Solids

1. Binding types
2. Crystal lattices
3. Lattice vibrations
4. Electrons in crystal lattices

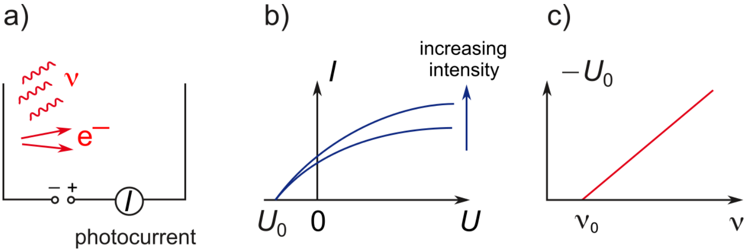
Photoemission Spectroscopy

Electrons in crystal lattices

- Drude model
- Sommerfeld model
- Bloch waves
- Energy bands and Fermi surfaces
- Electron dynamics and Electron hole bands
- Photoemission Spectroscopy
- Semiconductors
- Ferromagnetism
- Superconductivity

Photoemission Spectroscopy 1

The photoelectric effect at the beginning of the 20th century.



$$\boxed{E_{kin} = |eU_0|}$$

$$\boxed{E_{kin} = h\nu - W_A}$$

Photoemission Spectroscopy 1 Comment 1

The figures summarize the results of the photoelectric effect.

With the results of these measurements, A. Einstein showed in 1905 that the energy of electromagnetic waves is quantized.

When a photoelectrode is illuminated, electrons can be released, resulting in a photocurrent when a second electrode is nearby.

If the second electrode is positively charged, the photocurrent increases with increasing voltage and reaches a maximum value.

When a negative voltage is applied to the second electrode, there is a voltage at which the photocurrent can be reduced to zero.

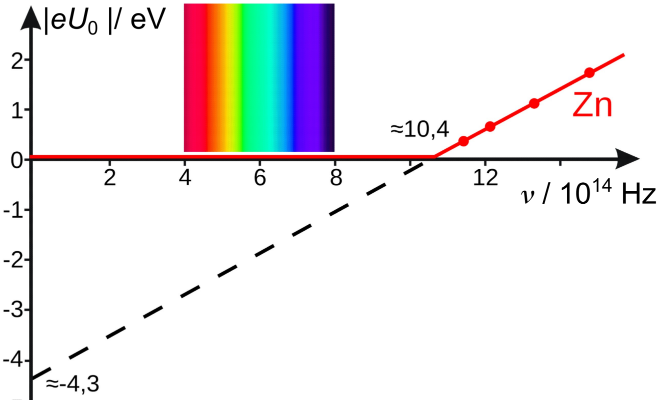
Photoemission Spectroscopy 1 Comment 2

If quantitative experiments are to be performed, it is important that monochromatic light is used.

If the voltage U_0, at which the photocurrent falls to zero, is plotted against the frequency of the light used, a straight line results whose slope is Planck’s constant h.

Photoemission Spectroscopy 2

$$\boxed{E_{kin} = h\nu - W_A}$$



Photoemission Spectroscopy 2 Comment

The interpretation of the experiment is easy.

The electrons are bound to the solid with at least the energy W_A.

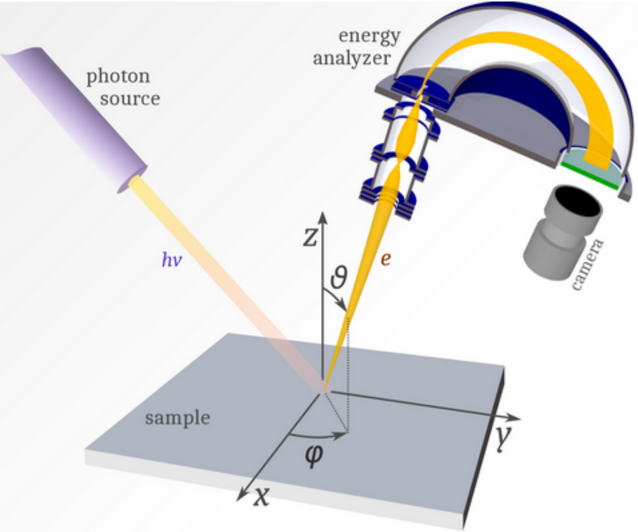
If the energy of the photons exceeds this energy, electrons can be knocked out of the solid.

The kinetic energy is determined by the energy of the photons reduced by the binding energy of the electrons.

The work function $W_A = U_0/e$ of the electrons results from the intersection of the straight line with the voltage axis.

W_A is in the range of a few eV.

Photoemission Spectroscopy 3



Photoemission Spectroscopy 3 Comment

If you want to analyze the photoelectrons more precisely, i.e. carry out photoelectron spectroscopy, you need an ultra-high vacuum system, a strong photon source whose frequency can be tuned best, and an electron detector that can determine the direction and the energy of the photoelectrons.

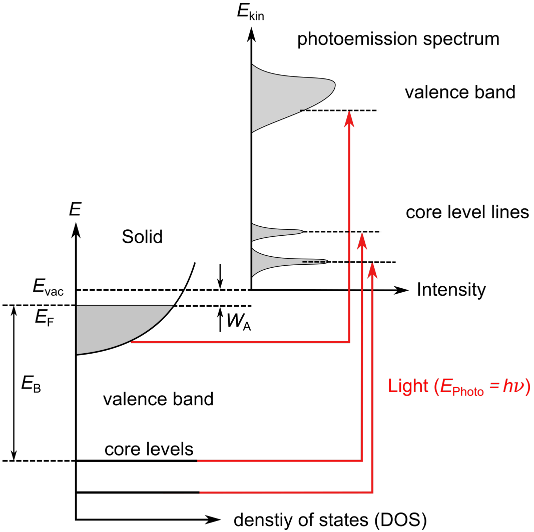
The figure outlines the experimental setup.

The photoelectrons are guided to the entrance slit of the detector by electron optics.

The detector consists of two metallic spherical shells to which a voltage is applied.

The electric field between the spherical shells deflects the electrons depending on the speed and directs them to a position-sensitive detector, which can thus determine the number of incident electrons depending on the electron speed.

Photoemission Spectroscopy 4



- The kinetic energy of the photoelectrons is determined by

$$\boxed{E_{kin} = h\nu - W_A - E_B}$$

- The kinetic energy of the measured photoelectrons is set by the experiment.

Photoemission Spectroscopy 4 Comment 1

The figure outlines how a photoemission spectrum comes about.

The left side of the figure shows the energy level diagram of a solid.

The energy is plotted against the density of states.

The conduction electrons are shown at the highest energy.

The work function W_A separates the Fermi energy E_F from the energy of the vacuum E_{vac}.

The binding energy of the electrons is measured against the Fermi energy.

Directly at the Fermi energy, the binding energy E_B is zero.

Photoemission Spectroscopy 4 Comment 2

This results in the formula framed in red for the kinetic energy of the photoelectrons.

The energy of the photon is reduced by the work function W_A and the binding energy of the electrons E_B.

If the energy of the photons is high enough, the bound core electrons of the atoms can also be excited.

The spectrum of the photons used usually ranges from the UV to the soft X-ray range.

The right side of the figure shows the photoemission spectrum, which results from the sketched energy structure of the solid.

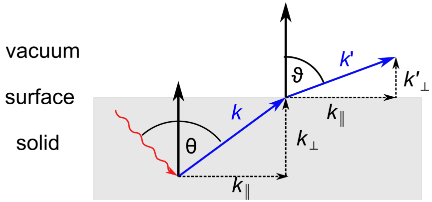
Photoemission Spectroscopy 4 Comment 3

As shown on the previous slide, the photoelectrons can be measured at different angles with respect to the surface.

The kinetic energy of the measured photoelectrons is set by the energy analyzer.

In an experiment, the energy of the photoelectrons can either be scanned for a fixed observation angle, or else the observation angle for a fixed energy of the photoelectrons.

Photoemission Spectroscopy 5



Only momentum parallel to the surface is conserved

$$\boxed{k_{\parallel} = \frac{1}{\hbar}\sqrt{2m_e E_{kin}}\,\sin\vartheta}$$

but $k'_{\perp} \neq k_{\perp}$ and not determined by a simple formula.

- The wavenumber of the photons is small compared to the 1st Brillouin zone.
  The momentum of the photons can always be neglected.
- The conduction electrons are knocked out of their quantum states without changing the momentum of the electrons.
- As in optics, the electron waves are refracted on the surface.

Photoemission Spectroscopy 5 Comment 1

As already noted for Brillouin and Raman scattering, the wavenumber of light in UV and soft X-rays is small compared to the dimensions of 1st Brillouin zone.

If a conduction electron is excited, the momentum transfer by the photon can be neglected.

The conduction electron is knocked out of its quantum state by the photon without changing the momentum of the electron.

If the wave of the excited electron hits the surface, refraction occurs, similar to optics, and there is also a critical angle of total reflection, similar to optics.

As in optics, the component of the wave vector does not change parallel to the surface during the transition from solid to vacuum (cf. 2nd lecture).

Photoemission Spectroscopy 5 Comment 2

In Maxwell's equations of optics, this condition was already sufficient to define the law of refraction at least for an isotropic refractive index.

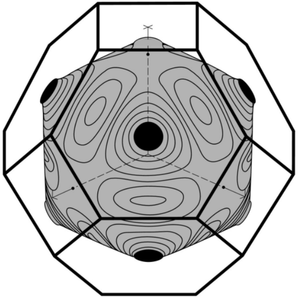
However, the transition from an electron wave in a solid to a plane wave in a vacuum is not as simple or well defined.

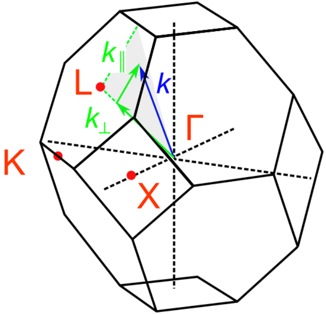
There is therefore no simple formula for the relationship between $k_\perp$ and $k'_\perp$.

However, the formula outlined in red shows that the component of the wave vector parallel to the surface can easily be calculated from the kinetic energy of the photoelectron.

Photoemission Spectroscopy 6

Angular resolved photoemission spectroscopy (ARPES) results from Cu(111) surface





Photoemission Spectroscopy 6 Comment 1

As an example, consider the photoemission spectrum for the (111) face of a single copper crystal.

A diagonal of the cubic unit cell is thus perpendicular to the surface.

The figure on the left shows the 1st Brillouin zone of copper, with the Fermi surface showing the characteristic bulges near the L point.

In a ring around the L point, the k states reach Fermi energy.

The k-states in the black circular area around the L-point do not have the Fermi energy, but with the notation of the figure on page 4 they have a certain binding energy E_B.

Photoemission Spectroscopy 6 Comment 2

The figure on the right shows the 1st Brillouin zone with the wave vector of an electron that will be excited by a photon.

The wave vector can be broken down into a component parallel $\vec{k}_{||}$ and a component perpendicular to the surface $\vec{k}_{\perp}$.

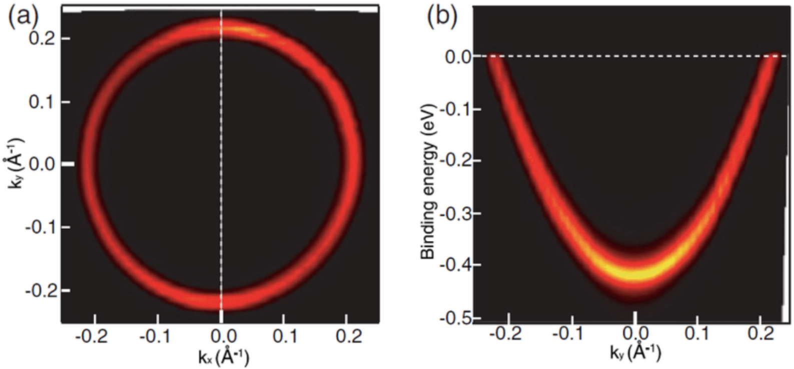
When the (111) plane is used, the component $\vec{k}_{\perp}$ is parallel to a line connecting the Γ point with the L point of the hexagonal face of the 1st Brillouin zone.

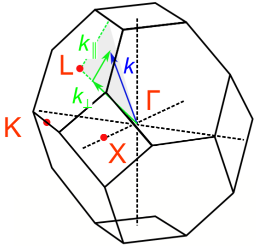
The kinetic energy and the angle ϑ in vacuum can be determined experimentally.

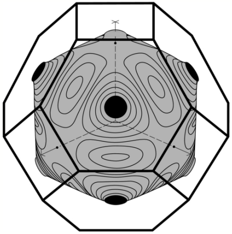
By adjusting the kinetic energy and the angle ϑ in an appropriate way, $\vec{k}_{||}$ can be set and the energy be scanned.

Photoemission Spectroscopy 7

ARPES results from Cu(111) surface







$$E_{kin} = h\nu - W_A - E_B$$

Photoemission Spectroscopy 7 Comment 1

The figures show the photoemission spectra near the L point.

Intensity is encoded by color. The intensity is high (red) when E_{kin} and $\vec{k}_{||}$ correspond to occupied k-states.

As sketched on page 4, the intensity is proportional to the density of states under the selected experimental conditions.

In the figure a) on the left, the observation angle (i.e. $\vec{k}_{||}$) is varied a fixed kinetic energy $E_{\mathrm{kin}} = h\nu - W_{\mathrm{A}} - E_{\mathrm{B}}$ of the photoelectrons.

The occupied k states are arranged in a ring around the (1,1,1)-direction.

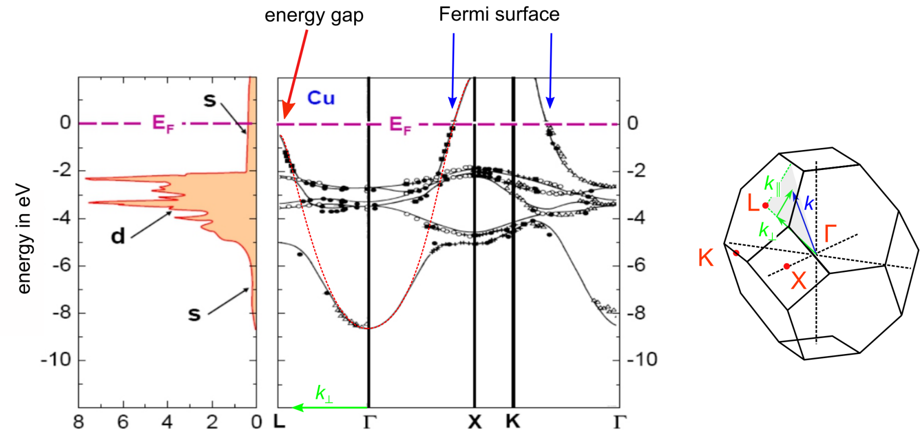
In figure b) the kinetic energy of the photoelectrons is scanned at different observation angles in such a way that $\vec{k}_{||}$ points in a certain direction called y.

Photoemission Spectroscopy 7 Comment 2

The energy of the occupied *k* states forms a parabola whose minimum lies on the connecting line between the Γ point and the L point.

Photoemission Spectroscopy 8

The figure shows the band structure of copper again for comparison.



Photoemission Spectroscopy 8 Comment

The left side of the band structure shows the energy change along a line connecting the Γ point and the L point.

The green vector shows the component $k_\perp$ of the $\vec{k}$ vector when the Cu(111) surface is used.

Only the parallel component $k_{||}$ is fixed by the experimental conditions.

The perpendicular component $k_\perp$ has to be derived indirectly, since the simple law of refraction in optics cannot be applied to electron waves.

The comparison with the band structure shows that the minimum of the parabola in the APRES measurement corresponds to the maximum of the energy band between Γ and L.

Revision

Summary in Questions 1

1. What determines the kinetic energy of a photoelectron?
2. Consider the experiment shown on slide Photoemission Spectroscopy 7. Suppose that photons with a wavelength of 100 nm are used in the experiment. The work function of copper is 4.3 eV. The kinetic energy measured by the detector is set to a fixed value. Which energy of the detector has to be selected if the Fermi energy is to be determined?
3. Which energy has to be chosen if the top of the 4s band is to be measured at the L point?