Photoemission from Valence Bands, Dispersion and Fermi Surface Mapping

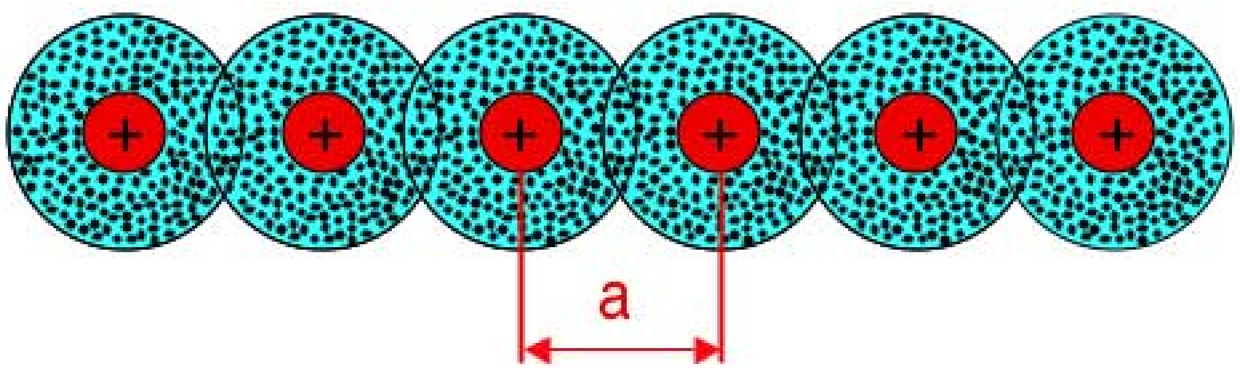
Jürg Osterwalder
Physik-Institut, Unversität Zürich, Winterthurerstr. 190,
CH-8057 Zürich, Switzerland - osterwal@physik.unizh.ch
http://www.physik.unizh.ch/groups/grouposterwalder/

Lecture 1

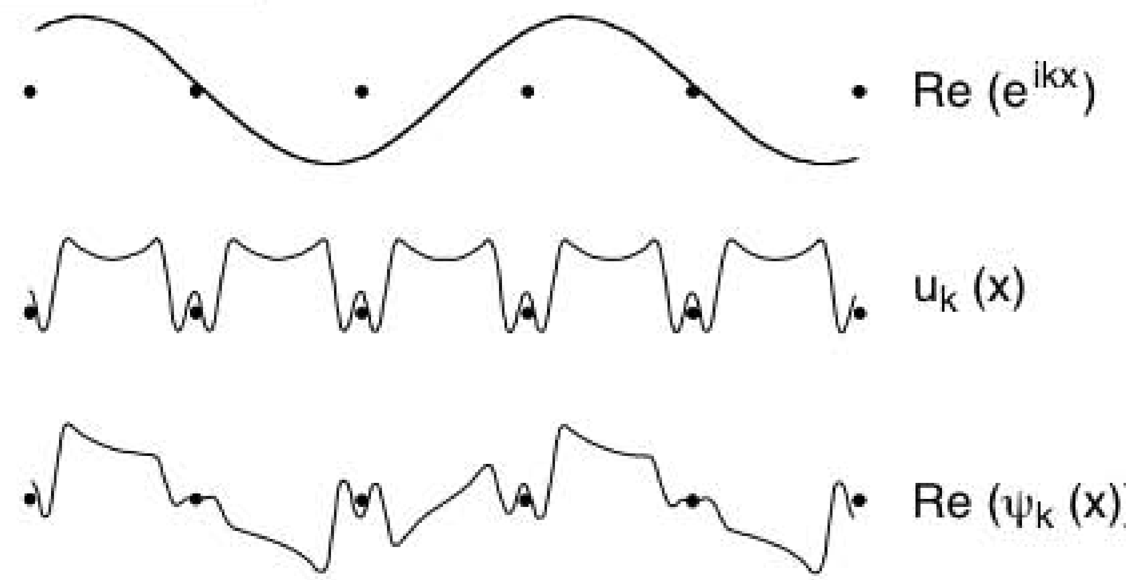
- Electronic Band Structure in 1-3 Dimensions
- Photoemission from a Periodic Potential - the 3-Step Model
- A 1D Example: p(2x1) O-Cu(110) -> Band Mapping
- Intensities in Valence Photoemission: Polarization and Atomic Effects
- A 2D Example: The Shockley Surface State on Cu(111)
- A Few Words about Surface States in General
- Constant Energy Mapping in 3D Systems
- A Few Words about the Fermi Surface in General
- 3D Examples for Fermi Surface Mapping: Cu, Al
- Intensities in Valence Photoemission: Diffraction Effects

Electronic Bandstructure in 1 Dimension

chain of atoms:



wave functions:

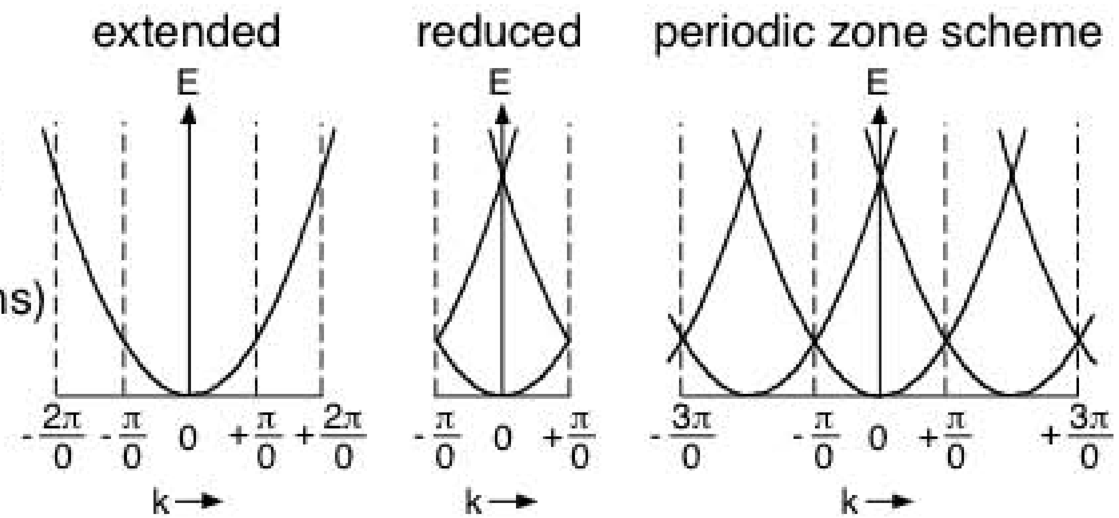


Bloch functions $\psi_k(x) = u_k(x)\, e^{ikx}$

dispersion relation (reciprocal space):

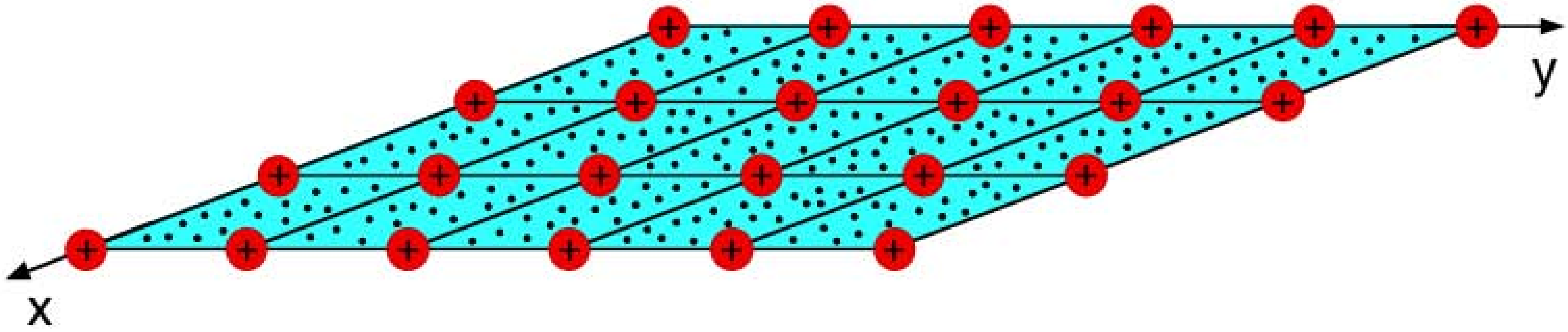
$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$$

(free electrons)

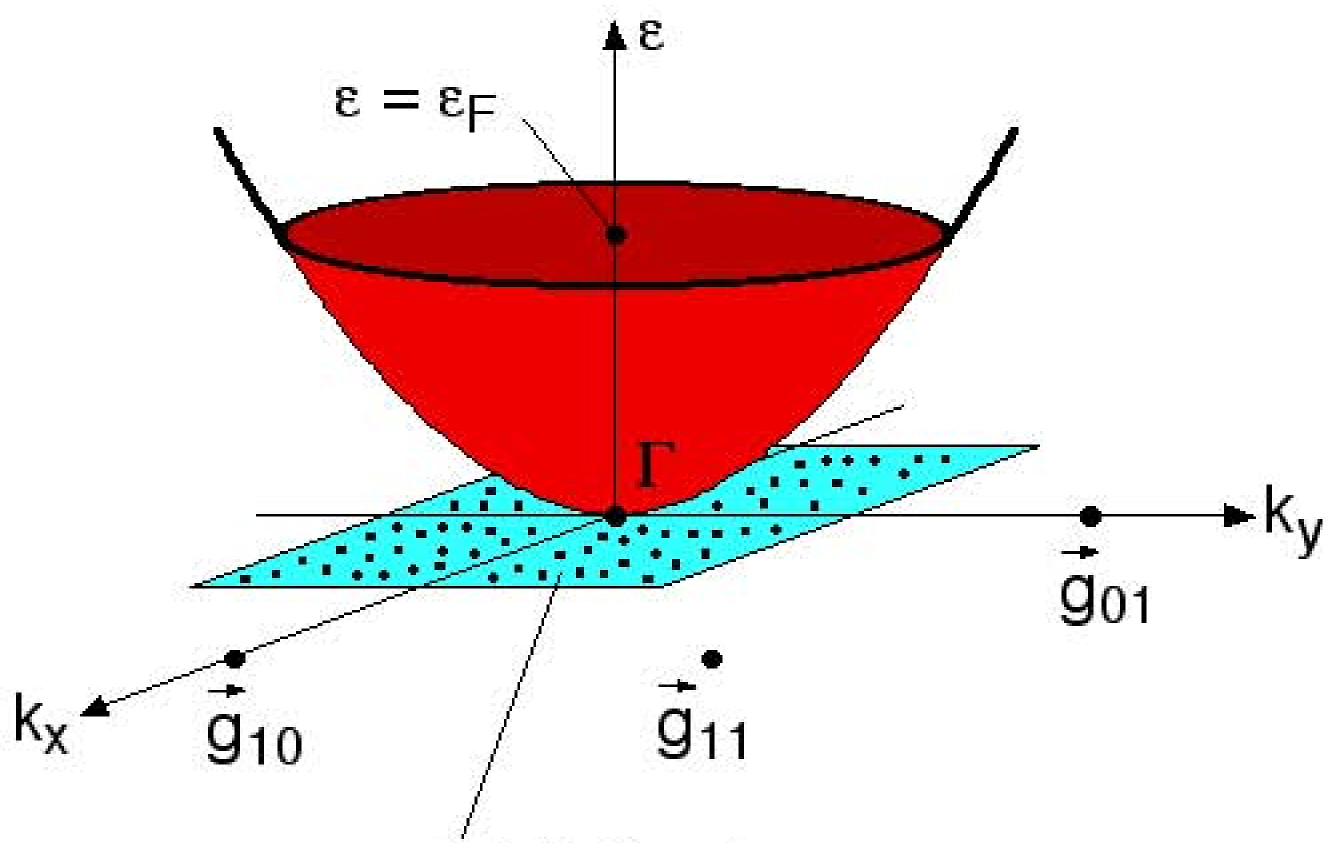


Electronic Structure in 2 Dimensions

(Plane of atoms)



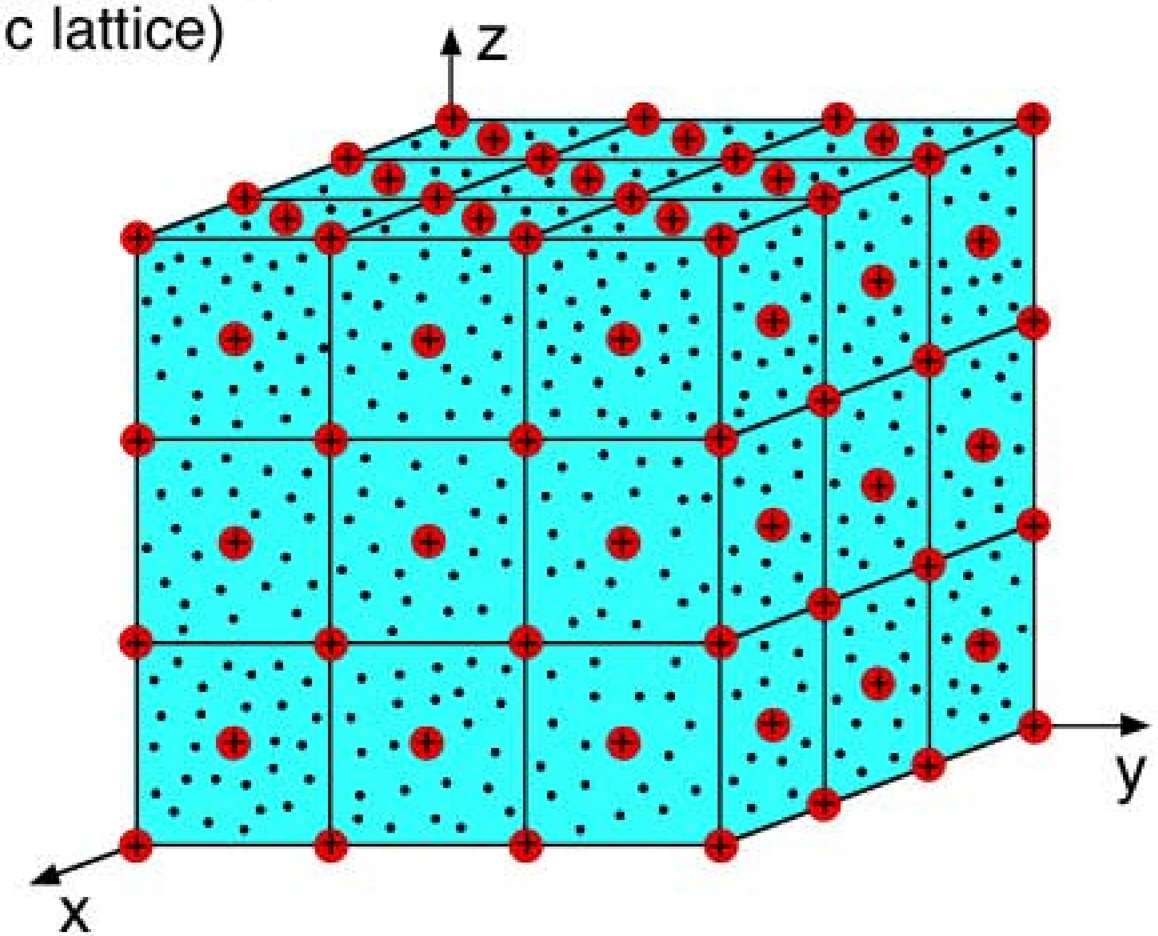
dispersion relation



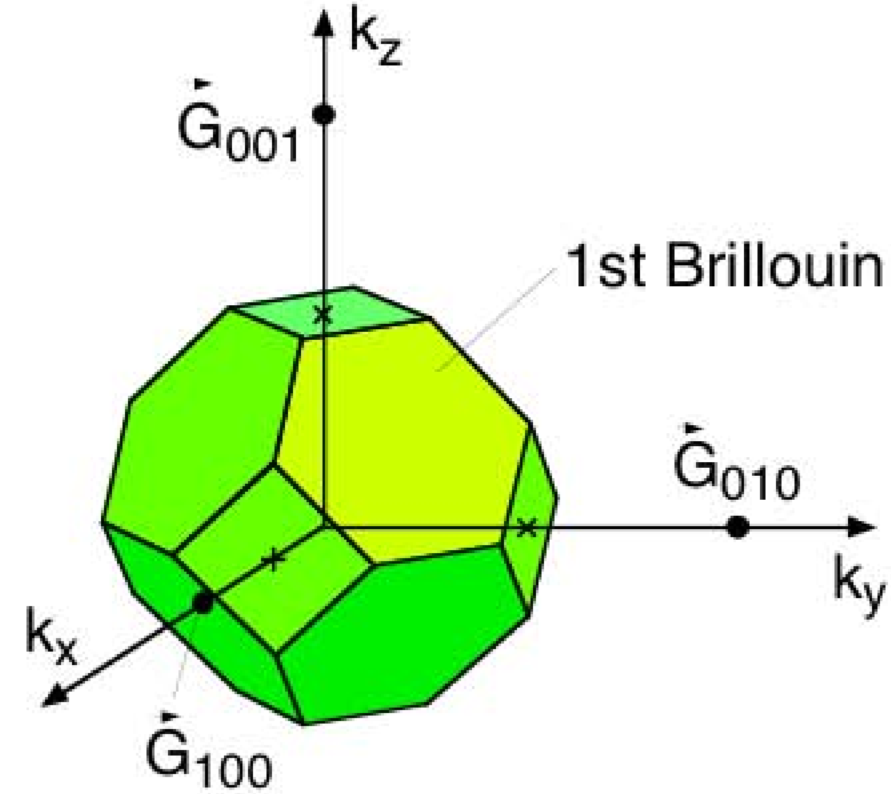
Electronic Structure in 3 Dimensions

real space:

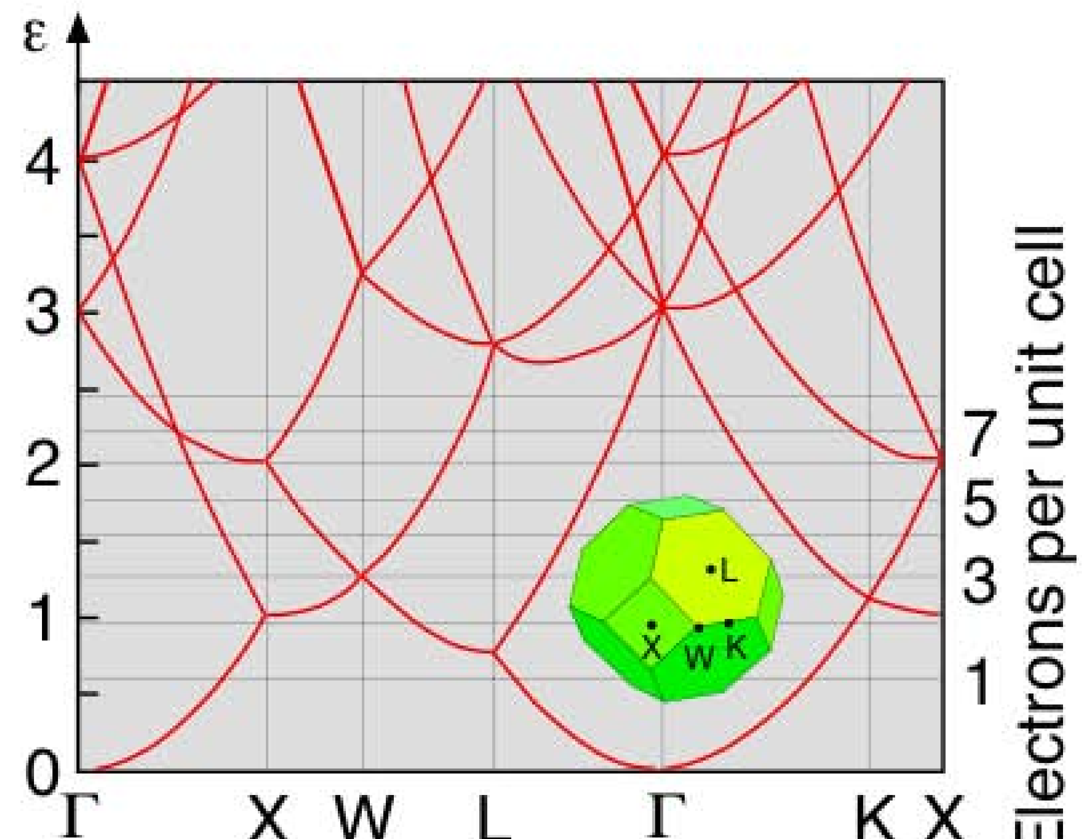
(face-centered cubic lattice)



reciprocal space:



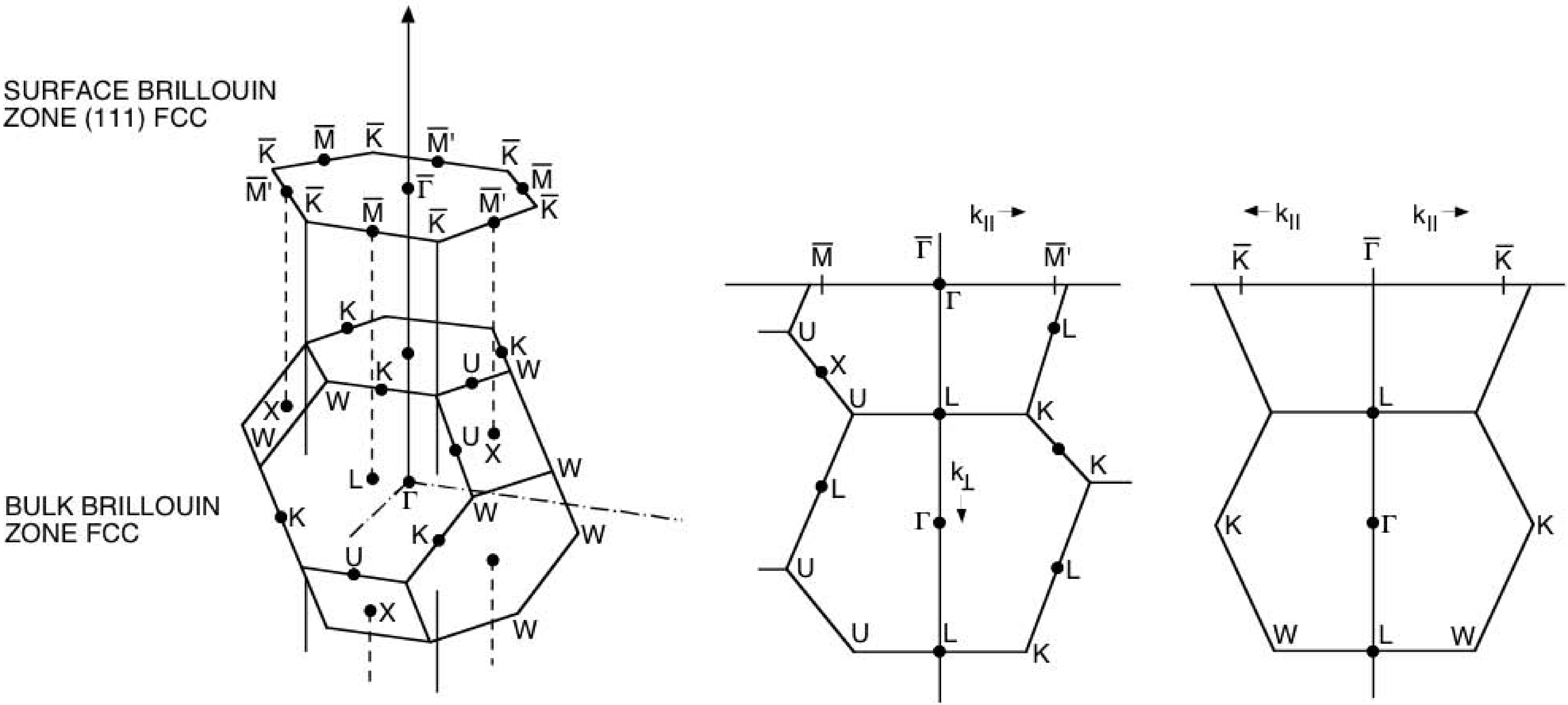
dispersion relation:



The Geography of Reciprocal Space

Surface and Bulk Brillouin Zones for face-centered cubic (fcc) Lattices

(111) Surface



From E. W. Plummer, W. Eberhardt
Adv. Chem. Phys. 49, 533 (1982)

Photoemission of a free electron

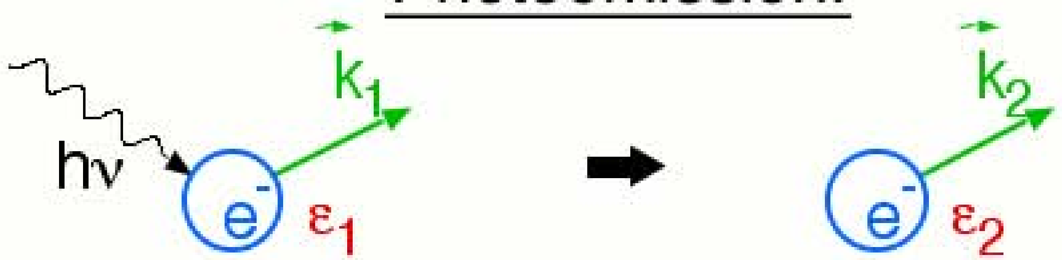
	Energy	Momentum
free electron	$\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$	$\hbar\vec{k}$
photon (hν)	$\varepsilon(\vec{k}) = \lvert\hbar\vec{k}\rvert c$	$\hbar\vec{k}$

wave numbers k

e^- : $k = 0.51 \sqrt{\varepsilon\,[\mathrm{eV}]}\ \mathrm{Å}^{-1}$

hν : $k = 0.51 \cdot \varepsilon\,[\mathrm{eV}] \cdot 10^{-3}\,\mathrm{Å}^{-1}$

Photoemission:



Conservation Laws:

$$\varepsilon_1 + h\nu = \varepsilon_2$$

$$\vec{k}_1 + \vec{k}_{h\nu} = \vec{k}_2$$

··· cannot be simultaneously fullfilled !

⇨ prozess forbidden

Atoms, Molecules: Recoil

Solids : Recoil (= reciprocal lattice vector)

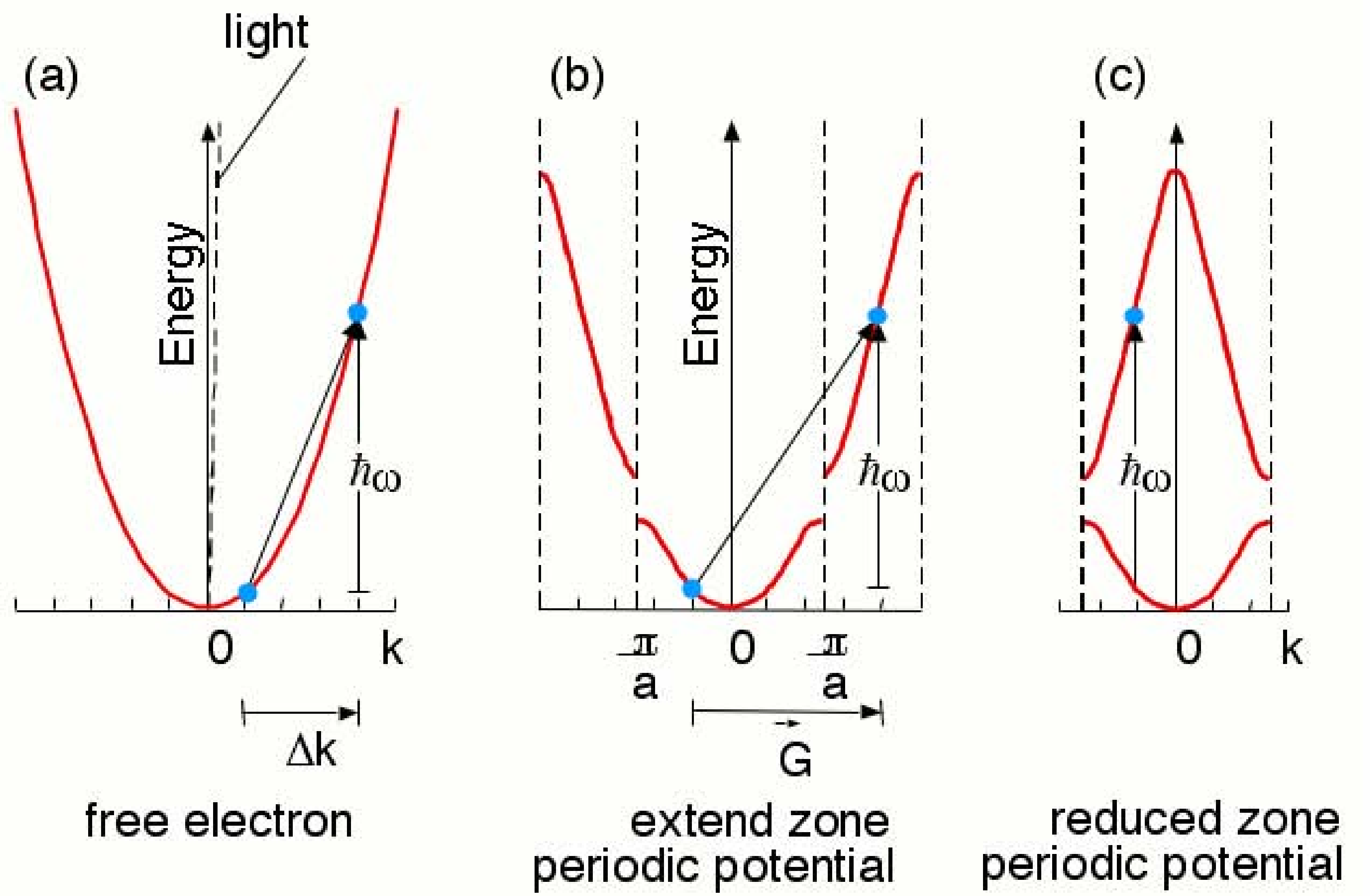
Photoemission from a Periodic Potential

Conservation Laws:

$$\varepsilon_i(\vec{k}_i) + h\nu = \varepsilon_f(\vec{k}_f)$$

$$\vec{k}_i + \vec{k}_{h\nu} + \vec{G} + \vec{g} = \vec{k}_f$$

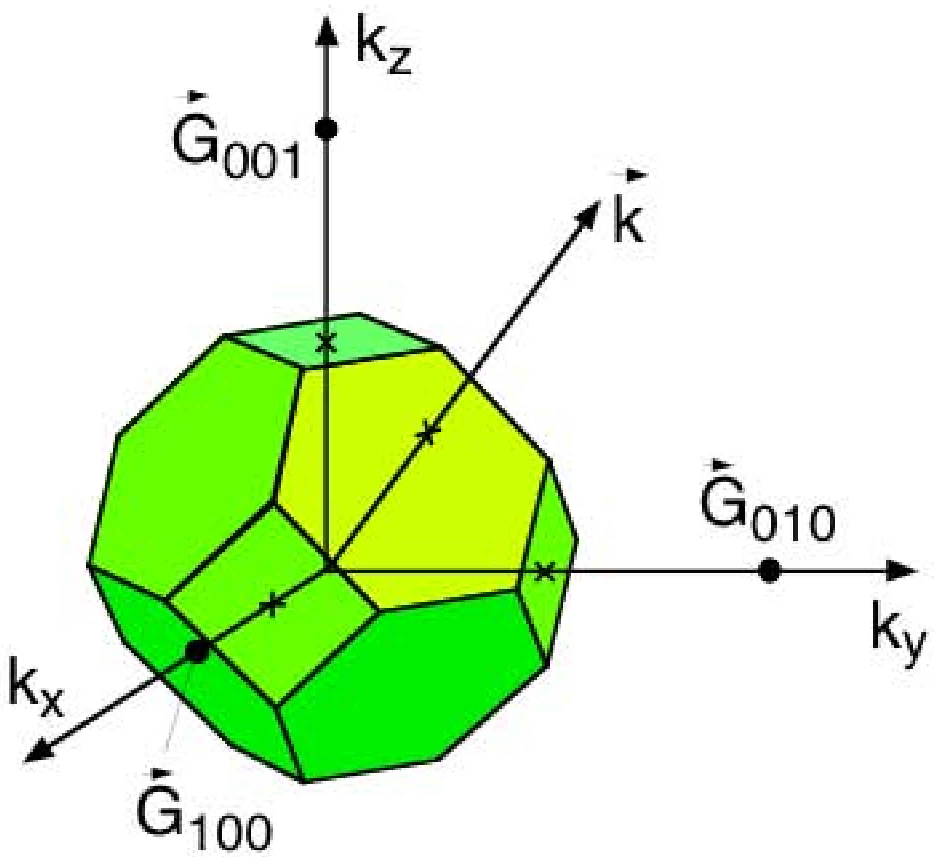
$\vec{k}_{h\nu} \approx 0$; $\vec{g}$: reconstructed surface



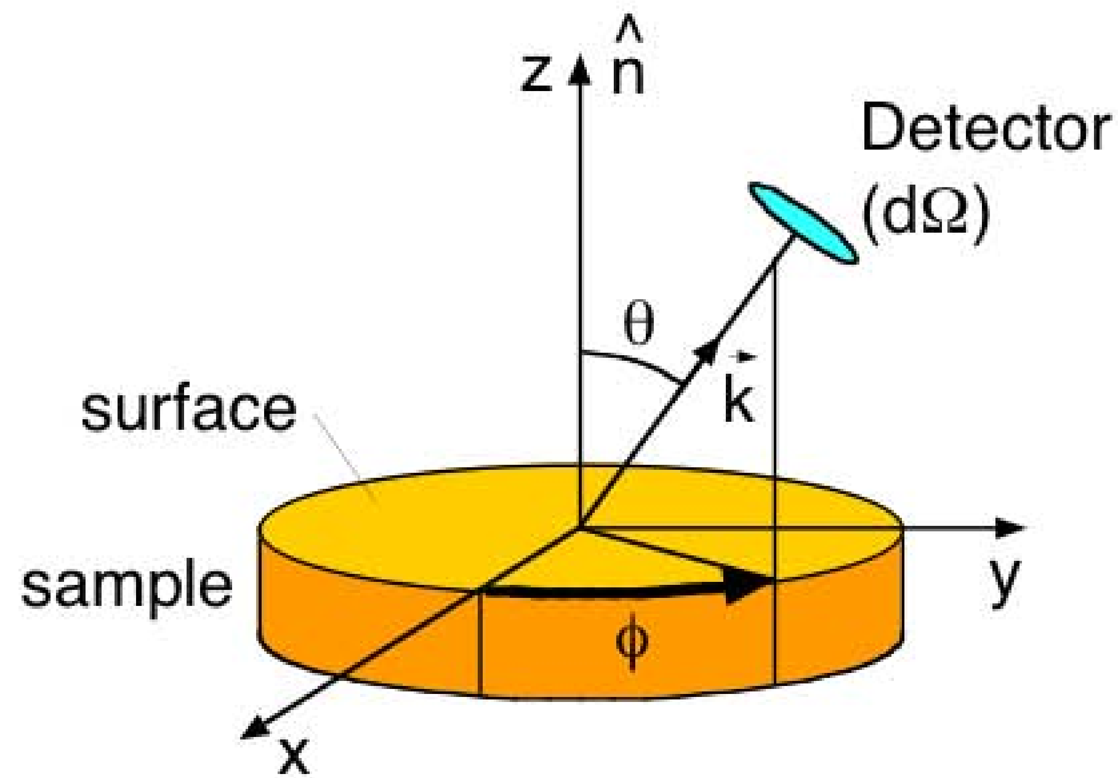
→ Direct Transitions

Measurement of the Photoelectron Momentum

reciprocal space:



real space:



direction: $\hat{k} = \theta, \phi$ (watch for refraction)

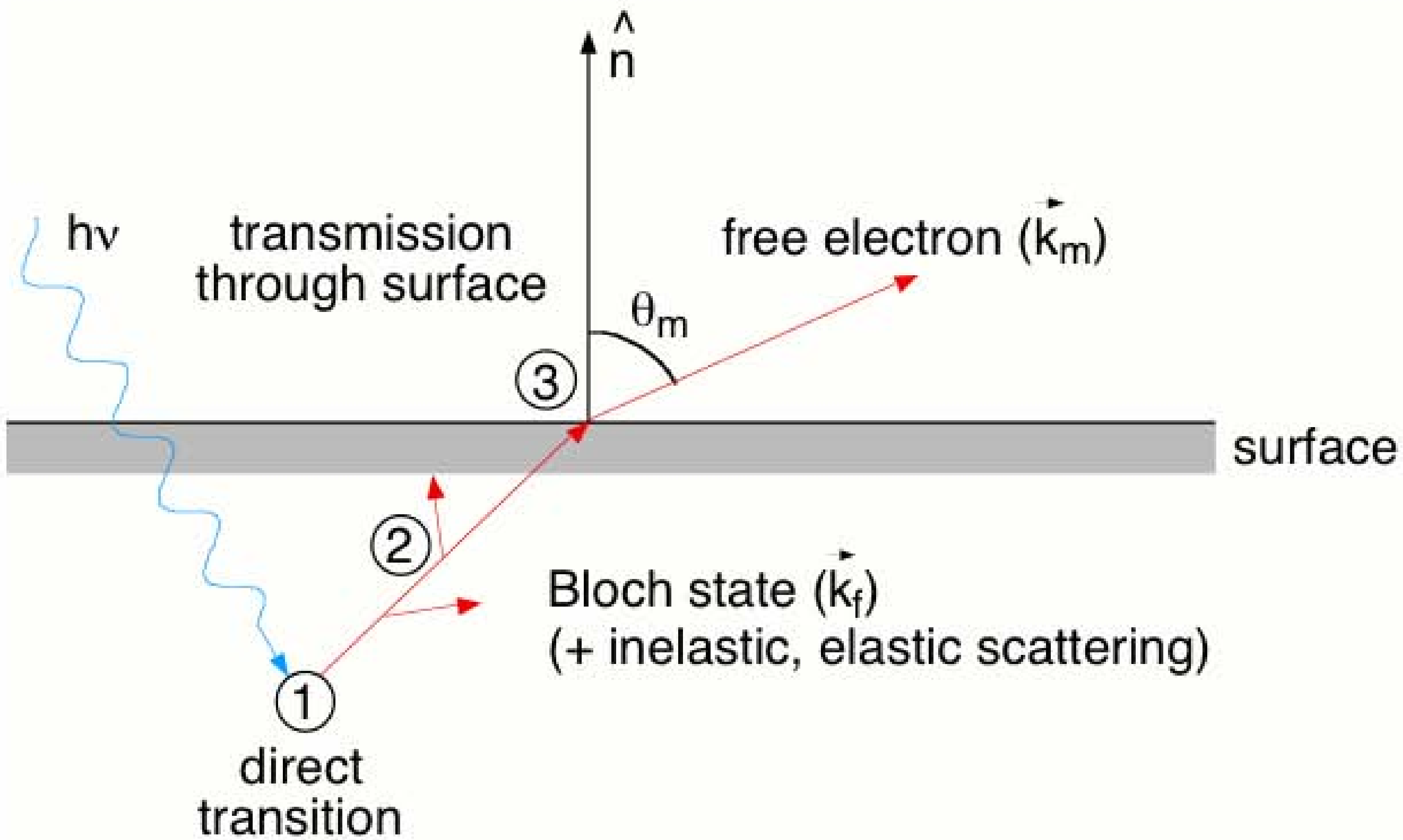
magnitude: from $\varepsilon_f(\vec{k})$ (ε_f is measured)

Problem: $\varepsilon_f(\vec{k})$ usually not known

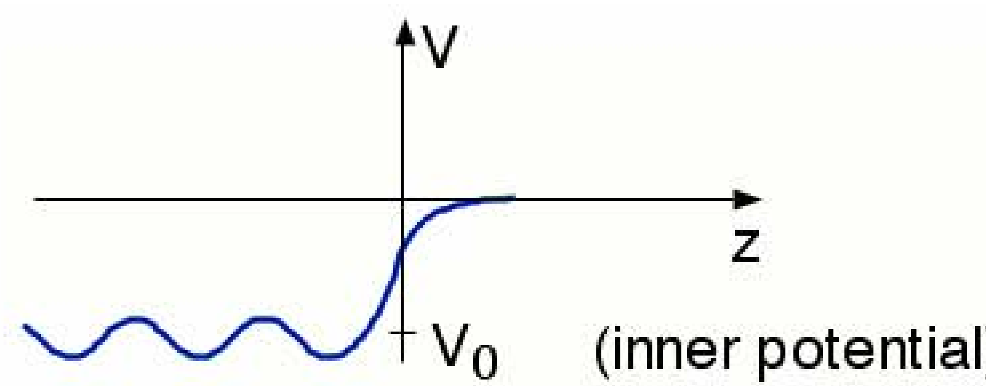
Solution: free electron final state

$$\varepsilon_f(k) = \frac{\hbar^2 k^2}{2m}$$

The 3-Step Model



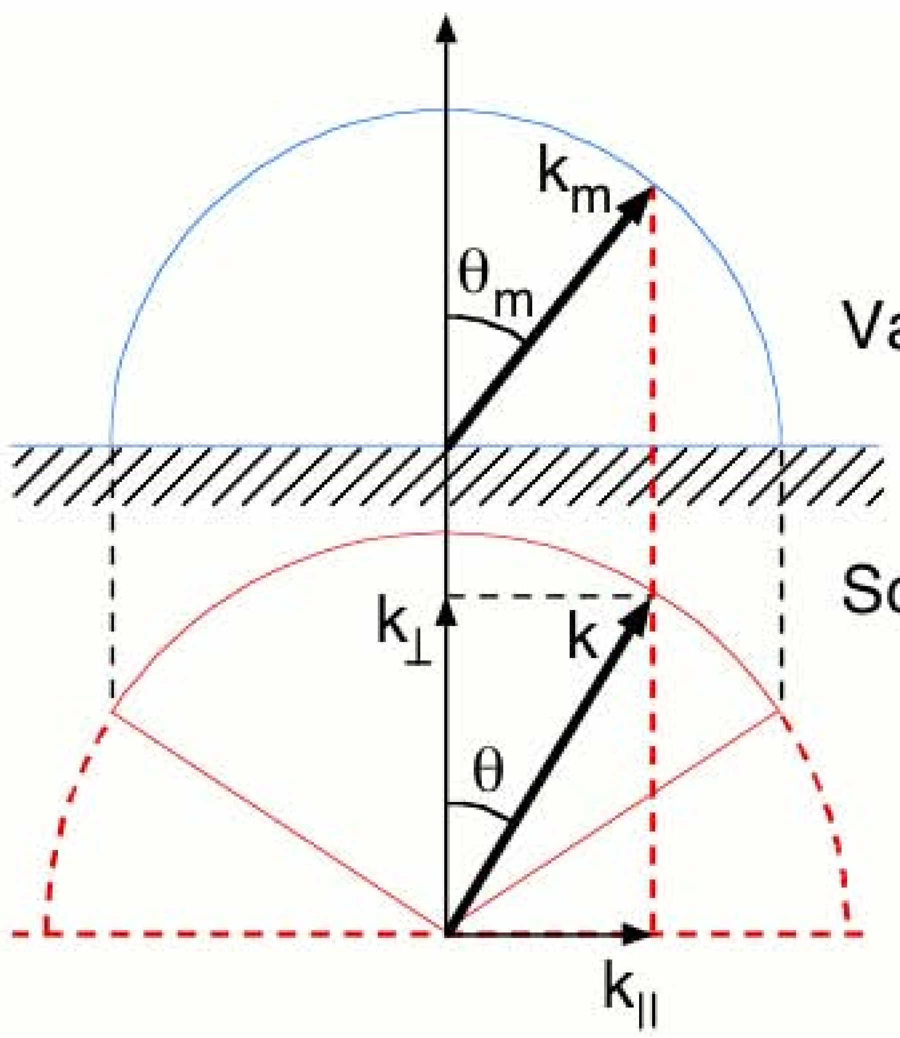
1. Photoexcitation
2. Propagation to surface
3. surface potential step → Refraction



periodicity within surface → $\vec{k}_{f\parallel} = \vec{k}_{m\parallel}$

surface potential step → $\vec{k}_{f\perp} > \vec{k}_{m\perp}$

Refraction at the Surface Potential Step



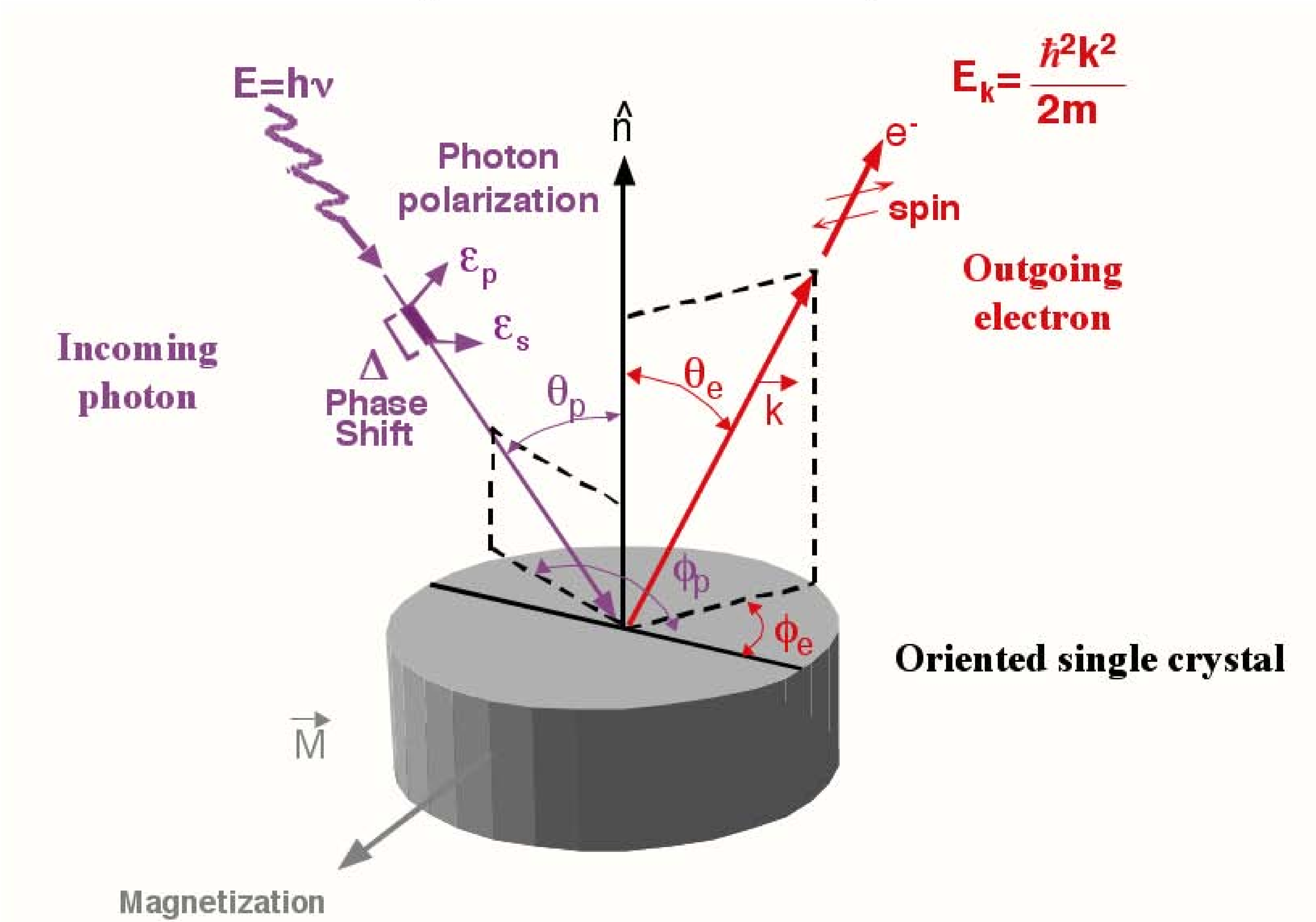
$E_{kin} \approx 17eV$

$E_{kin} \approx 28eV$

$$\sin\theta = \sin\theta_m \sqrt{\frac{h\nu - \Phi}{h\nu - \Phi + V_0}}$$

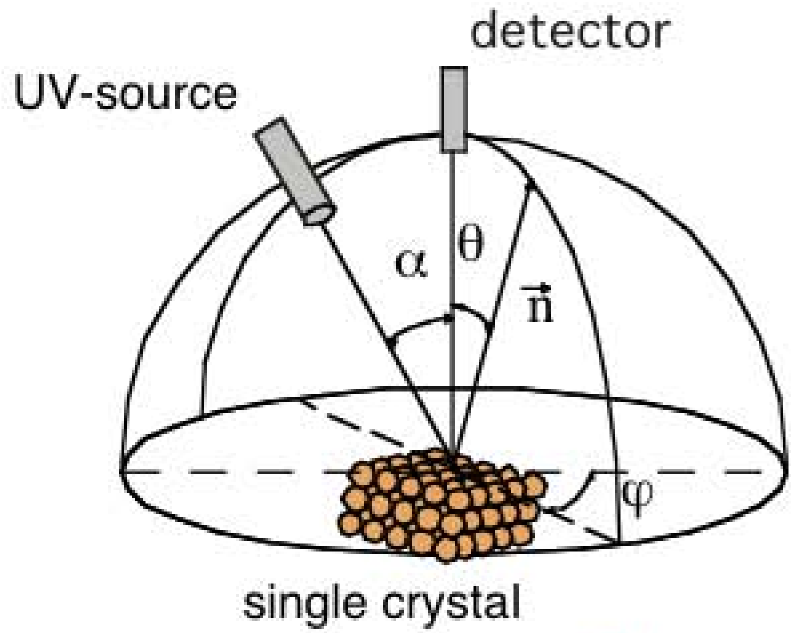
Φ : work function
V_0 : inner potential

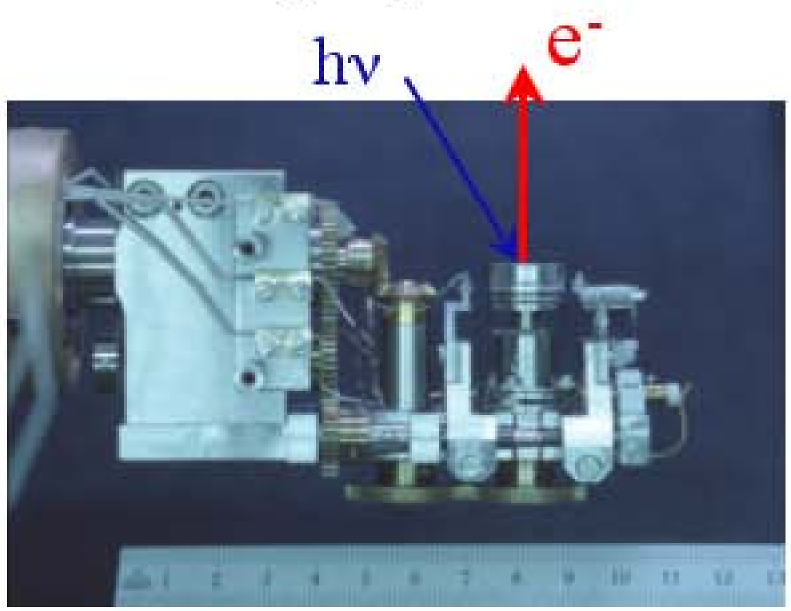
The photoemission experiment

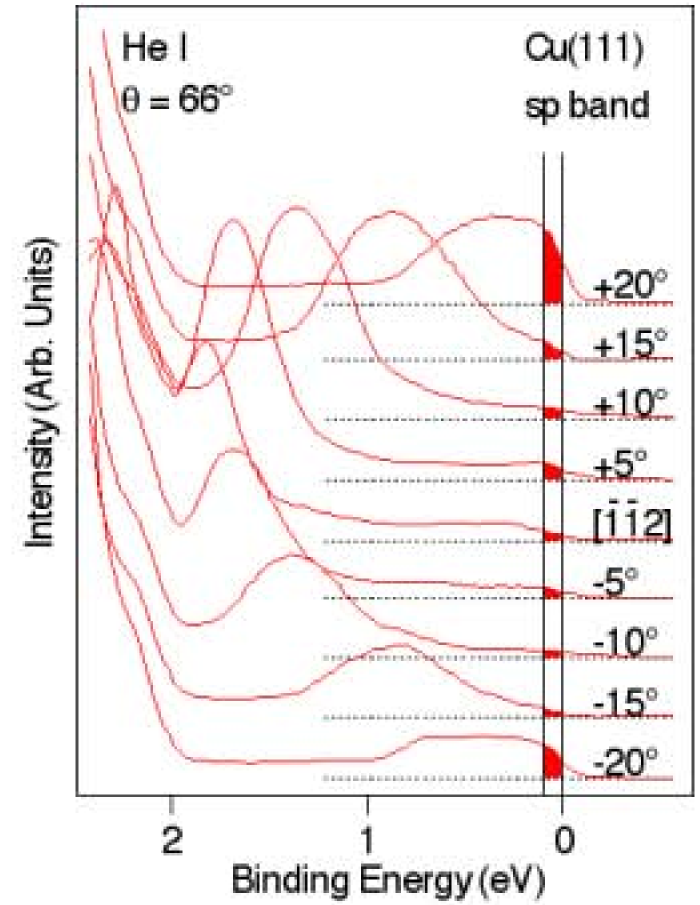


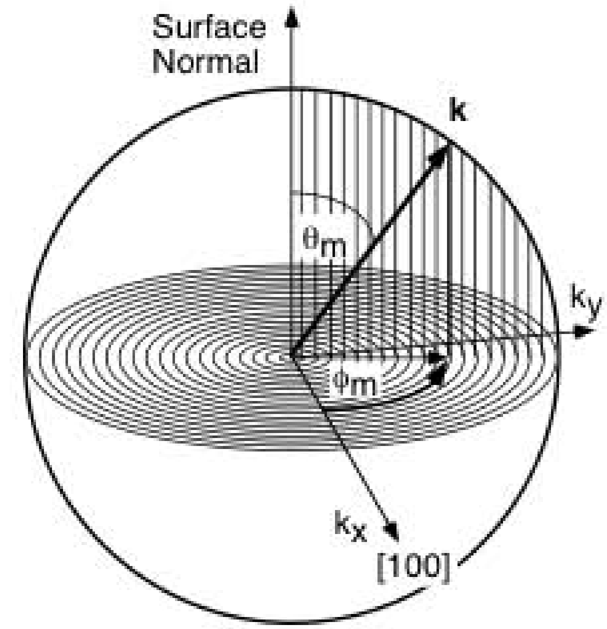
Courtesy G. Paolucci

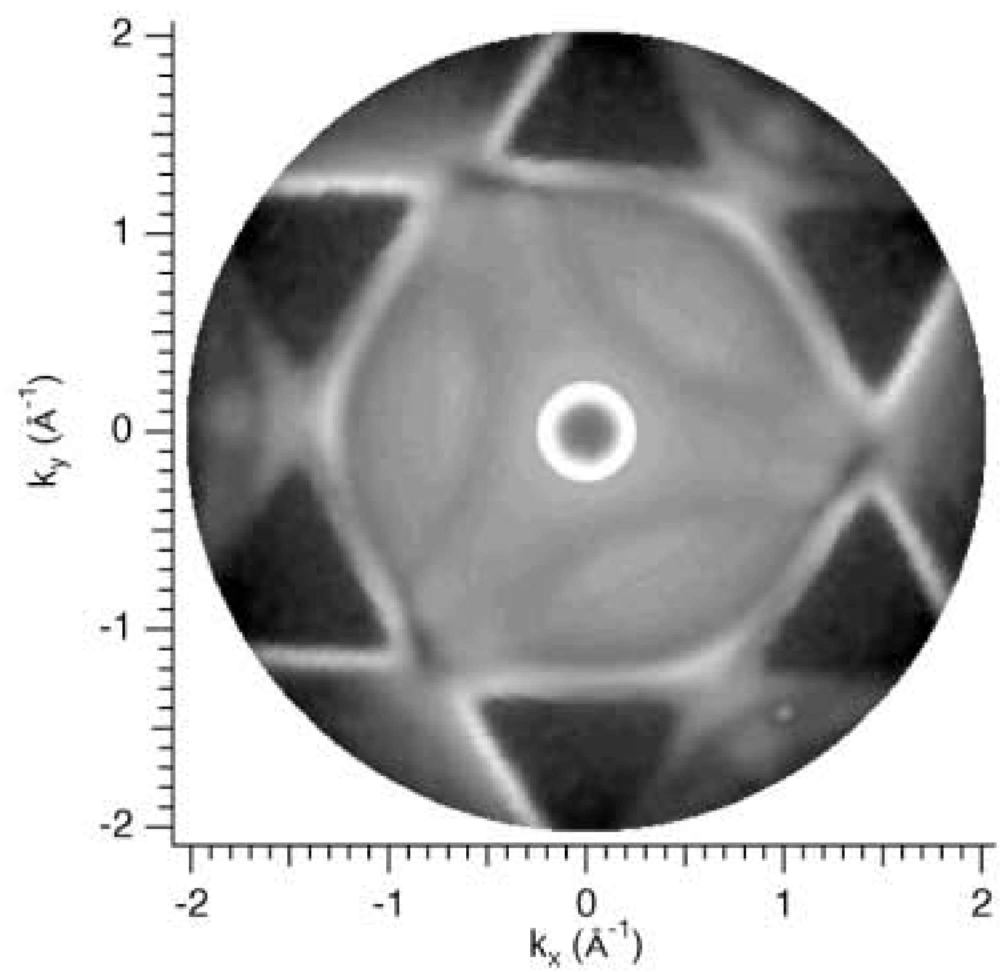
Fermi Surface Mapping by Photoemission

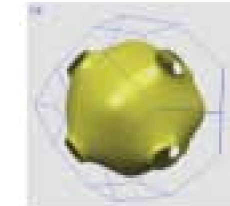




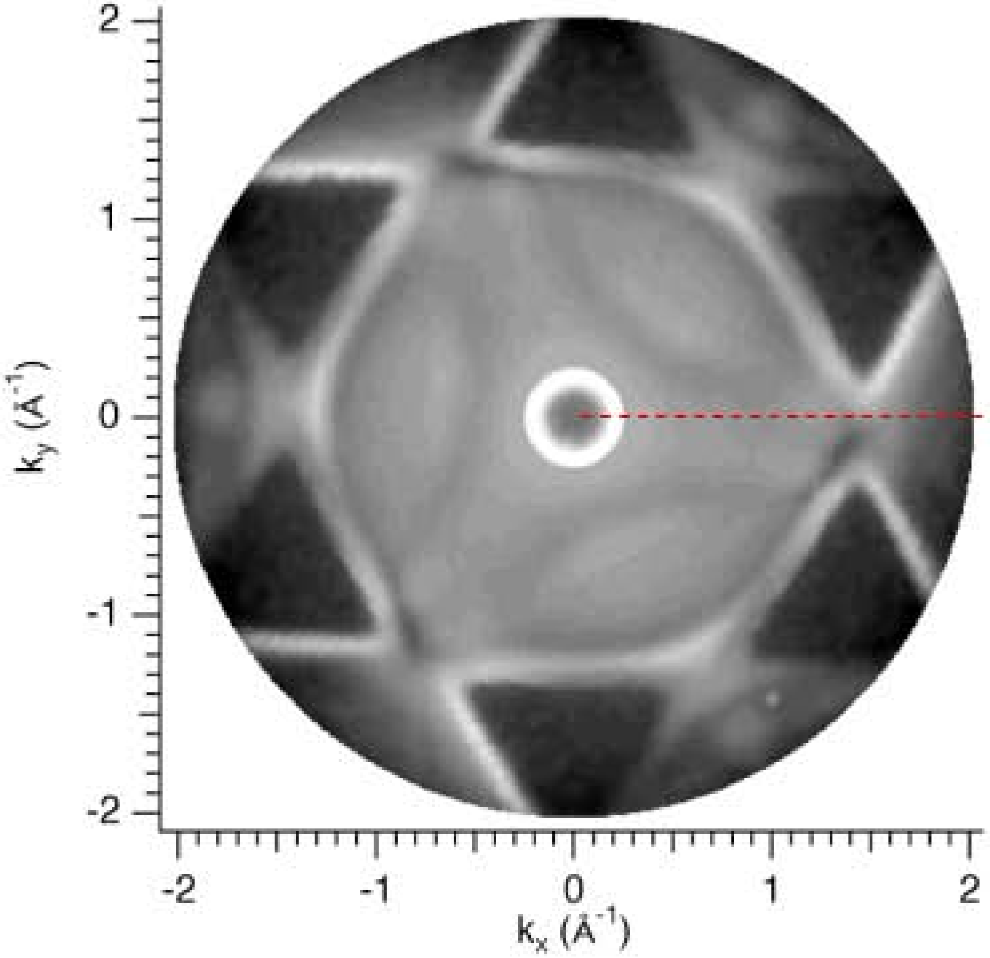






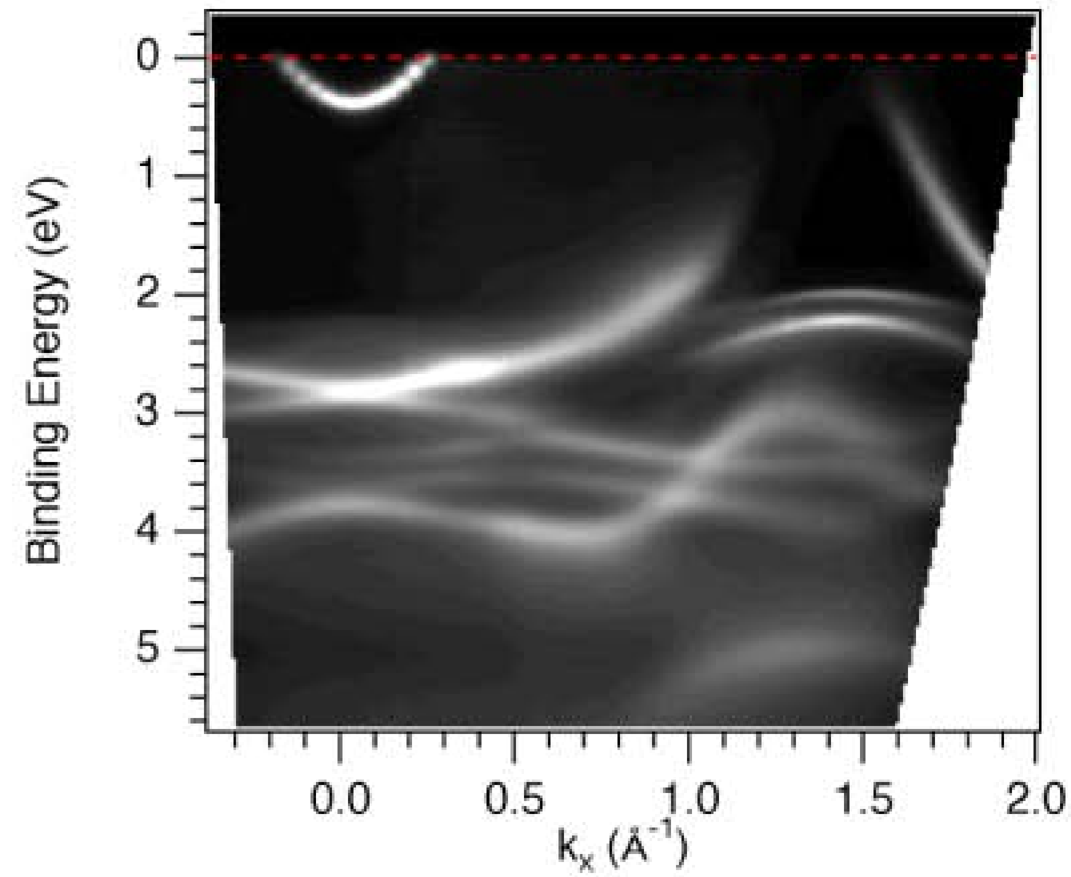


Angle-Resolved Photoemission from Cu(111)



$E_i = E_{fermi}$, scanning of (θ, ϕ):

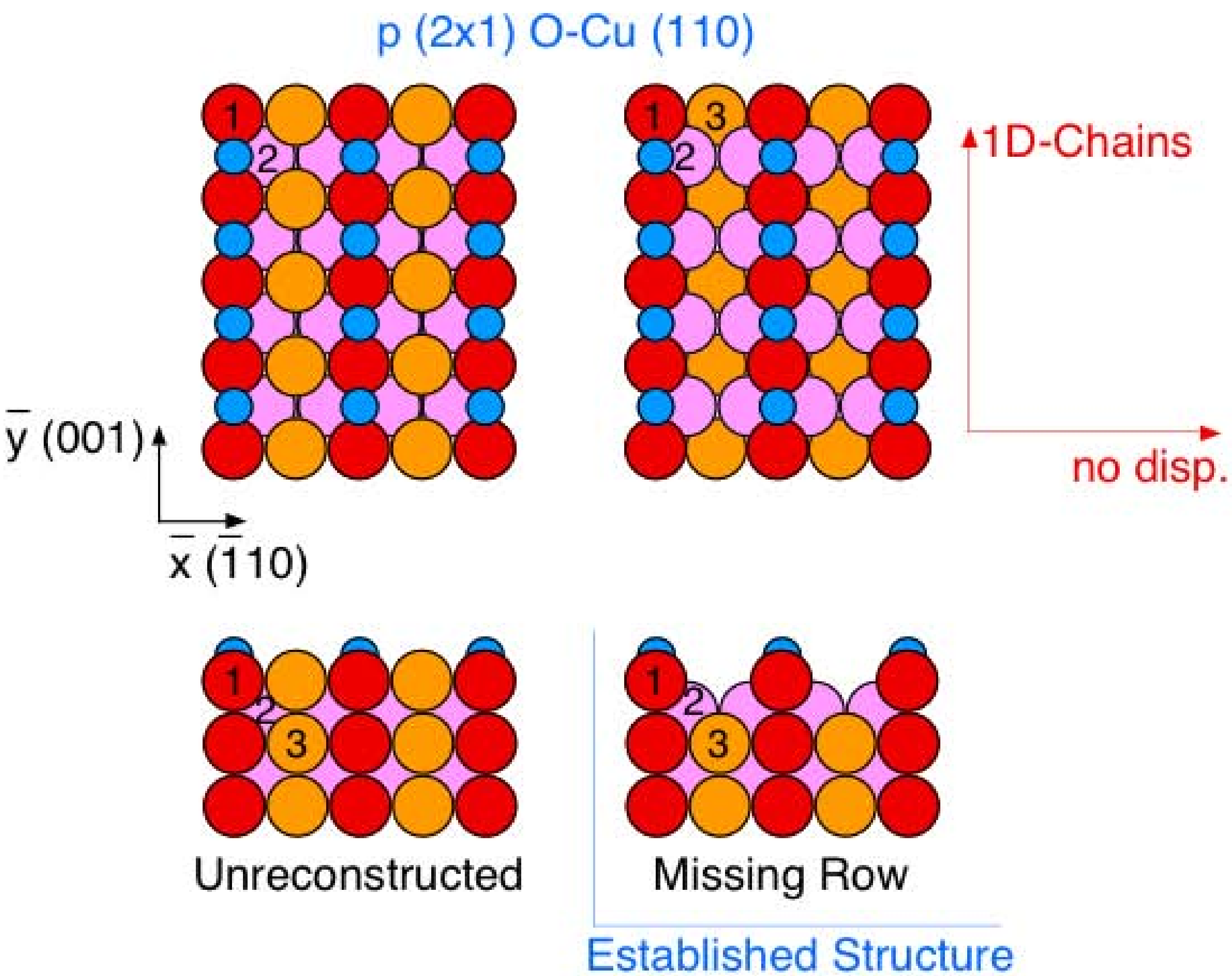
Cut through the bulk Fermi surface

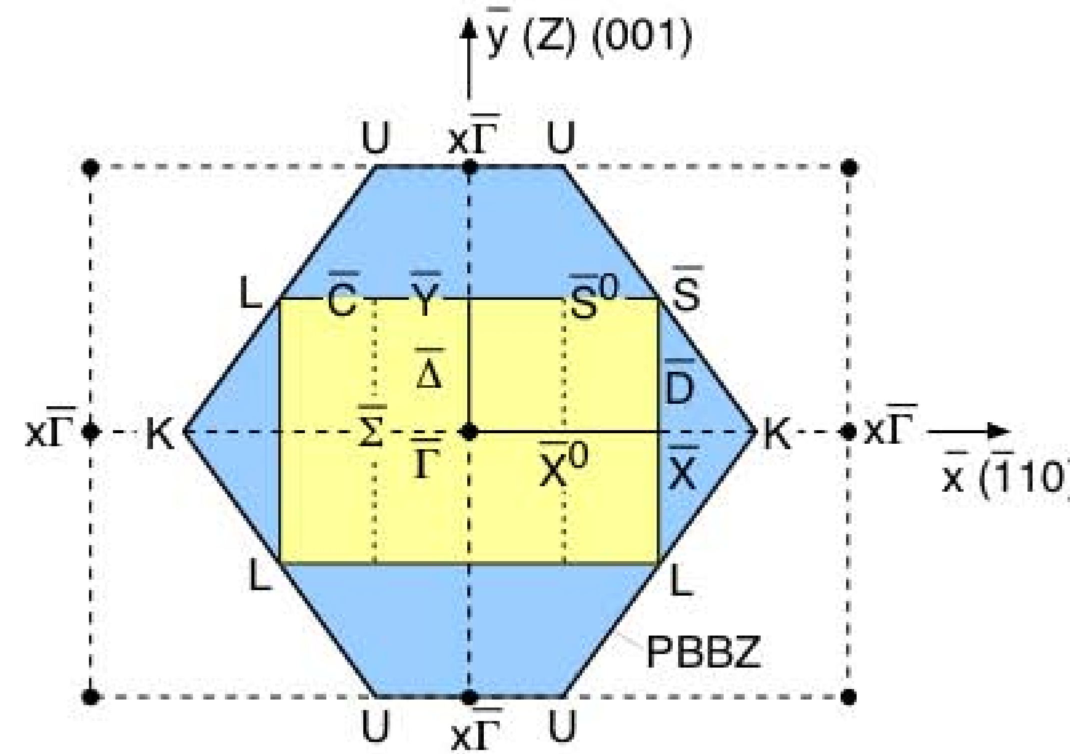


scanning of E_i *and* θ:

Band structure along curved line in 3D k - space

A One-Dimensional Example:

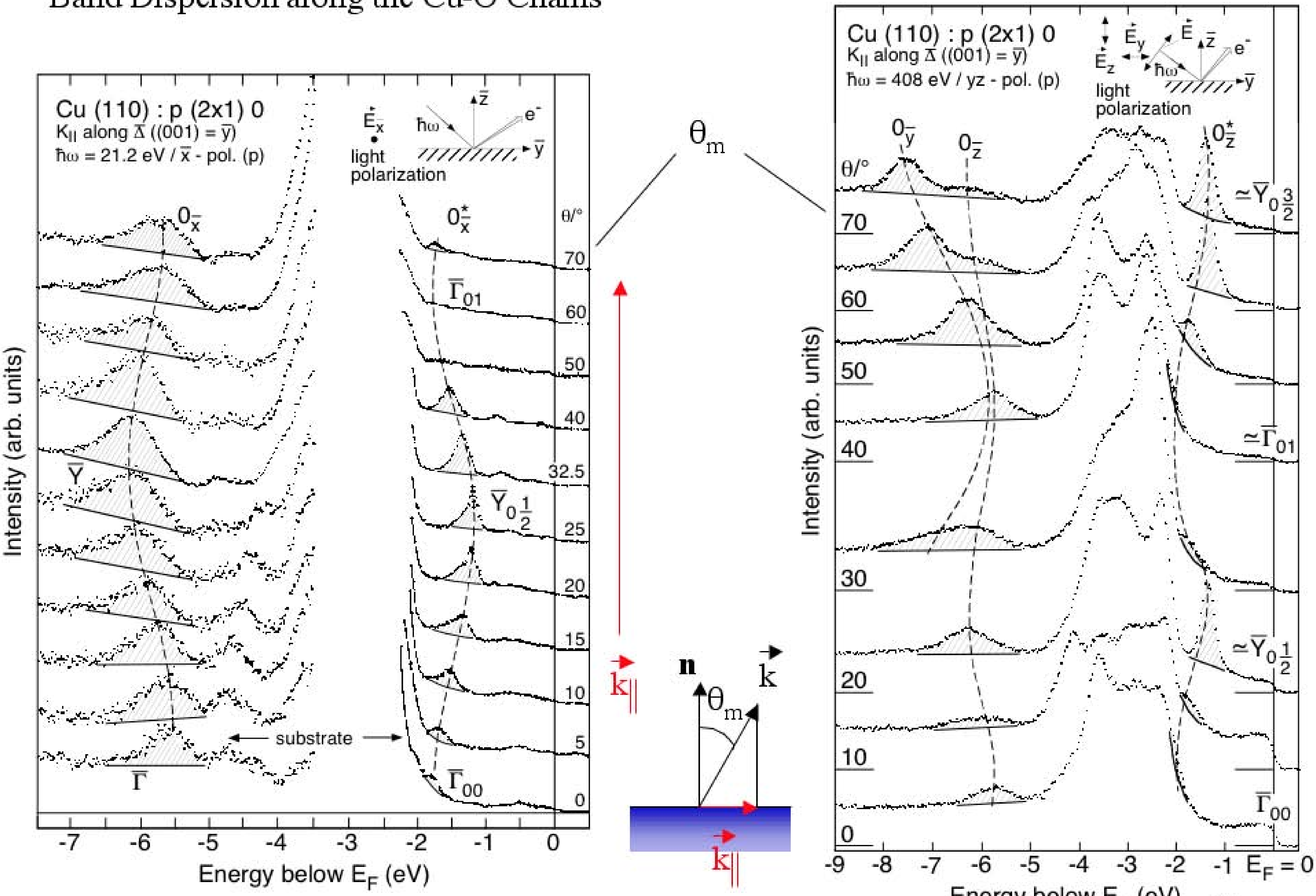




fcc (110) surface Brillouin zone (SBZ)

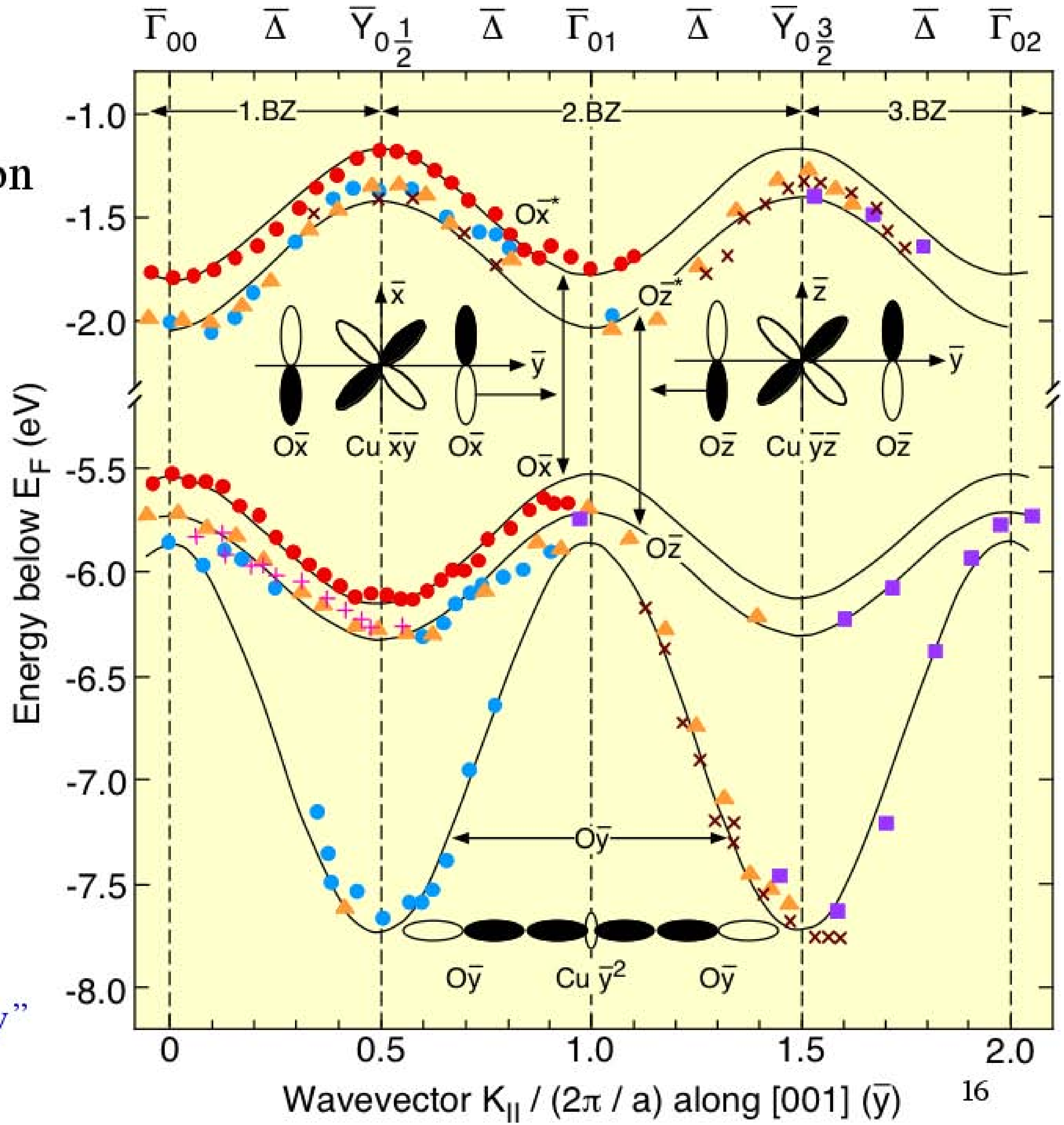
From S.Hüfner, "Photoelectron Spectroscopy" (Springer)

Band Dispersion along the Cu-O Chains



From S.Hüfner, "Photoelectron Spectroscopy" (Springer)

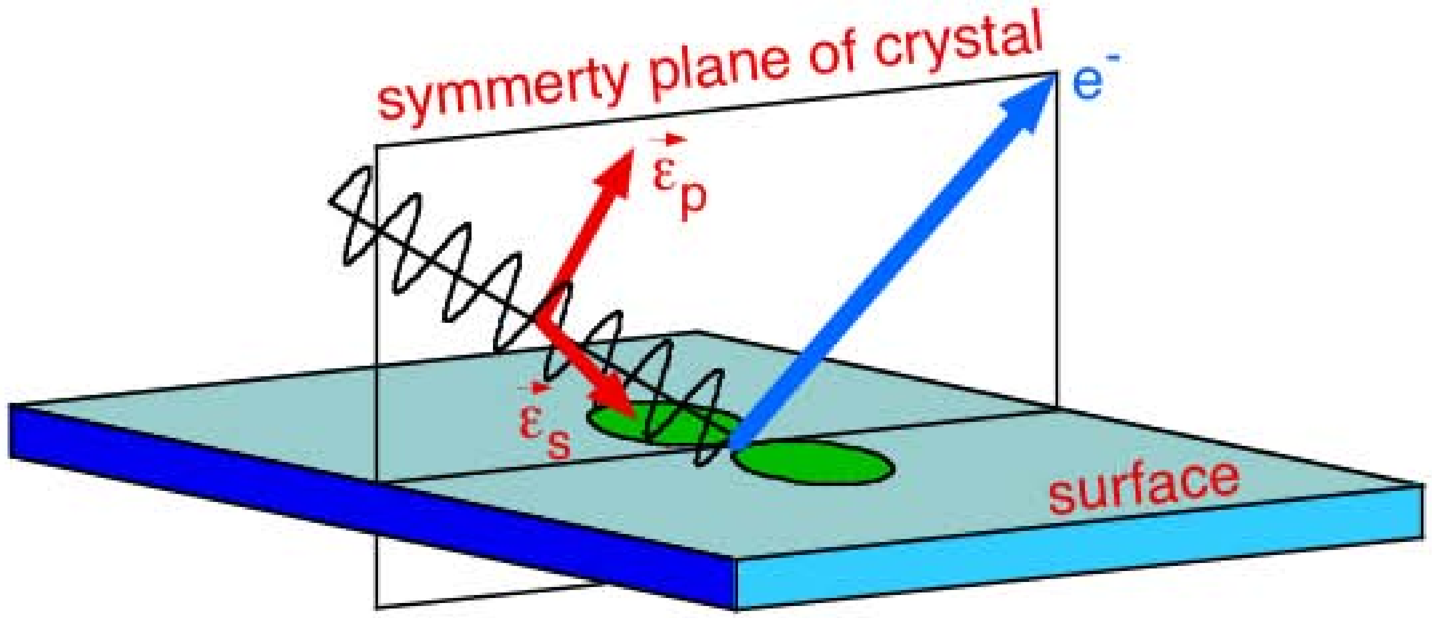
Finding all the States - Interpretation



Often a simple tight binding model works quite well !

From S.Hüfner, "Photoelectron Spectroscopy" (Springer)

Intensities in Valence Photoemission - Symmetry Effects



$\vec{\varepsilon}_p$ photon polarization in...

$\vec{\varepsilon}_s$ ...perpendicular ("senkrecht") to...scattering plane

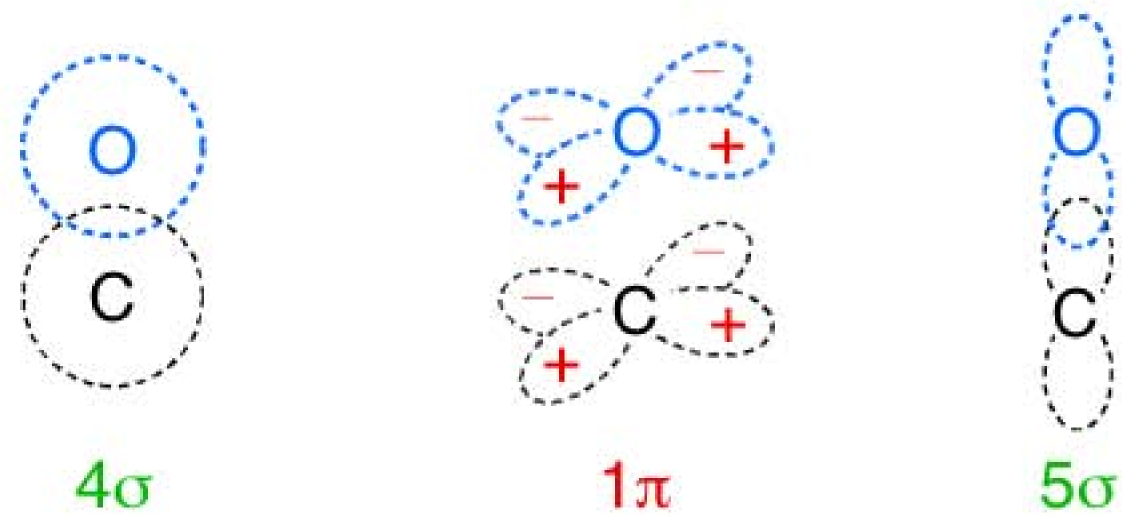
photoemission matrix element:

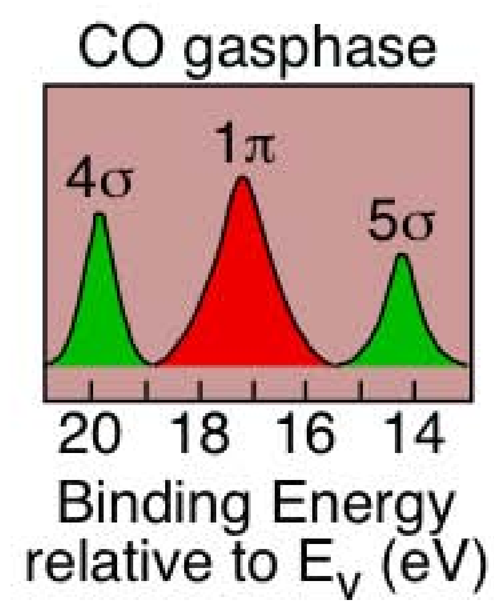
$$\left| \langle \phi_{f,kin} \right| \vec{r}_k \cdot \vec{\varepsilon} \left| \phi_{i,k(\vec{r}_k)} \rangle \right|^2 \rightarrow \text{Intensity}$$

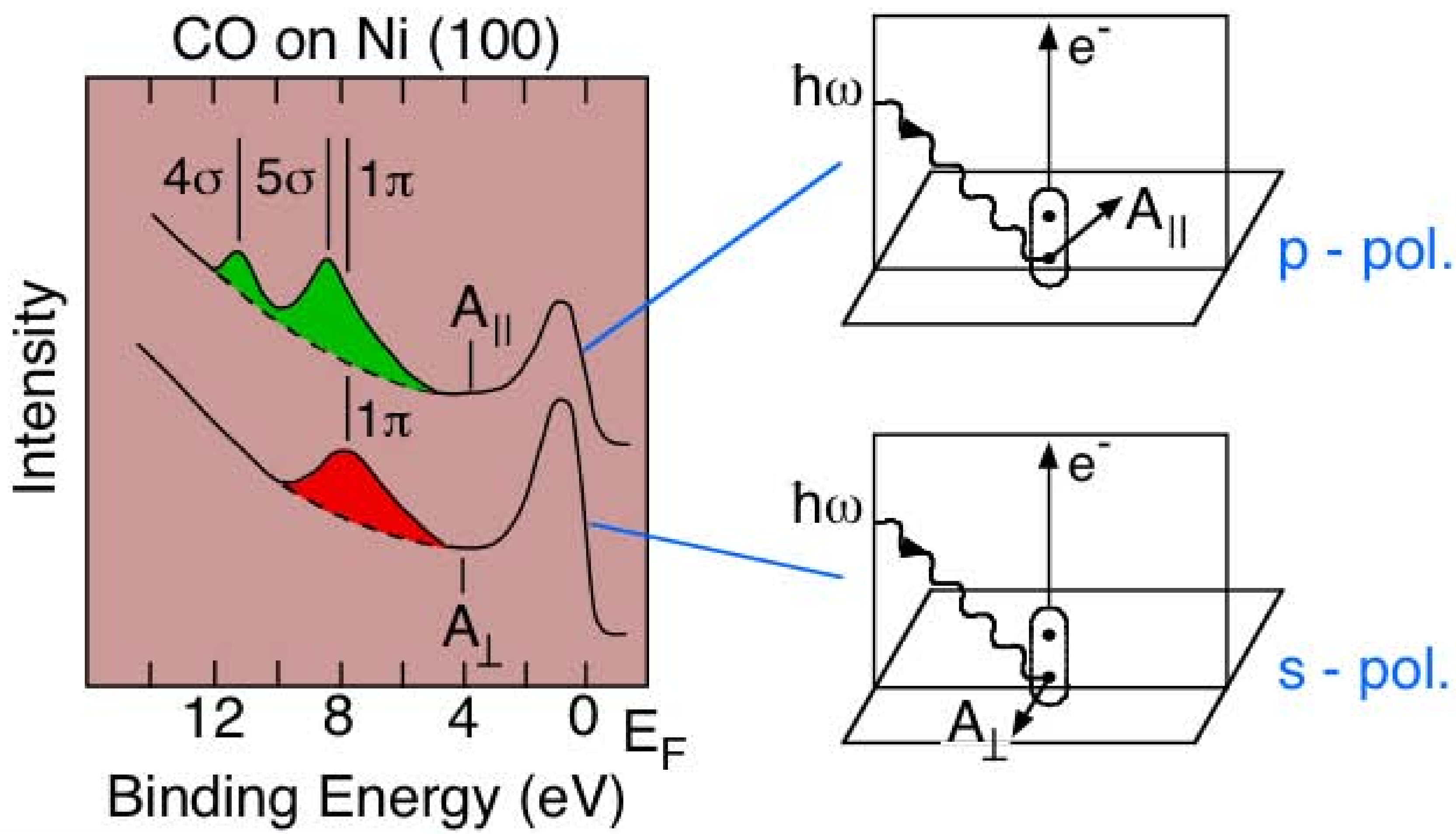
mirror reflection symmetries:

p - pol.	+1	+1	-1	0
	+1	+1	+1	max.
s - pol.	+1	-1	-1	max.
	+1	-1	+1	0

CO Molecular Orbitals







from Hüfner

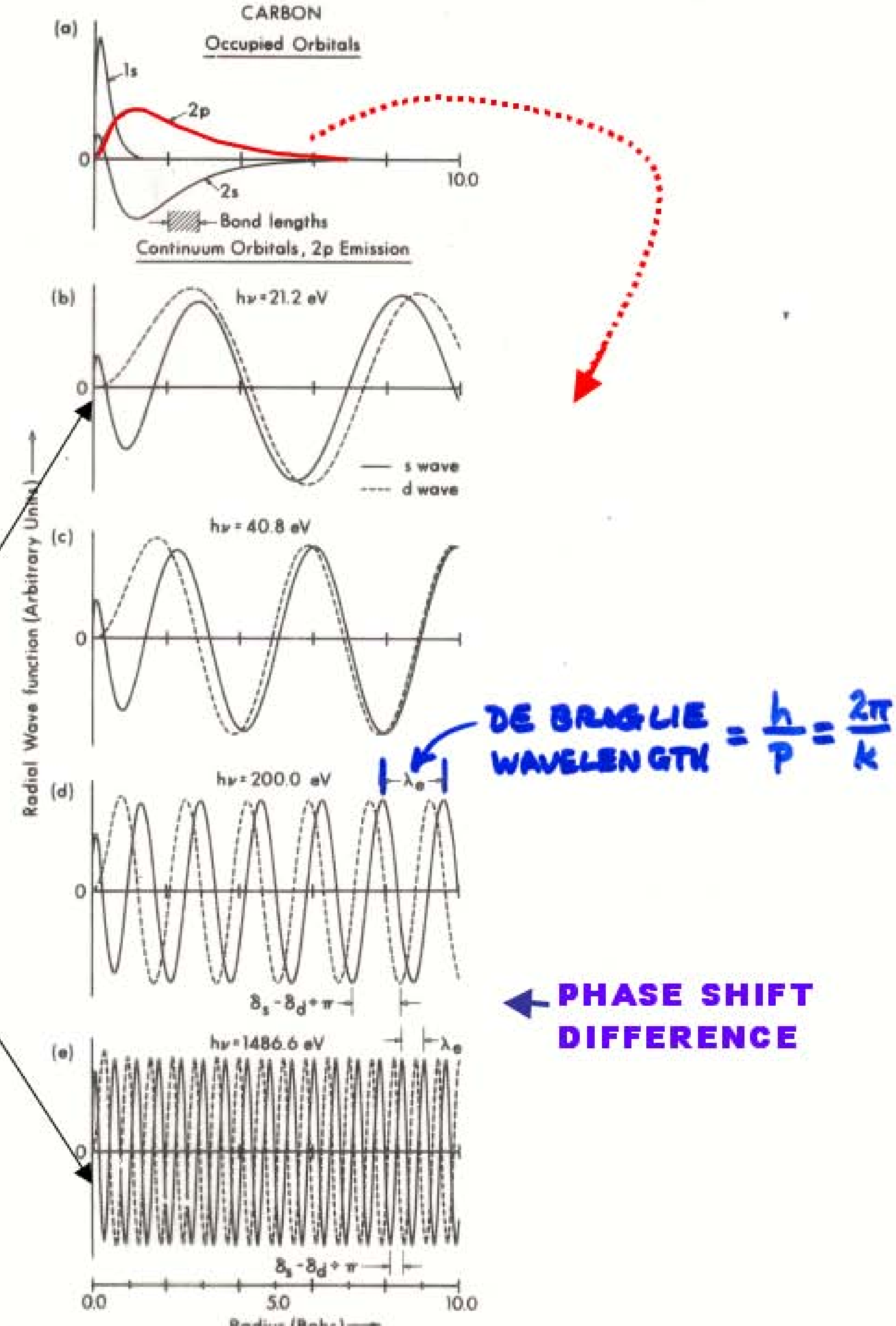
Intensities in Valence Photoemission - Atomic Effects

$$m_{i,f} \sim \langle \phi_{f,kin} | \vec{r}\cdot\vec{\varepsilon} | \phi_{i,k} \rangle$$

as for core levels

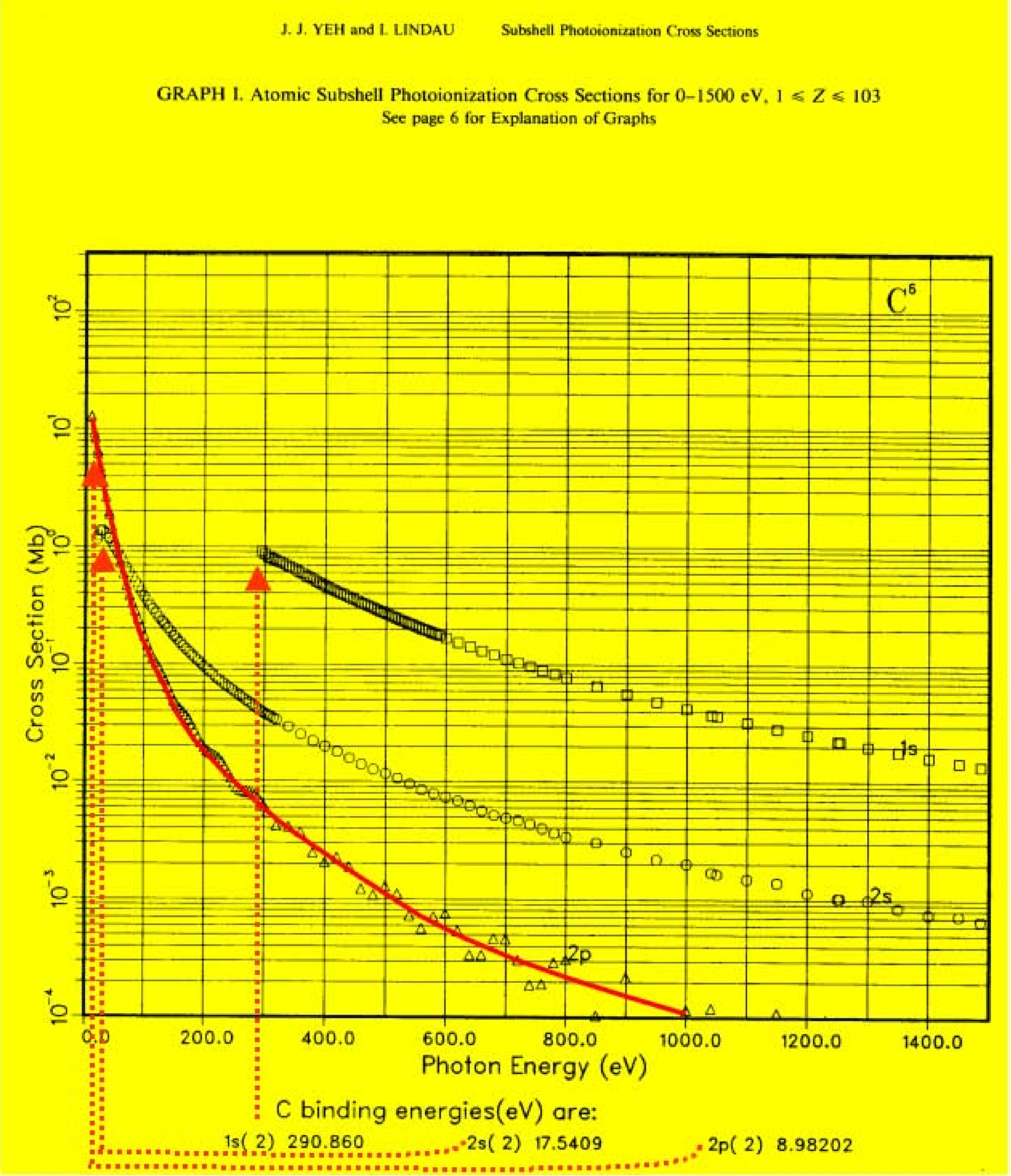
RADIAL MATRIX ELEMENTS TO $\ell \pm 1$ = s and d CHANNELS:

… for various energies



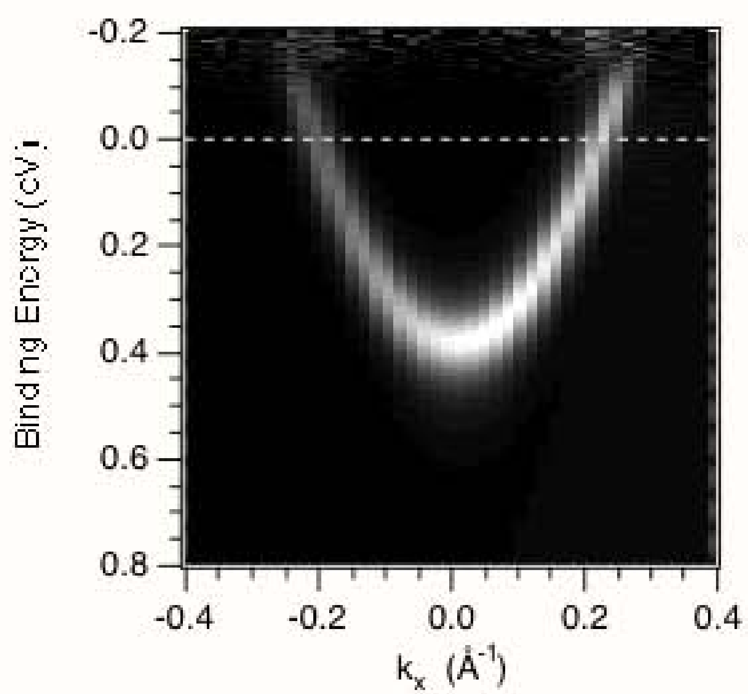
From C. S. Fadley's Lectures

Plus other examples
from Yeh and Lindau
in Sec. 1.5 of
X-Ray Data Booklet,
and plots for all elements at:
http://ulisse.elettra.trieste.i/
elements/WebElements.html

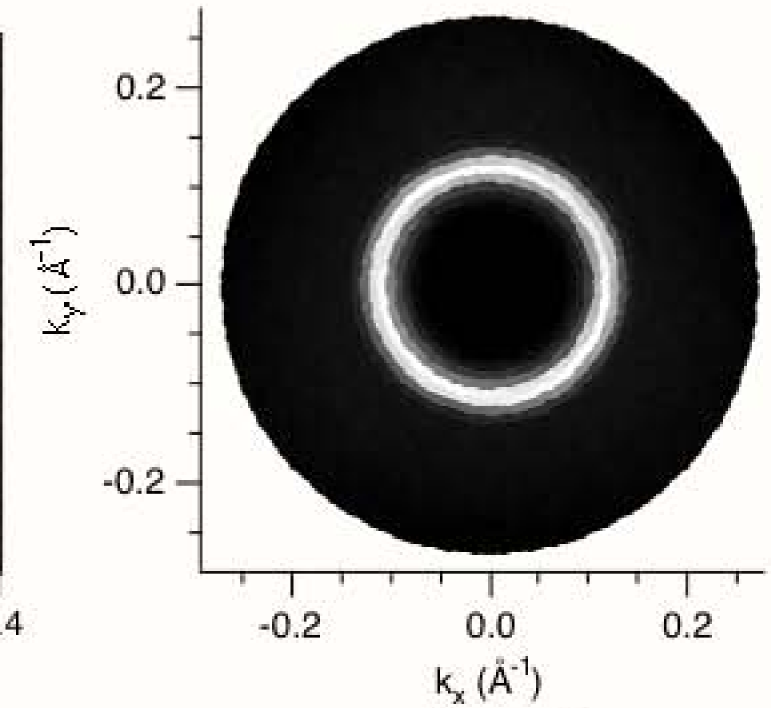


From C. S. Fadley's Lectures

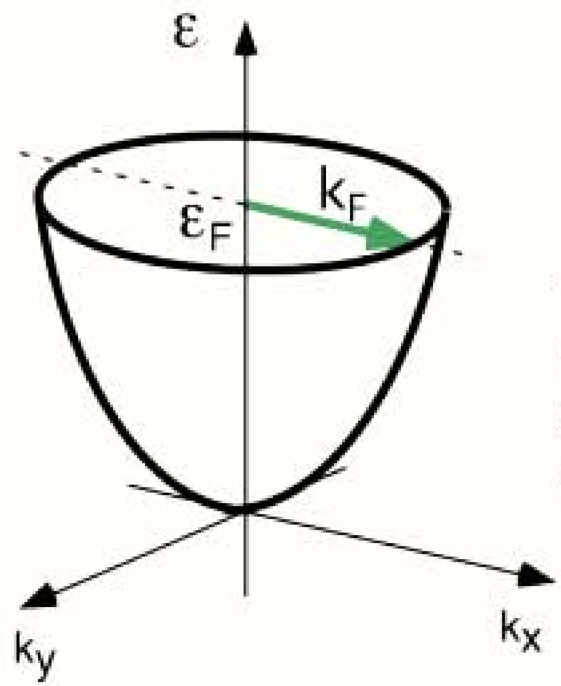
A 2D Example: The Shockley Surface State on Cu(111)



Energy dispersion



Fermi surface



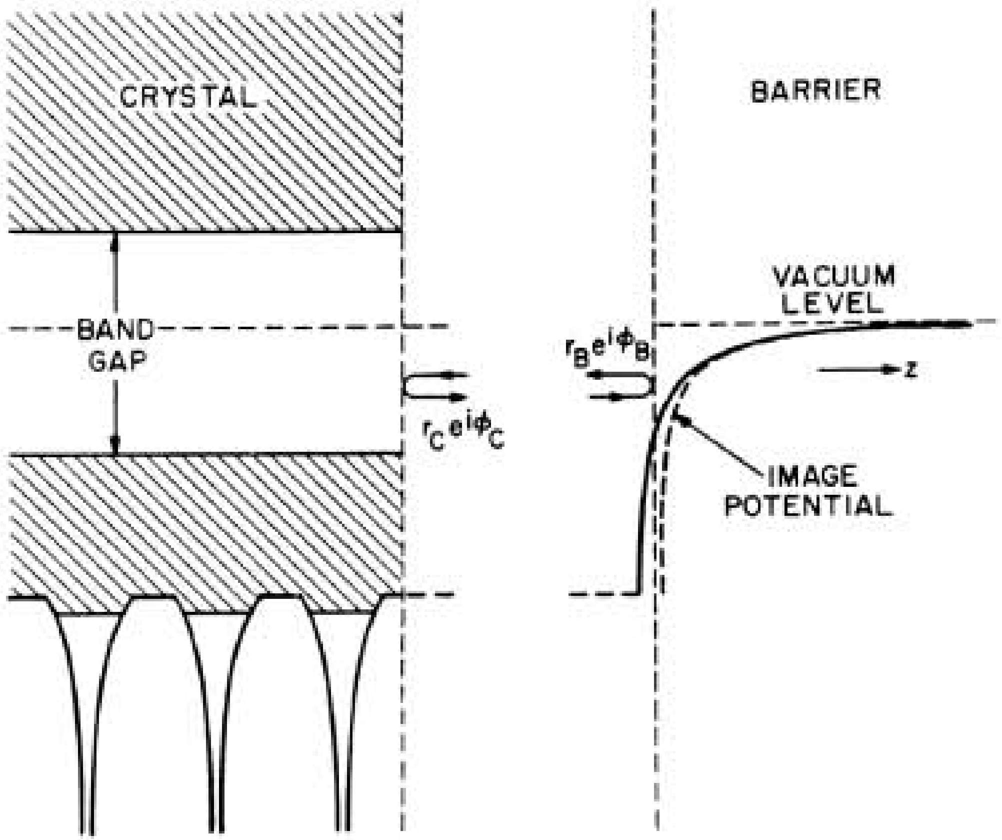
2D free electron gas

binding energy:	390 meV
effective mass:	0.42 m_e
Fermi wave length:	2.9 nm
coherence length:	~ 10 nm (300K)

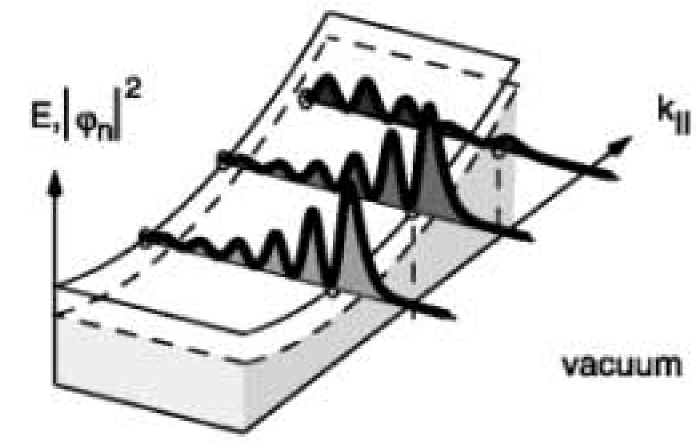
Courtesy F. Baumberger

Multiple reflection model for surface states:

(N.V. Smith, PRB **32**, 3549 (1985))



N.V. Smith, PRB **32**, 3549 (1985)



Surface state wave functions for different $k_{//}$

(from Kliewer et al. Science 288, 1399 (2000))

$$\phi_c + \phi_b = 2\pi n$$

$$\text{Cu(111)},\ n = 0:\ E_B = 0.3eV, m^* = 0.5m_e$$

Courtesy F. Baumberger

The Long-Range Image Potential Near a Metal Surface

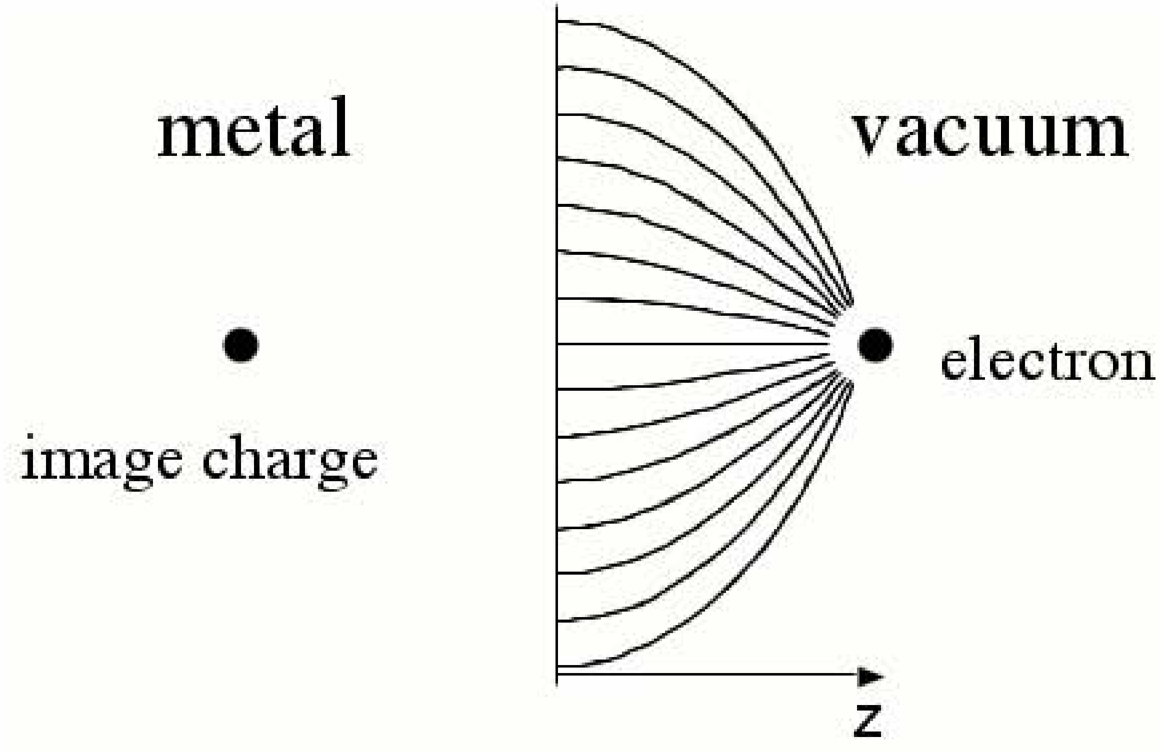
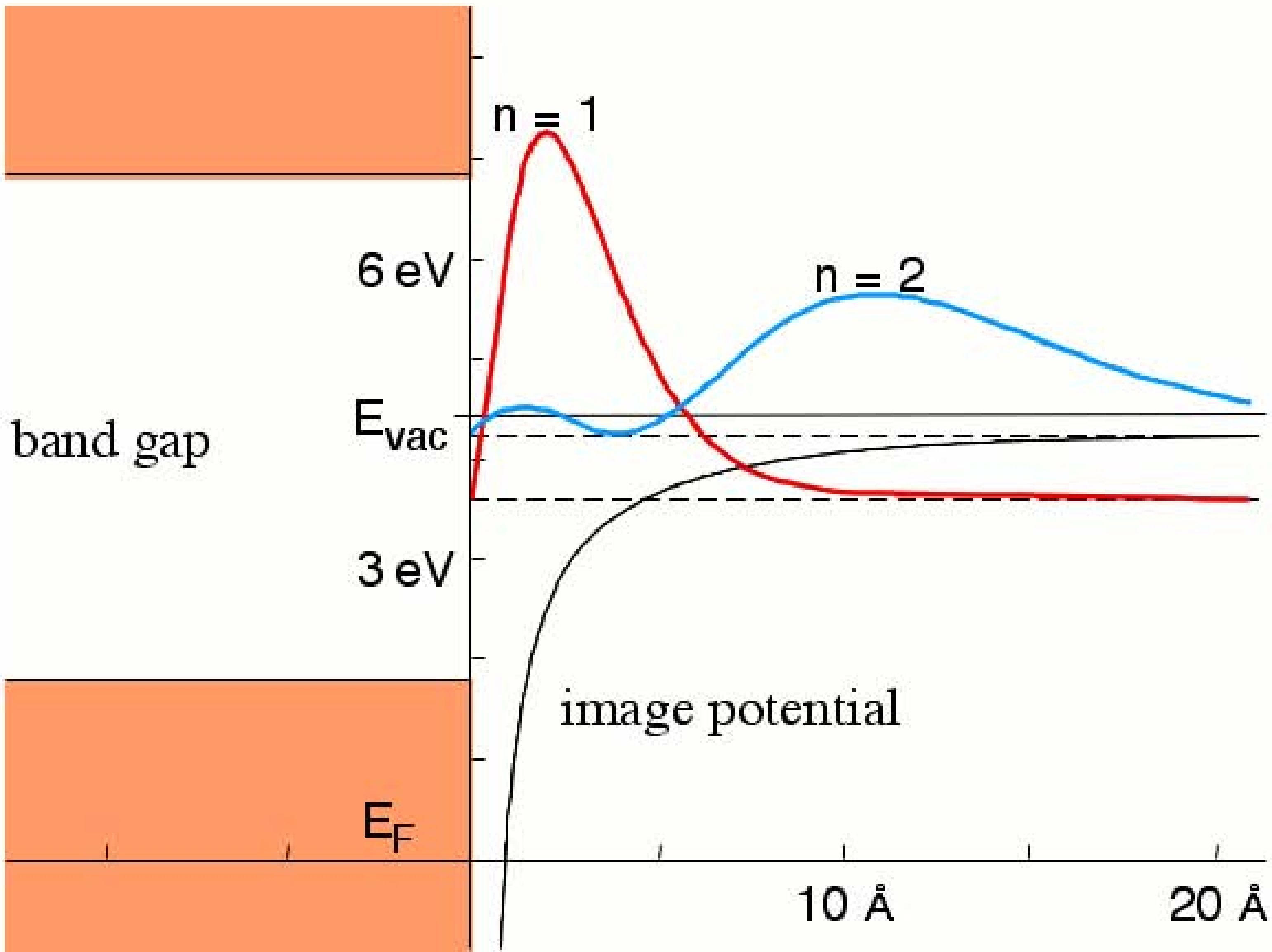


Image Potential States:

$E_B = 0.85\ \text{eV} / (n+a)^2$

(hydrogen-like Rydberg Series, with 'quantum defect' a accounting for electron reflectivity at the metal surface)



T. Fauster,
Appl. Phys. A 59, 63 (1994)

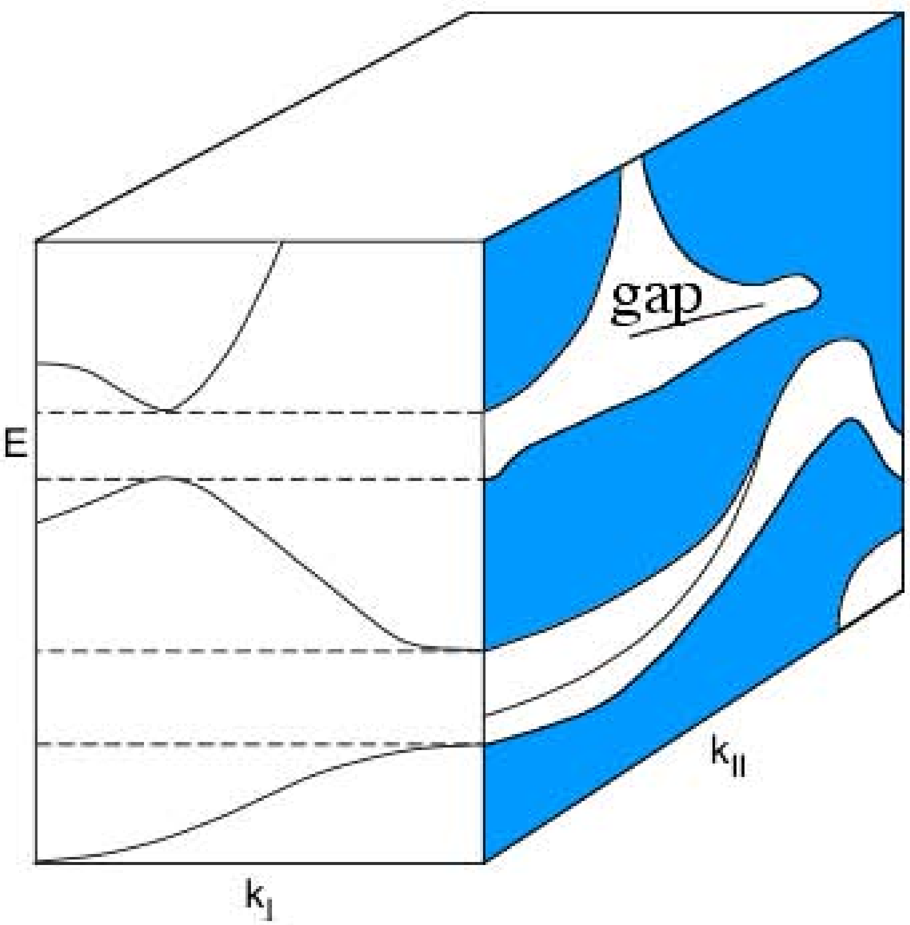
Where do surface states live in k space?

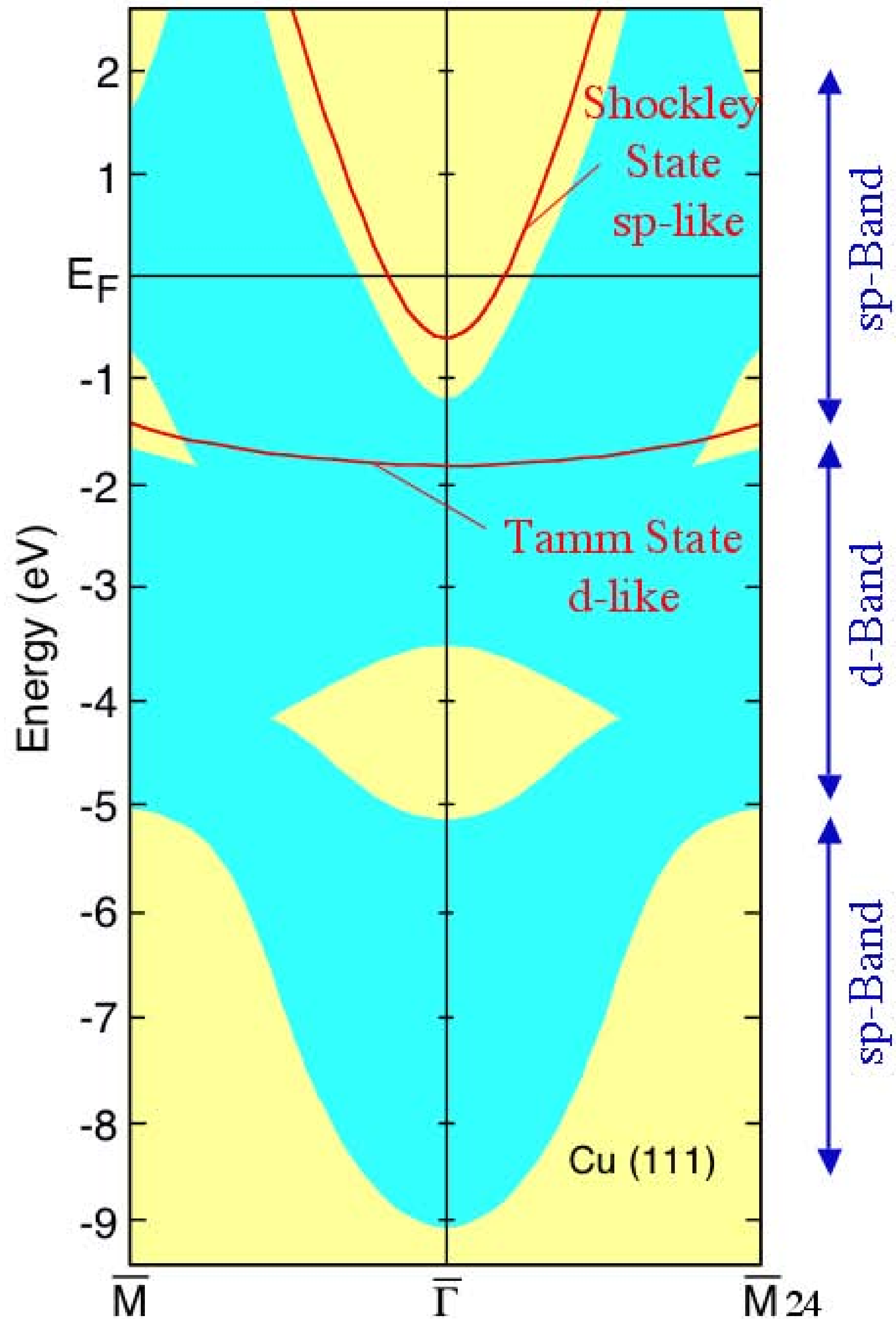
Experimental identification:

-"crud test" (sensitivity to adsorbates)

-no dispersion in k_{perp} (use synchrotron rad.)

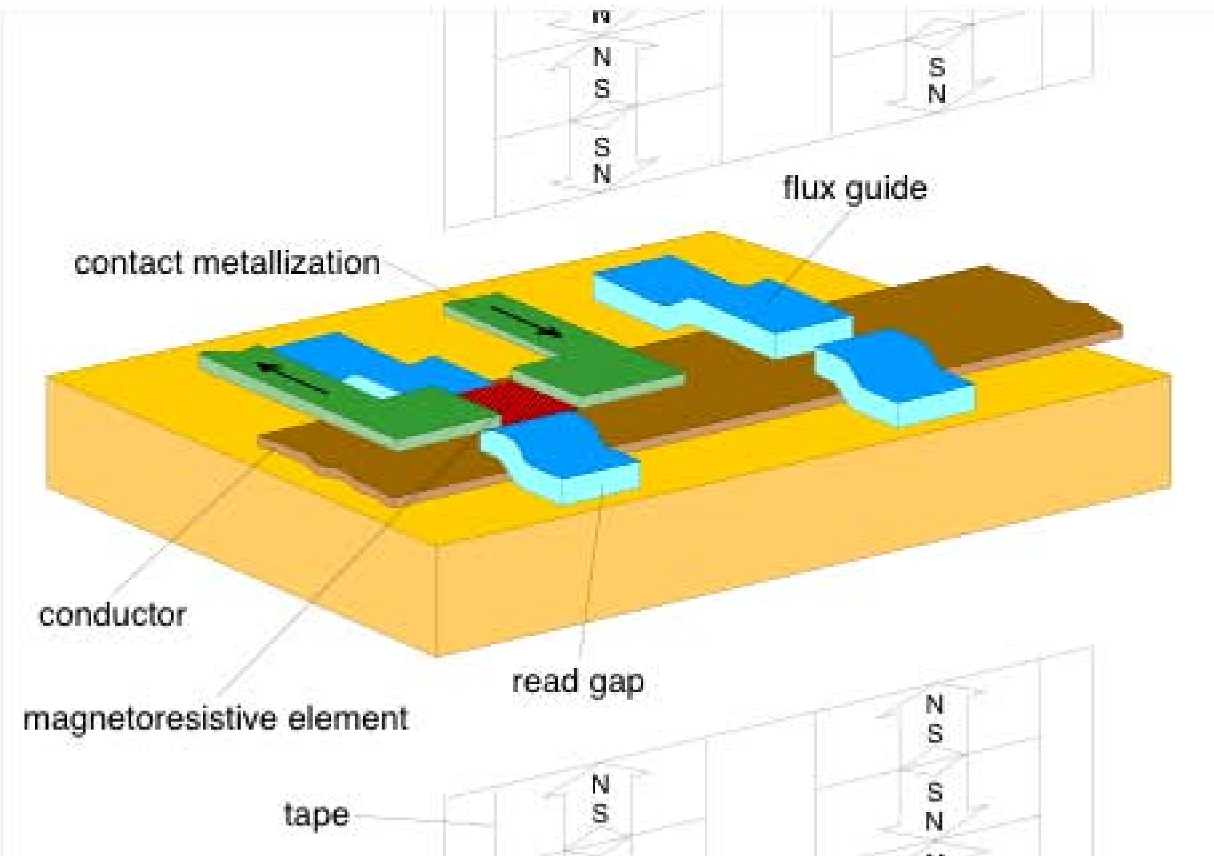
-lives in projected band gap





A 3D Example:
the Bulk Fermi Surface
of Copper

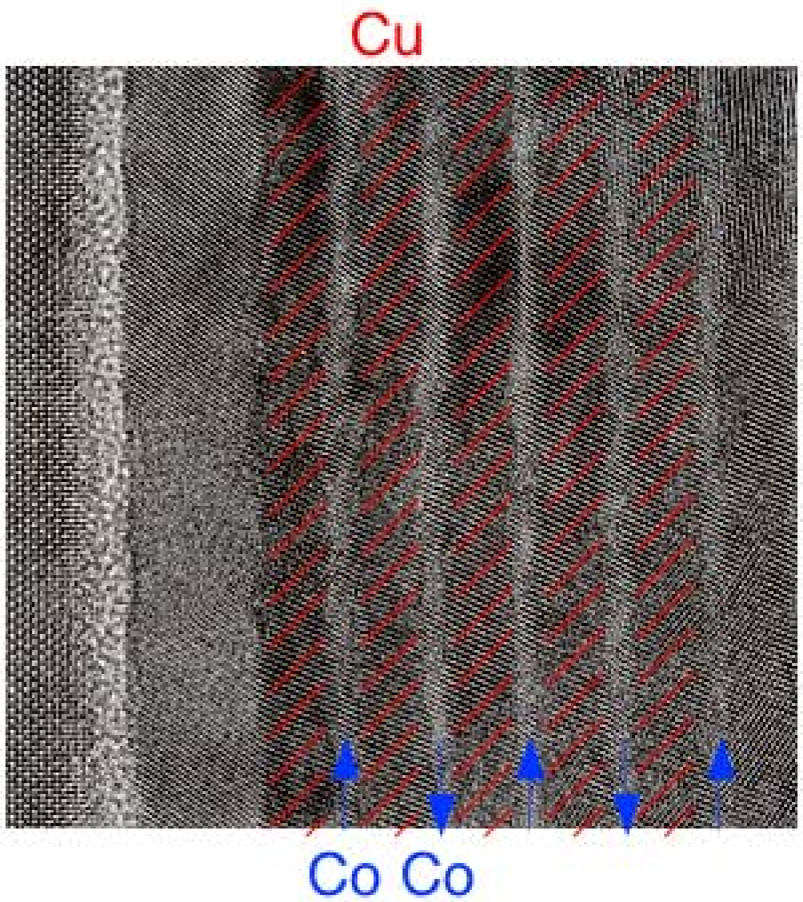
Application:
Magnetic Read Heads
Based on Giant Magneto-
Resistance in Magnetic
Multilayers

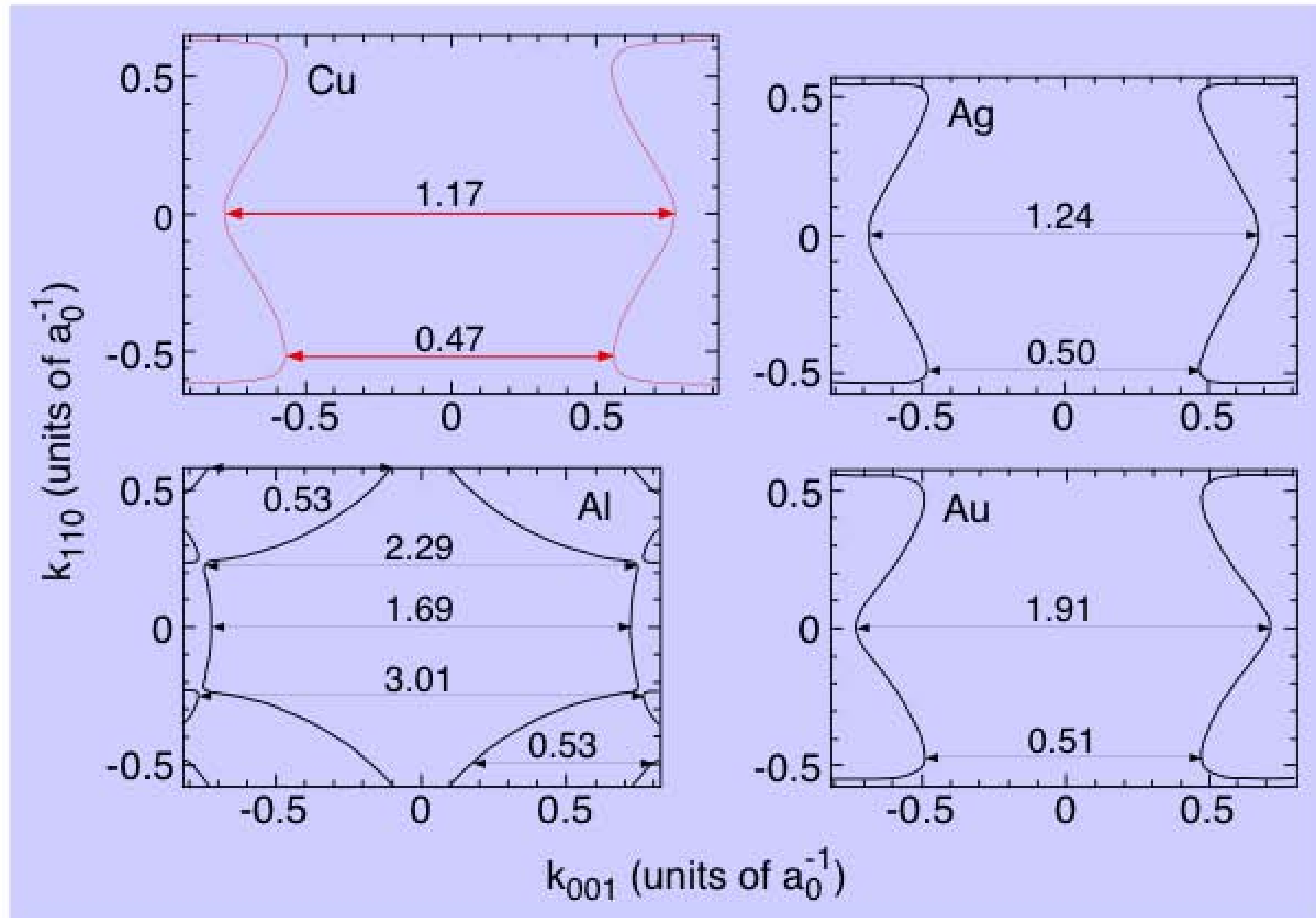


PHYSICAL REVIEW B VOLUME 48, NUMBER 10 1 SEPTEMBER 1993-II

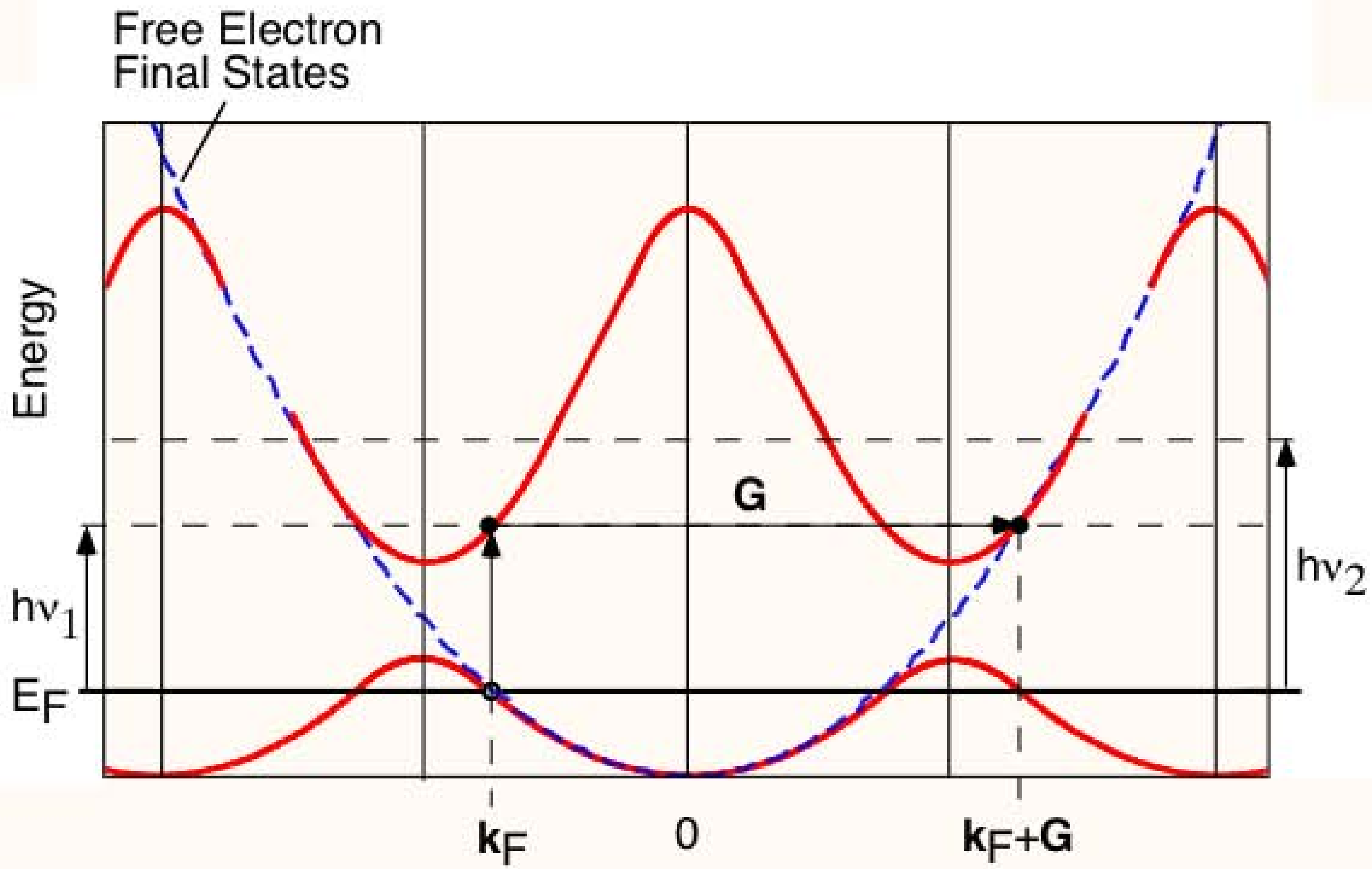
Exchange coupling in magnetic heterostructures

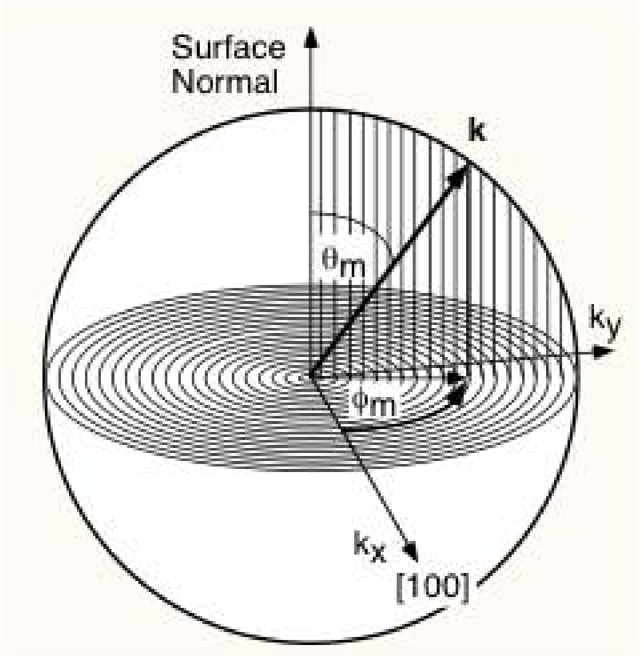
M. D. Stiles
National Institute of Standarts and Technology, Gaithersburg, Maryland 20899
(Received 3 May 1993)





Direct Transitions from the Fermi Surface





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

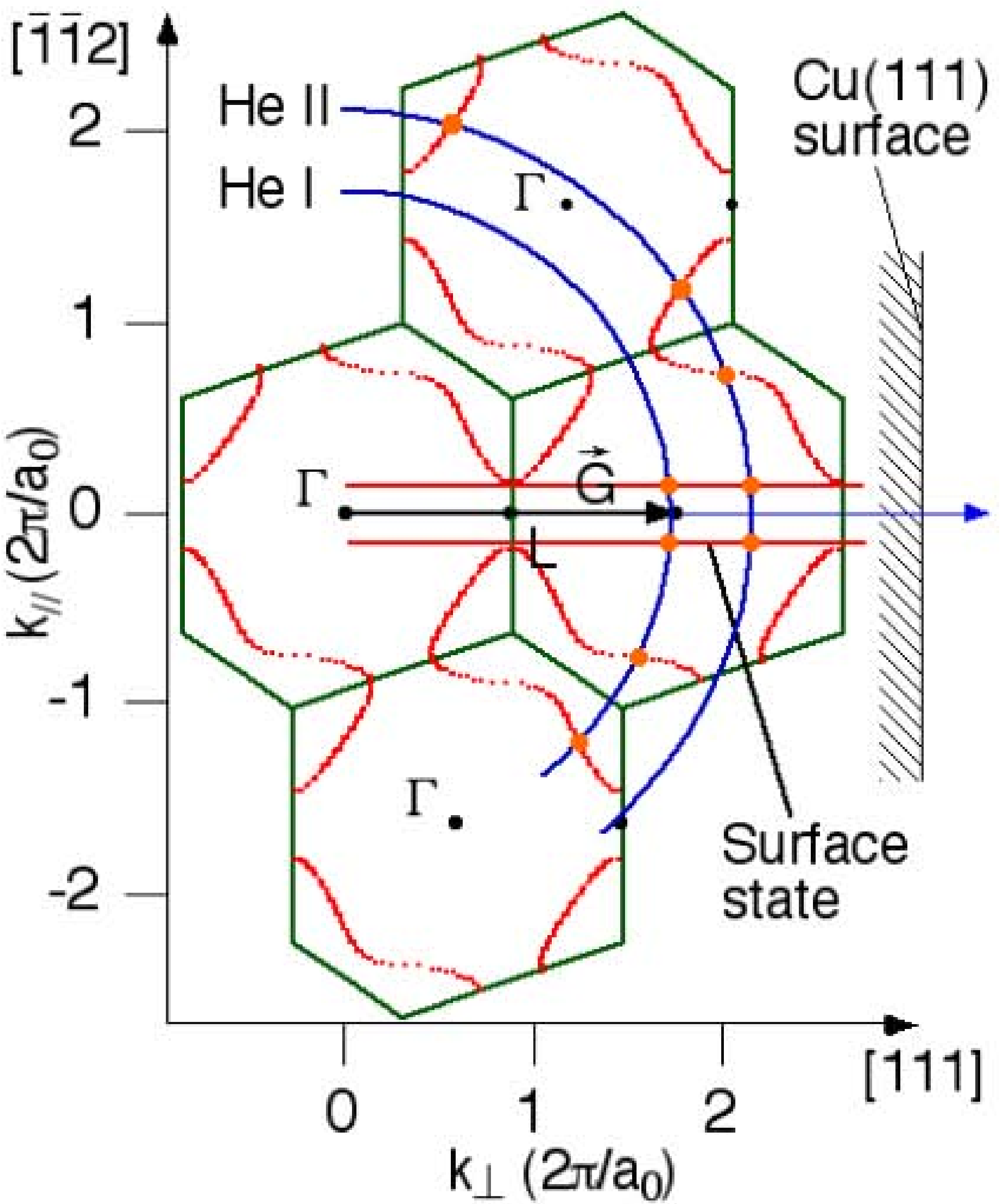
$$|\vec{k}_{||}| = \frac{1}{\hbar}\sqrt{2mE_{kin}^m}\sin\theta_m$$

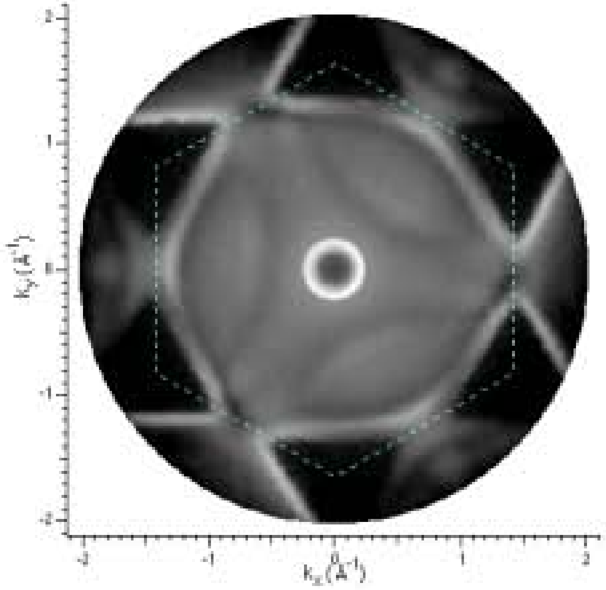
$$k_\perp = \frac{1}{\hbar}\sqrt{2m(E_{kin}^m + V_0)}\cos\theta_m$$

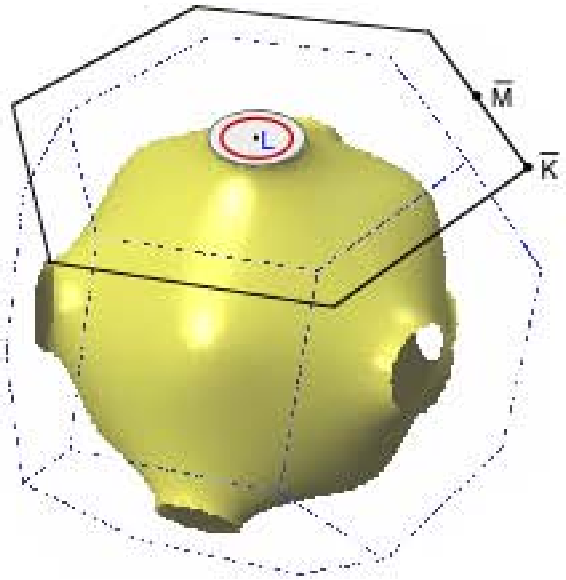
Refraction: $\sin\theta = \sin\theta_m\sqrt{\frac{E_{kin}^m}{(E_{kin}^m + V_0)}}$

Fermi surface mapping

Section along $(1\bar{1}0)$ plane in reciprocal space







In the photoemission process:

Energy conservation:

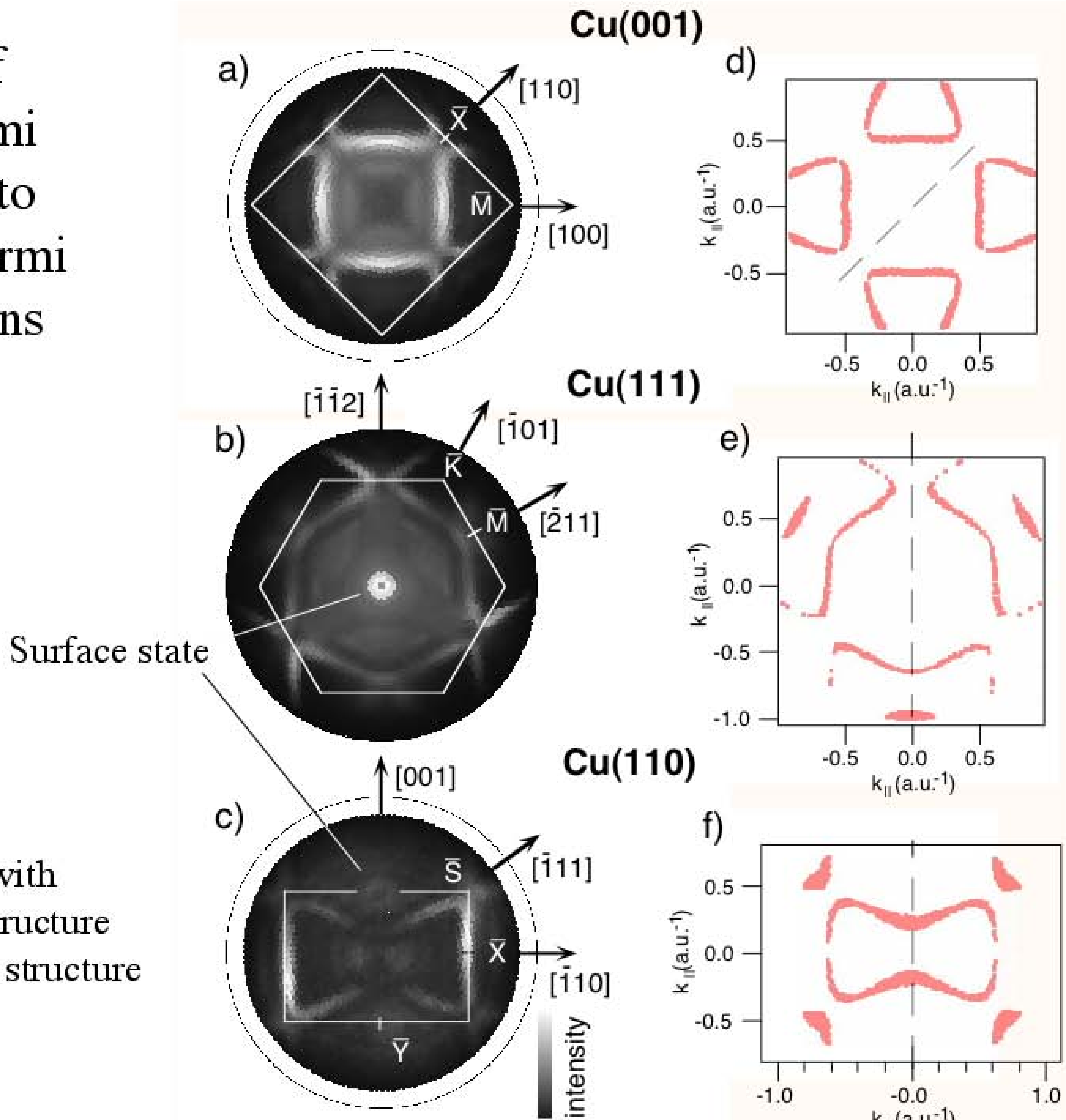
$$E_f = E_i + h\nu$$

Momentum conservation:

$$\vec{k}_f = \vec{k}_i + \vec{G}$$

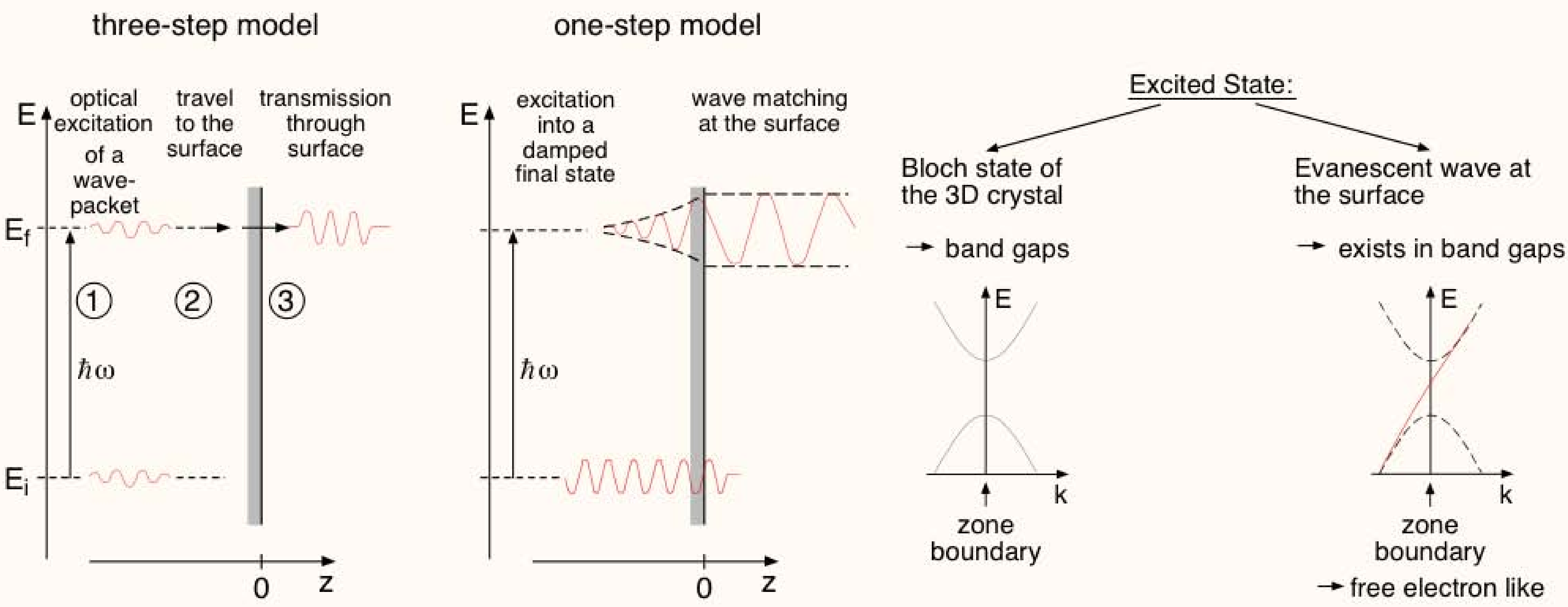
P. Aebi et al. Surf. Sci. 307-309, 917 (199

Comparison of Measured Fermi Surface Maps to Calculaded Fermi Surface Sections

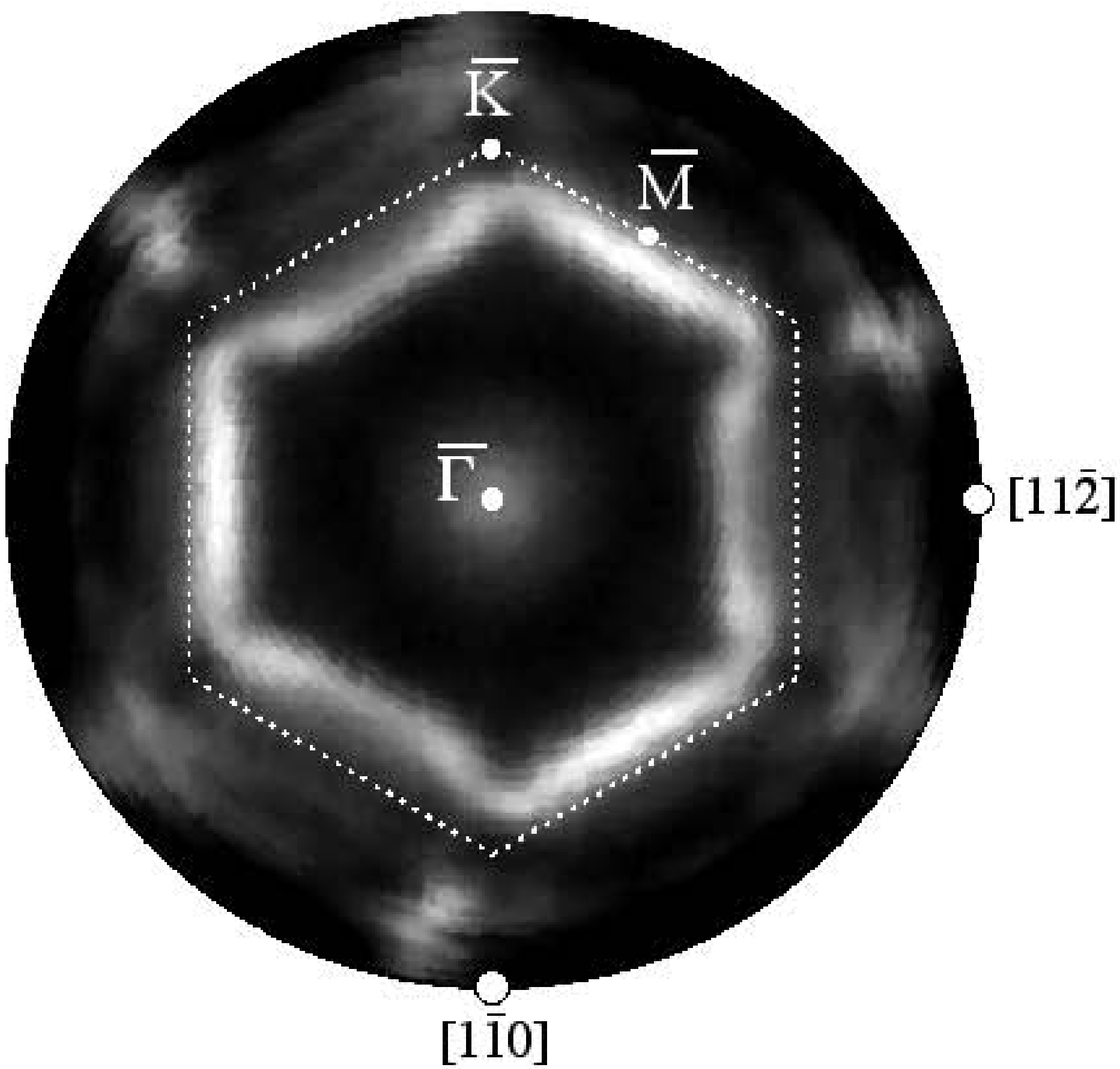


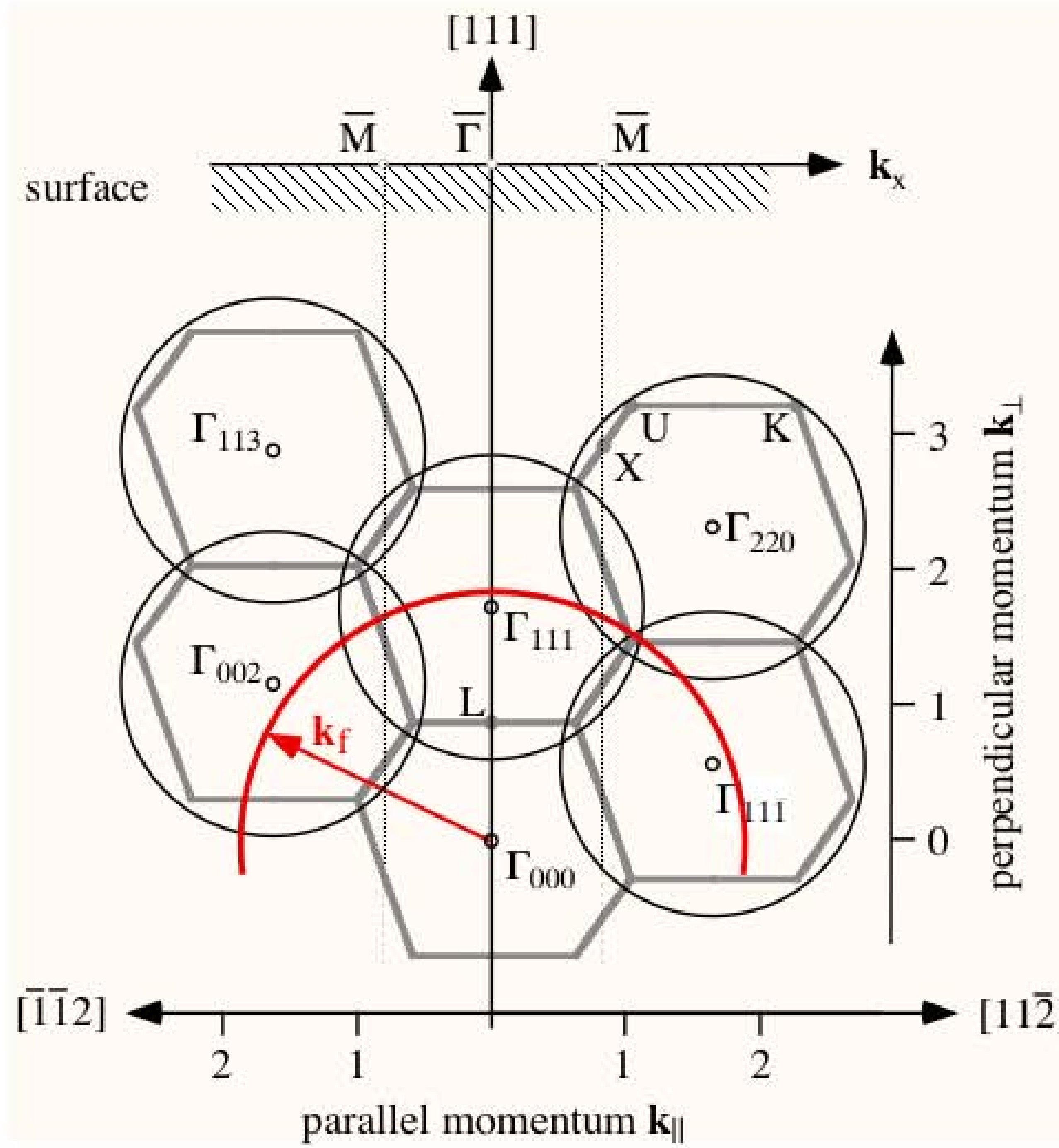
Calculations done with the Wien2k band structure code, assuming the structure of bulk Cu.

Comments on the Free Electron Final State



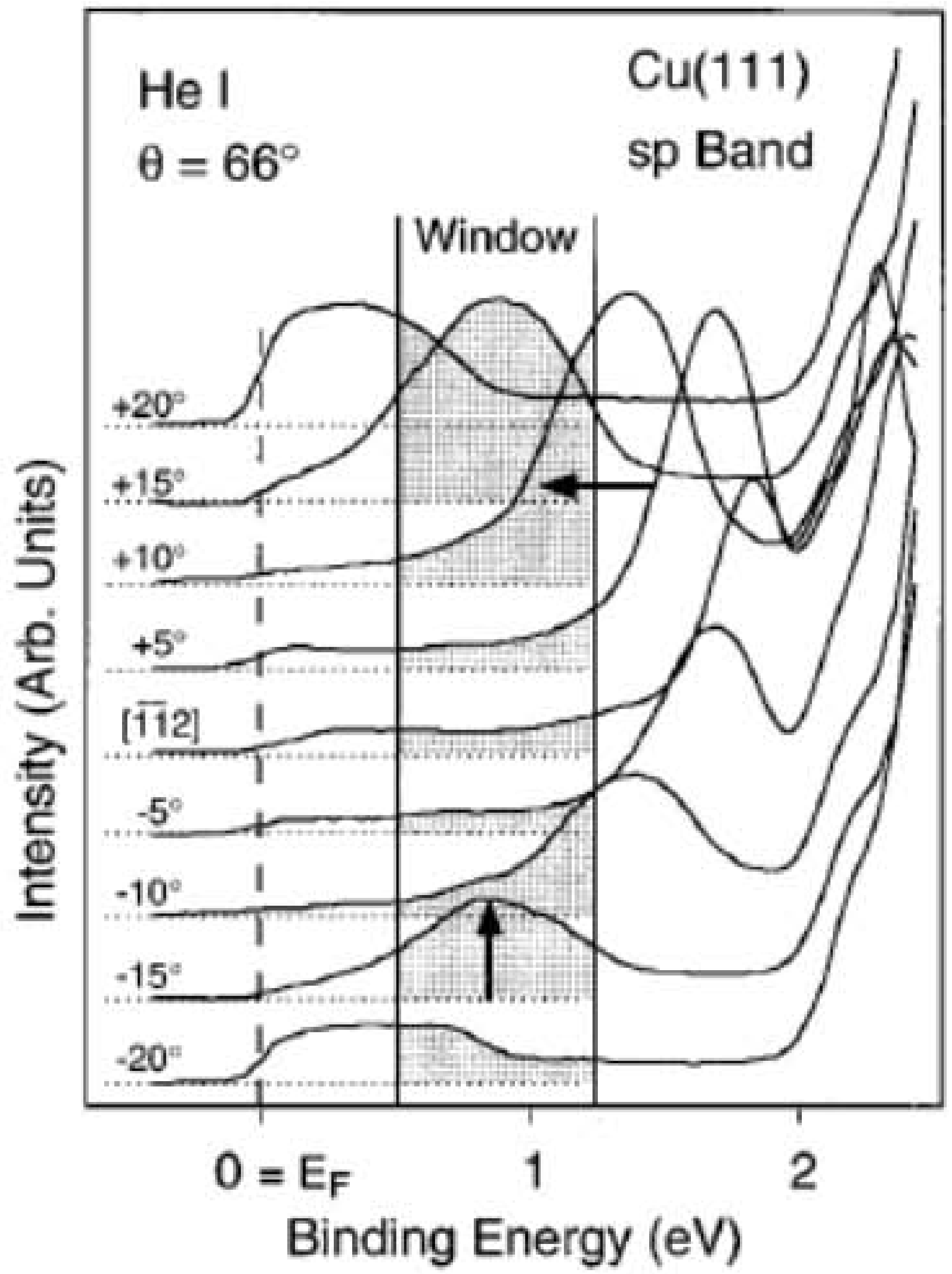
The Fermi Surface of Aluminium

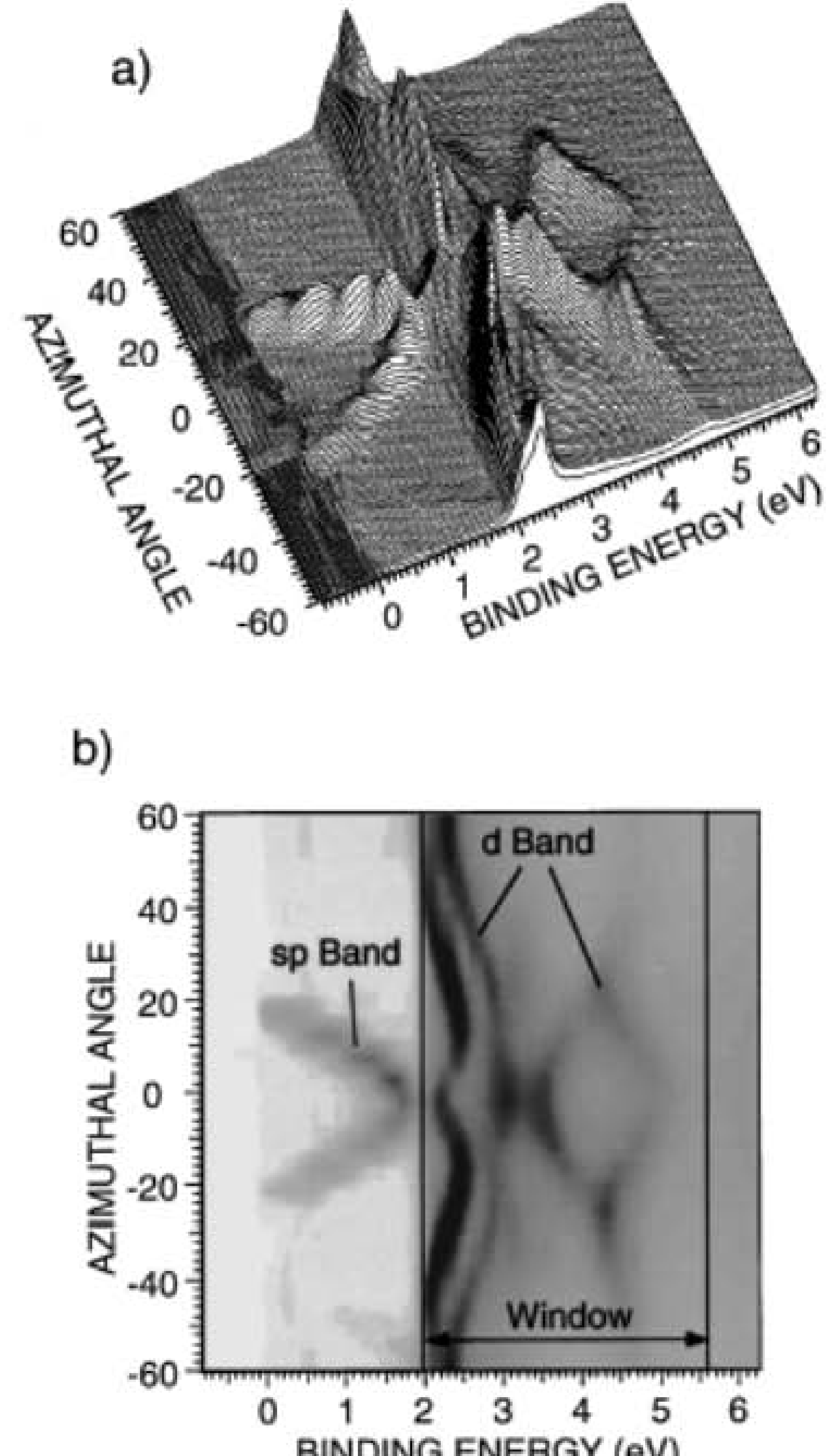




Courtesy R. Fasel

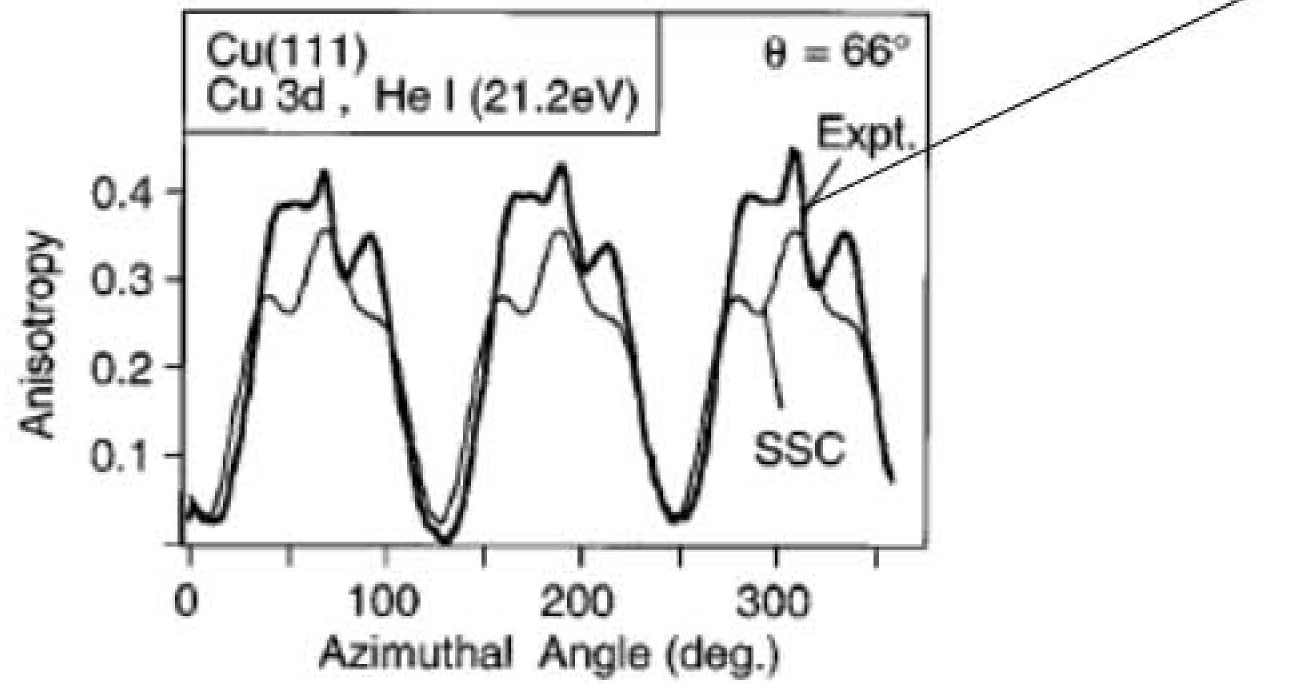
Intensities in Valence Photoemission - Diffraction Effects





Integration of Intensities over the Entire d-Band Region

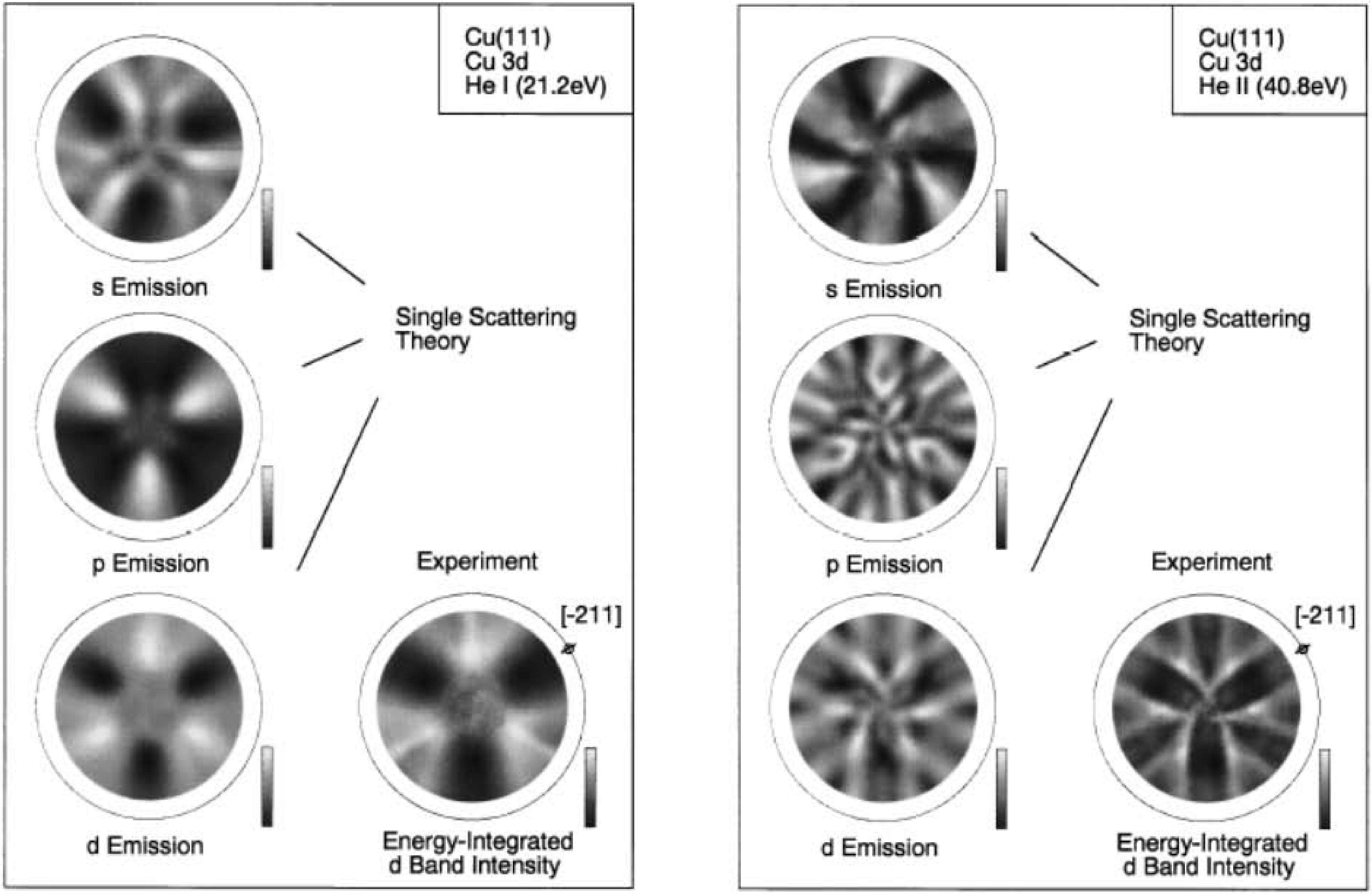
Choose energy window large enough so the d-band peak never leaves the window => the intensity variation of the peaks can be monitored



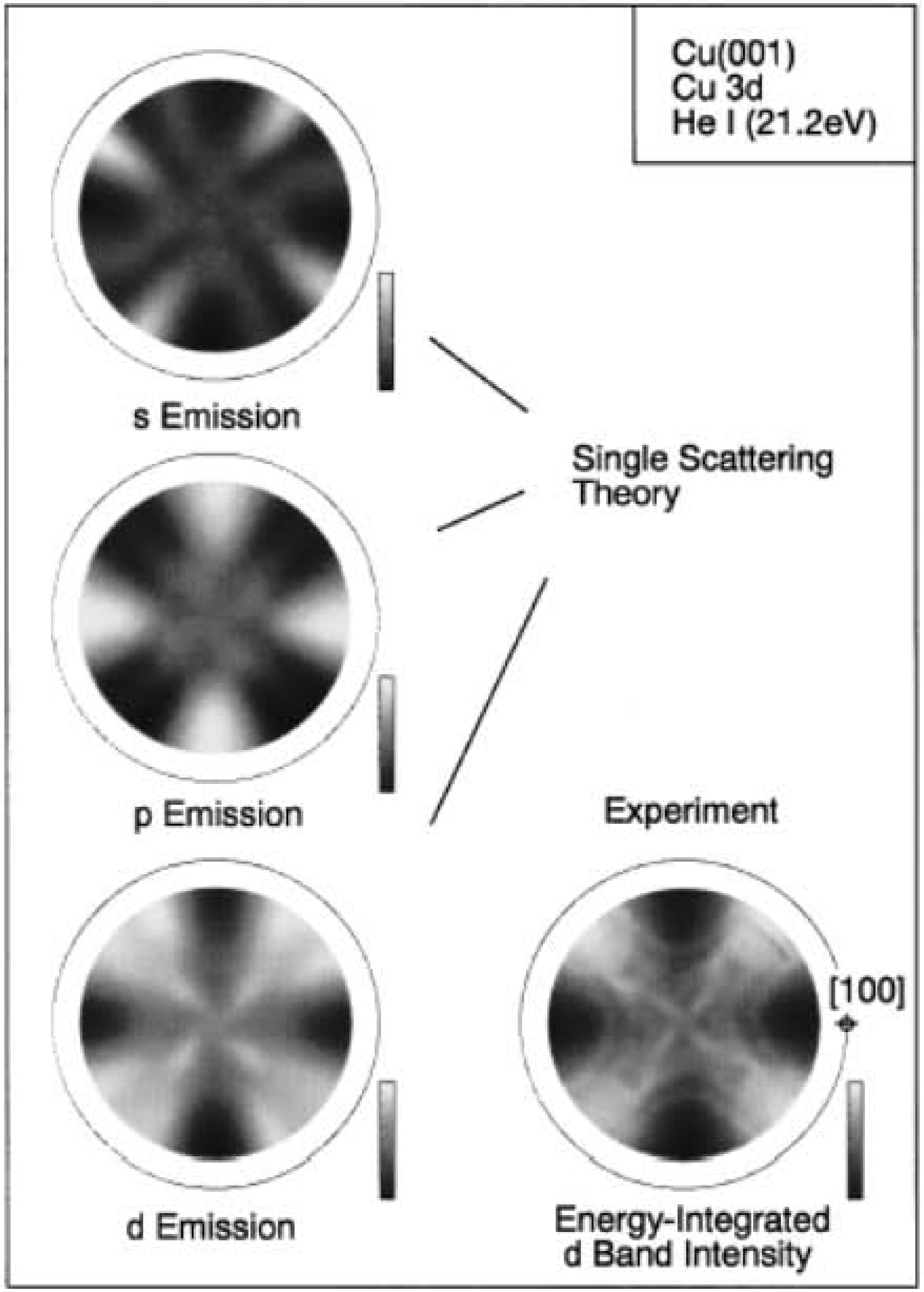
Theoretical curve: Single Scattering Cluster (SSC) calculation for a cluster representing a Cu(111) surface from a localized full d shell (like in x-ray photoelectron diffraction (XPD), hence

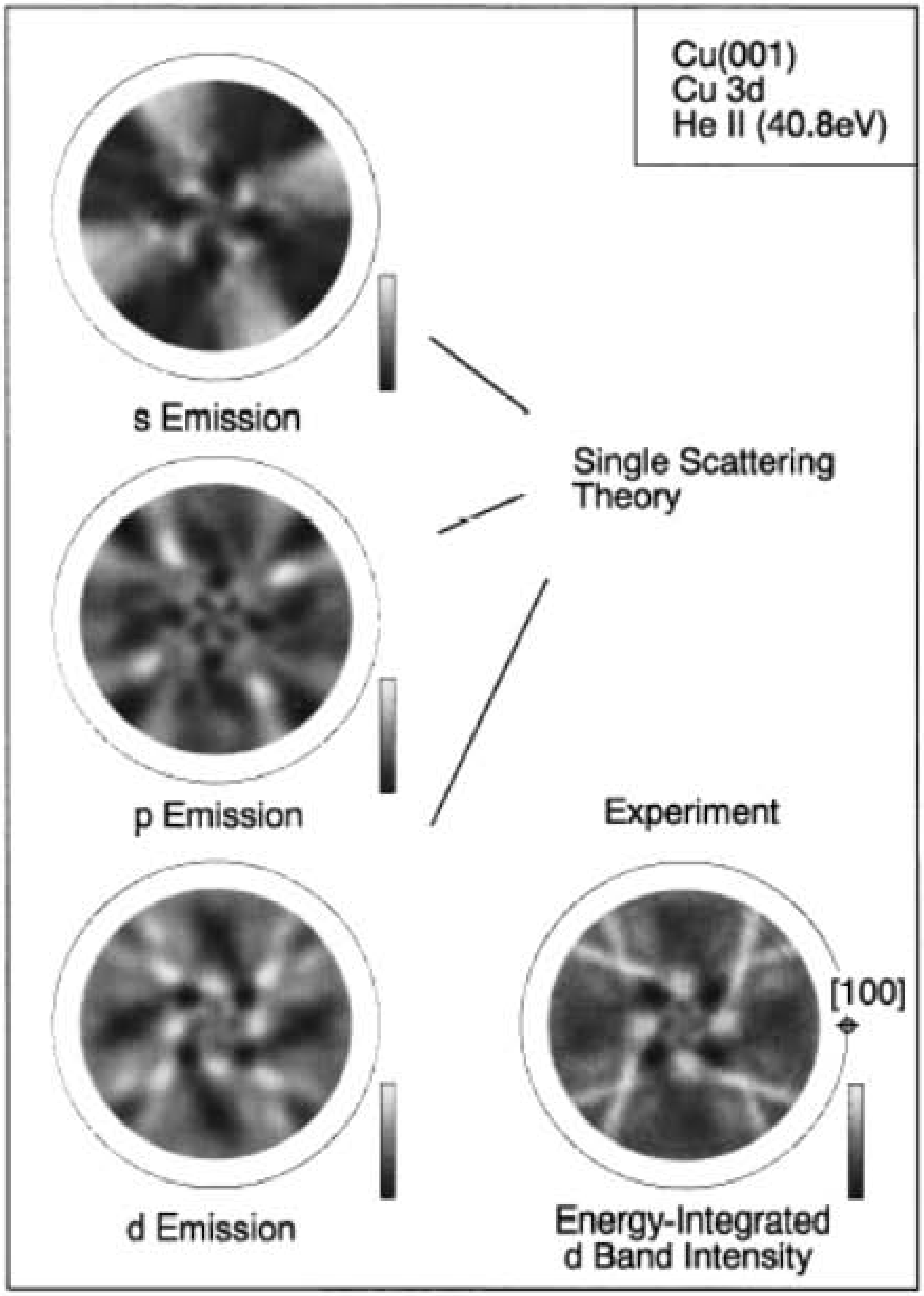
ultraviolet photoelectron diffraction (UPD)

J. Osterwalder et al., PRB 53, 10209 (1996)



J. Osterwalder et al., PRB 53, 10209 (1996)

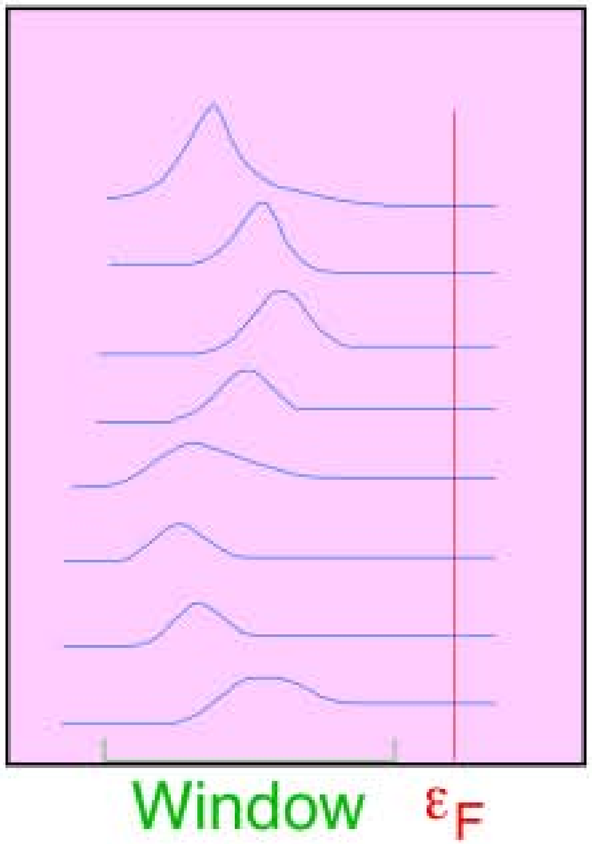




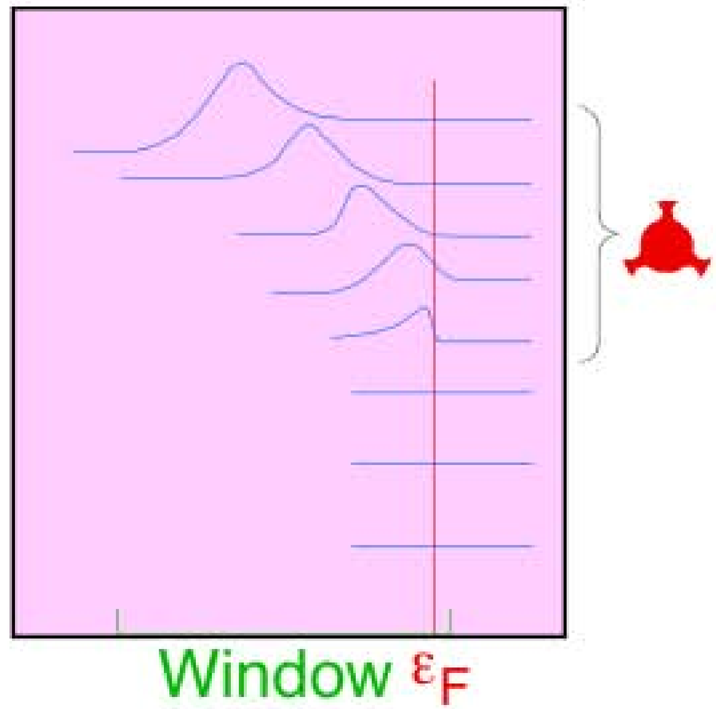
J. Osterwalder et al., PRB 53, 10209 (1996)

UPD and Photoemission Intensities

filled shells:



unfilled shells: ?

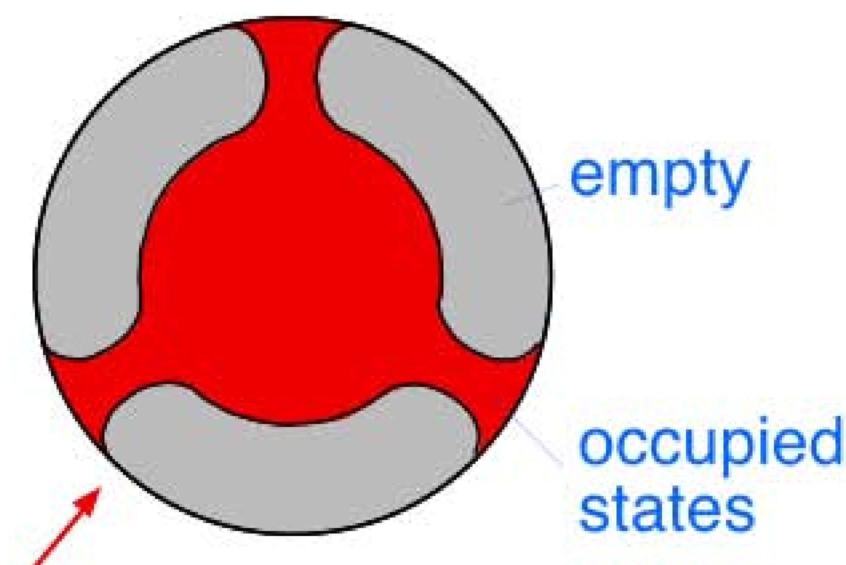


direct transition
is lost at Fermi surface.

direct transition
never disperses
out of measurement
window (e.g. Cu 3d).

UPD describes overall
band intensities !

(sum rule over
several subbands)



UPD may describe intens.
in occupied $\vec{k}$-Region

But: Must know angular momentum compos.
of occupied (cristal field) states !