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The Bandstructure of Solids by Angle-Resolved Photoemission

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Advanced Light Source

www-bl7.lbl.gov/BL7/who/eli/eli.html

Outline

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- Introduction to Condensed Matter Theory

- Single-electron picture
  - angle-resolved photoemission
    - energy and momentum conservation
  - matrix elements effects
    - Symmetry
    - Resonant Enhancment
  - Dimensionality
    - Surface states
    - Quantum-confined states
    - Non-periodic systems

- Beyond the single-electron picture
  - Many-body interactions and the spectral function
  - The ground states of metals
    - Electron-phonon coupling
    - High-Tc superconductors: electron-[???] coupling

Bibliography

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- S. Hufner, Photoelectron Spectroscopy, 2nd ed. Berlin; Springer, 1996
- S. D. Kevan, ed., Angle-Resolved Photoemission: Theory and Current Applications, Amsterdam; Elsevier 1992

The Advanced Light Source

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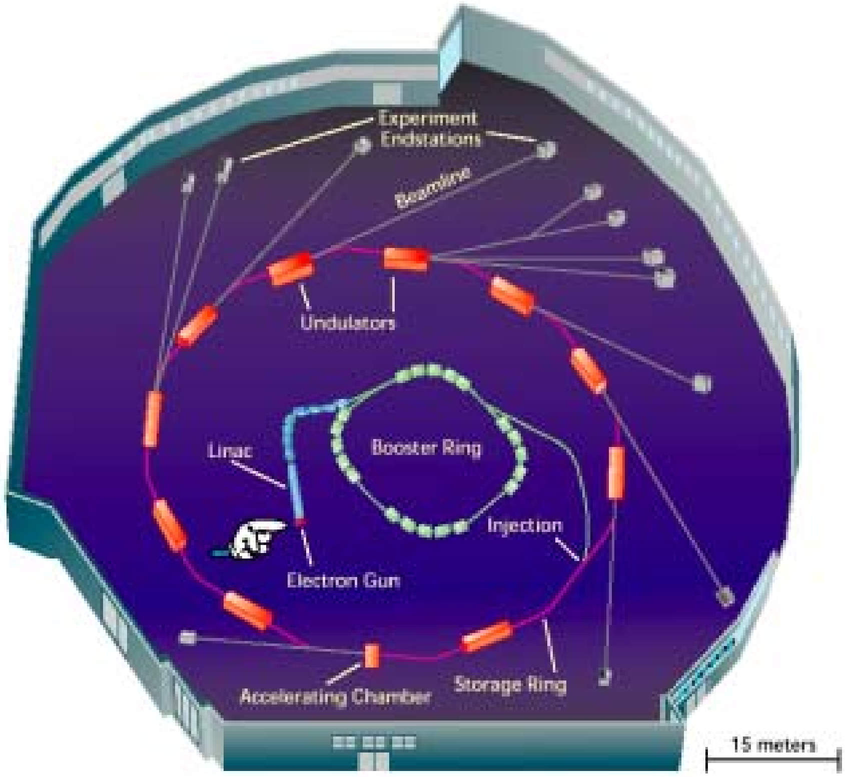

Condensed Matter in a Nutshell

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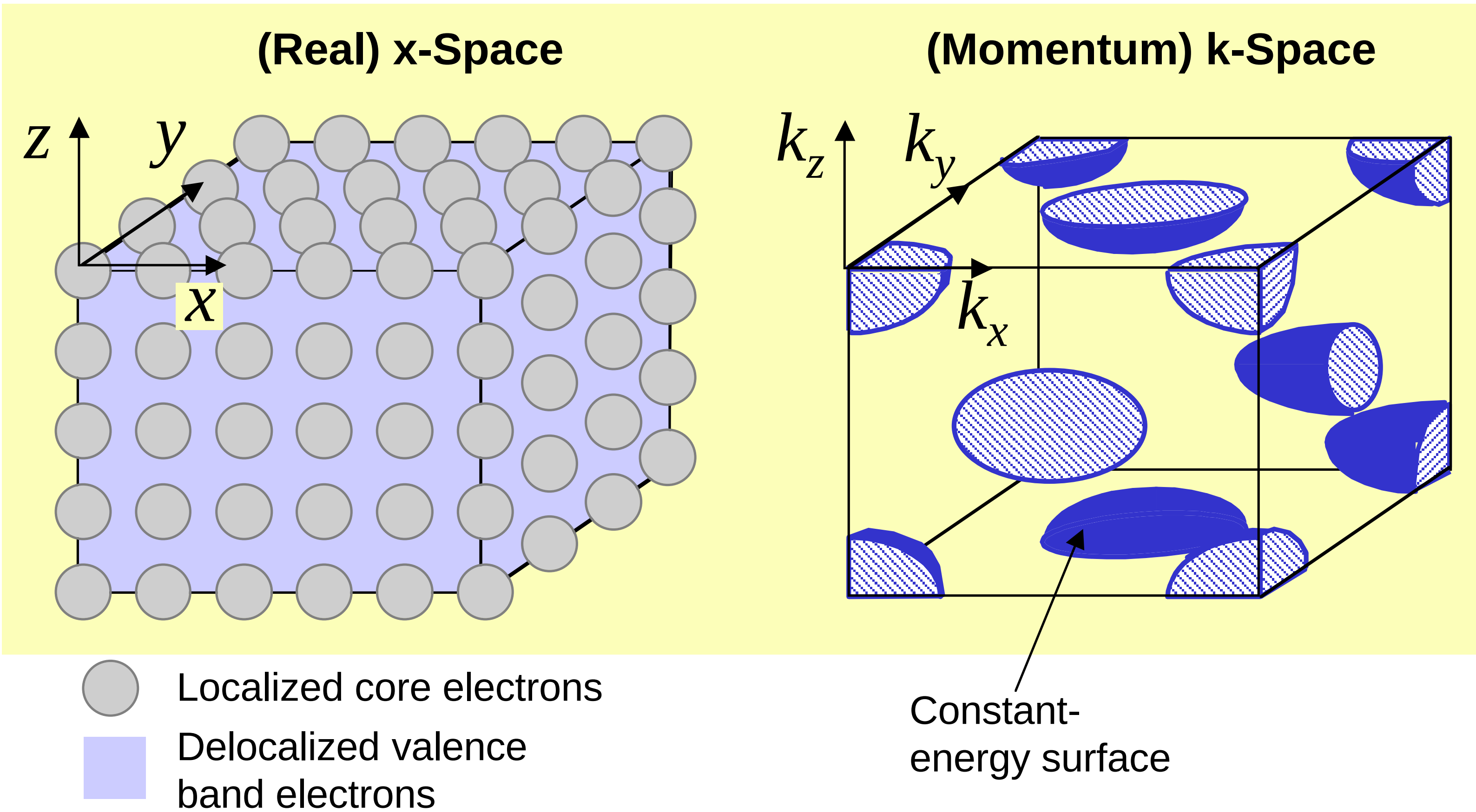
1. Real vs. Reciprocal Space



Constant Energy Surfaces

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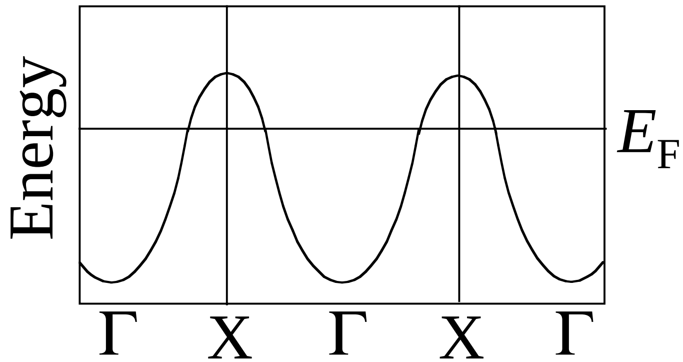
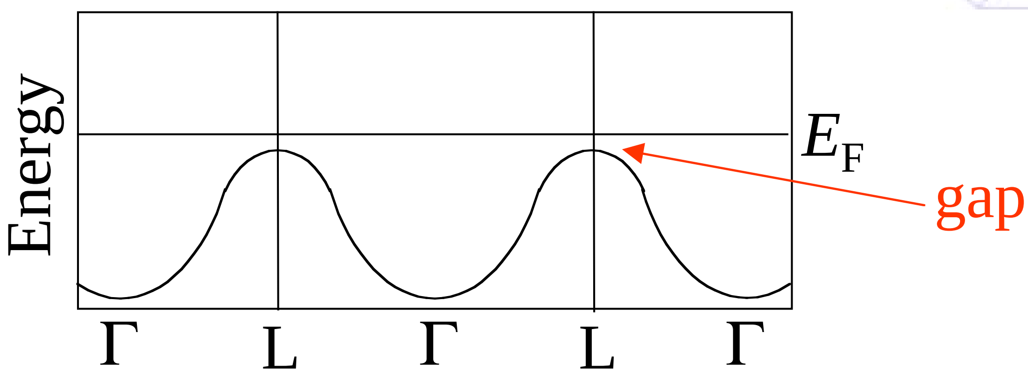
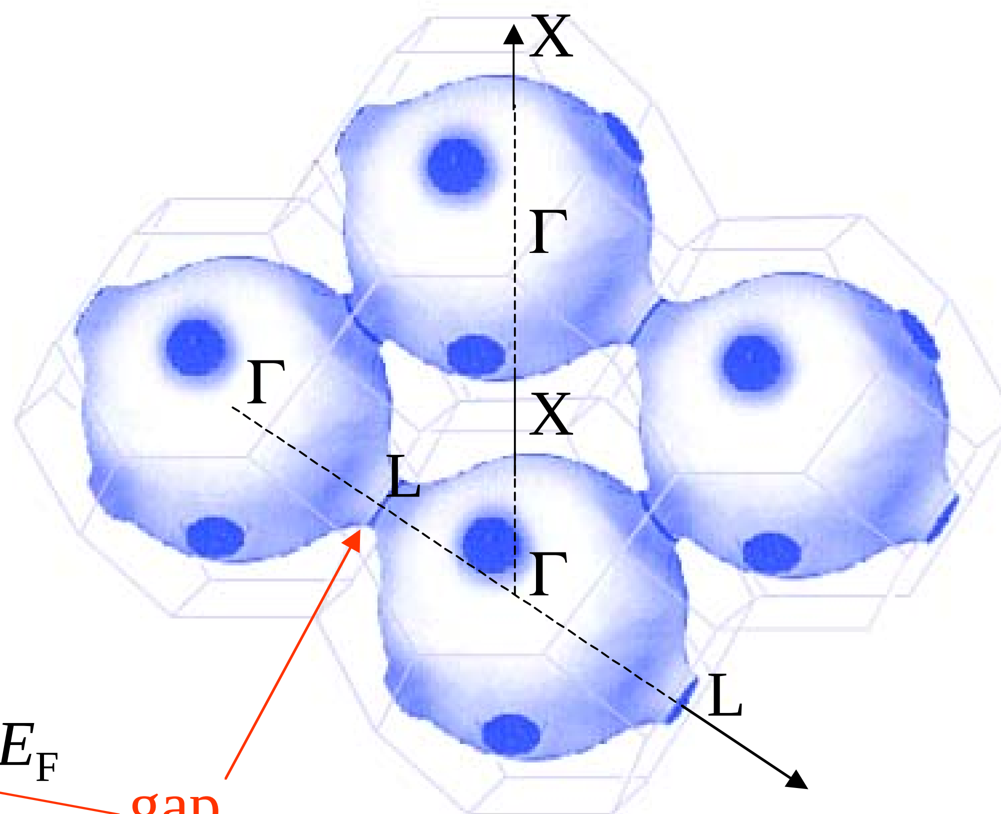
$$E_{Bind} = \frac{1}{2} m v^2$$
$$= p^2 / 2m = \hbar^2 k^2 / 2m$$





e.g. Copper



Effective Mass *m** indicates degree of localization

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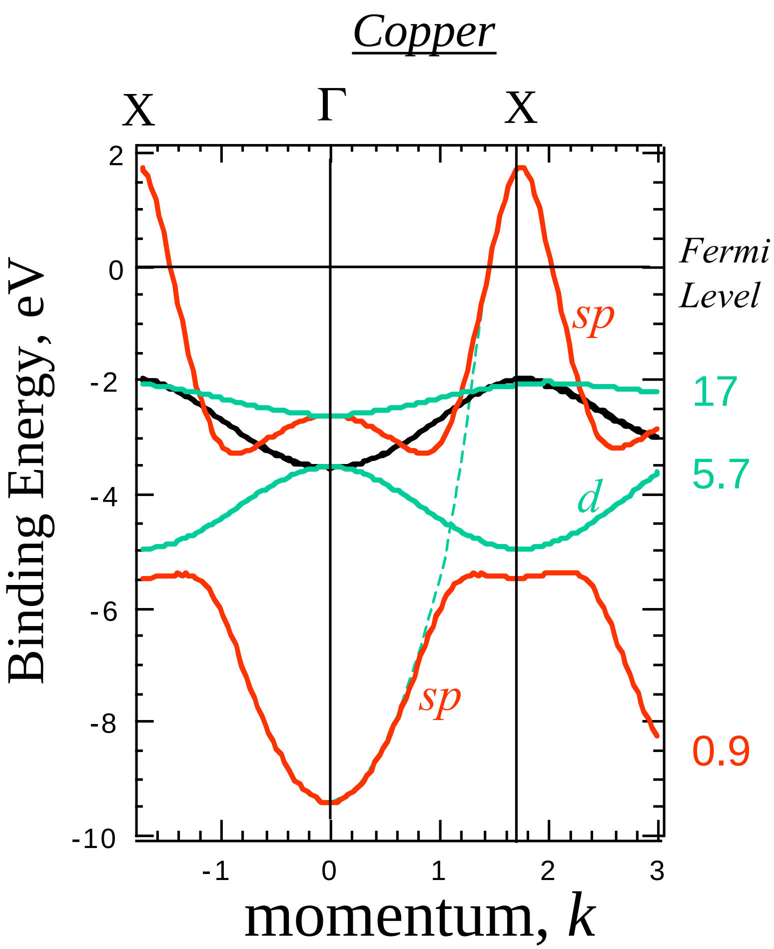
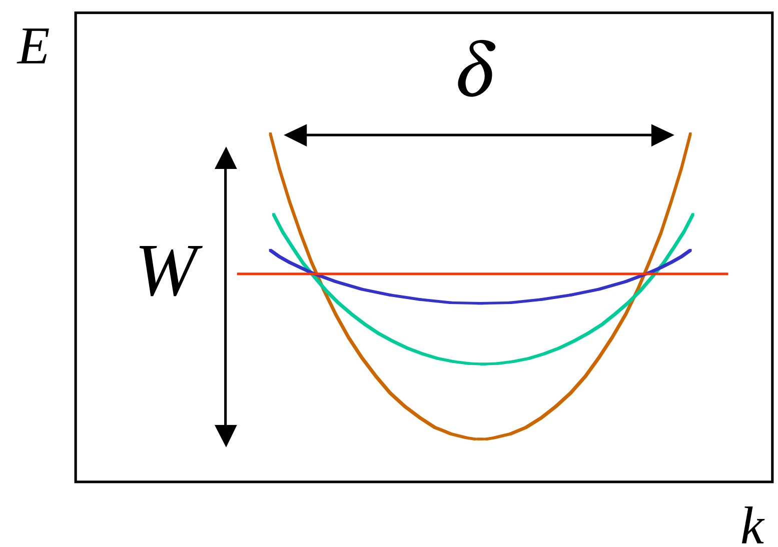
$$E = \frac{m^* v^2}{2} = \frac{\hbar^2 k^2}{2m^*}$$



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



Angle-Resolved Photoemission

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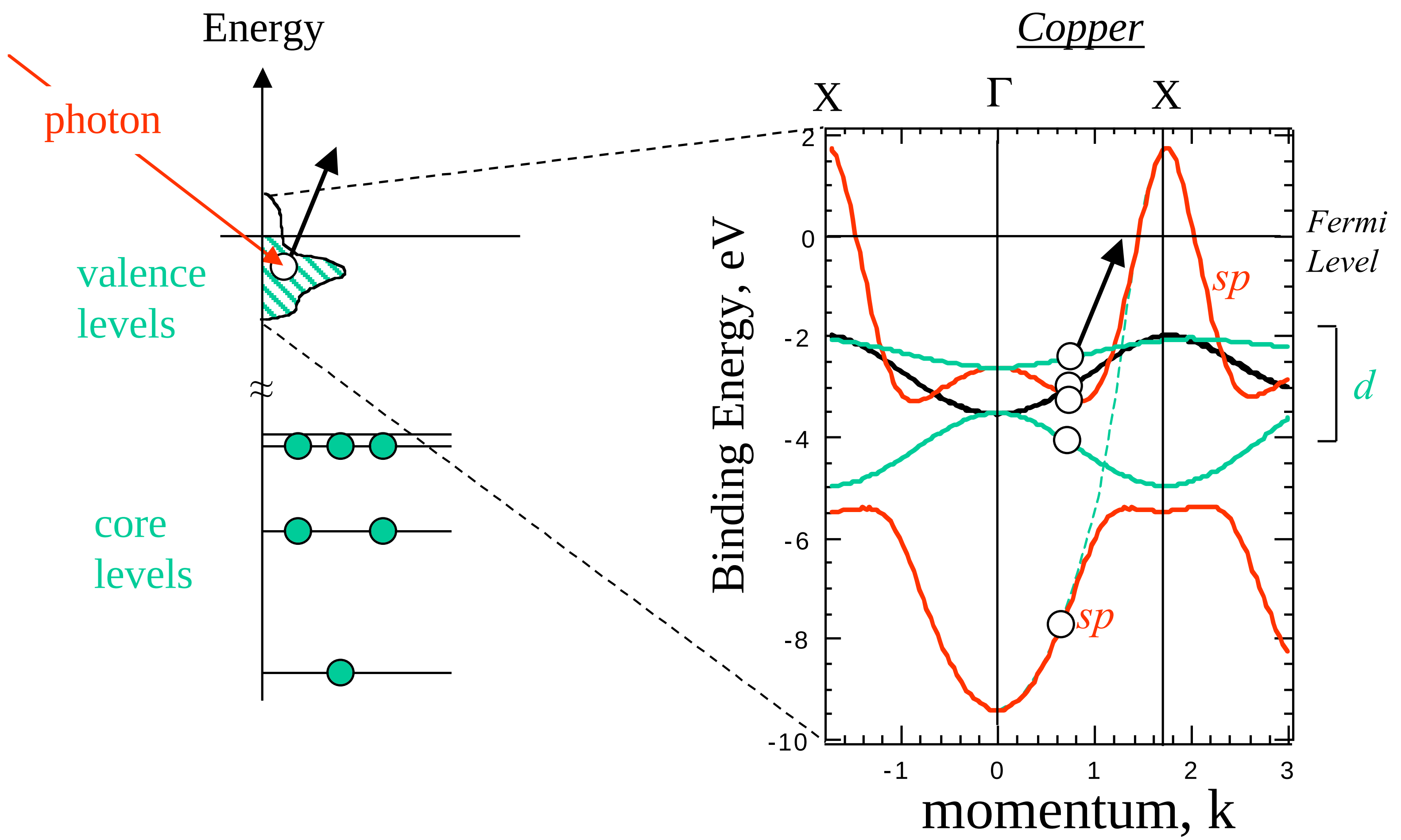

Typical Experimental Result

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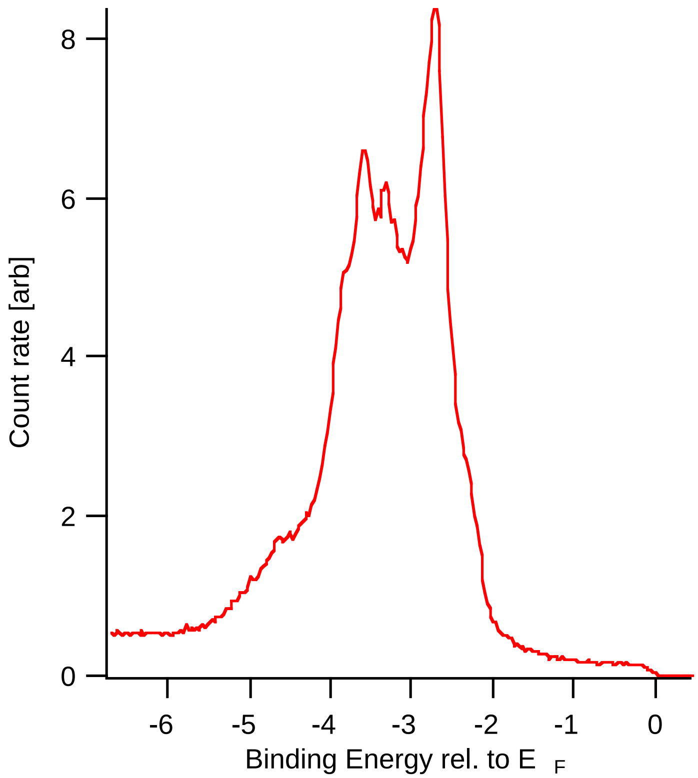
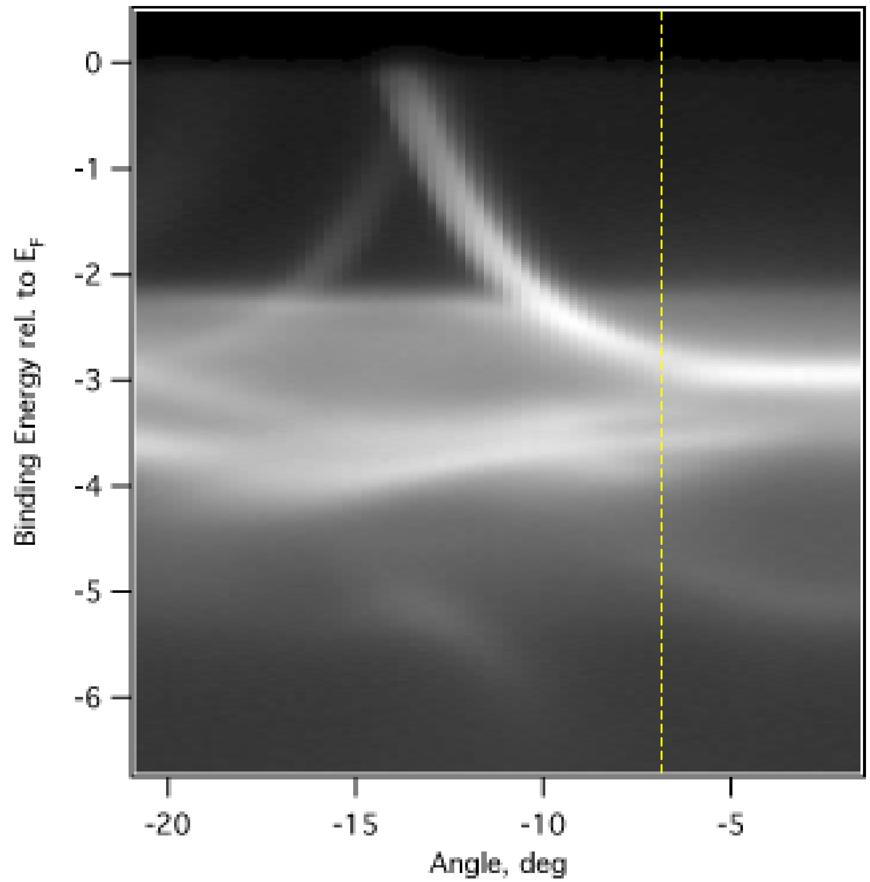


A spectrum at a single polar angle



Accumulate spectra as the angle is scanned

Experimental Geometry

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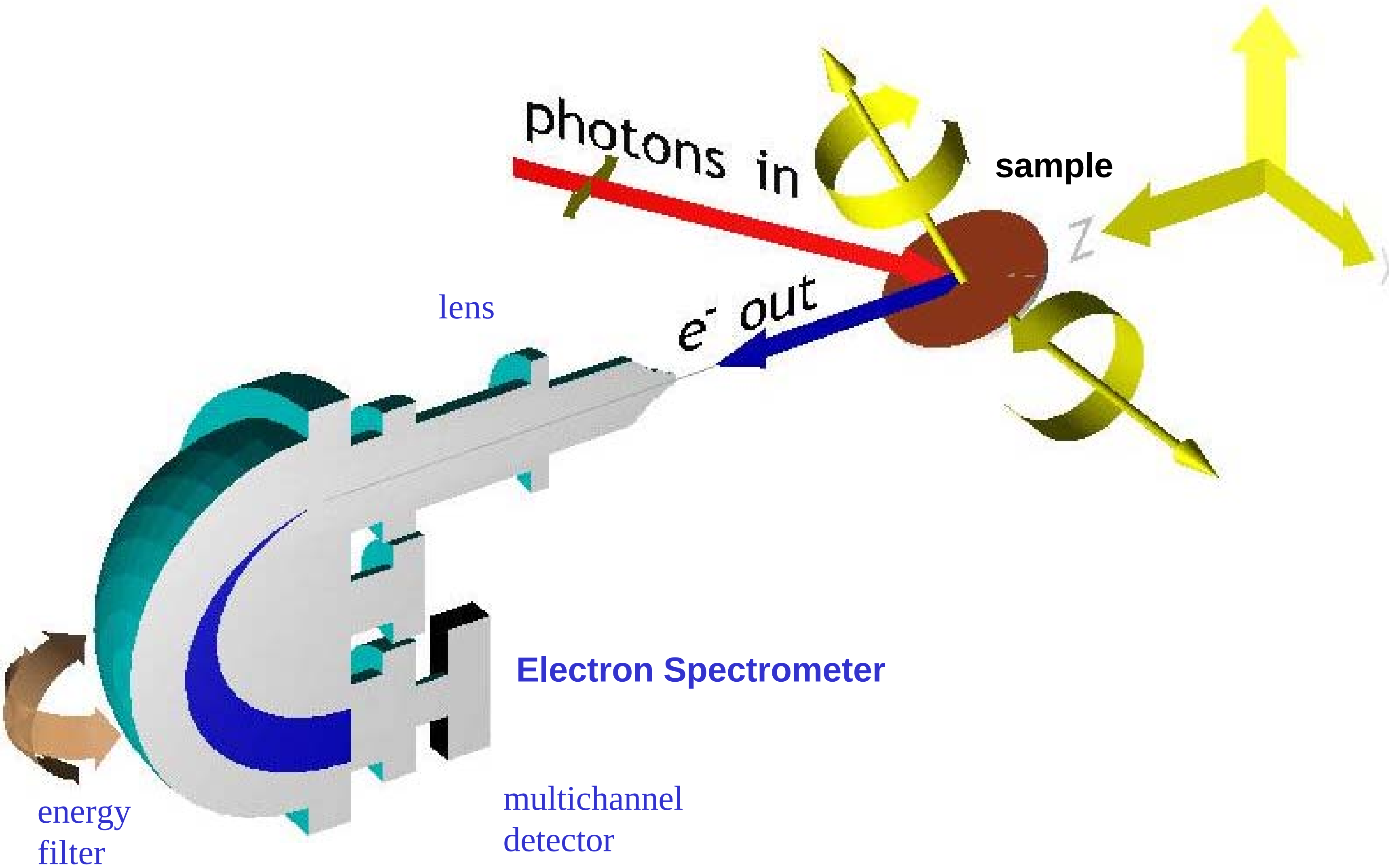

Hemispherical Detector Types

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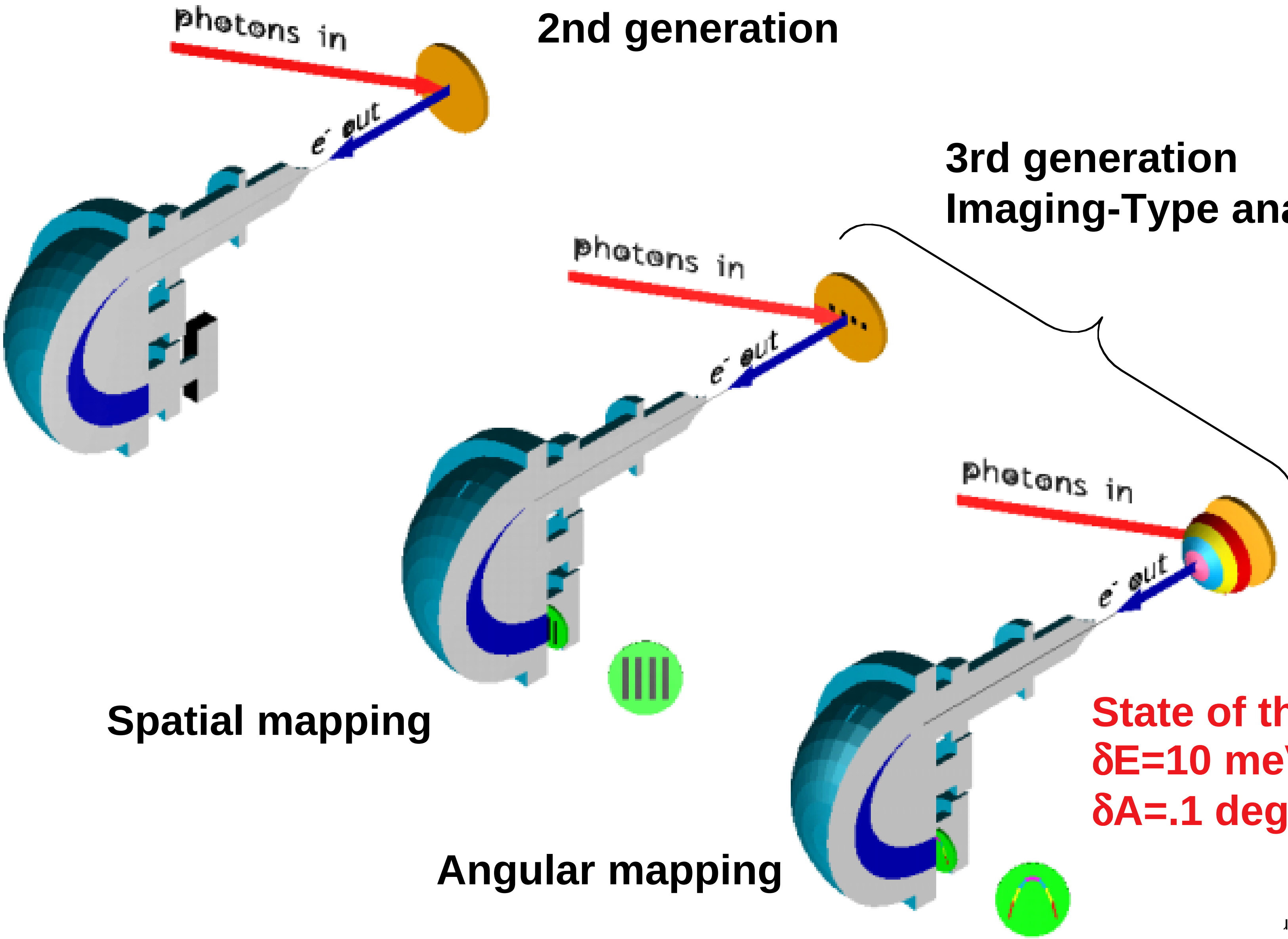
2nd generation

3rd generation
Imaging-Type analyzer



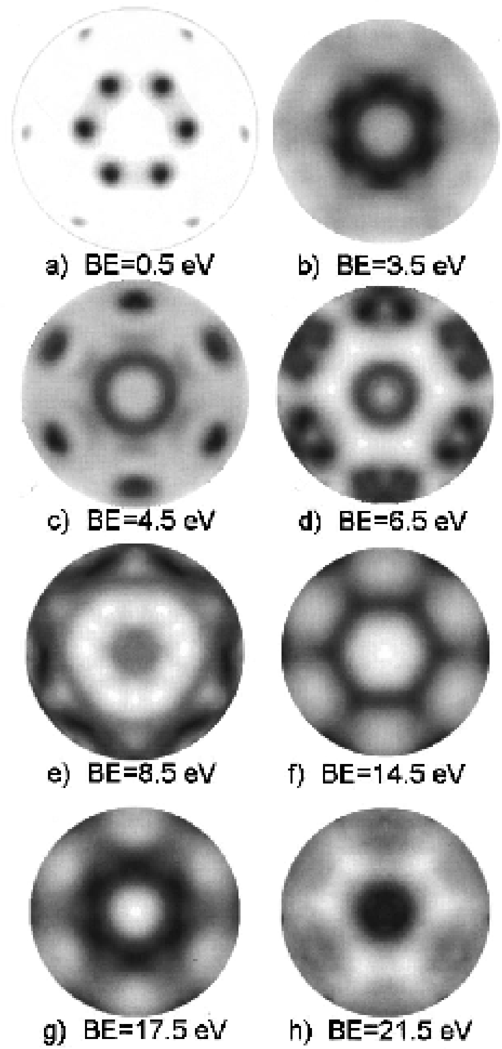
Spatial mapping

Angular mapping

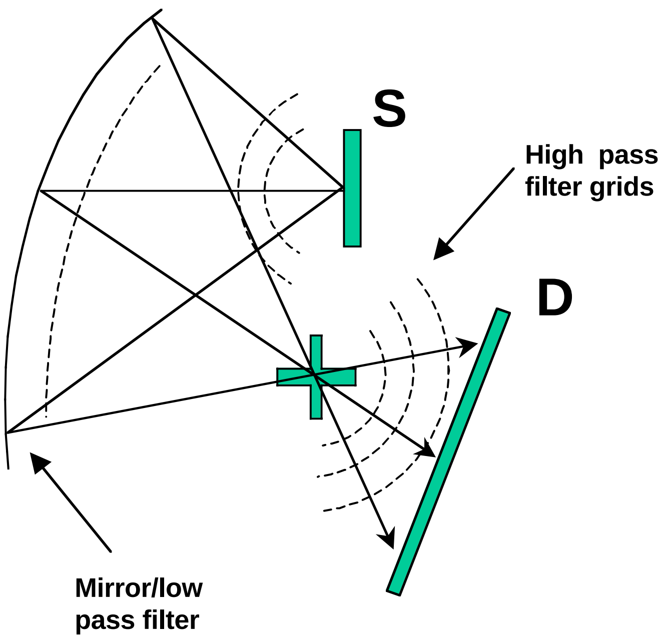
State of the art:
δE=10 meV
δA=.1 degrees

Imaging Detectors

Graphite constant-energy maps



Elliptical mirror analyzer



Fast, but poorer resolution

Heske et al, PRB 59,4680 (1999)

Three Step Model

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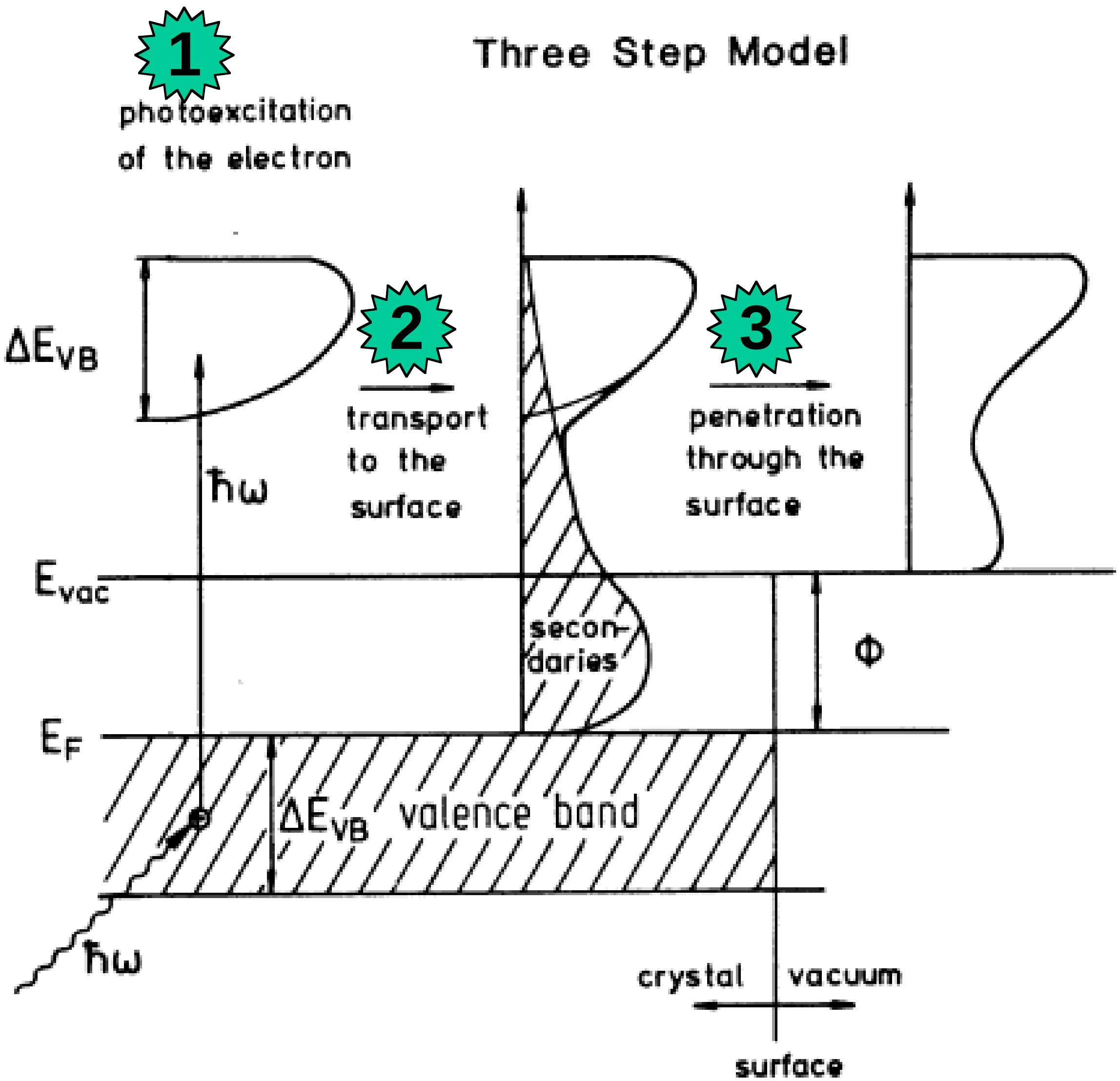
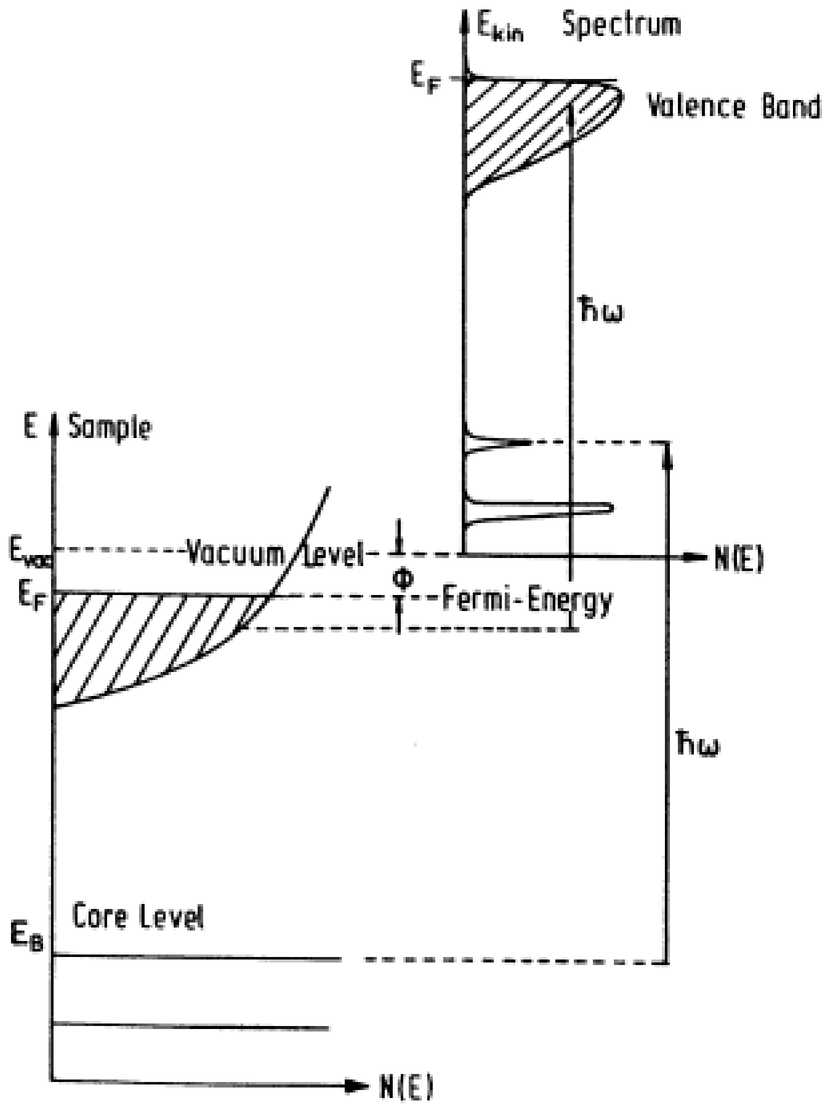


1

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

Momentum Conservation

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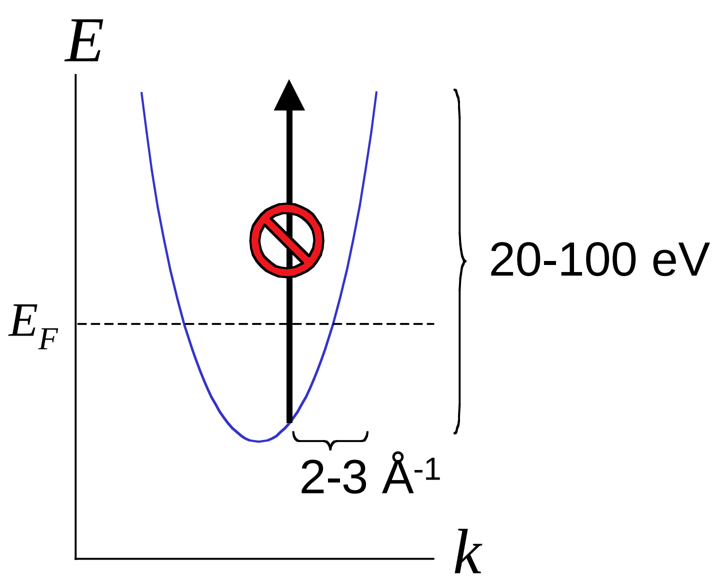
Photon Momentum $p = \hbar\kappa = h/\lambda$

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

Typical photon wavenumber

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

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



- **The photons impart very little momentum in the photoemission process**
- **Therefore photon-stimulated transitions are not allowed for free electrons**

Momentum Conservation

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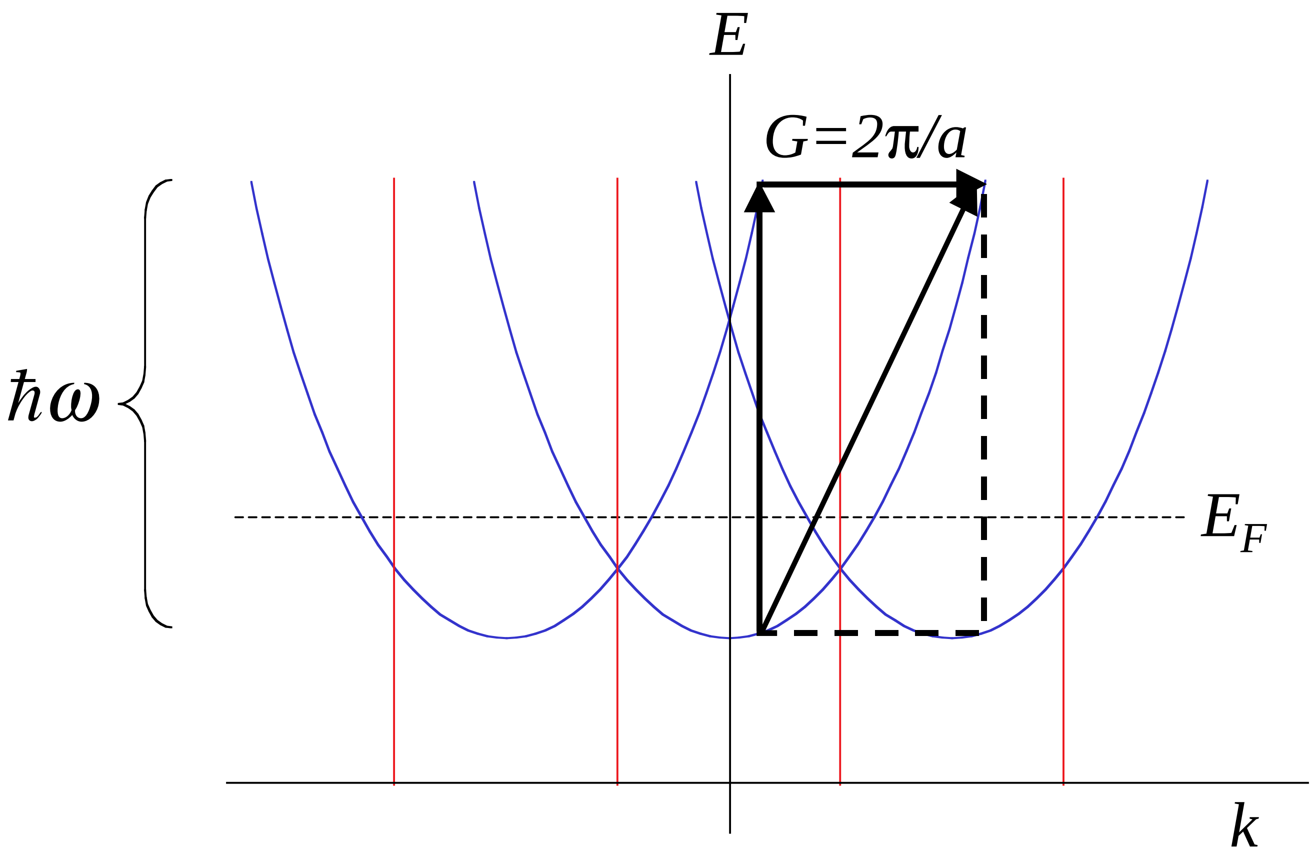
- **Momentum Conservation demands "vertical" transitions**
- **The role of crystal translational symmetry is crucial**
  - **i.e. no photoemission is allowed from truly free electrons.**



2 Transport to the surface

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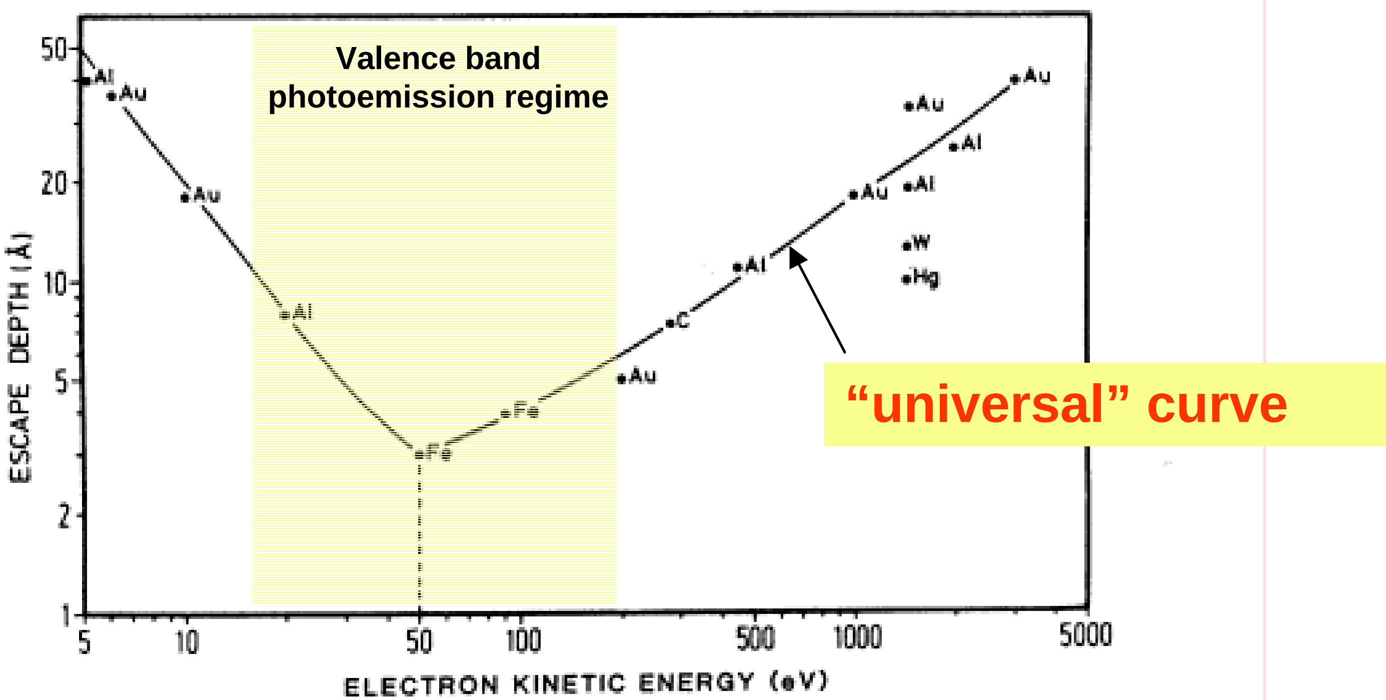
- **Inelastic scattering by electron-electron interaction leads to a loss of electrons reaching the surface**
  - **Valence band measurements are sensitive to only within the first few atomic layers of the material**
  - **Spectral peaks have a "loss tail" towards lower kinetic energies**



3 Transmission through the surface

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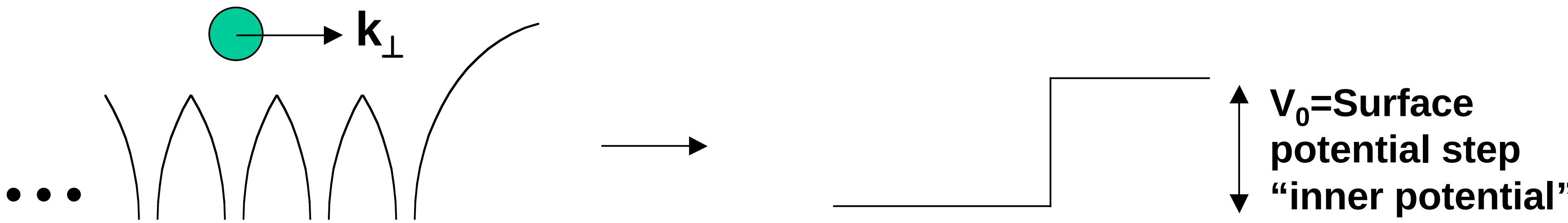
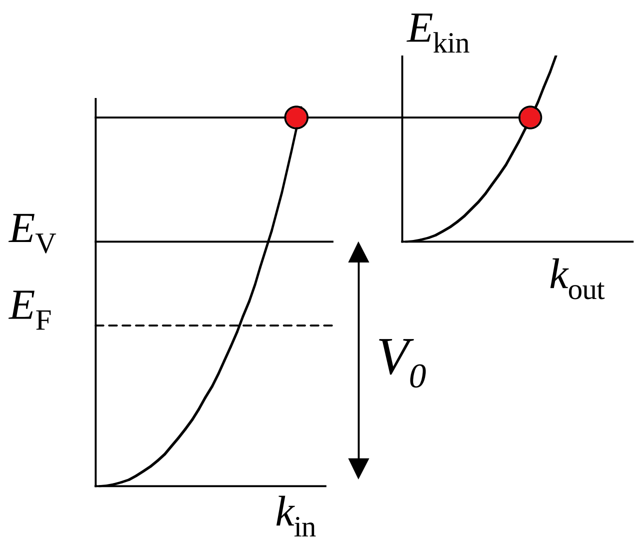
The potential barrier at the surface slows the electron in the direction normal to the surface.

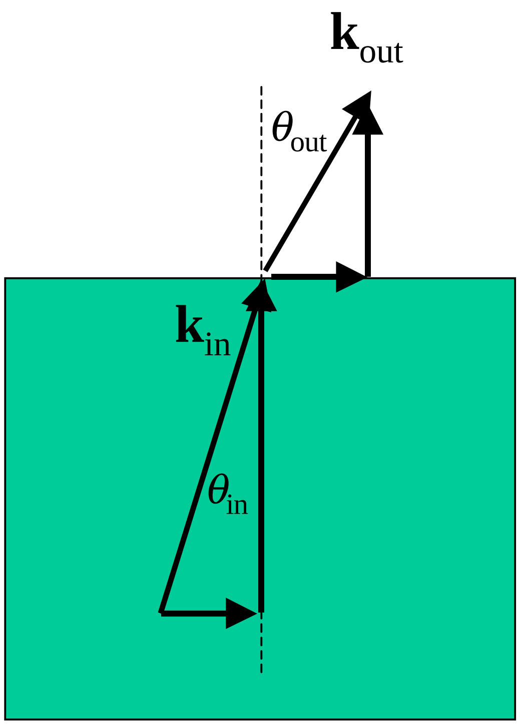


Free-electron final state model



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

Surface Electron Diffraction



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

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

Experimental Determination of V_0

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- **We don't normally have a priori knowledge of V_0.**
- **Methods to determine V_0:**
  - **Adjusted to make experiment agree with theory**
    - **Not too satisfactory**
  - **Adjusted to make bands have the symmetry of the solid**
    - **More reasonable, and normally easy to achieve**

Determination of V_0

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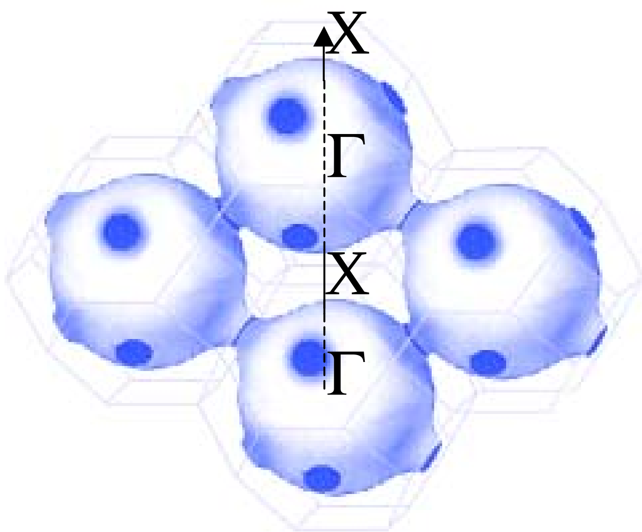

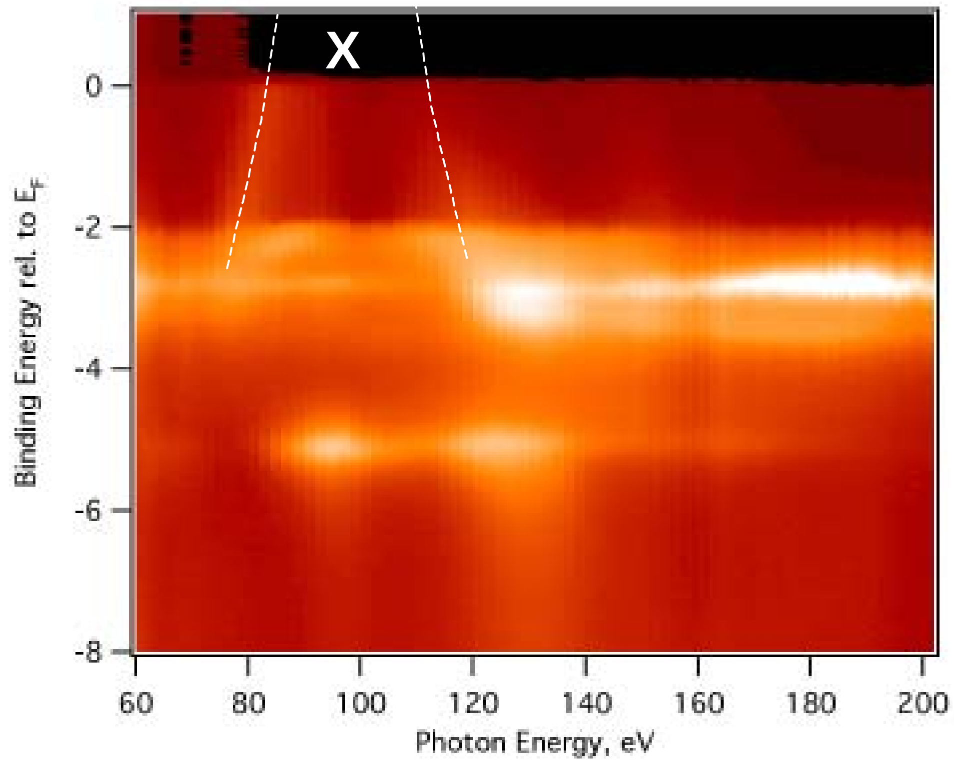

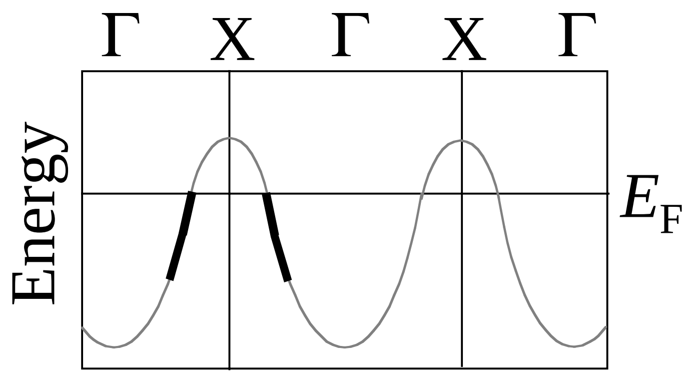

Case Study: Cu(100)

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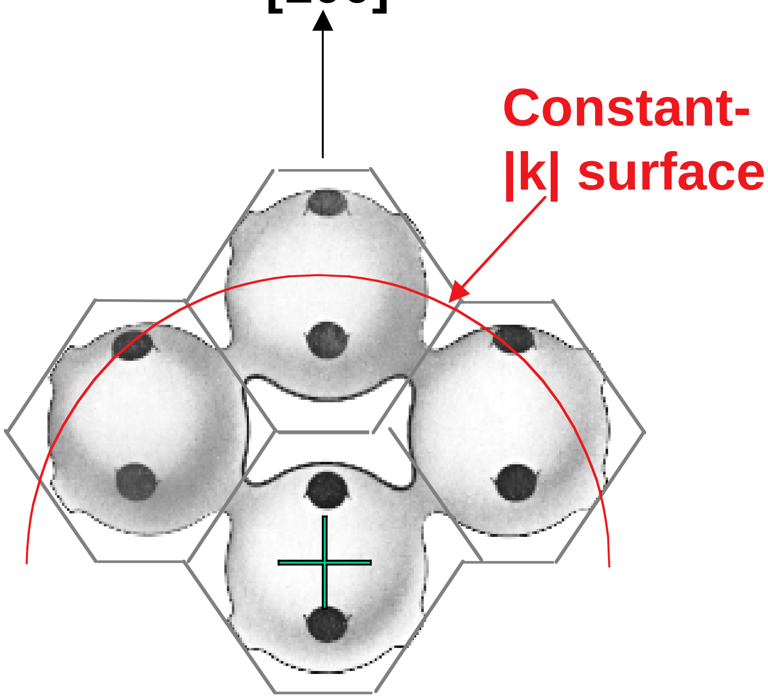
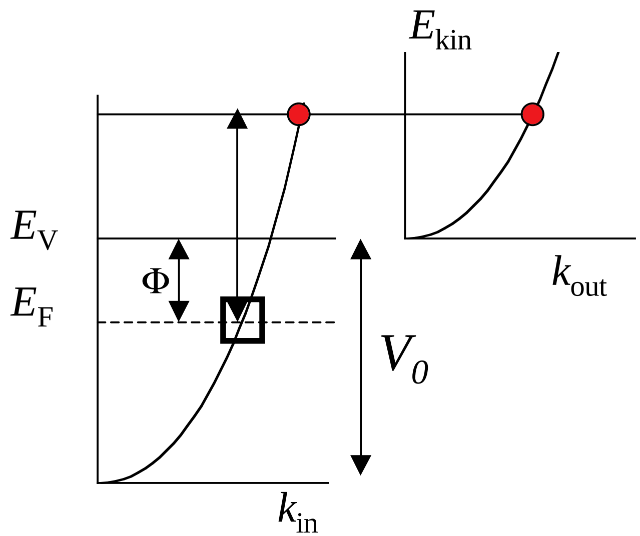
Surface normal [100]



- Fix the photon energy to a constant value,e.g. hν=83 eV
- This means the electrons will have constant energy
- The electrons detected have constant |k| and therefore lie on a sphere in k-space



Constant-|k| cut through Fermi surface of Cu(100)

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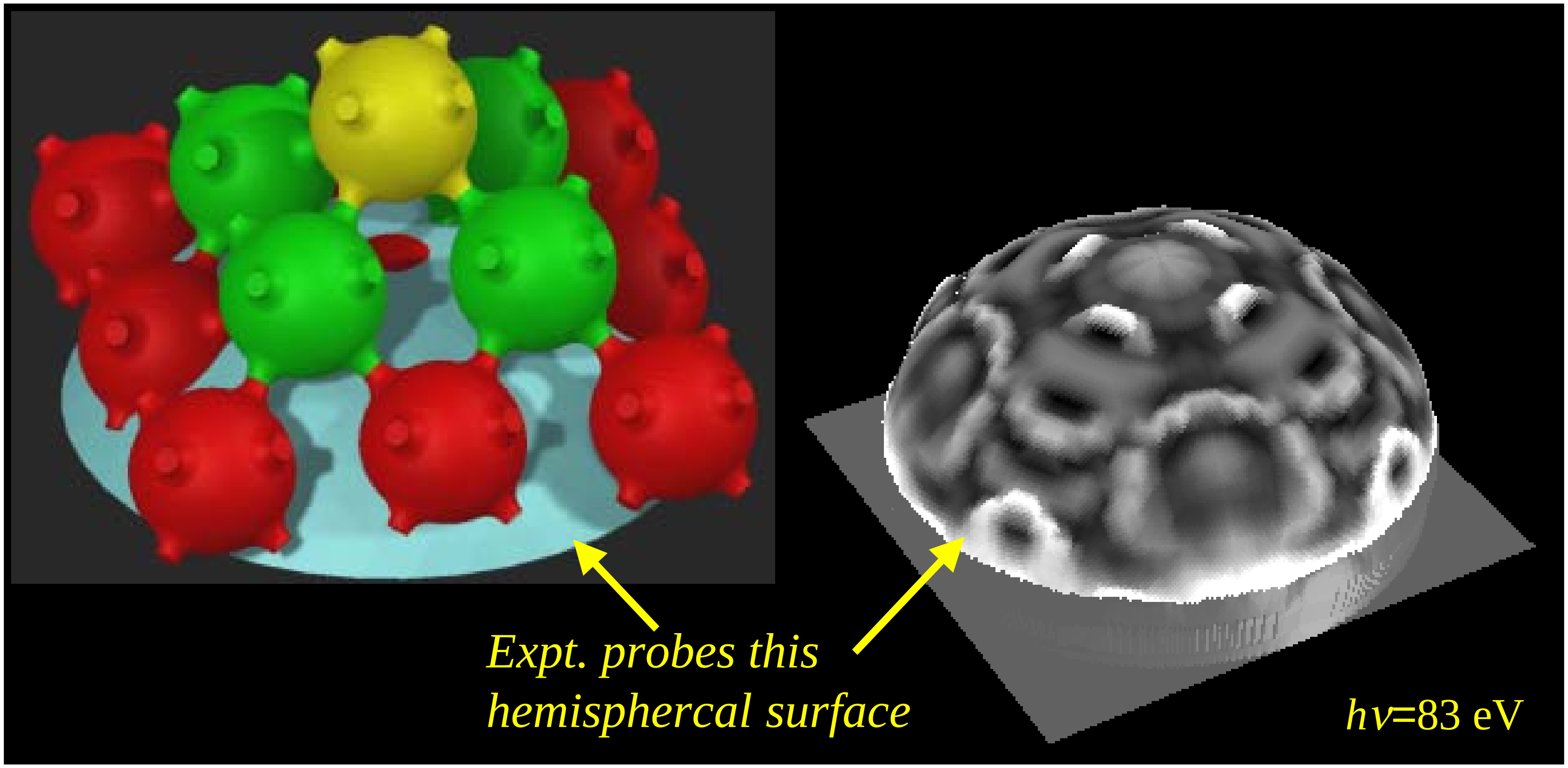
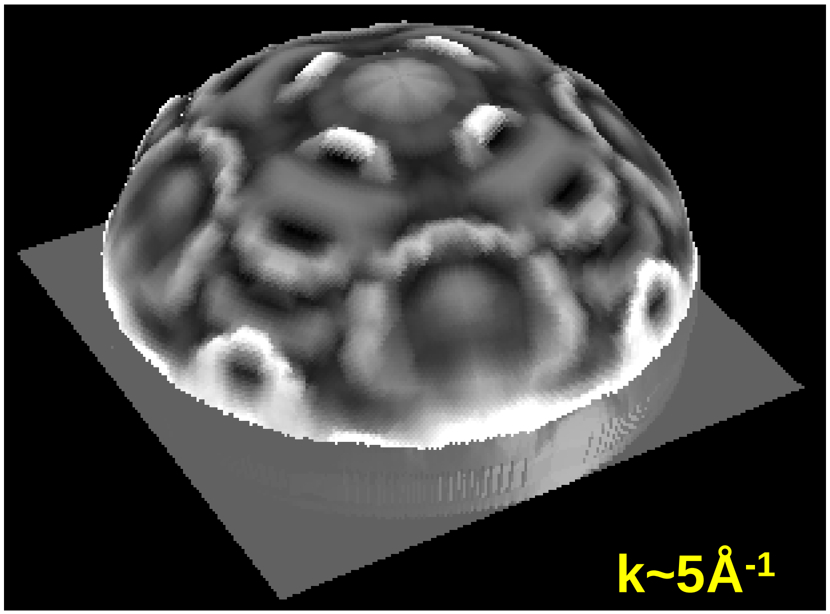
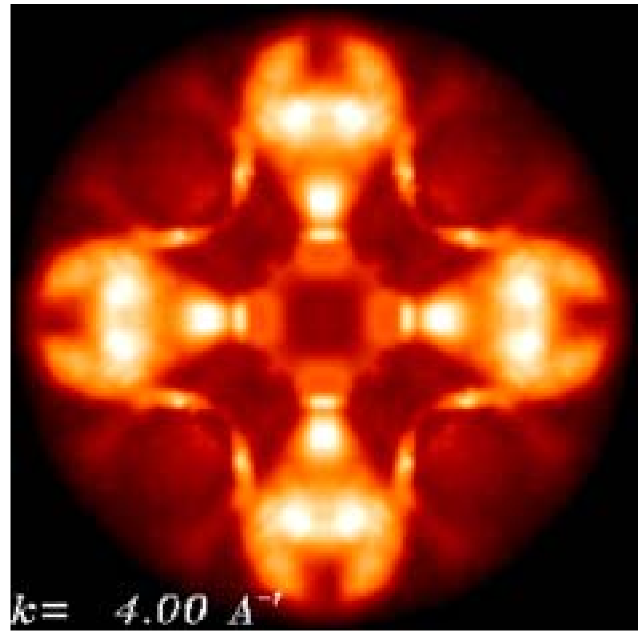
model **data**

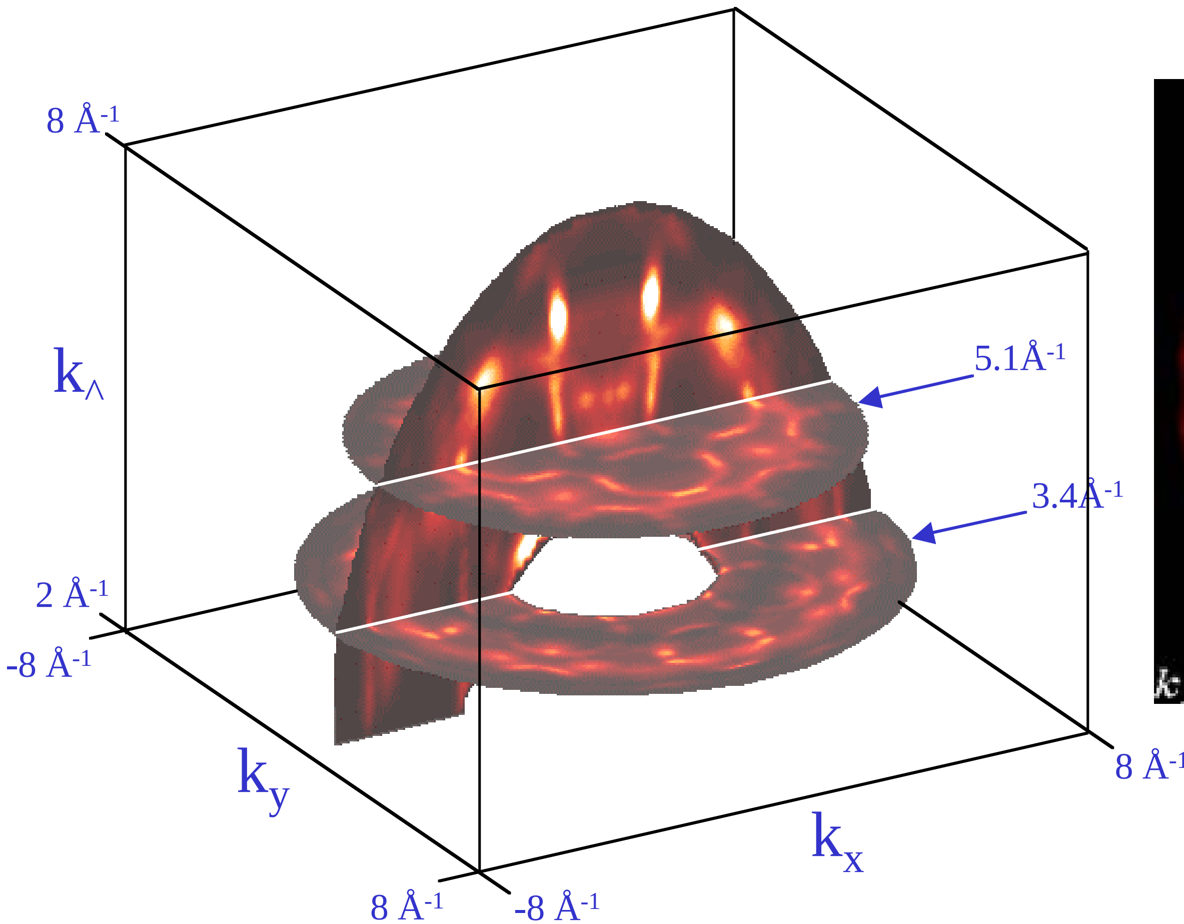


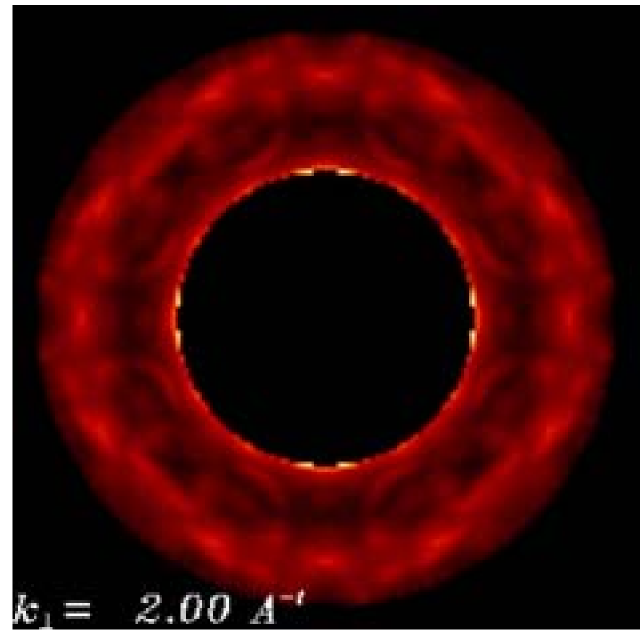
Animation of constant-|k| cuts





Resampling Copper (100) Fermi Surface to get a Volume Data Set in k-space





Copper (100) Fermi Surface Animation

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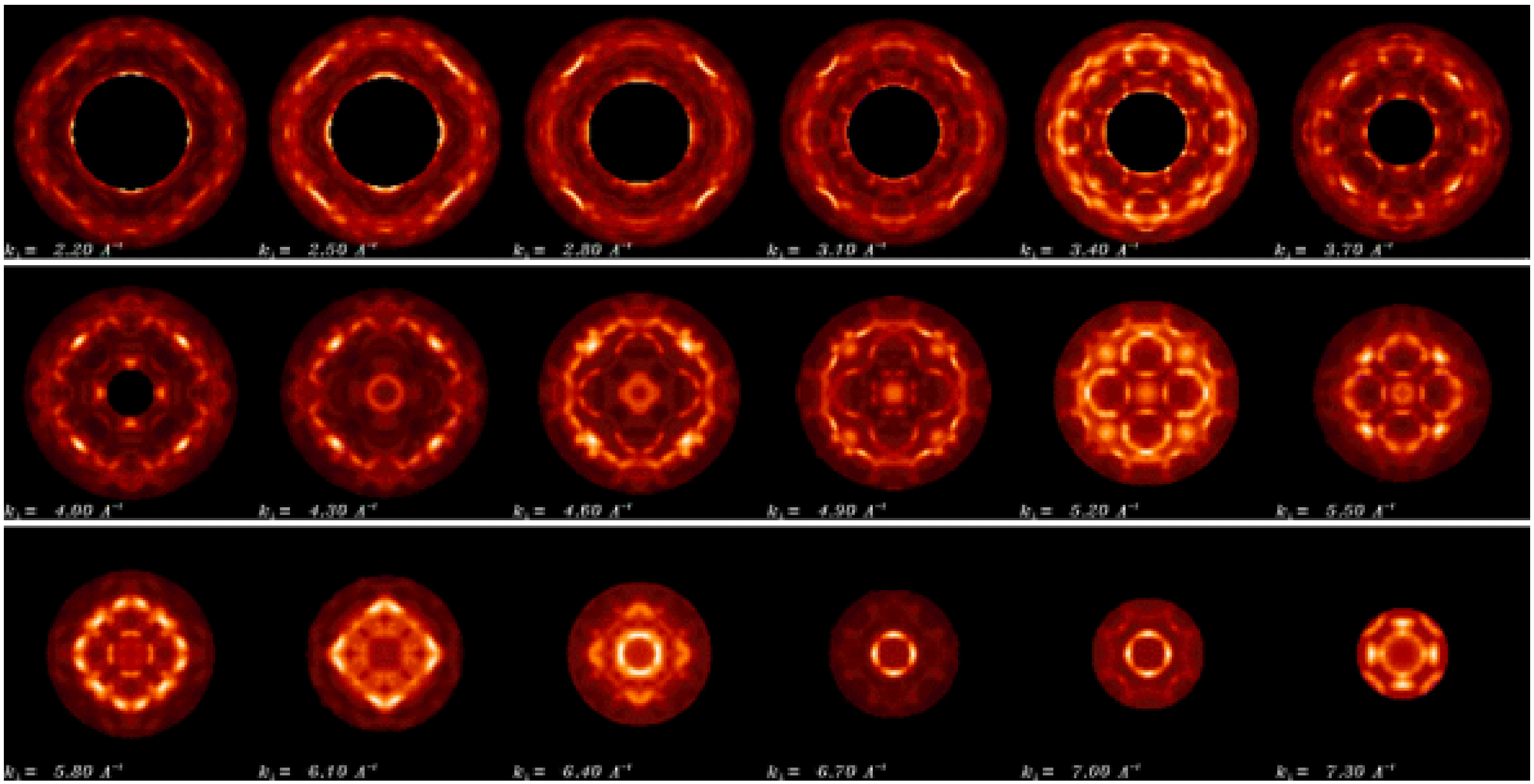

$k_z = 2.2$ to $7.0\ Å^{-1}$, $\Delta k_z = 0.3\ Å^{-1}$

Intensity Effects

- **Matrix Element Effects**
  - **Cross section - atomic-like effect**
  - **Cooper minimum - atomic-like effect**
  - **Symmetry Selection Rules - crystalline effect**
- **Resonant Photoemission**

Matrix Element for Photoemission

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- **Perturbation Theory gives Fermi's Golden Rule for transition probability**

$$w = \frac{2\pi}{\hbar}\left|\left\langle \psi_f \left| H_{\text{int}} \right| \psi_i \right\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

- **For dipole allowed transitions,**

$$H_{\text{int}} = \frac{e}{mc}\mathbf{A}\cdot\mathbf{p}$$

Illustration of cross-section effect

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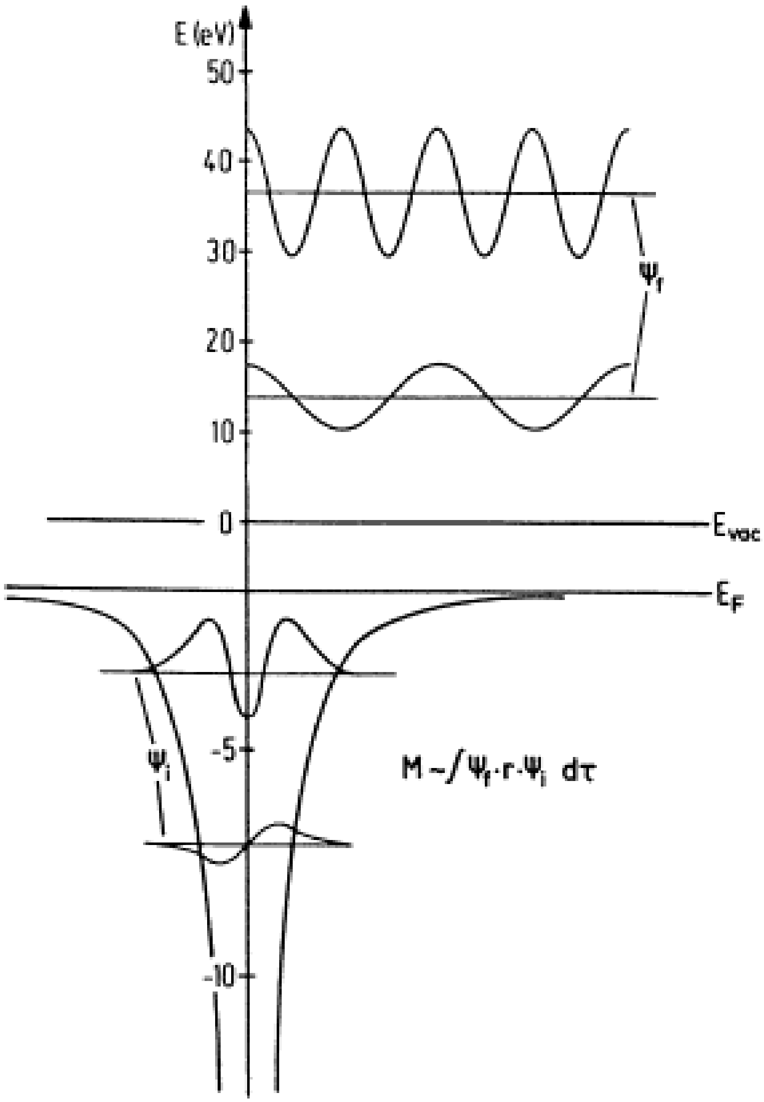

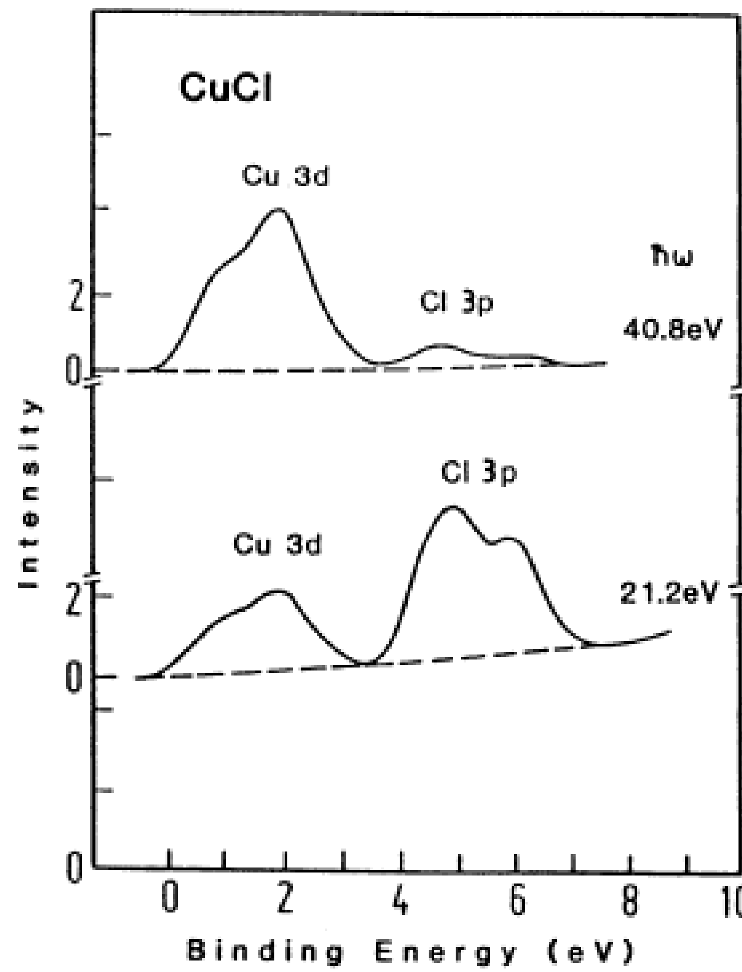

A. Goldmann et al, PRB 10, 4388 (1974).

The Cooper Minimum

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

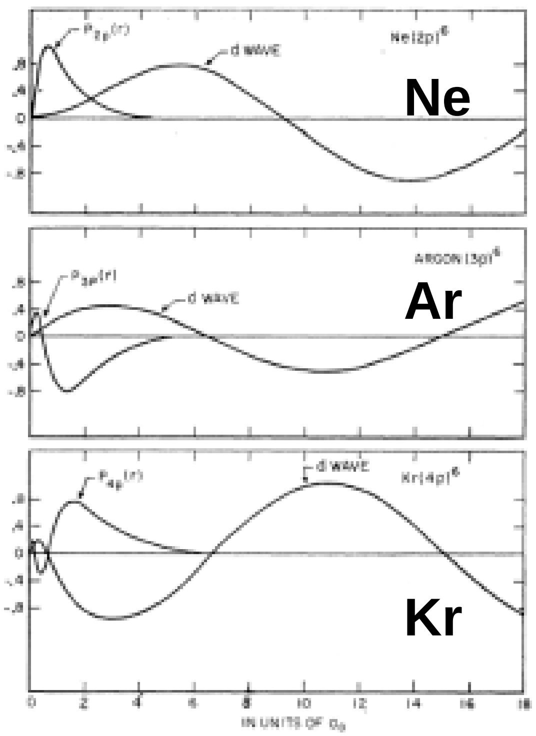
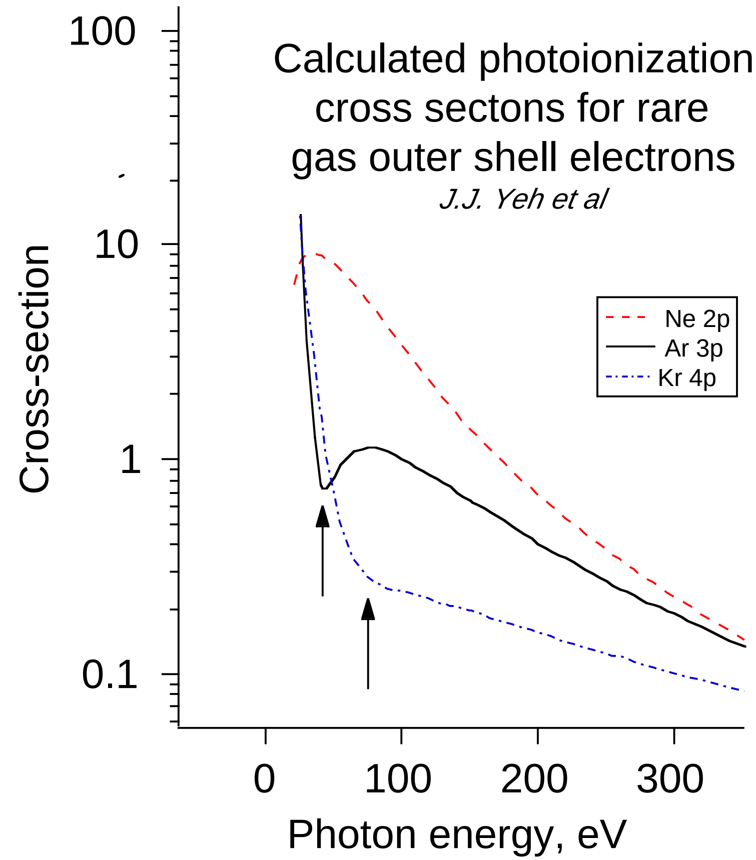


Fig. 2. Outer subshell radial wave functions and d waves for ε=0 for Ne, Ar, and Kr.



Application of Cooper Minimum

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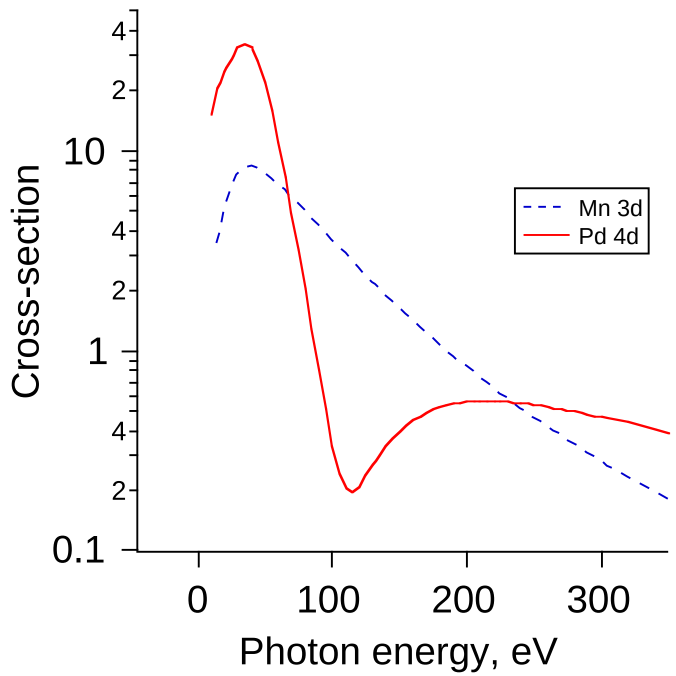
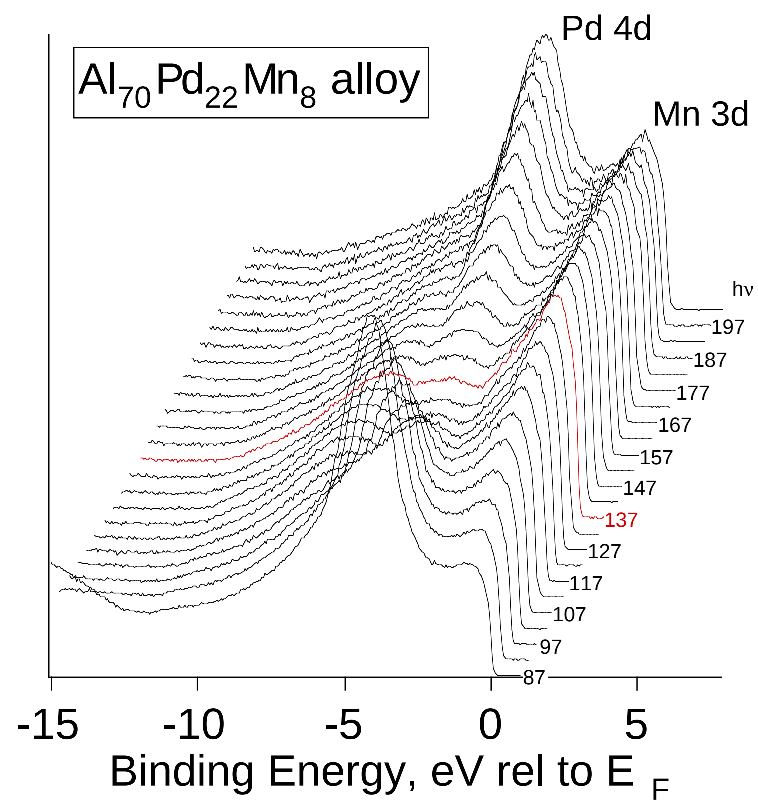
Calculation
J.J.Yeh



Expt.
Rotenberg et al



Symmetry Selection Rules

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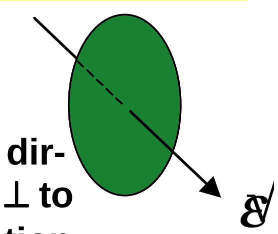
$$\left|M_{fi}\right|^2 \sim \left|\underbrace{\left\langle \psi_f \middle| \mathbf{A}\cdot\mathbf{p}\right|}_{\text{Fixed by geometry}}\underbrace{\left.\psi_i\right\rangle}_{\text{Sample-dependent}}\right|^2$$

- **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 $\perp$ to polarization vector

Odd in this direction

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

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

Some examples

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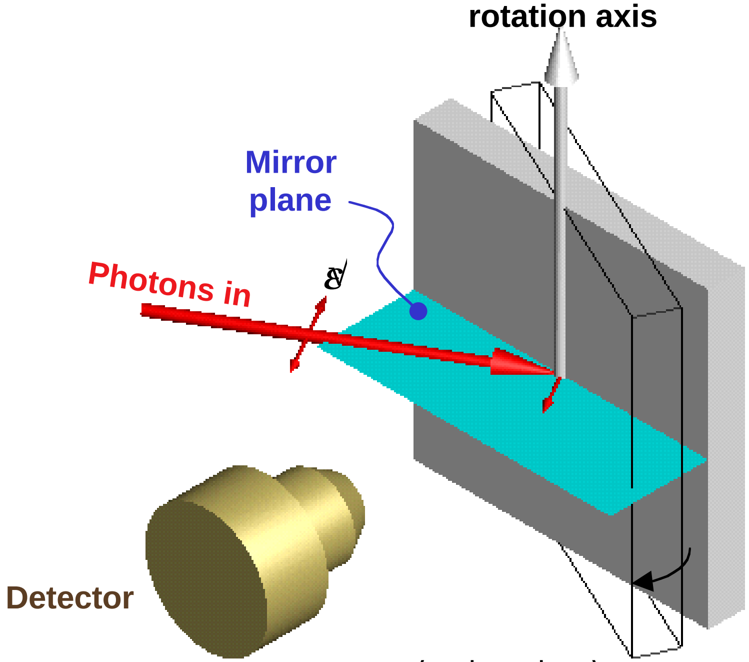
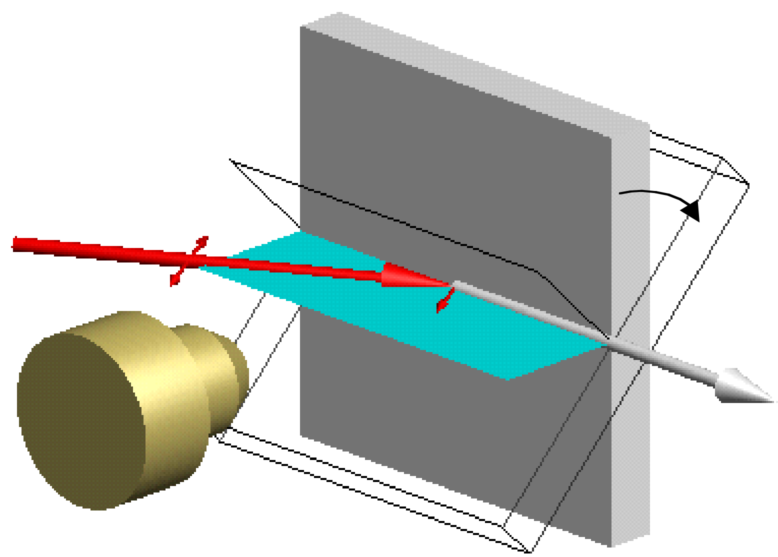
$$\left|M_{fi}\right|^2 \sim \left|\left\langle \psi_f \left| \mathbf{A}\cdot\mathbf{p} \right| \psi_i \right\rangle\right|^2 \text{ non-zero for } \begin{cases} \langle + | - | - \rangle \\ \langle + | + | + \rangle \end{cases}$$



$\langle + | + | + \rangle$



Only even initial states are observed at all rotation angles

Mixture of even and odd states

Resonant Photoemission

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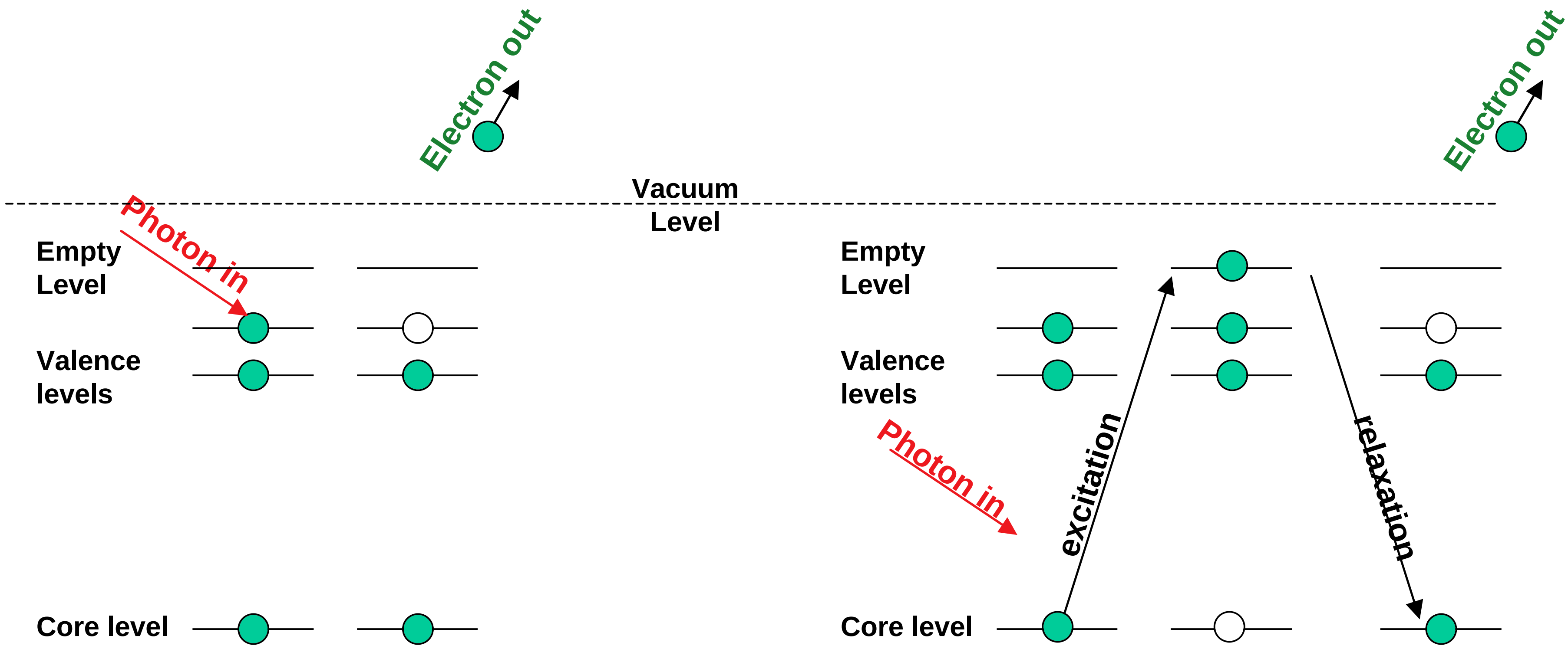

Resonant Photoemission

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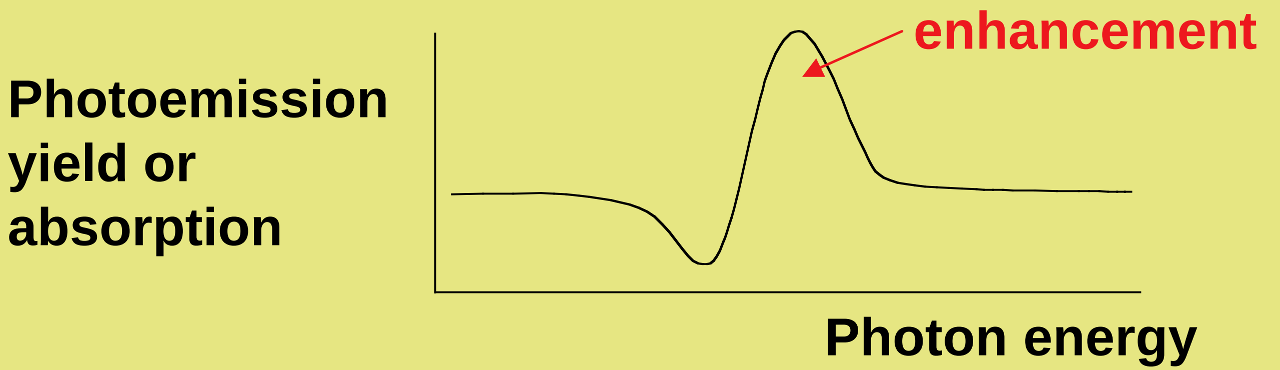
- These processes (non-resonant and resonant photoemission) have the same initial and final states.
- As quantum mechanics dictates, these independent channels will interfere when added coherently

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



- 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.

Resonant photoemission example

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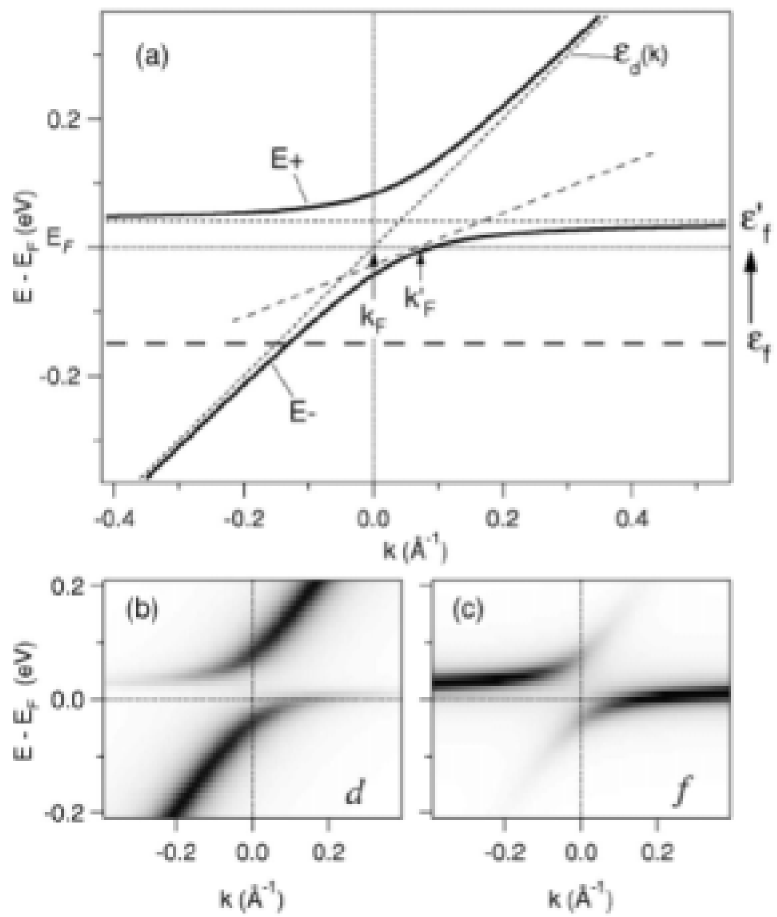
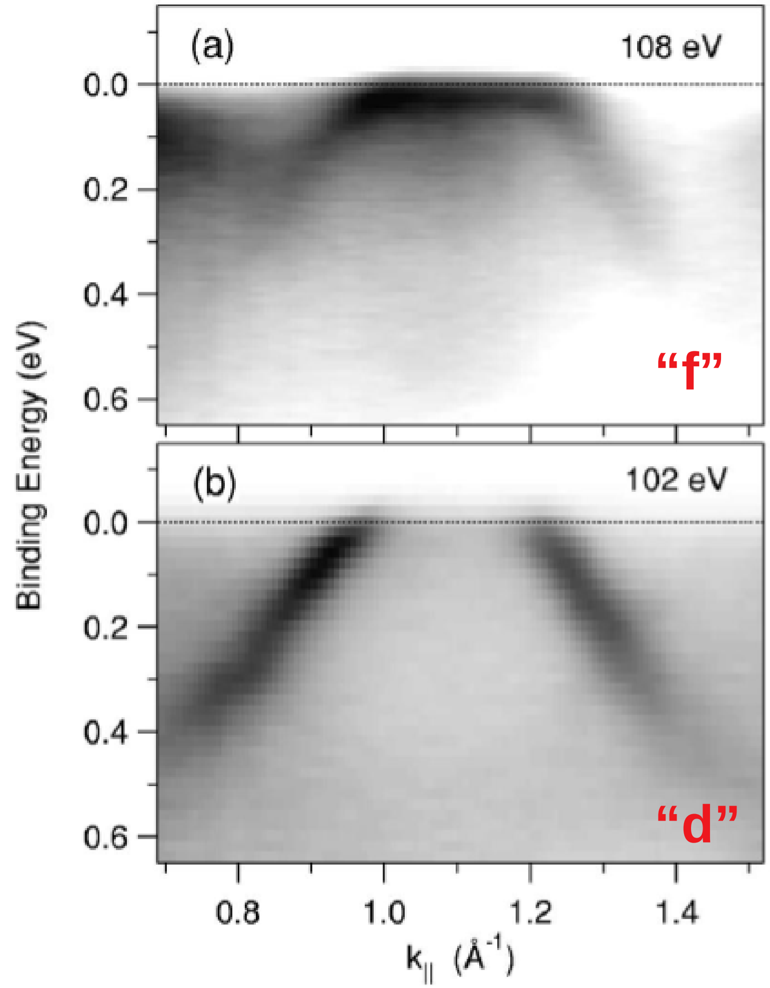
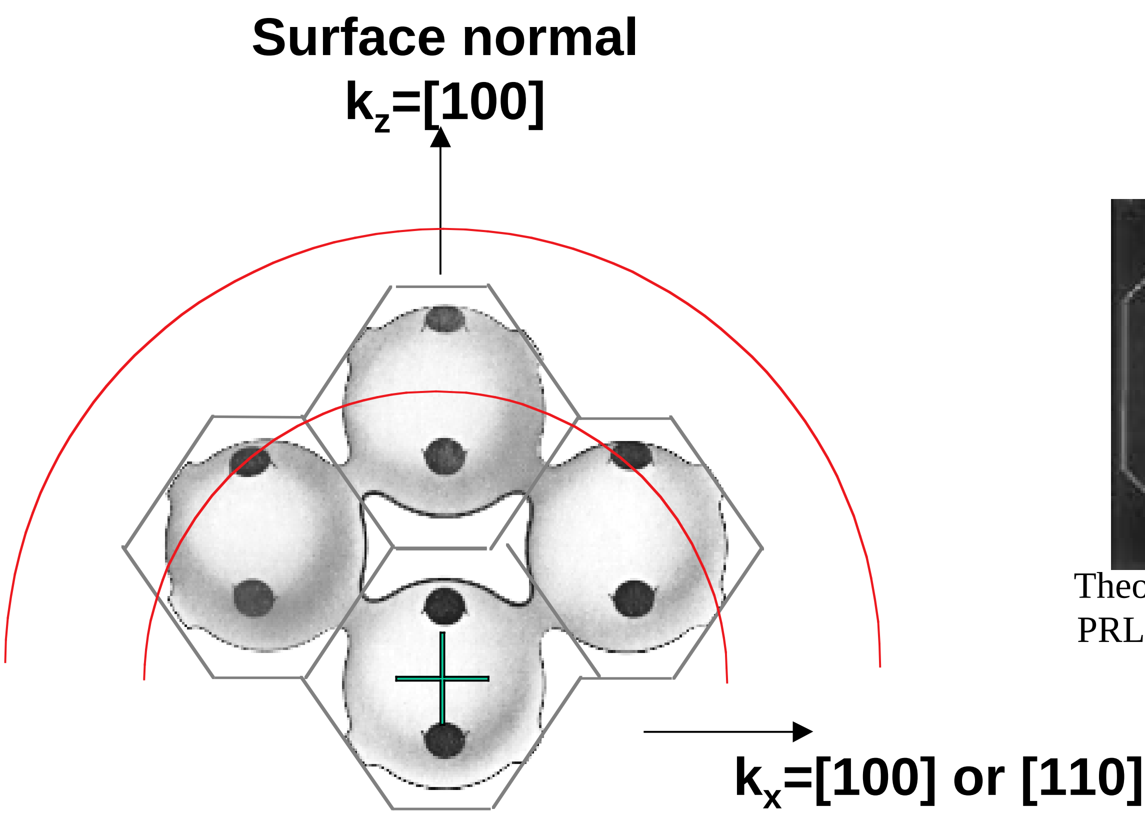
The mixture between d- and f-levels in URu_2Si_2 can be sorted out using resonant bandmapping

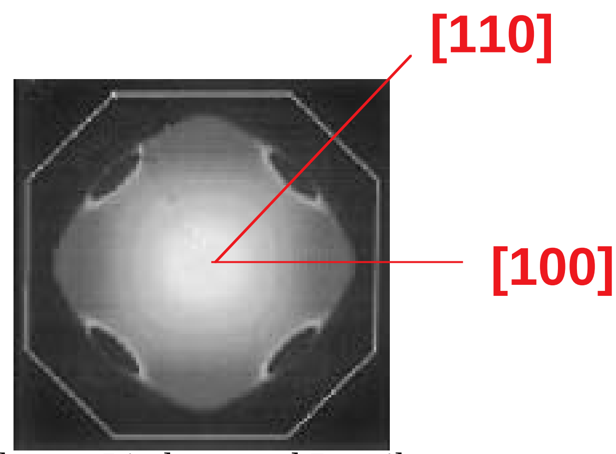




J. D. Denlinger et al, J. Electr. Spectr. Rel. Phenom. 117-118 (2001) 347

Surface Effects in Cu(100)





Theory, Lindroos and Bansil,
PRL **77**, 2985-2988 (1996).

By varying the photon energy and the polar angle, we can sample states in the k_x-k_z plane (for a fixed azimuth).
What do we find?

cuts through $k_{||}$-k_z plane

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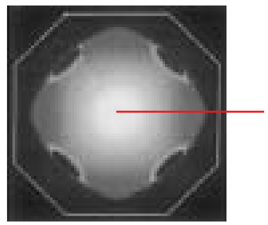
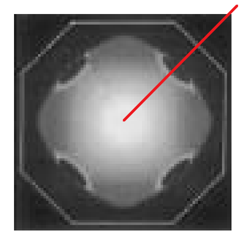
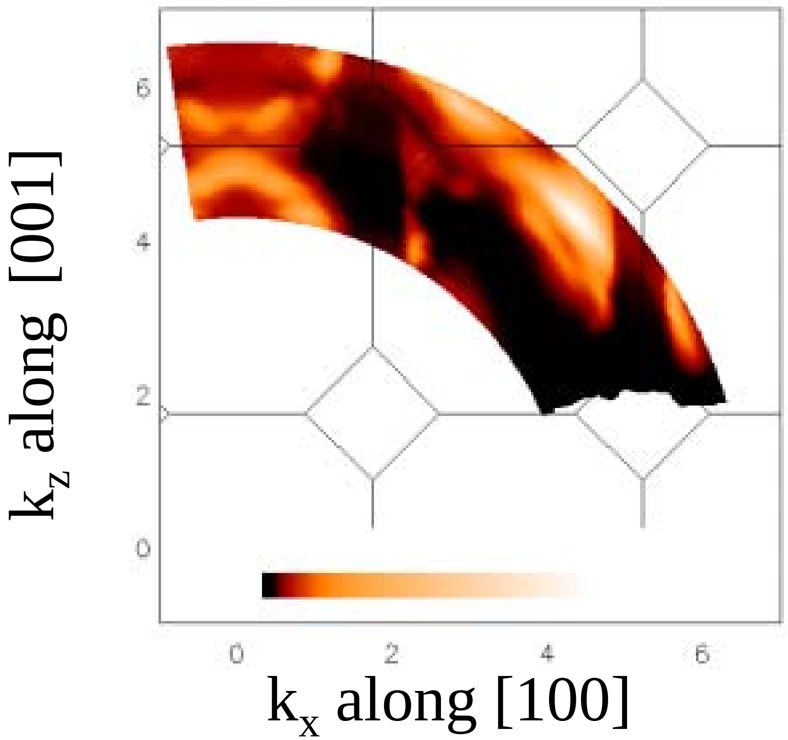
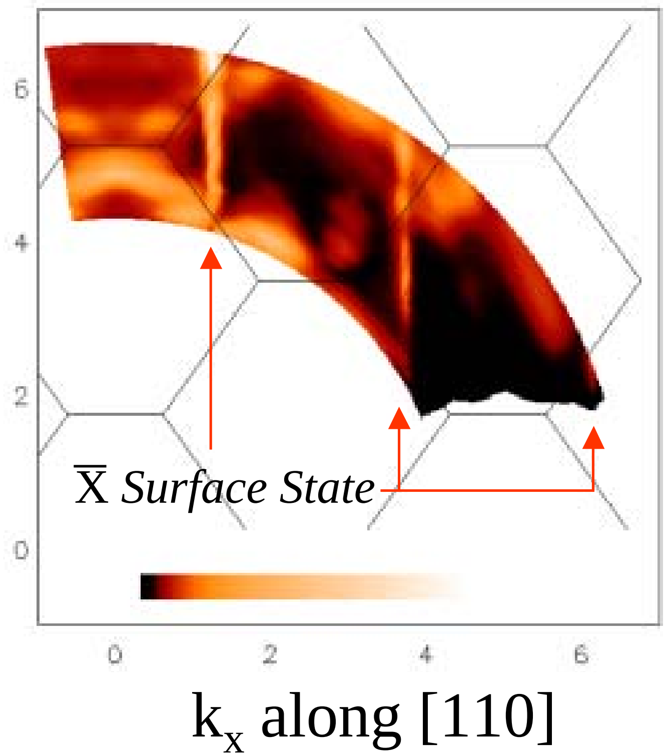
top





side





Surface Effects

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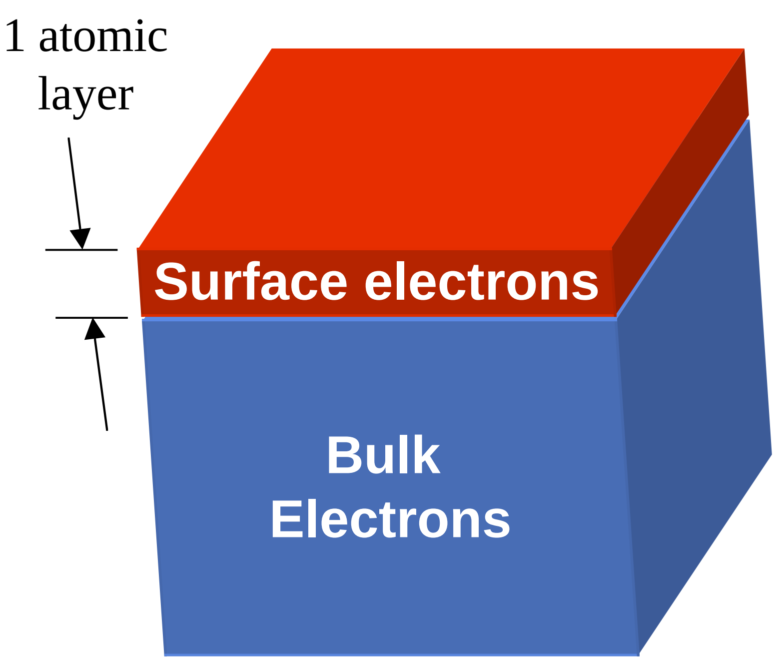
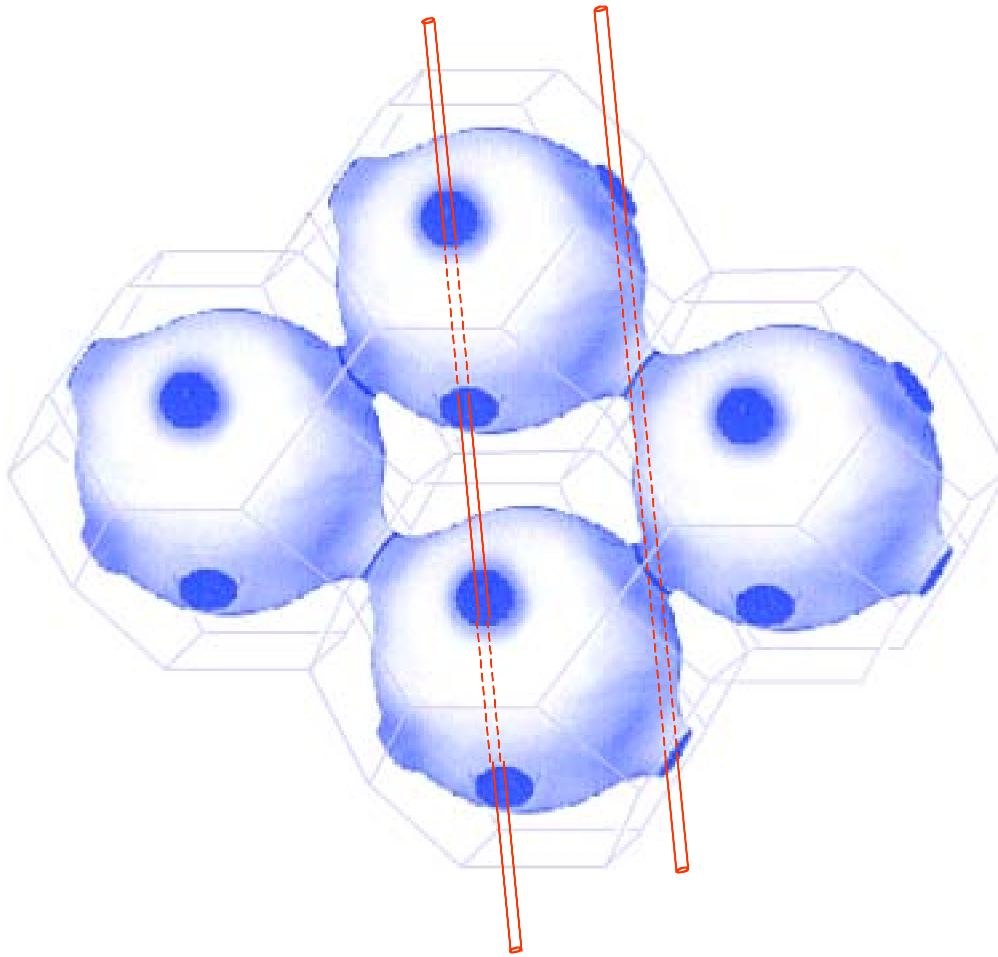


Real Space



Momentum Space

Fermi Surface Mapping

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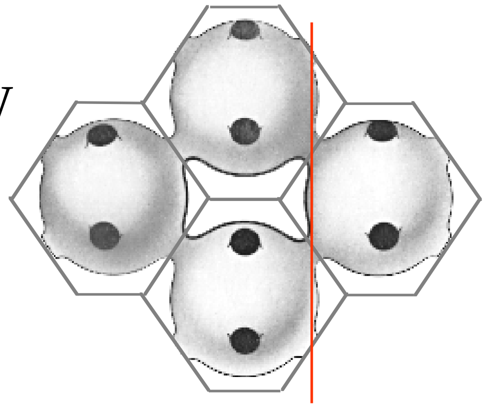
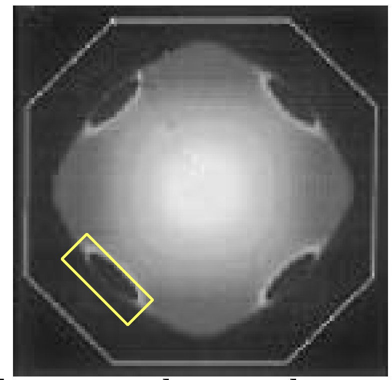
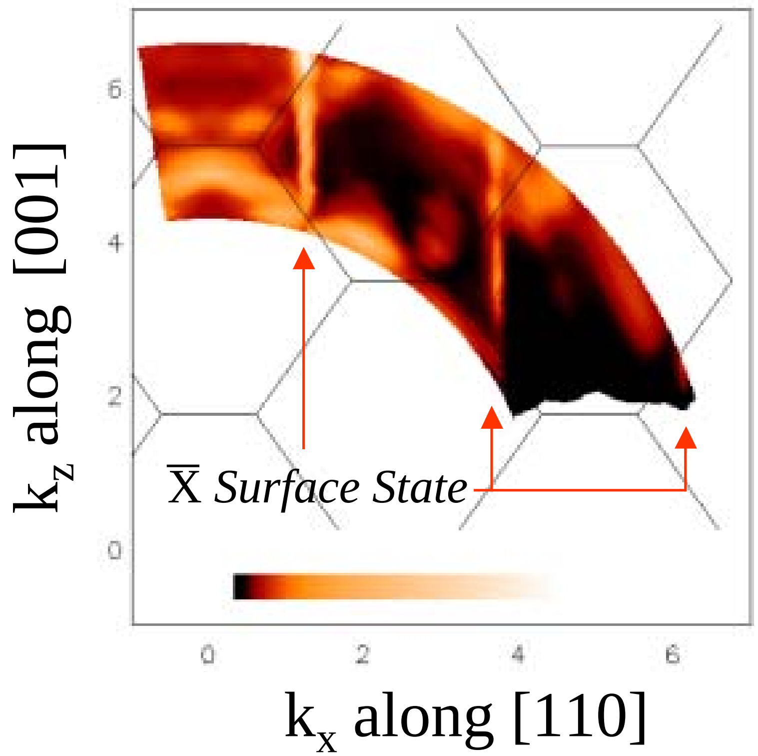
Side view

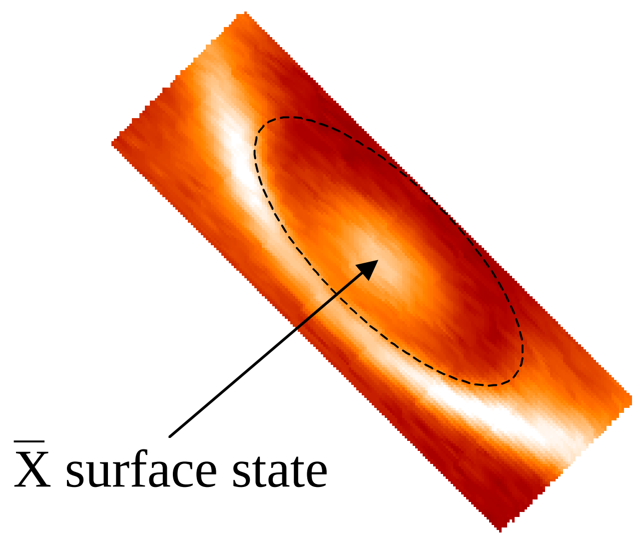




Top View

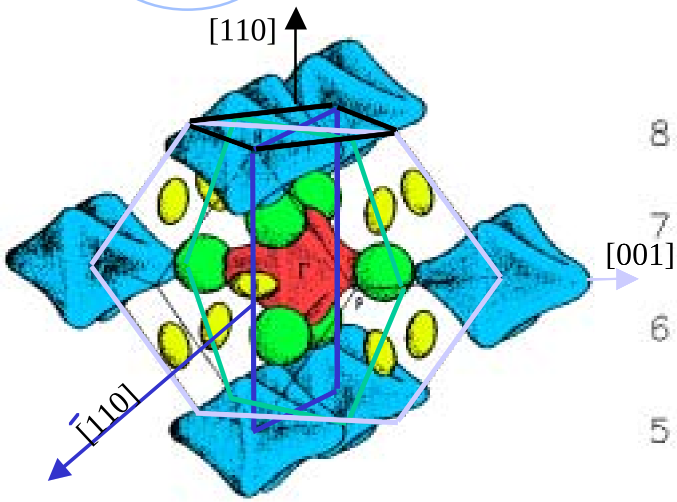
Theory, Lindroos and Bansil, PRL **77**, 2985-2988 (1996).

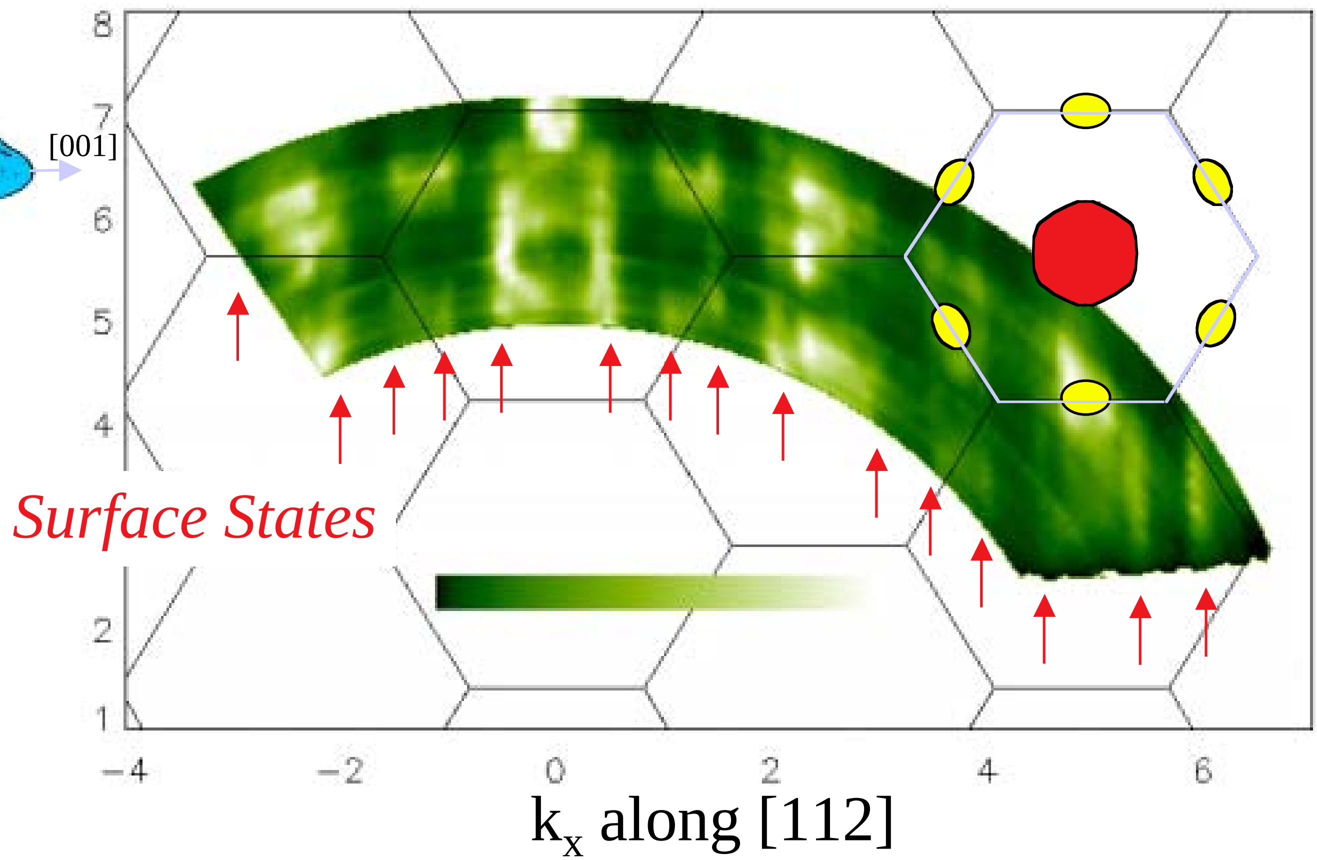




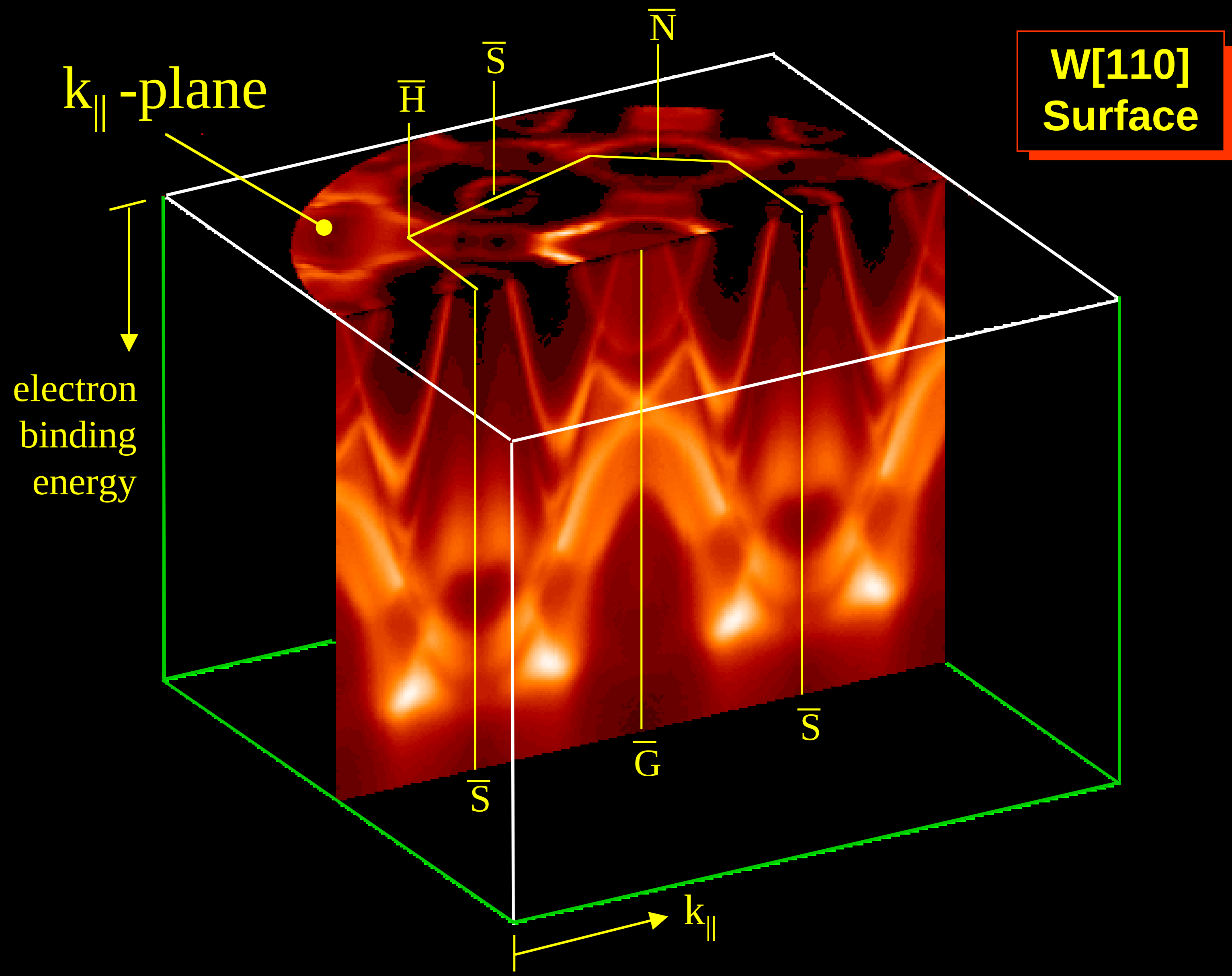
Another example: W(110)

ALS





Band Mapping and Fermi Contours



Surface States vs Bulk States

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- **Surface states are highly localized in real space, therefore completely delocalized in k-space along k_z.**
  - **NO DISPERSION OF SURFACE STATES in k_z direction**
- **Energy and momenta of surface and bulk states cannot overlap (otherwise, why would the states be localized to the surface?)**
- **Surface states have sharper linewidths than bulk due to a geometrical effect**

Bulk State linewidths

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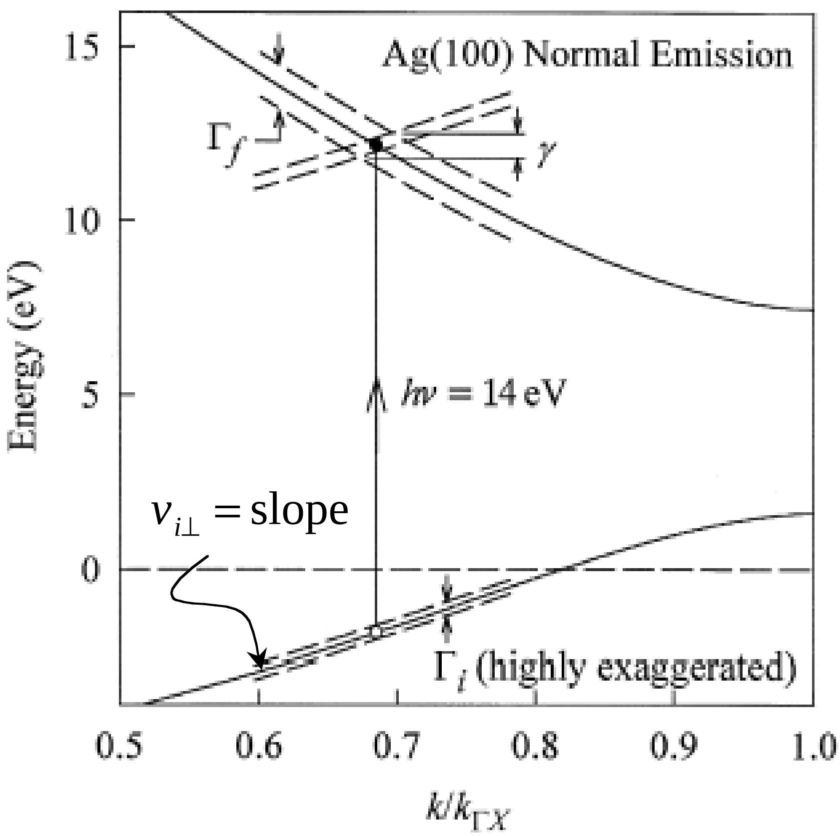

→ **Surface normal**

- **The total linewidth has contributions from both initial and final bands**

$$\gamma = \frac{\dfrac{\Gamma_i}{|v_{i\perp}|} + \dfrac{\Gamma_f}{|v_{f\perp}|}}{\left|\dfrac{1}{v_{i\perp}} - \dfrac{1}{v_{f\perp}}\right|}$$

T. C. Chiang, Chem. Phys. 251 (2000) 133.

Implications for surface states

ALS

• **Bulk bands may satisfy**

$$\left(v_{i\perp} = v_{f\perp}\right) \Rightarrow \left(\gamma \rightarrow \infty\right)$$

implying artificially large linewidths.

• **Surface states bands do not disperse along $k_\perp$, i.e.**

$$\left(v_{i\perp} = 0\right) \Rightarrow \left(\gamma \rightarrow \Gamma_i\right)$$

So there is no "geometrical" broadening of surface states. This is important when we come to the topic of lineshape analysis later on.

One-dimensional states?

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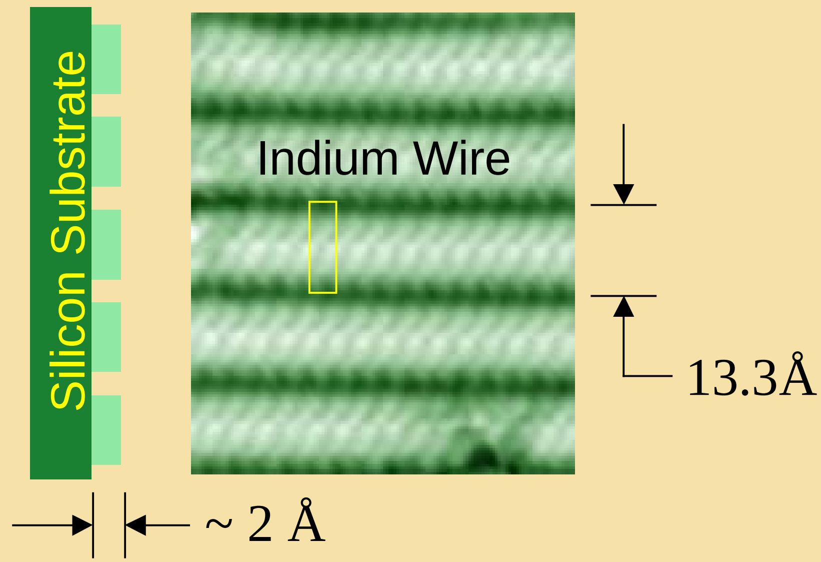
Real-Space

(STM Image)

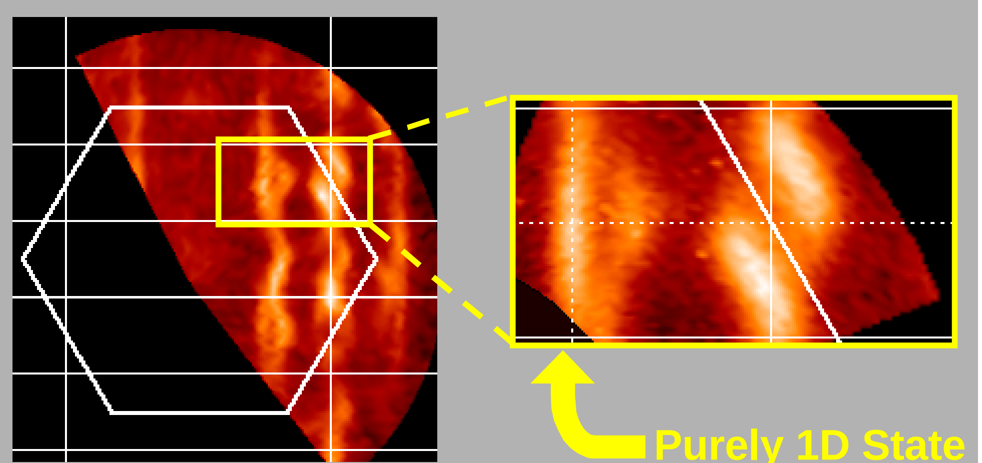


Reciprocal-Space

(Angle-Resolved Photoemission)

Fermi-Edge DOS

Yeom et al, PRL 82, 4898 (1999)



H. W. Yeom, S. Takeda, I. Matsuda, K. Horikoshi, T. Ohta, T. Nagao, Univ. of Tokyo
S. Hasegawa, Japan Science and Technology Corporation
J. Schaefer, S. D. Kevan, University of Oregon
E. Rotenberg, Advanced Light Source

Quantum-confined states

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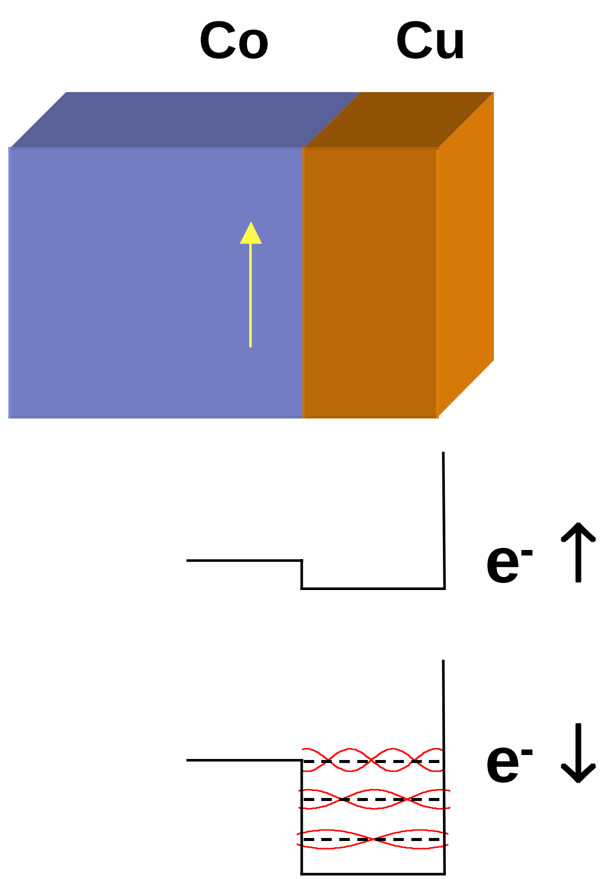
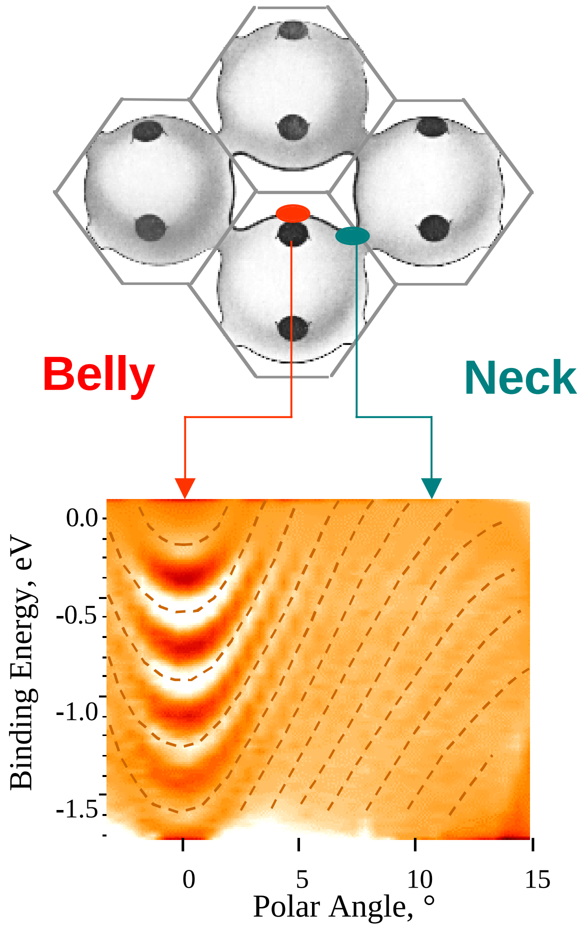




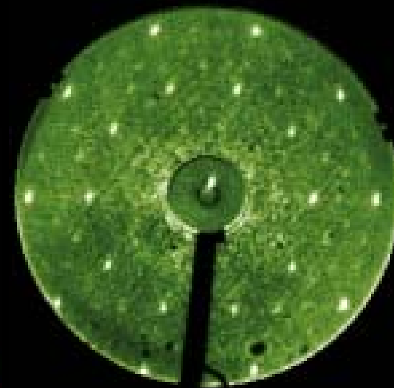
Data from Kawakami Thesis, UCB

J. Unguris et al, PRL 67,140 (1991).
P. Segovia et al, PRL 77,3455 (1996)

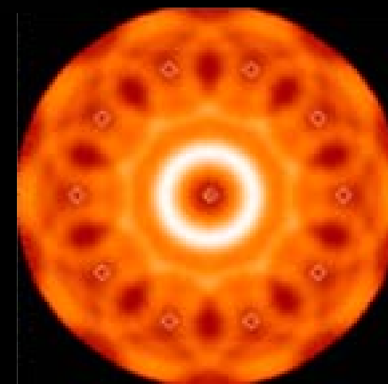
Non-periodic materials?

Perfect long-range order without periodicity!

Hypothetical structure,
after Yamamoto et al

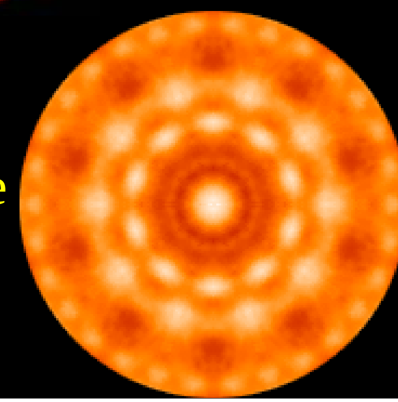


Surface Diffraction



Free-Electron
(s-p bands)

Fermi Surface
(d-bands)

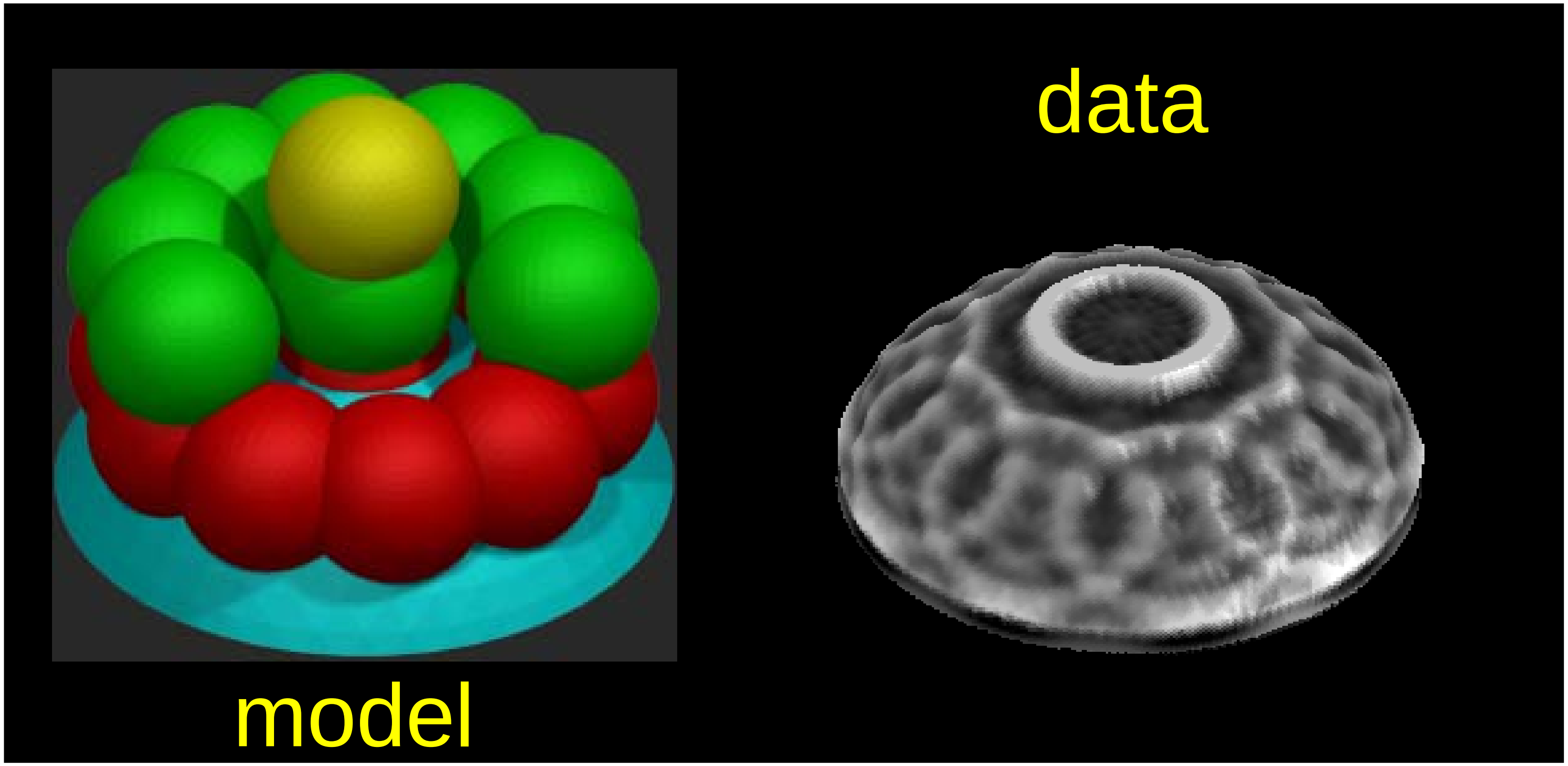


E. Rotenberg, W. Theis, P. Gille, K. Horn, Nature 406, 602 (2000).

Model for distribution of states in k-space

ALS

Here we present cross-sections of the constant-energy surfaces in three-dimensional reciprocal space, acquired by measuring constant-energy (|**k**|) electrons vs emission angle. The spherical bodies arise from the free-electron-like dispersion relations.



Beyond the one-electron picture

- **Assumptions so far:**
  - **Each electron was treated as an independent particle in a background of the other electrons**
    - **Fact: the other electrons respond to the presence of the core hole**
  - **No interactions between electrons and other excitations**
    - **Facts:**
      - **Electron-electron interaction**
      - **Electron-phonon interaction**
  - **How can photoemission picture be modified to include these effects?**
  - **How do these effects lead to interesting ground states of metals?**
    - **Superconductivity**
    - **Giant Magnetoresistance**
    - **Density Waves**

What materials do we study?

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- **Metals**
  - Metal electrons can sustain excitations down to zero energy
  - So they can couple to low-energy excitations in the system
    - Phonons, spin excitations, etc.
  - Metals are trapped in a high energy state.
    - High kinetic energy from conduction electrons
    - No favorable lattice structure in which to form insulator
    - Metals look to subtle many body interactions to form low-energy ground states

- **Low-dimensional materials (2D, 1D)**
  - Sharp linewidths
  - Many-body effects are enhanced because in lower dimensions, the quasiparticles have fewer degrees of freedom to avoid each other
  - Geometrical effect (next slide)

- **Low temperatures**
  - Because interesting ground states are usually below a critical temperature
  - To reduce smearing of the electrons near the Fermi level

The Fermi Surface

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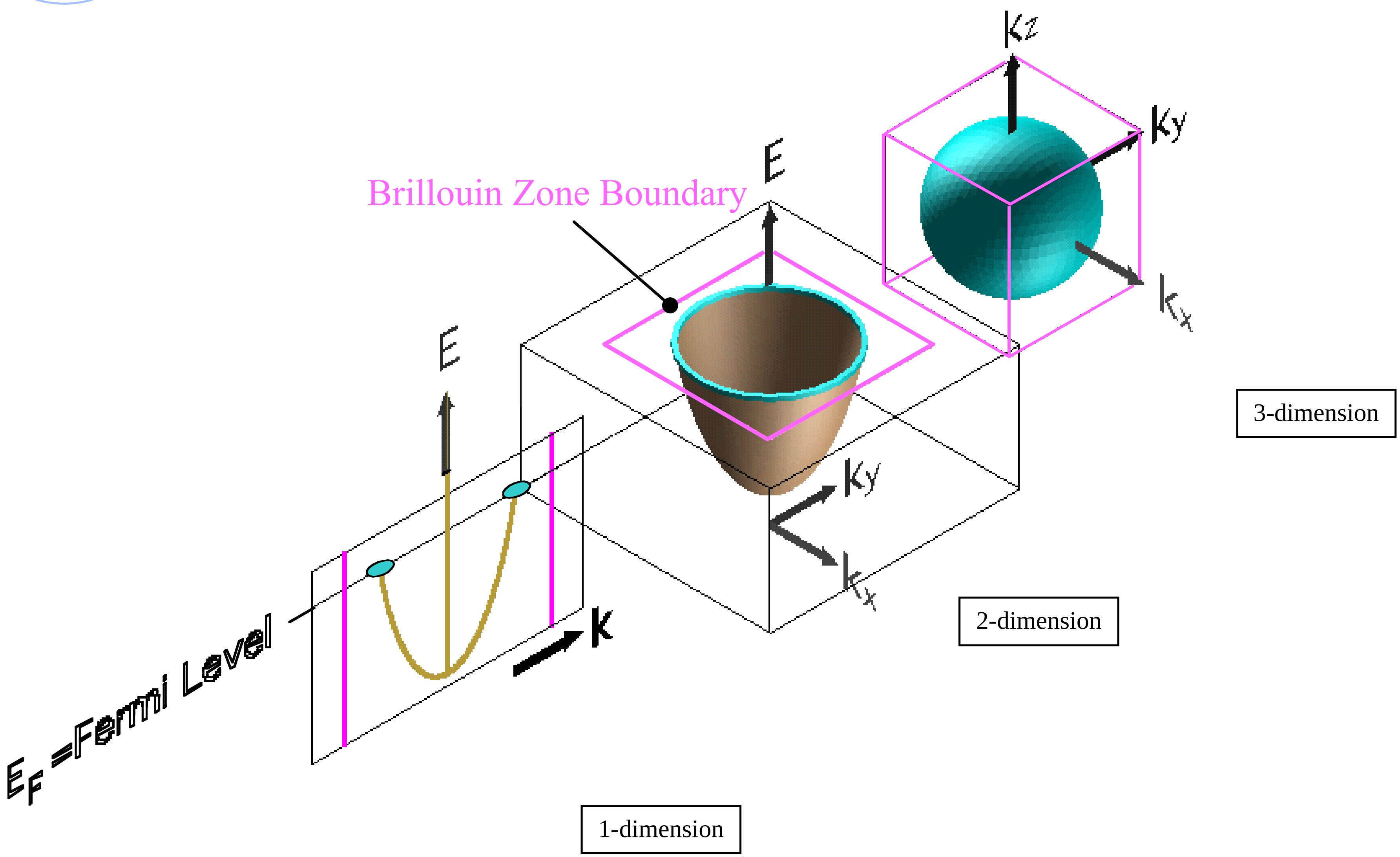

Formalism for many-body treatment

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Transition Probability $$w = \frac{2\pi}{\hbar} \left| \left\langle \psi_f \middle| H_{\text{int}} \middle| \psi_i \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

$$\psi_i(N) = \phi_{ik} \psi_{i\mathbf{k},R}(N-1)$$ "R" means "remaining"

$$\psi_f(N) = \underbrace{\phi_{f\mathbf{k}}}_{\text{One-electron state}} \underbrace{\psi_{f\mathbf{k},R}(N-1)}_{\text{State of remaining electrons}}$$

$$\left\langle \psi_f \middle| H_{\text{int}} \middle| \psi_i \right\rangle = \left\langle \phi_f \middle| H_{\text{int}} \middle| \phi_i \right\rangle \sum_s c_s$$

$$c_s = \left\langle \psi_{fsR}(N-1) \middle| \psi_{i\mathbf{k},R}(N-1) \right\rangle$$

Possible relaxed final states

The spectral function

ALS

We can now write

$$I \propto \sum_{f,i,\mathbf{k}} \left| \left\langle \phi_f \left| H_{\text{int}} \right| \phi_i \right\rangle \right|^2 A(\mathbf{k}, E)$$

Where the spectral function

$$A(\mathbf{k}, E) = \sum_s |c_s|^2 \delta(E_F + E_s(N-1) - E_0(N) - \hbar\omega)$$

This is what we measure in a photoemission spectrum!

The Green's Function

In practical terms, we treat the wavefunction in perturbation theory as

$$\psi(\mathbf{r}) = \psi_i(\mathbf{r}) + \int d\mathbf{r}' \underbrace{G(\mathbf{r},\mathbf{r}')}_{\text{Green's Function}} \underbrace{H_{\text{int}}(\mathbf{r}')}_{\text{Perturbation}} \underbrace{\psi_i(\mathbf{r}')}_{\text{Initial state}}$$

The spectral function and the Green's function are related:

$$A(k,E) = \frac{1}{\pi}\,\mathrm{Im}(G(k,E))$$

This is a simplification--we are now dealing with Green's functions, not wavefunctions!

The self-energy function

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We recover the free-electron case easily:

$$G_0(k,E) = \frac{1}{E - E_k^0 - i\delta}$$

$$A_0(k,E) = \delta(E - E_k)$$

$$E_k^0 = \hbar^2 k^2 / 2m$$

We modify the equations to handle the interacting case:

$$G(k,E) = \frac{1}{E - E_k - \Sigma(k,E)}$$

How the binding energies are modified

$$A(k,E) = \frac{1}{\pi} \frac{\operatorname{Im}\Sigma(k,E)}{\left[E - E_k^0 - \operatorname{Re}\Sigma(k,E)\right]^2 + \left[\operatorname{Im}\Sigma(k,E)\right]^2}$$

How the spectral lines look

$$\Sigma(k,E) = \underbrace{\operatorname{Re}\Sigma(k,E)}_{\text{Change in energy}} + i\underbrace{\operatorname{Im}\Sigma(k,E)}_{\text{Change in lifetime}}$$

Change in lifetime

Change in energy

Summary of the formalism

ALS

$$G(k,E) = \frac{1}{E - E_k - \Sigma(k,E)}$$

$$A(k,E) = \frac{1}{\pi} \frac{\operatorname{Im}\Sigma(k,E)}{\left[E - E_k^0 - \operatorname{Re}\Sigma(k,E)\right]^2 + \left[\operatorname{Im}\Sigma(k,E)\right]^2}$$

$$\Sigma(k,E) = \operatorname{Re}\Sigma(k,E) + i\operatorname{Im}\Sigma(k,E)$$

In practise, an experimentalist does not have to be an expert in the many-body physics.

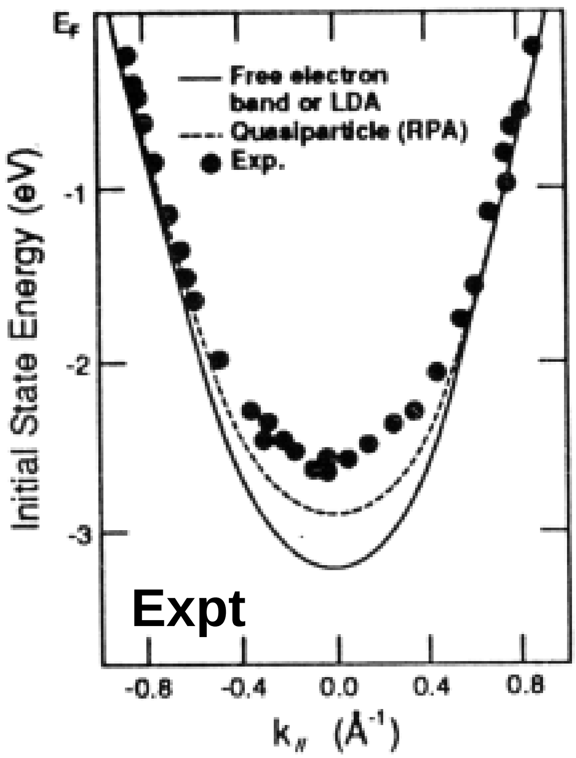
One can often look up the self-energy function and use it to simulate spectra.

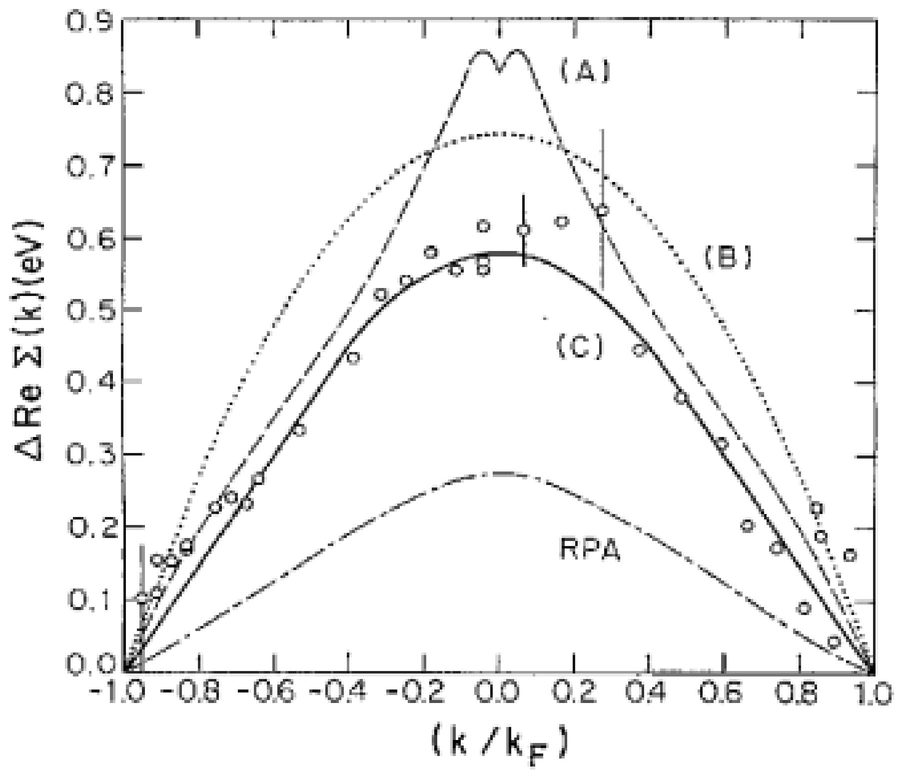
Theorists can easily look up experimental self-energies and compare to their models.

Simple example: bandwidth of Na metals

ALS

The bandstructure of Na deviates from the free-electron model

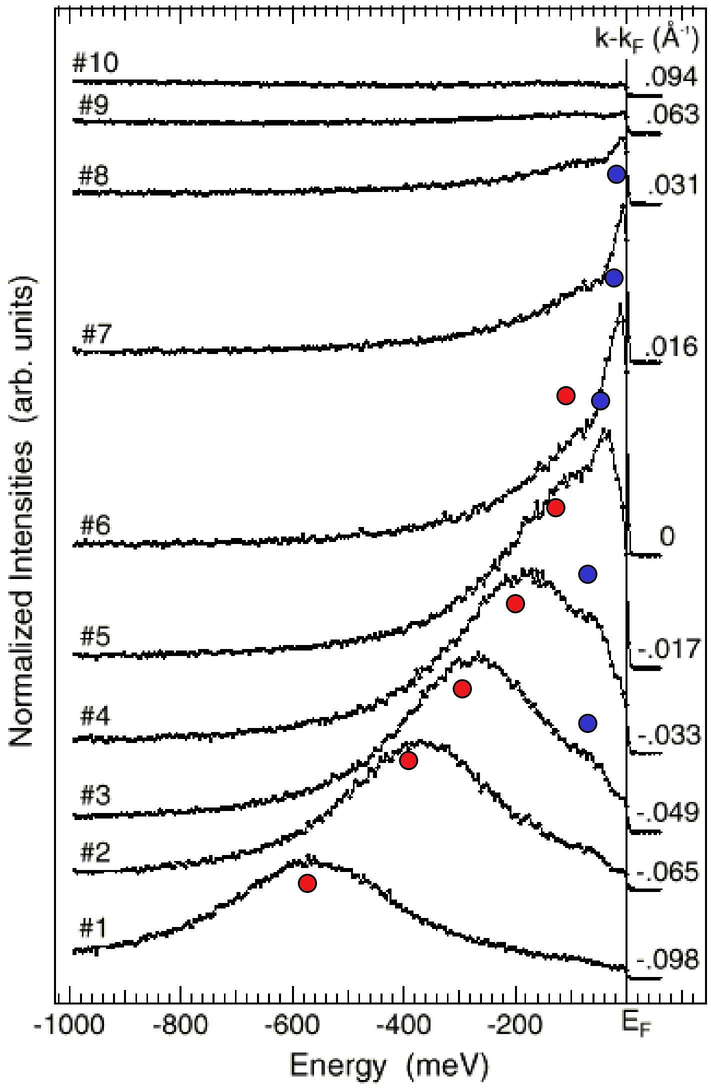




In-Whan Lyo and E. W. Plummer, PRL 60,1558 (1988).

More complicated: electron-phonon coupling

ALS



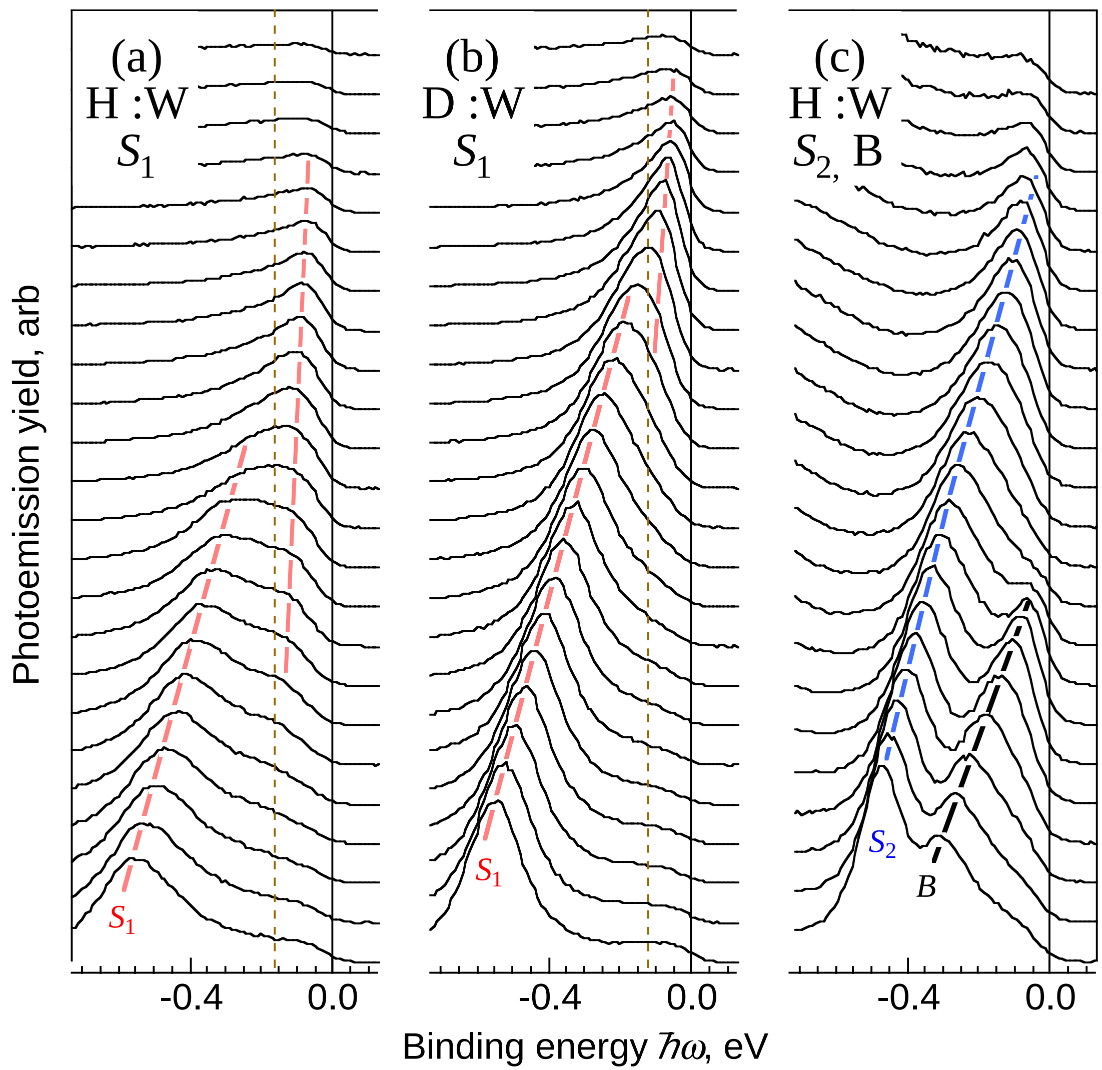
Surface state of Be(0001)
T=12K

Two states, not one!

Hengsberger et al, PRL 83,592 (1999).

Another el-ph coupling example

ALS

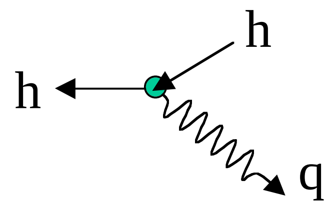


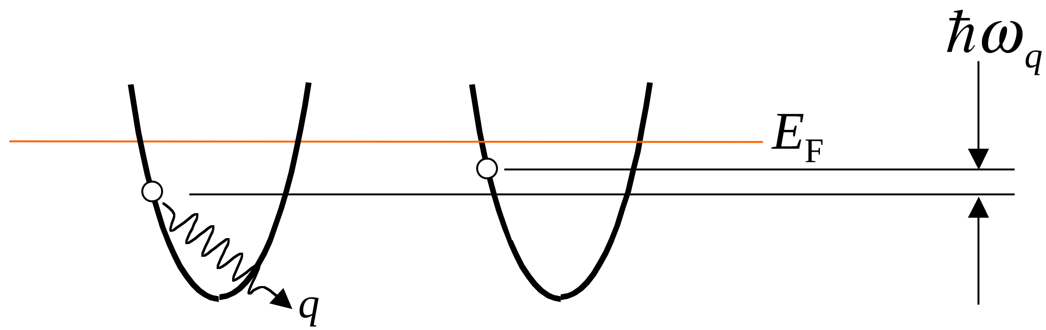
Single monolayer H atoms on W(110)

Many-body interactions

ALS

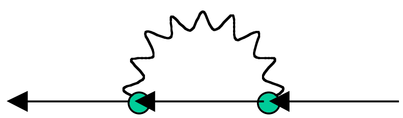
Hole emits (decays) to phonon

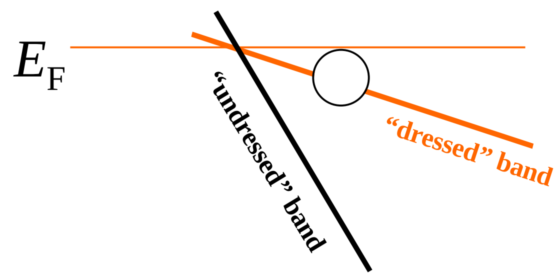




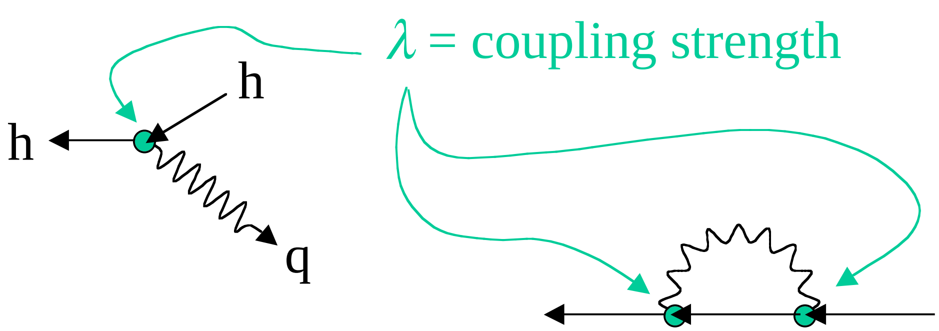
Hole emits and reabsorbs phonon

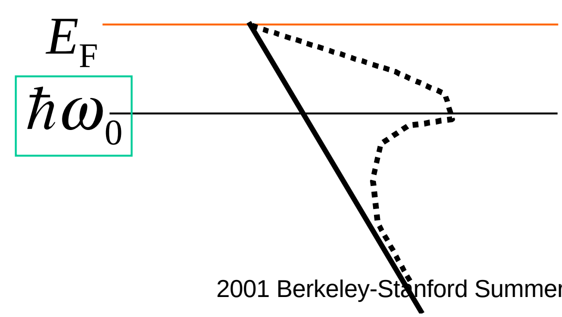
"dressed hole w/virtual cloud"



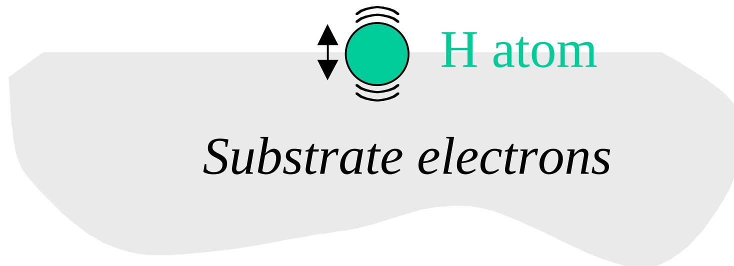


Slope changes
=> Smaller velocity
=> Higher mass





Formalism *single-oscillator model*



ω=electron energy

k=electron momentum

$\Sigma(\omega;\ \lambda,\ \omega_0)$=self-energy function (theoretical model)

$A(\omega,k)$ = what we measure

= photoemission spectrum

= measure the valence band spectrum as a function of angle (k)

What can we get out of the experiment?

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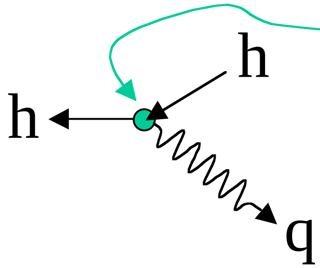
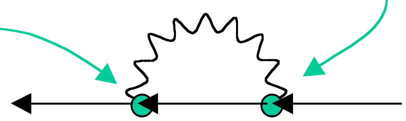
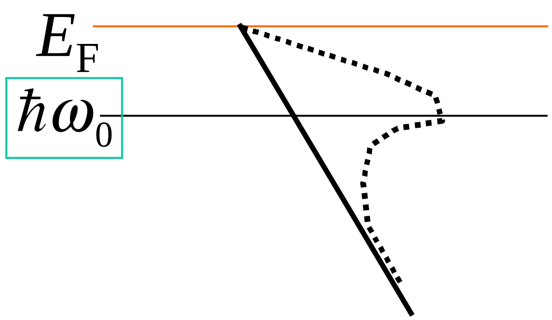
2 important parameters

λ = coupling strength







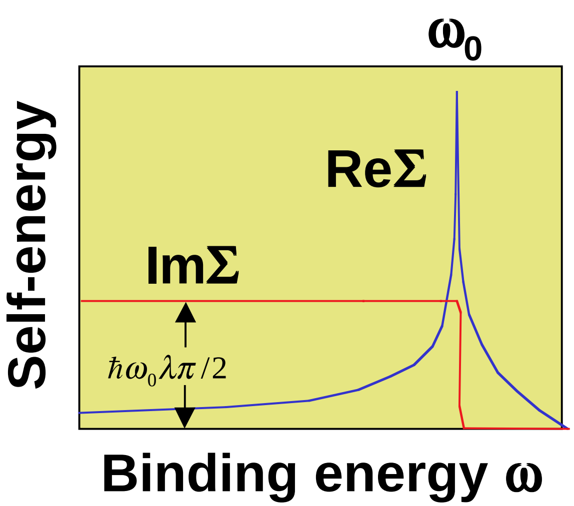
Self-energy function for electron-phonon coupling

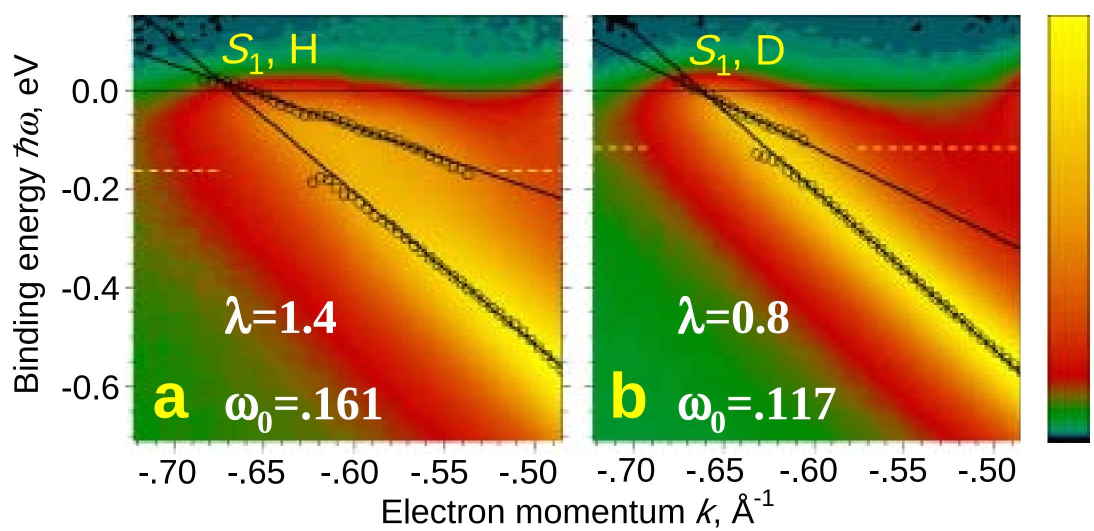
$$\Sigma(\omega) = \int_{-E_F}^{\infty} d\varepsilon \int_0^{\omega_m} d\omega' \alpha^2 F(\omega') \left\{ \frac{1 - f_{\varepsilon,T} + n_{\omega',T}}{\omega - \varepsilon - \omega' + i\delta} + \frac{f_{\varepsilon,T} + n_{\omega',T}}{\omega - \varepsilon + \omega' + i\delta} \right\}$$

We take an Einstein model for the optical vibration mode

$$F(\omega) \sim \delta(\omega - \omega_o)$$

$$\text{coupling strength} = \lambda = 2\int \frac{\alpha^2 F(\overline{\omega})}{\overline{\omega}} d\overline{\omega}$$





Possibility of 2-d superconductivity?

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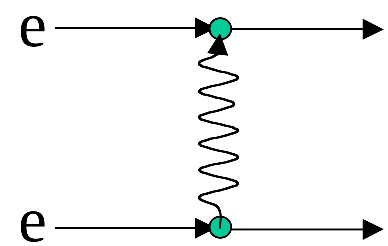
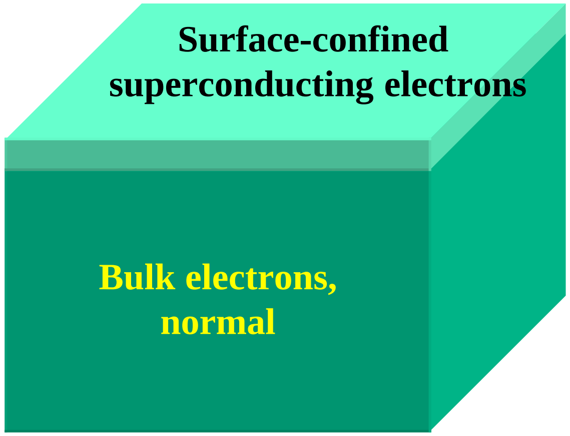
Now that we understand the "node" then we can understand more complicated processes, e.g.

<u>superconductivity</u>

--> formation of Cooper pairs
--> net attraction between electrons
--> critical temperature T_c
--> energy gap Δ



Electron-electron interaction via phonon exchange



e.g. For Be surface expt*,

λ =1.15

ω_0=70 meV

Predict superconductor with $T_c \leq 70$ K !

But, not seen so far down to 12K[†]

*Jensen et al 1998

[†]Baer et al 1999

How does H on W(110) stack up?

ALS

Strong-coupling theory of superconductivity

	Matl	λ	w0 [K]	Tc(theory)	Tc(expt)
	W	0.28	390	0.01	0.012
	Mo	0.41	460	0.84	0.92
	Be	0.24	1000	**0.02**	0.026
3-D	Hg	1	72	3.56	4.16
	Pb	1.12	105	6.25	7.19
	Nb	0.82	277	9.20	9.22
	Pd	0.15	274	0.00	not SC
	PdH	0.75	475	12.67	10
2-D	H:W	0.5-1.4	1932	**50-150**	?
	Be surf	1.15	1000	**70.21**	?

But, can you really make a superconductor by coupling to **optical** phonons? The usual treatment is for **acoustic** phonons.

Bardeen, Cooper, Schriefer 1957; McMillan 1968

Coupling to excitations with finite momentum transfer

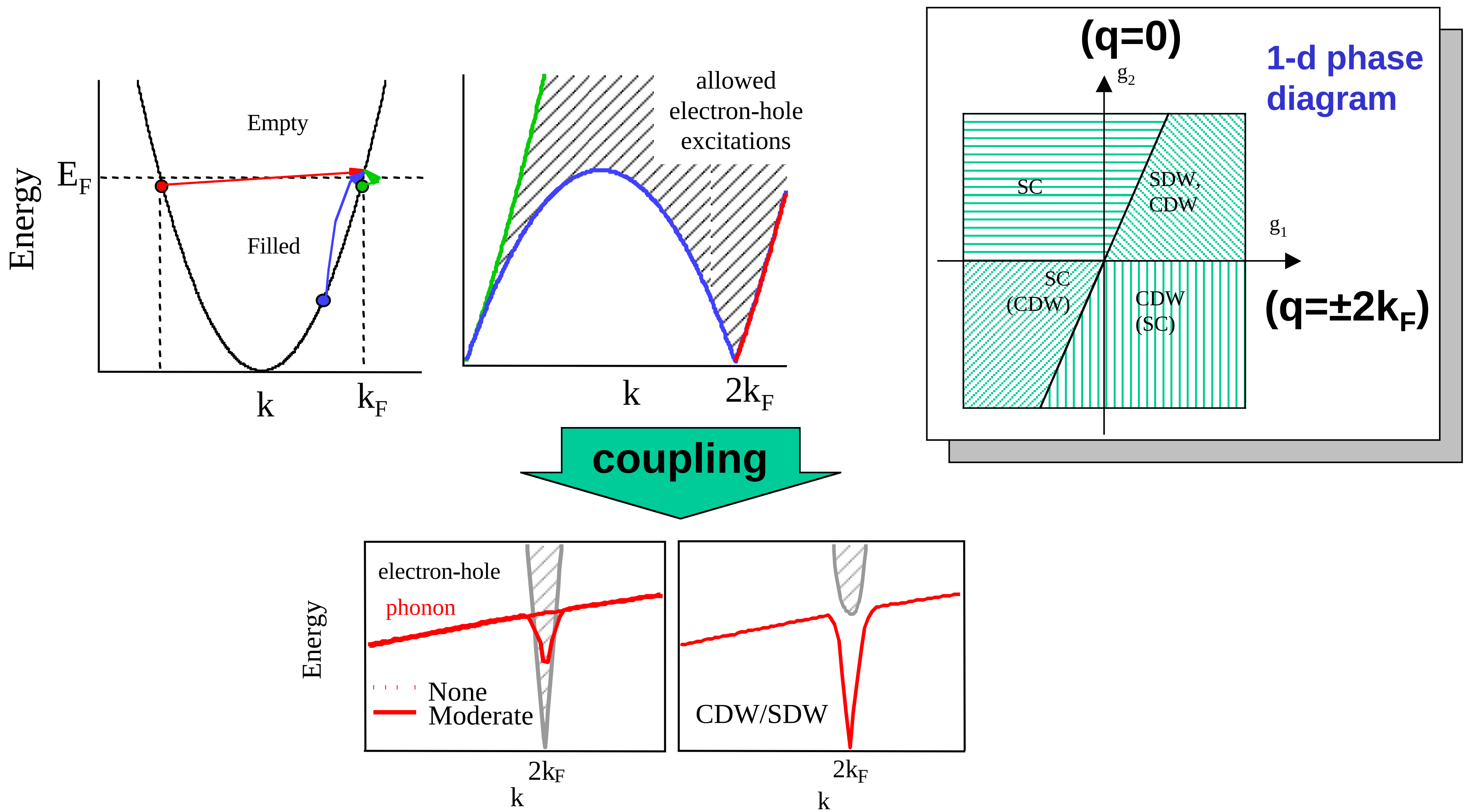
ALS

- **In the previous discussion, momentum transfer between electrons and phonons (or other excitations) was not important.**

- **In the <u>density wave</u> ground state, the exchange of momentum becomes crucial**

- **For example, the spin-density wave ground state of Cr metal.**

Density Wave Formation



G. Grüner, Density Waves in Solids, Addison-Wesley 1994

Electronic Response Function

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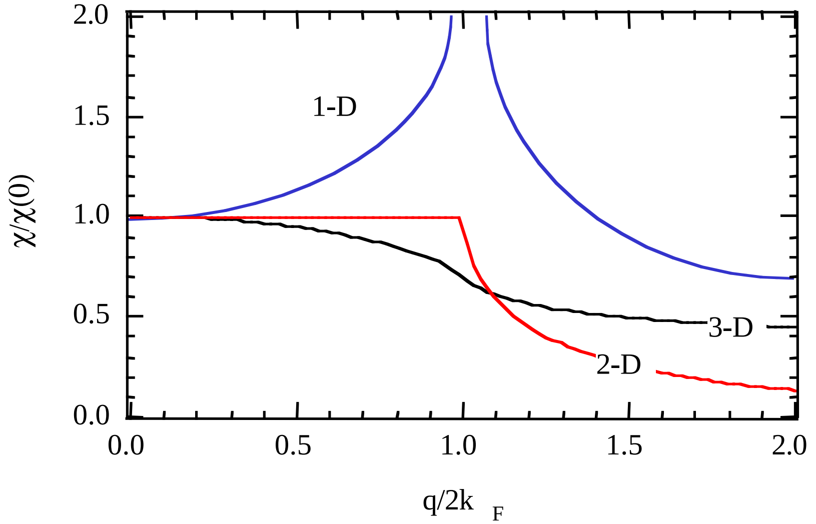
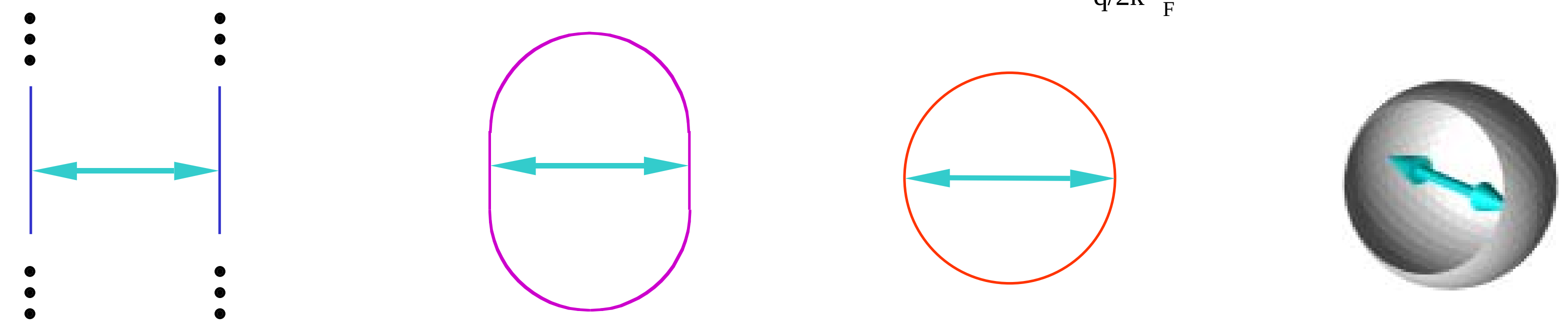
Response function

$$\chi(q) = \int \frac{dk^d}{(2\pi)^d} \frac{f_k - f_{k+q}}{E_k - E_{k+q}}$$





pure 1-dimensional
Fermi Contours
"Perfect nesting"

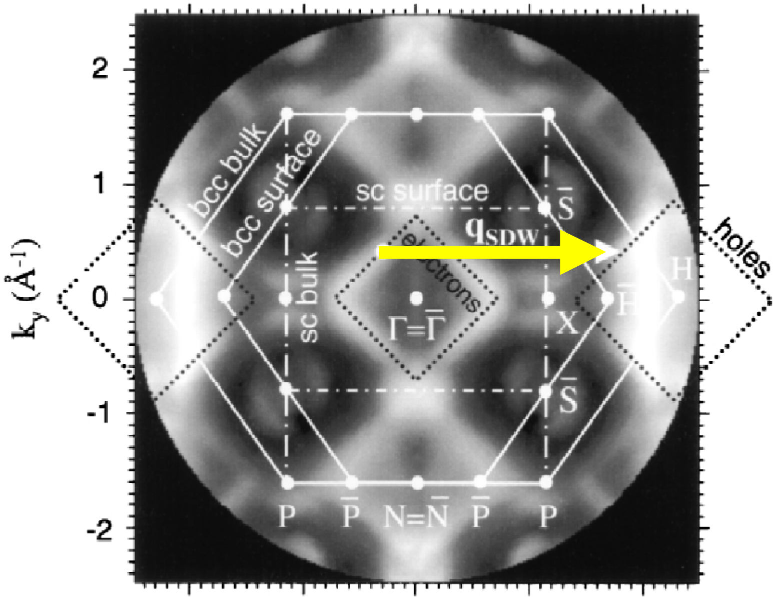
somewhere
in between
"Well-nested"

pure 2-dim
Fermi Contour
"Not nested"

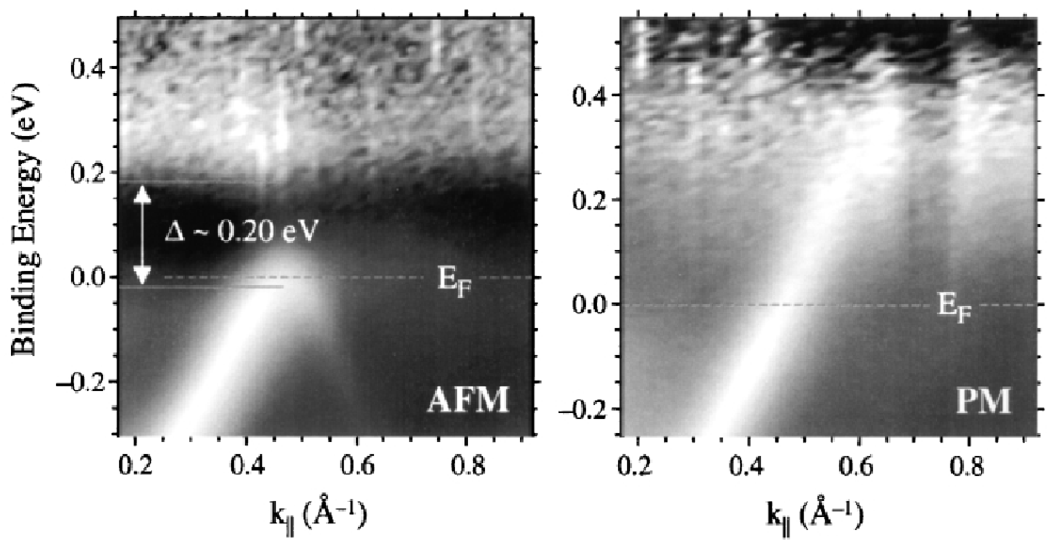
pure 3-dim
Fermi Contour
"Not nested"

Cr(110) Spin-Density Wave Gap Formation

ALS



Fermi surface gives us the Nesting condition

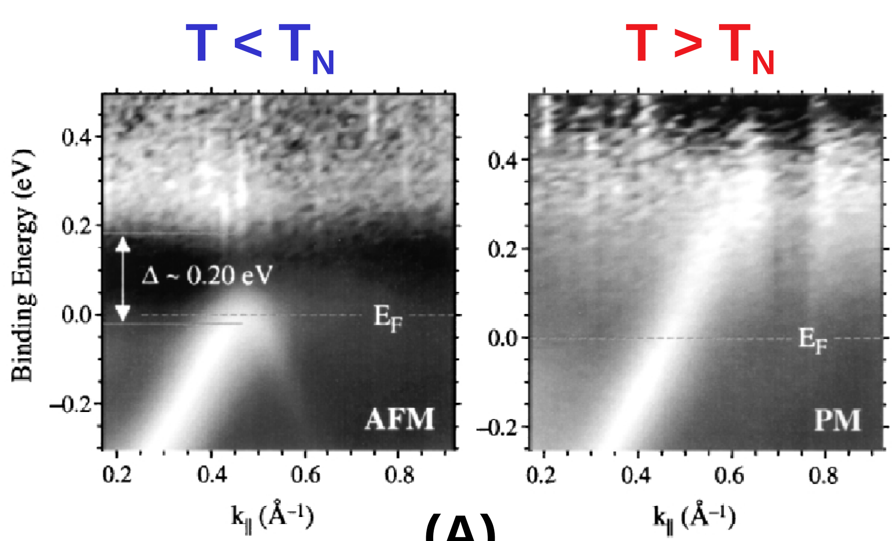


Band structure measurements show the energy gap formation…

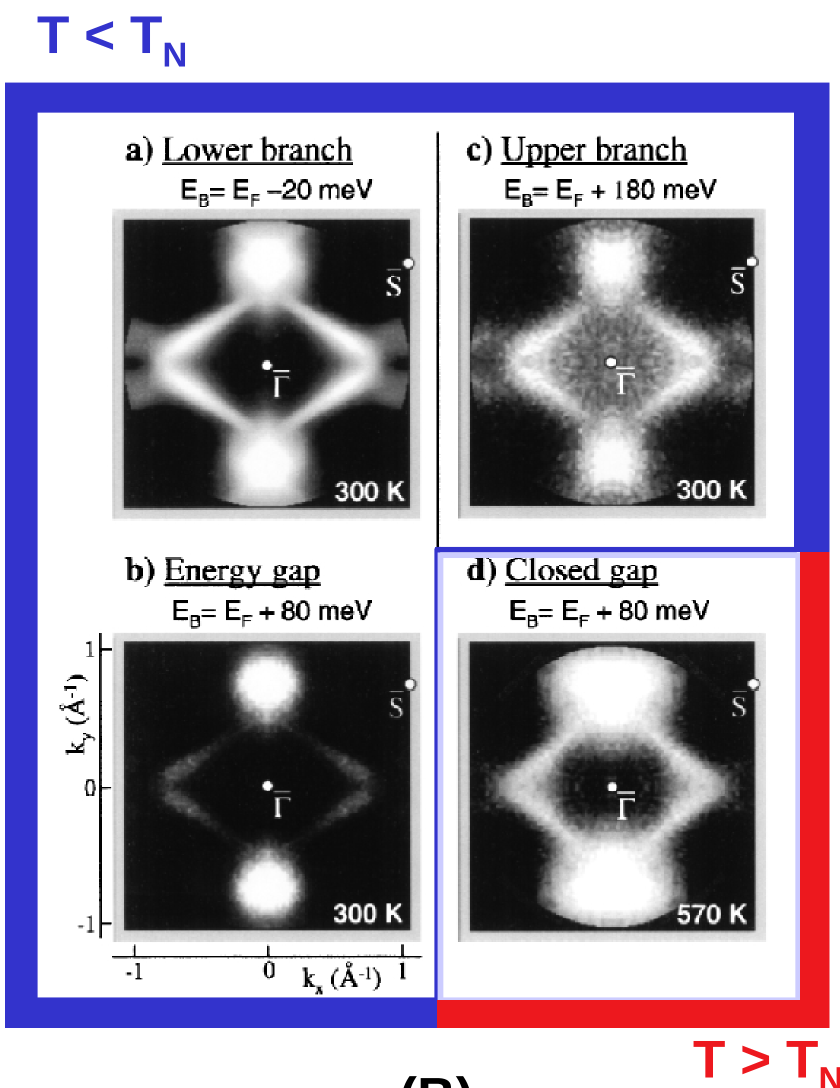
Schaefer, Rotenberg, Kevan, Blaha, Hufner PRL83(10)2069(1999).

ALS

And temperature-dependent measurements of the Fermi surface show the gap is isotropic



(A)



(B)

Other interesting systems

ALS

- **High-T_c superconductors**
  - **cuprates**
- **Collosal Magnetoresistance materials**
  - **Manganates**

- **These materials have exotic ground states whose nature is still under debate.**

- **Intense efforts continue to measure and understand the spectral functions of these materials.**

- **Angle-resolved photoemission "is, for this problem, the experiment that will play the role that tunneling played for BCS"-- Philip Anderson, Princeton Univ.**

Summary and outlook

- **A full description of the states in a solid is given by the energy-momentum spectral function *A(*k*,E).***
- **Angle-resolved photoemission delivers!**
- **With spin-resolved detectors (still a developing field) angle-resolved photoemission will become a complete probe.**