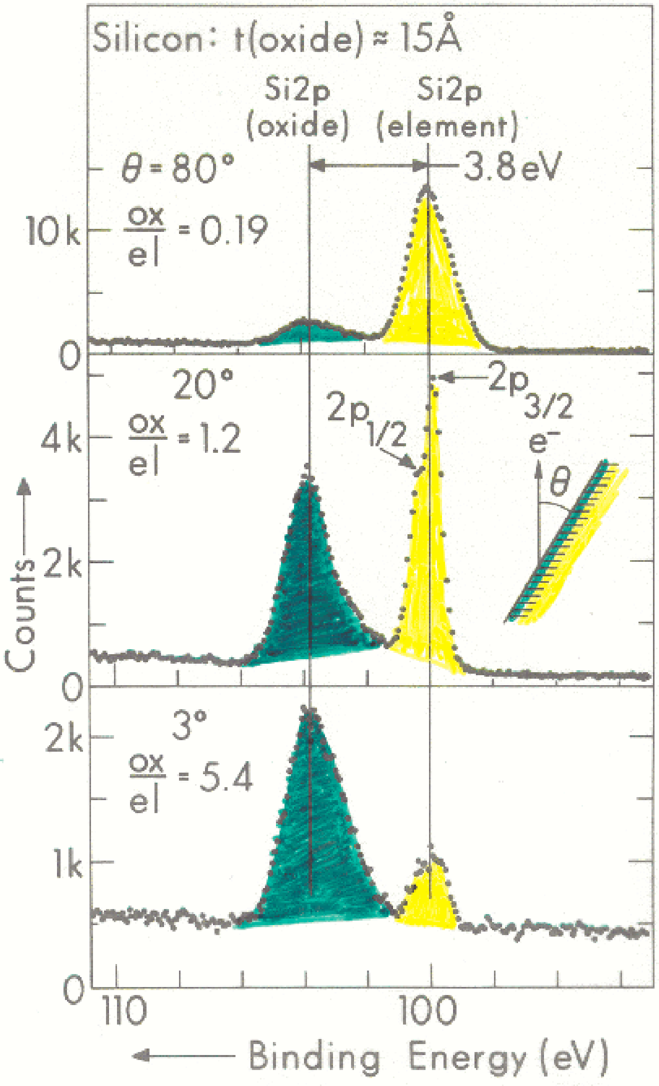


θ =20°

More Surface Sensitive

θ = 90°

Less Surface Sensitive



Information depth = d sinθ

d = Escape depth ~ 3 λ

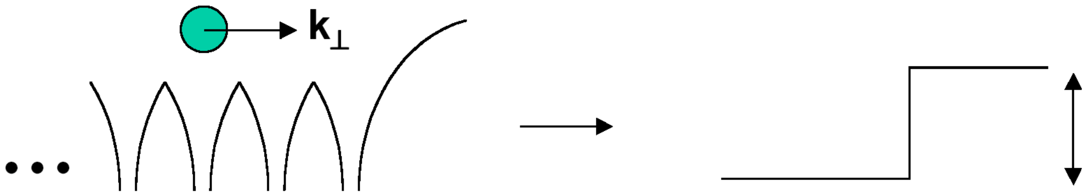
θ = Emission angle relative to surface

λ = Inelastic Mean Free Path

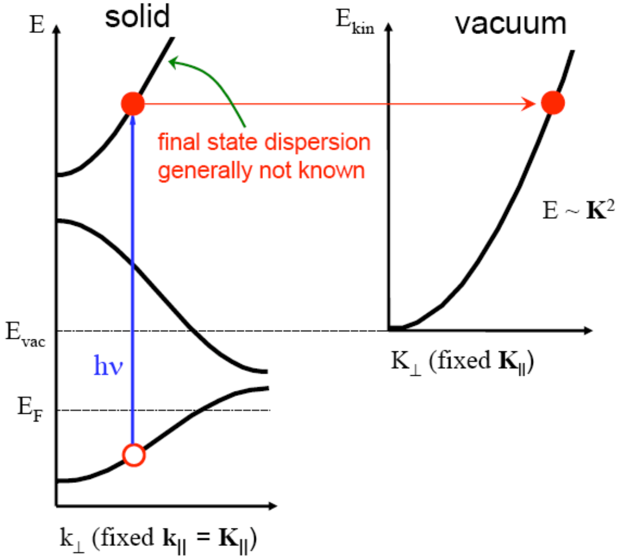
3 Transmission through the surface

At the surface the crystal symmetry is conserved in the surface plane but is broken perpendicularly to the surface: the component of the electron momentum parallel to the surface plane ($k_{//}$) is conserved, but $k_{\perp}$ is not

The potential barrier at the surface slows the electron in the direction normal to the surface.

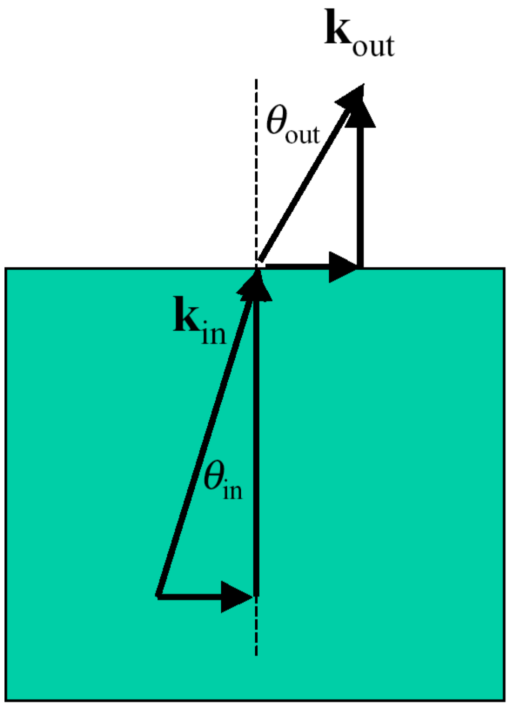


V_0=Surface potential step "inner potential"



We match the free-electron parabolas inside and outside the solid to obtain the wavevector k inside the solid

At the surface the crystal symmetry is conserved in the surface plane but is broken perpendicularly to the surface: the component of the electron momentum parallel to the surface plane ($k_{//}$) is conserved, but $k_{\perp}$ is not



Kinematic relations

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

$$k_{out,\|} = k_{in,\|} \equiv k_{\|}$$

"Snell's Law"

$$k_{\|} = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

Critical angle for emission from bulk states

$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$

First important results:

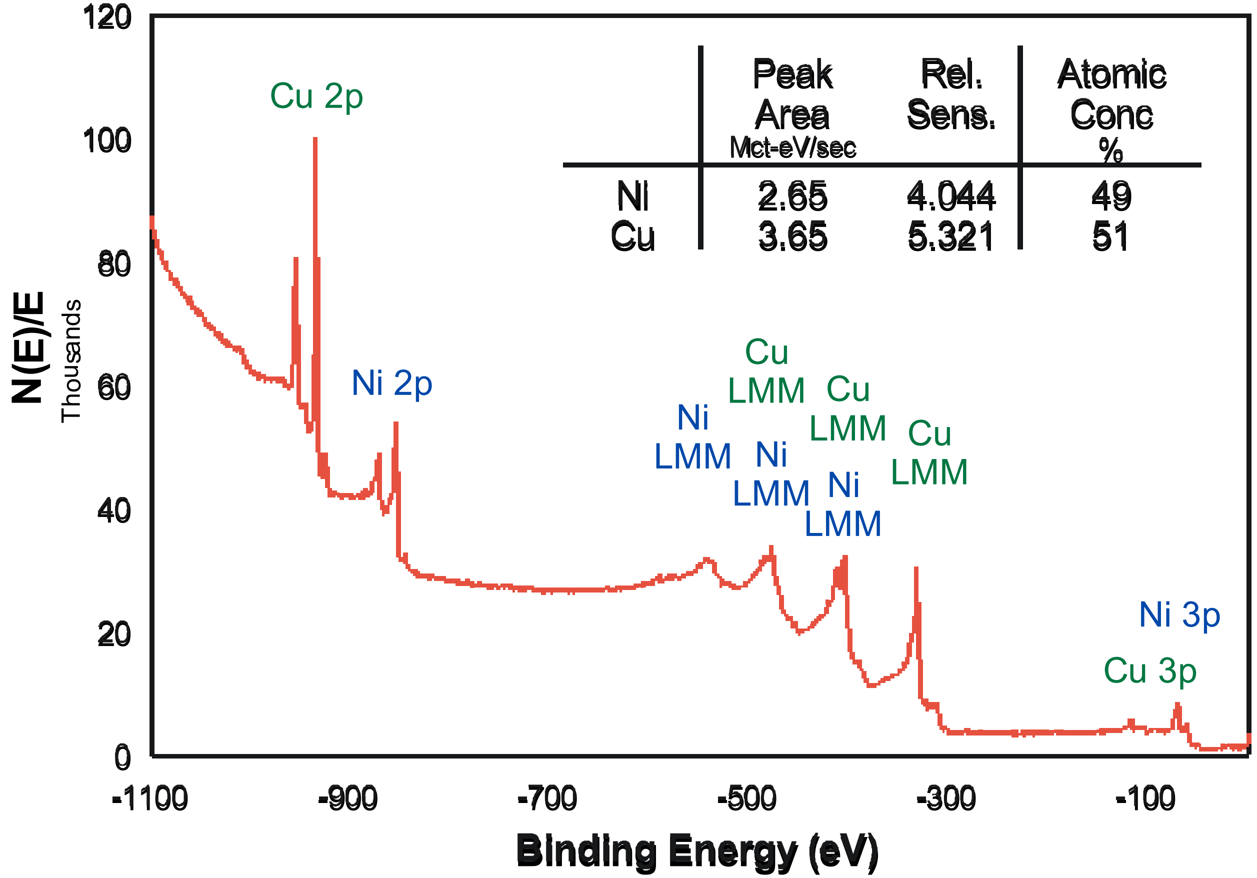
$E_{kin}=h\nu-|E_B|-\phi_A$

$$k_{//}=\sqrt{\frac{2m^*E_k}{\hbar^2}}\sin\theta_{out}\approx 0.512\sqrt{E_k}\sin\theta_{out}$$

Band mapping is therefore completely determined for 1D or 2D systems and surface states for which $k_{//}$ is a good quantum number

Anyway, as we will see later, $k_{\perp}$ is uniquely determined once E_{kin} and $k_{//}$ are fixed

XPS of Copper-Nickel alloy



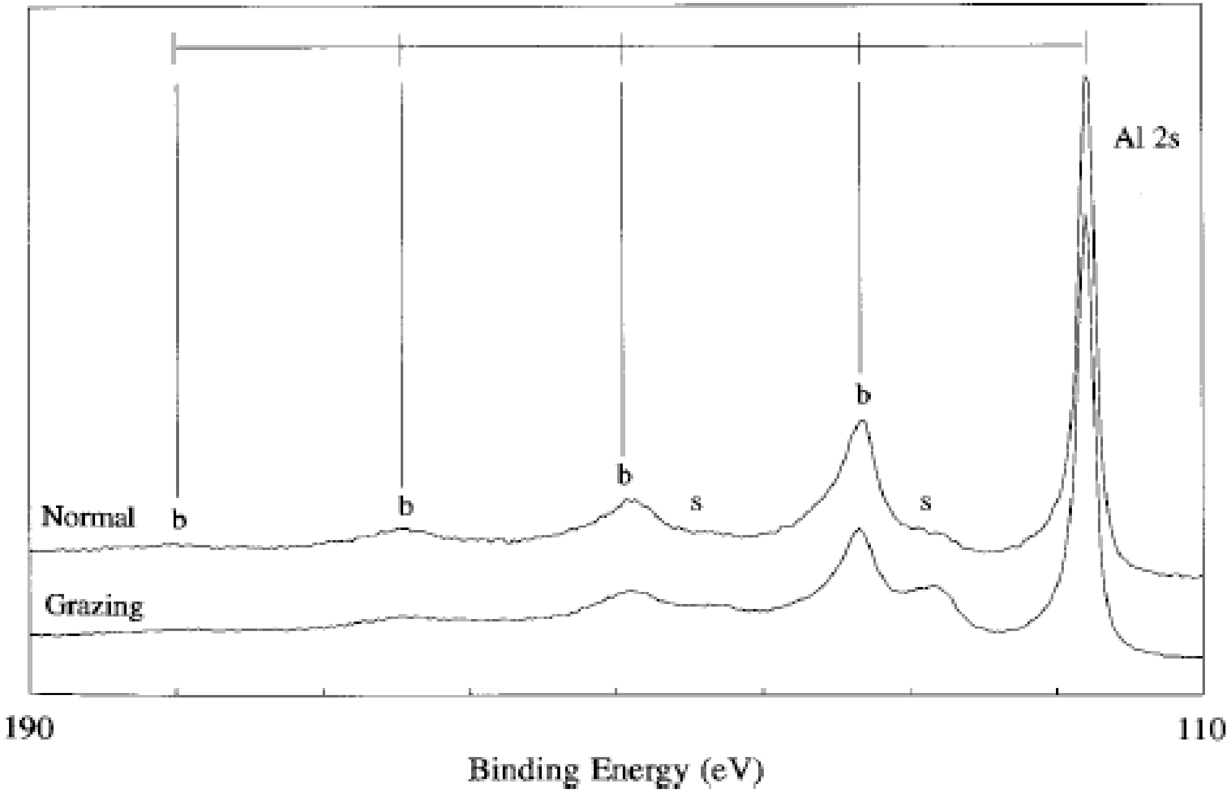
	Peak Area Mct-eV/sec	Rel. Sens.	Atomic Conc %
Ni	2.65	4.044	49
Cu	3.65	5.321	51

XPS: Core Level Photoemission

Plasmon Loss Peaks

For some materials, there is an enhanced probability for loss of a specific amount of energy due to interaction between the photoelectron and other electrons.

Al 2s spectrum of sapphire (Al_2O_3)



S: surface plasmon
B: bulk plasmon

Some photoelectrons lose more than once

The Sudden Approximation

Assumes the remaining orbitals (often called the passive orbitals) are the same in the final state as they were in the initial state (also called the *frozen-orbital approximation*). Under this assumption, the XPS experiment measures the negative Hartree-Fock orbital energy:

Koopman's Binding Energy

$$E_{B,K} \cong -\varepsilon_{B,K}$$

Actual binding energy will represent the readjustment of the N-1 charges to minimize energy (relaxation):

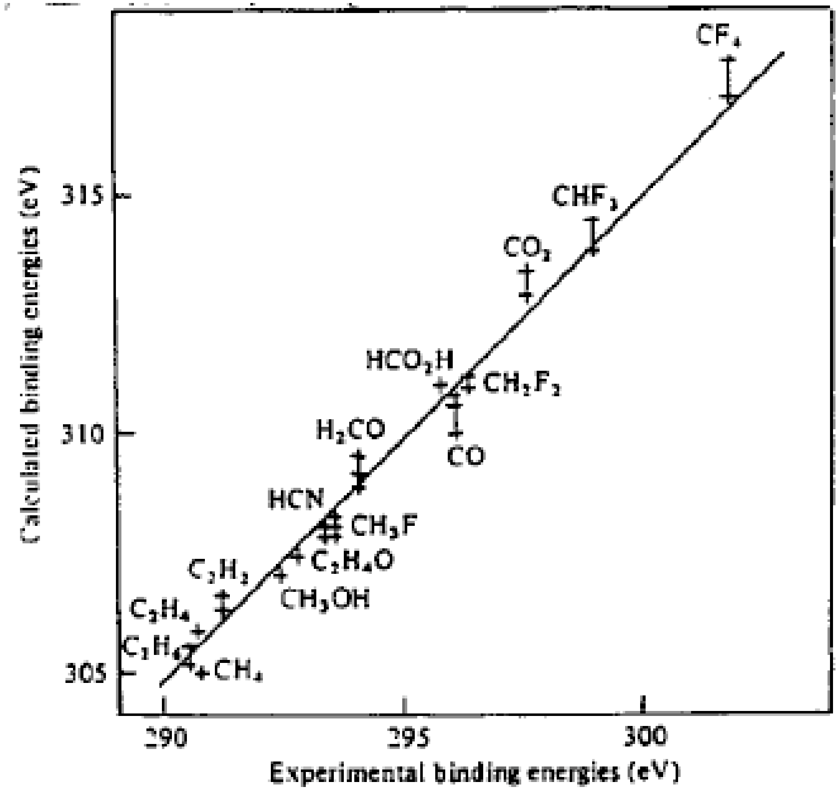
$$E_B = E_f^{\,N-1} - E_i^{\,N}$$

Koopman's Theorem

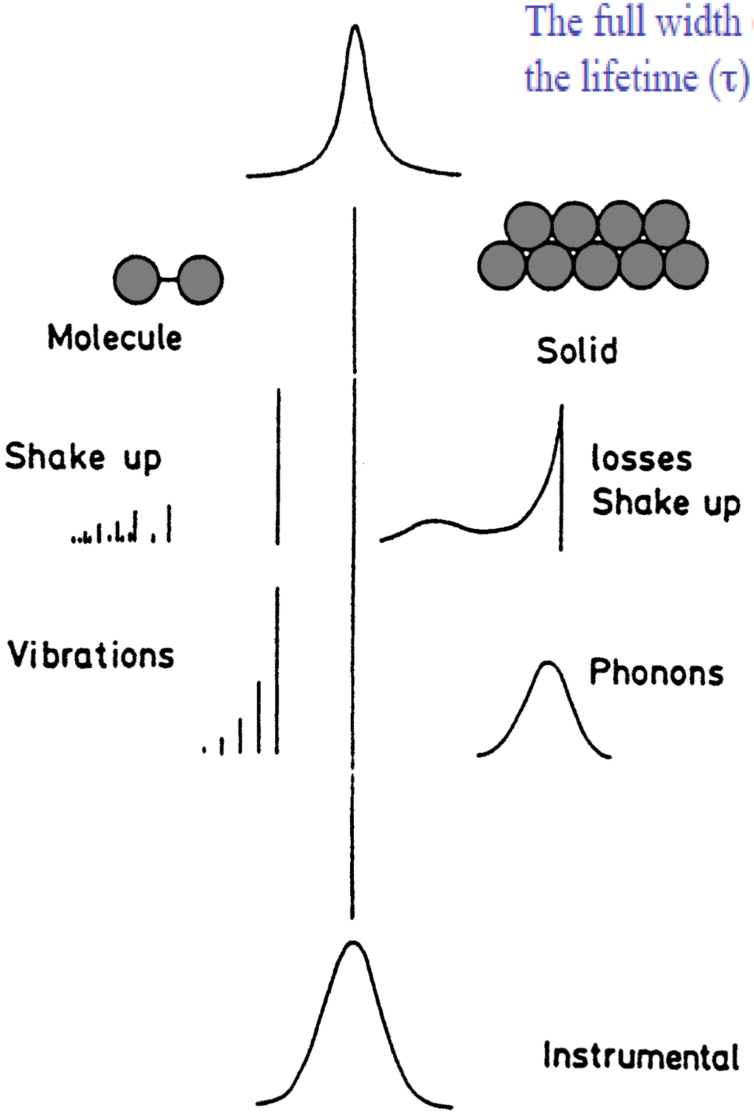
The BE of an electron is simply the difference between the initial state (atom with n electrons) and final state (atom with n-1electrons (ion) and free photoelectron)

$$BE = E_{final}(n-1) - E_{initial}(n)$$

If no relaxation* followed photoemission, BE = - orbital energy, which can be calculated from Hartree Fock. *this "relaxation" refers to electronic rearrangement following photoemission – not to be confused with relaxation of surface atoms.



Core level line shapes



The full width (Γ) of a spectral line is given by the lifetime (τ) of the final state

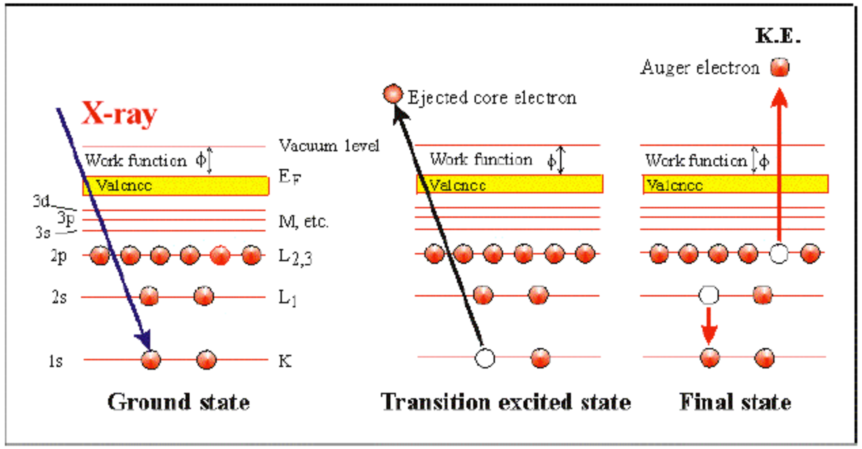
$$\Gamma = \hbar/\tau$$

Lifetime of core hole states is determined by sum of the rate for all decay channels

Auger and fluorescence (X-ray emission)

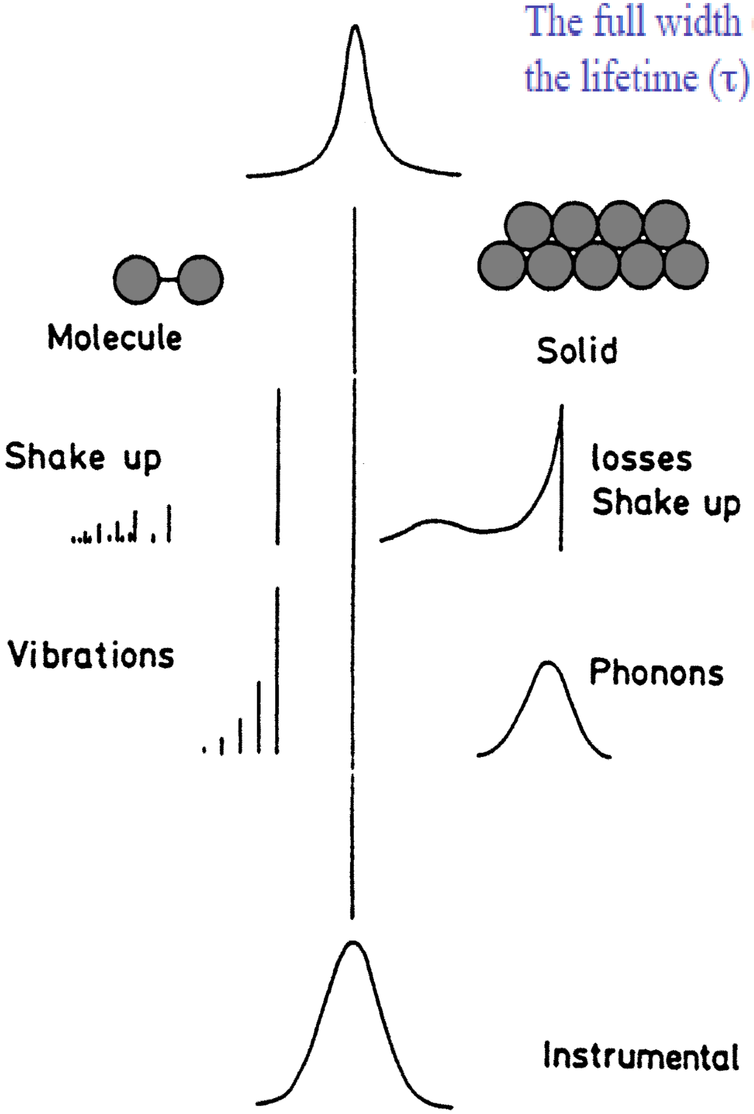
$$\Gamma = \Gamma_{aug} + \Gamma_{fluo}$$

X-ray Induced Auger Electrons



K.E. is independent of the x-ray photon energy. However, in the B.E. scale, Auger peak positions depend on the x-ray source.

Core level line shapes



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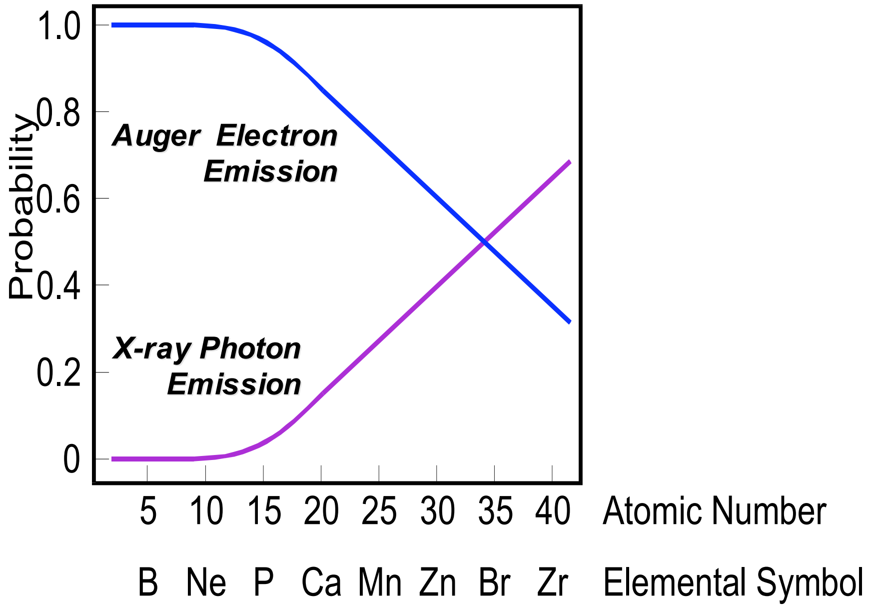
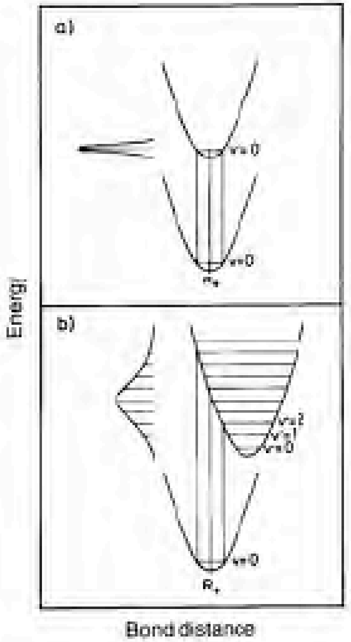
Auger and fluorescence (X-ray emission)

$$\Gamma = \Gamma_{aug} + \Gamma_{fluo}$$

Note: the light elements have a low cross section for X-ray emission.



Vibrations Core Levels



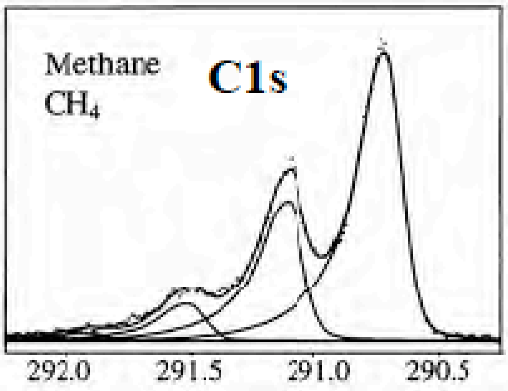
Frank Condon Principle

Core levels are non bonding orbitals

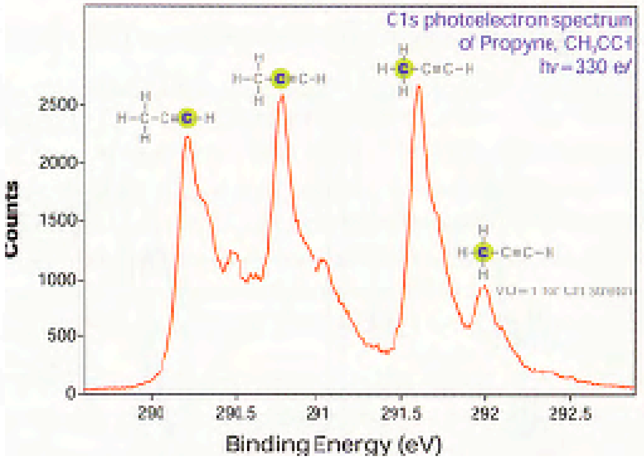
No vibrational excitations expected?

Relaxation in the ionized state

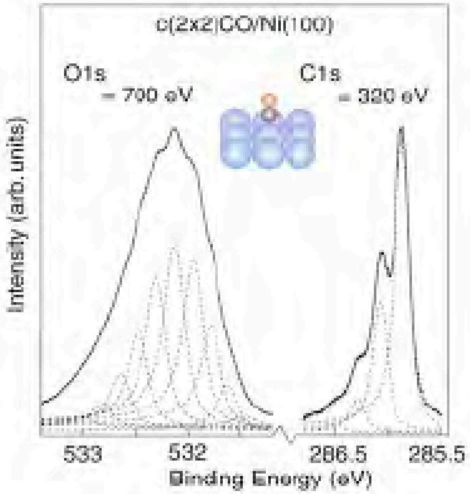
Different potential energy curves



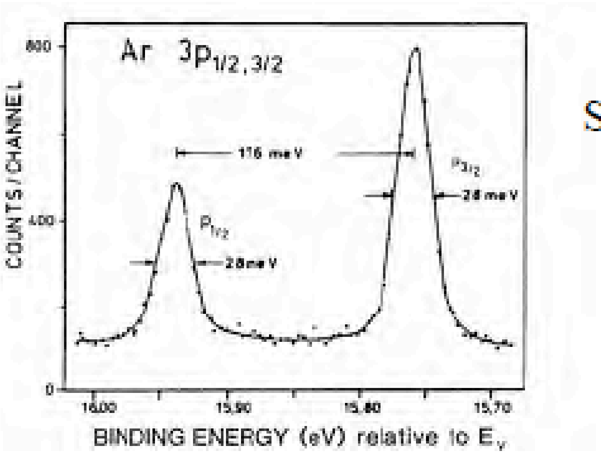
Chemical shifted components



Adsorbed CO on Ni



Spin-orbit splitting



$$3p^6 + h\upsilon \rightarrow 3p^5 \approx (3p)^{-1}$$

Spin and angular momentum interaction $J = l \pm s$

For $l = 1$ and $s = +1/2$ $J = 3/2$

$s = -1/2$ $J = 1/2$

Two lines seen in spectrum $3p_{3/2}$ and $3p_{1/2}$

Intensities ratio of the two lines given by the population of the orbitals

$$(2J_{3/2} + 1)/(2J_{1/2} + 1) = 4/2 = 2$$

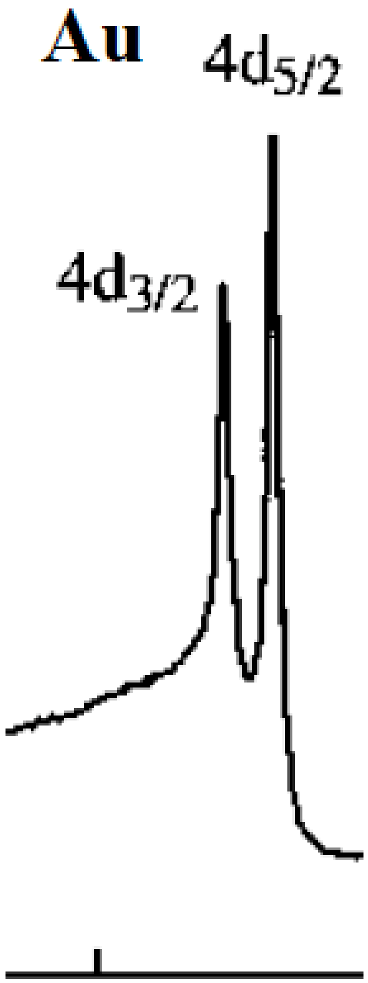
$$\boxed{\begin{array}{l} \text{p shell} \rightarrow p_{3/2} \text{ and } p_{1/2} \text{ ratio} \rightarrow 2:1 \\ \text{d shell} \rightarrow d_{5/2} \text{ and } d_{3/2} \text{ ratio} \rightarrow 3:2 \\ \text{f shell} \rightarrow f_{7/2} \text{ and } f_{5/2} \text{ ratio} \rightarrow 4:3 \end{array}}$$

For p, d and f peaks, two peaks are observed.

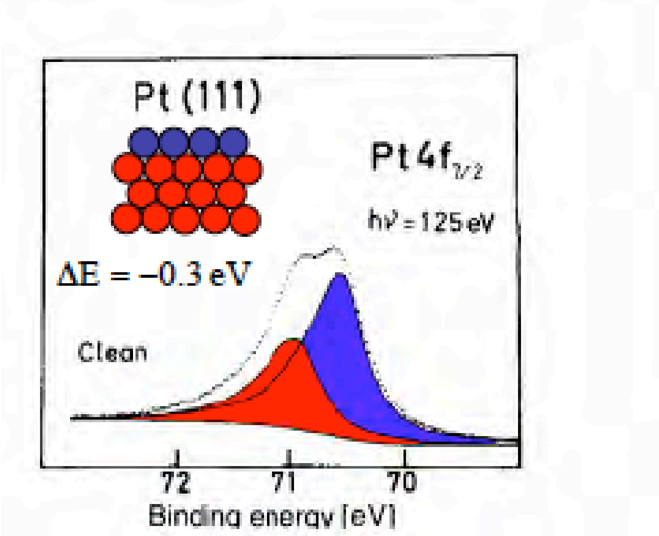
The separation between the two peaks are named **spin orbital splitting**. The values of spin orbital splitting of a core level of an element in different compounds are nearly the same.

The **peak area ratios** of a core level of an element in different compounds are also nearly the same.

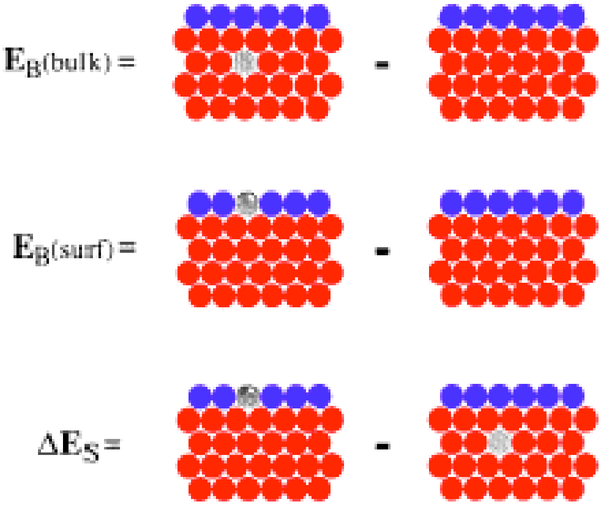
Spin orbital splitting and peak area ratios assist in element identifications.

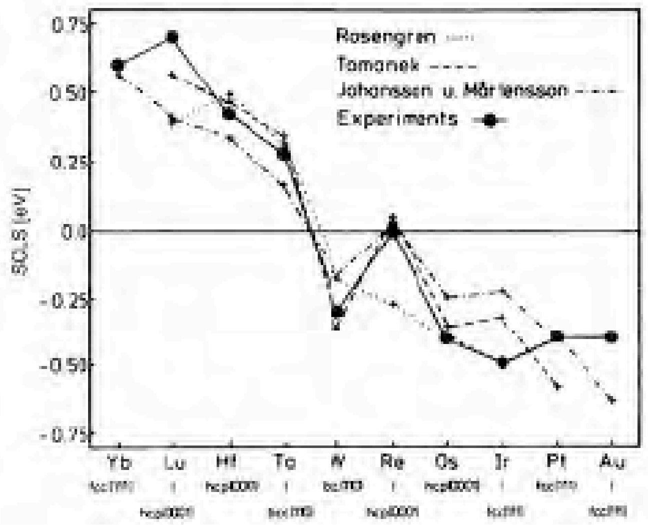


Surface Core Level Shift (SLCS)



$$E_b = E_{TOT}^{Final} - E_{TOT}^{Ground}$$





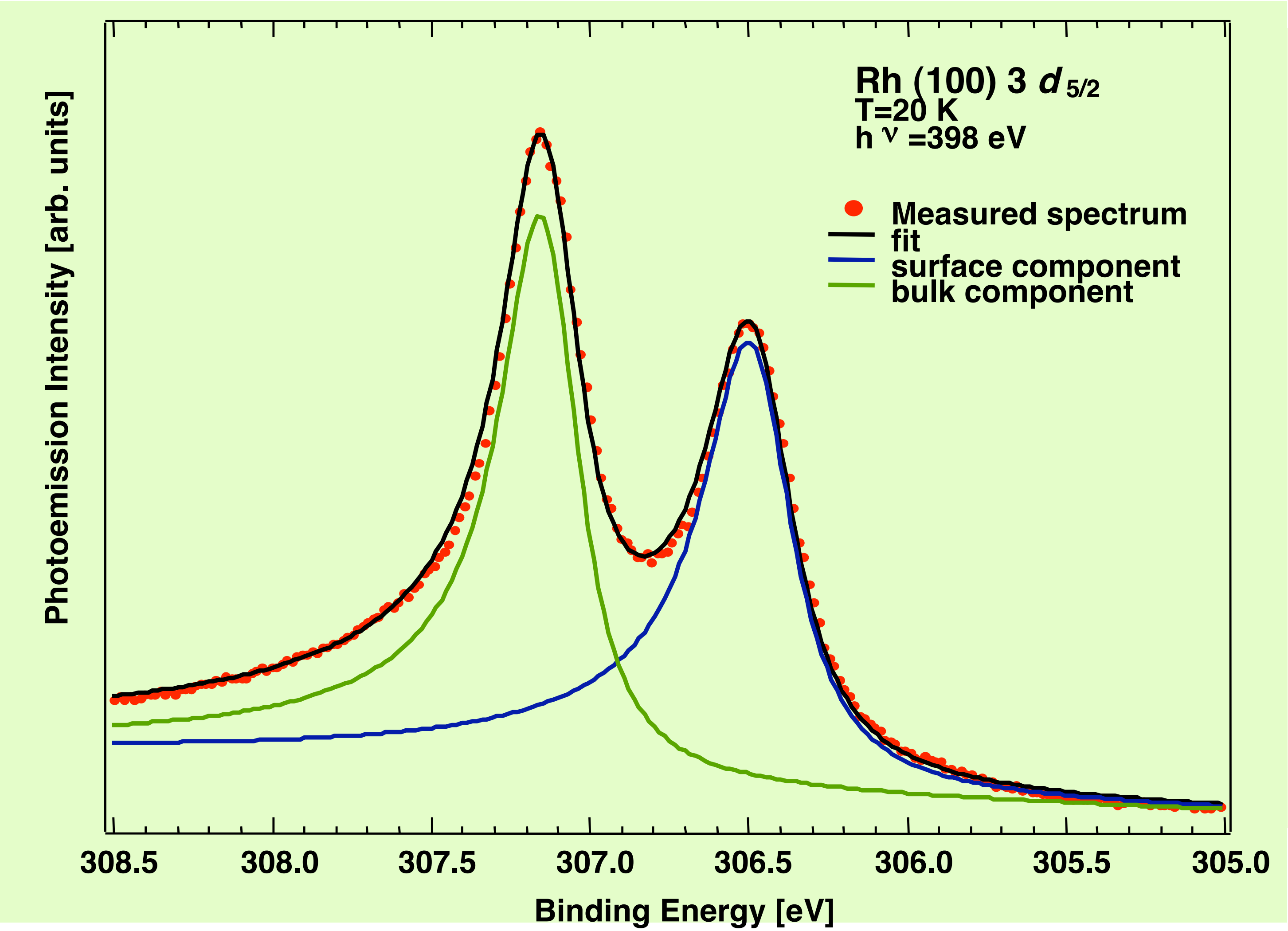
Variation across the 5d series

ΔE_S Surface segregation energy for Z+1 impurity in Z metal

We have a lower binding energy for Au at the surface than in bulk for Pt (111)

The more open surfaces have a larger ΔE_S

High resolution spectrum measured in less than 1 minute



Chemical Effects in XPS

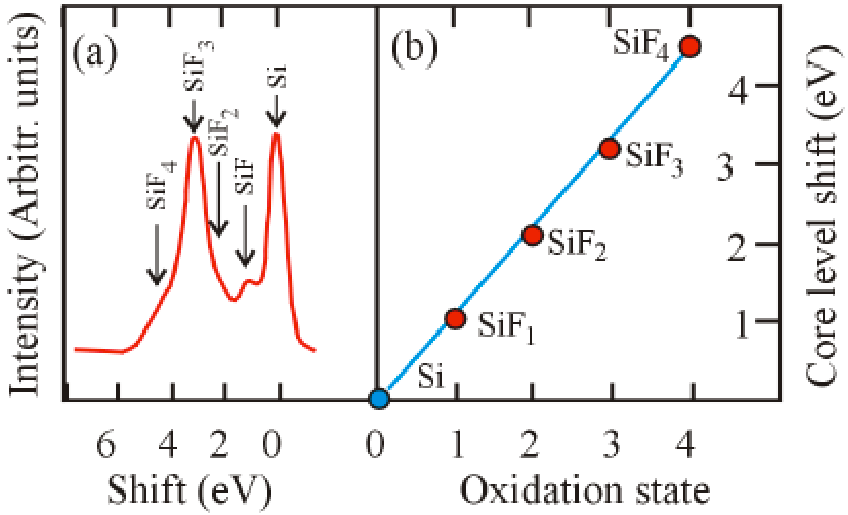
Chemical shift: change in binding energy of a core
electron of an element due to a change
in the chemical bonding of that element.

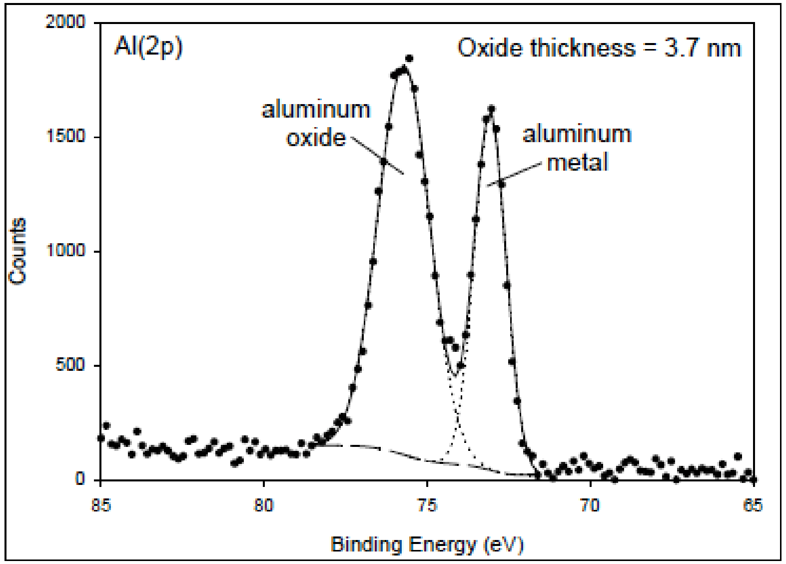
Qualitative view: Core binding energies are determined by:

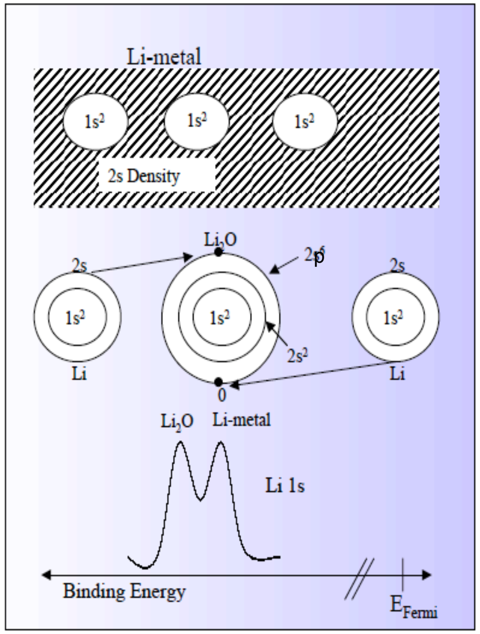
- electrostatic interaction between it and the nucleus, and reduced by:
- the electrostatic shielding of the nuclear charge from all other electrons in the atom (including valence electrons)
- removal or addition of electronic charge as a result of changes in bonding will alter the shielding

Withdrawal of valence electron charge → increase in BE
(oxidation)
Addition of valence electron charge → decrease in BE

Chemical Shifts



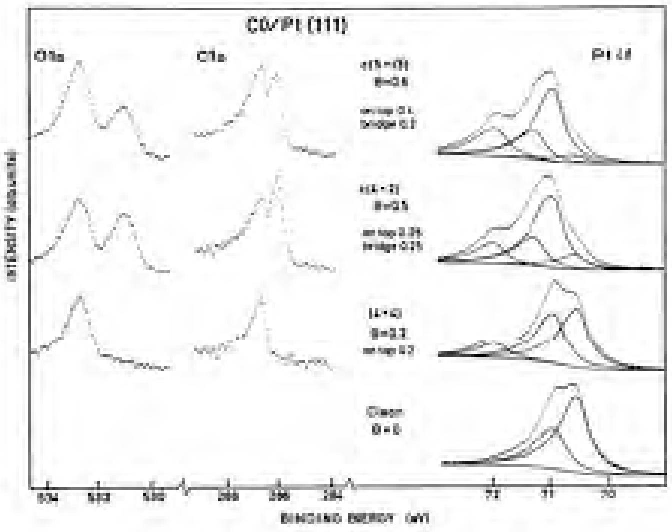


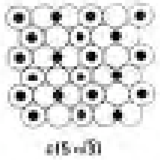


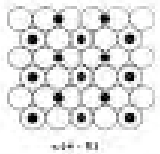
Binding Energy is lower due to increased screening of the nucleus by 2s conduction by 2s electrons

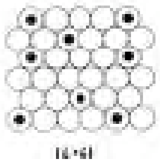
Binding Energy is higher because Li 2s electron density is lost to oxygen

PE spectrum

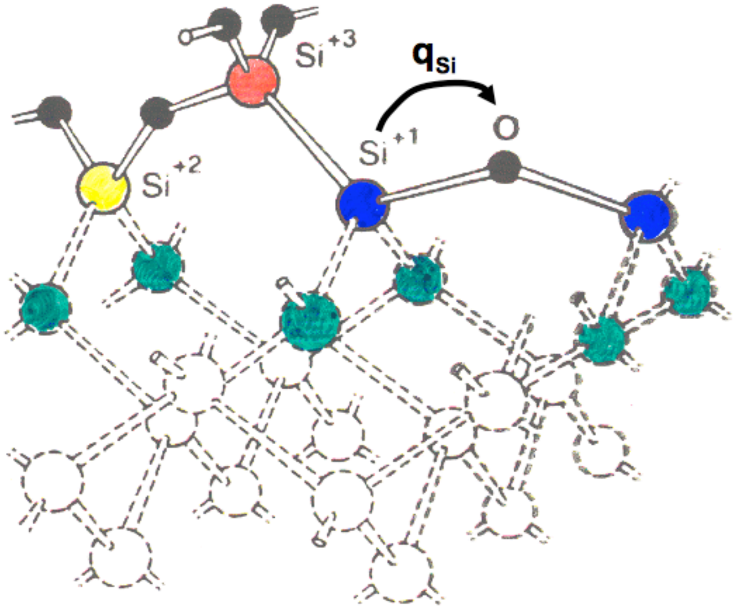


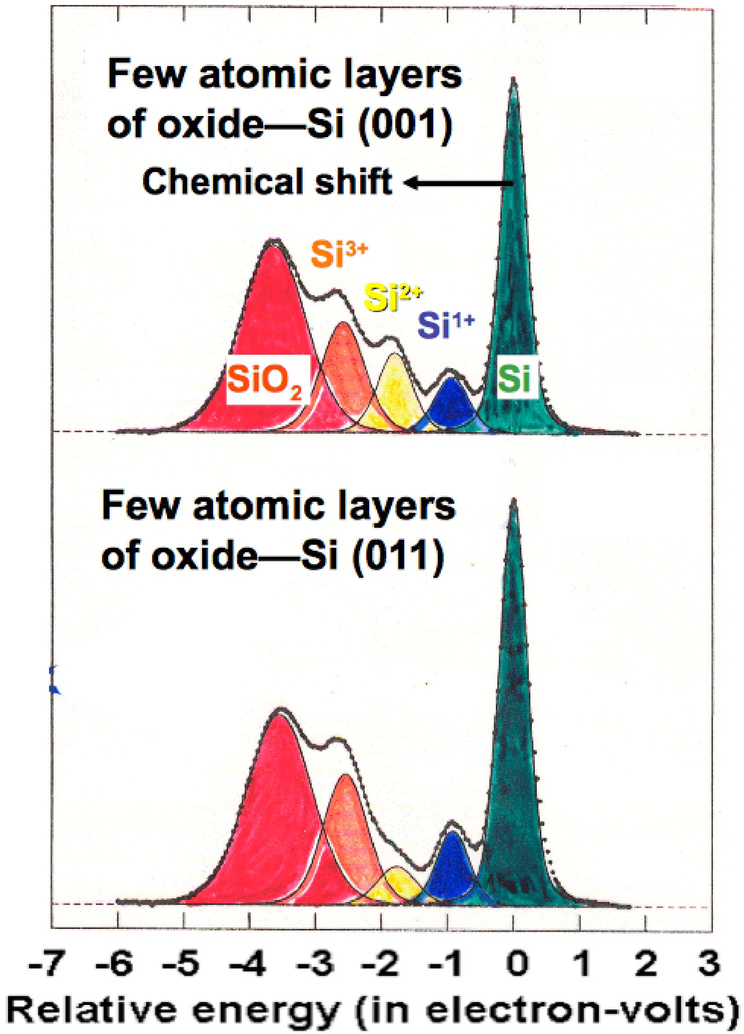




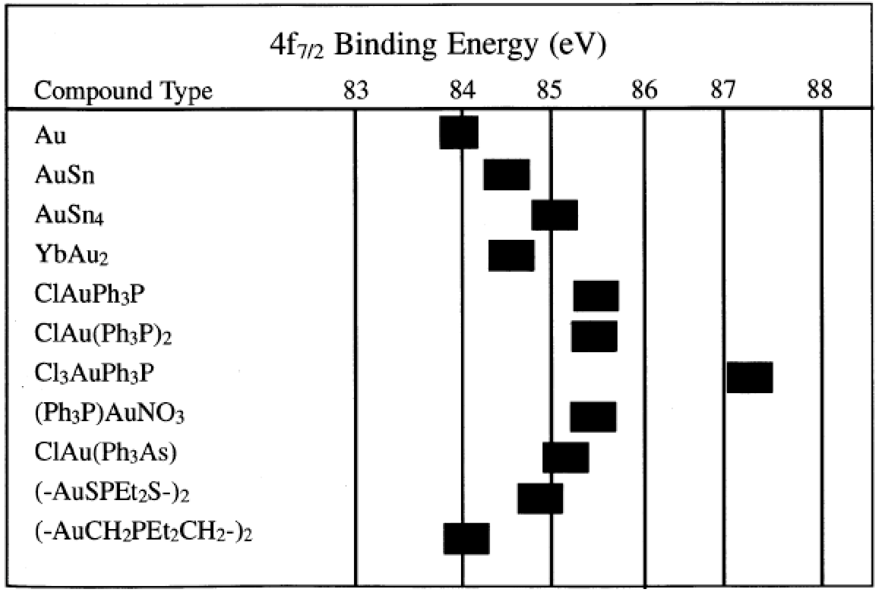


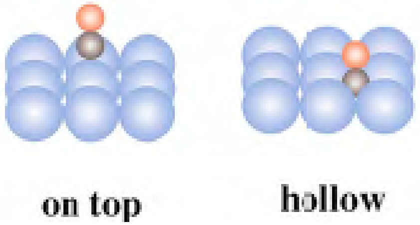
Chemical shifts:
Looking into the silicon dioxide layer with photoelectron spectroscopy

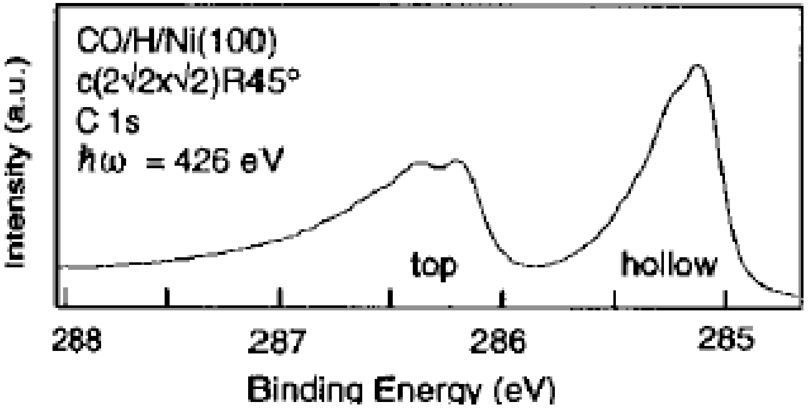




Chemical Shift







Ground state picture

Koopmans teorem $\boxed{E_b = -\varepsilon_b}$ orbital eigenvalue

Assuming the remaining electrons inert

Relaxation

Valence electrons change due to electron removal

$$\boxed{E_b = -\varepsilon_b + E_{relax} + E_{corr}}$$

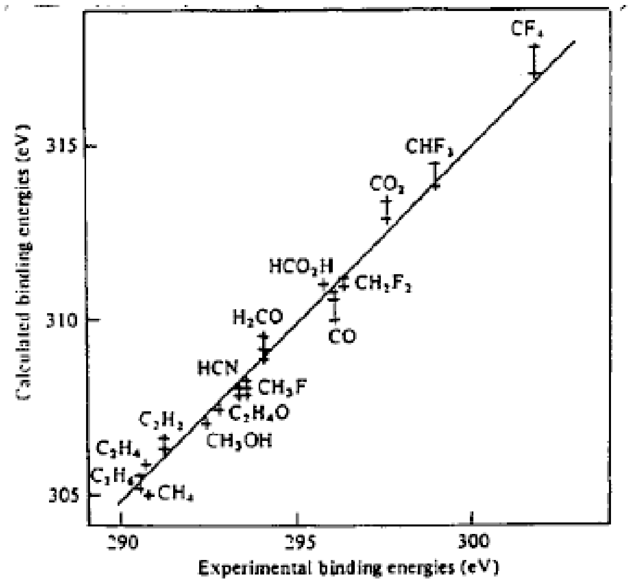
relaxation energy

correlation energy

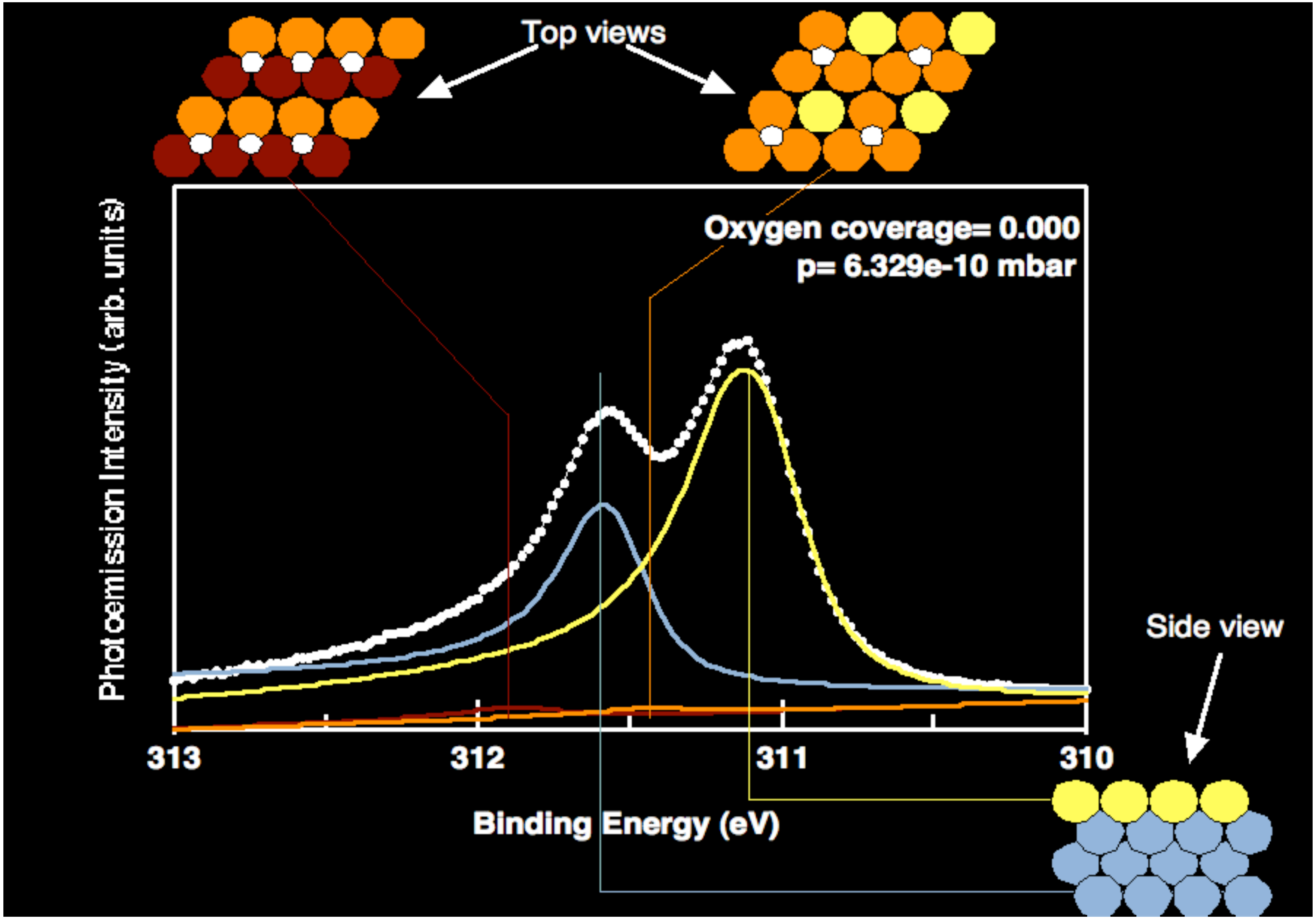
Difference in total energy

$$\boxed{E_b = E_{TOT}^{Ground} - E_{TOT}^{Final}}$$

total energy of the whole system including all interacting atoms

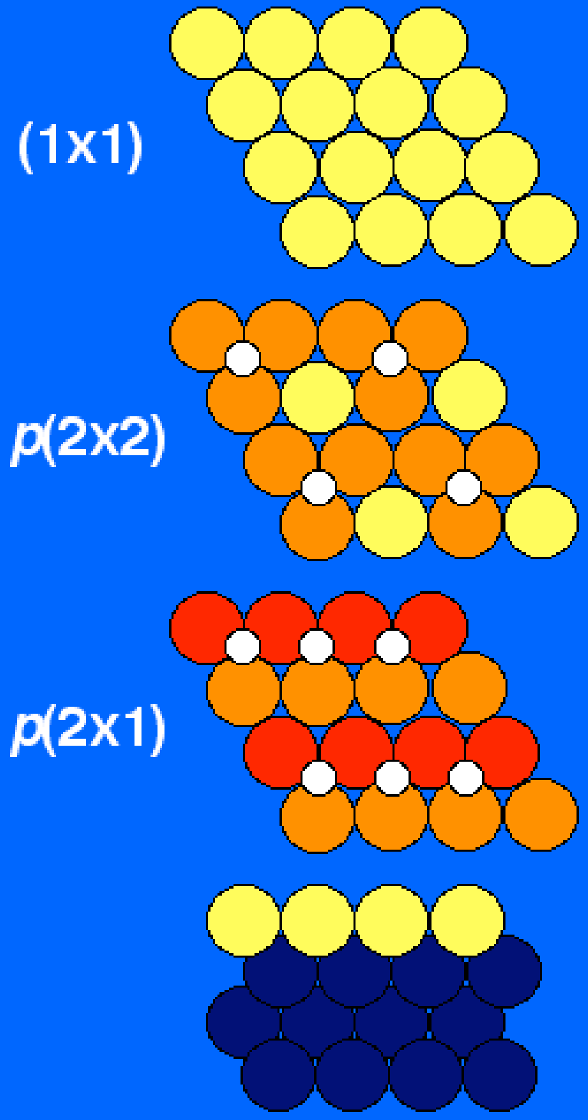


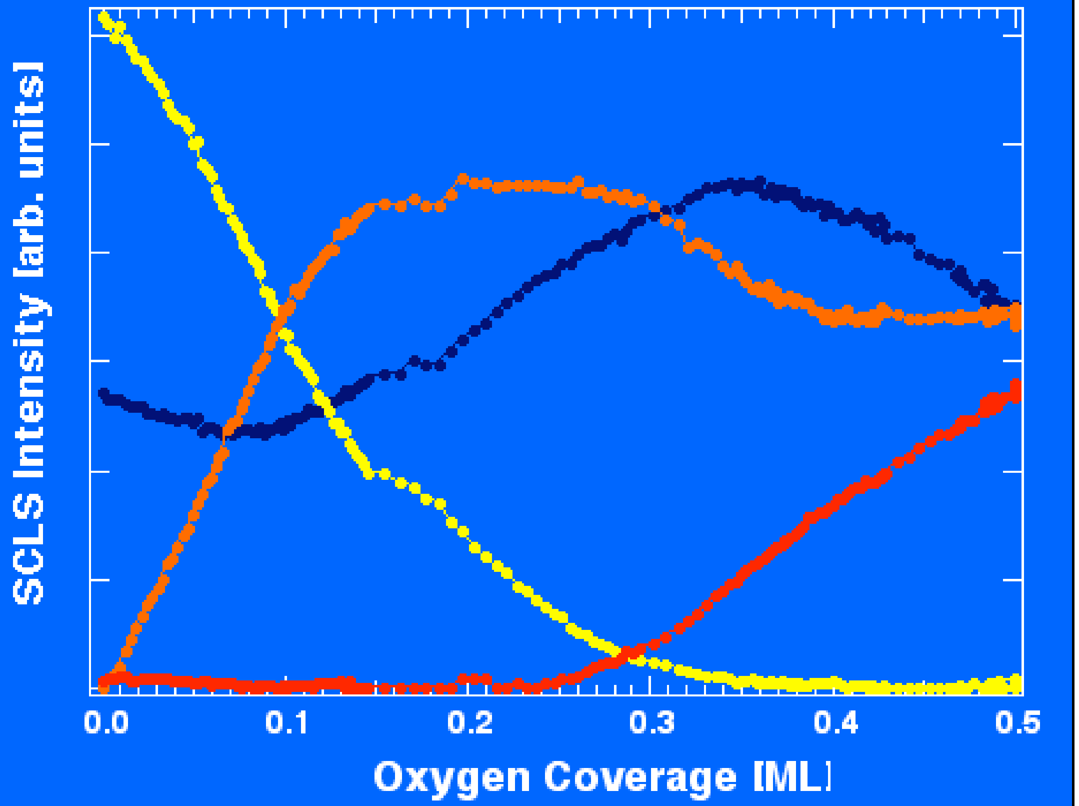
Rh(111): evolution of Rh $3d_{5/2}$ during O_2 dosing



p(2x2)
Θ=0.25 ML

p(2x1)
Θ=0.5 ML

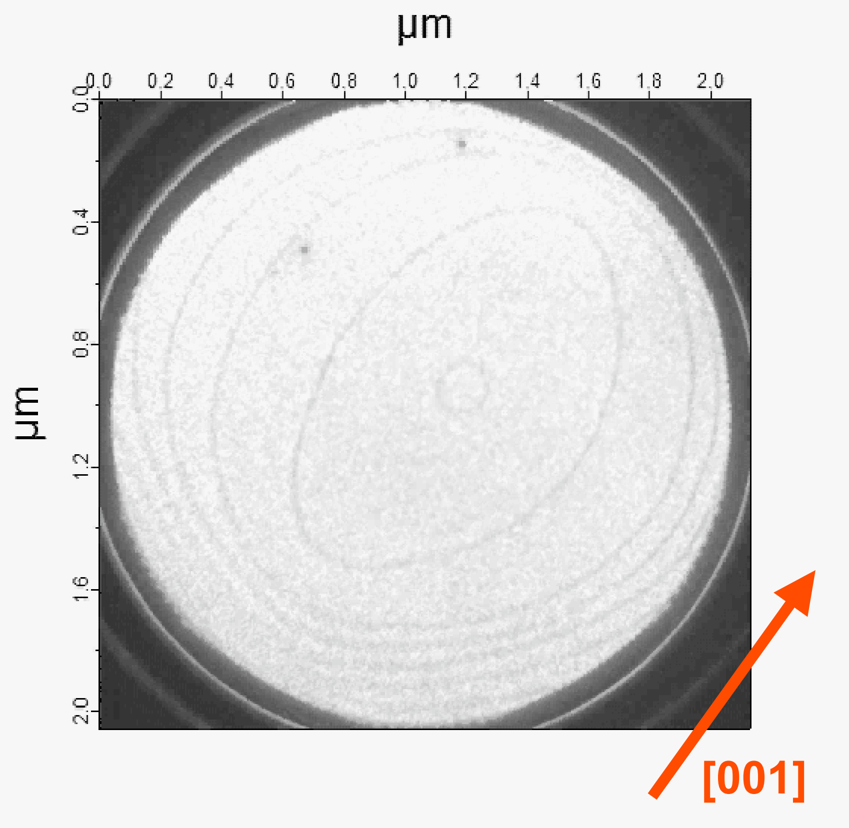




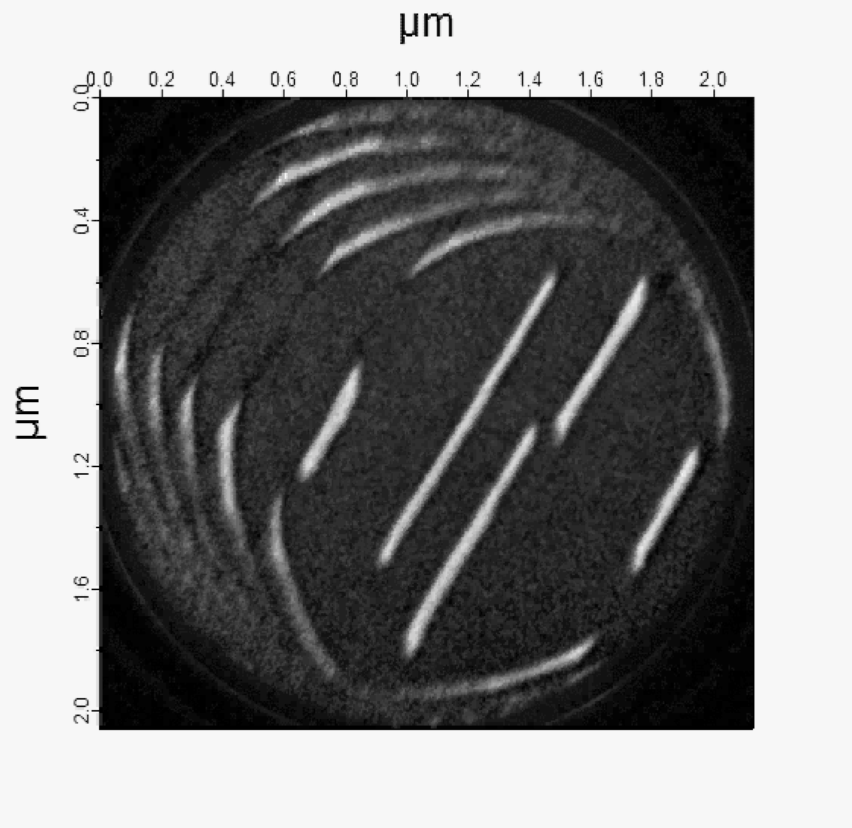
Chemical reaction in real time at the nanoscale

NanoSpectroscopy beamline

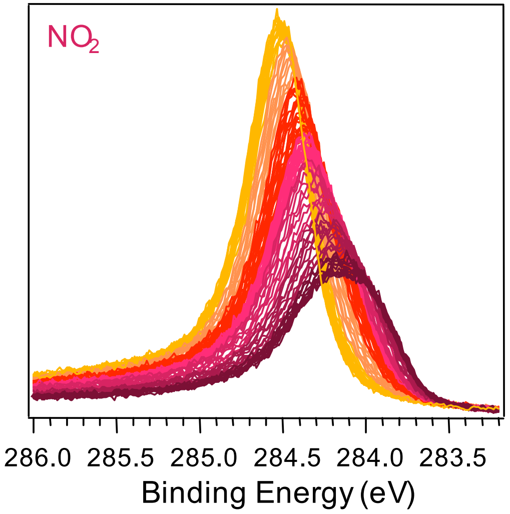
Pd deposited on 0.25 ML O / W(110)
T = 850° C
Super-saturation growth of Pd

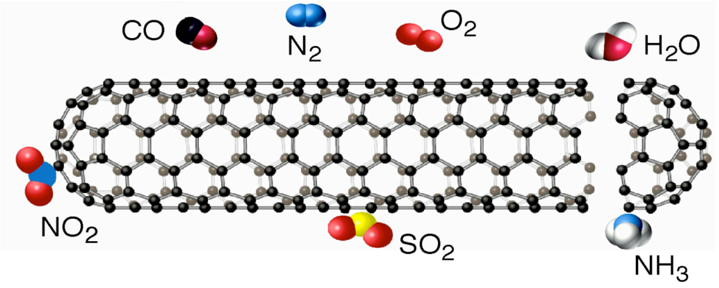


0.25 ML O / W(110)
T = 850° C
Pd desorption



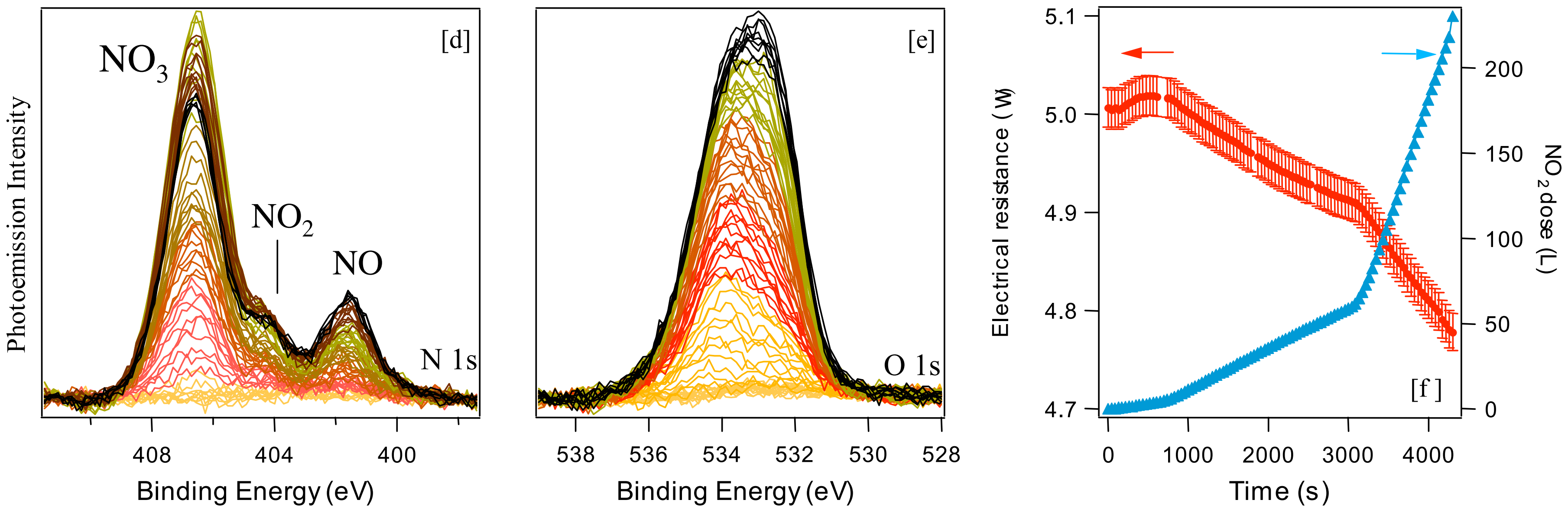
Fast photoemission: evolving chemical reactions





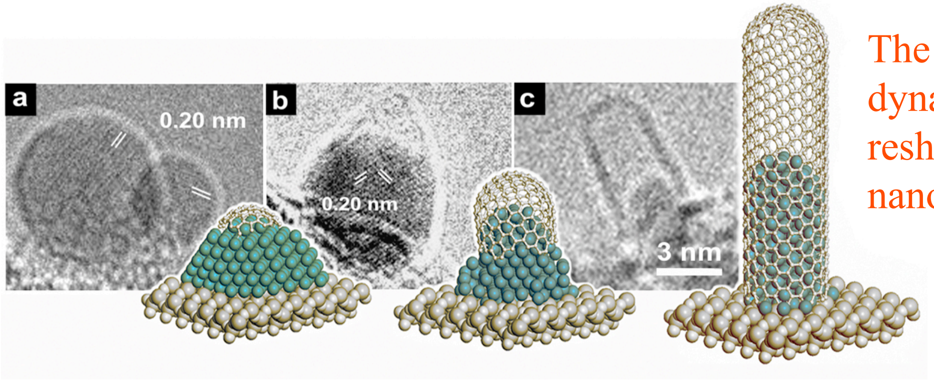
Variation of 1% after ~ 40 L,
i.e. after 10 ppb of toxic molecule in 4 sec.

SnO$_2$-based sensor: some ppm in 1 min.



Catalyst dynamics during surface-bound carbon nanotube nucleation

S. Hofmann, M. Cantoro, S. Pisana, A. Parvez, A.C. Ferrari, F. Cervantes-Sodi, J. Robertson, R. Sharma, G. Du,
C. Ducati, C. Mattevi, C. Cepek, R. Dunin-Borkowski, S. Lizzit, L. Petaccia, A. Goldoni, NanoLetters 7 (2007)

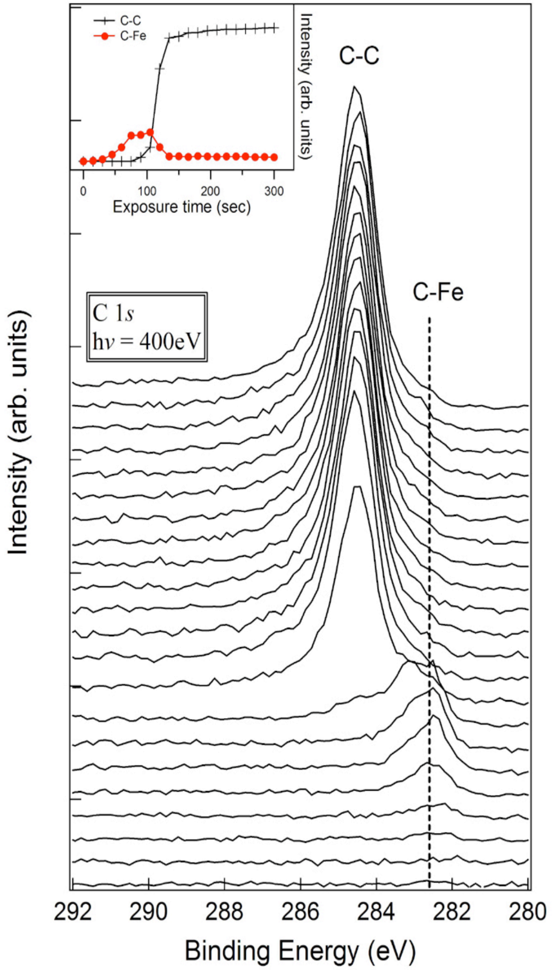


The formation of graphitic carbon leads to the dynamic reshaping of the catalyst particle. This reshaping defines the morphology of the carbon nanotube.

For SWNT we observe crystalline phase contrast from the transition metal catalyst nano-particles. The 0.20 nm reflection observed is expected for metallic fcc Ni(111), but also for Ni_2O_3(200) and Ni_3C(113).

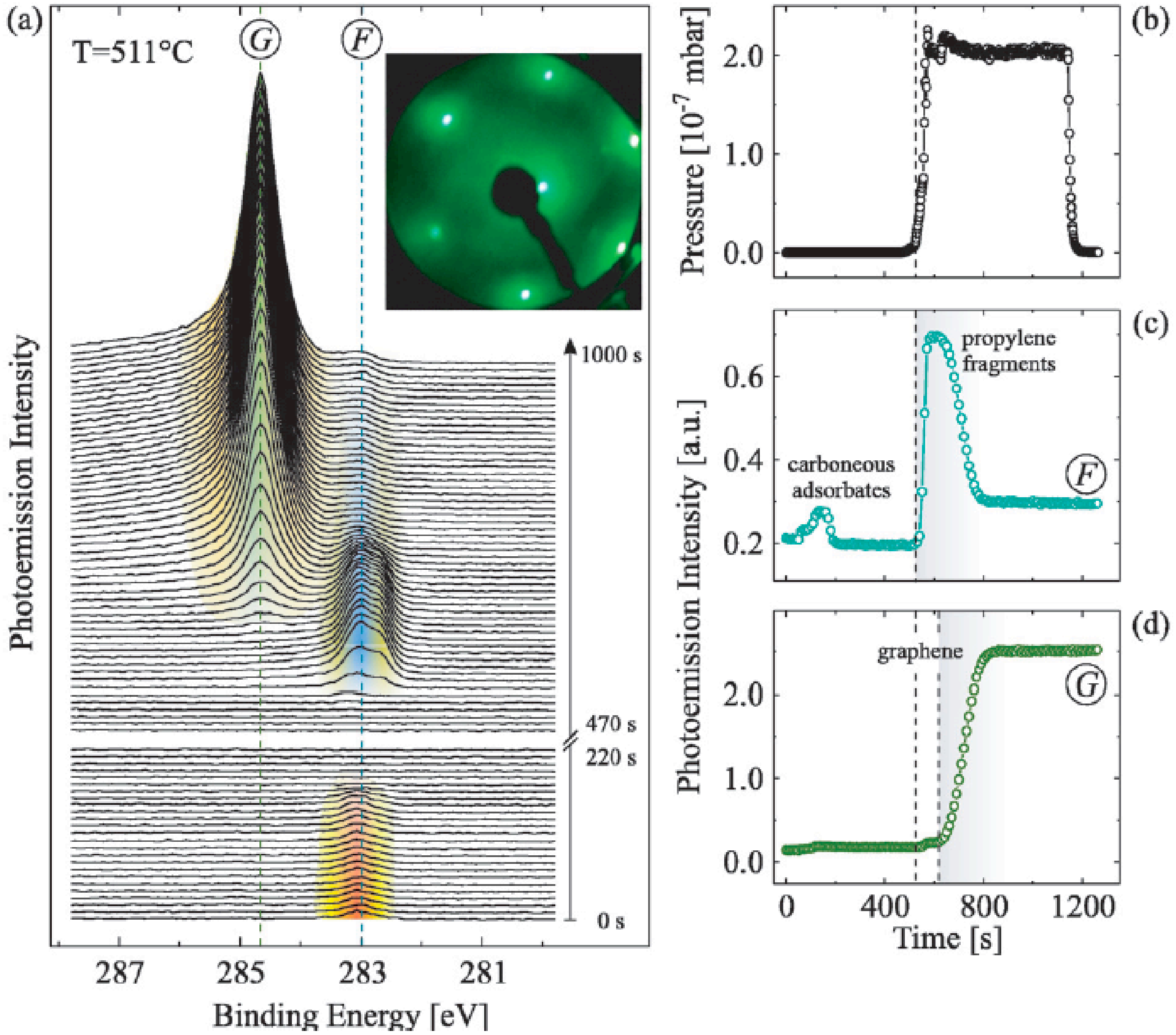
We have highlighted some of the progress made towards an atomistic CNT growth model by combining in-situ TEM and XPS. Selective acetylene chemisorption and the formation of a carbon-rich surface layer were observed on otherwise crystalline transition metal nano-particles. Structural selectivity is determined by the dynamic interplay between carbon network formation and catalyst particle deformation.

The catalyst is active in its metallic state; Fe and Ni films that were deliberately oxidised before annealing showed a lower/no nanotube yield on C_2H_2 exposure.



Graphene grown on Ni(111)

A. Gruneis et al., New J. Phys. 11 (2009) 073050

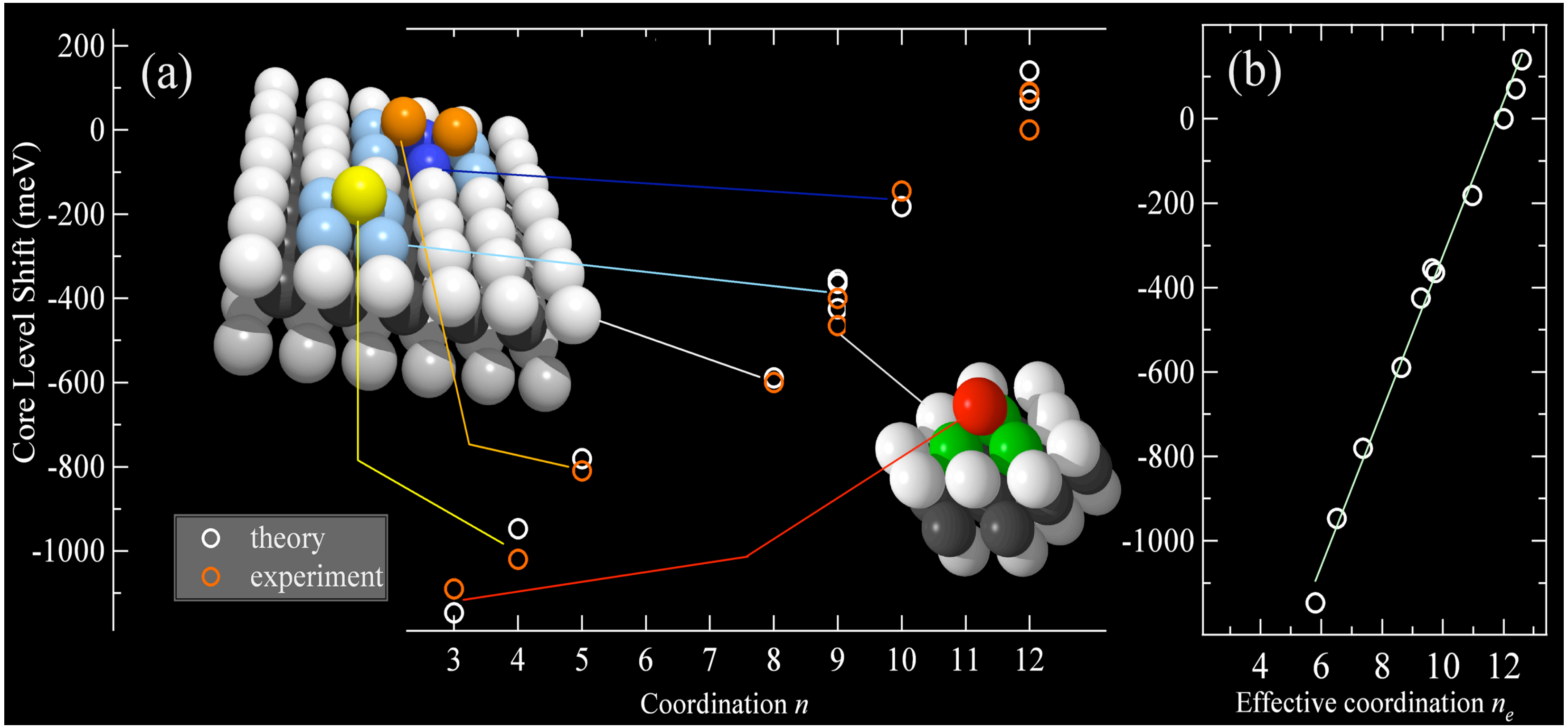


Highly under-coordinated atoms at Rh surfaces: interplay of strain and coordination effects on core level shift

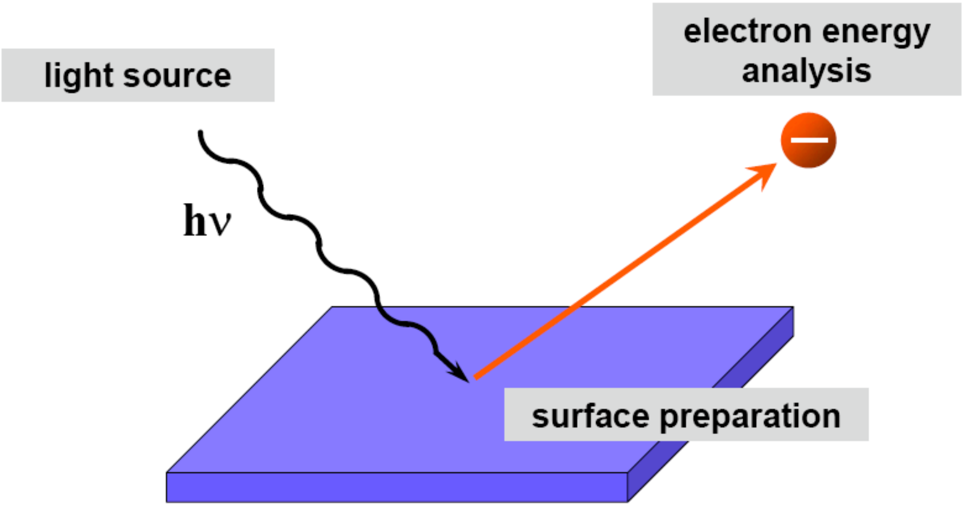
A. Baraldi, L. Bianchettin, E. Vesselli, S. de Gironcoli, S. Lizzit, L. Petaccia, G. Zampieri, G. Comelli and R. Rosei,
New J. Phys. **9** (2007) 143

There is a good agreement with theory when all the relaxation effect are taken into account (coordination number vs local bond strain)

The surface core level shift depends linearly with the effective coordination



Instrumentation and recent implementations

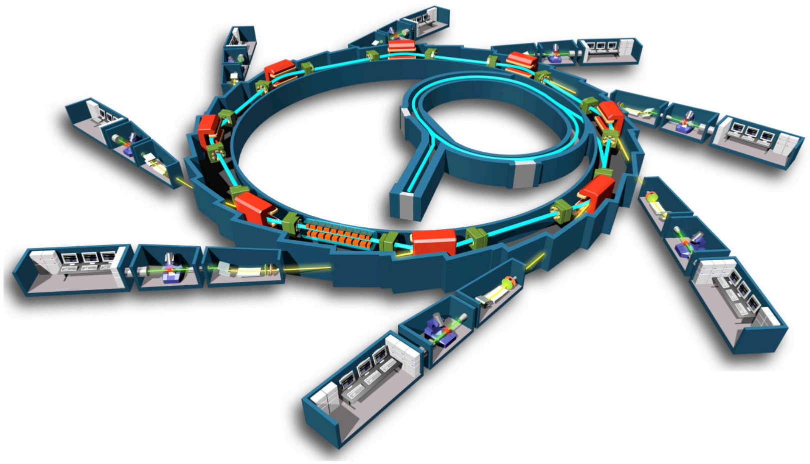


light source

electron energy analysis

hν

surface preparation

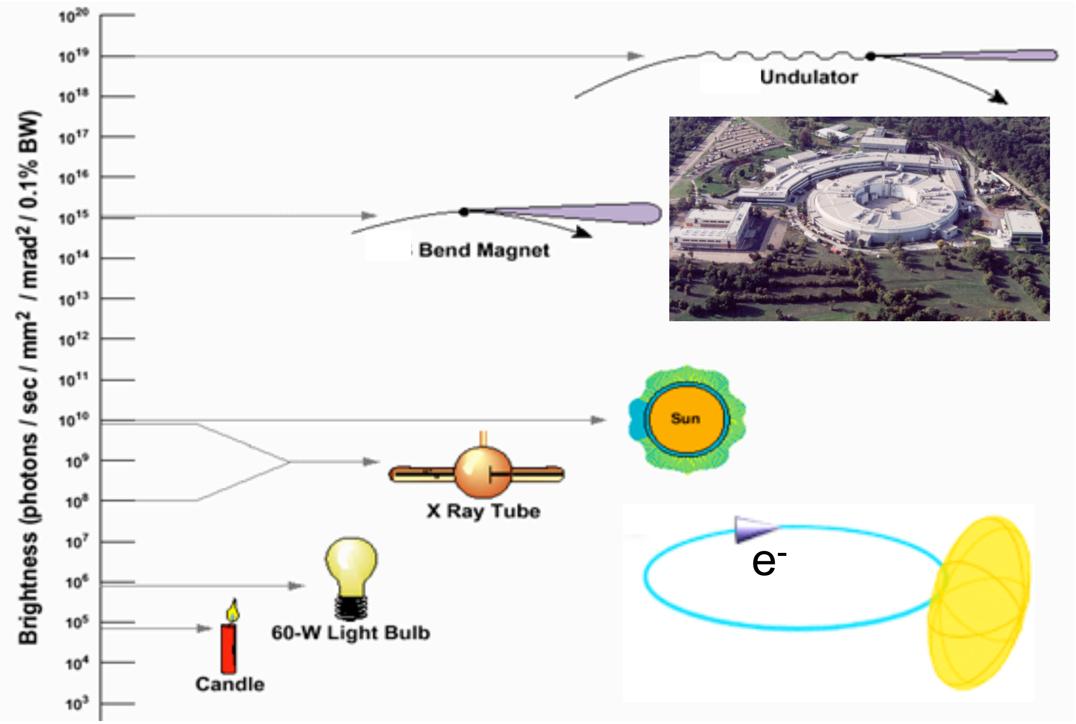


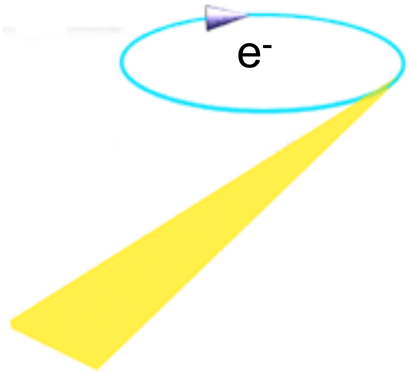
Laboratory sources:
- rare gas discharge lamps
- x-ray tubes

Synchrotron radiation:
- tunable, **hν = 10 eV…10 keV**
- polarized (linear and circular)
- brilliant
- temporal structure

More properties on the Synchrotron Light

1. **Intensity** – many orders of magnitude higher than a conventional lab. source: fast experiments allowed on small sample

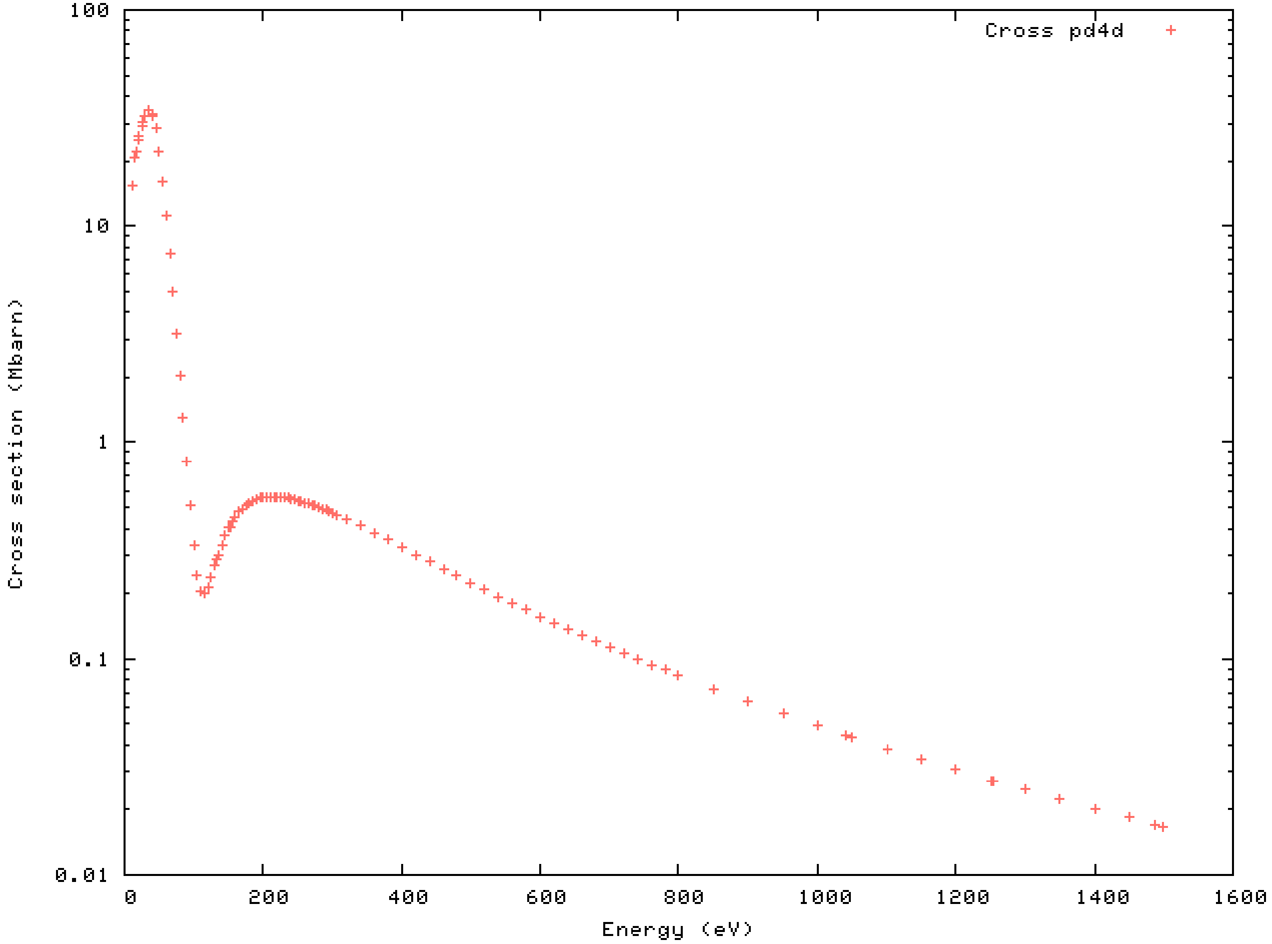




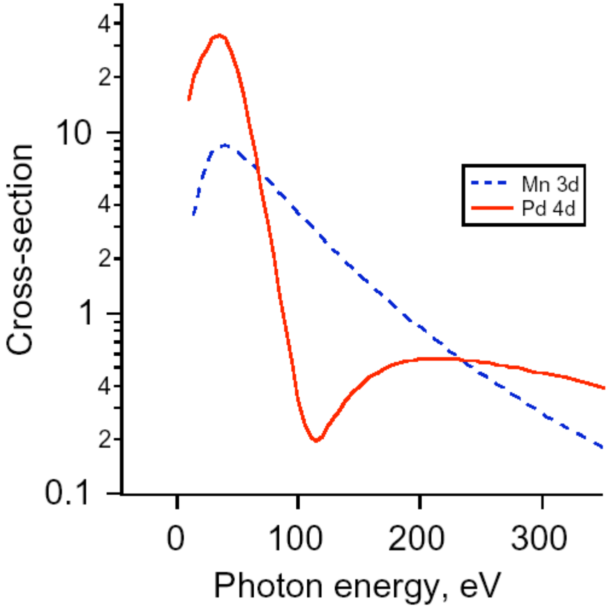
2. **Brightness and tunability** – Allow to focalize the beam up to nanometers
3. **Polarization** – all kinds of polarizations
4. **Pulsed time structure** – The light is produced by electron packets: the distance between the packets is the time scale

Change the photon energy to be more (or less) sensitive to one atomic element

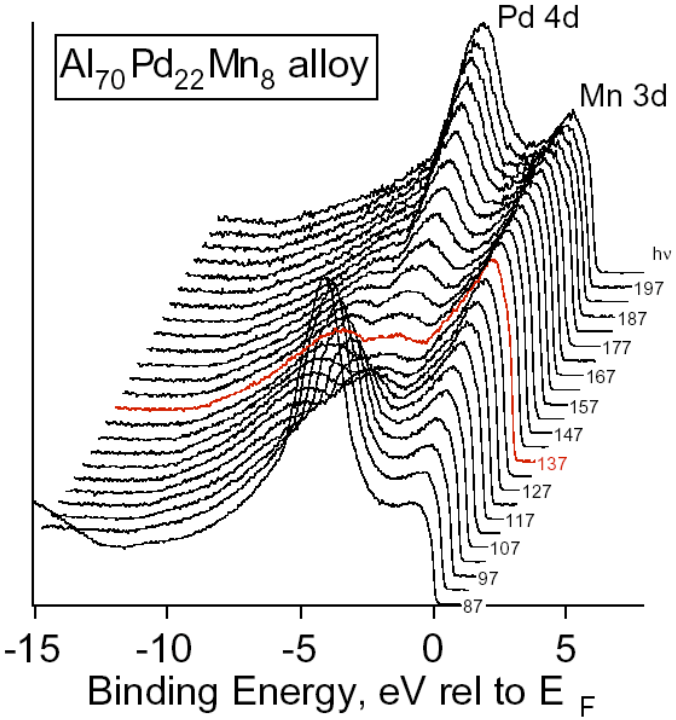
Photoionization Cross-Sections of Pd 4d



Calculation
J.J.Yeh



Expt.
Rotenberg et al



Gd@C_{82} resonant photoemission

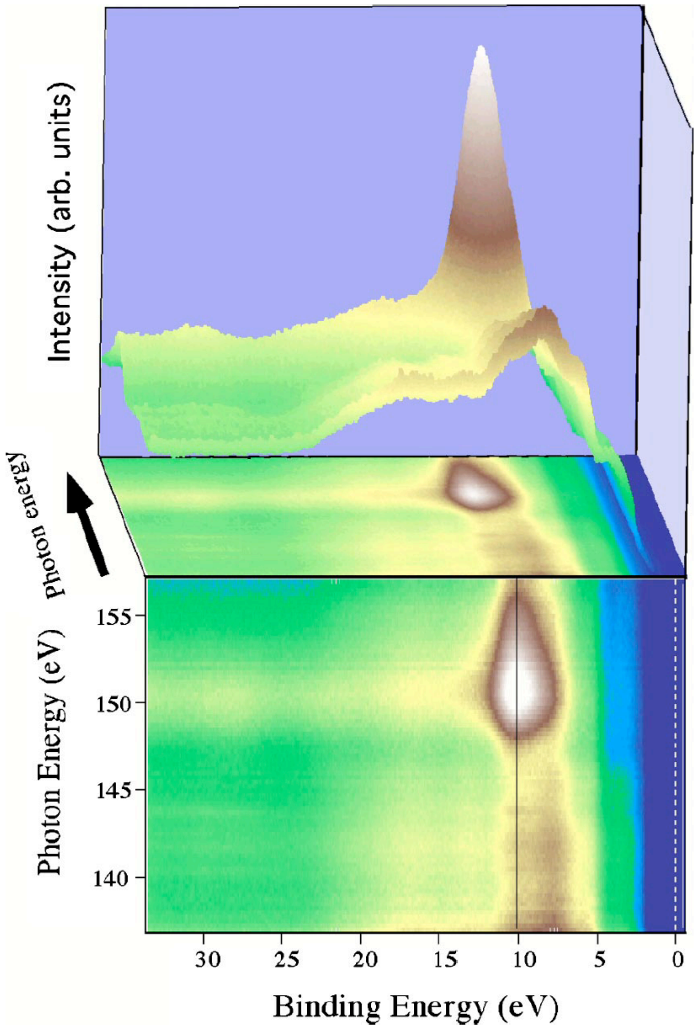
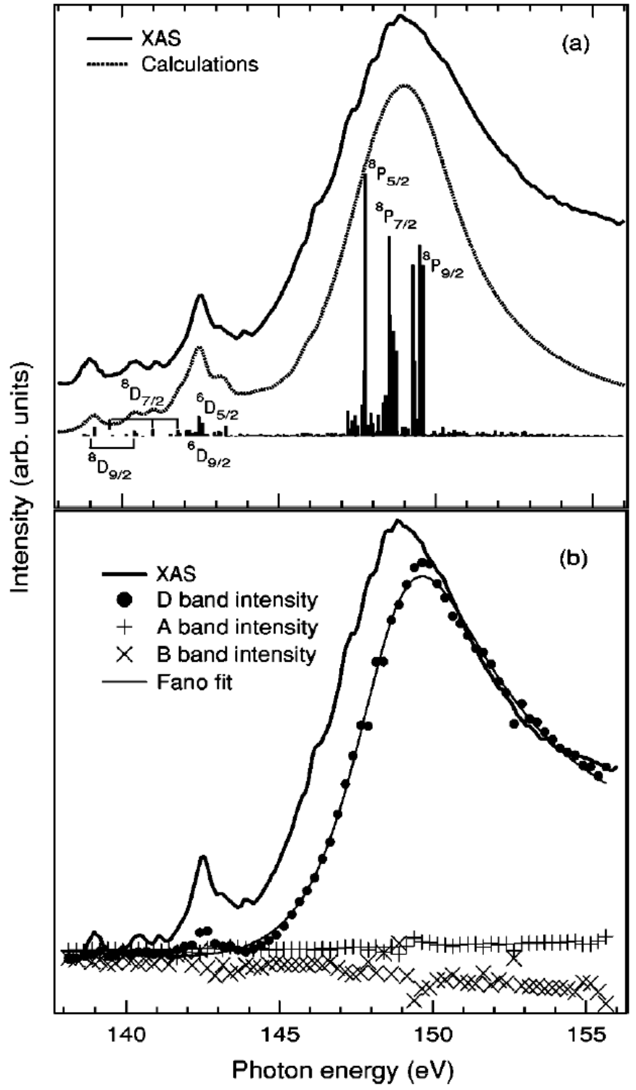
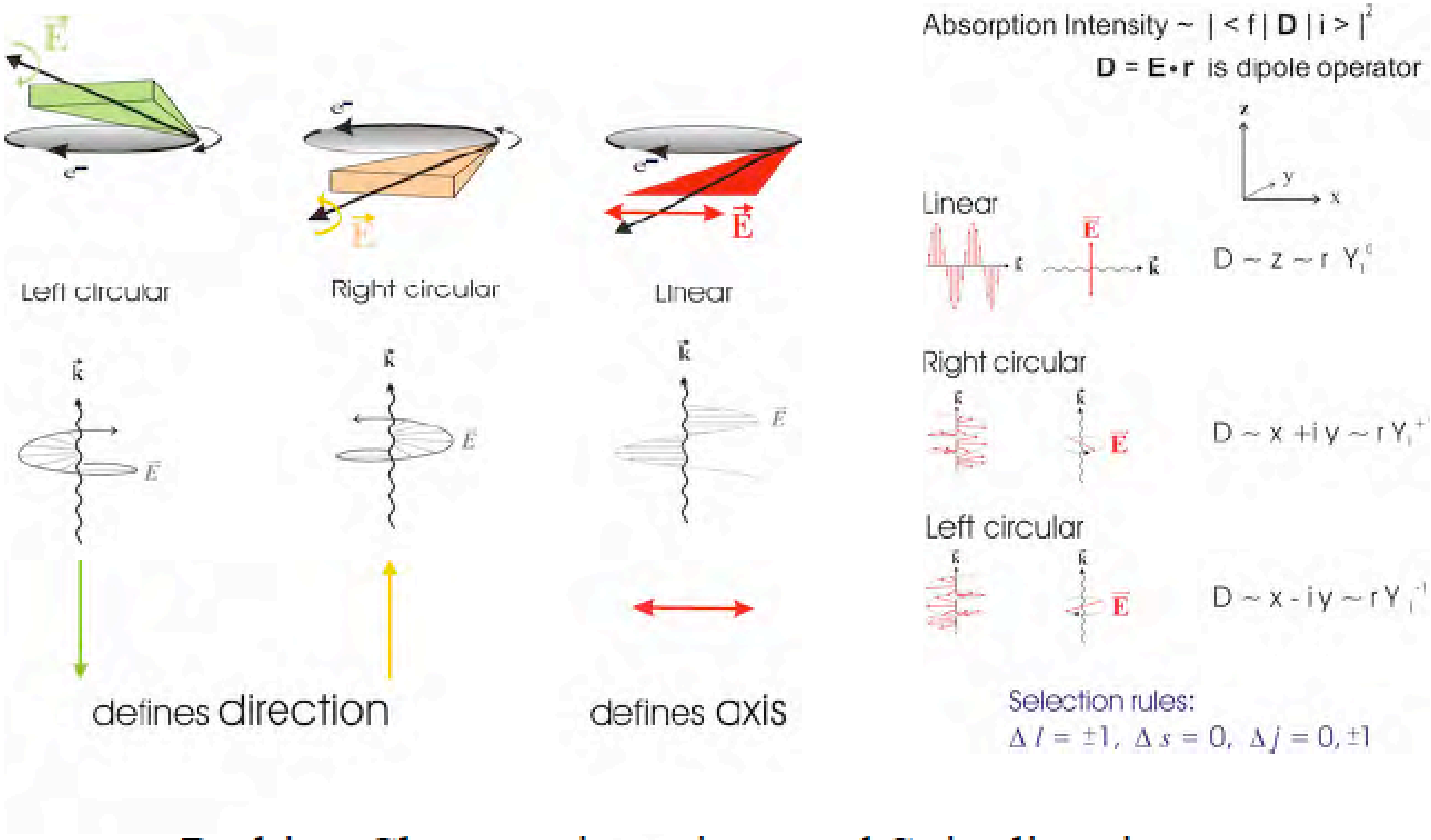


FIG. 3. (Color online) Resonant photoemission valence band spectra collected at the Gd $4d \rightarrow 4f$ edge.



Polarization Change



Absorption Intensity ~ $|\langle f|\mathbf{D}|i\rangle|^2$

$\mathbf{D} = \mathbf{E}\cdot\mathbf{r}$ is dipole operator

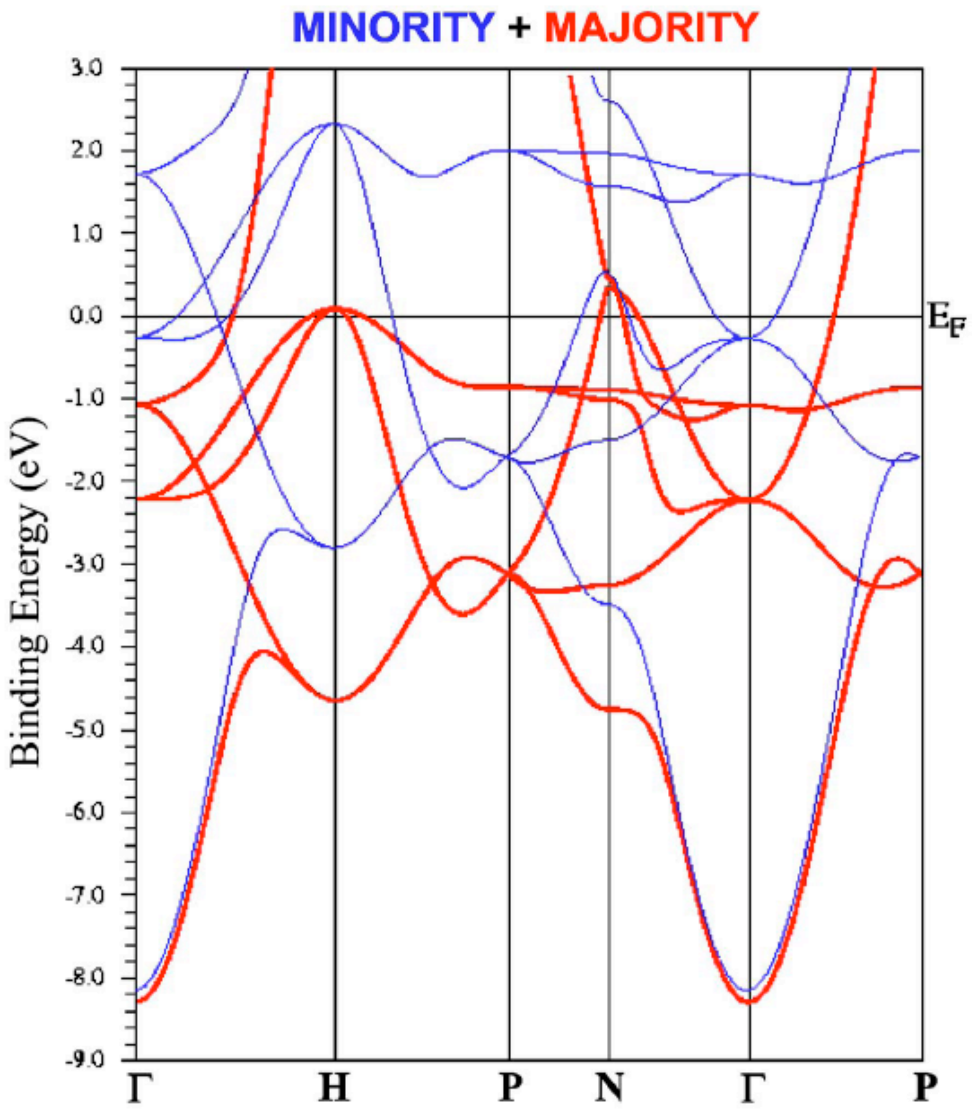
Linear: $D \sim z \sim r\,Y_1^0$

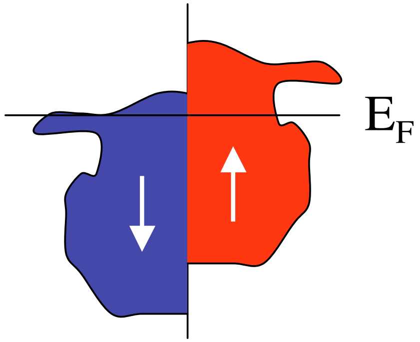
Right circular: $D \sim x + iy \sim r\,Y_1^{+1}$

Left circular: $D \sim x - iy \sim r\,Y_1^{-1}$

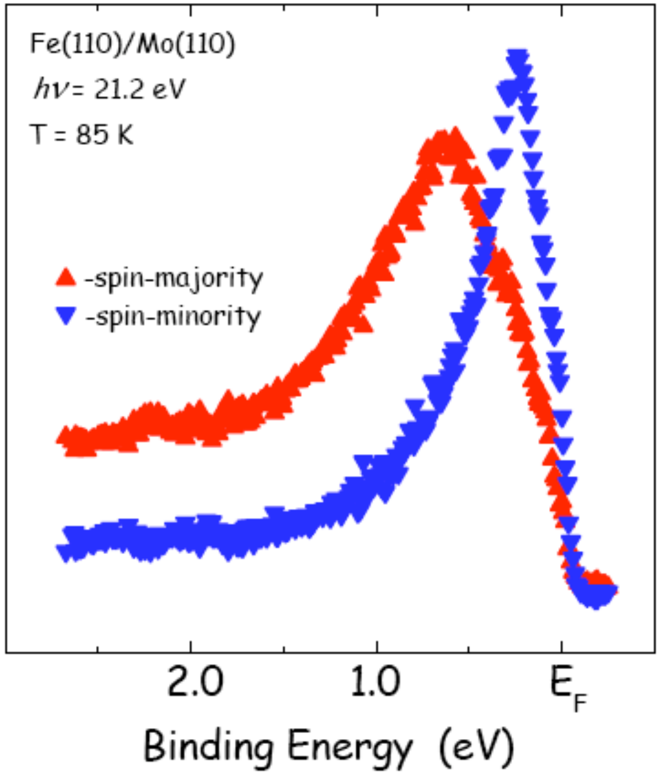
Selection rules:
$\Delta l = \pm 1,\ \Delta s = 0,\ \Delta j = 0, \pm 1$

Probing Charge orientations and Spin directions





"in-plane" polarization in ferromagnetic iron films



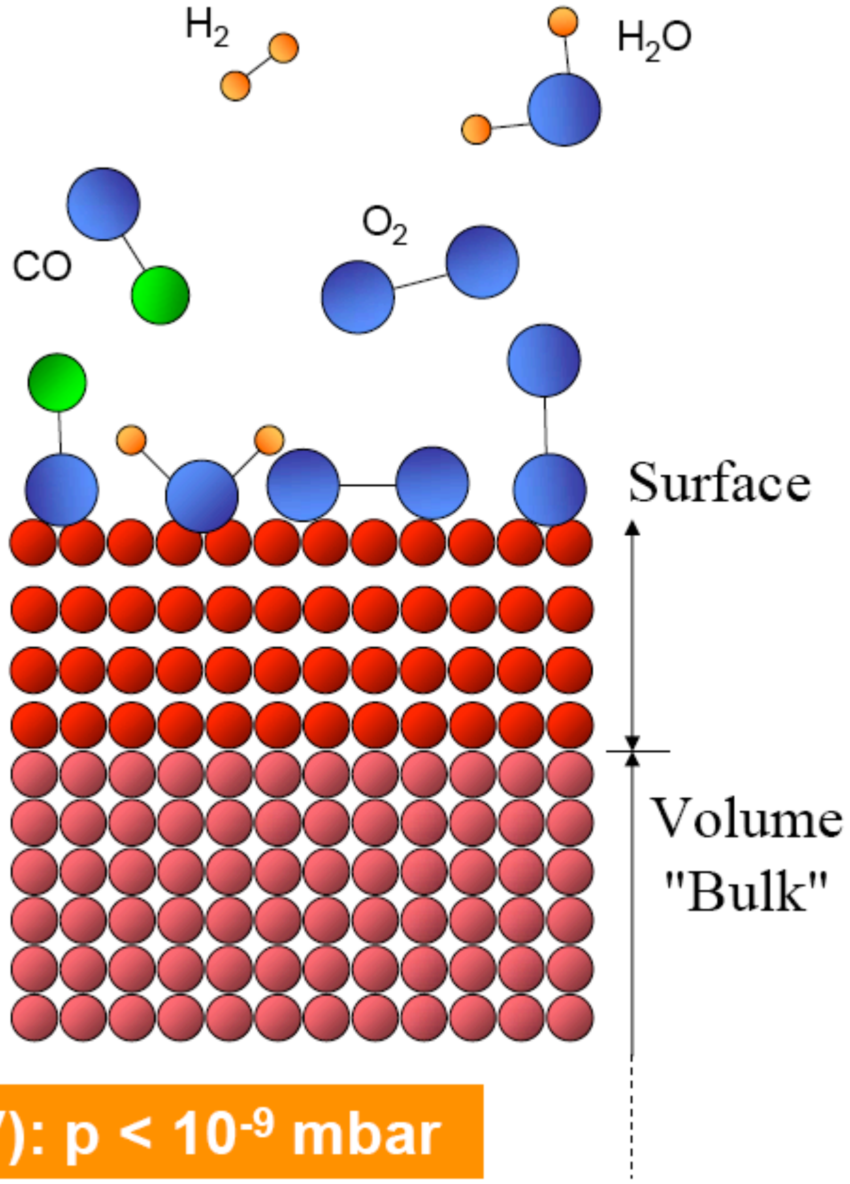
Surface preparation: good surface quality and UHV

Surface contamination:

lifetime of clean surface limited by adsorption of residual gas atoms and molecules !

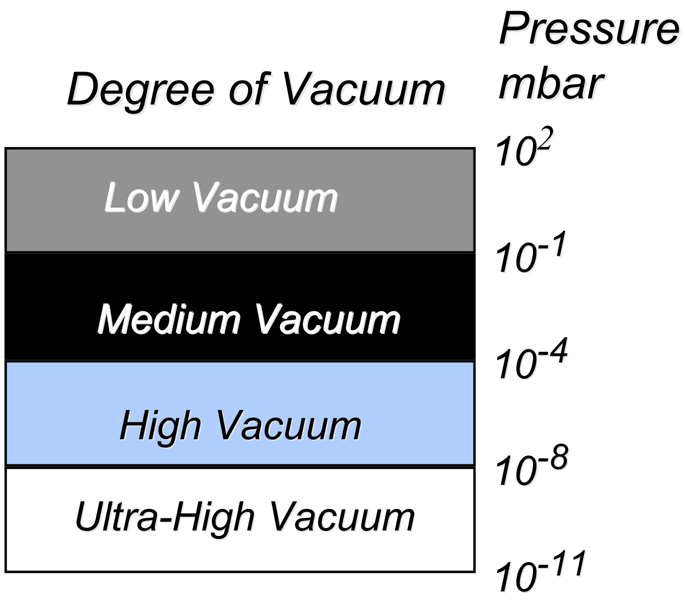
Time T_{ML} for monolayer formation at given vacuum pressure:

pressure	T_{ML}
1000 mbar	6×10^{-9} s
1 mbar	6×10^{-6} s
10^{-3} mbar	6×10^{-3} s
10^{-6} mbar	6 s
10^{-9} mbar	6×10^{3} s = 1.5 hours



⇒ need ultrahigh vacuum (UHV): $p < 10^{-9}$ mbar

Surface preparation: good surface quality and UHV



- *Remove adsorbed gases from the sample.*
- *Eliminate adsorption of contaminants on the sample.*
- *Prevent arcing and high voltage breakdown.*
- *Increase the mean free path for electrons, ions and photons.*

Angle resolved photoemission: definitions and the non-interacting electrons

Part I

Papers: S. Hüfner et al., J. Electron Spectroscopy Rel. Phenom. 100 (1999)
A. Damascelli et al., Rev. Modern Phys. (2005)
F. Reinert et al., New J. Phys. 7 (2005)
X.J. Zhou et al., J. Electron Spectroscopy Rel. Phenom. 126 (2002)

Thanks to: A. Damascelli, Z.X. Shen, R. Claessen, Ph. Hofmann and E. Rotemberg from whose I have taken slides and figures

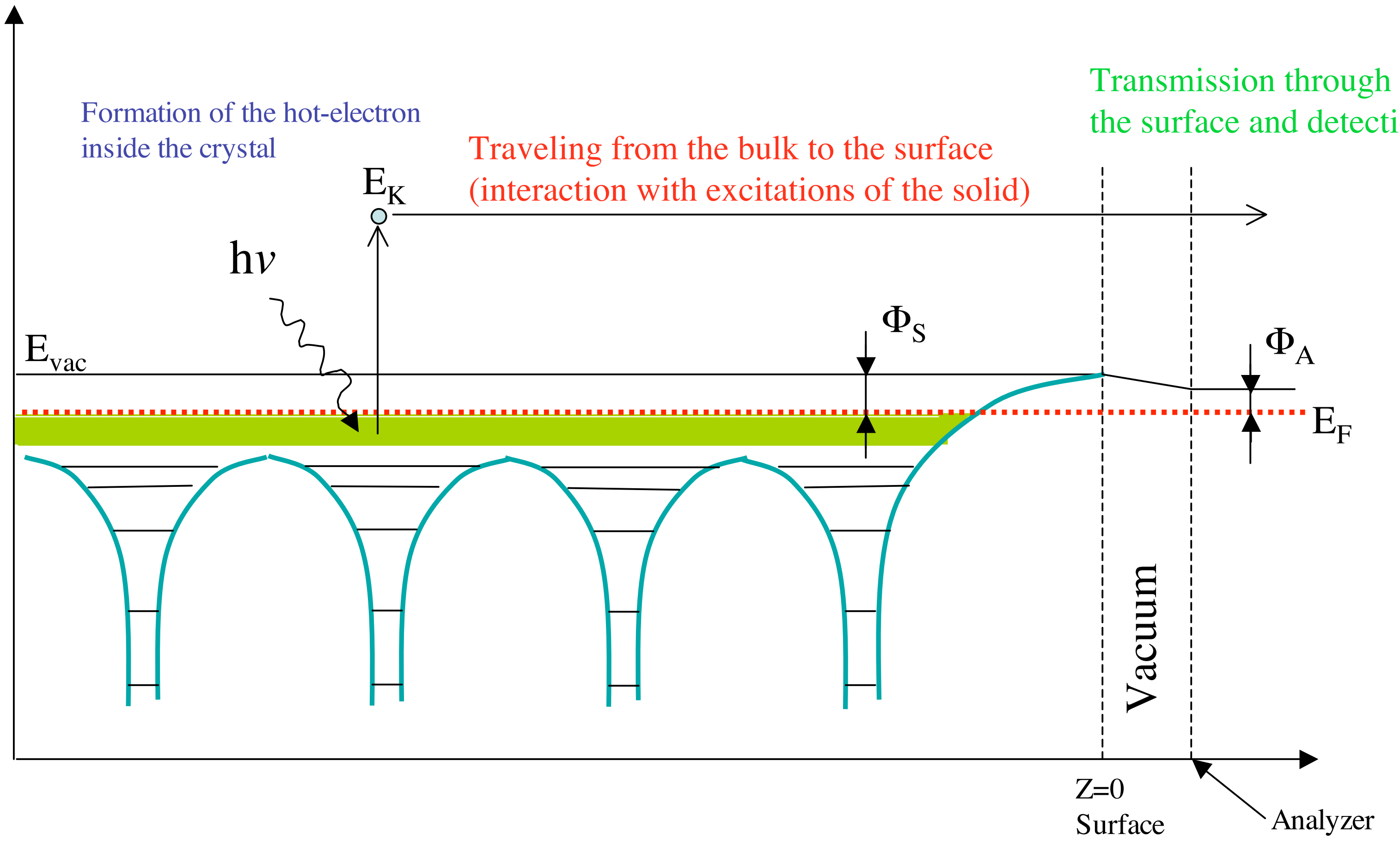
Outline

- General introduction
- The three-step model
- Bulk and surface states
- The non-interacting electrons
- Fermi surface for the non-interacting electrons
- Density of states and effective mass m*
- Instrumentation and recent implementation
- The one-step model

An approximate (but useful) model: Three-step model

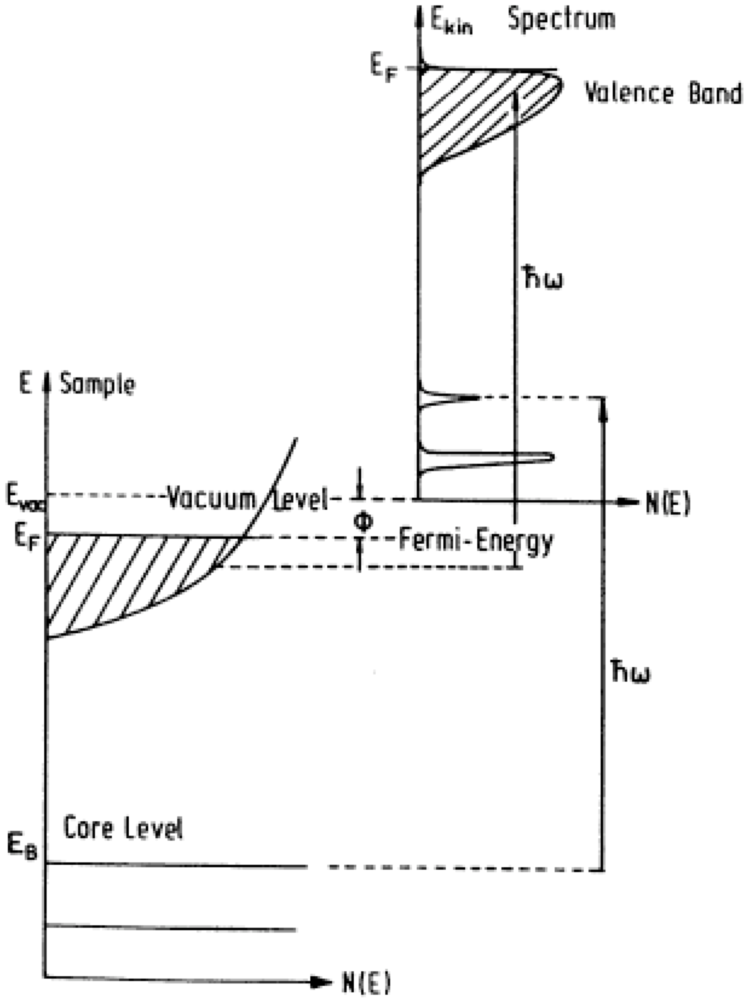
Energy conservation: $E_k = h\nu - |E_B| - \phi_A$

Note: when sample and analyzer are in electrical contact, the electron kinetic energy does not depend on the sample work function. The Fermi level position depends exclusively on the analyzer work function and therefore it is an absolute reference, valid also for insulators, which obviously do not exhibit a metallic Fermi edge.



1

Photoexcitation process



Energy conservation

$$E_{kin} = \hbar\omega - \Phi - |E_B|$$

Measured Kinetic Energy

Measureed Photon Energy

Measured Work Function

Electron Binding Energy

①

Photoexcitation process: Momentum conservation

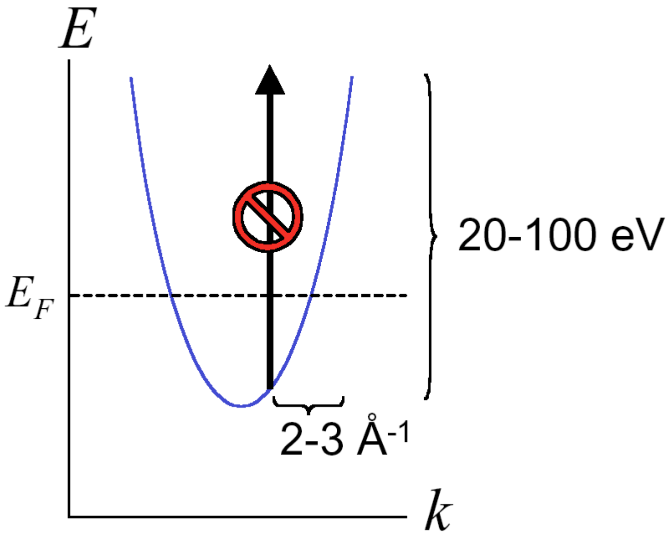
Photon Momentum $p = \hbar \mathrm{q} = h/\lambda$

Photon Energy $E = h\nu = hc/\lambda$

Typical photon wavenumber

$$\mathrm{q} = 2\pi \frac{E}{hc} = 2\pi \frac{E\ [\mathrm{eV}]}{12400\ [\mathrm{eV\text{-}\mathring{A}}]}$$

$$= .01 \text{ to } .05\ \mathring{A}^{-1} \quad (\text{for } E = 20 \text{ to } 100 \text{ eV})$$

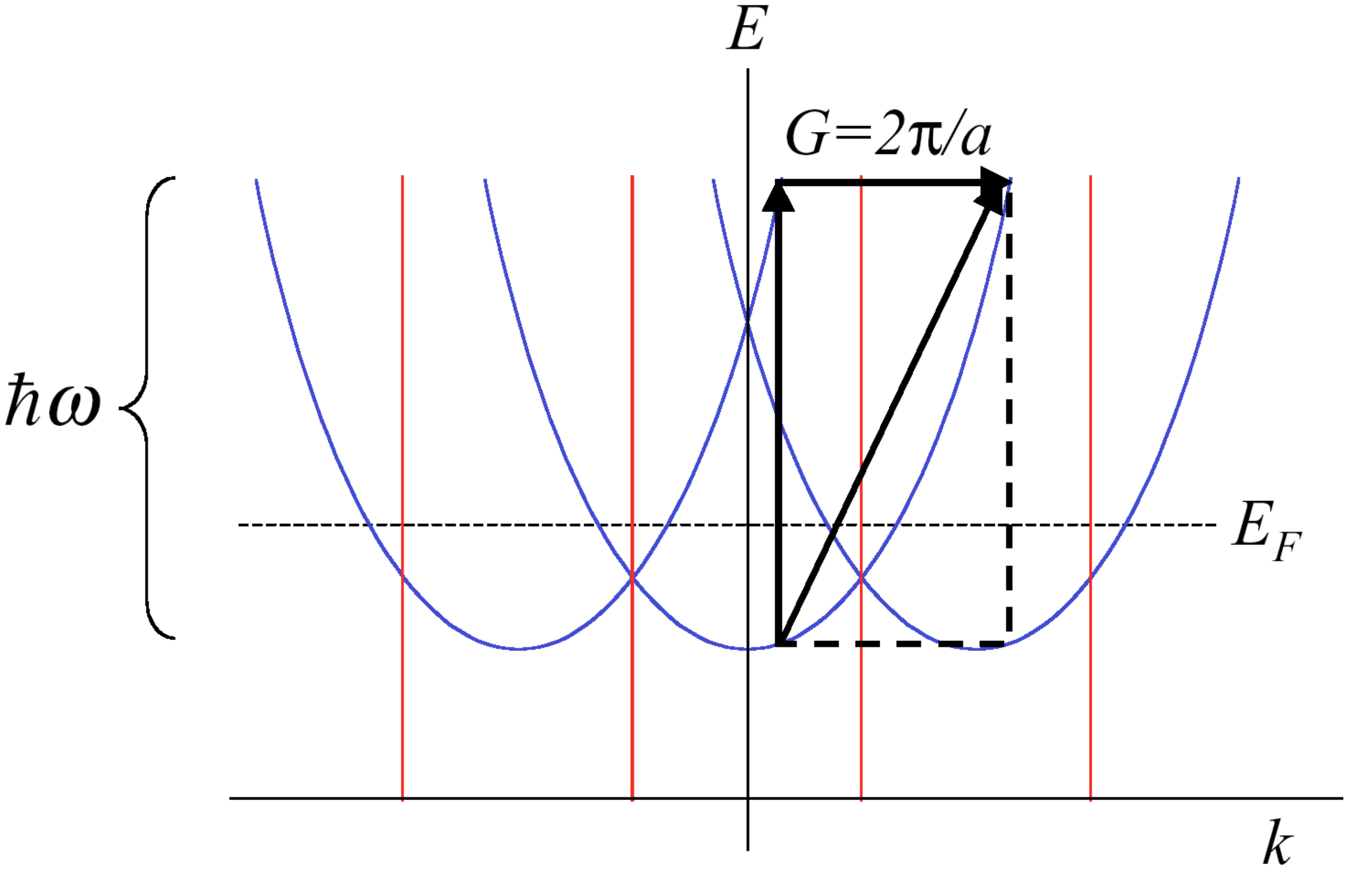


- **The photons impart very little momentum in the photoemission process, i.e. vertical transitions**

- **Therefore photon-stimulated transitions are not allowed for free electrons (energy and momentum conservation laws cannot be satisfied at the same time).**

In order to satisfy both energy and momentum conservation:

- **The role of crystal translational symmetry is crucial**
  - **i.e. no photoemission is allowed from truly free electrons.**

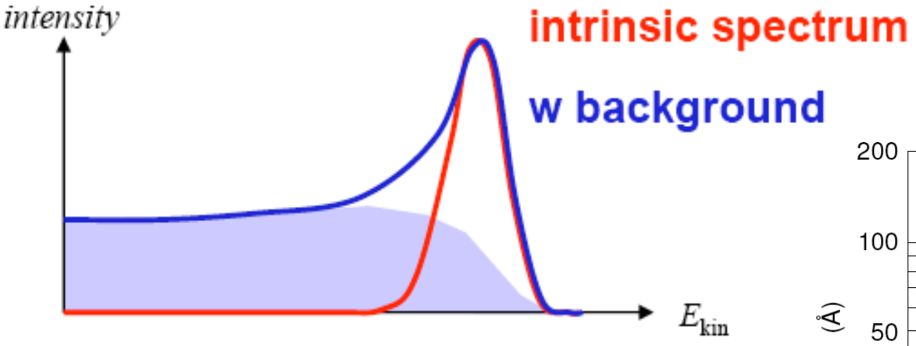


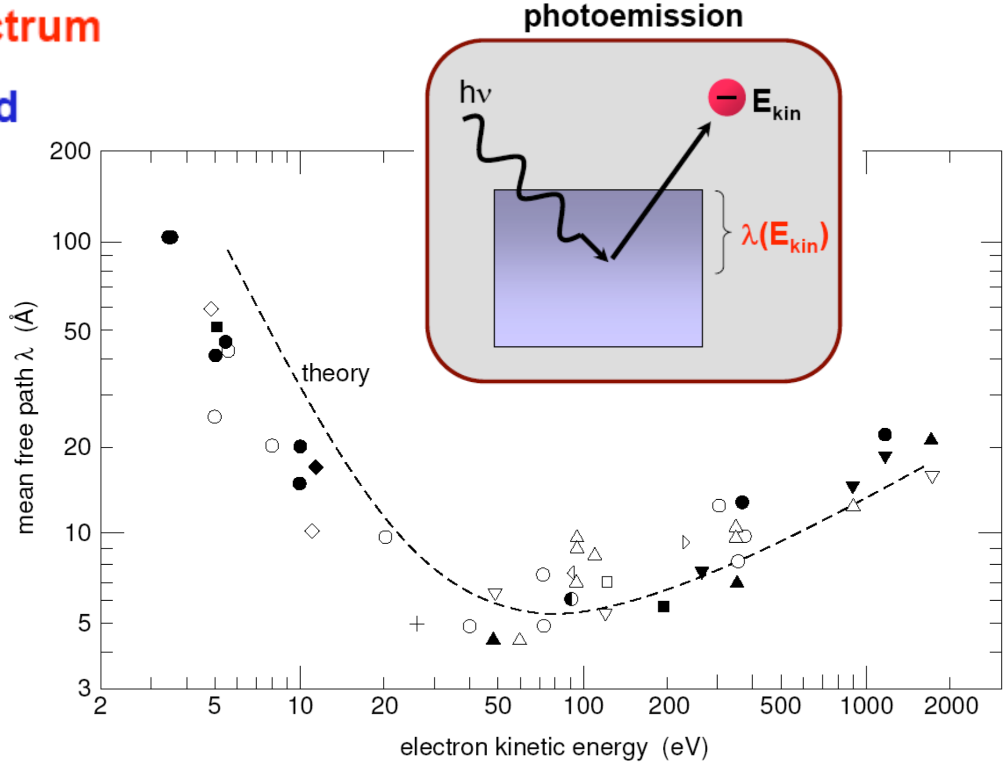
$$E_f=E_i+h\nu \quad \& \quad \mathbf{k}_f=\mathbf{k}_i+\mathbf{G}$$

2 Transport to the surface

Inelastic scattering of the hot-electrons (electron-electron, electron-phonon, impurities etc…) produces a loss of electrons and a loss of energy

- **Valence band measurements are sensitive to only within the first few atomic layers of the material**
- **Spectral peaks have a “loss tail” towards lower kinetic energies**

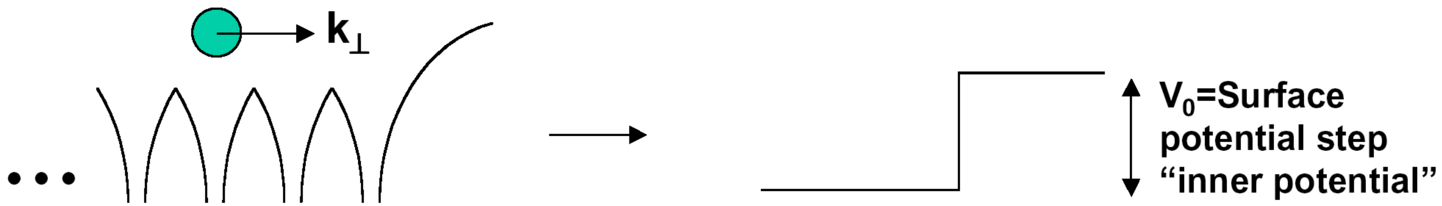




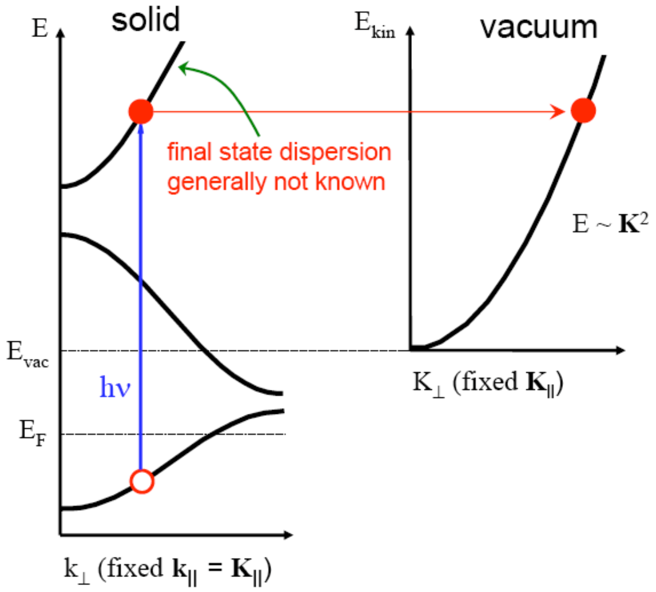
3 Transmission through the surface

At the surface the crystal symmetry is conserved in the surface plane but is broken perpendicularly to the surface: the component of the electron momentum parallel to the surface plane ($k_{//}$) is conserved, but $k_{\perp}$ is not

The potential barrier at the surface slows the electron in the direction normal to the surface.



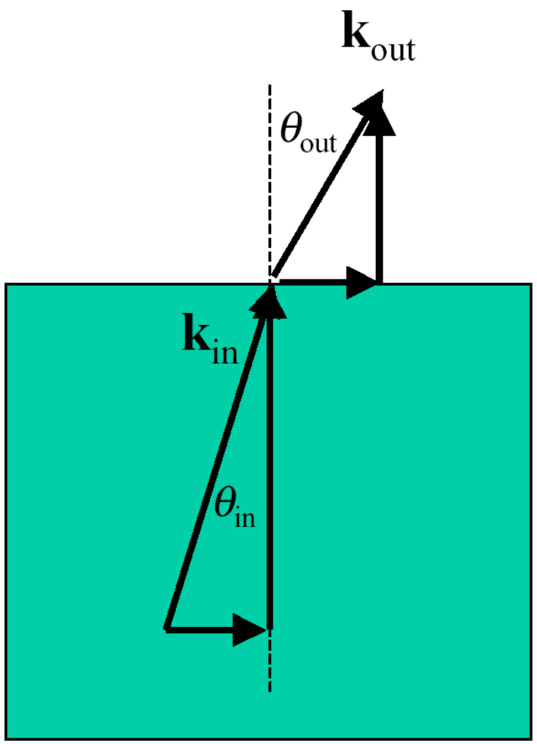
V_0=Surface potential step "inner potential"



final state dispersion generally not known

We match the free-electron parabolas inside and outside the solid to obtain the wavevector k inside the solid

At the surface the crystal symmetry is conserved in the surface plane but is broken perpendicularly to the surface: the component of the electron momentum parallel to the surface plane ($k_{//}$) is conserved, but $k_{\perp}$ is not



Kinematic relations

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

$$k_{out,\|} = k_{in,\|} \equiv k_\|$$

“Snell’s Law”

$$k_\| = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

Critical angle for emission from bulk states

$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$

First important results:

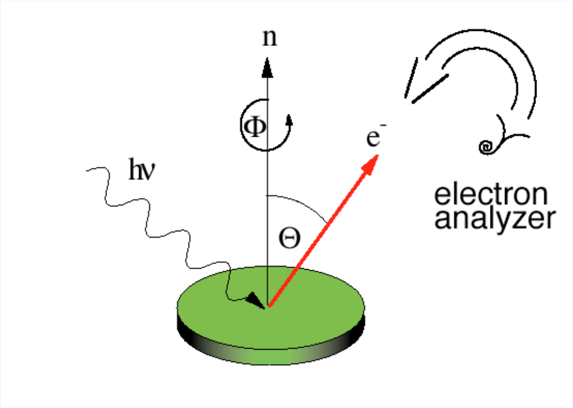
$E_{kin}=h\nu-|E_B|-\phi_A$

$$k_{//} = \sqrt{\frac{2m^* E_k}{\hbar^2}}\sin\theta_{out} \approx 0.512\sqrt{E_k}\sin\theta_{out}$$

Band mapping is therefore completely determined for 1D or 2D systems and surface states for which $k_{//}$ is a good quantum number

Anyway, as we will see later, $k_{\perp}$ is uniquely determined once E_{kin} and $k_{//}$ are fixed

Angle-resolved photoemission from (quasi) 2D systems: a simple picture



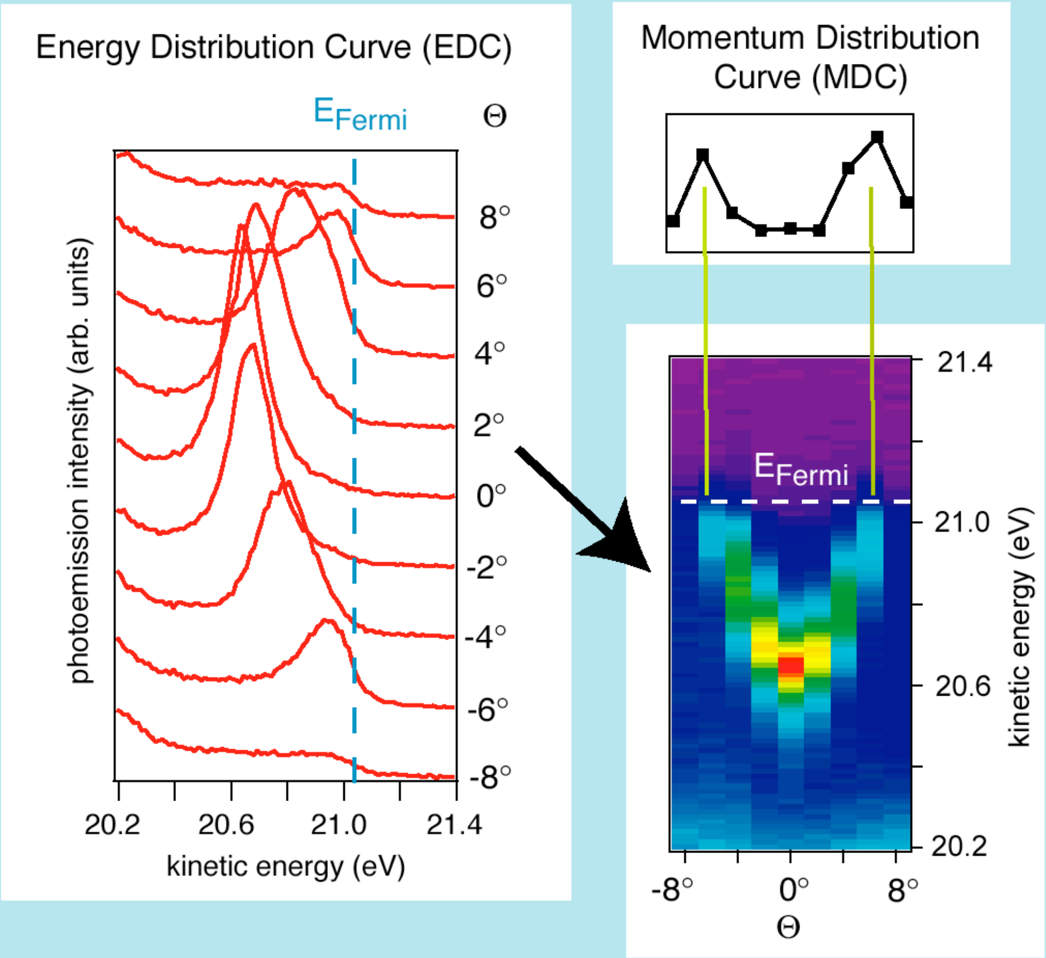
- measure E_{kin}, Θ, Φ.

$$k_x = \sqrt{\frac{2m}{\hbar^2}} \sin\Theta \cos\Phi \sqrt{E_{kin}}$$

$$k_y = \sqrt{\frac{2m}{\hbar^2}} \sin\Theta \sin\Phi \sqrt{E_{kin}}$$

obtain $E_{bin}(k_x,k_y)$, i.e. the occupied band structure

Example: Cu(111) surface state

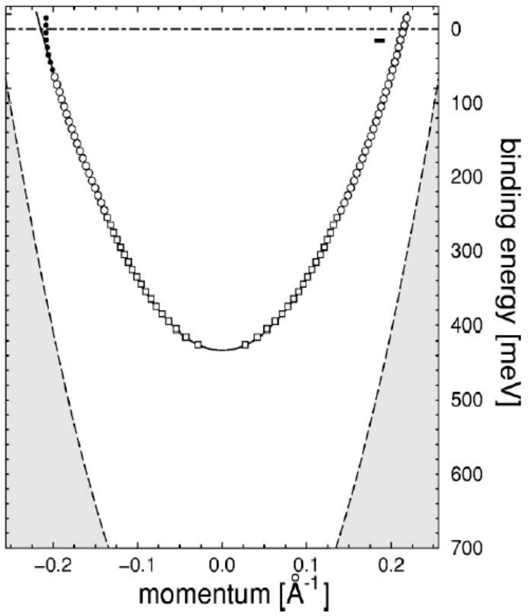


Courtesy of Ph. Hofmann

Shockley Surface States of Nobel Metal (111) Surfaces

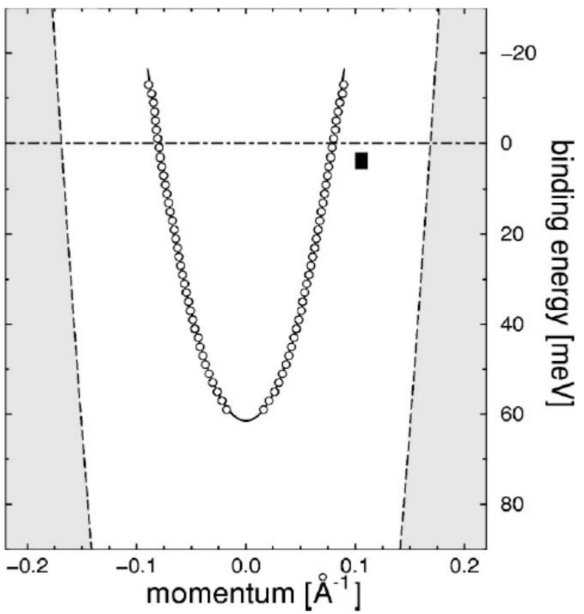
Cu(111)

Z=29



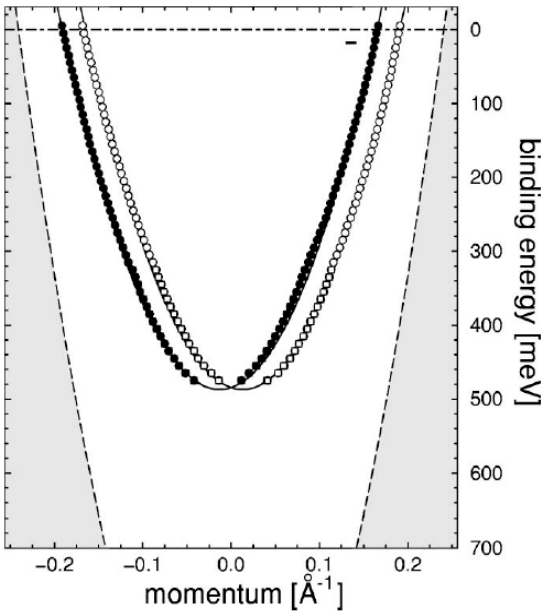
Ag(111)

Z=47



Au(111)

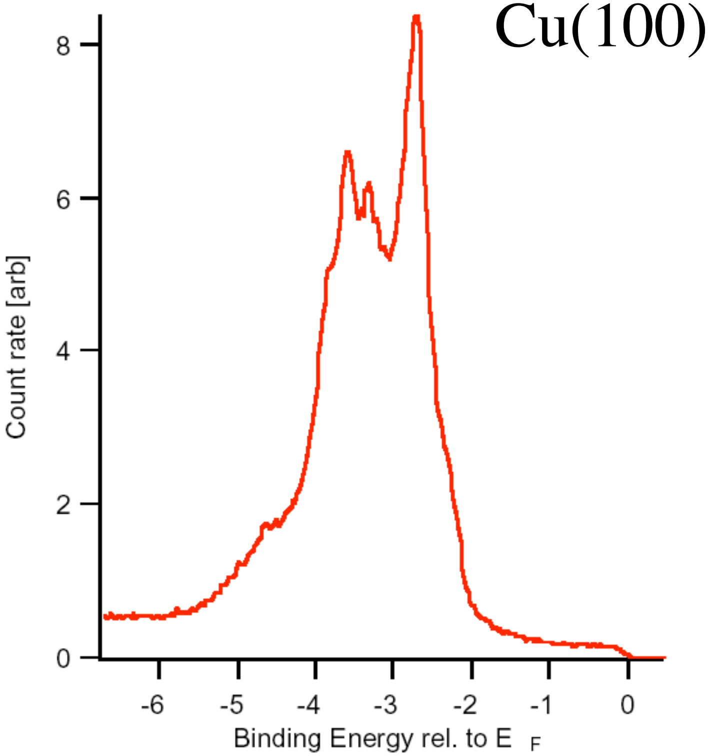
Z=79

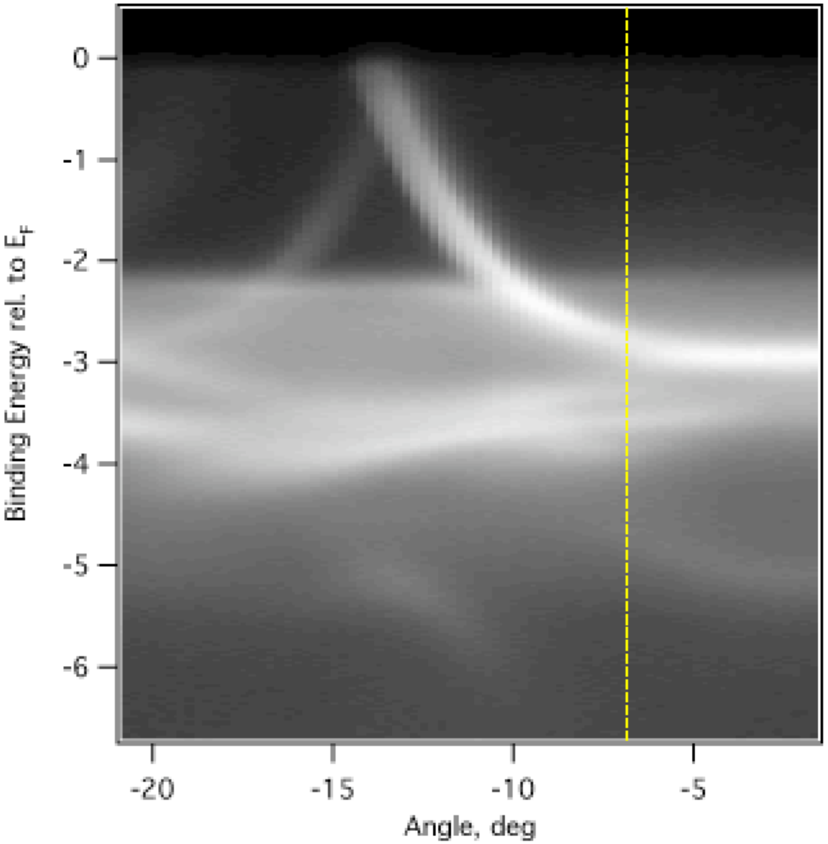


Two parabolas: spin-orbit splitting

PES Experiment, Reinert, Nicolay, Ehm, and Hüfner, PRB 63, 115415 (2001)

How a photoemission spectrum looks like in general?

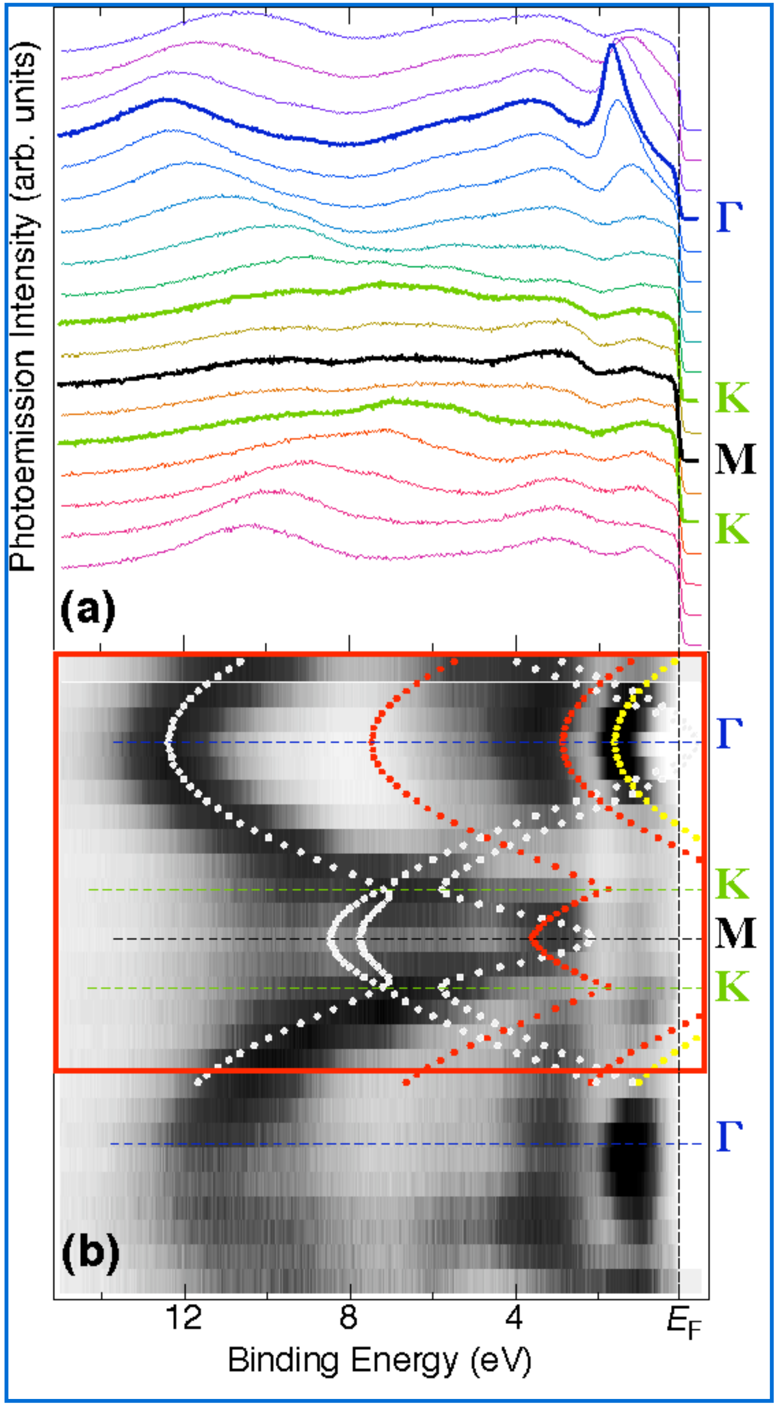


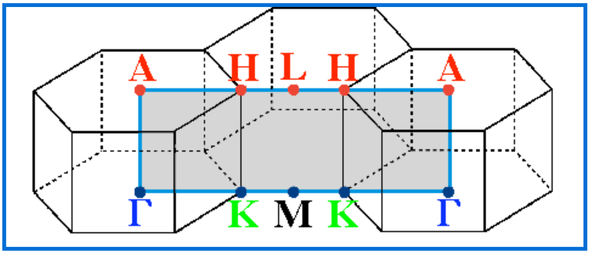


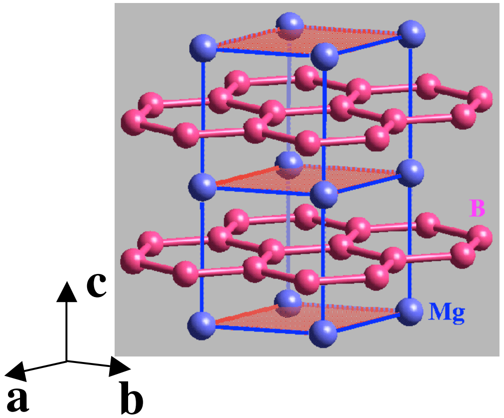
A spectrum at a single polar angle

Accumulate spectra as the angle is scanned

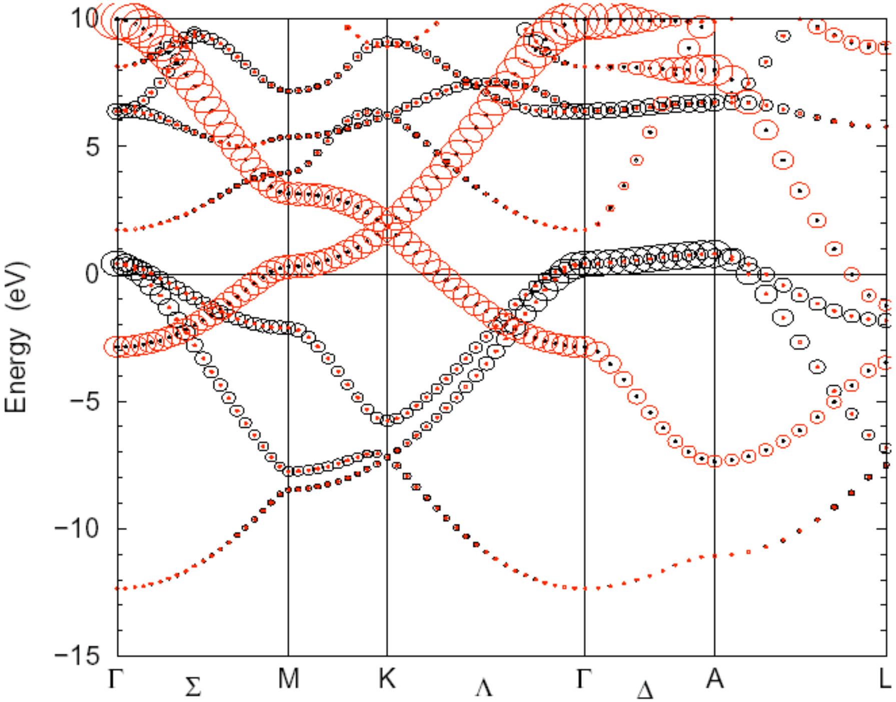
Bulk or surface states? Why bulk bands are quite sharp anyway?







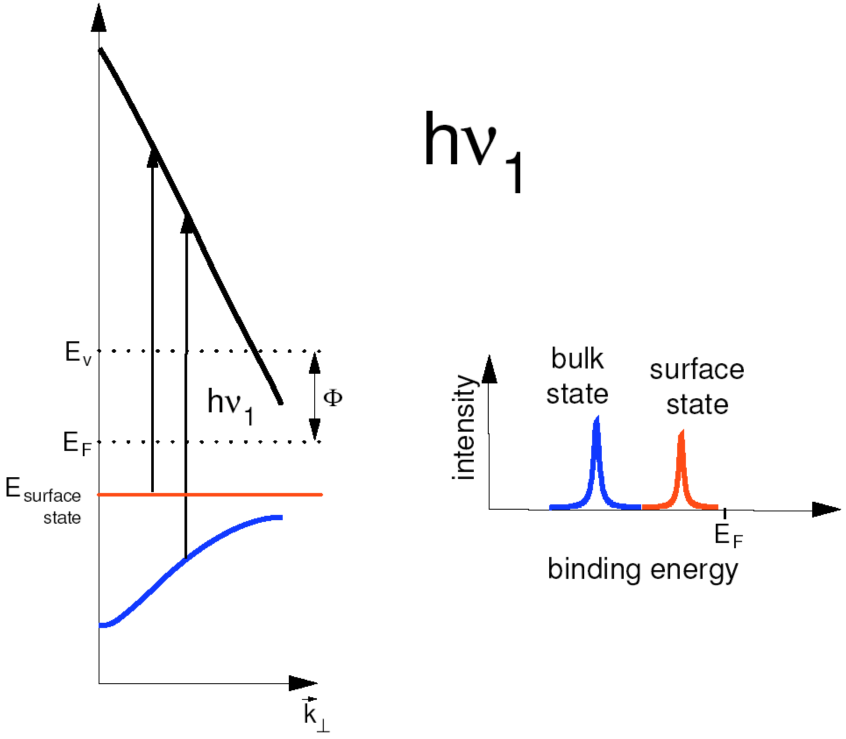
MgB_2

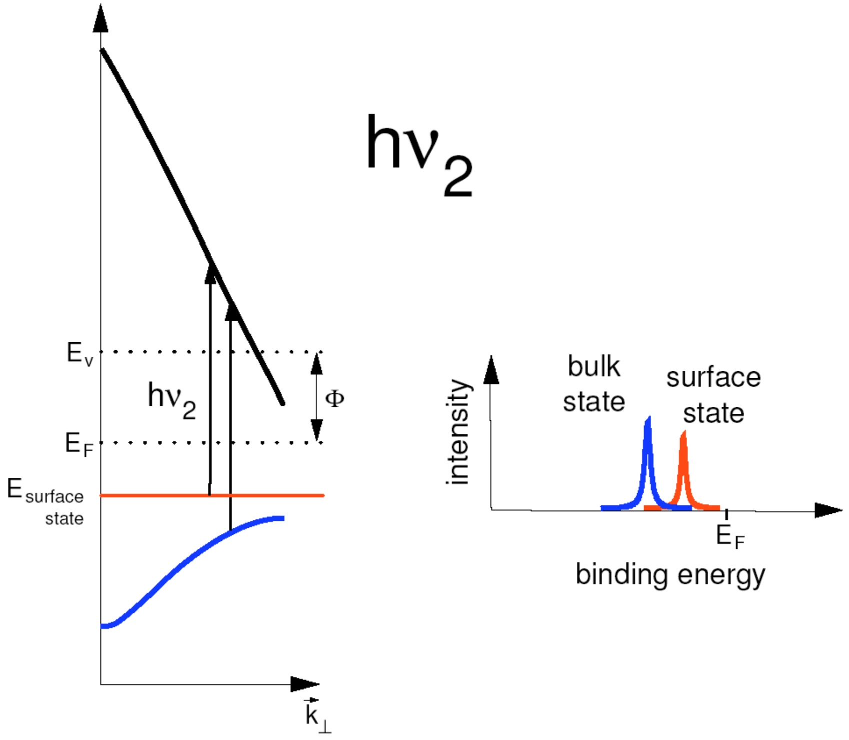


Photon energy: 105eV (ΔE≈50meV)
in-plane dispersion along Γ– K – M– K – Γ

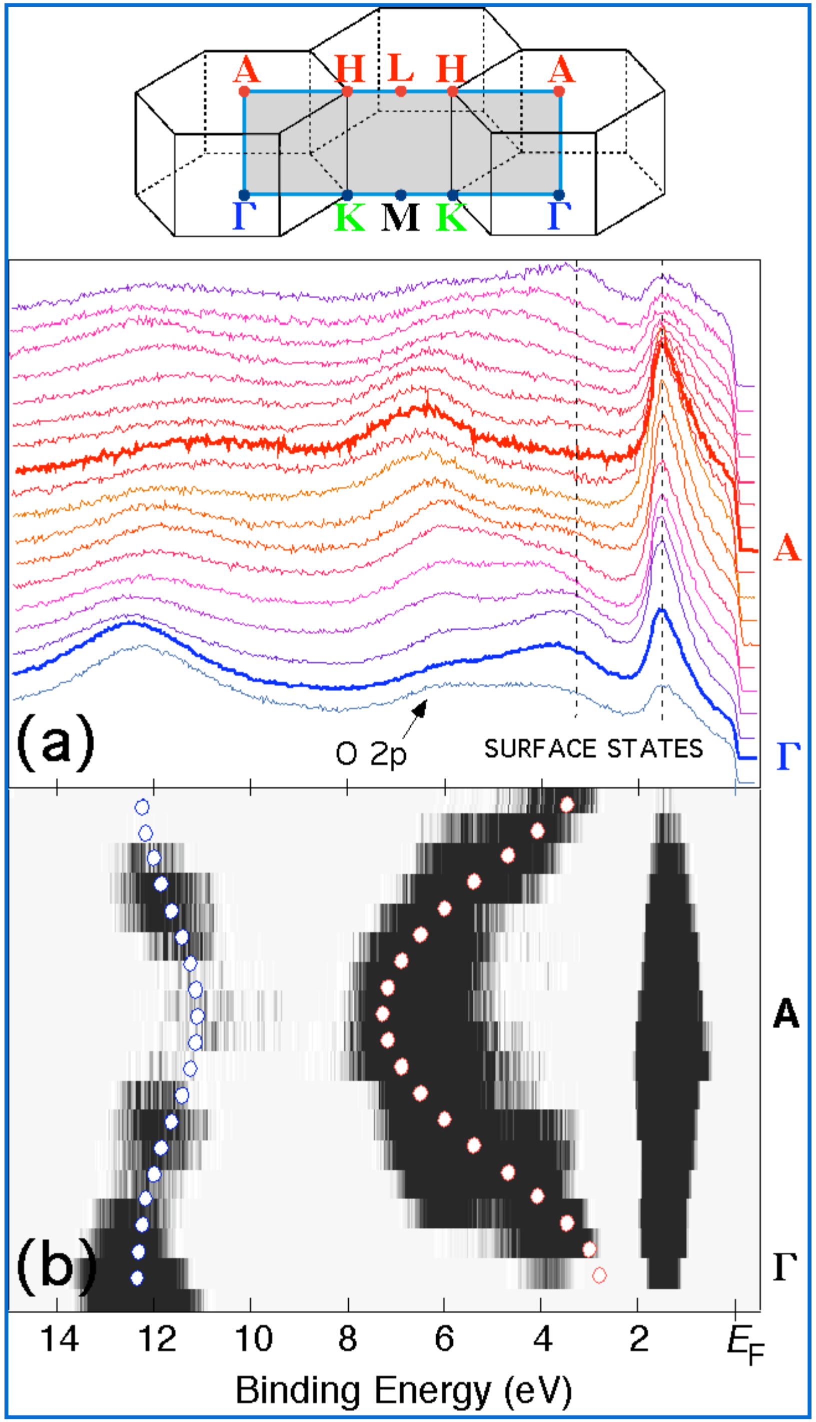
How we can recognize surface states from bulk bands?

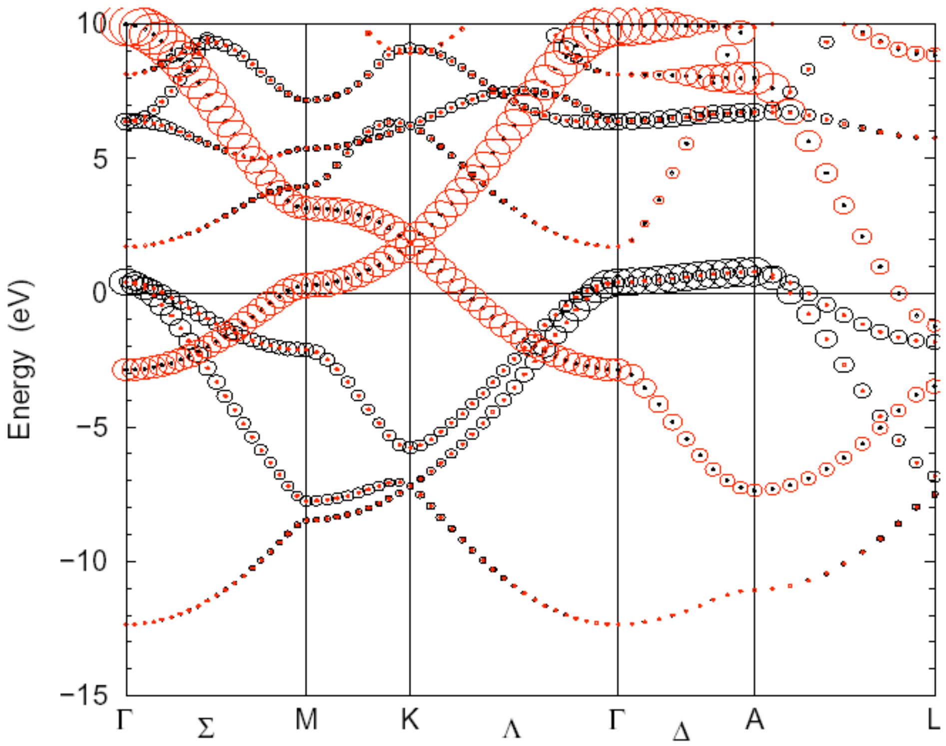
Simple: fix $\mathbf{k}_{//}$ and change $\mathbf{k}_{\perp}$. Bulk states should have dispersion, surface states should not.





Easiest way: fix $\mathbf{k}_{//}=0$ ($\underline{\Gamma}$, normal emission) and change the photon energy





I.I.Mazin V.P.Antropov, Physica C **385**, 49 (2003)

Γ– A direction

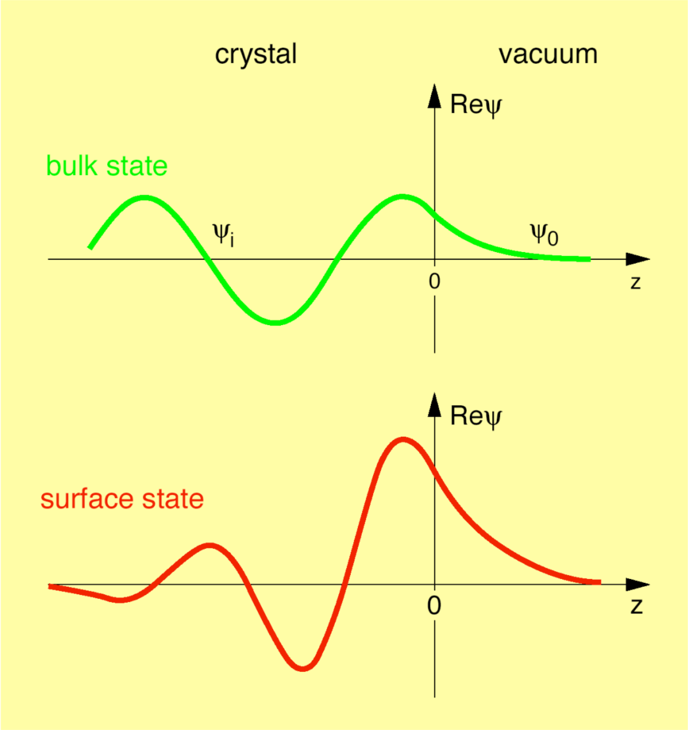
Normal emission geometry

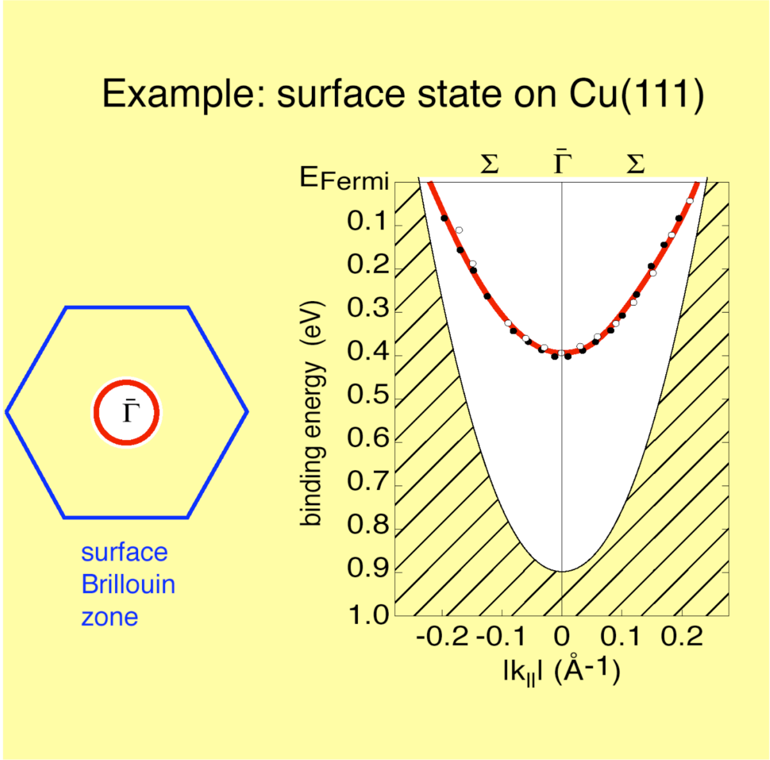
Photon energy: 95 eV - 185 eV (ΔE≈50meV)

No dispersive peak at 1.65 eV:
Mg terminated $MgB_2(0001)$ surface state

Weak no dispersive peak at 3.2 eV:
B terminated $MgB_2(0001)$ surface state
(B terminated domains)

Electronic surface states: a simple picture




Example: surface state on Cu(111)

- new solutions of the Schrödinger equation at the surface
- exponential decay in bulk and vacuum
- described by two-dimensional wave number $k_{||}$

Bulk wave functions crossing a surface: the decay into the vacuum

Consider the Bloch wave in the bulk $\psi_k(r) = u(r)e^{ikr}$ (k and r are vectors)

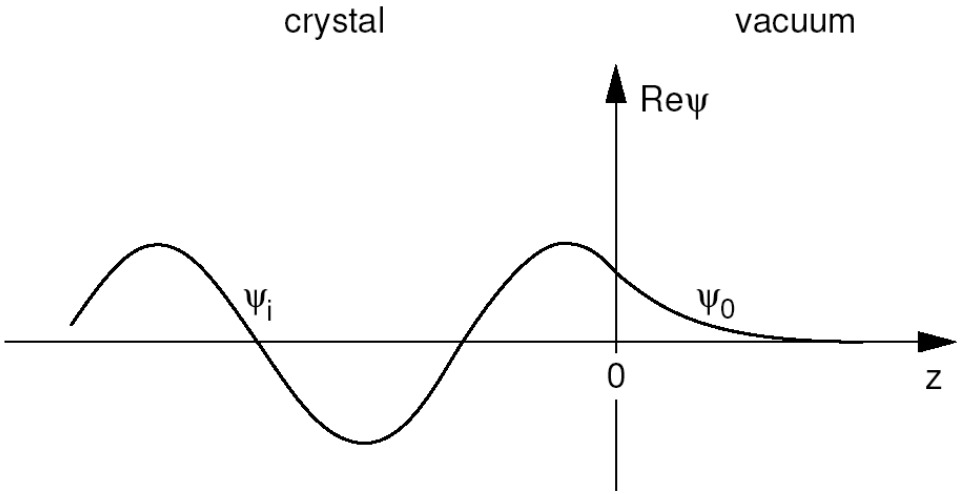
In the mathematical derivation of the Bloch theorem, nothing requires k to be a real number (**k** is real only in the approx. of an infinite crystal: Born-von Karman boundary conditions)**.** In general **k** can be a complex number, so there are solution also in the form:

$$\psi_k(r) = [u(r)e^{i\,\mathrm{Re}(k)\,r}]e^{-\,\mathrm{Im}(k)\,r}$$ (remember k and r are vectors)

This wave function grows without limit in the direction of **k** and decays exponentially in the direction opposite to **k.**

$$\psi_k(r) = [u(r)e^{i\,\mathrm{Re}(k)r}]e^{-\mathrm{Im}(k)r}$$

Since inside the crystal the charge density is always finite and periodic, this solution has no relevance, but it is relevant by crossing the surface because the charge density goes to zero in the vacuum: **for a bulk state we have to match the periodic wave inside the crystal with and exponential decay into the vacuum**



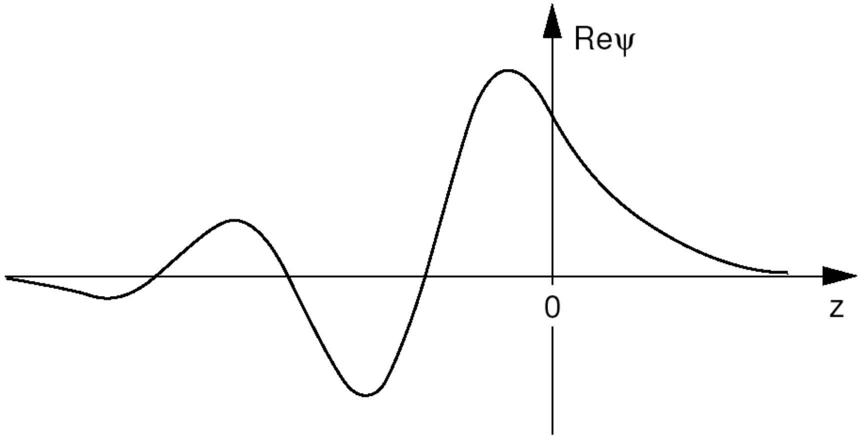
The form of the surface wave functions

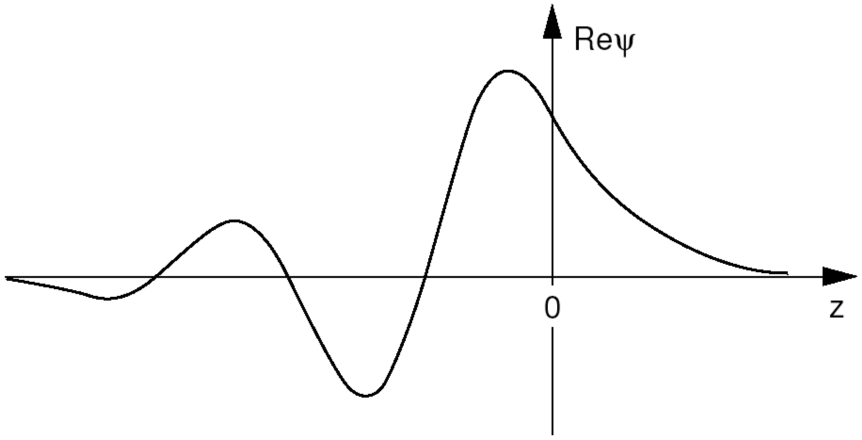
The wave functions at the surface do obey to the crystal symmetry in the surface plane only, but not perpendicularly because in this direction the translational invariance (periodicity) is lost (vacuum on one side, bulk crystal on the other).

The surface state wave function inside the crystal should be in the form:

$$\psi_k(r) = [u(r_{//})e^{ik_{//}r_{//}}e^{i\,\mathrm{Re}(q)z}]e^{-\mathrm{Im}(q)z}$$

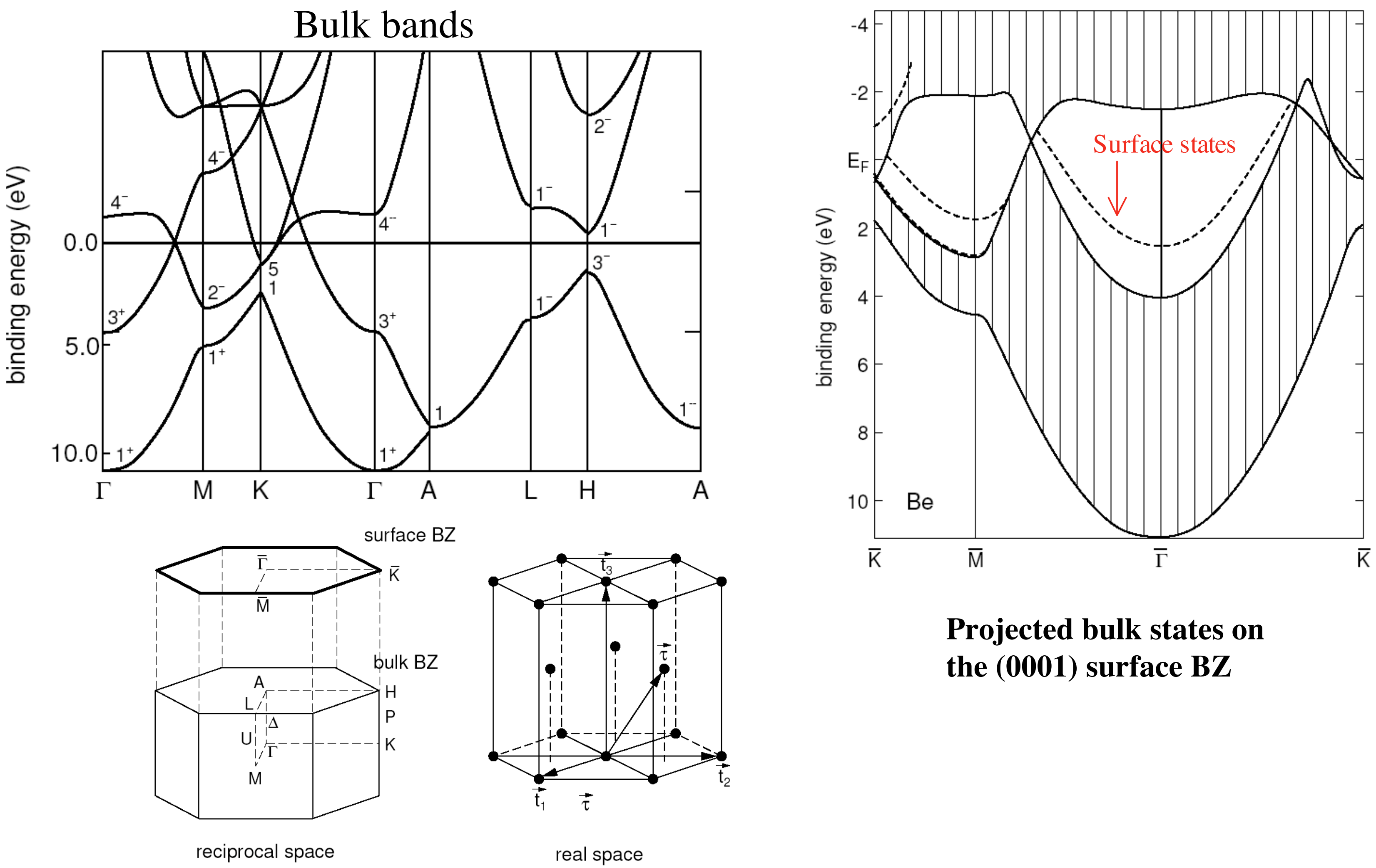
i.e. a periodic function modulated by an exponential decay from the surface into the bulk, which should then match an exponential decay function into the vacuum.





These states are characterized by the momentum $k_{//}$ and energy $E(k_{//})$. $K_{\perp}$ is no more a good quantum number. **True surface states cannot be degenerate with bulk states (i.e. for every $k_{\perp}$ there should not be any bulk state with the $k_{//}$ and $E(k_{//})$ of the surface state),** otherwise they can propagate periodically and infinitely into the bulk and therefore are no more surface states.

Surface states live in the projected bulk band gaps



reciprocal space

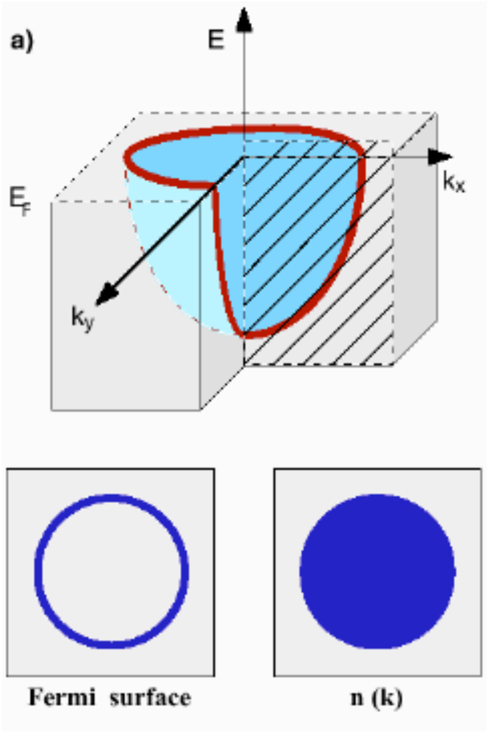
real space

Projected bulk states on the (0001) surface BZ

Figure 7.5: Real space structure and Brillouin zone of Be. The Be(0001) surface is the closed packed surface on top of the real-space hexagon. The surface Brillouin zone of Be(0001) is also shown. It is the projection of the bulk Brillouin zone in the (0001) direction.

Understanding the Solid State: Electrons in Reciprocal Space

Many properties of a solids are determined by electrons near E_F (conductivity, magnetoresistance, superconductivity, magnetism)



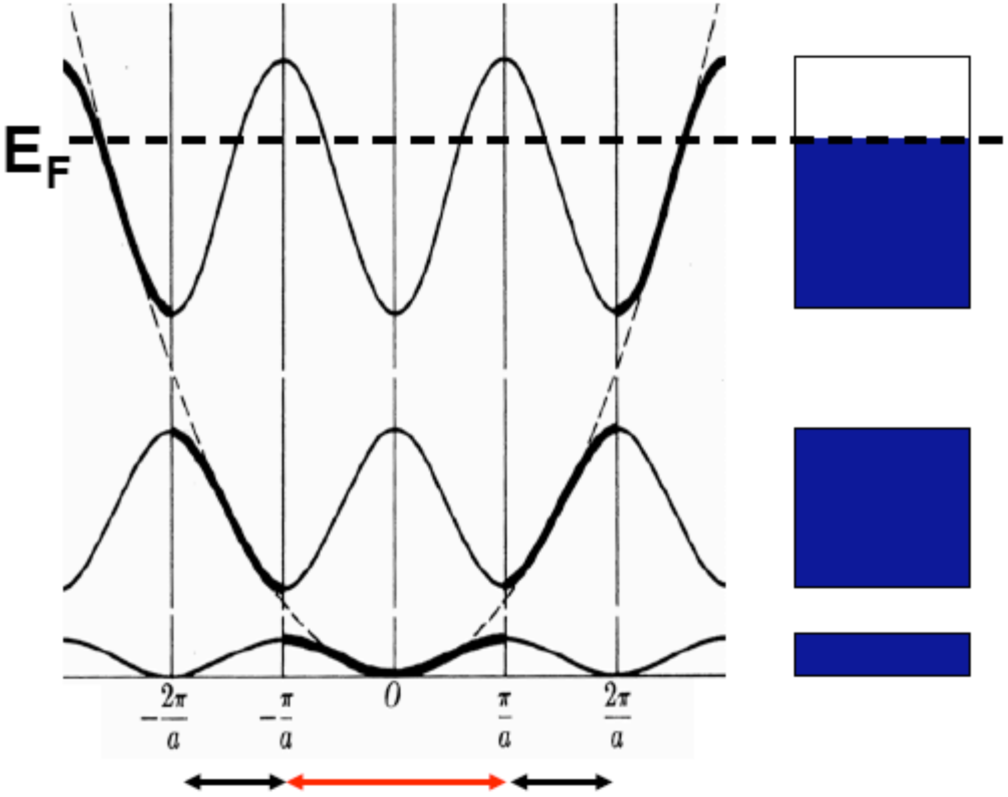
Fermi surface

n (k)

Only a narrow energy slice around E_F is relevant for these properties ($kT=25$ meV at room temperature)

Allowed electronic states

Repeated-zone scheme



Second Brillouin zone

First Brillouin zone

Second Brillouin zone

Mathematical formulation

The problem is to find a function $\phi(\mathbf{r}_1, \mathbf{r}_2,\ldots,\mathbf{r}_n)$ of the $\mathbf{r}_i$ coordinates of the n valence electrons such that:

$$\left[-\sum_i \frac{\hbar^2\nabla_i^{\;2}}{2m} + \sum_i U(r_i) + \sum_{ij} \frac{e^2}{|r_i - r_j|}\right]\phi(r_1, r_2 ..., r_n) = \varepsilon\phi(r_1, r_2 ..., r_n)$$

Kinetic energy

Electron-electron Coulomb energy (many electrons problem)

Potential energy in the ion electric field
Whit ions fixed at lattice positions R, each contribute as $U_0(\mathbf{R}-\mathbf{r}_i)$ and $U(\mathbf{r}_i)=\Sigma_R\, U_0(\mathbf{R}-\mathbf{r}_i)$

Hopeless problem; an exact solution is out of question

The simplest approx: free electrons (or quasi-free)

We ignore everything (which can be thought more or less constant or at least not introducing large perturbations) apart the kinetic energy term.

$$\left[-\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + U_0\right]\phi(\bar{r}_1, \bar{r}_2 \ldots, \bar{r}_n) = \varepsilon\phi(\bar{r}_1, \bar{r}_2 \ldots, \bar{r}_n)$$

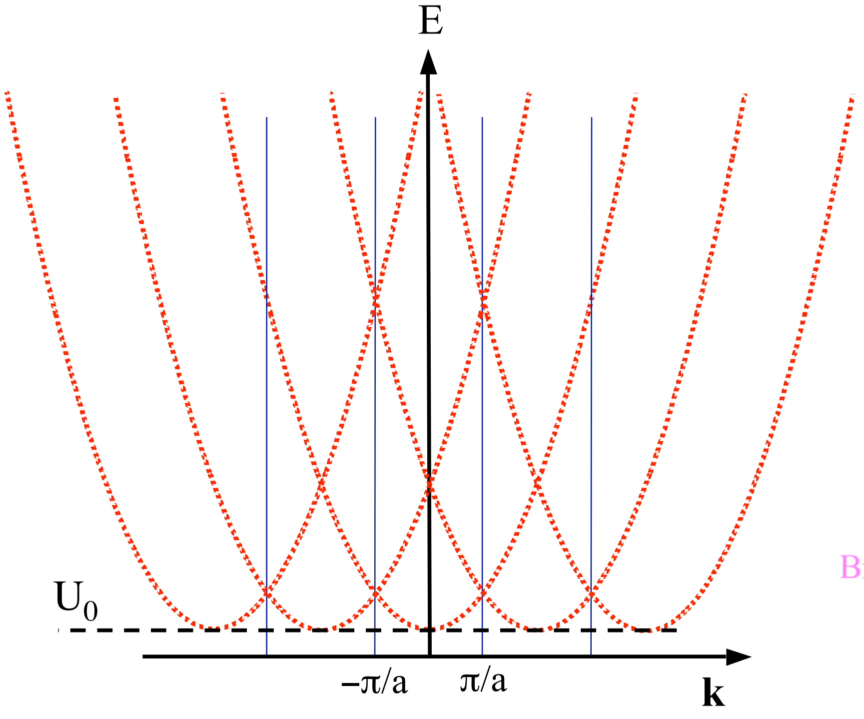
Solution: $$\varepsilon = \sum_i \frac{\hbar^2 k_i^2}{2m} + U_0$$

$$\phi(\bar{r}_1, \bar{r}_2 \ldots, \bar{r}_n) = \phi_1(\bar{r}_1)\phi_2(\bar{r}_2)\ldots\phi_n(\bar{r}_n)$$

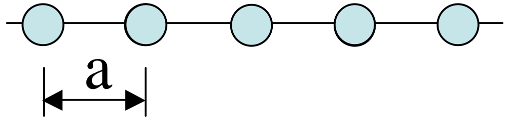
$$\phi_j(\bar{r}) = \frac{1}{\sqrt{V}} e^{i\bar{k}_j \cdot \bar{r}}$$

The **k** are restricted by suitable boundary conditions that depend on the crystal symmetry. If we assume that the unit cell is a parallelepiped of edges a_x, a_y and a_z we have $k_x = h\, 2\pi/a_x$, $k_y = k\, 2\pi/a_y$, $k_z = l\, 2\pi/a_z$

Example: 1D case



Free-electron parabola+boundary conditions

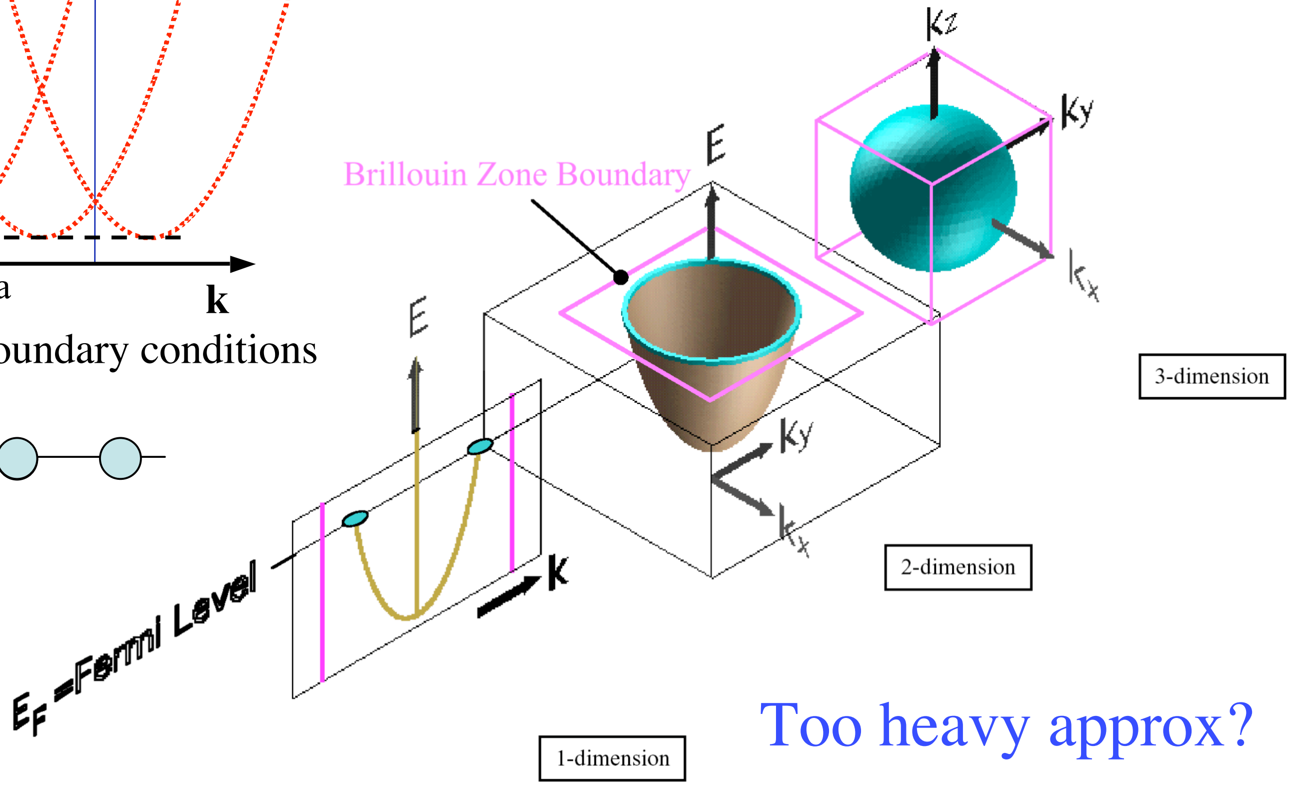


Concepts:

Fermi level: the energy of the highest state occupied by valence electrons according to their fermionic nature.

Fermi surface: the iso-energetic surface at E_F in the reciprocal lattice (diameter 2 k_F)

Fermi velocity: $V_F = \hbar k_F/m$



Too heavy approx?

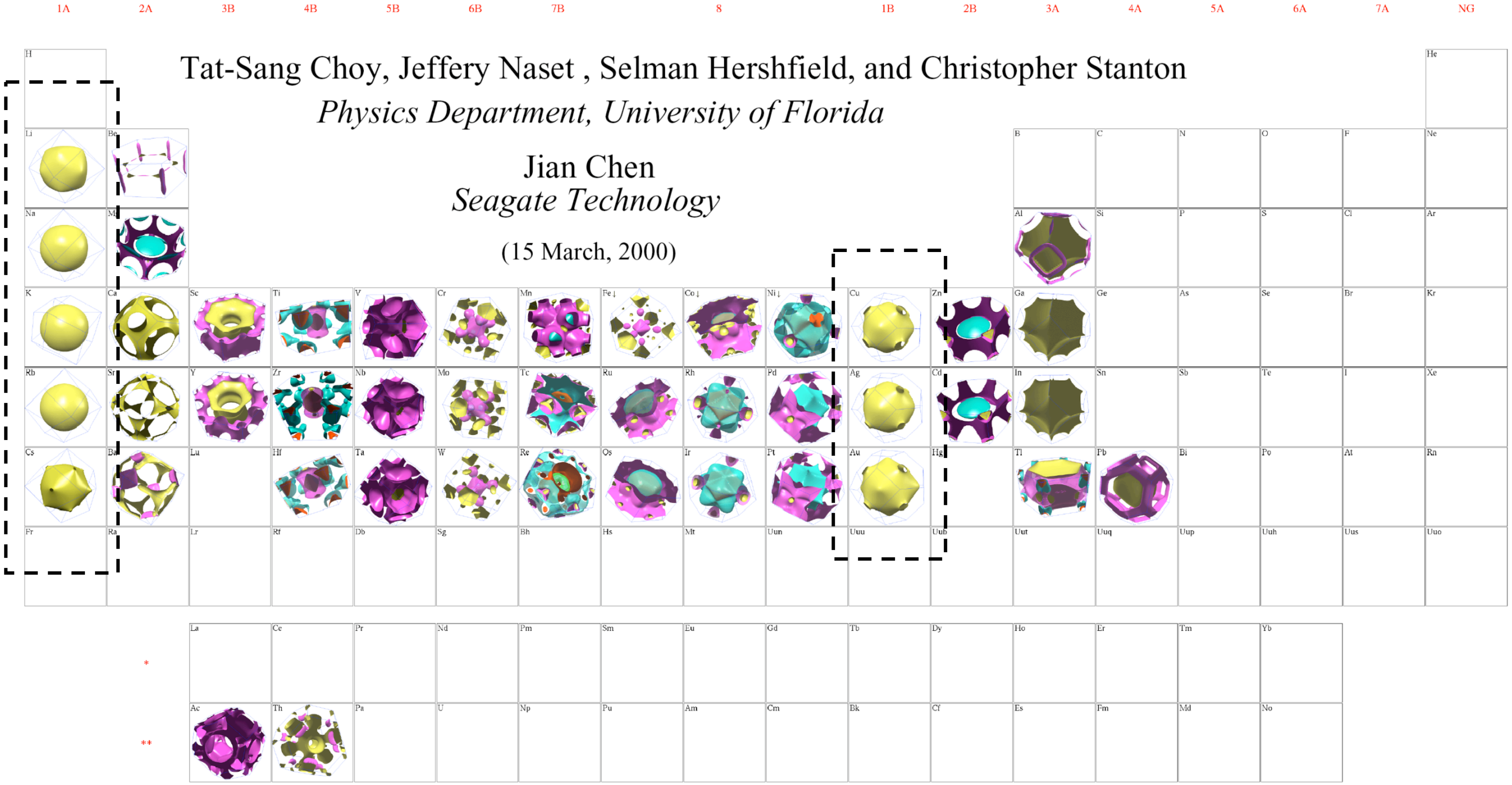
Periodic Table of the Fermi Surfaces of Elemental Solids

http://www.phys.ufl.edu/fermisurface

Tat-Sang Choy, Jeffery Naset , Selman Hershfield, and Christopher Stanton
Physics Department, University of Florida

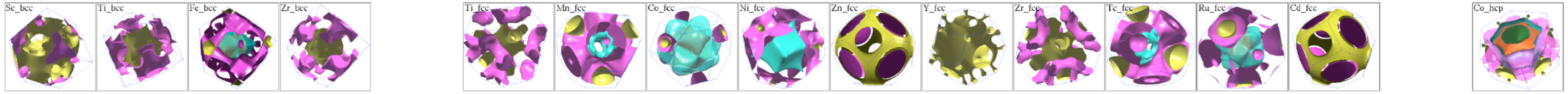
Jian Chen
Seagate Technology

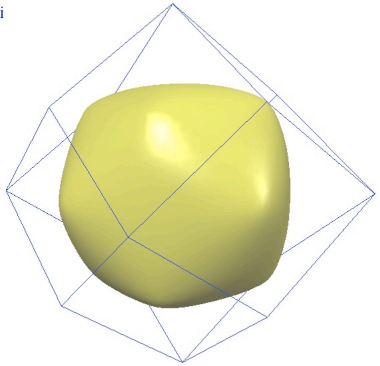
(15 March, 2000)



Ferromagnets:

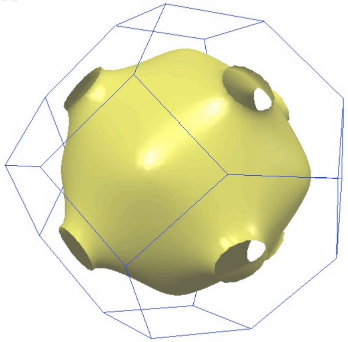
Alternate Structures :



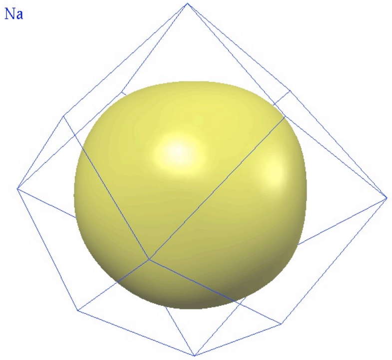


Li

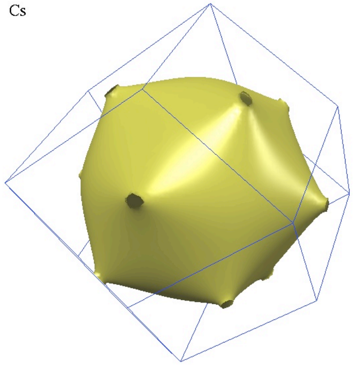
Alkali & noble metals (bcc) and (fcc)



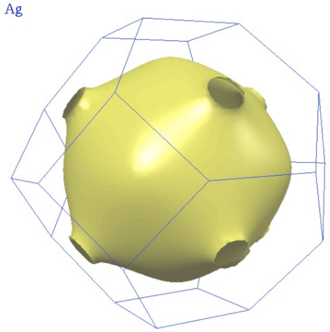
Cu



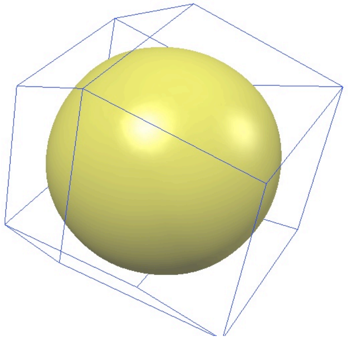
Na



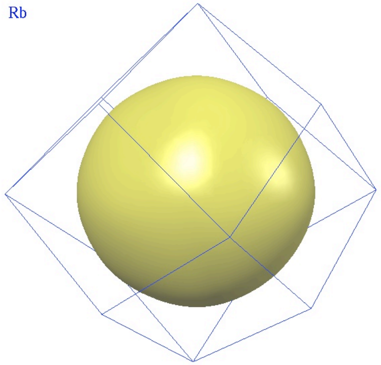
Cs



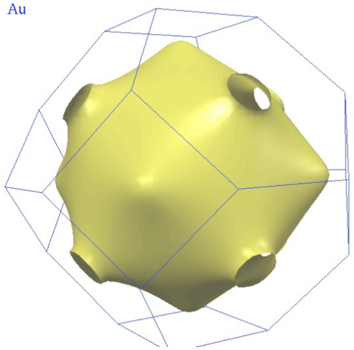
Ag



K



Rb



Au

How to Determine Fermi Vectors by Angle-Resolved Photoemission

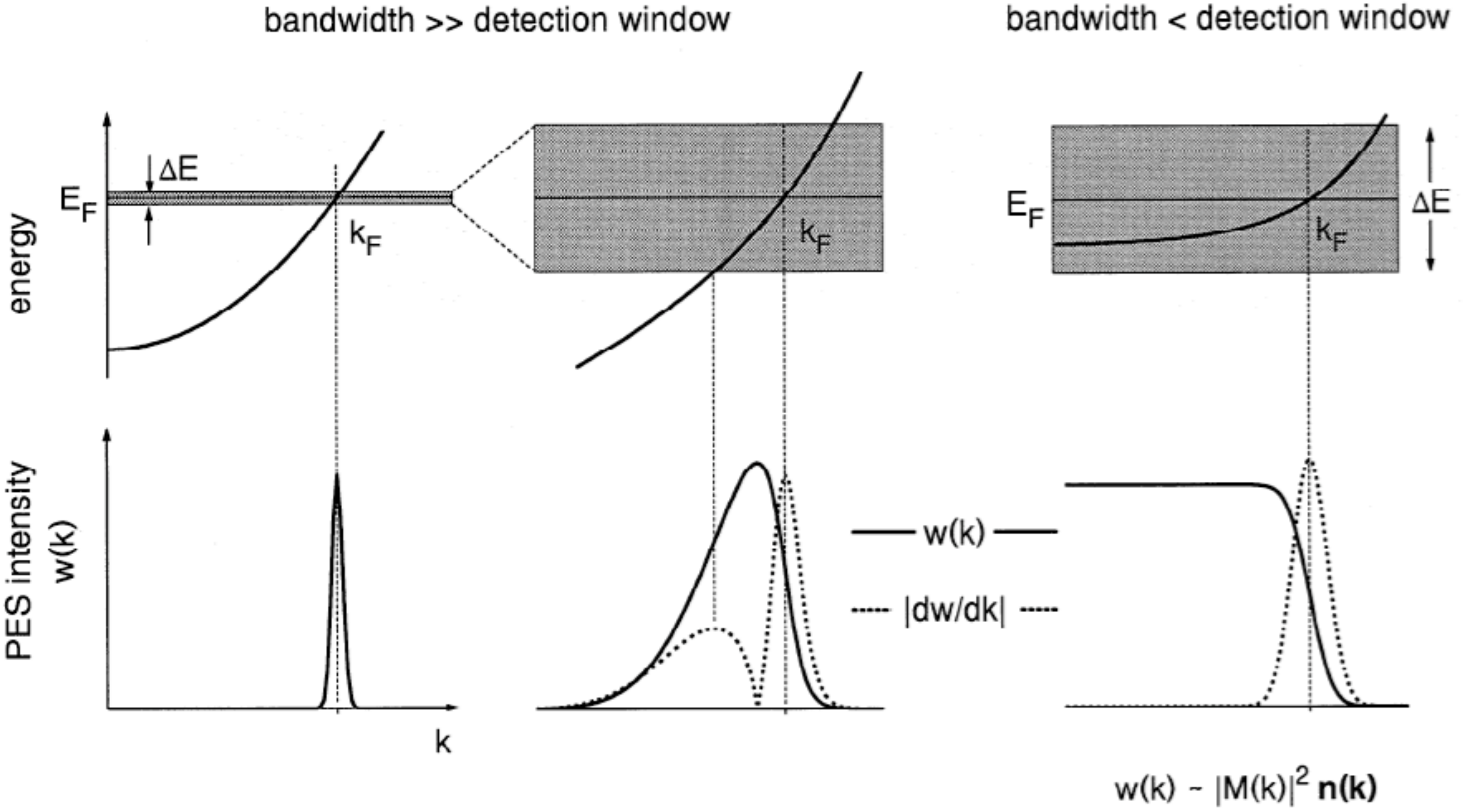
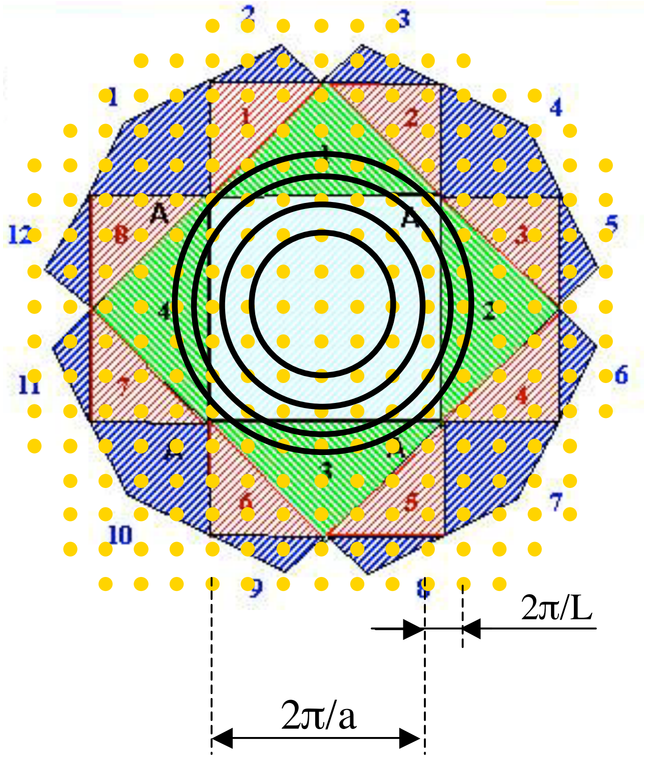


Fig. 8. Schematic behavior of the detected photoelectron intensity near a Fermi level crossing for wide band (left and center) and narrow band systems (right).



Typically a/L ~ 10^{-7}-10^{-8}
i.e. states almost continuous

DENSITY OF STATES N(E)

N° of available electronic states
per unit of energy and volume

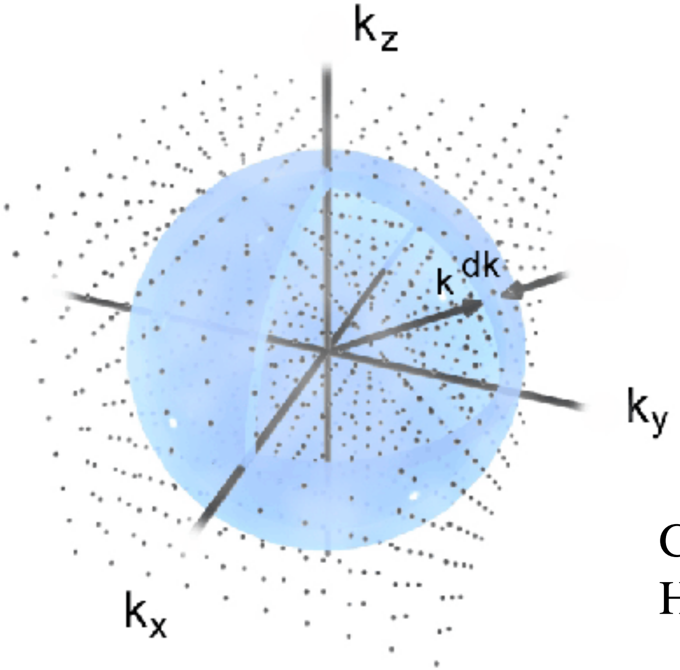
2D case

Consider adjacent constant energy contours E and E+∂E.
How many k points in the skin ∂E between them?

$$n(k) = \frac{\pi k^2}{4\pi^2 / L^2} \Leftrightarrow n(E) = \frac{2\pi m E}{4\pi^2 \hbar^2 / L^2}$$

$$N(E) = \frac{1}{L^2} \frac{\partial n(E)}{\partial E} = \frac{m}{2\pi \hbar^2} = \text{constant}$$

(Times 2 to account for the spin)



DENSITY OF STATES N(E)

N° of available electronic states per unit of energy and volume

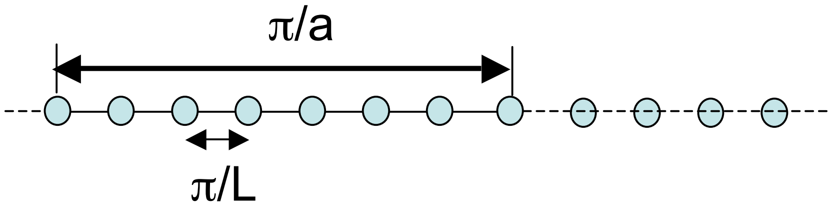
3D case

Consider adjacent constant energy spheres E and E+∂E.
How many k points in the skin ∂E between them?

$$n(k) = \frac{\frac{4}{3}\pi k^3}{8\pi^3 / L^3} \Leftrightarrow n(E) = \frac{\frac{4}{3}\pi(2mE/\hbar^2)^{3/2}}{8\pi^3 / L^3}$$

$$N(E) = \frac{1}{L^3}\frac{\partial n(E)}{\partial E} = \frac{(2m)^{3/2}}{4\pi^2\hbar^3}E^{1/2} \propto E^{1/2}$$

(Times 2 to account for the spin)



DENSITY OF STATES N(E)

N° of available electronic states
per unit of energy and volume

What about 1D case?

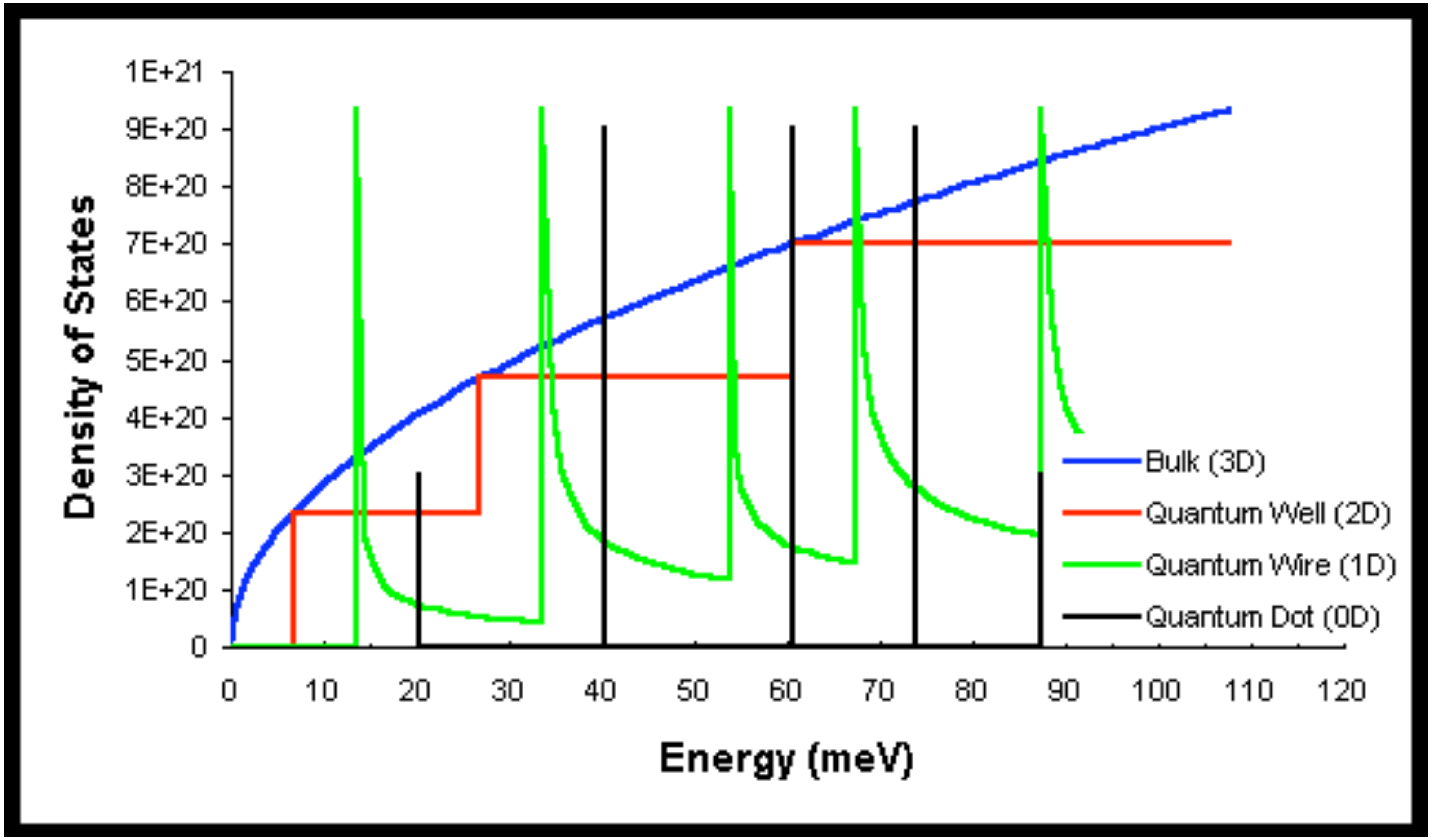
$$n(k) = \frac{k}{2\pi / L} \Leftrightarrow n(E) = \frac{(2mE / \hbar^2)^{1/2}}{2\pi / L}$$

$$N(E) = \frac{1}{L}\frac{\partial n(E)}{\partial E} = \frac{(2m)^{1/2}}{4\pi\hbar E^{1/2}} \propto E^{-1/2}$$

(Times 2 to account for the spin)

Square root (van Hove) singularity, typical of 1D problems

Quantum Confinement and Dimensionality



The effective mass m*

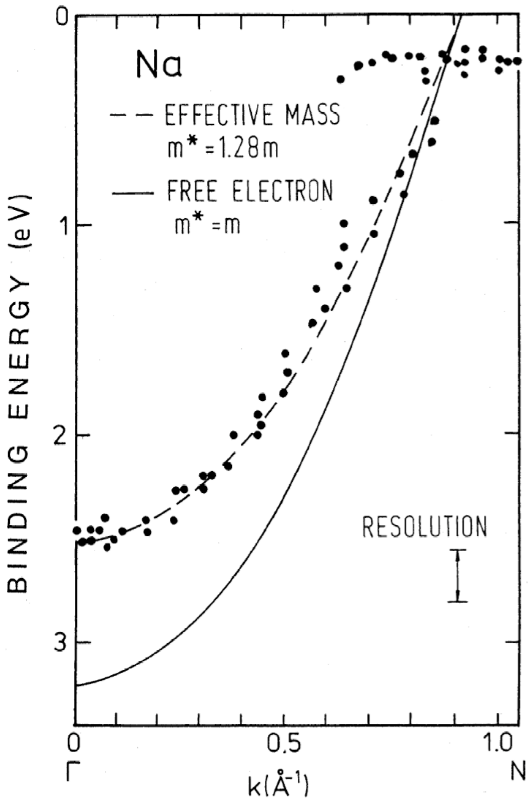
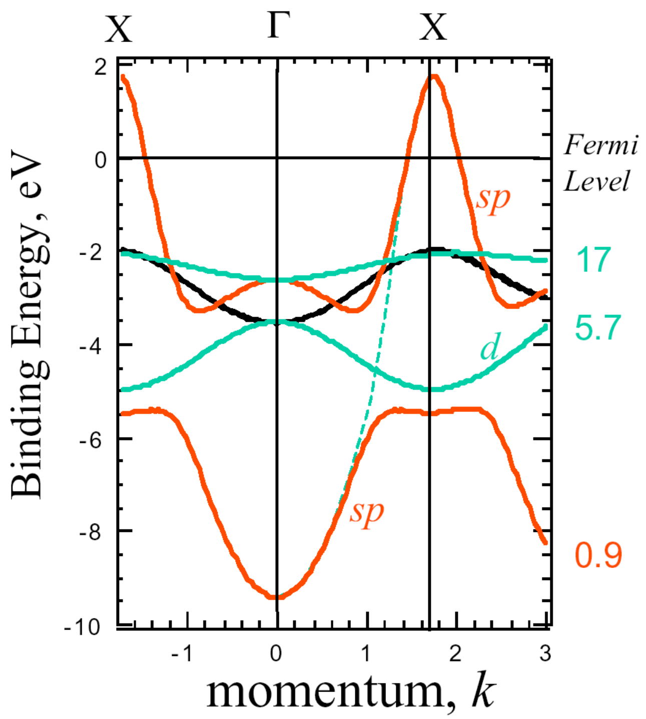


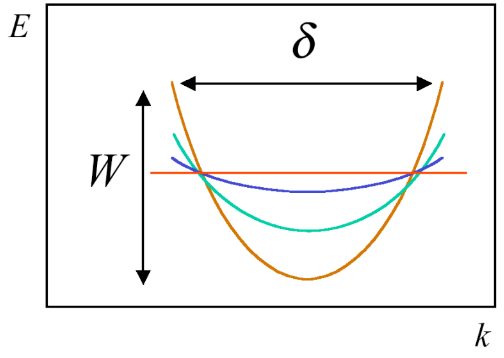
Fig. 2. Experimental band structure of Na obtained by ARPES along the ΓN direction (dots). The solid and dashed curves represent parabolic dispersion curves obtained for a free-electron mass (m_e) and for an effective mass of $m^* = 1.28 \times m_e$, respectively [12,13].

Copper



$$E = \frac{\hbar^2 k^2}{2m^*} \Rightarrow m^* = \frac{\hbar^2 k^2}{2E}$$

$$\boxed{m^* = \frac{0.946\,\delta[\text{Å}^{-1}]^2}{W[\text{eV}]}}$$



Effective mass

- more general definition of m*
- double differentiate $E(k) = \hbar^2 k^2 /(2m^*) + V_0$ w.r.t. k

⇨ $d^2E / dk^2 = \hbar^2 / m^*$

or

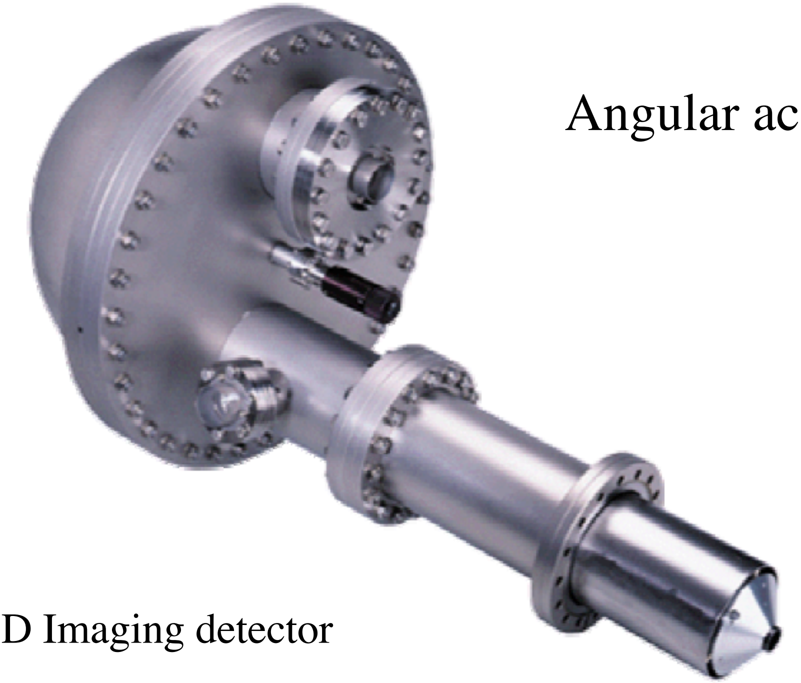
⇨ $m^* = \hbar^2 /(d^2E / dk^2)$

effective mass given by the curvature of $E(k)$

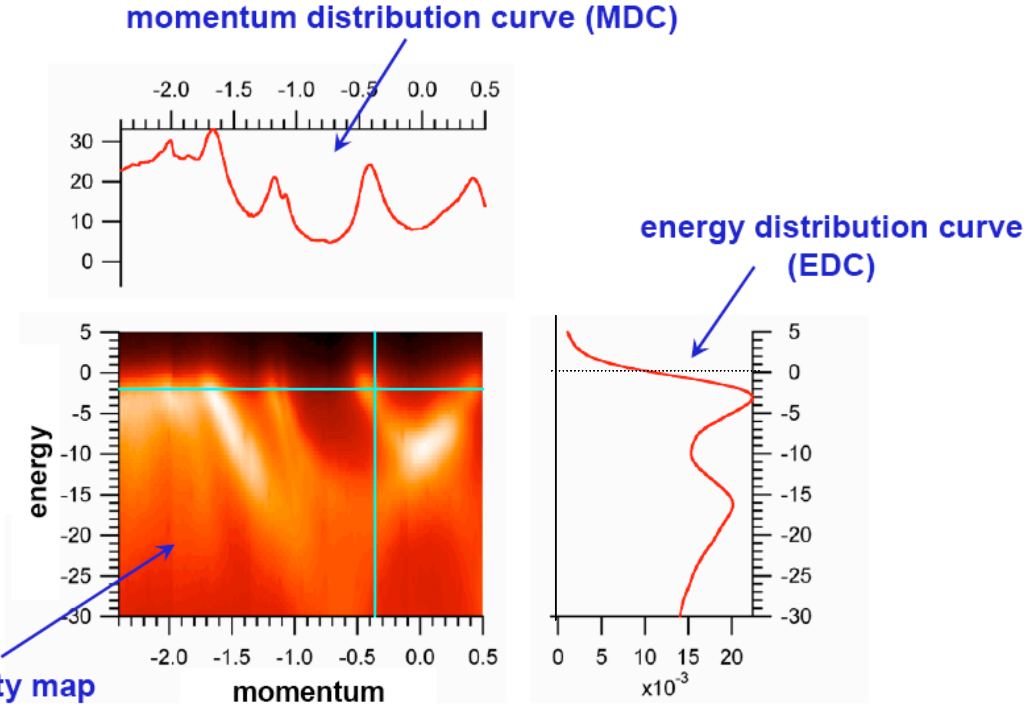
- leads to negative m* near top of a band: holes, rather than electrons

Photoelectron detection

hemispherical energy analyzer



Angular acquisition max 35˚ at the same time

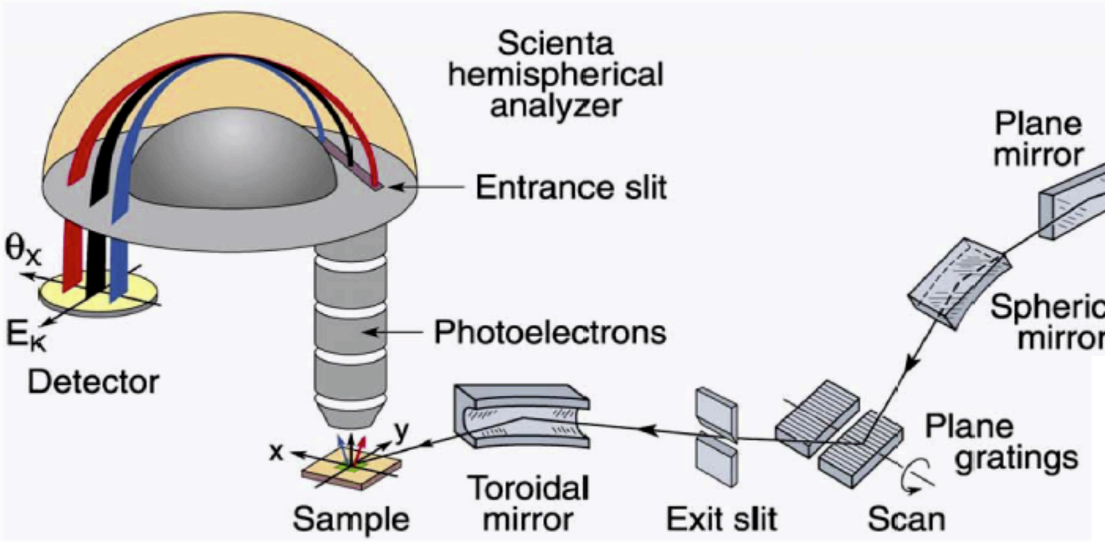

momentum distribution curve (MDC)

energy distribution curve (EDC)

intensity map

CCD Imaging detector

State-of-the-art



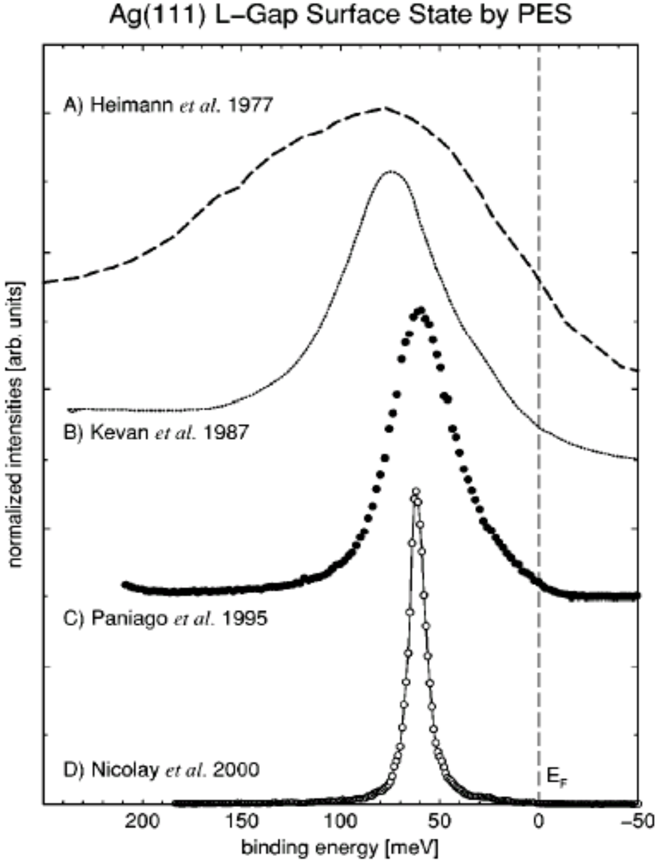
Parallel multi-angle recording

- Improved **energy resolution**
- Improved **momentum resolution**
- Improved **data-acquisition efficiency**

	ΔE (meV)	*Δθ*
past	*20-40*	*2°*
now	*2-10*	*0.2°*

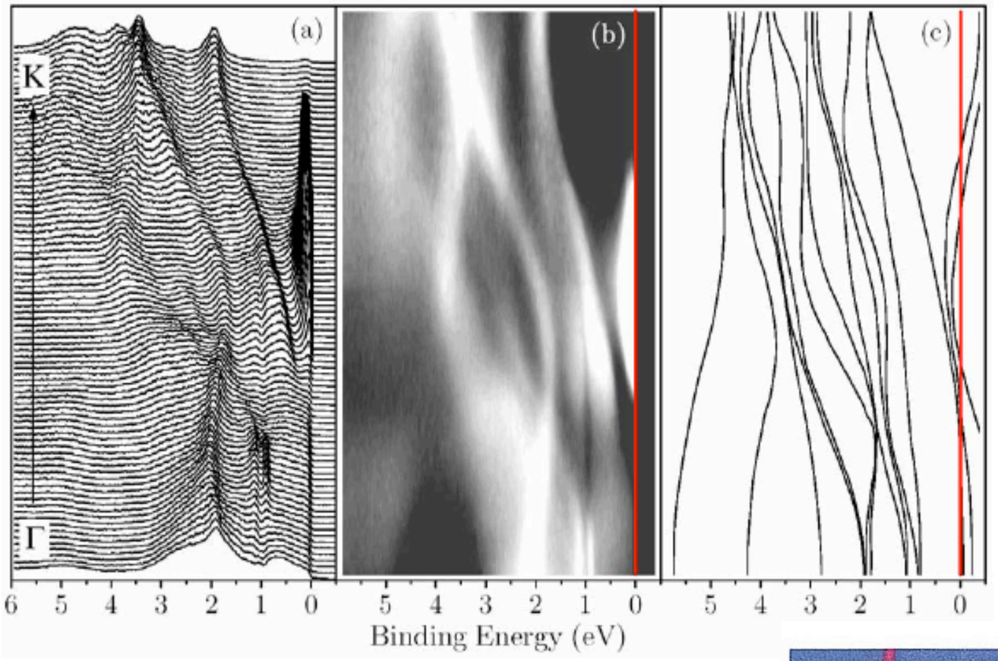
courtesy of A. Damascelli

Ag(111) L–Gap Surface State by PES



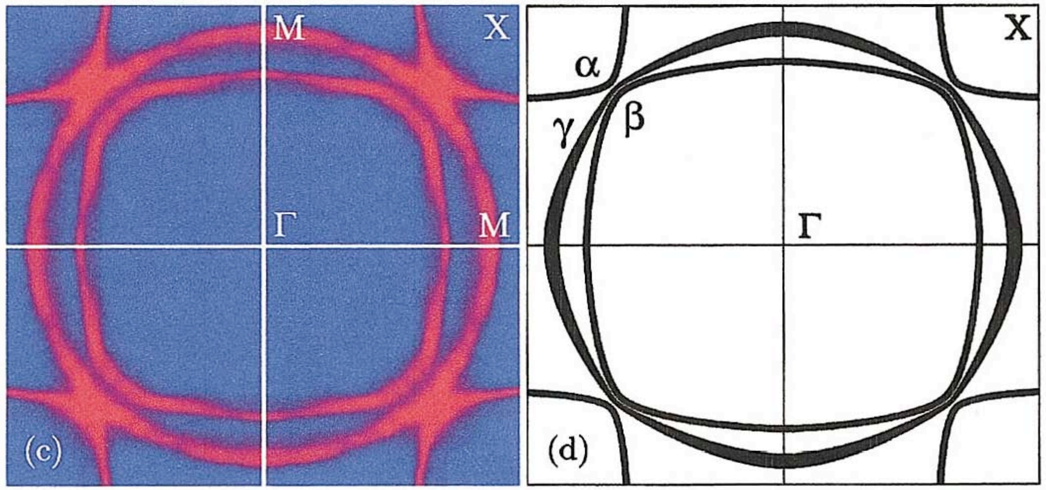
Clear and nice representation of the data

$NbSe_2$ Damascelli *et al*. (2000)



Band dispersions

Fermi surface



Sr_2RuO_4 cleaved at 180 K
T= 10 K hν=28 eV

Local-density-approximation
band-structure calculation

Summary: advantages and limitation of ARPES

Advantages

- **Direct information about the electronic states!**
- Straightforward comparison with theory - little or no modeling.
- High-resolution information about **BOTH energy** and **momentum**

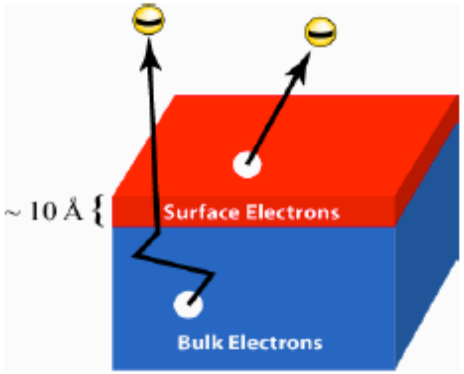
  → band structure $E(\mathbf{k})$

  → Fermi surface $\mathbf{k}(E_F)$
- Sensitive to "**many-body**" effects

  → spectral function $A^{<}(\mathbf{k},E)$

  (if photohole localized ⊥ surface)
- **Surface-sensitive probe**

Limitations



- **Not bulk sensitive**
- 3dim k-space information difficult to obtain
- Requires clean, atomically flat surfaces in **ultra-high vacuum**
- Cannot be studied as a function of pressure (or magnetic field)

One-step model and the non-interacting electrons

Part II

Papers: S. Hüfner et al., J. Electron Spectroscopy Rel. Phenom. 100 (1999)
A. Damascelli et al., Rev. Modern Phys. (2005)
F. Reinert et al., New J. Phys. 7 (2005)
X.J. Zhou et al., J. Electron Spectroscopy Rel. Phenom. 126 (2002)

Thanks to: A. Damascelli, X. Shen, R. Claessen, Ph. Hofmann and E. Rotemberg from whose I have taken slides and figures

One-step model: Matrix elements

The process at the heart of photoemission is the interaction of a photon with a many electron system in the ground state $|N,i\rangle$. The **transition probability** from the ground state to a final state $|N,f\rangle$ where the photoelectron is detected with a kinetic energy E_{kin} is given by the **Fermi Golden Rule:**

$$I(E_{kin}) = \frac{2\pi}{\hbar}\sum_f \left|\langle N,f|H_{int}|N,i\rangle\right|^2 \rho\left(E_f^N\right)\delta\left(E_f^N - E_i^N - h\nu\right)$$

$|N,i\rangle$ and $|N,f\rangle$ Eigenstates of the unperturbed Hamiltonian

$$H_{int} = -\frac{e}{m}\left(A\cdot\nabla + \frac{1}{2}\mathrm{div}A \cancel{-\frac{e}{\hbar}|A|^2}\right)$$

Negligible in case of small field strength (but relevant for lasers)

This term is small inside the crystal and changes very slowly in space (i.e. div A can be neglected apart at the surface where it may affect the lineshape of photoemission peaks)

We are left with:

$$H_{int} \approx -\frac{e}{m} A \cdot \nabla = -\frac{e}{m} A \cdot p$$

Dipole approx: $A = A_0 \exp(i\mathbf{qr}) \sim A_0$

Because q is negligible compared to BZ size (or photon wavelength small compared to inter-atomic spacing)

So the transition probability reduces to:

$$I(E_{kin}) = \frac{2e^2\pi}{m^2\hbar} \sum_f \left| \langle N, f | A_0 p | N, i \rangle \right|^2 \rho\left(E_f^N\right) \delta\left(E_f^N - E_i^N - h\nu\right)$$

$$I(E_{kin}) = \sum_f |M_{fi}|^2 \rho\left(E_f^N\right) \delta\left(E_f^N - E_i^N - h\nu\right)$$

Up to now everything is many-body!!!!

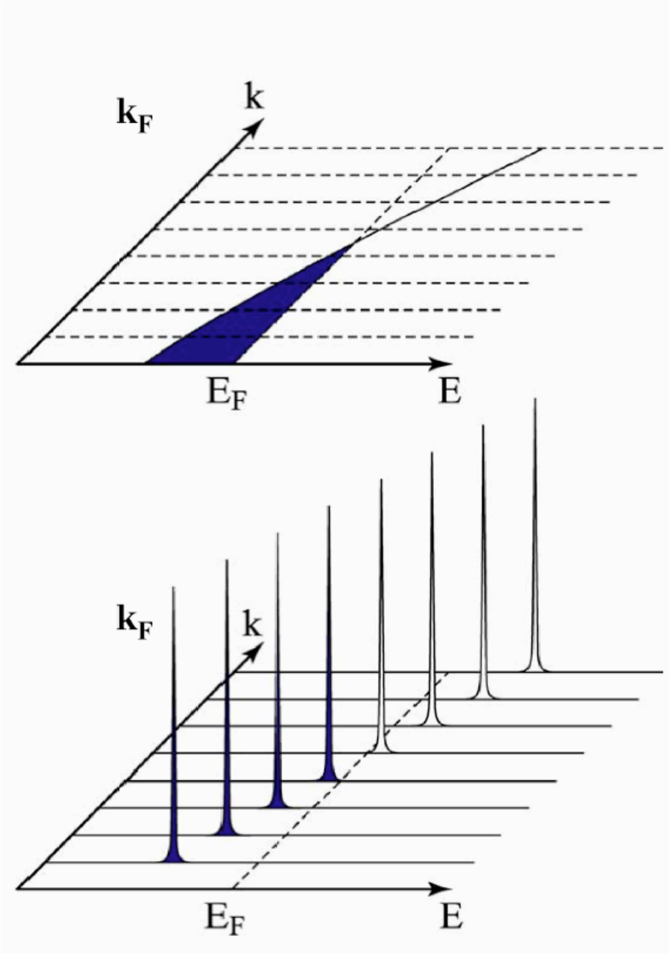
Single particle approximation

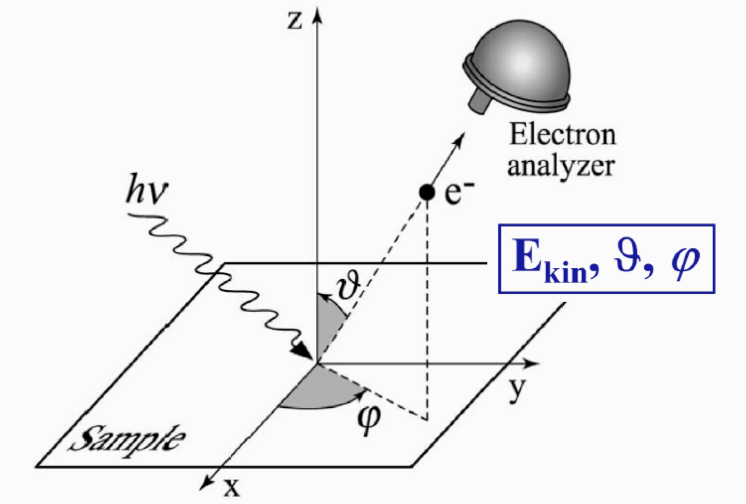
In the limit of non-interacting electrons the N-electron wave function can be written as the product of single electron wave functions. We can assume that before and after the photoemission process the remaining N-1 electrons are not affected by the photoelectron excitation, so we can write the transition probability as:

$$I(E_{kin}) = \frac{2e^2\pi}{m^2\hbar}\sum_f A_0^2 \left|\langle k_f|p|k_i\rangle\right|^2 \rho(E_{kf})\,\delta\left(E_{kin}^{kf} - E^{ki} - h\nu\right)\delta\left(k_{f//} - k_{i//} - g\right)$$

Interpretation: the photon is adsorbed by a single electron of initial state $|k_i\rangle$ in the solid which make a transition to a photoelectron state $|k_f\rangle$ (plane wave) in the vacuum. The conservation of the momentum component parallel to the surface plane has been included.
The remaining N-1 electrons are just “spectators”!!

The photoelectron spectrum consists of “spikes” at energies E_{kin}





Energy Conservation

$$E_{kin} = h\nu - \phi - |E_B|$$

Momentum Conservation

$$\mathbf{p}_{||} = \hbar \mathbf{k}_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

The intensity is modulated by the matrix element $|M_{fi}|^2=|<k_f|A_0p|k_i>|^2$

Symmetry selection rules

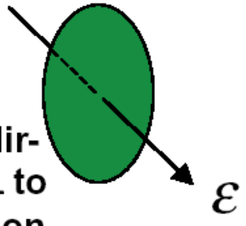
$$\left|M_{fi}\right|^2 \sim \left|\left\langle \underbrace{\psi_f \middle| \mathbf{A}\cdot\mathbf{p}}_{\text{Fixed by geometry}} \middle| \underbrace{\psi_i}_{\text{Sample-dependent}} \right\rangle\right|^2$$

- **The sample has mirror-plane symmetries.**
- **Each part of the matrix element has its own possible symmetry with respect to the sample plane.**
- **Whether a transition is allowed or forbidden depends on a combination of experimental geometry and the details of the wavefunctions**

$$\left|\psi_f\right\rangle$$

Is a plane wave, always even w.r.t. sample mirror plane

$$\mathbf{A}\cdot\mathbf{p}$$



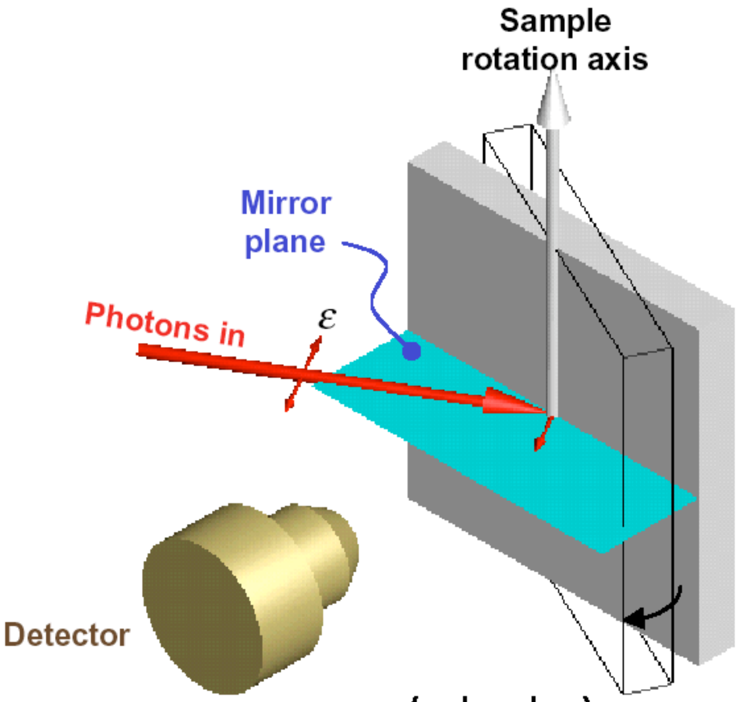
Even in directions ⊥ to polarization vector

Odd in this direction

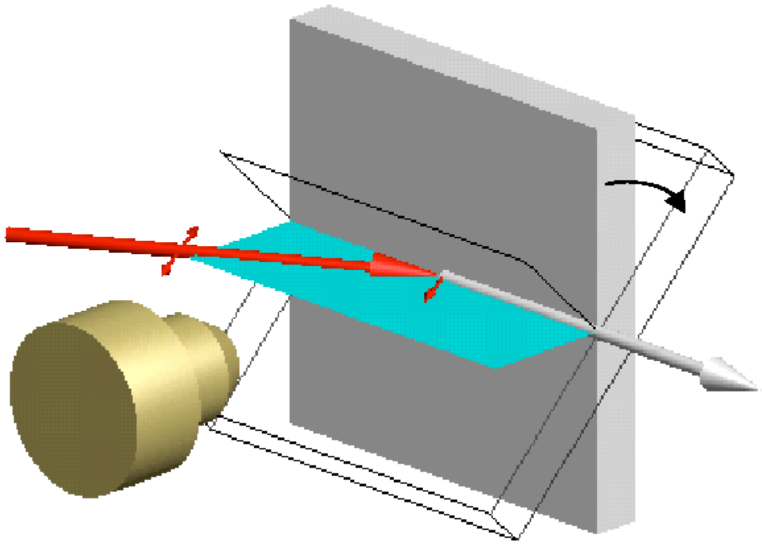
$$\left|\psi_i\right\rangle$$

Can be even or odd, depending on location in Brillouin Zone

$$\left|M_{fi}\right|^2 \sim \left|\langle\psi_f|\mathbf{A}\cdot\mathbf{p}|\psi_i\rangle\right|^2 \text{ non - zero for } \begin{cases}\langle +|-|-\rangle\\ \langle +|+|+\rangle\end{cases}$$



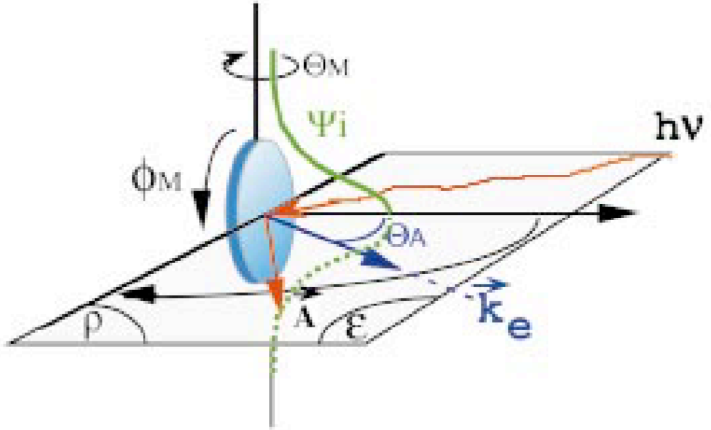
$$\langle +|+|+\rangle$$



Only even initial states are observed at all rotation angles

Mixture of even and odd states

a) even detection



b) odd detection

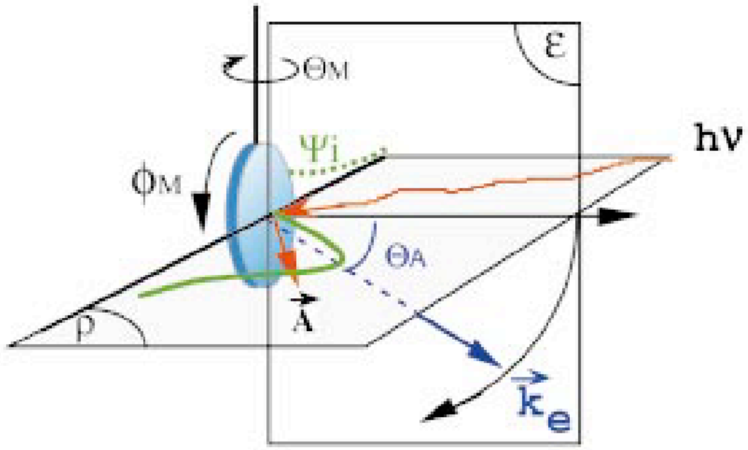
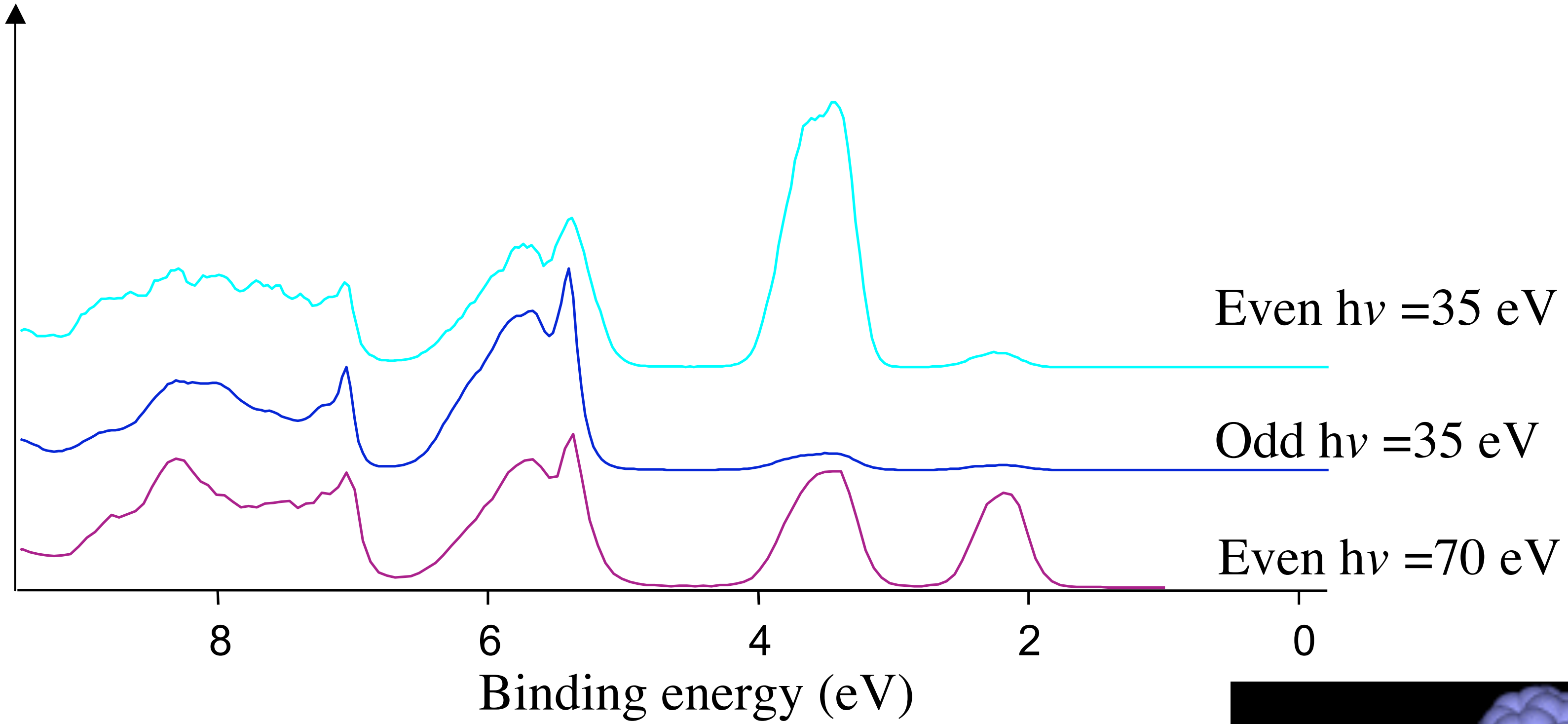
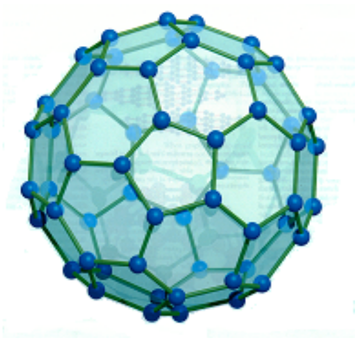
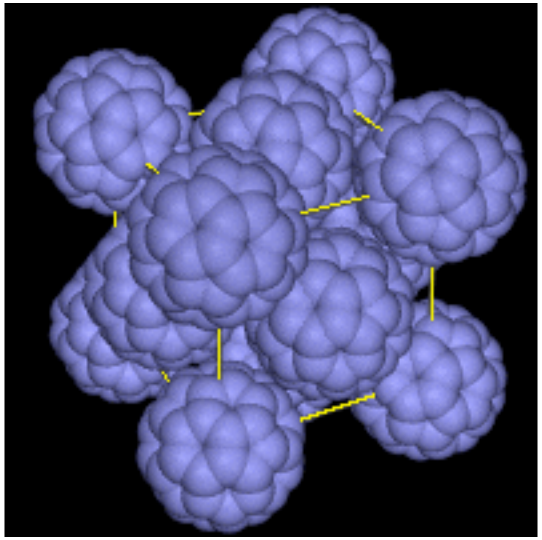


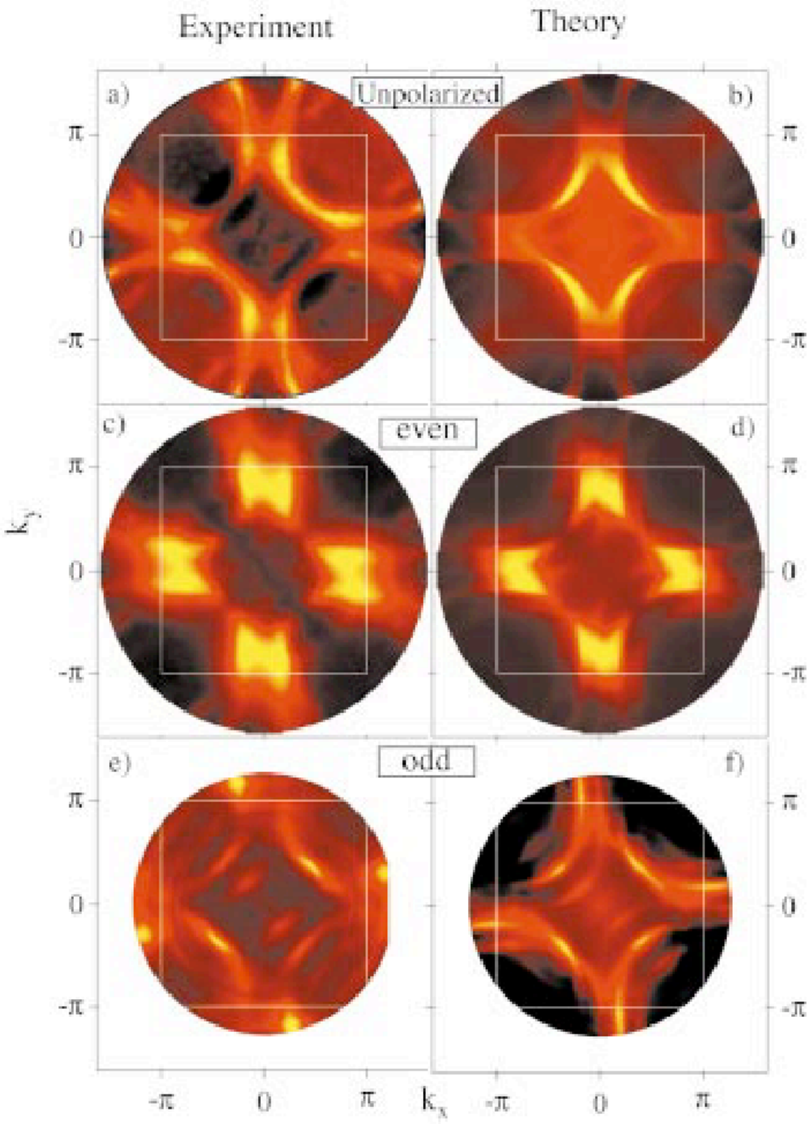
FIG. 1. (Color) The meaning of “even” and “odd” detection geometry in the present ARPES experiments is explained. $\vec{k}_e$ points toward the detector. In the even case, the detector moves in the plane of incident light (horizontal plane) in which the synchrotron light is polarized. In the odd case, the detector moves in a perpendicular plane as shown. The sample is kept fixed. For initial states lying in a mirror plane (e.g., along the $\bar{\Gamma}$-$\bar{M}$ line), the even polarization selects emission only from states symmetric with respect to the mirror plane, while the odd polarization couples to antisymmetric states as discussed in the text. The detector is rotated along the vertical and horizontal axis to access states throughout the (k_x, k_y) plane.

Matrix effects on a molecular crystal: C_{60}

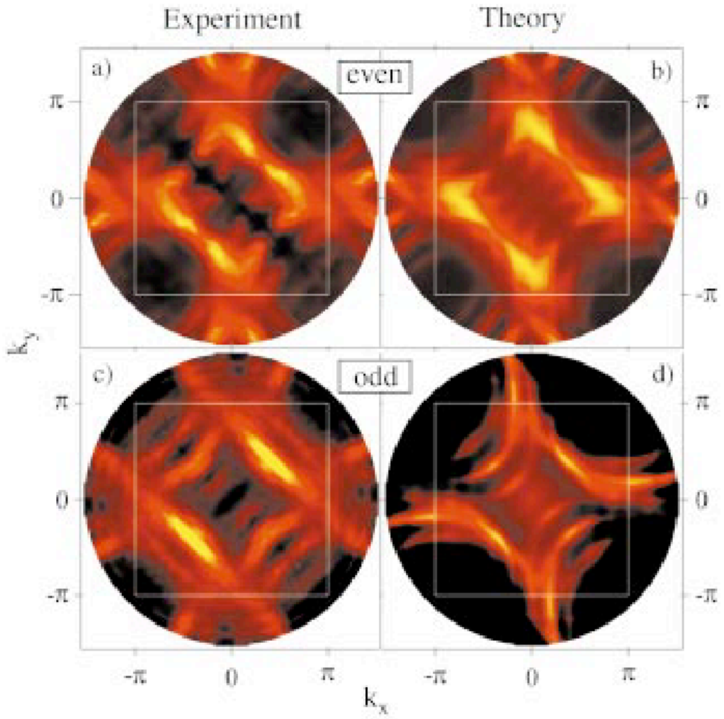








hν = 21..2 eV



hν = 35 eV

M.C. Asensio et al., PRB (2003)

Matrix effects on the Fermi surface shape in Bi2212

Cooper Minimum

- **Cooper (1962) pointed out that the cross-section for photoemission will have a minimum for emission whenever the radial wavefunction has a node.**

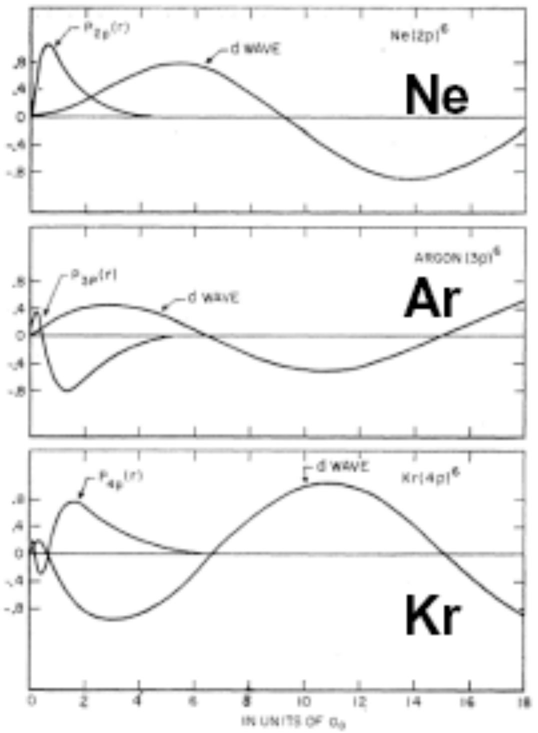
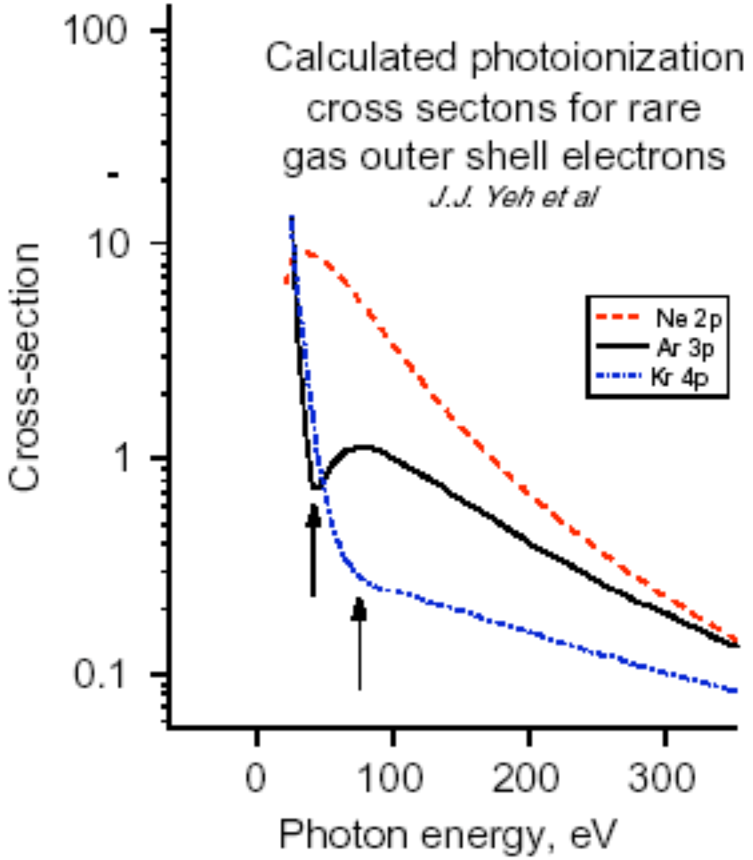
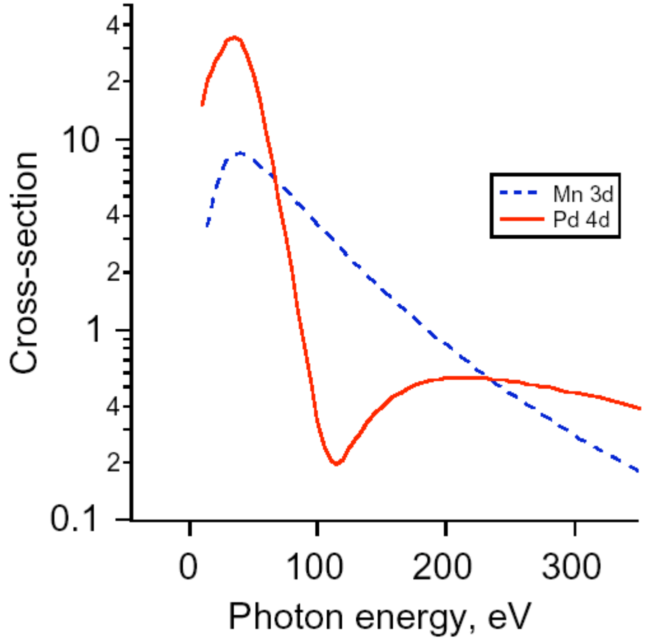


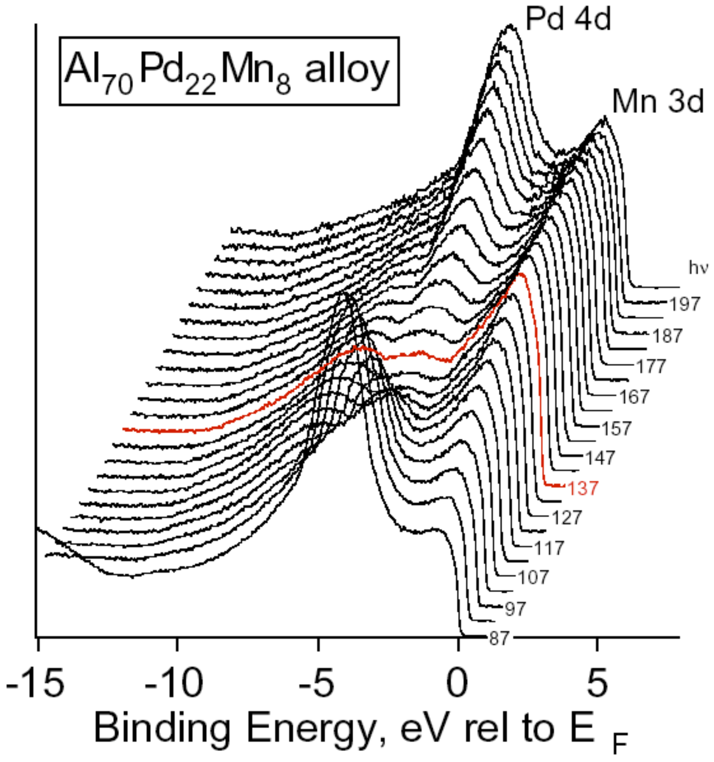
FIG. 2. Outer subshell radial wave functions and d waves for ε=0 for Ne, Ar, and Kr.


Calculated photoionization cross sectons for rare gas outer shell electrons
J.J. Yeh et al

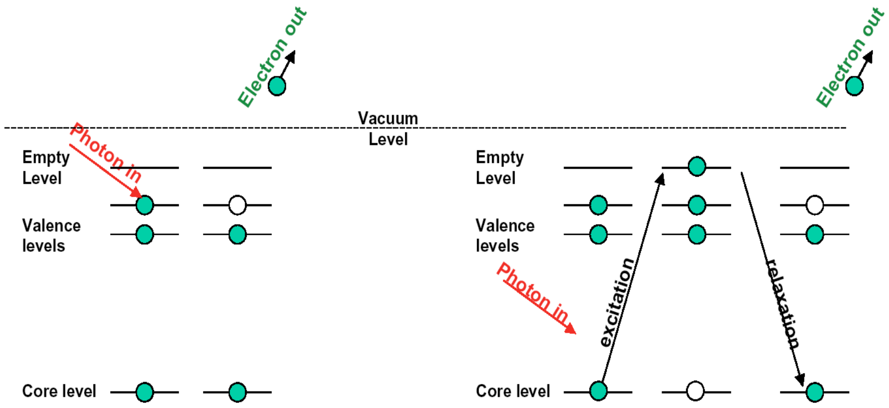
Calculation
J.J.Yeh



Expt.
Rotenberg et al

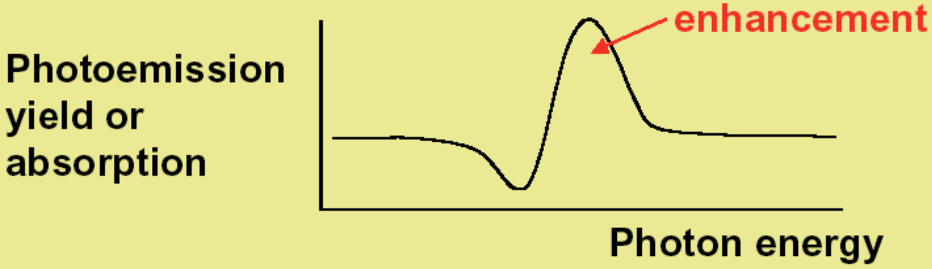


Resonant photoemission



- **These processes (non-resonant and resonant photoemission) have the same initial and final states.**
- **As quantum mechanics dictates, these independent channels will interfere when added coherently**

$$|M_{fi}|^2 = \left|\langle f|H_{NR}|i\rangle + \langle f|H_R|i\rangle\right|^2$$



- **Not all valence electrons are enhanced equally!**
- **Only those with overlap to the core hole are enhanced**
- **This can be very useful to get projections of the valence bands to the individual atoms.**

Two constrains on the time scale of the process:

1) To have a coherent interfering process the time scale of the two channels must be comparable.

2) The the excited electron must remain localized on the same atom of the core hole for a time scale bigger or comparable to the core hole lifetime

Gd@C$_{82}$ resonant photoemission

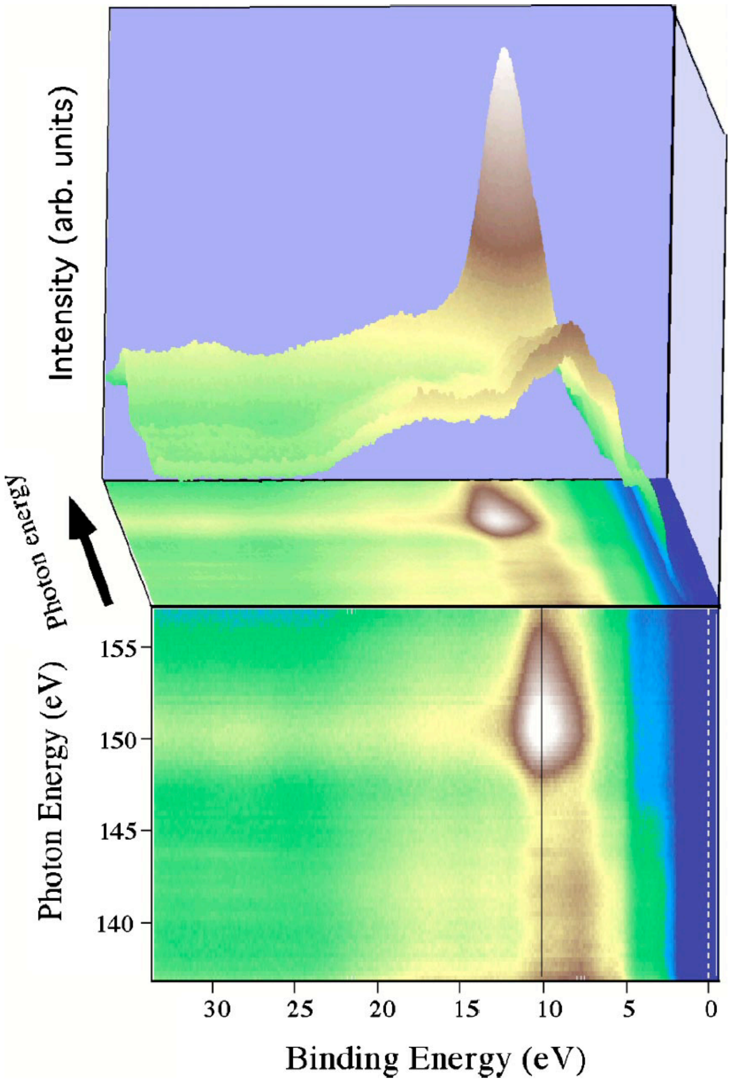
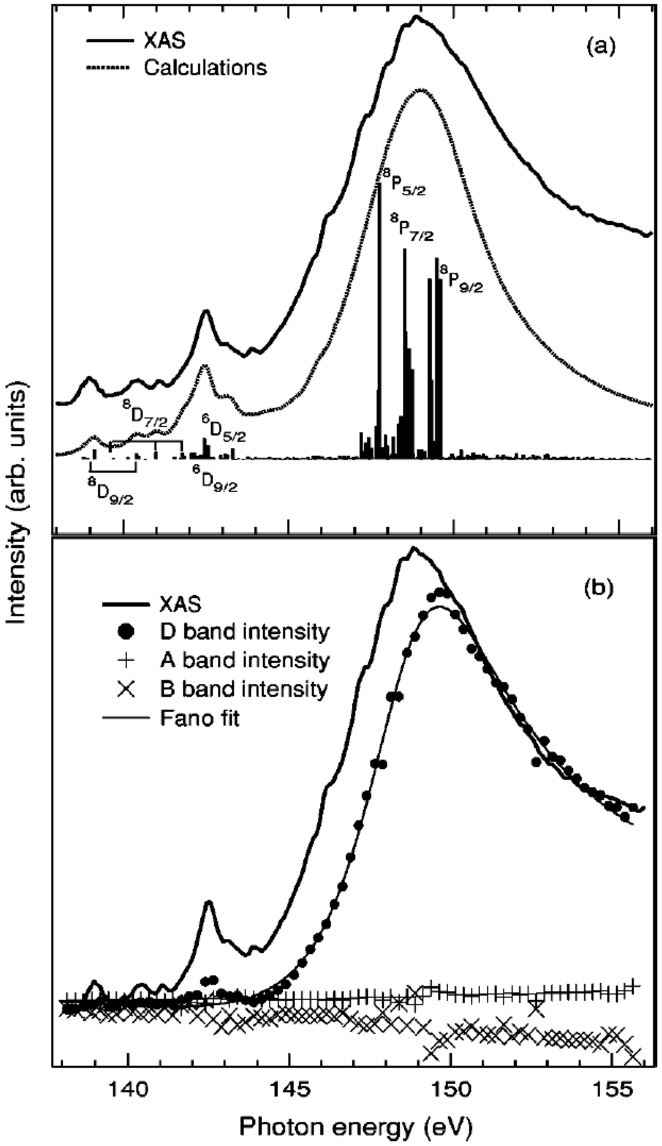
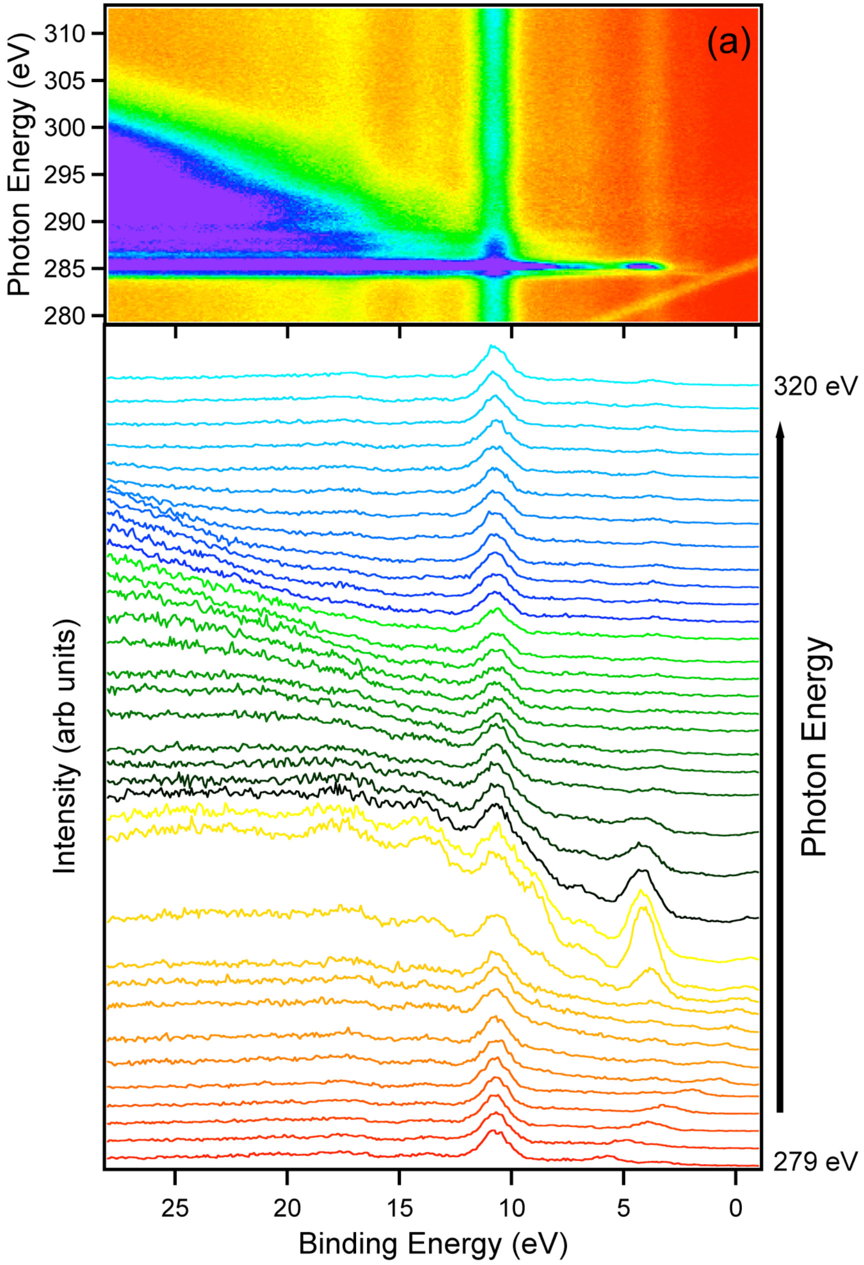
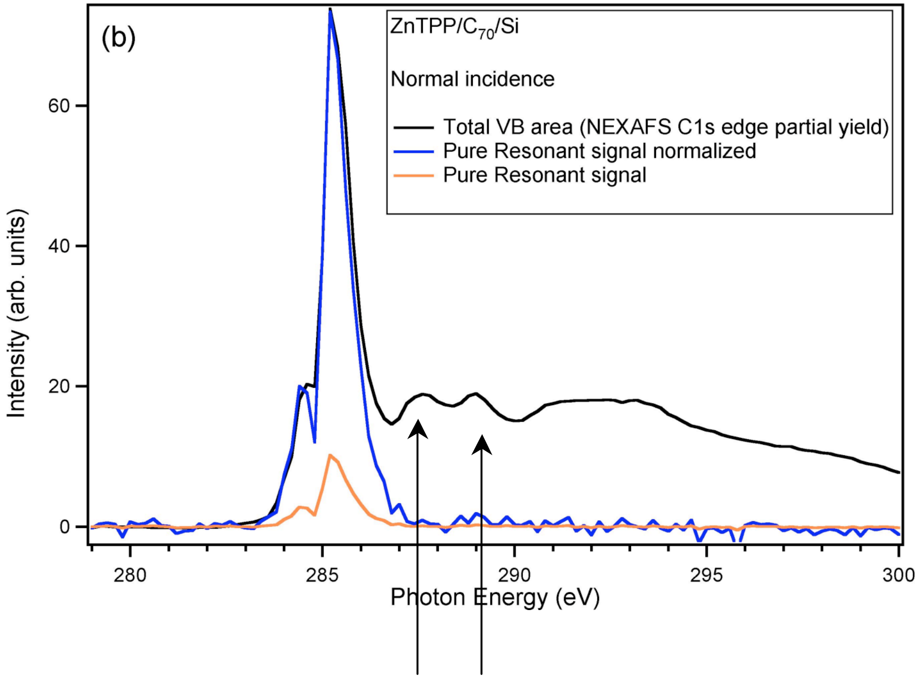


FIG. 3. (Color online) Resonant photoemission valence band spectra collected at the Gd $4d \rightarrow 4f$ edge.



Resonant Photoemission: Charge transfer time scale





When excited to these states, C1s core electrons delocalize well before the core hole decay.

Remember: The the excited electron must remain localized on the same atom of the core hole for a time scale bigger or comparable to the core hole lifetime