The Abdus Salam
International Centre for Theoretical Physics

United Nations
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1936-31

Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications

7 - 25 April 2008

Angle Resolved photoemission:photoemission and the non-interacting electrons

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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, 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

The photoelectric effect

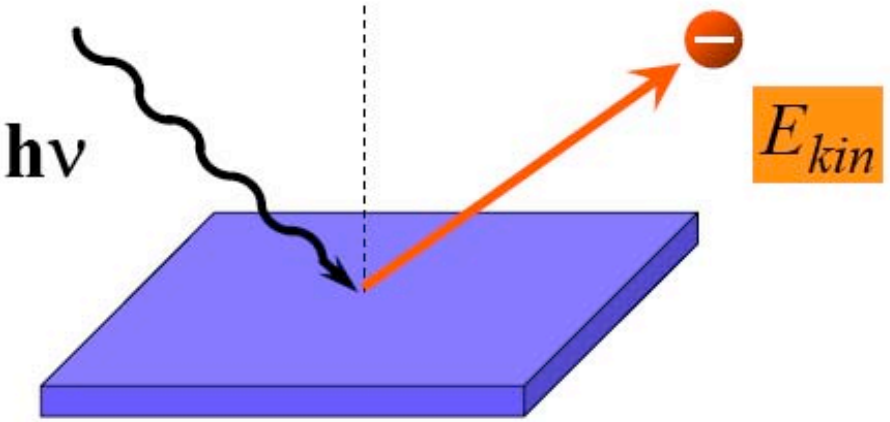
Theoretical explanation by A. Einstein (1905):
QUANTIZATION OF LIGHT

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

Die kinetische Energie solcher Elektronen ist

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

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

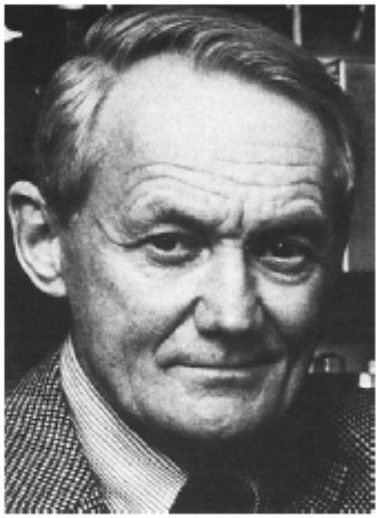


early experiments by:
- H. Hertz (1886)
- W. Hallwachs (1888)
- P. Lenard (1902)

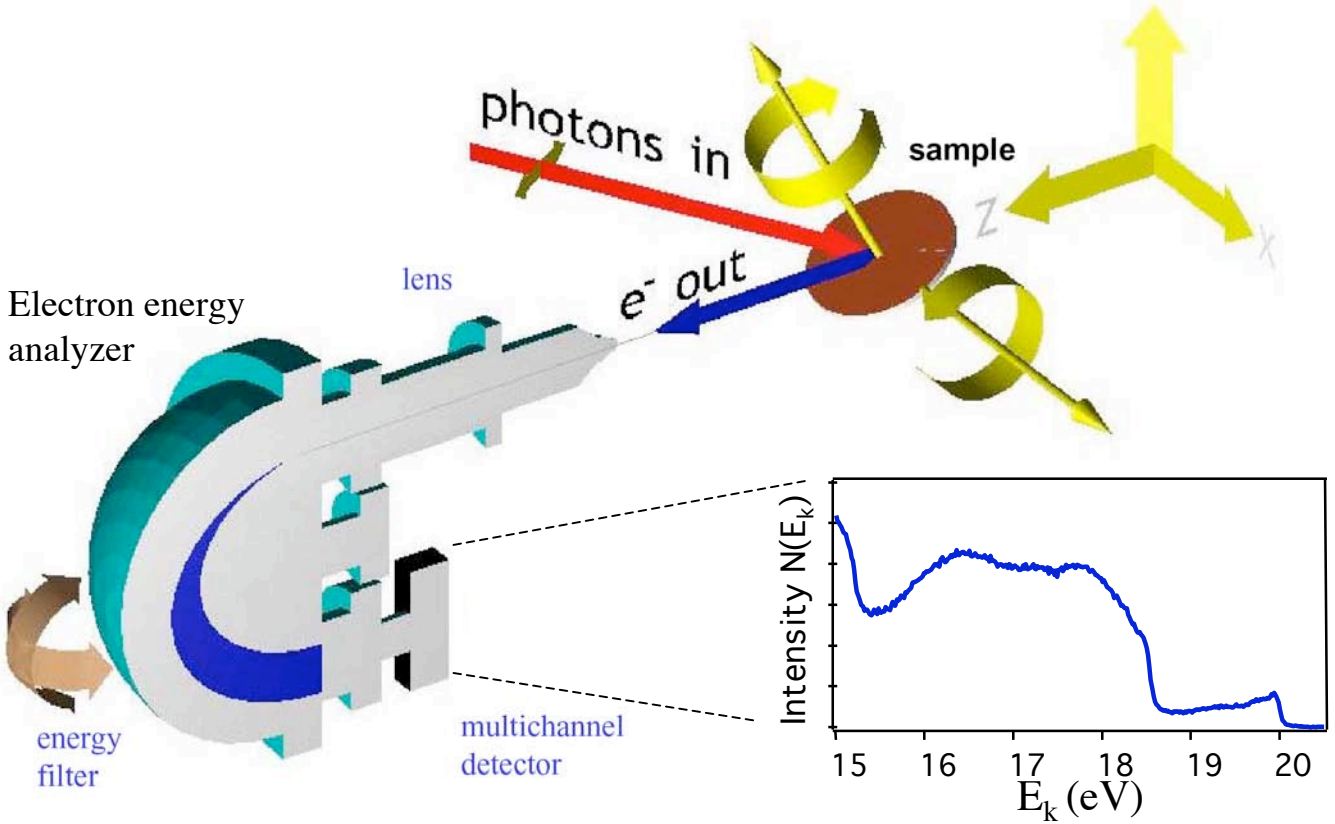
Photoelectron spectroscopy

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

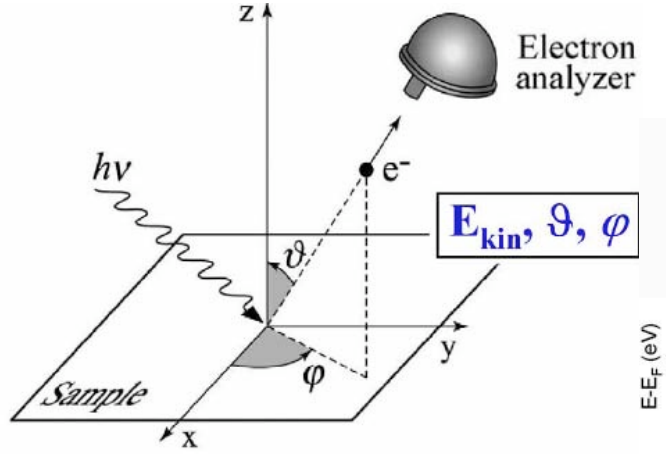


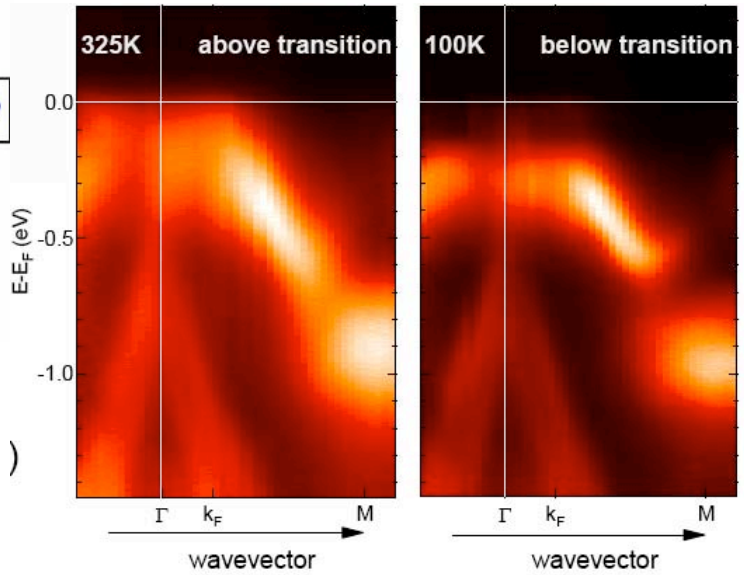
What kind of information carries a photoelectron ?

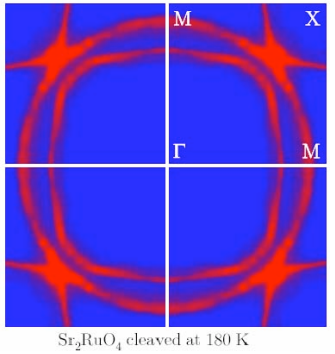
Angle-resolved photoemission is the most general tool for the investigation of the occupied band structure of solids. Band mapping based on direct transitions has been successfully applied to numerous material.

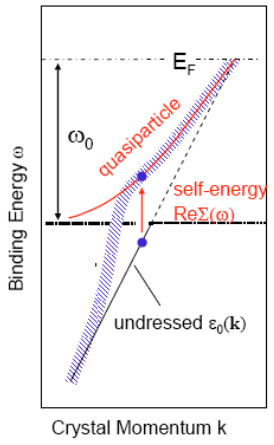
The momentum dependence of the quasi-particle peak lineshape along the Fermi surface is a very sensitive probe of all the scattering (many body) processes.

Spin, light polarization and temperature dependences give information on magnetic behaviour, symmetries, electron-boson interactions, phase transitions … and more …









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.

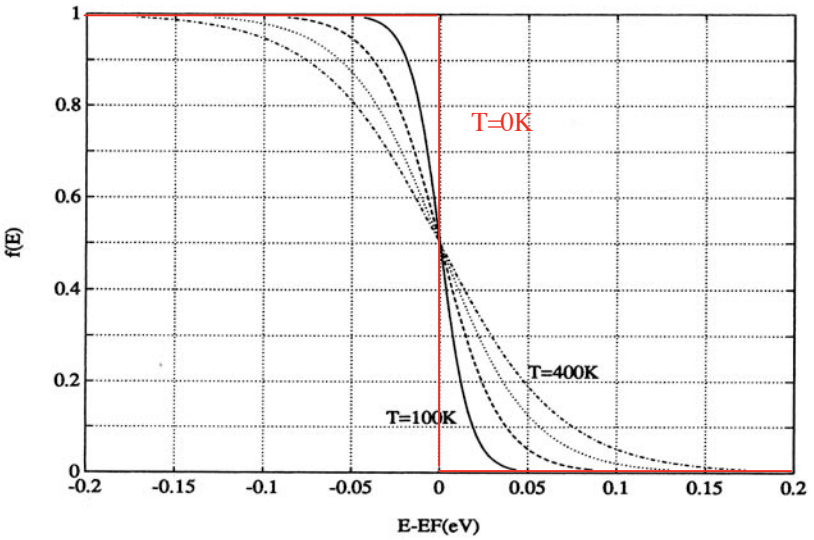
$$f(E) = \frac{1}{1 + e^{(E - E_F)/kT}}$$

E_F = Fermi energy or Fermi level

k = Boltzmann constant =

1.38×10^{-23} J/K = 8.6×10^{-5} eV/K

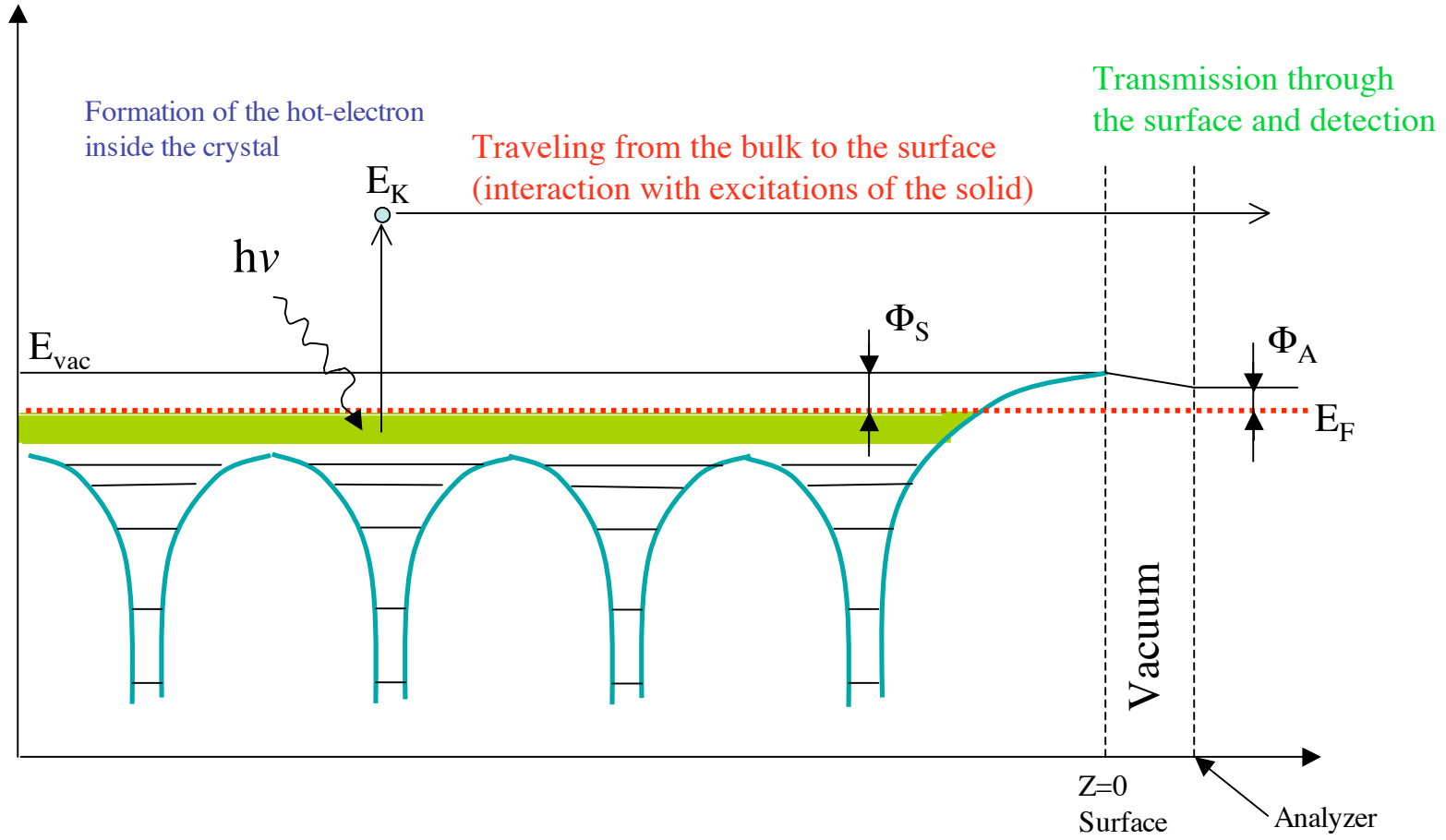
T = absolute temperature in K



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.



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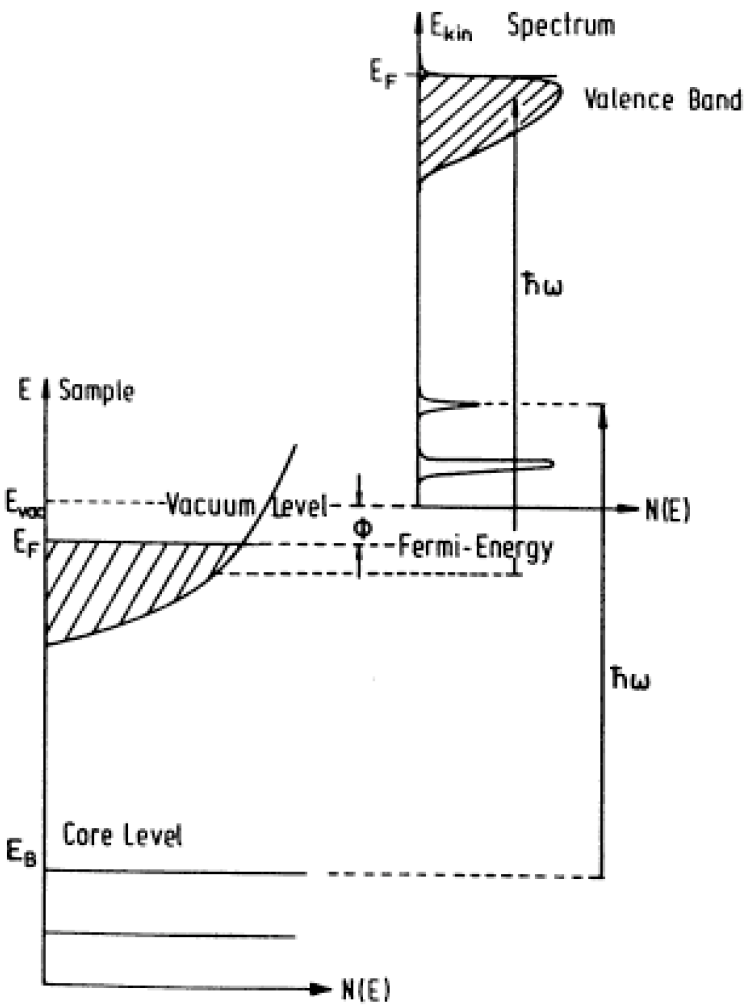
Photoexcitation process



Energy conservation

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

- E_{kin}: Measured Kinetic Energy
- $\hbar\omega$: Measureed Photon Energy
- Φ: Measured Work Function
- $|E_B|$: Electron Binding Energy

Photoexcitation process: Momentum conservation

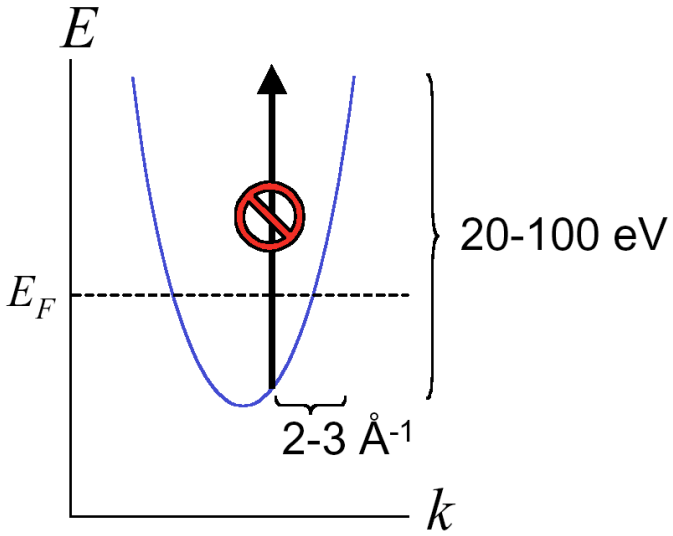
Photon Momentum $p = \hbar q = h/\lambda$

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

Typical photon wavenumber

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

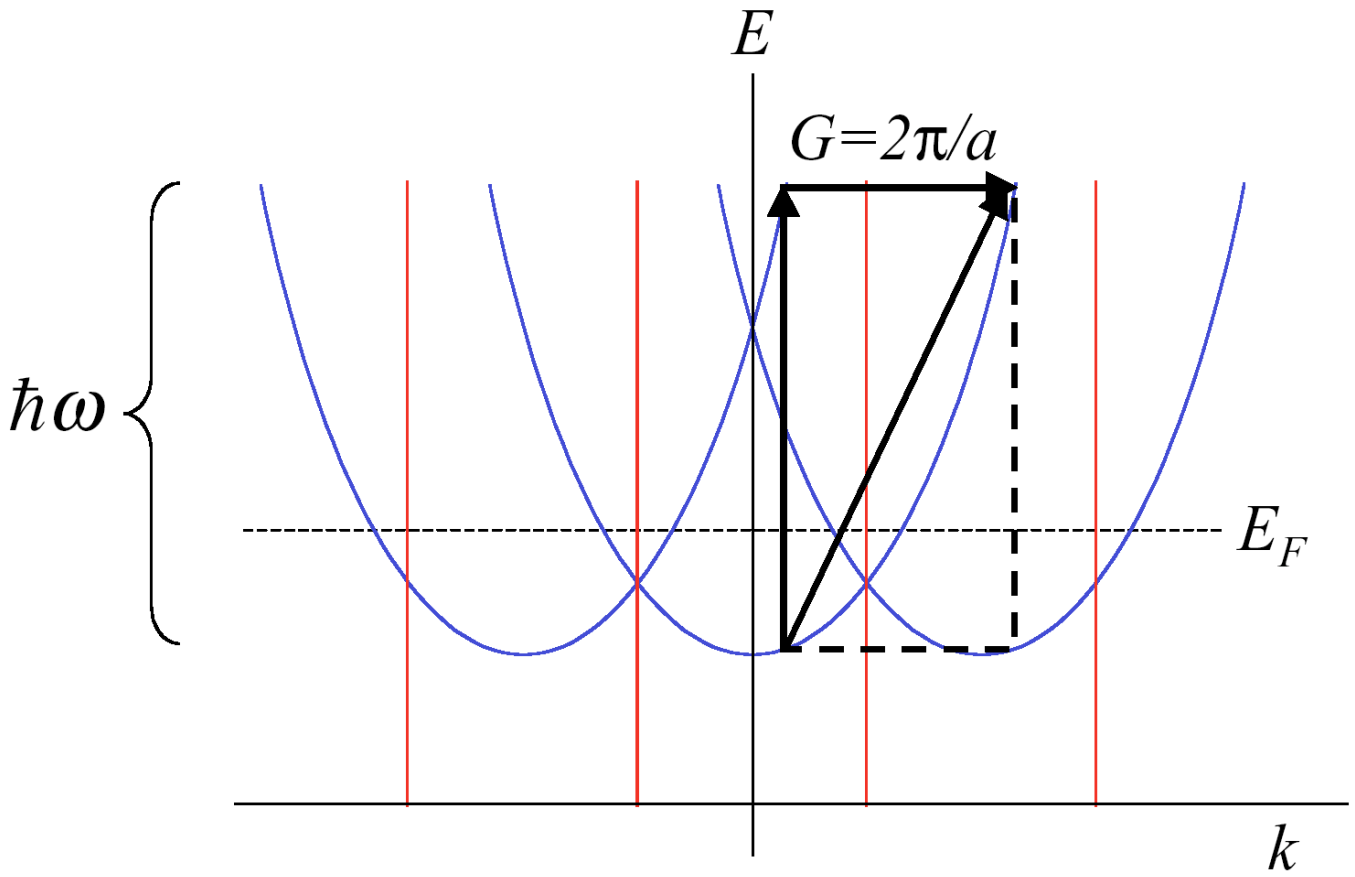
$$= .01 \text{ to } .05 \text{ Å}^{-1} \quad (\text{for } E = 20 \text{ to } 100 \text{ eV})$$



- **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).**

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.**

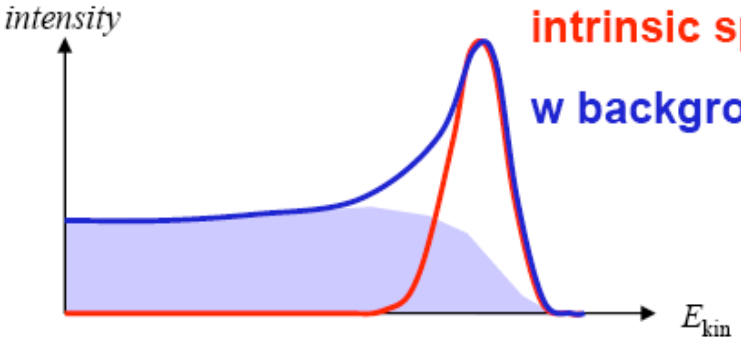


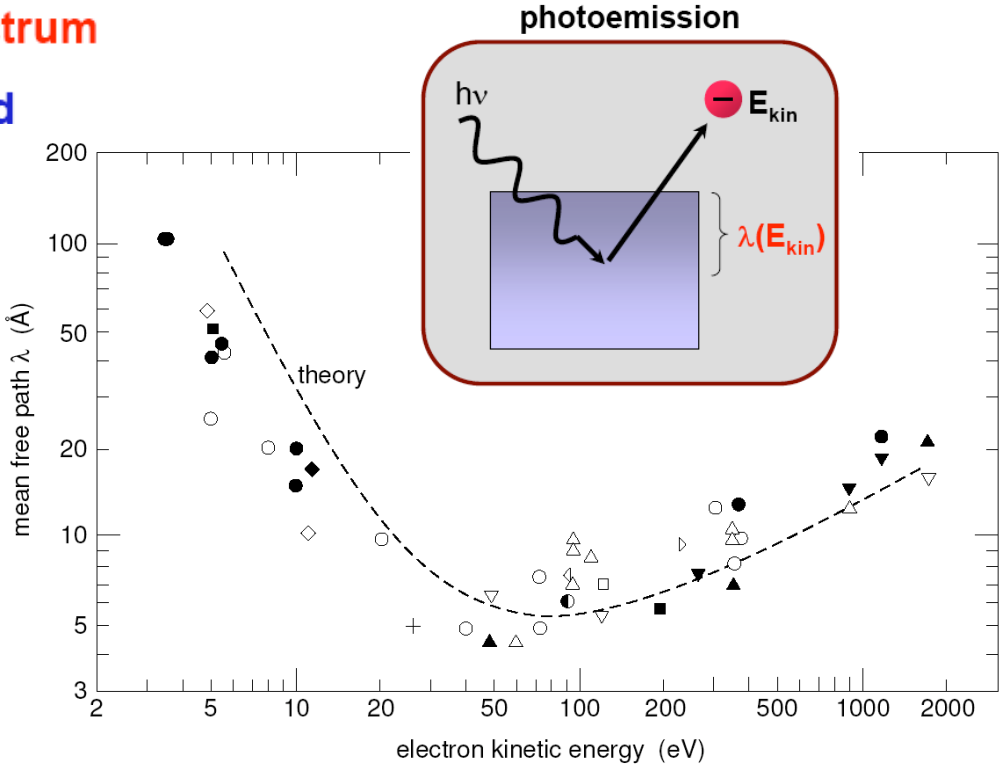
$E_f = E_i + h\nu$ & $\mathbf{k}_f = \mathbf{k}_i + \mathbf{G}$

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**

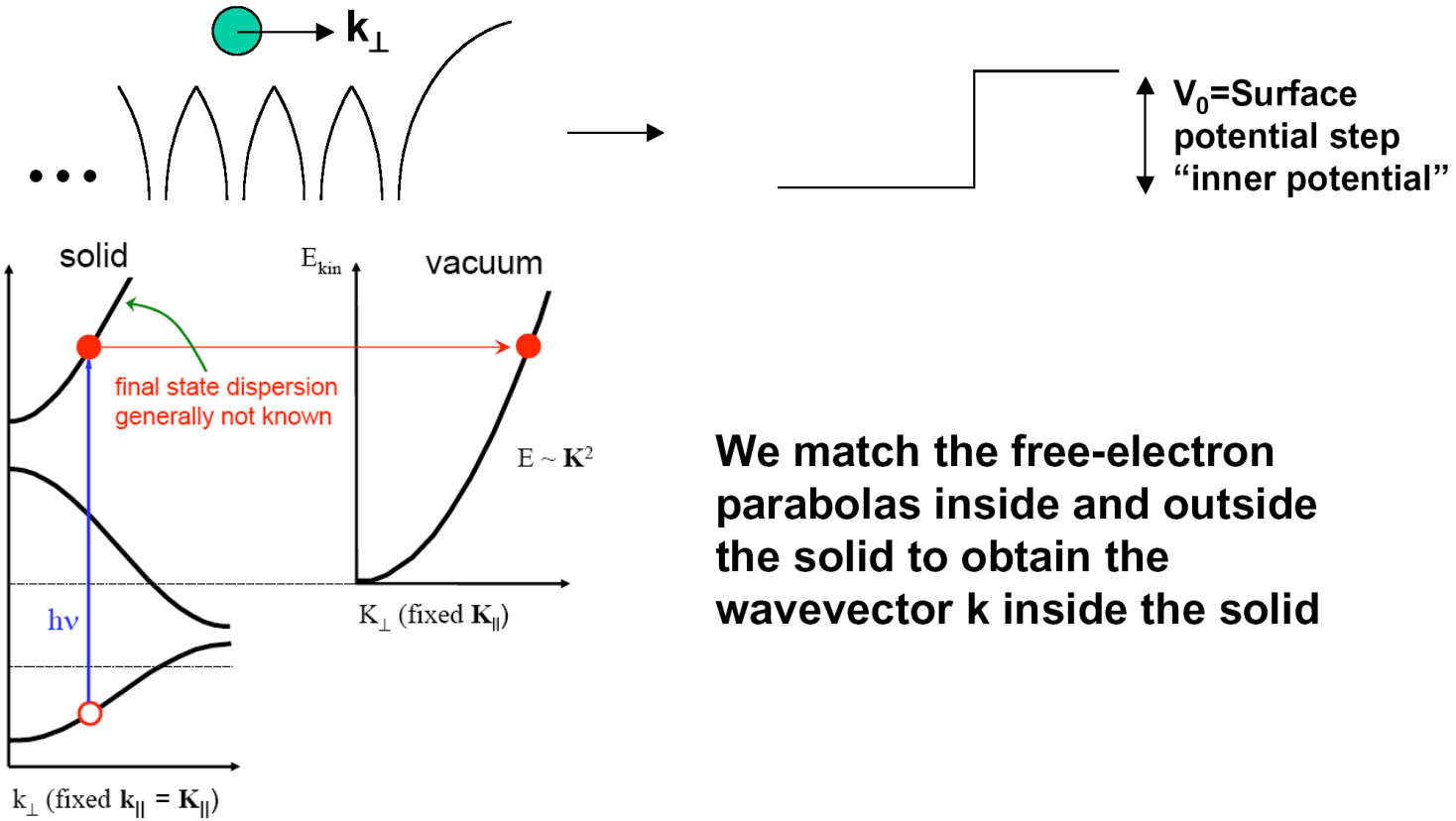




3 Transmission through the surface

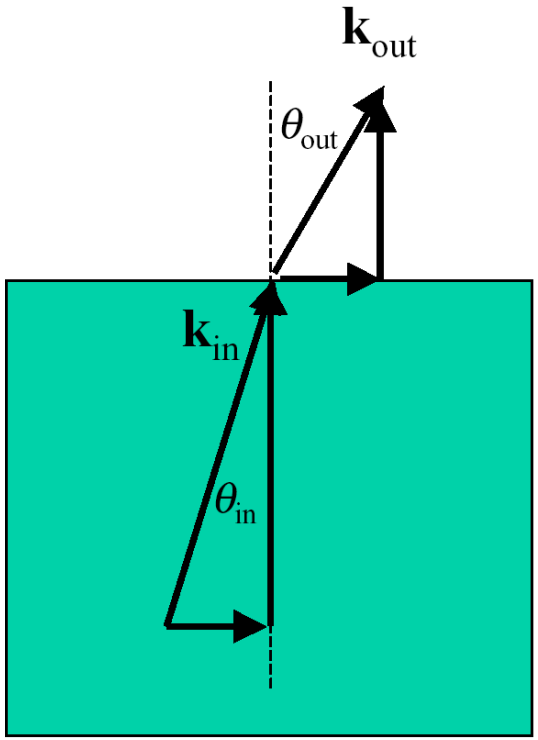
At the surface the crystal symmetry is conserved in the surface plane but is broken perpendicularly to the surface: the component of the electron momentum parallel to the surface plane ($k_{//}$) is conserved, but $k_{\perp}$ is not

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



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

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

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

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

"Snell's Law"

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

Critical angle for emission from bulk states

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

First important results:

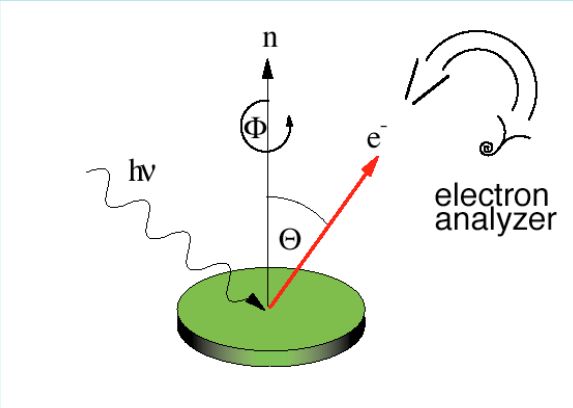
$$E_{kin}=h\nu-|E_B|-\phi_A$$

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

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



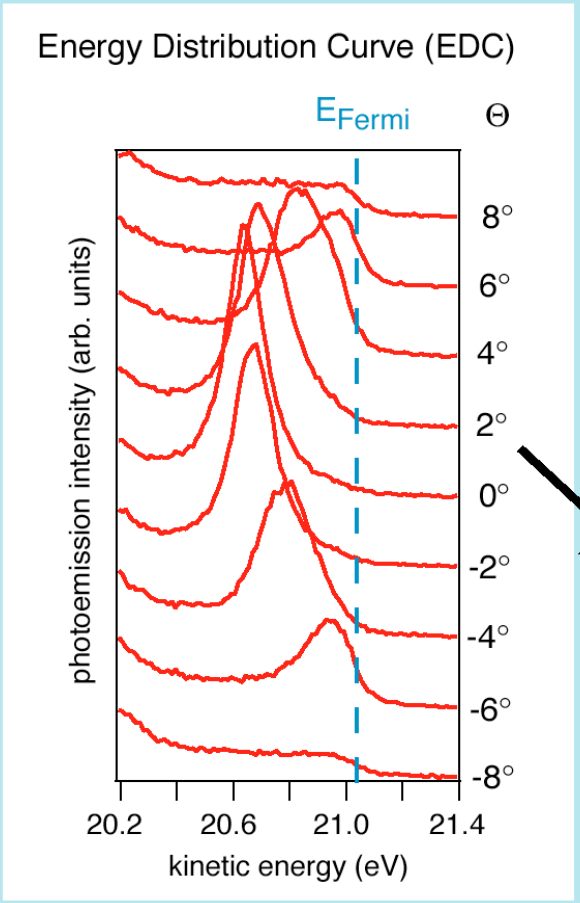
- measure E_{kin}, Θ, Φ.

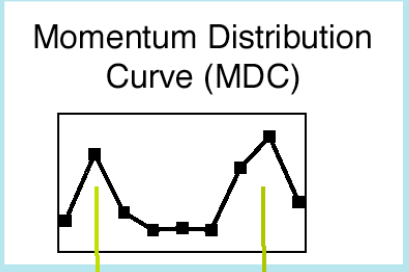
$$k_x = \sqrt{\frac{2m}{\hbar^2}} \sin\Theta \cos\Phi \sqrt{E_{kin}}$$

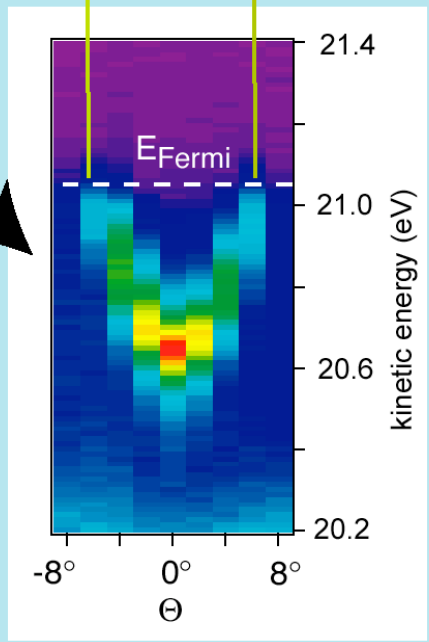
$$k_y = \sqrt{\frac{2m}{\hbar^2}} \sin\Theta \sin\Phi \sqrt{E_{kin}}$$

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

Example: Cu(111) surface state







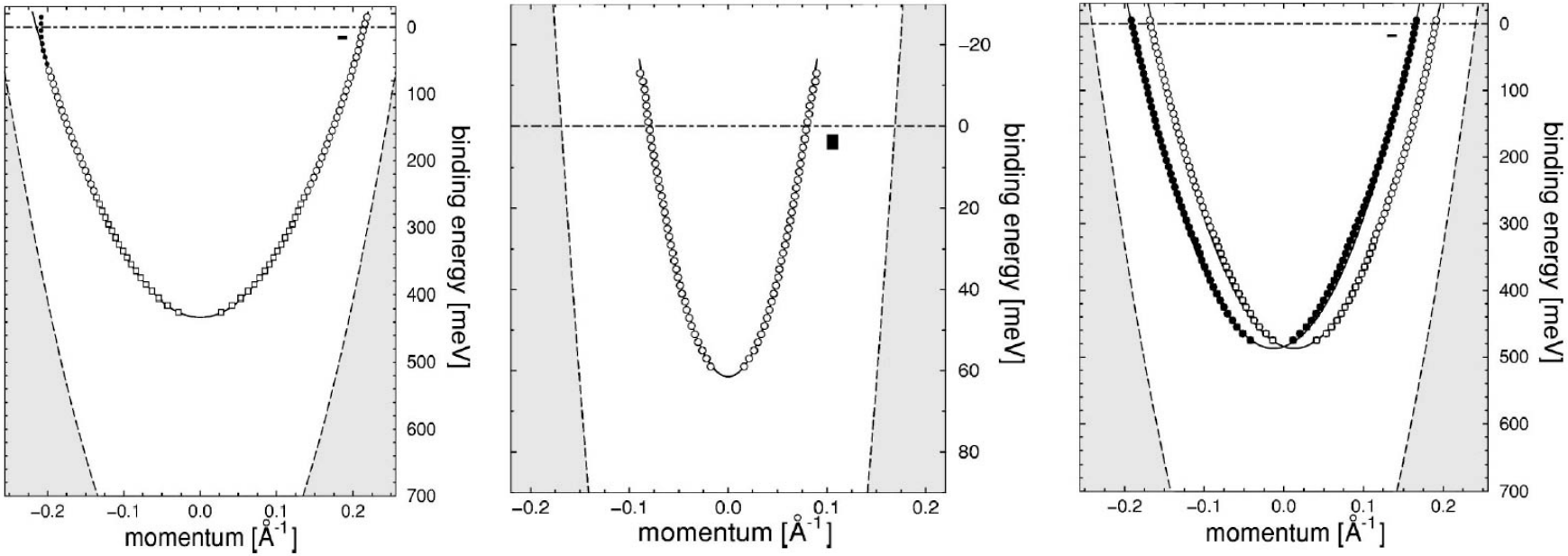
Courtesy of Ph. Hofmann

Shockley Surface States of Nobel Metal (111) Surfaces

Cu(111)
Z=29

Ag(111)
Z=47

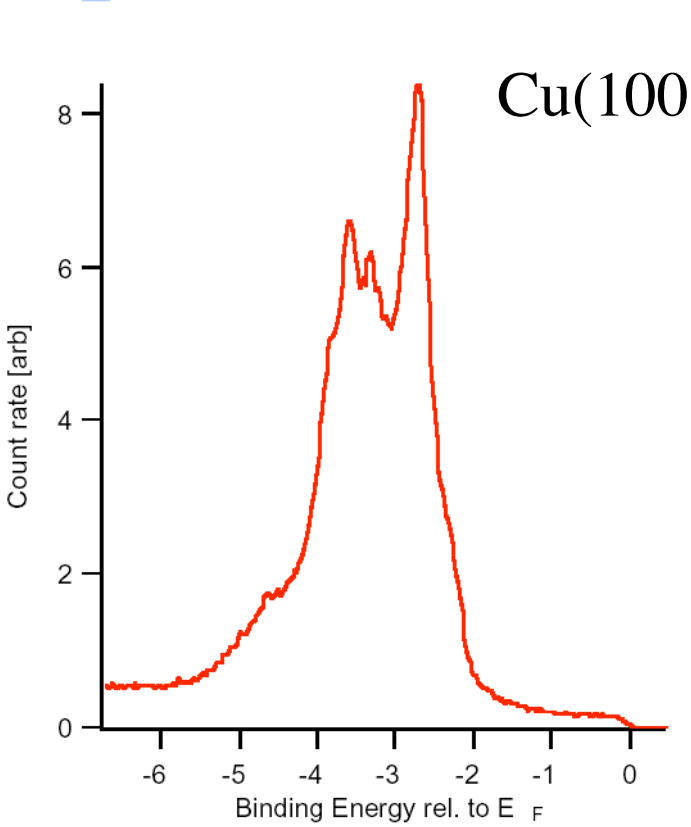
Au(111)
Z=79



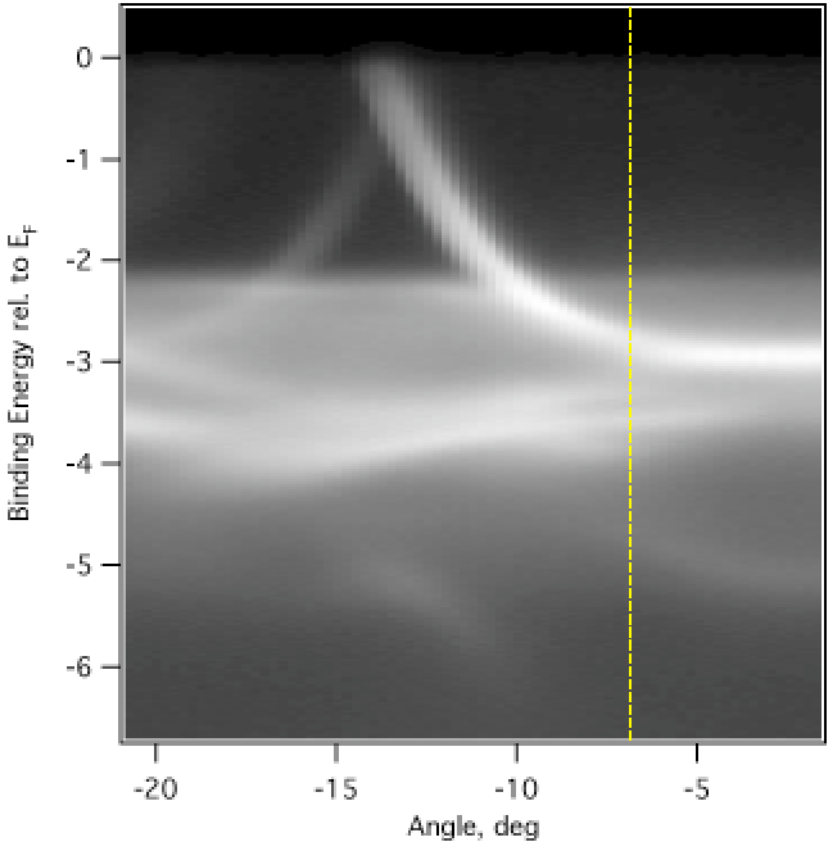
Two parabolas: spin-orbit splitting

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

How a photoemission spectrum looks like in general?

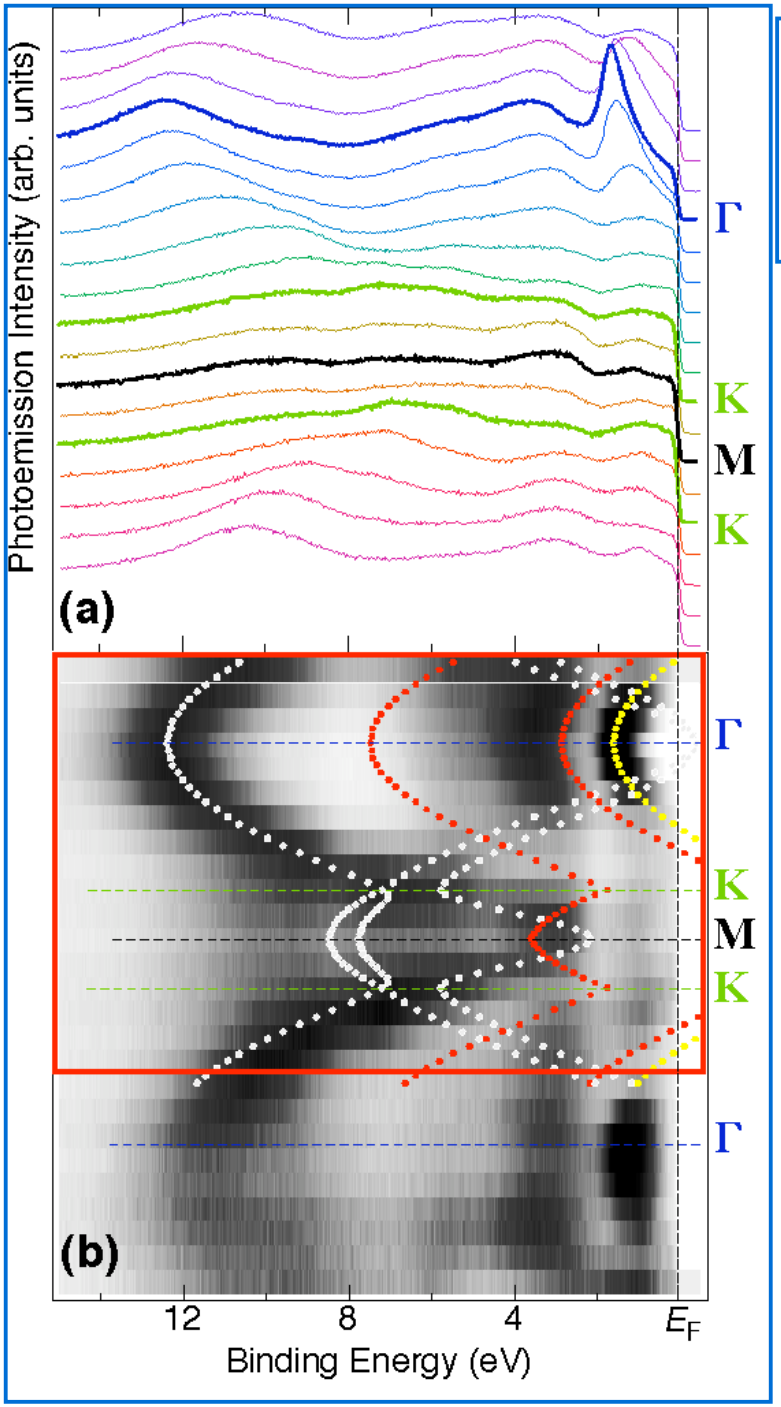


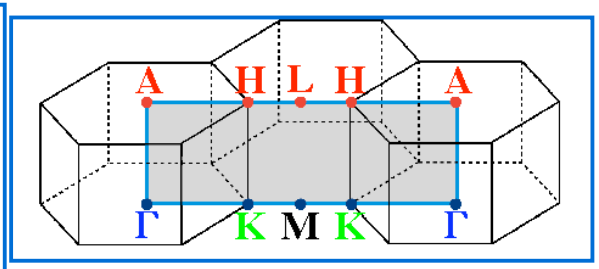
A spectrum at a single polar angle

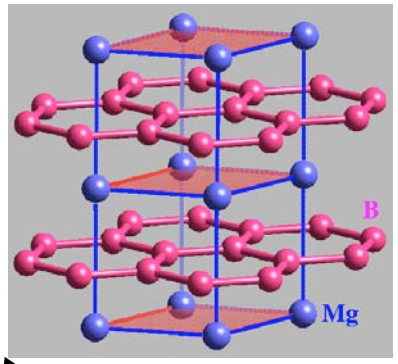


Accumulate spectra as the angle is scanned

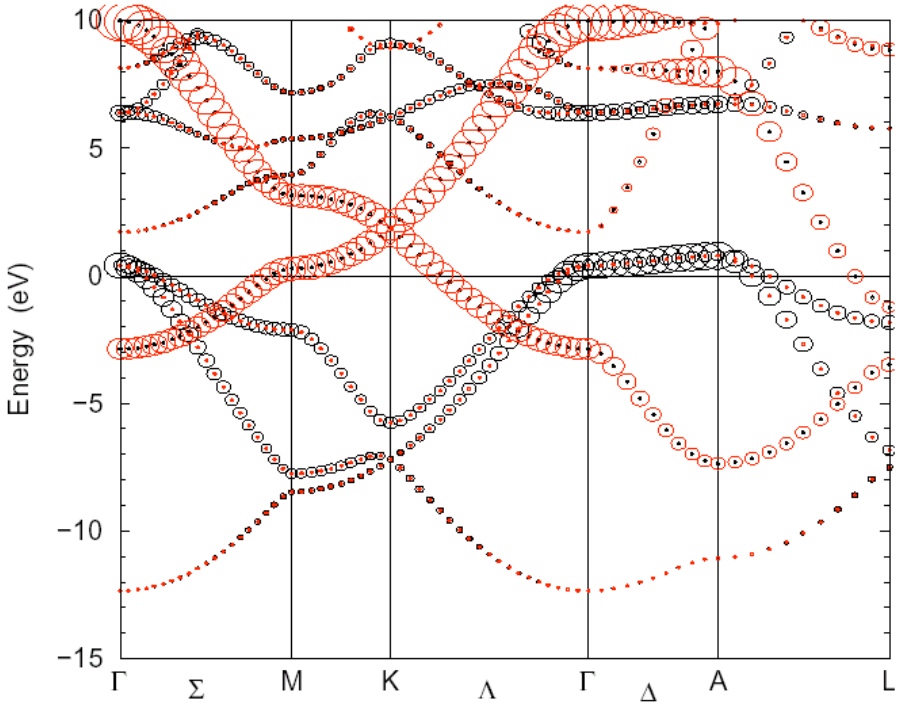
Bulk or surface states? Why bulk bands are quite sharp anyway?







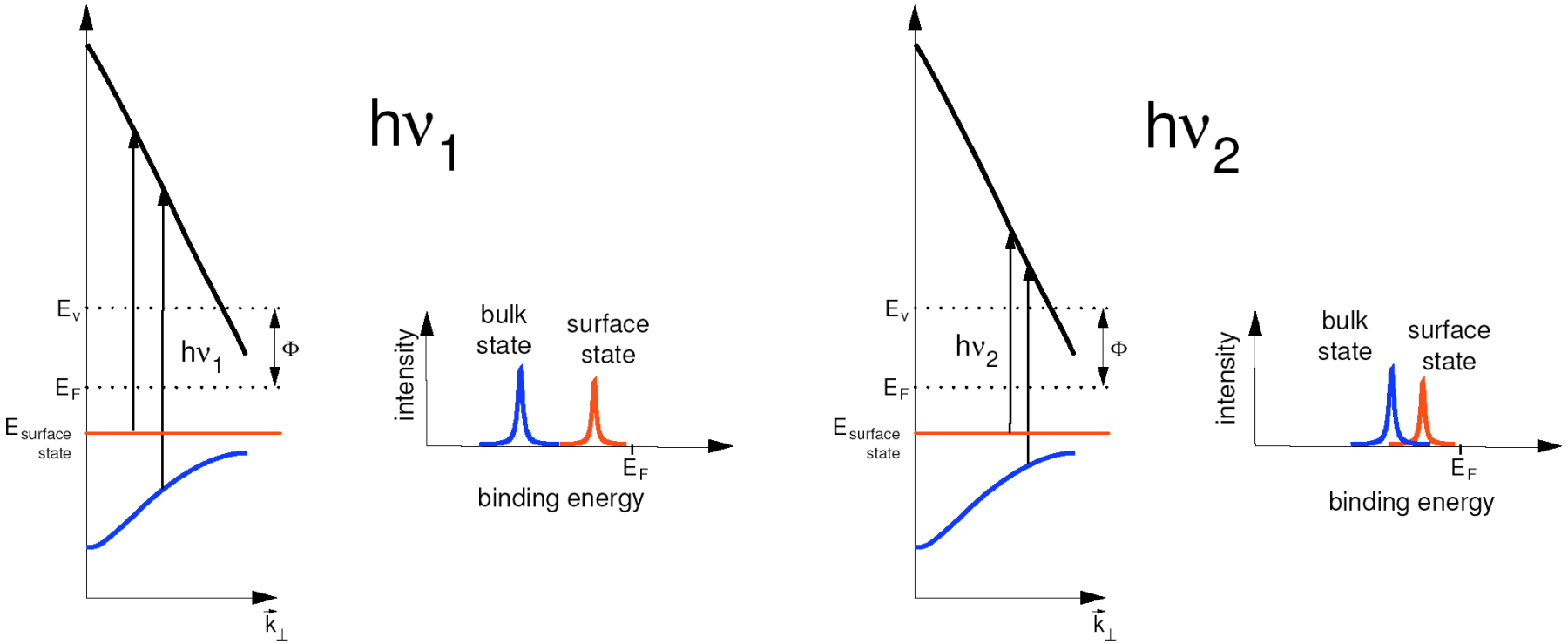
MgB_2



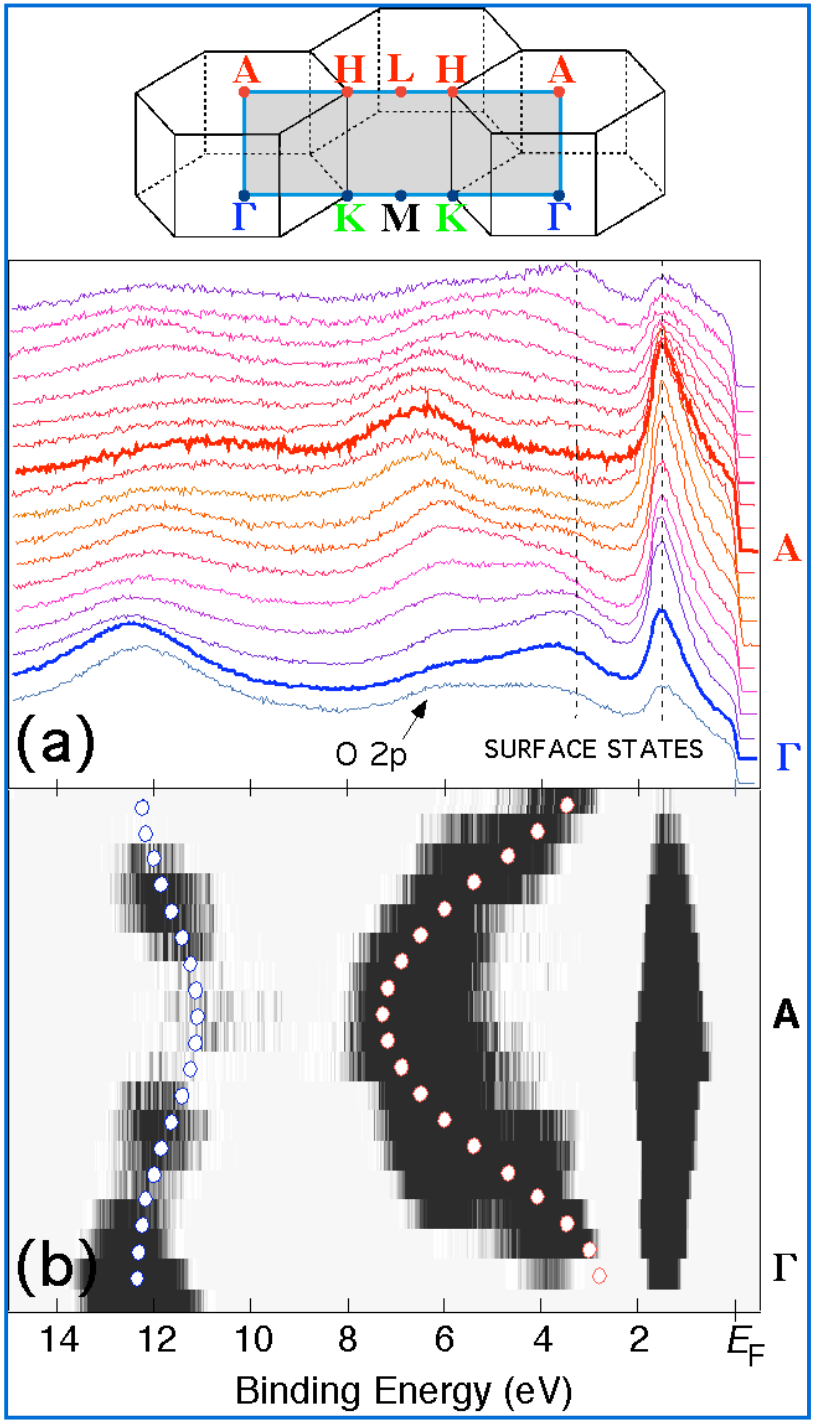
Photon energy: 105eV (ΔE≈50meV)
in-plane dispersion along Γ– K – M– K – Γ

How we can recognize surface states from bulk bands?

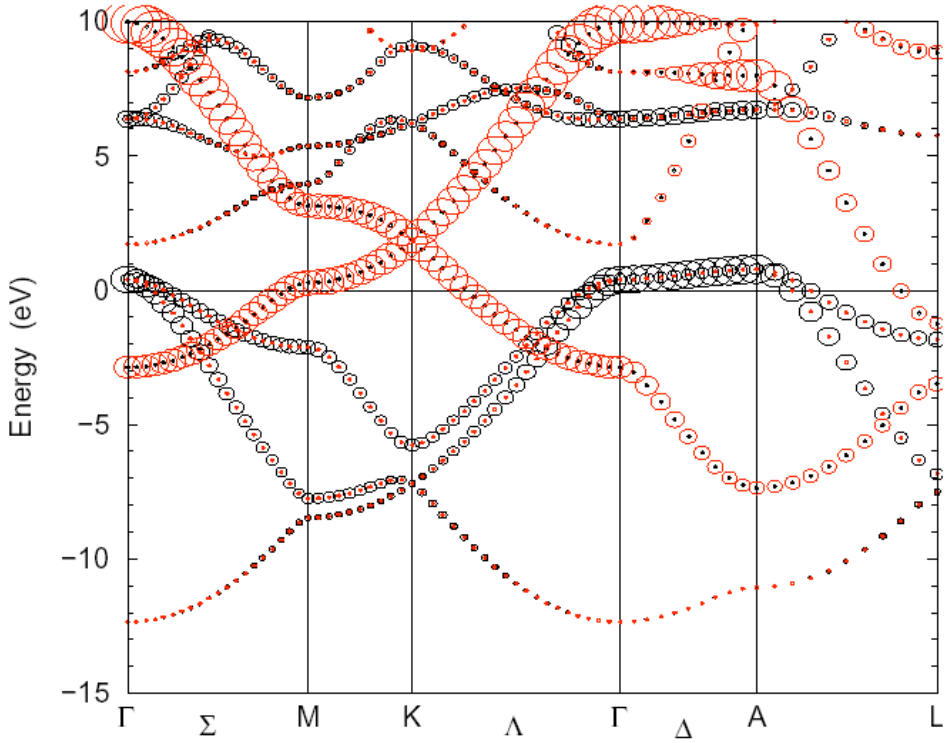
Simple: fix $\mathbf{k}_{//}$ and change $\mathbf{k}_{\perp}$. Bulk states should have dispersion, surface states should not.



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

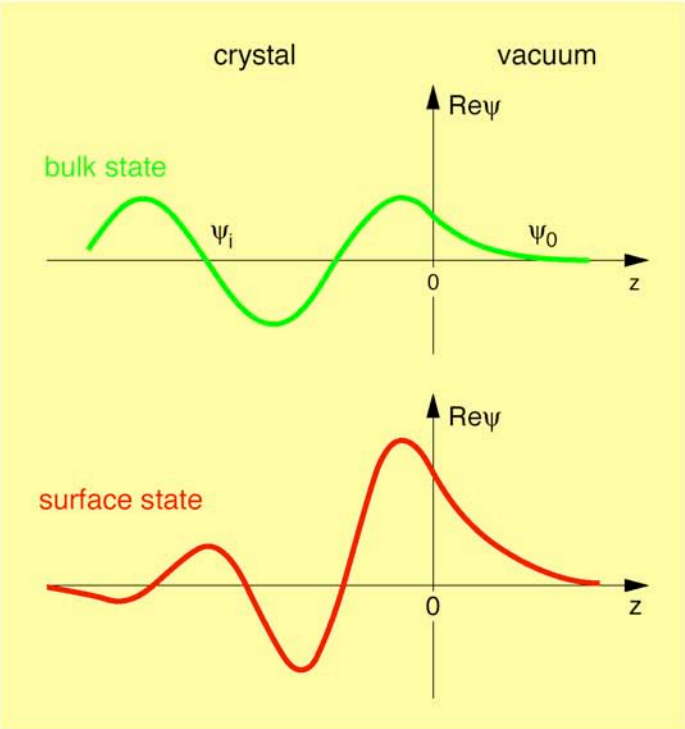
Normal emission geometry

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

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

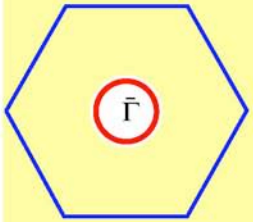
Weak no dispersive peak at 3.2 eV:
B terminated MgB_2(0001) surface state
(B terminated domains)

Electronic surface states: a simple picture

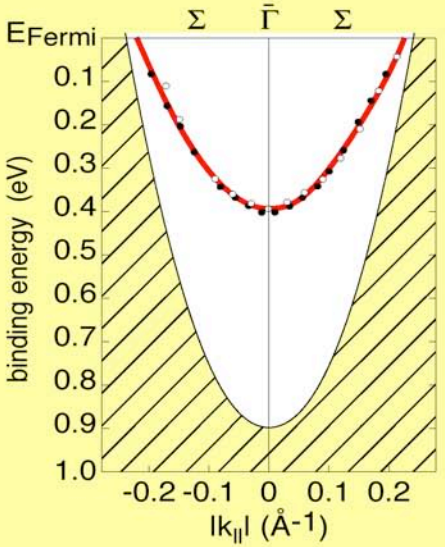


- new solutions of the Schrödinger equation at the surface
- exponential decay in bulk and vacuum
- described by two-dimensional wave number $k_{||}$

Example: surface state on Cu(111)



surface Brillouin zone



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)

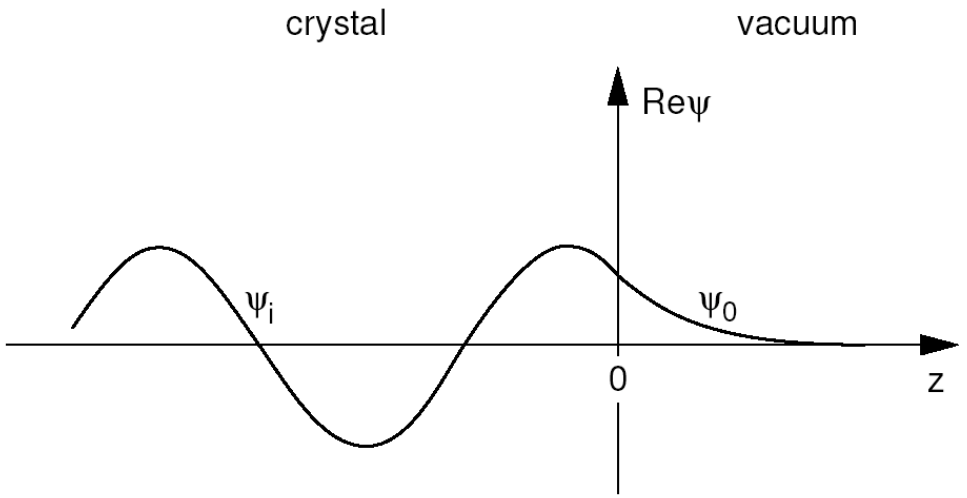
In the mathematical derivation of the Bloch theorem, nothing requires k to be a real number (**k** is real only in the approx. of an infinite crystal: Born-von Karman boundary conditions)**.** In general **k** can be a complex number, so there are solution also in the form:

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

$$\psi_k(r) = [u(r)e^{iRe(k)r}]e^{-Im(k)r}$$

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**



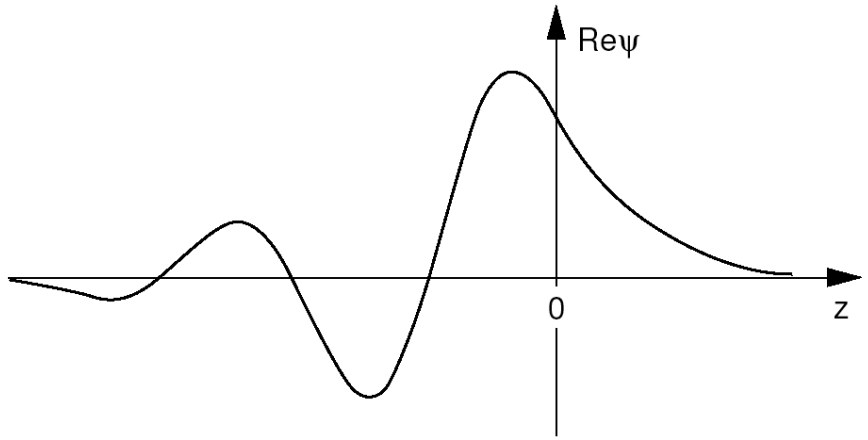
The form of the surface wave functions

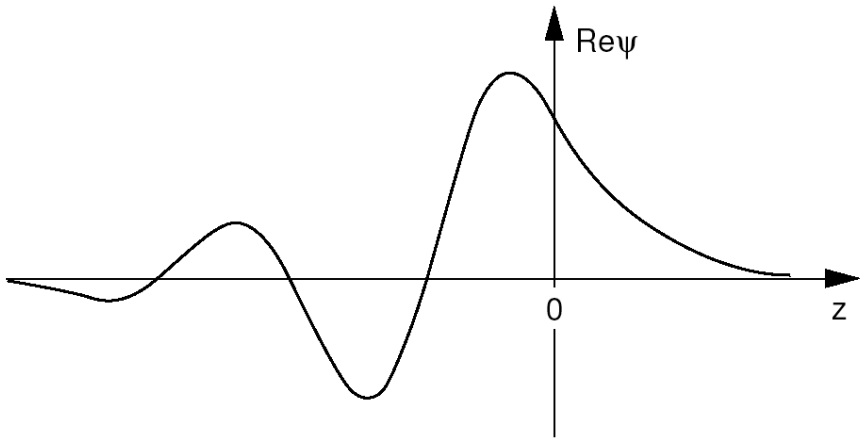
The wave functions at the surface do obey to the crystal symmetry in the surface plane only, but not perpendicularly because in this direction the translational invariance (periodicity) is lost (vacuum on one side, bulk crystal on the other).

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

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

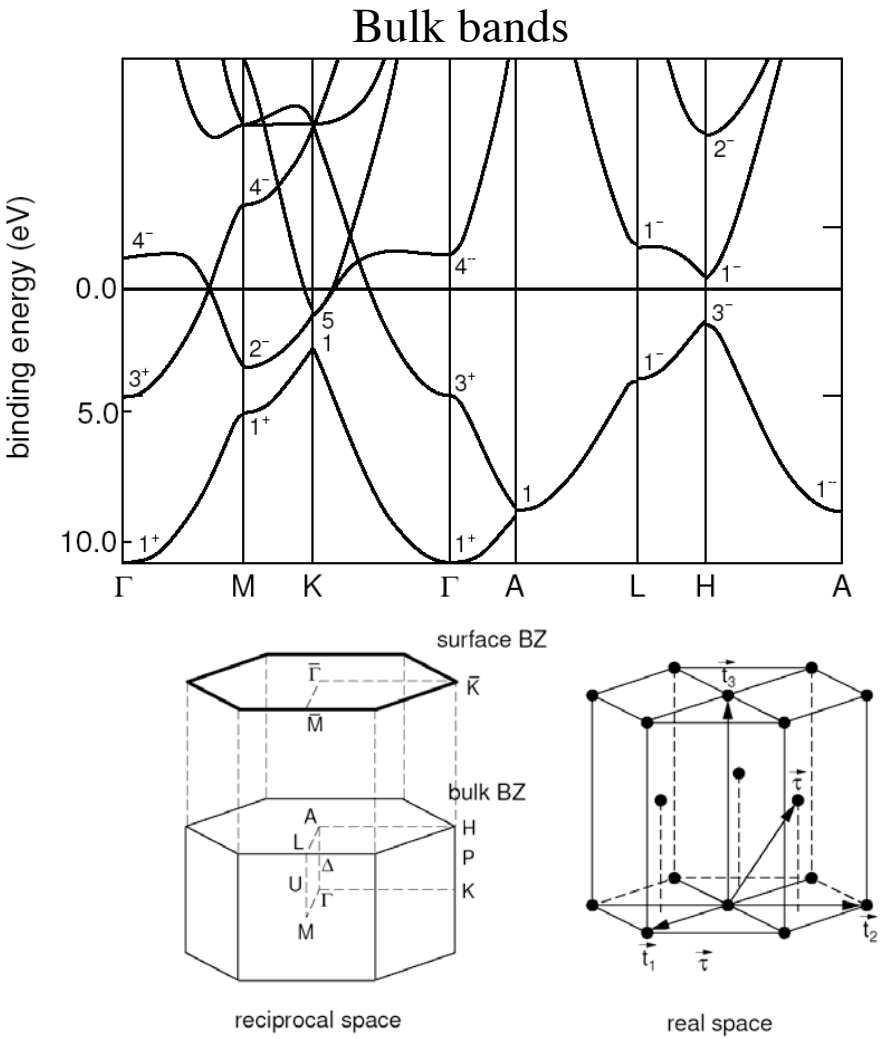
i.e. a periodic function modulated by an exponential decay from the surface into the bulk, which should then match an exponential decay function into the vacuum.

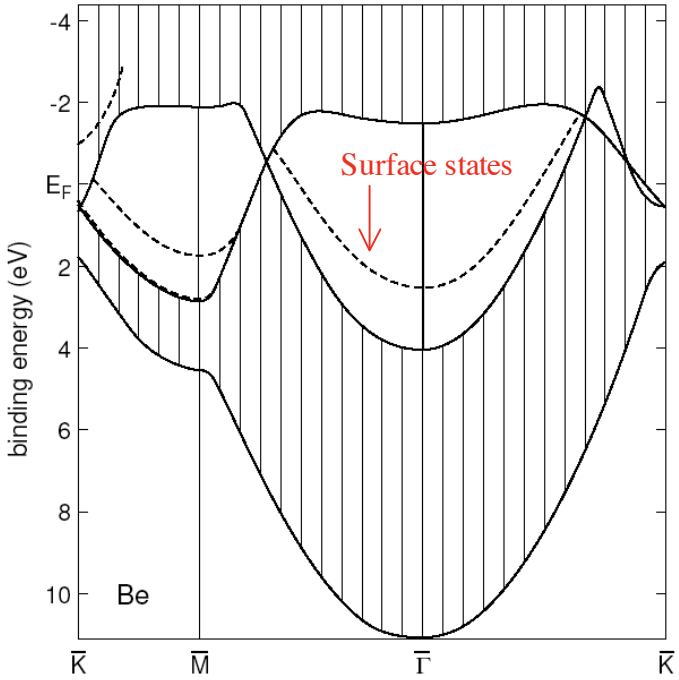




These states are characterized by the momentum $k_{//}$ and energy $E(k_{//})$. $K_{\perp}$ is no more a good quantum number. **True surface states cannot be degenerate with bulk states (i.e. for every $k_{\perp}$ there should not be any bulk state with the $k_{//}$ and $E(k_{//})$ of the surface state),**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



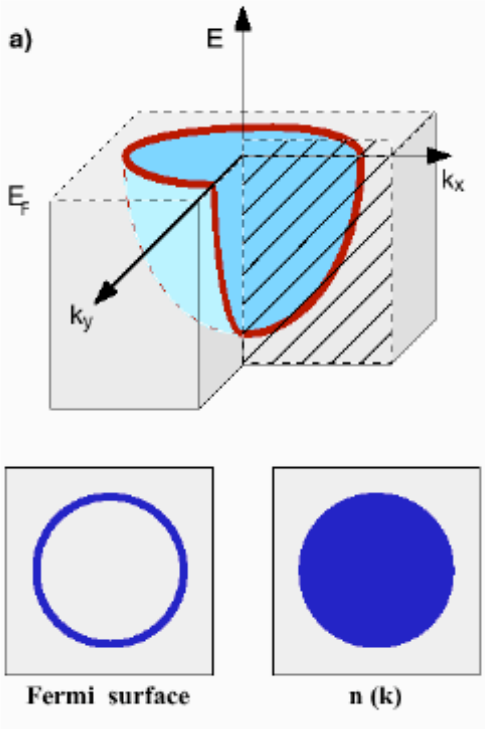


Projected bulk states on the (0001) surface BZ

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.

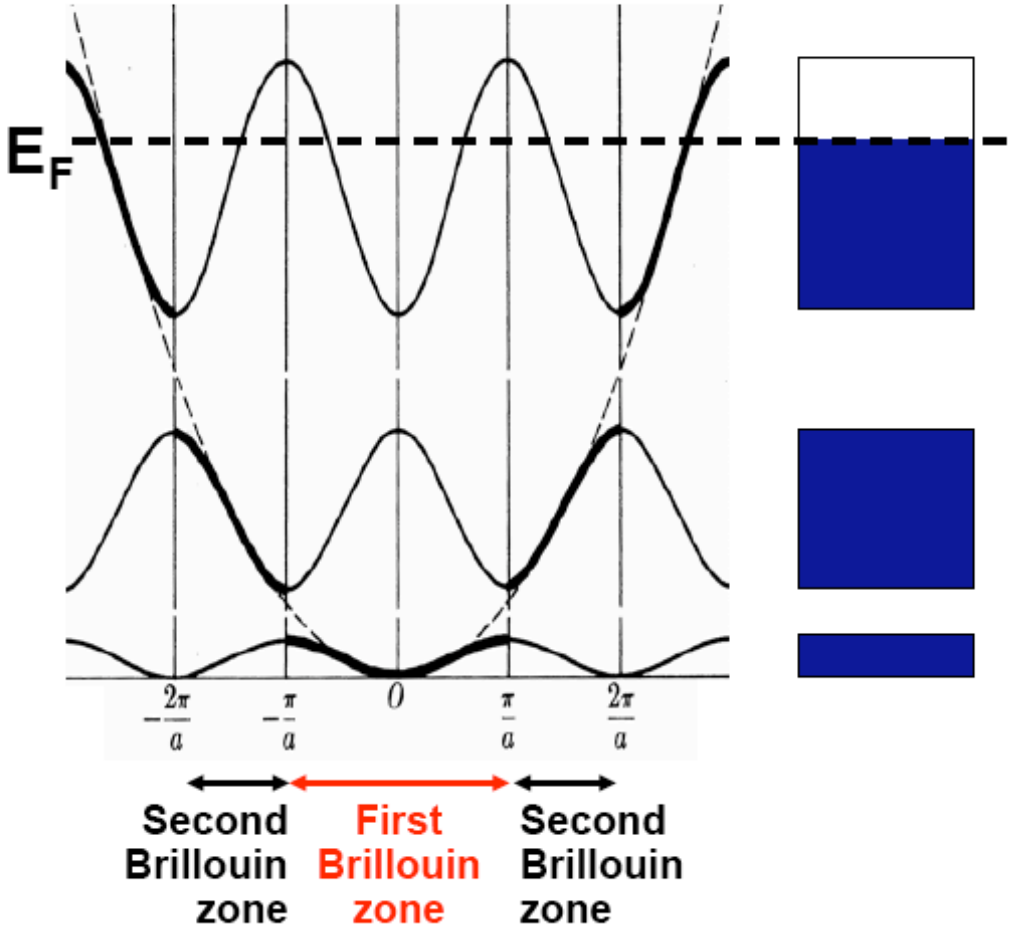
Understanding the Solid State: Electrons in Reciprocal Space

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



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



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:

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

Kinetic energy

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 $U(\mathbf{r}_i)=\Sigma_R\, U_0(\mathbf{R}-\mathbf{r}_i)$

Electron-electron Coulomb energy (many electrons problem)

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.

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

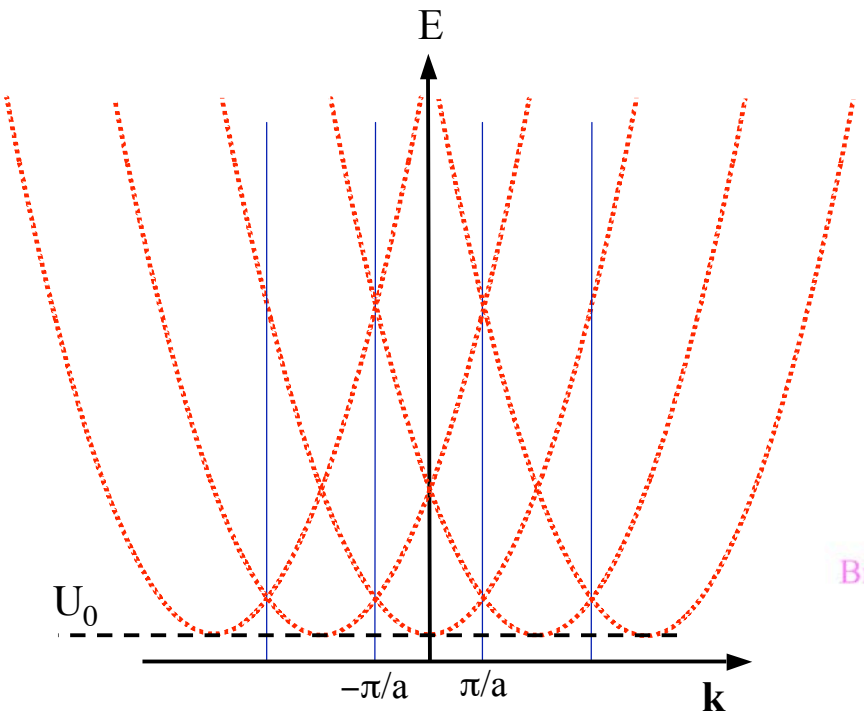
Solution: $$\varepsilon = \sum_i \frac{\hbar^2 k_i^2}{2m} + U_0$$

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

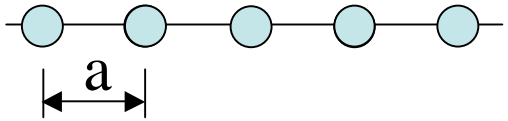
$$\phi_j(\bar{r}) = \frac{1}{\sqrt{V}} e^{i\bar{k}_j \cdot \bar{r}}$$

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

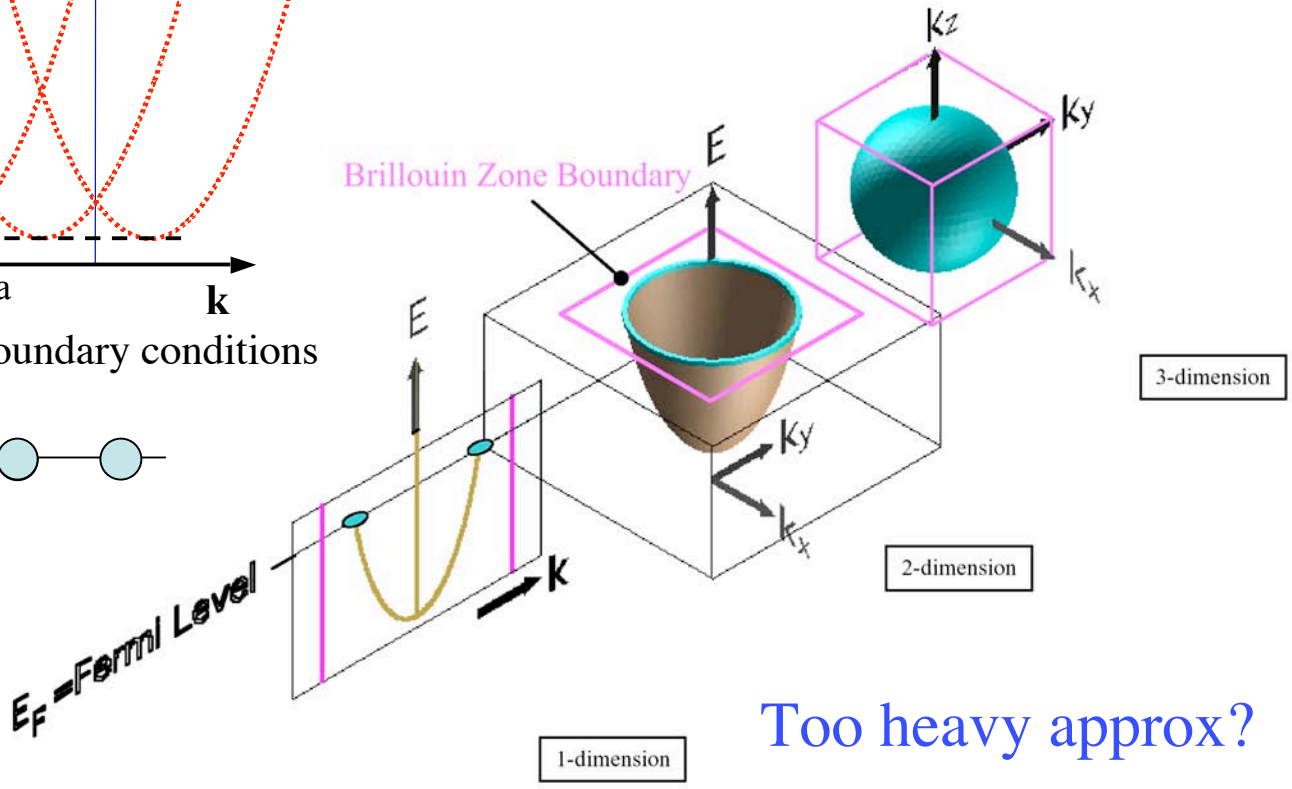


Concepts:

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

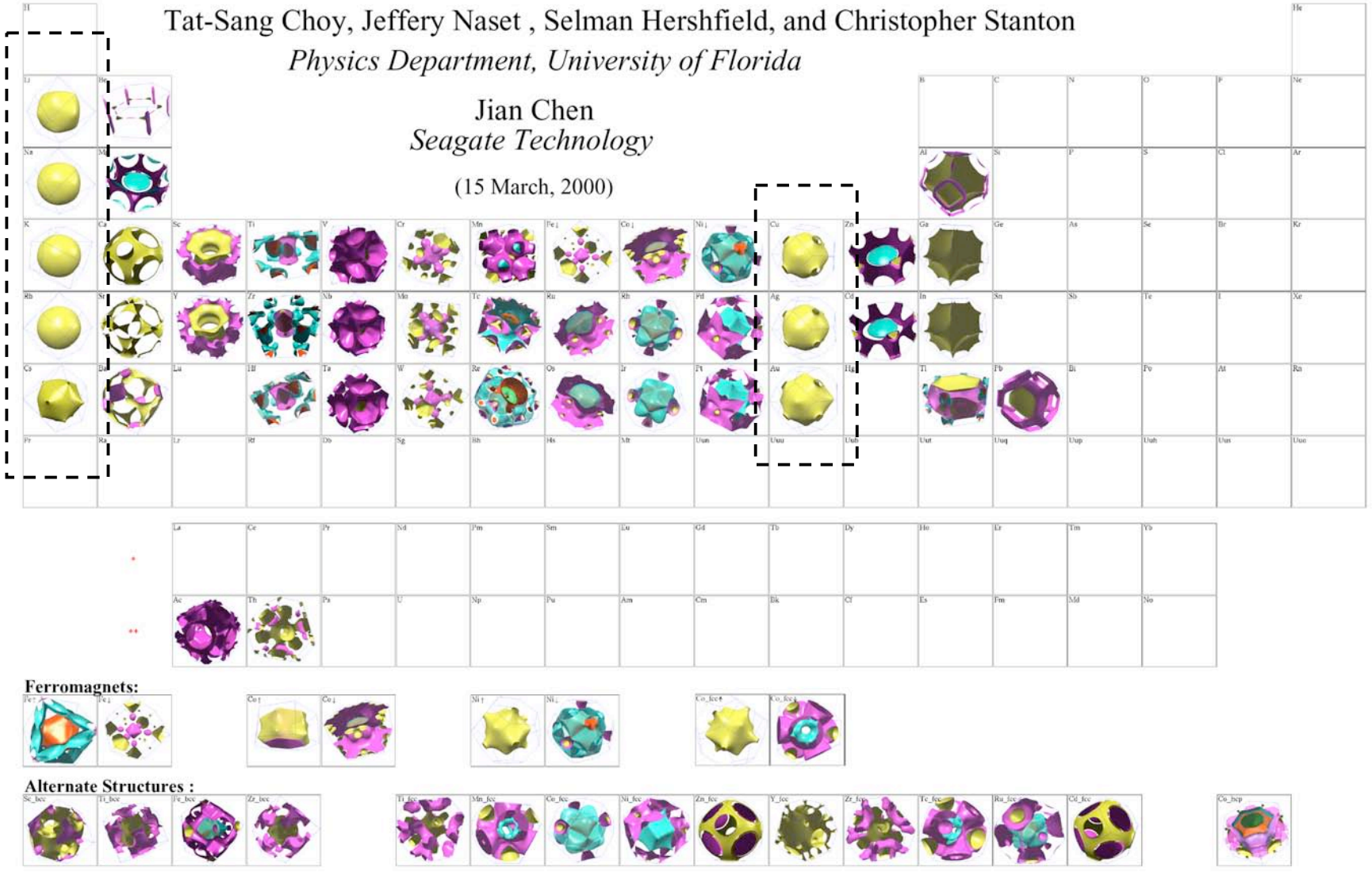
Tat-Sang Choy, Jeffery Naset , Selman Hershfield, and Christopher Stanton

Physics Department, University of Florida

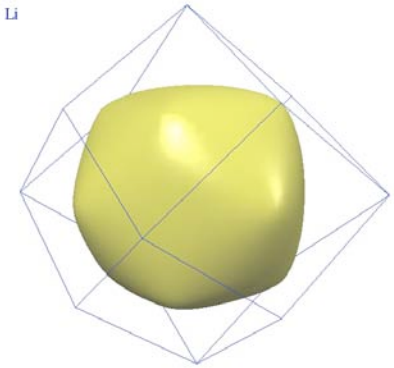
Jian Chen

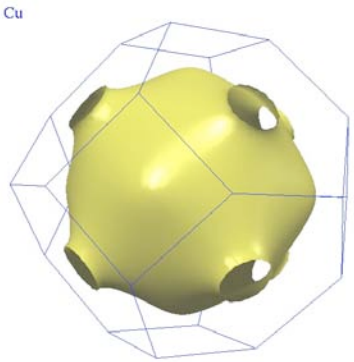
Seagate Technology

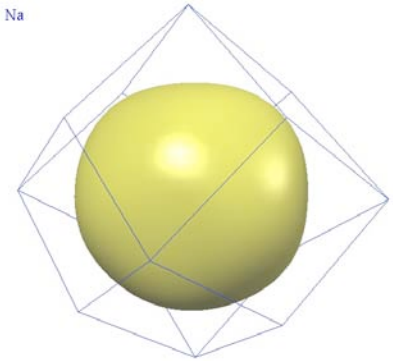
(15 March, 2000)

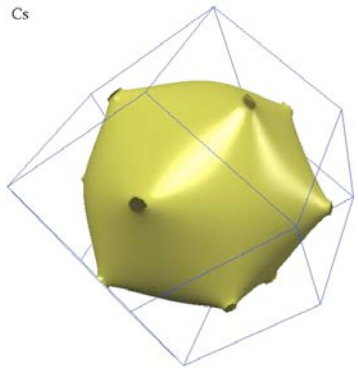


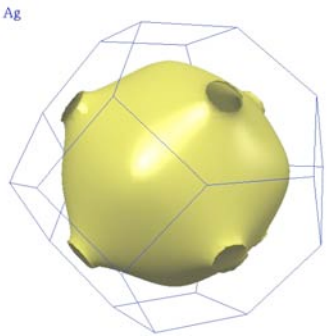
Alkali & noble metals (bcc) and (fcc)

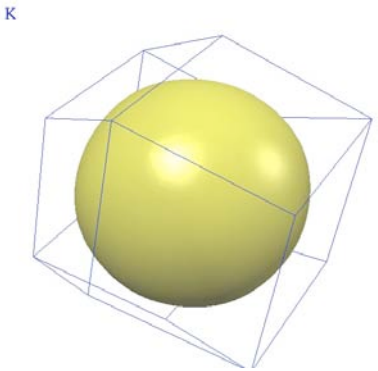


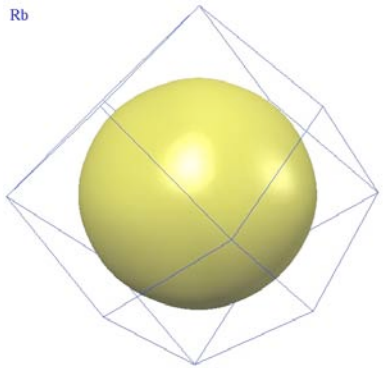


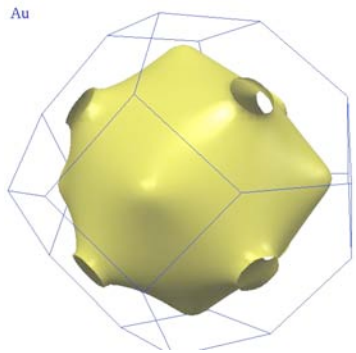












How to Determine Fermi Vectors by Angle-Resolved Photoemission

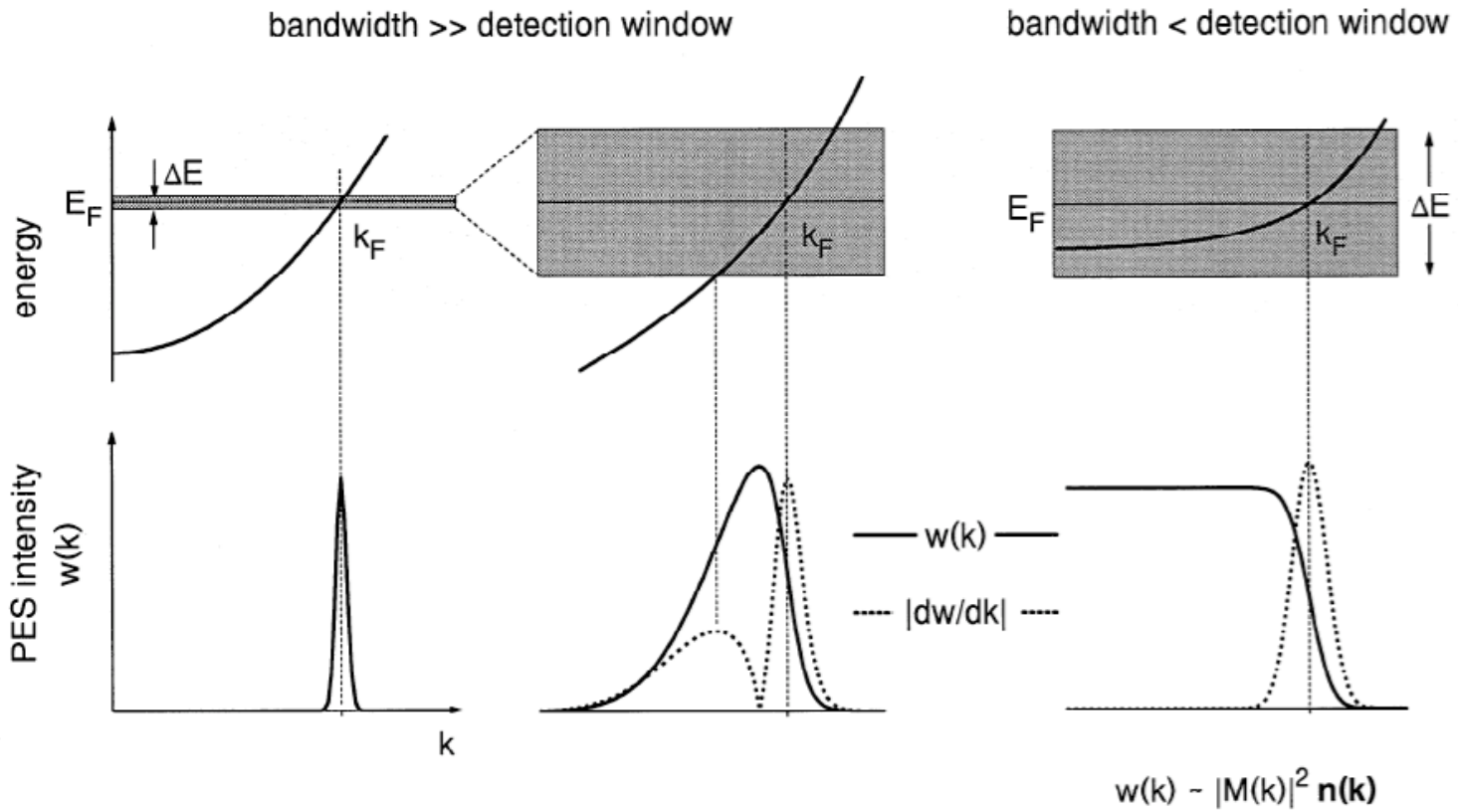
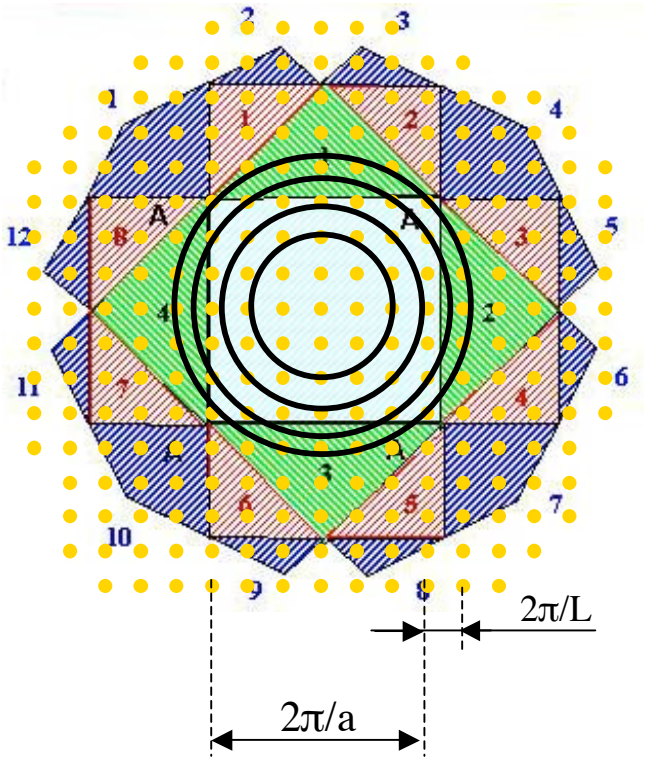


Fig. 8. Schematic behavior of the detected photoelectron intensity near a Fermi level crossing for wide band (left and center) and narrow band systems (right).



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

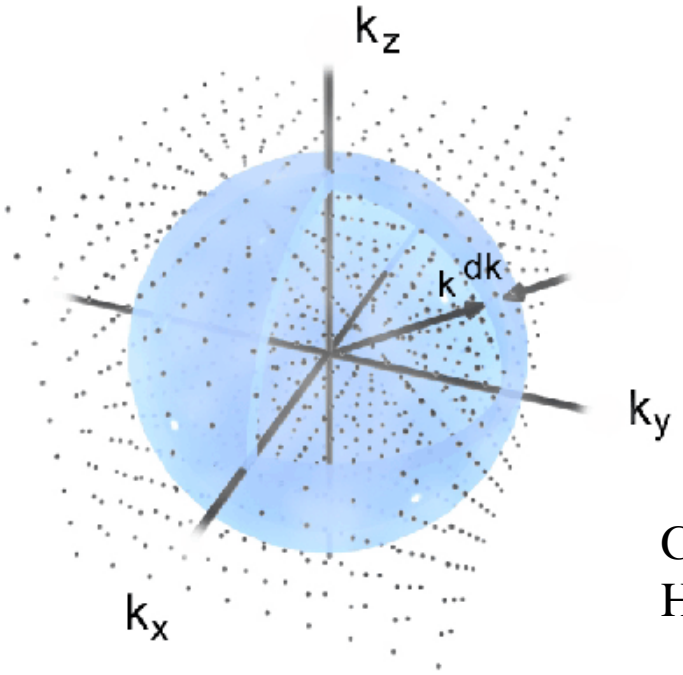
2D case

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

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

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

(Times 2 to account for the spin)



DENSITY OF STATES N(E)

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

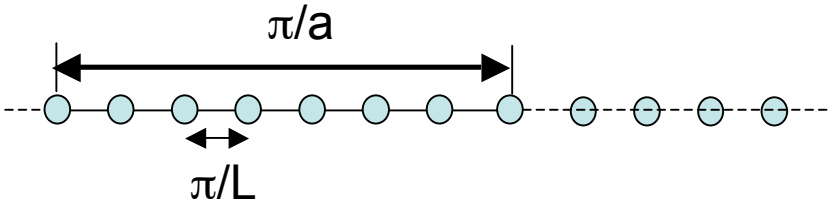
3D case

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?

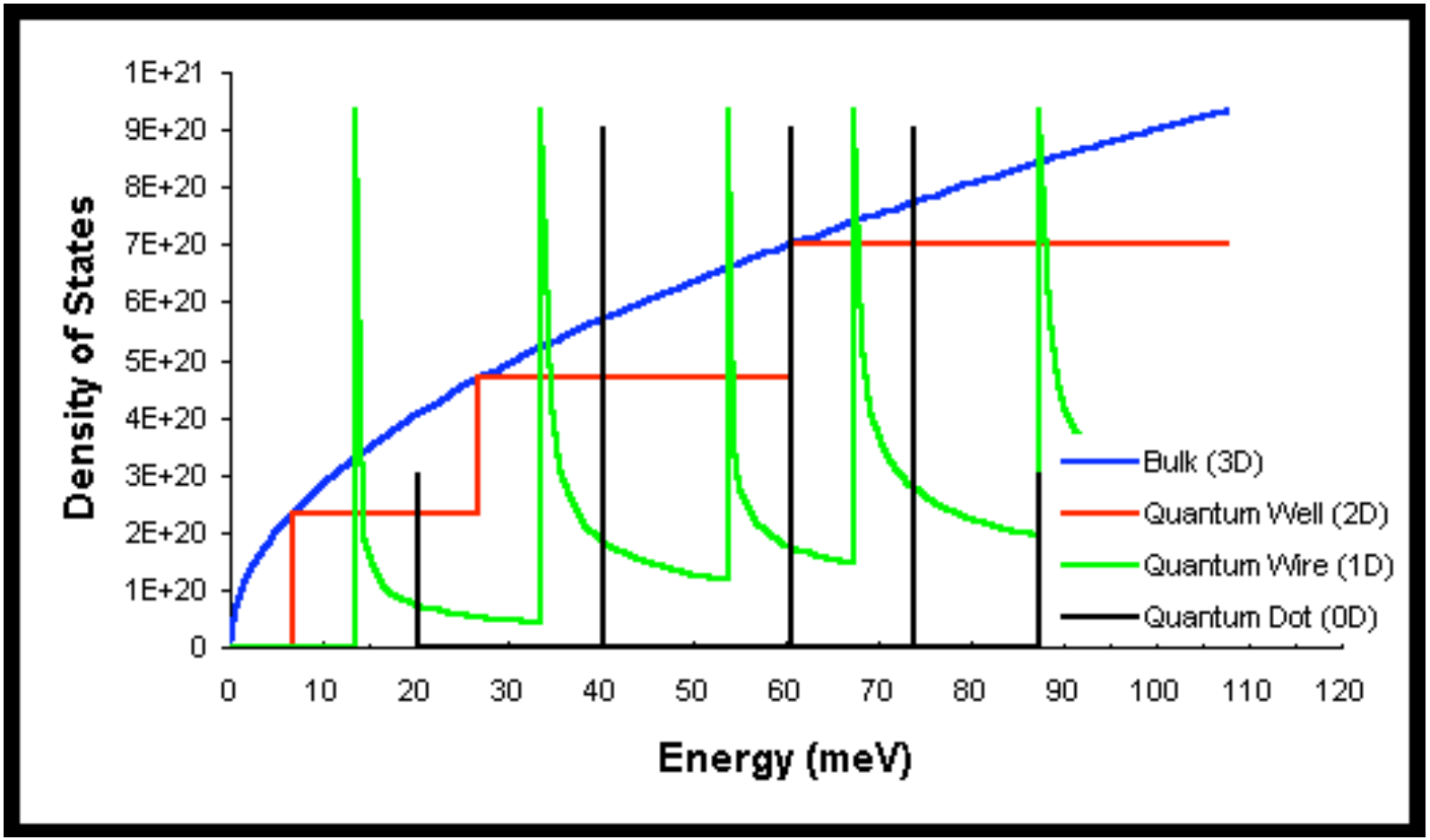
$$n(k) = \frac{k}{2\pi / L} \Leftrightarrow n(E) = \frac{(2mE/\hbar^2)^{1/2}}{2\pi / L}$$

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

(Times 2 to account for the spin)

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

Quantum Confinement and Dimensionality



The effective mass m*

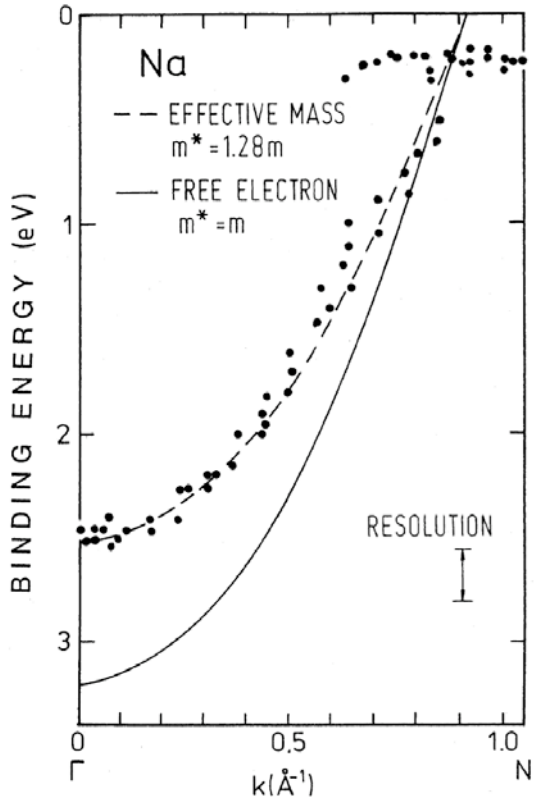
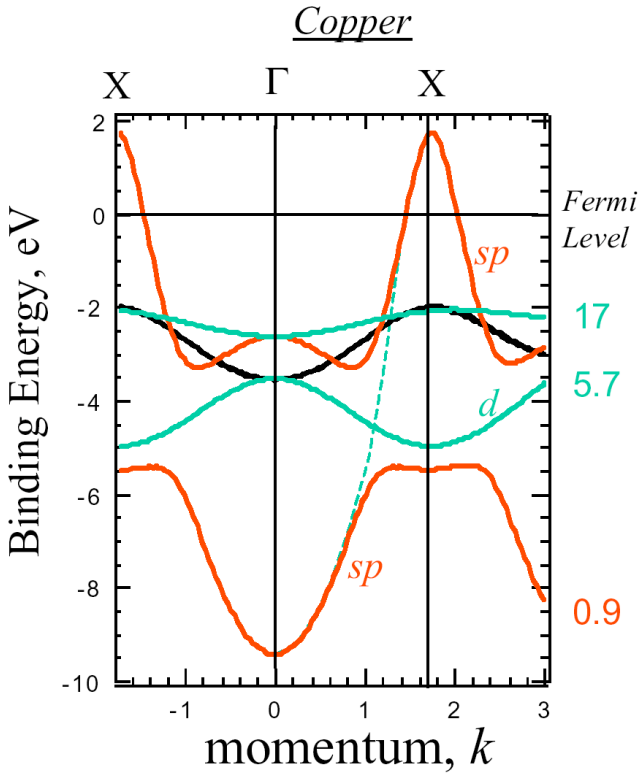
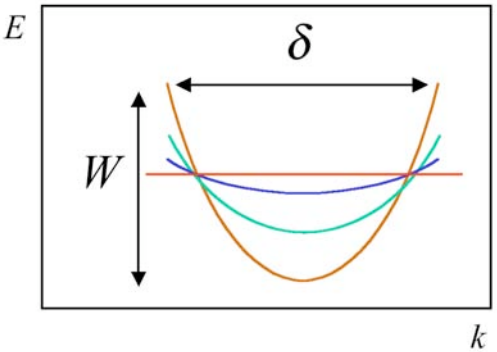


Fig. 2. Experimental band structure of Na obtained by ARPES along the ΓN direction (dots). The solid and dashed curves represent parabolic dispersion curves obtained for a free-electron mass (m_e) and for an effective mass of $m^* = 1.28 \times m_e$, respectively [12,13].



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

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



Effective mass

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

$$\Rightarrow \quad d^2E / dk^2 = \hbar^2 / m^*$$

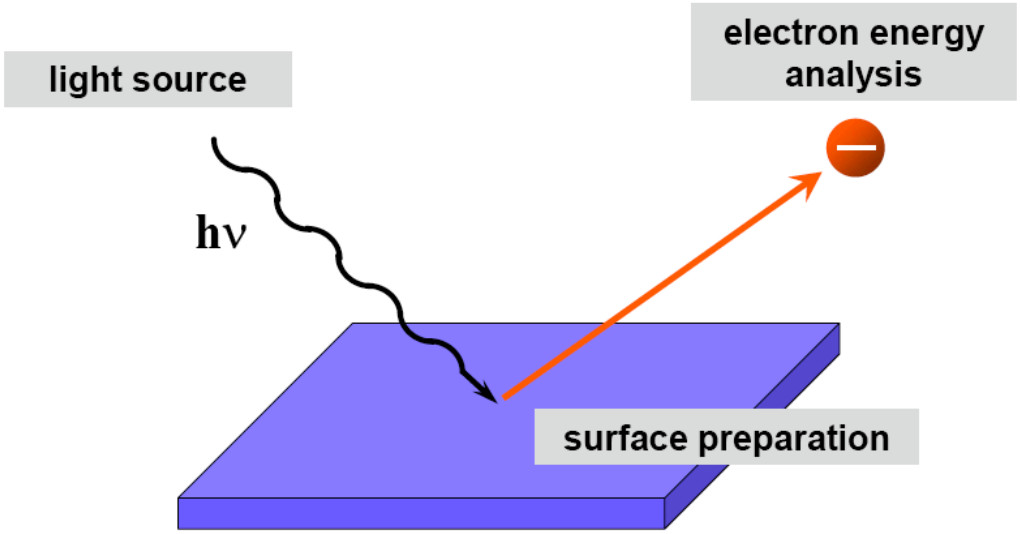
or

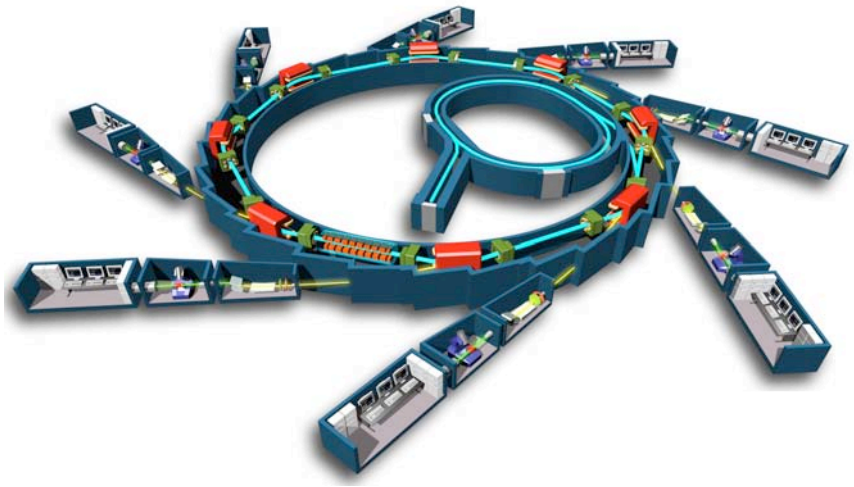
$$\Rightarrow \quad m^* = \hbar^2 / (d^2E / dk^2)$$

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

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

Instrumentation and recent implementations





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

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

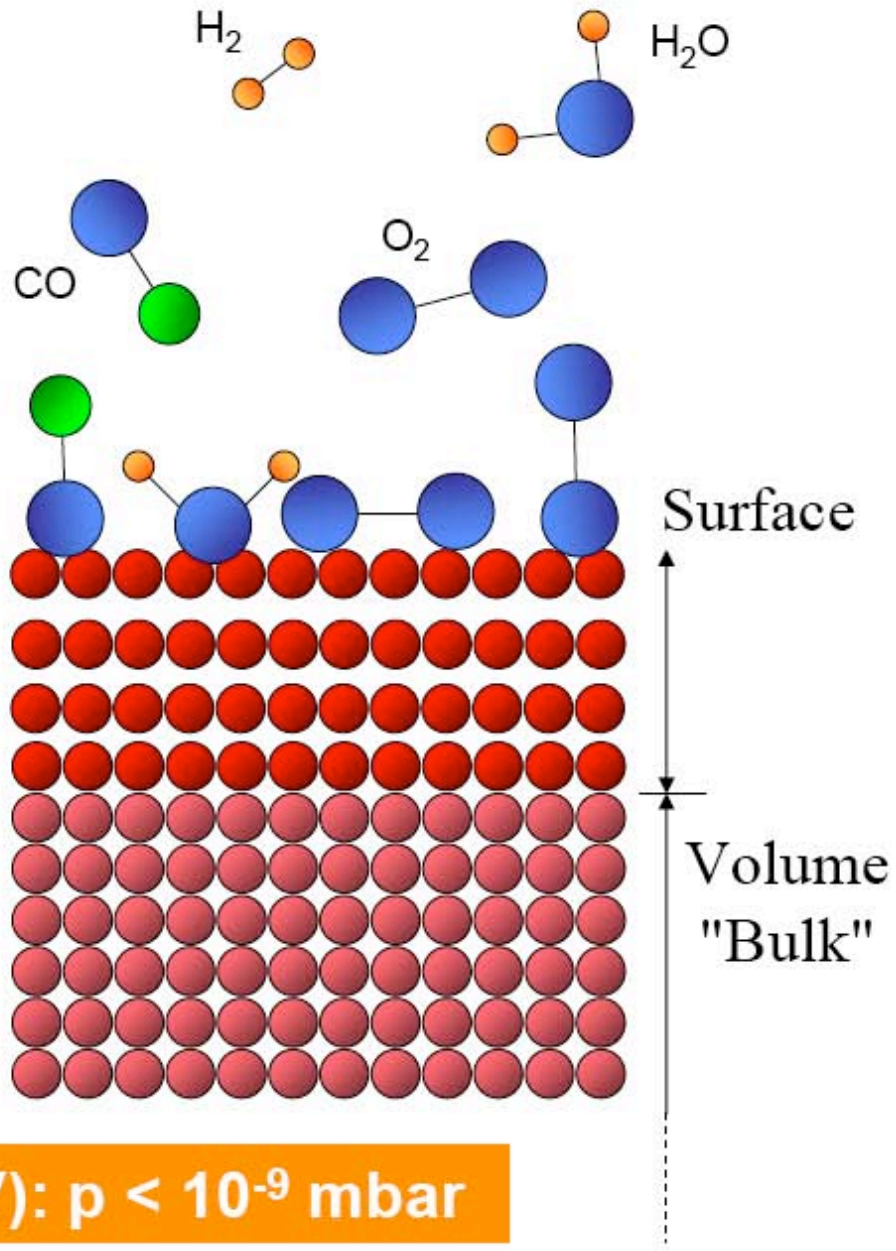
Surface preparation: good surface quality and UHV

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:

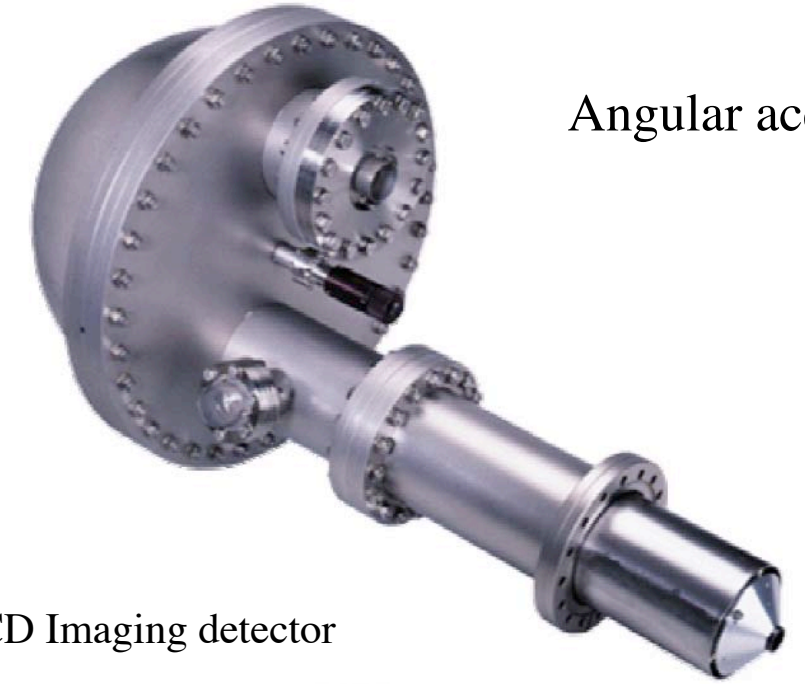
pressure	T_{ML}
1000 mbar	6×10^{-9} s
1 mbar	6×10^{-6} s
10^{-3} mbar	6×10^{-3} s
10^{-6} mbar	6 s
10^{-9} mbar	6×10^{3} s = 1.5 hours



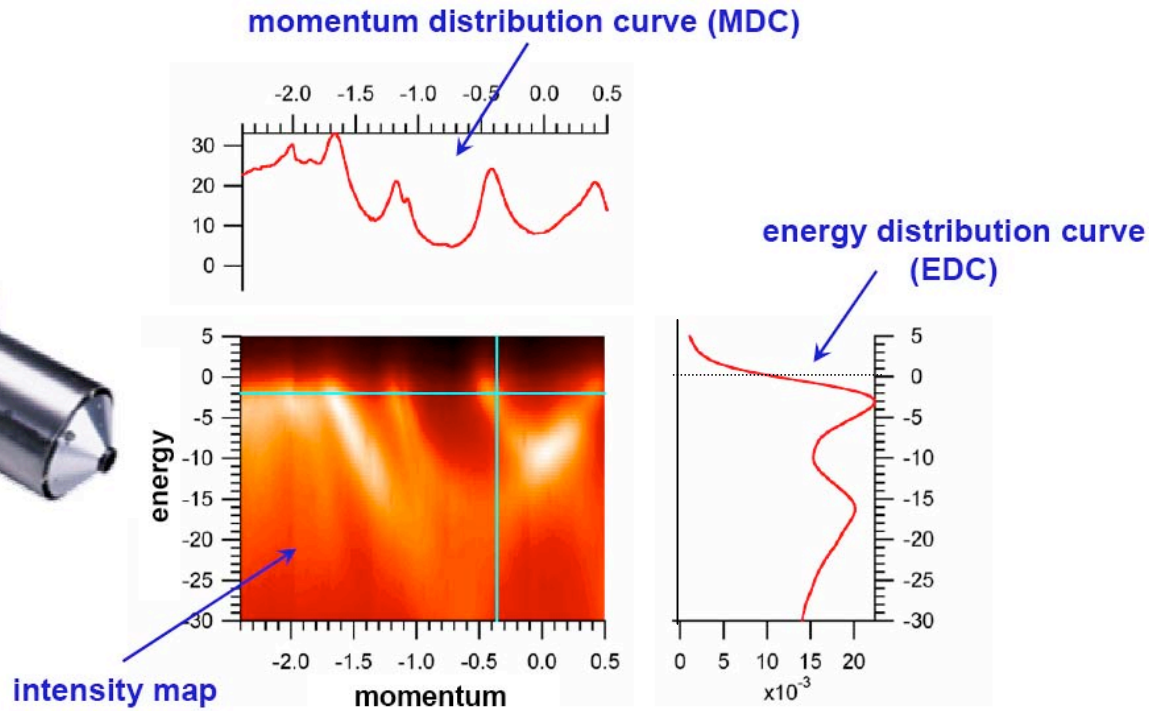
⇒ need ultrahigh vacuum (UHV): p < 10^{-9} mbar

Photoelectron detection

hemispherical energy analyzer

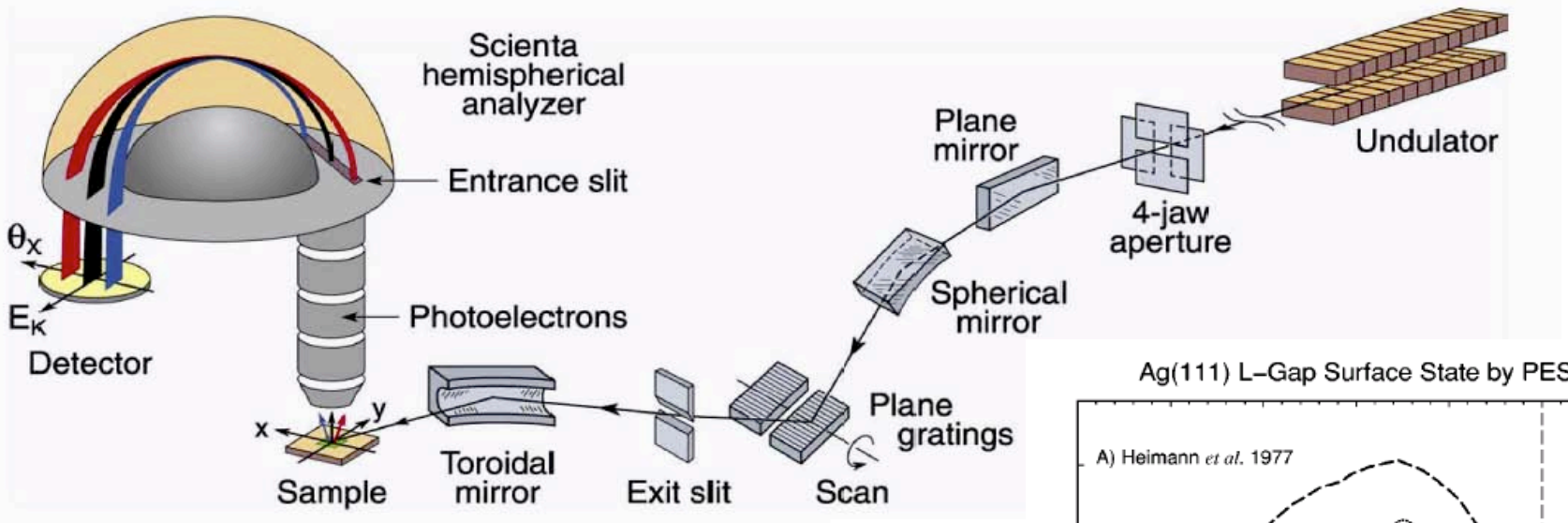


Angular acquisition max 35˚ at the same time



CCD Imaging detector

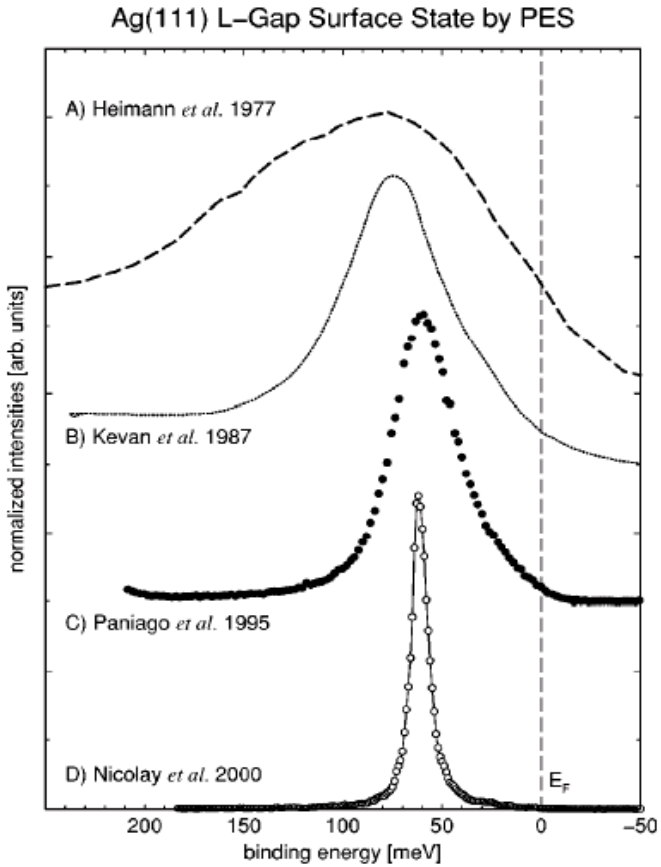
State-of-the-art



Parallel multi-angle recording

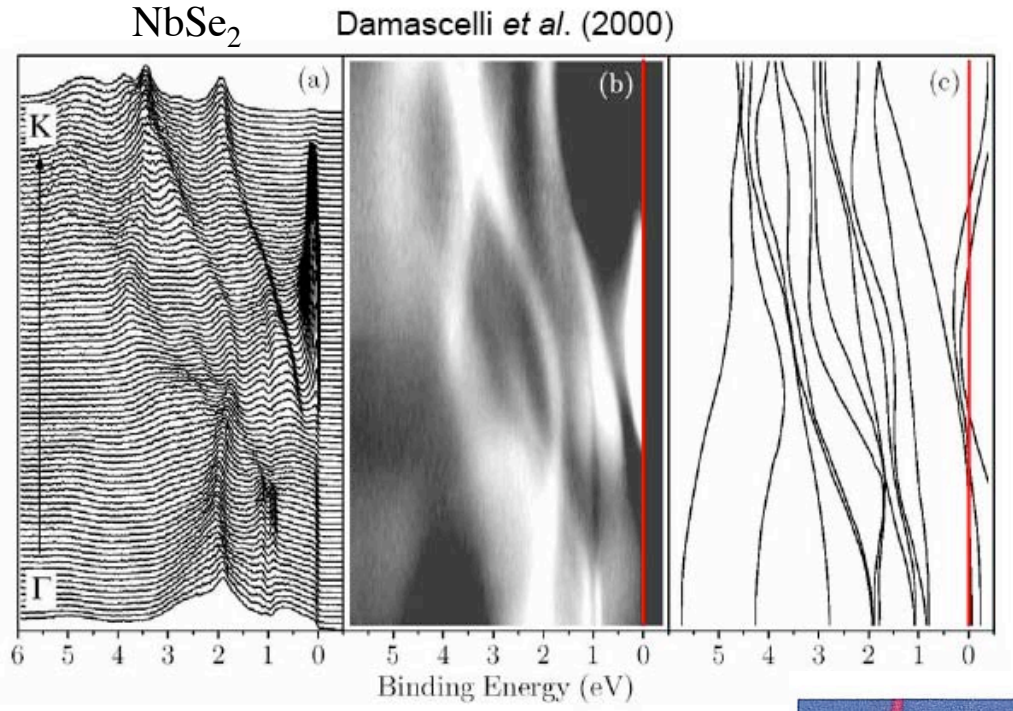
- Improved **energy resolution**
- Improved **momentum resolution**
- Improved **data-acquisition efficiency**

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



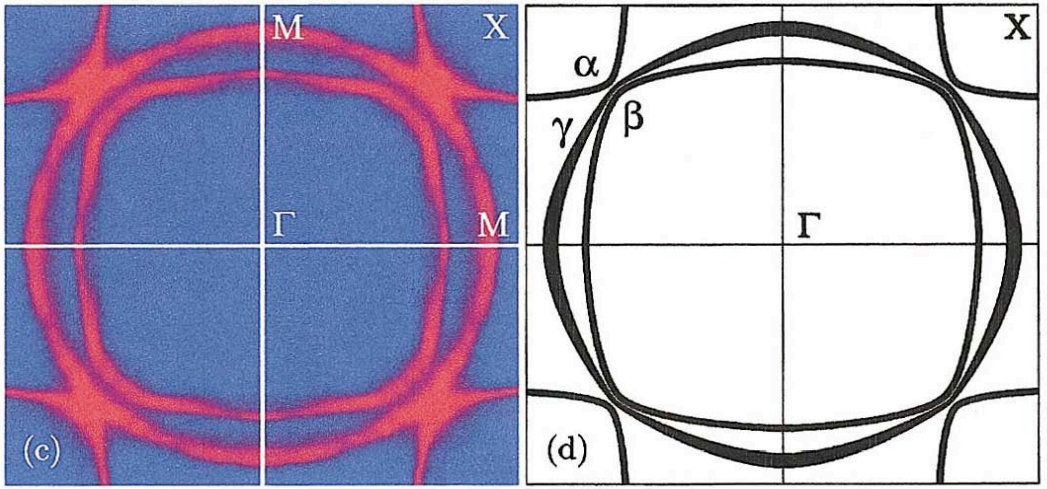
courtesy of A. Damascelli

Clear and nice representation of the data



Band dispersions

Fermi surface



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

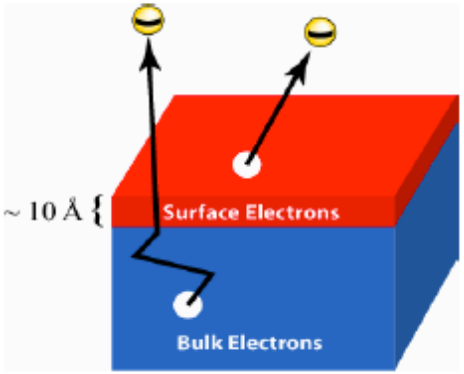
Local-density-approximation
band-structure calculation

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

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

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:

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

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

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

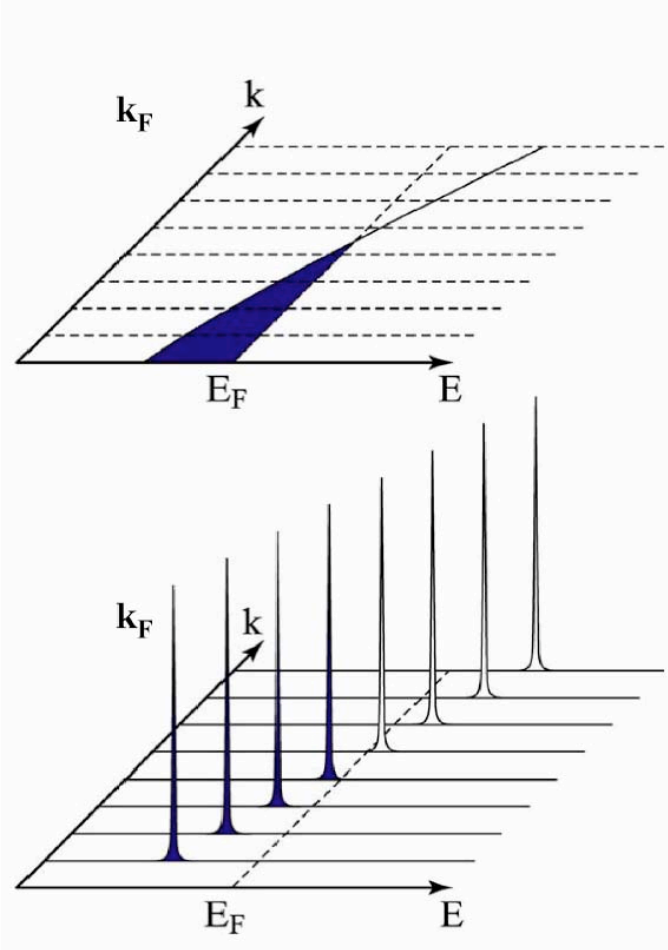
Single particle approximation

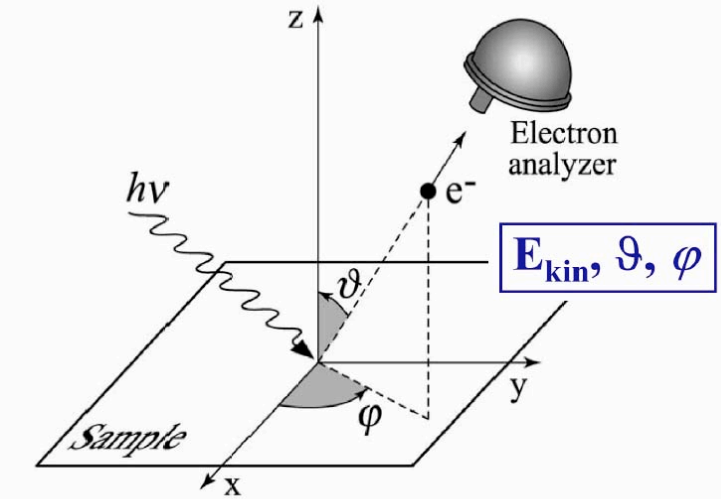
In the limit of non-interacting electrons the N-electron wave function can be written as the product of single electron wave functions. We can assume that before and after the photoemission process the remaining N-1 electrons are not affected by the photoelectron excitation, so we can write the transition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

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

The intensity is modulated by the matrix element $|M_{fi}|^2 = |\langle k_f | A_0 p | k_i \rangle|^2$

Symmetry selection rules

$$\left|M_{fi}\right|^2 \sim \left|\left\langle \psi_f \left| \mathbf{A}\cdot\mathbf{p} \right| \psi_i \right\rangle\right|^2$$

Fixed by geometry

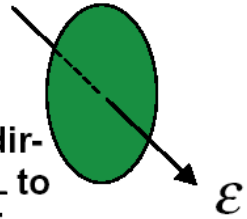
Sample-dependent

- 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

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



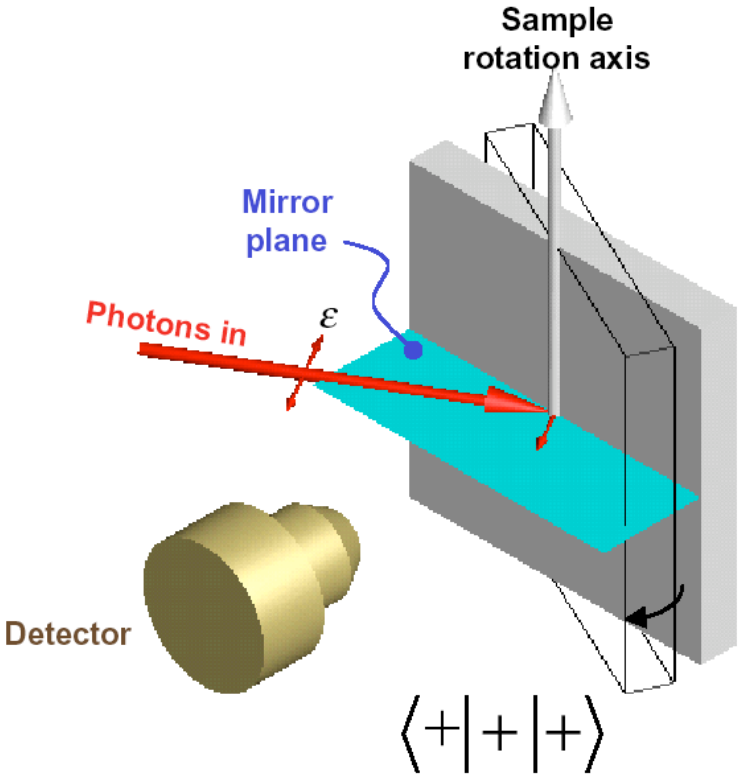
Even in directions ⊥ to polarization vector

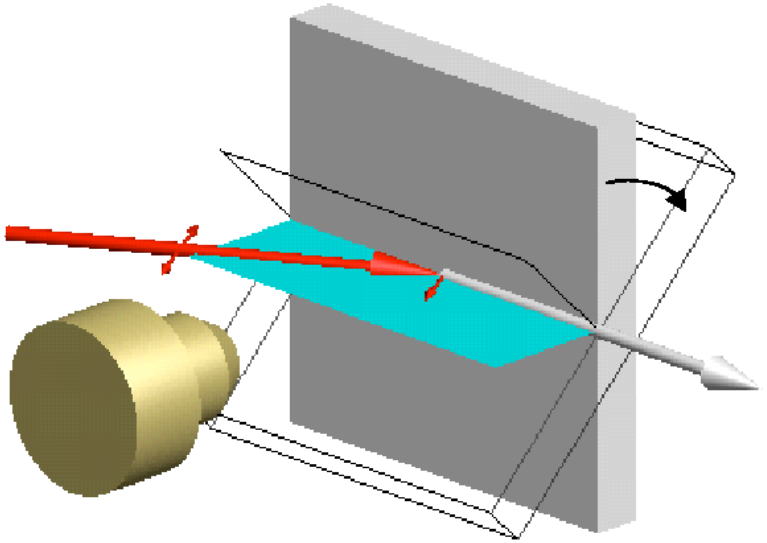
Odd in this direction

$\left|\psi_i\right\rangle$

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

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





Only even initial states are observed at all rotation angles

Mixture of even and odd states

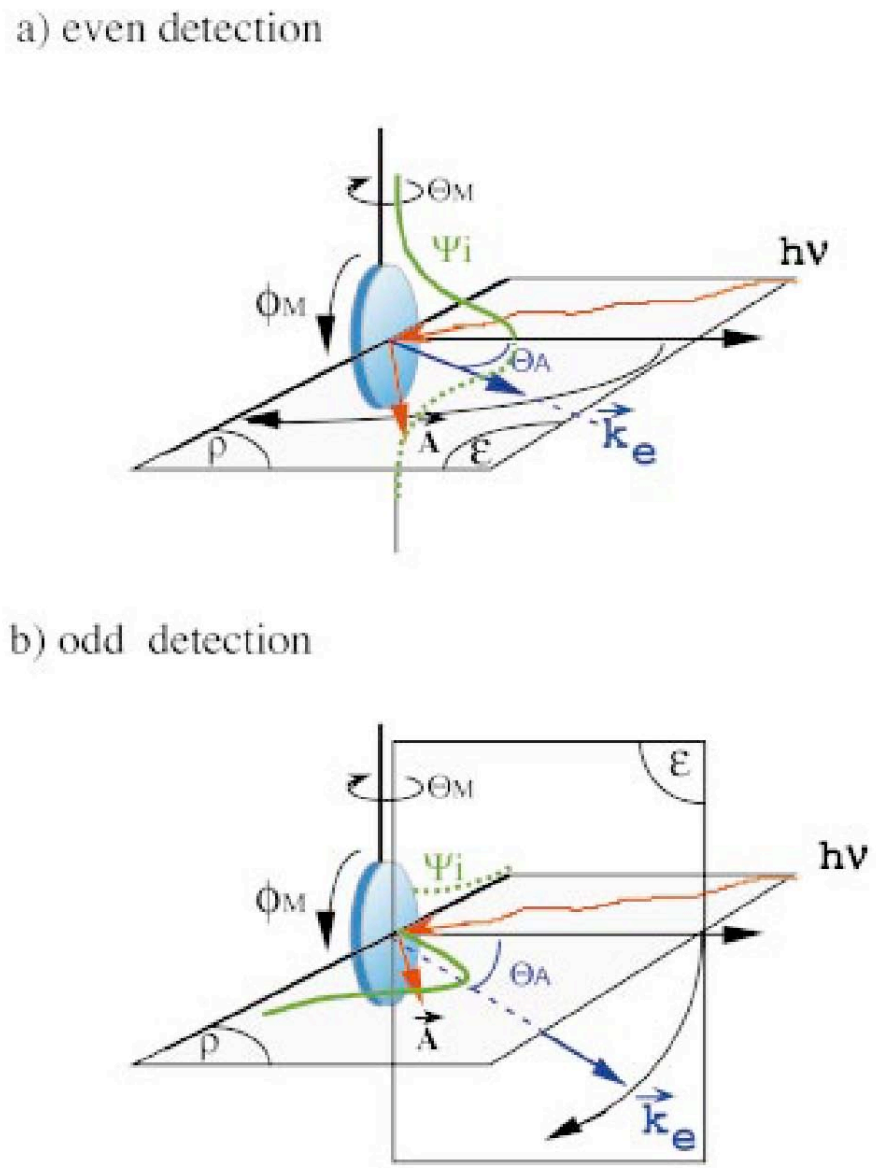
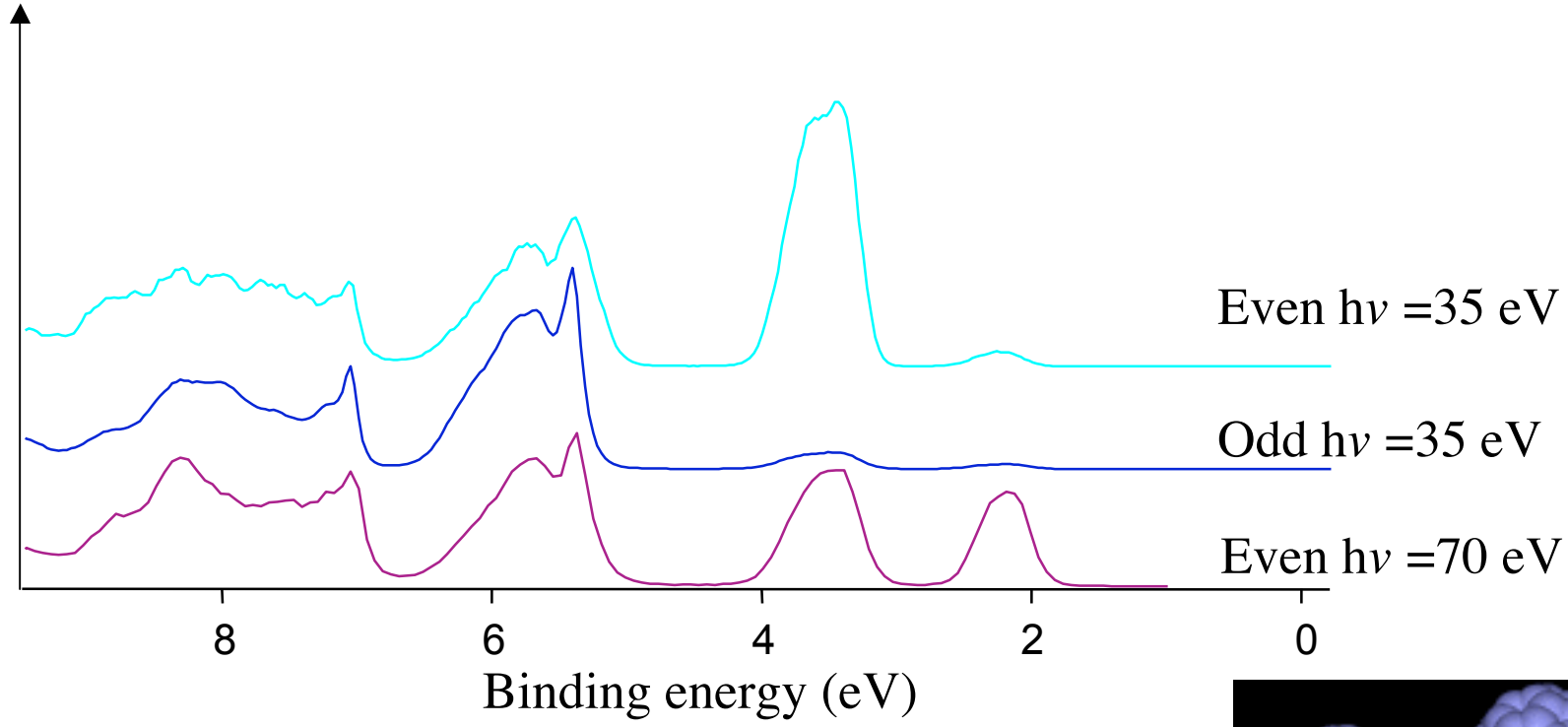
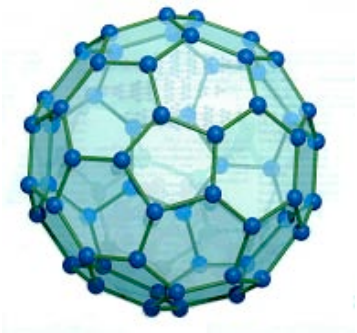
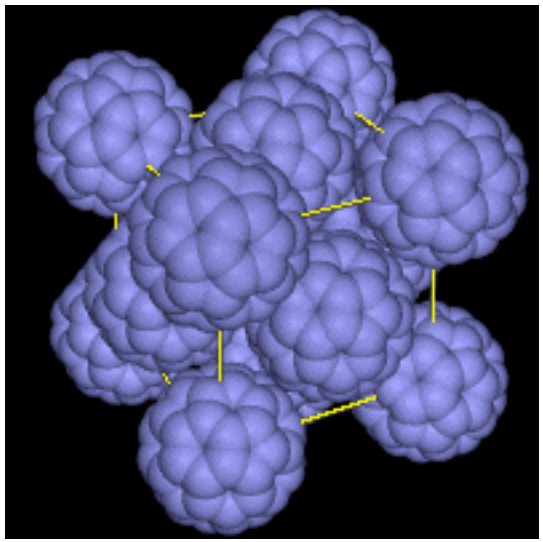


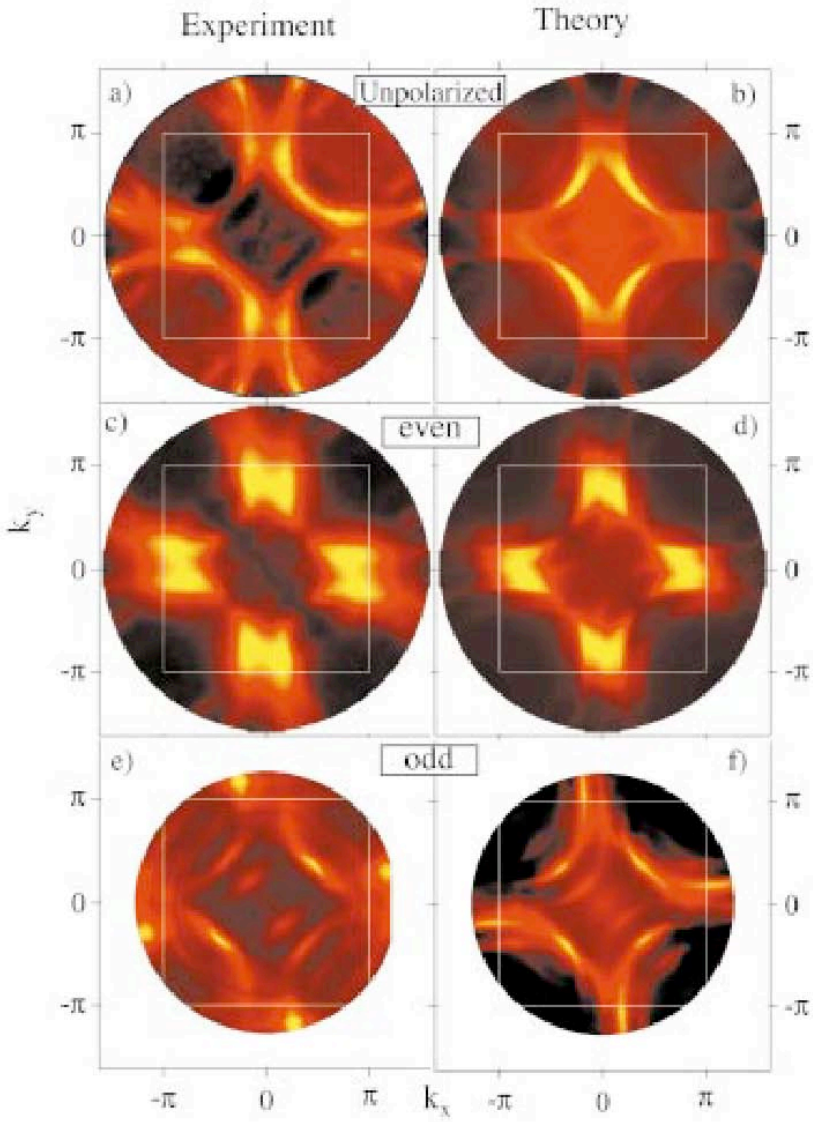
FIG. 1. (Color) The meaning of "even" and "odd" detection geometry in the present ARPES experiments is explained. $\vec{k}_e$ points toward the detector. In the even case, the detector moves in the plane of incident light (horizontal plane) in which the synchrotron light is polarized. In the odd case, 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}

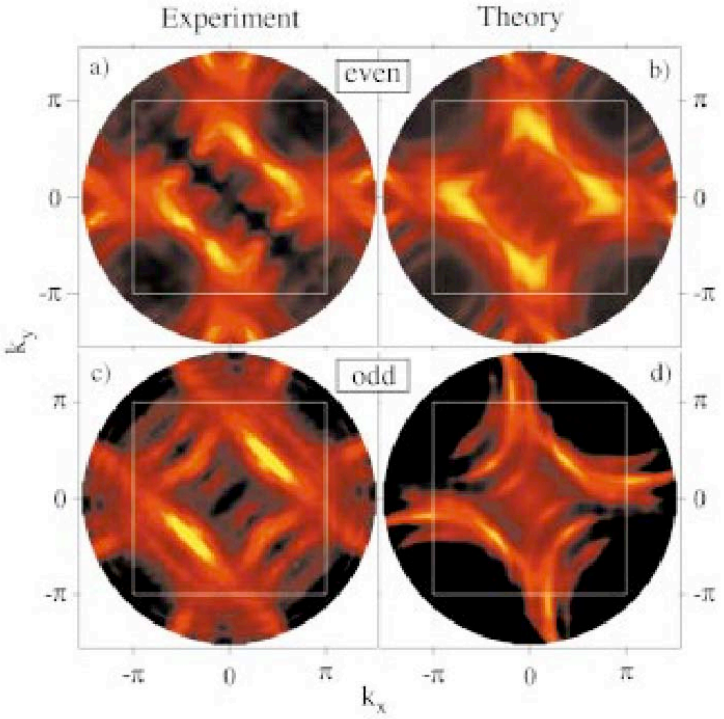








hν = 21..2 eV



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.**

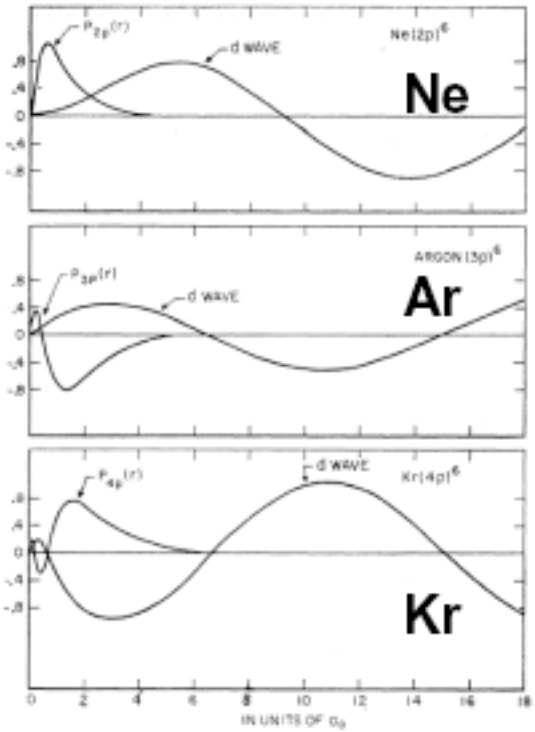
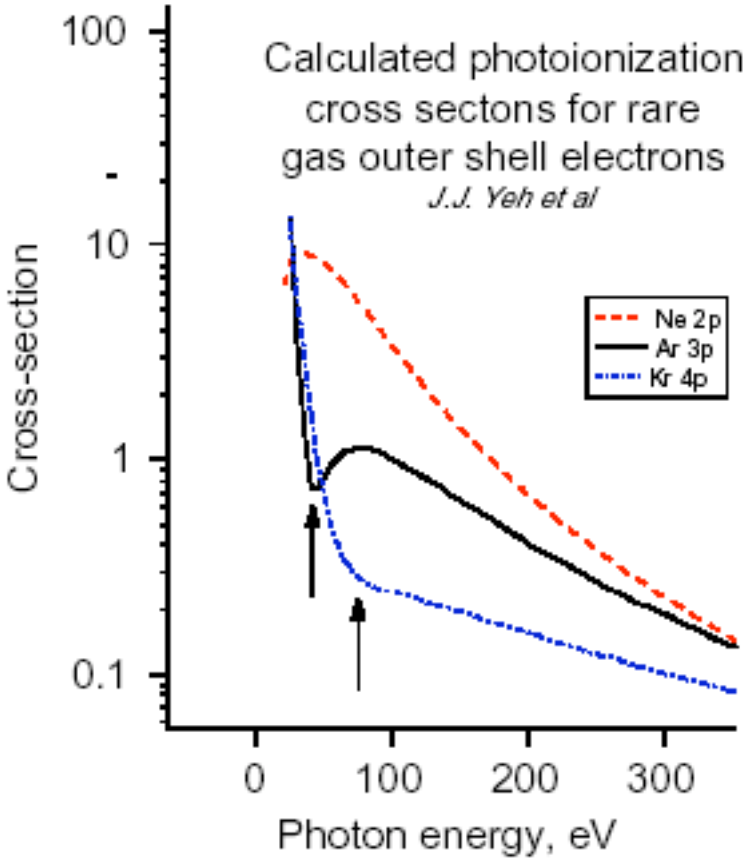
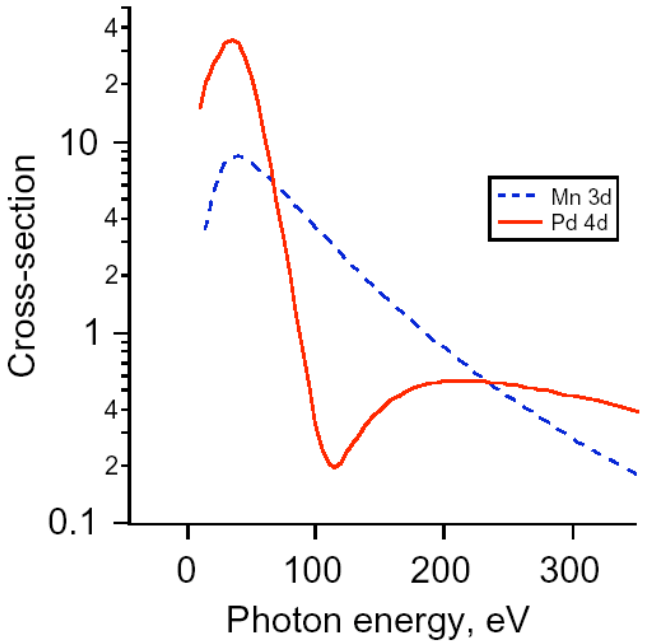


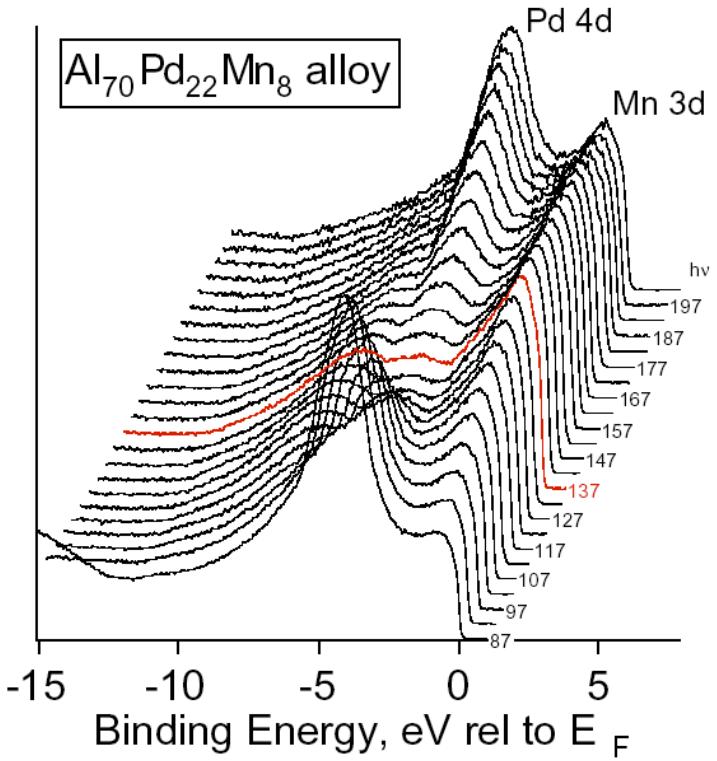
FIG. 2. Outer subshell radial wave functions and d waves for $\epsilon=0$ for Ne, Ar, and Kr.



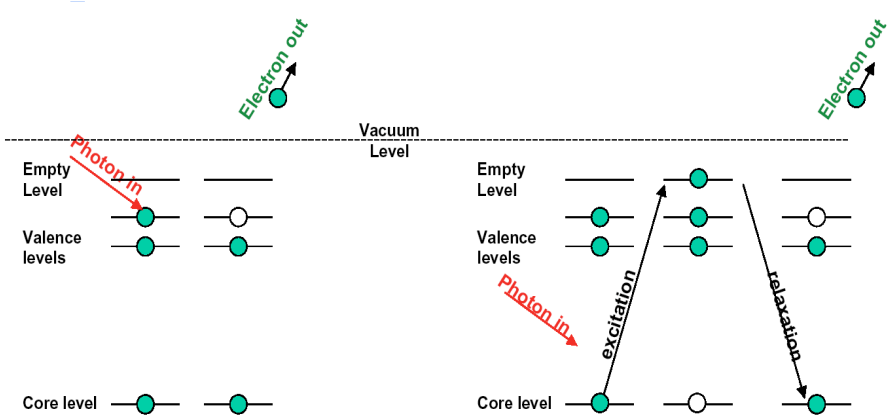
Calculation
J.J.Yeh



Expt.
Rotenberg et al

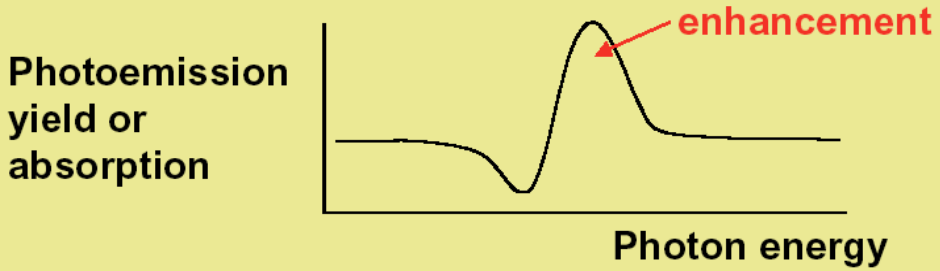


Resonant photoemission



- 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

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



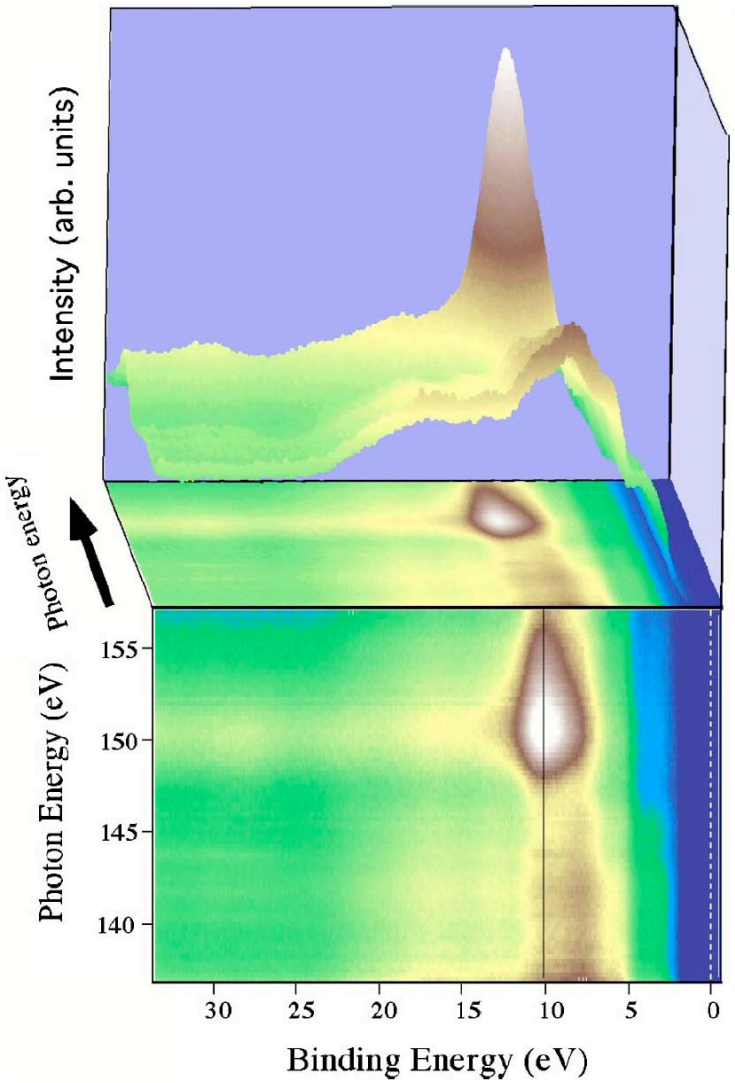
- Not all valence electrons are enhanced equally!
- Only those with overlap to the core hole are enhanced
- This can be very useful to get projections of the valence bands to the individual atoms.

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



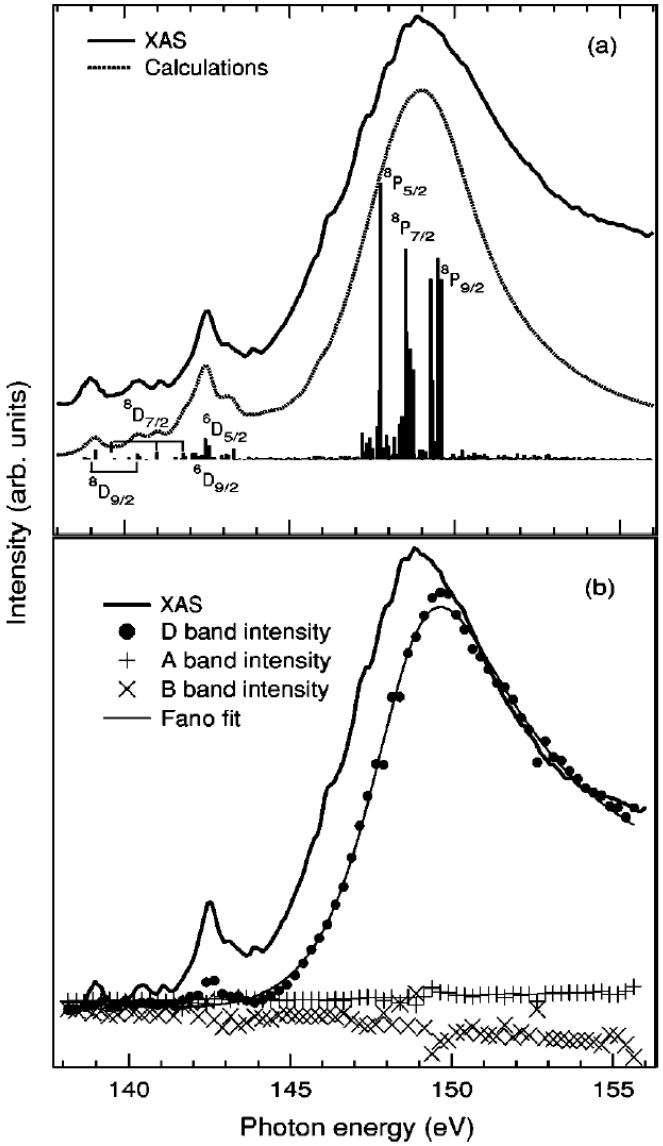
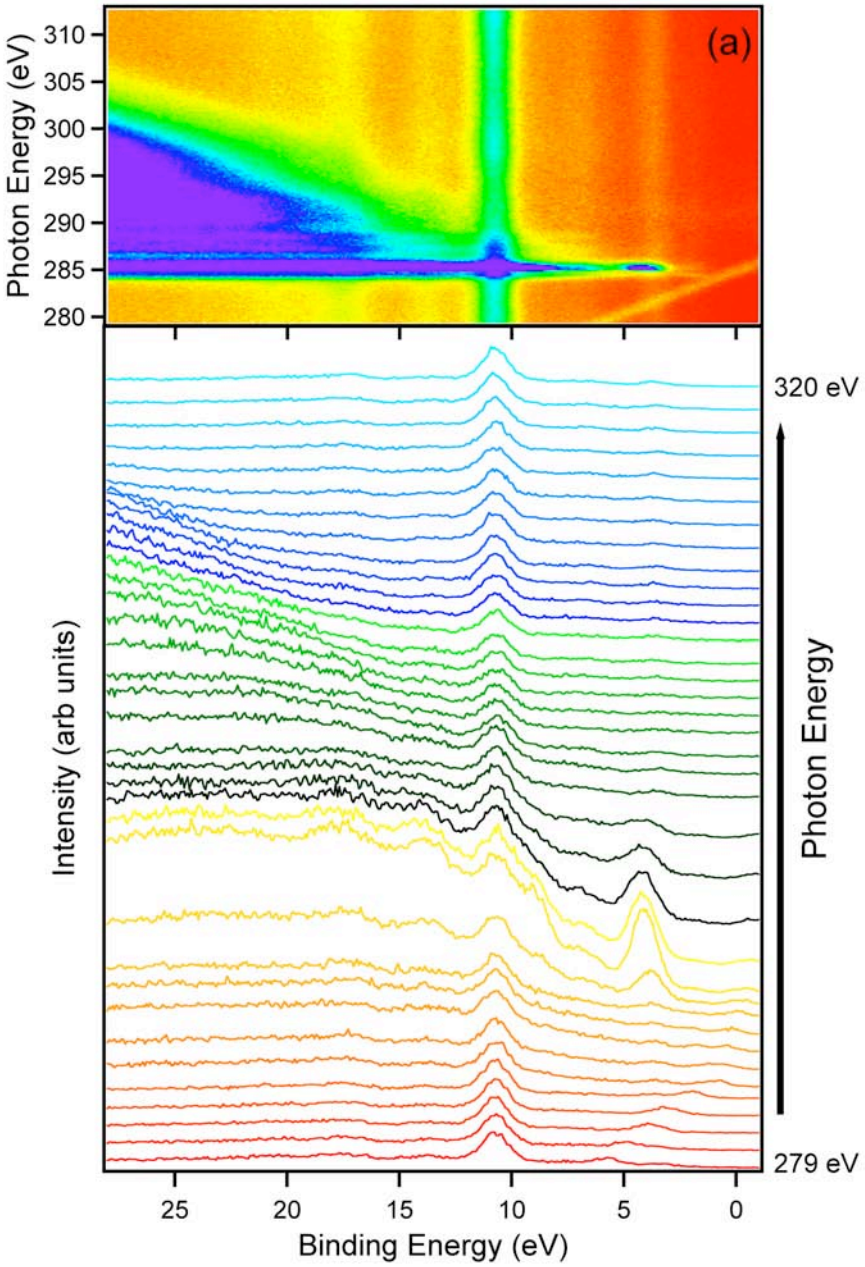
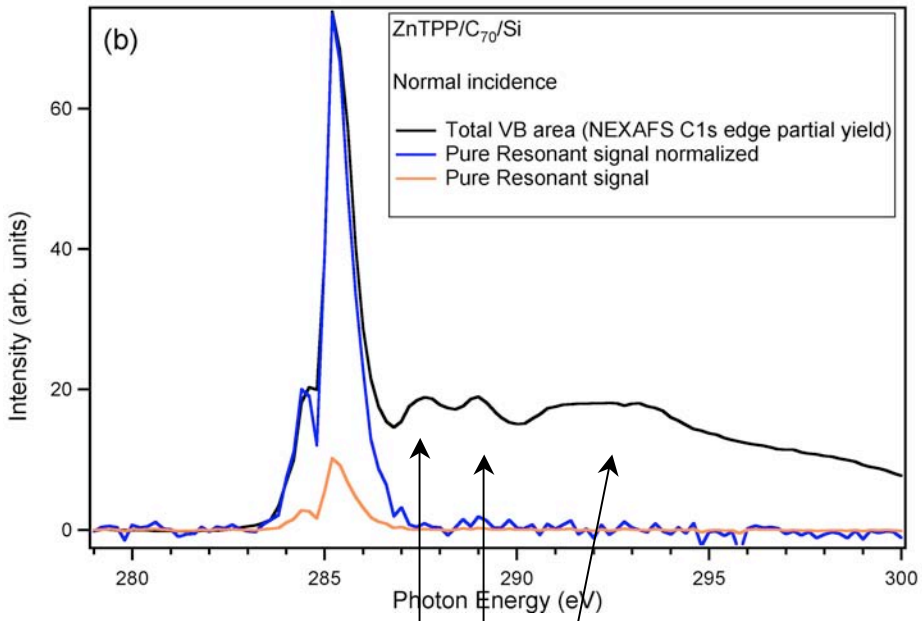
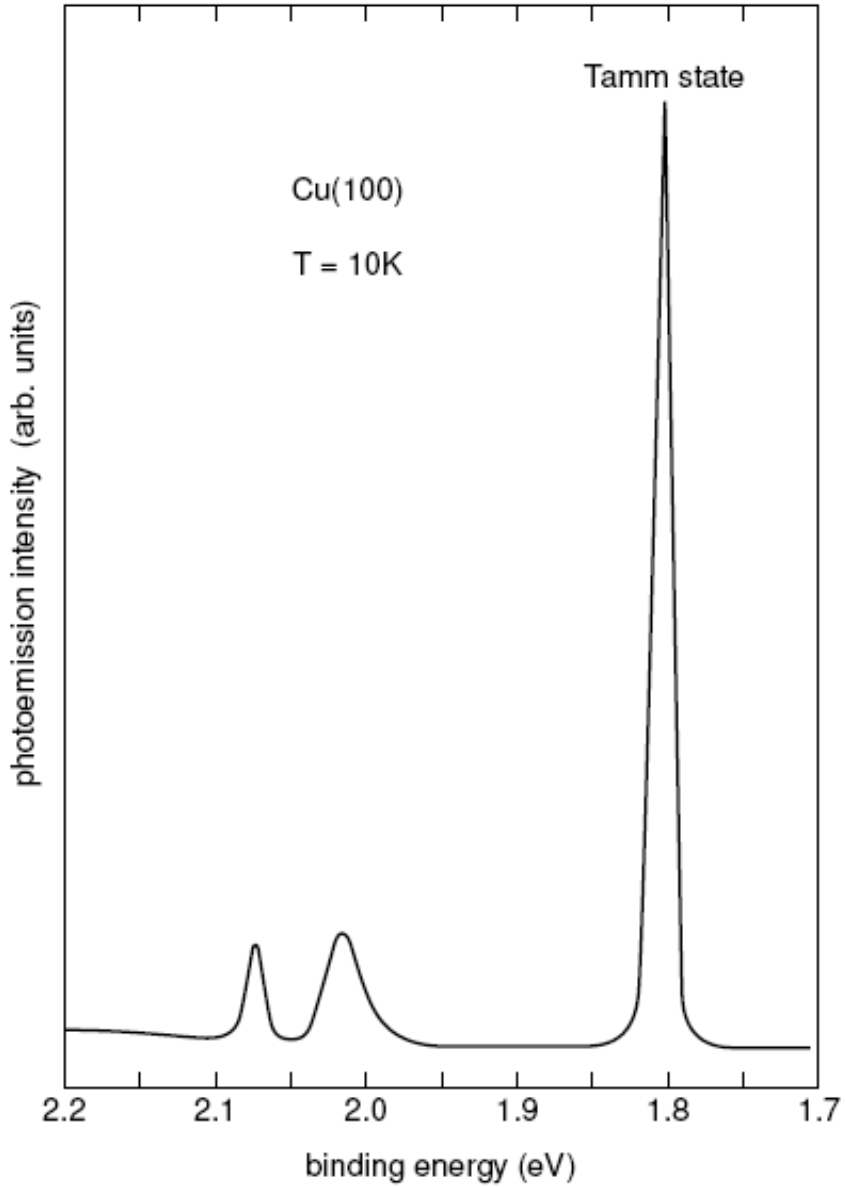


FIG. 3. (Color online) Resonant photoemission valence band spectra collected at the Gd $4d \rightarrow 4f$ edge.

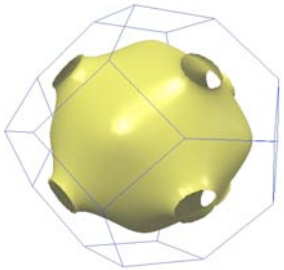




When excited to these states, C1s core electrons delocalize well before the core hole decay.


Tamm state
Cu(100)
T = 10K
photoemission intensity (arb. units)
2.2
2.1
2.0
1.9
1.8
1.7
binding energy (eV)

Bulk Fermi Surface mapping: case studies Cu

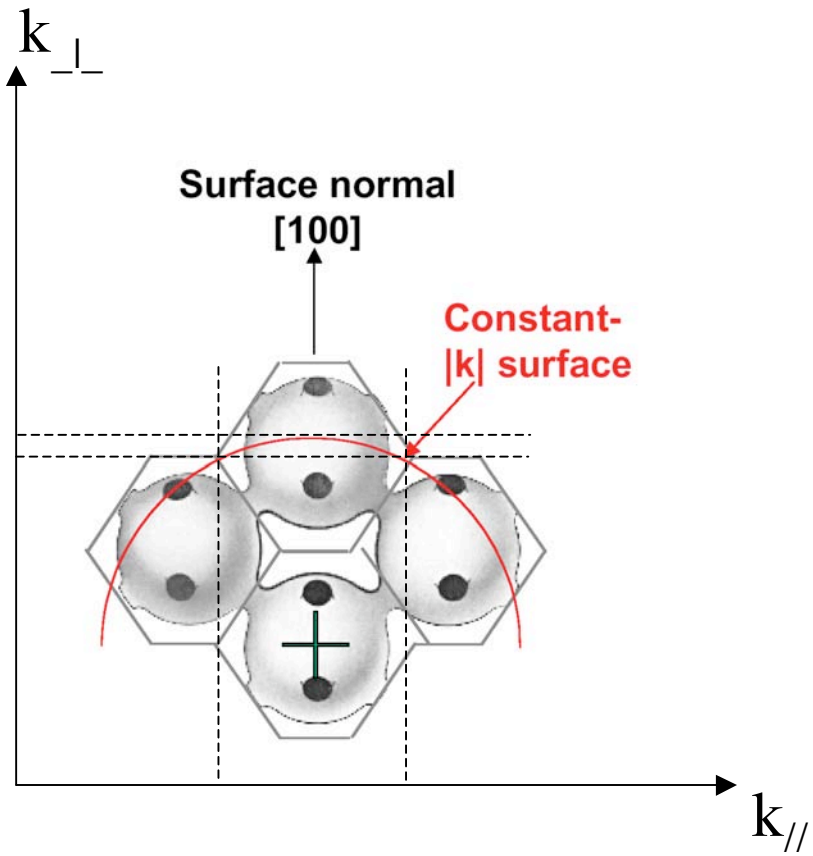


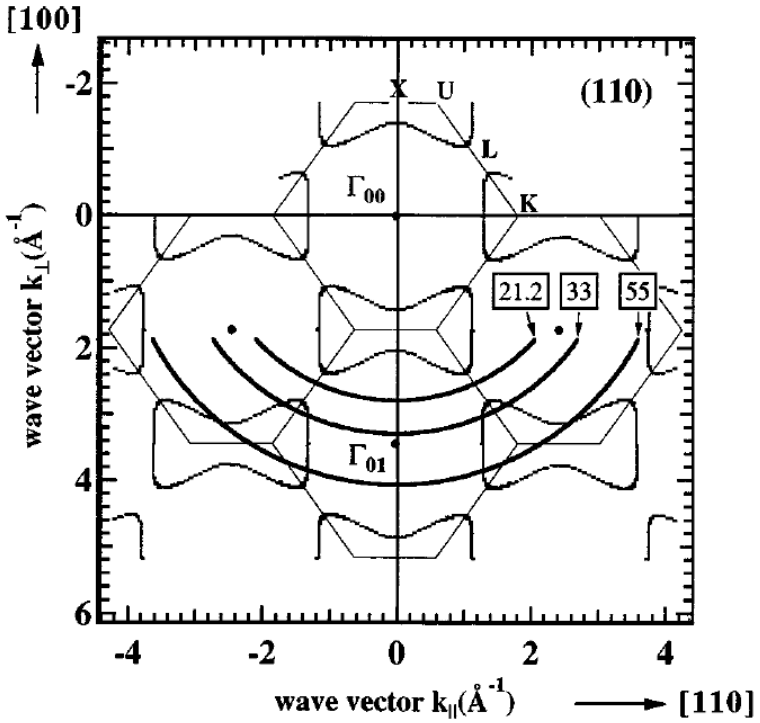
$$k_{out} = \sqrt{\frac{2m^*}{\hbar^2}E_{kin}}$$

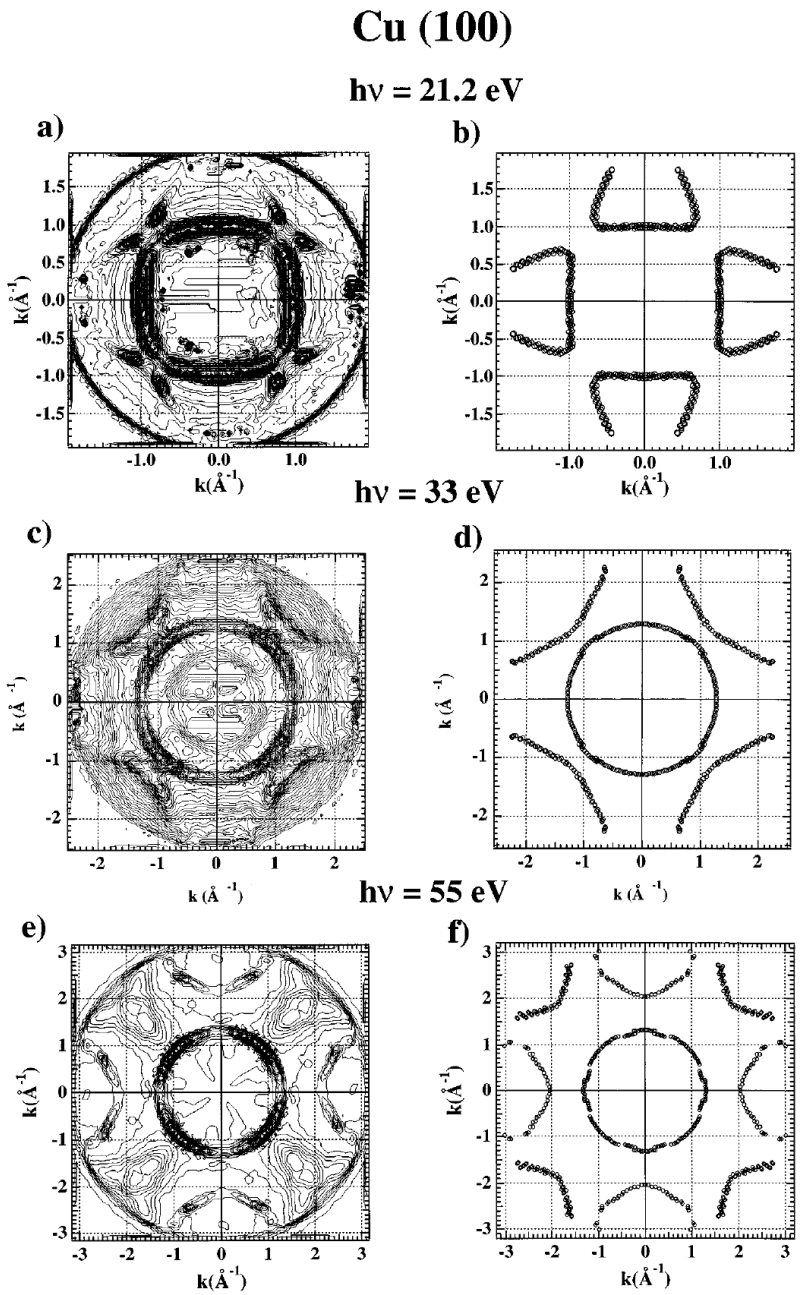
$$k_{in} = \sqrt{\frac{2m^*}{\hbar^2}(E_{kin} + V_0)}$$

$$k_{//out} = k_{//in} = \sin\theta_{out}\sqrt{\frac{2m^*}{\hbar^2}E_{kin}}$$

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







Slices of the Fermi surface in the $k_{//}$ plane at different $k_{\perp}$

$k_{\perp} = 2.83$ Å^{-1}

Less defined $k_{\perp}$ at low kinetic energy (broader Fermi contours, ie. thicker slices).

$k_{\perp} = 3.33$Å^{-1}

3D reconstruction of the Fermi surface shape is possible

$k_{\perp} = 4.11$ Å^{-1}

FIG. 3. On the left side, experimental photoelectron angular distributions from the Cu(100) Fermi surface at 21, 33, and 55 eV kinetic energies. On the right side, the results of a tight binding theoretical calculation for the same energies are indicated.