Solids

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

Electrons in crystal lattices

- Electrical conductivity and Ohm’s law
- Drude model
- Sommerfeld model
- Bloch waves
- Energy bands and Fermi surfaces
- Photoemission Spectroscopy
- Semiclassical Electron Dynamics
- Semiconductors
- Ferromagnetism
- Superconductivity

Quasi-free electrons in the sc-lattice

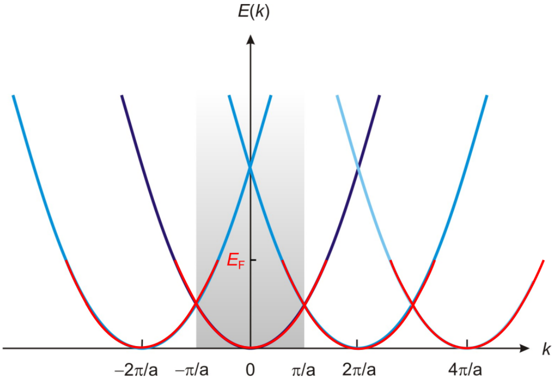
Energy bands and Fermi surfaces 5

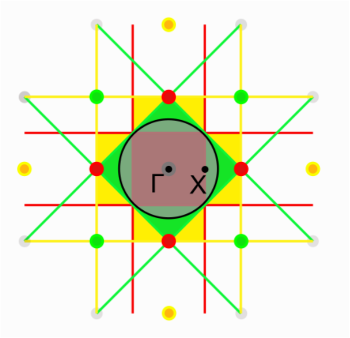
- Quasi-free electrons in the sc-lattice
- Sodium
- Copper
- Zinc
- Quasi-free electrons in the sc-lattice

Quasi-free electrons in the sc-lattice 1

three electrons per primitive unit cell of a simple cubic lattice

$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} = \frac{(3\pi^2 \cdot 3)^{\frac{1}{3}}}{a} = \frac{4.46}{a} > \frac{\pi}{a}$$





Quasi-free electrons in the sc-lattice 1 Comment

It may be helpful to consider the case of three free conduction electrons in a simple cubic lattice.

The Fermi wave number is easy to calculate.

The figure on the left shows the energy bands in the periodic zone scheme in the Γ-X direction. The occupied *k* states are marked in red.

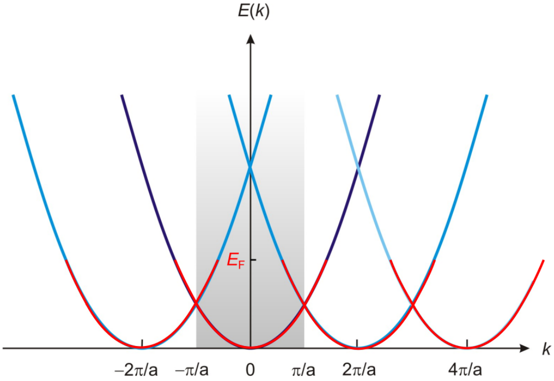
The figure on the right shows the Γ-X plane of the reciprocal lattice with the 1st Brillouin zone, 2nd Brillouin zone and 3rd Brillouin zone for the simple cubic lattice.

The circle indicates the Fermi sphere.

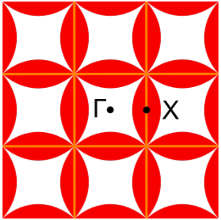
The *k* states of the 1st Brillouin zone are completely occupied and the *k* states of the 2nd Brillouin zone are partially occupied by electrons.

Therefore, the first energy band cannot contribute to conductivity.

Quasi-free electrons in the sc-lattice 2



periodic zone scheme 2nd band



Quasi-free electrons in the sc-lattice 2 Comment

The figure on the left again shows the band structure in the Γ-X direction.

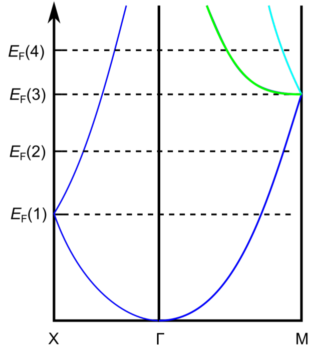
The figure on the right shows the occupied k states of the 2^{nd} energy band marked in red in the periodic zone scheme.

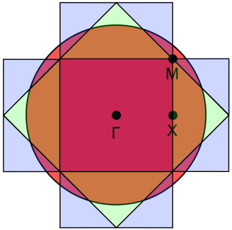
The red areas enclose white areas of unoccupied k states, i.e. the energy of the k states is greater than the Fermi energy $E(\vec{k}) > E_F$.

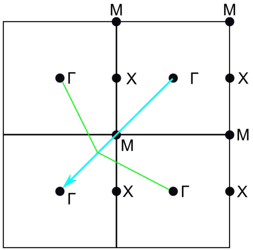
Quasi-free electrons in the sc-lattice 3

four electrons per
primitive sc cell

$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} = \frac{(3\pi^2 \cdot 4)^{\frac{1}{3}}}{a} = \frac{4.91}{a}$$







Quasi-free electrons in the sc-lattice 3 Comment 1

The middle figure shows the energy bands of quasi-free electrons in the simple cubic lattice along the ΓX and ΓM directions.

The dashed lines show the Fermi energies for 1, 2, 3, and 4 electrons per primitive cell of the sc lattice.

The green and light blue colors indicate the paraboloids contributing the the energy band in ΓM direction.

The green and light blue colors indicate the paraboloids contributing to the energy bands in ΓM direction.

The green line corresponds to two degenerate energies as indicated in the sketch below right.

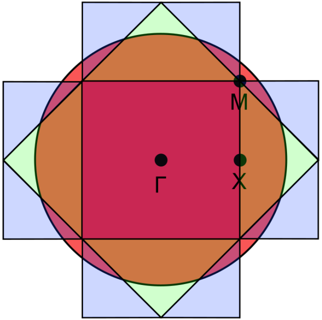
Quasi-free electrons in the sc-lattice 3 Comment 2

The sketch above right shows the Fermi sphere for four electrons.

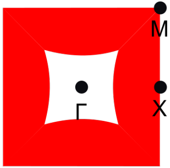
The 1st Brillouin zone is completely occupied, the 2nd Brillouin zone, 3rd Brillouin zone and 4th Brillouin zone are partly occupied.

Quasi-free electrons in the sc-lattice 4

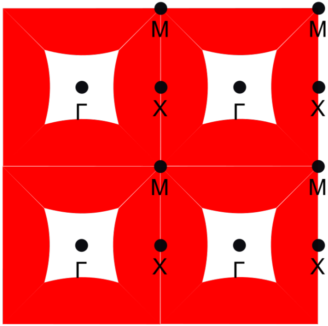
second energy band



reduzed scheme



periodic zone scheme



Quasi-free electrons in the sc-lattice 4 Comment

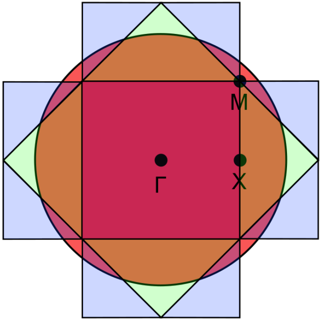
The middle figure shows the second band in the reduced zone scheme.

The figure on the right shows the second band in the periodic zone scheme.

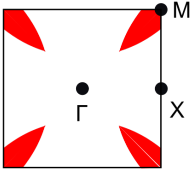
The Fermi surface completely encloses unoccupied k-states, i.e. in the white area $E(\vec{k}) < E_F$ applies.

Quasi-free electrons in the sc-lattice 5

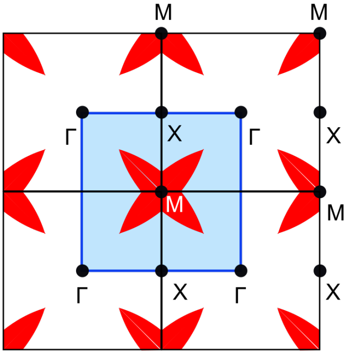
third energy band



reduced scheme



periodic zone scheme



Quasi-free electrons in the sc-lattice 5 Comment

The middle figure shows the third band in the reduced zone scheme.

The figure on the right shows the third band in the periodic zone scheme.

The center of the primitive cell is shifted to the M-point so that the Fermi surface is completely enclosed by the primitive cell.

The Fermi surface completely encloses occupied *k*-states, i.e. in the red areas $E(\vec{k}) < E_F$ applies.

The occupied *k*-states of the 4th Brillouin zone are also centered at the M-point.

The Fermi surface completely encloses occupied *k*-states.

Photoemission Spectroscopy

Electrons in crystal lattices

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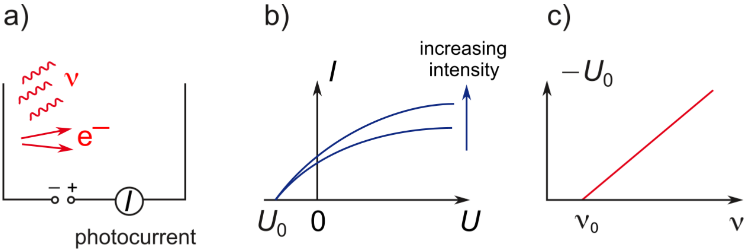
Photoemission Spectroscopy 1

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.

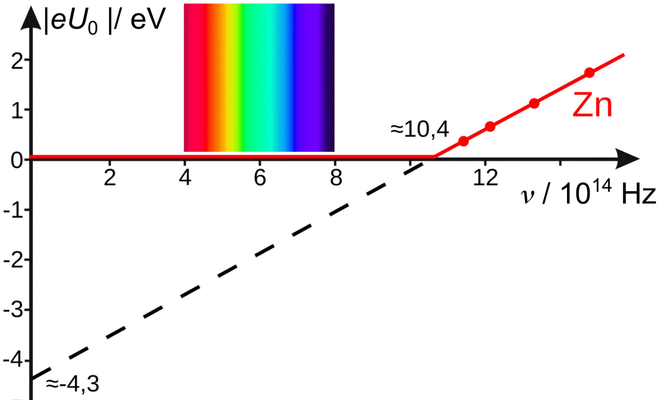
Photoemission Spectroscopy 1 Comment 2

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.

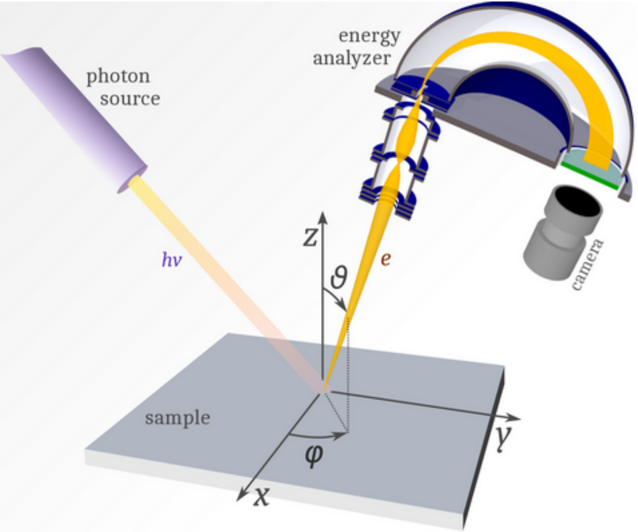
If the energy of the photons exceeds this energy, electrons can be knocked out of the solid.

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

Photoelectron spectroscopy requires an ultra-high vacuum system, a powerful photon source whose frequency can be best tuned, and an electron detector that can determine the direction and energy of the photoelectrons.

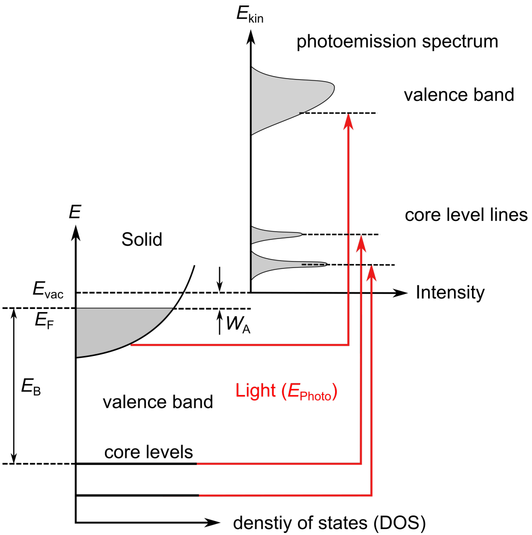
The figure outlines the experimental setup.

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 and kinetic energy of the incident electrons.

Photoemission Spectroscopy 4



- The kinetic energy of the photoelectrons is determined by

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

- 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 energy of the photons usually ranges from the UV to the soft X-ray range, i.e. $\approx$3 eV to 10 keV.

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

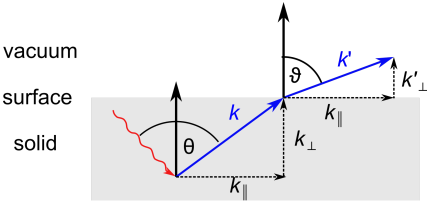
Photoemission Spectroscopy 4 Comment 3

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 1^{st} Brillouin zone.

If electrons are excited, the momentum transfer by the photons can be neglected.

The electrons are knocked out of their quantum states without changing the momentum of the electrons.

If the wave of the excited electrons 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.

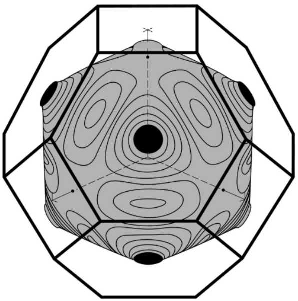
However, the transition from an electron wave in a solid to a plane wave in a vacuum is not as simple or well defined.

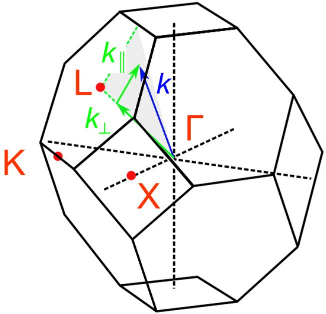
There is no simple formula for the relationship between $k_\perp$ and $k'_\perp$.

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 photoelectrons.

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 on the hexagonal face of the 1st Brillouin zone.

The binding energy E_B of the electrons states within the black area is greater than zero according to the definition in the figure on page 4.

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 $\vec{k}_{\perp}$.

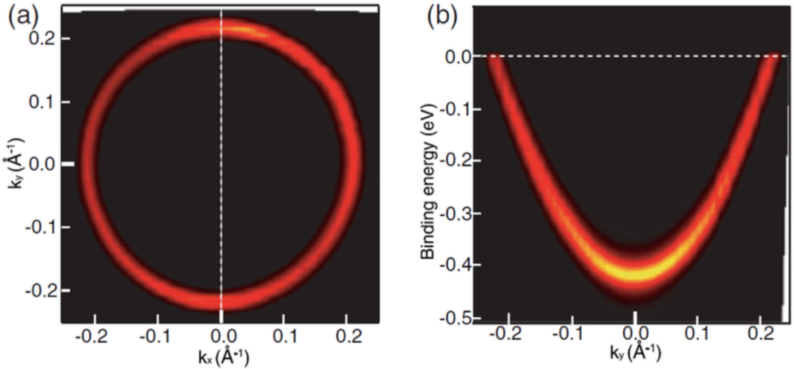
When the (111) plane is used, the component $\vec{k}_{\perp}$ is parallel to a line connecting the Γ point with the L point of the hexagonal face of the 1st Brillouin zone.

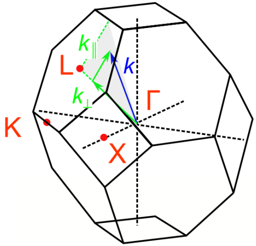
The kinetic energy of the photoelectrons and the observation angle ϑ are determined by the setting of the spectrometer.

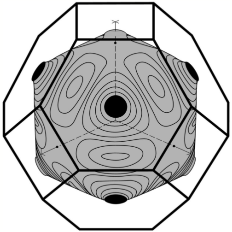
By adjusting the kinetic energy and the angle ϑ in an appropriate way, $\vec{k}_{||}$ can be set and the energy be scanned.

Photoemission Spectroscopy 7

ARPES results from Cu(111) surface







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 for 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.

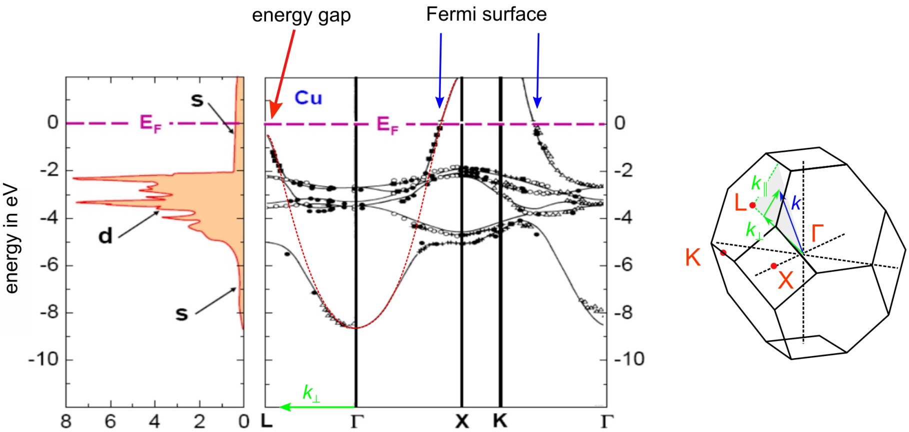
In figure b) the kinetic energy of the photoelectrons is scanned at different observation angles in such a way that $\vec{k}_{||}$ points in a certain direction called y.

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.

Electron dynamics

Electrons in crystal lattices

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Semiclassical Electron dynamics 1

How react electrons on quasi static applied electric and magnetic fields?

- The influence of the fields on the energy of the electrons is small and often much smaller than the thermal energy $k_B T$

Only electrons on the Fermi surface can respond to an applied $\vec{E}$ and $\vec{B}$ field

- The Schrödinger equation

$$\boxed{E\varphi_{\vec{k}}(\vec{r}) = \left(-\frac{\hbar^2\nabla^2}{2m} + E_{pot}(\vec{r})\right)\varphi_{\vec{k}}(\vec{r})}$$

is not suitable since $\underline{E_{pot}(\vec{r}) \neq E_{pot}(\vec{r}+\vec{R})}$

Semiclassical Electron dynamics 1 Comment 1

The discussion of electrical conductivity in the context of the Sommerfeld model (cf. Lecture 24) showed that the influence of an external electric and/or magnetic field on the energy of the conduction electrons is usually much smaller than the thermal energy.

The associated energies due to the applied electric and magnetic fields are small.

Therefore, only electrons in the thermally softened region of the Fermi surface contribute to electrical transport phenomena.

However, it turns out that the Schrödinger equation outlined in red cannot be solved even with standard perturbation theory.

Although the electric and magnetic fields are the same throughout the crystal, the associated potential energy (e.g. $E_pot(\vec{r}) = e\vec{r}\vec{E}$) depends on the location $\vec{r}$.

Semiclassical Electron dynamics 1 Comment 2

As a result, the potential energy in the crystal lattice is no longer periodic, and Bloch waves are no longer the solution to the Schrödinger equation.

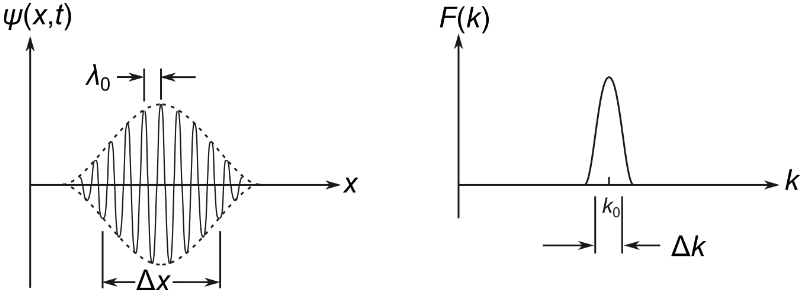
A purely theoretical solution to the problem was found in 1929 by Rudolf Peierls, who was then working in Arnold Sommerfeld’s group.

Peierls’ solution is very successful and is known as semiclassical electron dynamics.

The crucial idea of his approach is to group the Bloch waves into wave packets in order to be able to examine the influence of the external fields locally at the location of the wave packets.

Semiclassical Electron dynamics 2

wave packets



wave packets move with the group velocity

$$\boxed{v_x(\vec{k}_0) = \left.\frac{\partial \omega(\vec{k})}{\partial k_x}\right|_{\vec{k}=\vec{k}_0} = \frac{1}{\hbar}\left.\frac{\partial E(\vec{k})}{\partial k_x}\right|_{\vec{k}=\vec{k}_0}}$$

Semiclassical Electron dynamics 2 Comment

The figure illustrates the formation of a wave packet.

The Bloch waves around a wave vector $\vec{k}_0$ are superimposed with the amplitude $F(k)$.

This leads to a wave packet with the spatial extent Δx, and Δx and Δk are related by the uncertainty relation.

Since Δk is very much smaller than the dimensions of the 1^{st} Brillouin zone, the wave packets extend over many primitive unit cells of the crystal lattice.

Since the Bloch waves are taken from a specific energy band, the velocity of the wave packet is the group velocity, which is related to the energy dispersion $E(\vec{k}) = \hbar\omega(\vec{k})$ of the selected band.

The group velocity results from the derivation of the frequency with respect to the components of the wave vector.

Semiclassical Electron dynamics 3

equation of motion of a wave packet

$$\boxed{\hbar\dot{\vec{k}} = q\vec{E} + q\vec{v} \times \vec{B}} \quad \text{with} \quad q = -e$$

acceleration of a wave packet

$$a = \frac{dv}{dt} = \underline{\frac{d}{dt}\left(\frac{1}{\hbar}\frac{\partial E(k)}{\partial k}\right)} = \frac{1}{\hbar^2}\left(\frac{\partial^2 E(k)}{\partial k^2}\right)\hbar\dot{k}$$

comparison with Newton's equation of motion

$$a = m^{-1}F$$

effective mass tensor

$$\boxed{m^{-1} = \frac{1}{\hbar^2}\frac{\partial^2 E(k)}{\partial k^2}}$$

Semiclassical Electron dynamics 3 Comment 1

The remarkable result of Peierl's theory is that the equation of motion of a wave packet in an electromagnetic field is formally identical to Newton's equation of motion.

The theory of Peierls is therefore known as semiclassical electron dynamics.

The first equation, outlined in red, provides this amazingly simple result of a fairly sophisticated calculation.

The wave vector $\vec{k}$ refers to the center of gravity of the wave packet, which was named $\vec{k}_0$ in the first slide.

The index 0 is omitted below.

Semiclassical Electron dynamics 3 Comment 2

The time derivative of the crystal momentum $\hbar\vec{k}$ is equal to the sum of the electric force $q\vec{E}$ and the Lorentz force $q\vec{v} \times \vec{B}$.

In Newtonian mechanics, the time derivative of the momentum corresponds to the force $\vec{F}$.

If you calculate the acceleration of a wave packet, i.e. the derivation of the speed over time, it turns out that the acceleration is determined by an effective mass.

The reciprocal of the effective mass is proportional to the second derivative of the band energy with respect to the components of the wave vector.

Semiclassical Electron dynamics 3 Comment 3

The inverse effective mass is a tensor.

To simplify the notation, I use the scalar notation and omit the subscripts of the tensor.

The equation below, outlined in red, gives the formula for the reciprocal of the effective mass.

Semiclassical Electron dynamics 4

Fermi liquid theory (Lew Landau 1956):

Due to the Coulomb interaction, the electrons are never independent of each other and form a so-called Fermi liquid

- The excitations of a Fermi liquid are so-called quasiparticles.
- There is a one to one correspondence between the *k* states of the independent electron gas and the quasiparticles.
- The quasiparticles move with group velocity and obey the semiclassical electron dynamics.
- The interaction between the quasiparticles approaches zero when their energy approaches zero.

Semiclassical Electron dynamics 4 Comment 1

Despite the success of semiclassical electron dynamics, it is not clear how the wave packets of Peierls theory arise in nature.

It is also not clear why the Coulomb repulsion between electrons is not effective at all.

The answer to this questions was given by Lew Landau who published in 1956 his Fermi liquid theory for ^{3}Helium.

^{3}Helium is a fermion (spin 1/2) and liquid ^{3}Helium ($T_c = 3.19$ K) is a Fermi liquid.

Soon it became clear that his theory can also be applied to conduction electrons in a crystal lattice.

It is crucial for the Fermi liquid theory that the excitation energy is small.

Semiclassical Electron dynamics 4 Comment 2

Due to the interaction between the electrons they are never independent of each other.

Any excitation of an electron affects other electrons, leading to the formation of quasiparticles.

Once the quasiparticles are formed, the Coulomb repulsion between the quasiparticles becomes nearly ineffective.

Landau showed that when quasiparticles scatter due to the Coulomb interaction, the number of final states approaches zero as the energy of the quasiparticles approaches zero.

This effect effectively suppresses the scattering of the quasiparticles due to the Coulomb interaction.

Semiclassical Electron dynamics 4

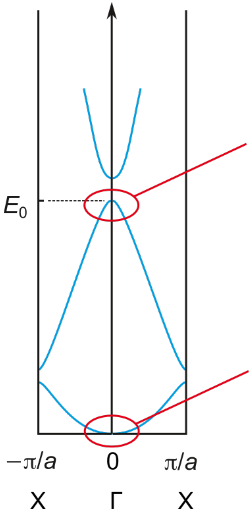
Comment 3

Landau also showed that there is a one-to-one correspondence between the independent electron states of the ground state and the quasiparticles.

The quasiparticles obey semiclassical electron dynamics.

Beyond these fundamental properties of quasiparticles, there are very subtle effects that allow the experimental test of the Fermi liquid theory.

Semiclassical Electron dynamics 5



$E(k) = E_0 + Bk^2$ and $B<0$

$1/m = 2B/\hbar^2 < 0$

$E(k) = E_0 + Ak^2$ and $A>0$

$1/m = 2A/\hbar^2 > 0$

Semiclassical Electron dynamics 5 Comment 1

The figure shows the reduced band scheme of nearly free electrond in a simple cubic lattice.

At the Γ point of the lowest band, the second derivative of the energy is positive and the effective mass is also positive.

At the peak of the second band, the second derivative of the energy is negative and the effective mass of the wave packets is negative.

Since the motion of a particle with negative mass is highly unusual in Newtonian mechanics, Newton's equation of motion is extended by -1:

$$a = \frac{1}{\hbar^2}\left(\frac{\partial^2 E(k)}{\partial k^2}\right)\hbar\dot{k} = \frac{1}{\hbar^2}\left(\frac{\partial^2 E(k)}{\partial k^2}\right)\cdot q(\vec{E}+\vec{v}\times\vec{B}) = -\frac{1}{\hbar^2}\left(\frac{\partial^2 E(k)}{\partial k^2}\right)\cdot(-q)(\vec{E}+\vec{v}\times\vec{B})$$

Semiclassical Electron dynamics 5 Comment 2

This changes the sign of the charge.

The wave packets at the top of the second band respond to the force of an applied electric or magnetic field with a negative mass, or alternatively with a positive charge.

Semiclassical Electron dynamics 6: “electron holes”

current density of a band

$$\vec{j} = -\frac{2e}{V} \sum_{\substack{\text{all occupied}\\ k\ \text{states}}} \vec{v}(\vec{k})$$

---

and

$$0 = -\frac{2e}{V} \sum_{\substack{\text{all } k \text{ states}\\ \text{of } 1^{\text{st}}\text{Brillouinzone}}} \vec{v}(\vec{k})$$

$$0 = -\frac{2e}{V} \sum_{\substack{\text{all occupied}\\ k\ \text{states}}} \vec{v}(\vec{k}) - \frac{2e}{V} \sum_{\substack{\text{all unoccupied}\\ k\ \text{states}}} \vec{v}(\vec{k}) = \vec{j} - \frac{2e}{V} \sum_{\substack{\text{all unoccupied}\\ k\ \text{states}}} \vec{v}(\vec{k})$$

and

$$\vec{j} = +\frac{2e}{V} \sum_{\substack{\text{all unoccupied}\\ k\ \text{states}}} \vec{v}(\vec{k})$$

Semiclassical Electron dynamics 6 Comment 1

The current density $j = \rho v$ is defined as the charge carrier density multiplied by the charge carrier velocity: i.e. $\vec{j} = \frac{-e}{V}\vec{v}$ for one electron with velocity $\vec{v}$ in volume V.

According to this definition, the current density of an energy band can be calculated by summing up all occupied k states.

Since each k state is occupied by two electrons, the charge of each k state is twice the negative elementary charge, i.e. $-2e$.

These considerations lead to the first underlined formula for the current density of an energy band.

Semiclassical Electron dynamics 6 Comment 2

The electric current density is zero when no electric field is applied to the solid because for every quasiparticle there is a quasiparticle propagating in exactly the opposite direction.

If a band is not completely occupied by electrons, this equilibrium can be disturbed by an external electric field and an electric current flows.

If a band is completely occupied by electrons, no current can flow even when an electric field is applied due to the periodicity of the band energy in the reciprocal lattice.

To illustrate this fact, consider the integral

$$\int_{x=0}^{2\pi} \sin(x)\mathrm{d}x = 0 = \int_{x=a}^{2\pi+a} \sin(x)\mathrm{d}x$$

Semiclassical Electron dynamics 6 Comment 3

When integrating over the period of a periodic function, the integration interval can be shifted without changing the value of the integral.

The equation in the second line formulates this fact for the *k* states.

This equation always holds, even when an external electric field is applied and the Fermi surface is shifted in *k*-space.

The electric field is so small that its influence on the energy bands is negligible. This is always the case as long as the electric field does not destroy the solid.

The sum over all *k* states can be divided into the occupied and the unoccupied *k* states.

The current density can thus be calculated by summing over all occupied *k* states, but also by summing over the unoccupied *k* states.

Semiclassical Electron dynamics 6 Comment 4

In this case the charge of the charge carriers is not twice the negative elementary charge but twice the positive elementary charge.

If the Fermi surface is simple (e.g. spherical or elliptical) and the second derivative of the energy $E(\vec{k})$ is negative due to the influence of the periodic potential, the electrons can be assigned a positive charge, and it is convenient to consider the unoccupied electron-hole states instead of the occupied k states to calculate the electric current.

Semiclassical electron dynamics 7

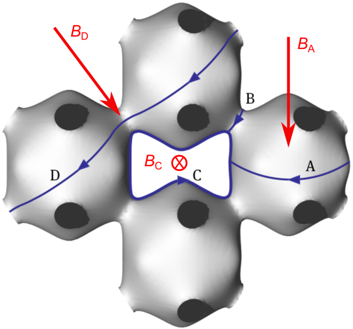
Motion in a homogeneous magnetic field

$$\boxed{\hbar\dot{\vec{k}} = \vec{F} = q\vec{v}\times\vec{B}} \quad \text{with} \quad \vec{v} = \frac{1}{\hbar}\frac{\partial E(\vec{k})}{\partial\vec{k}} \quad \text{and} \quad q = -e$$

- $E(\vec{k}) = \text{constant}$
- $\vec{k}_{||} = \text{constant}$

The orbits are determined by

$$\boxed{E(\vec{k},\vec{k}_{||} = \text{constant}) = \text{constant}}$$



→ there are closed and open orbits

Semiclassical electron dynamics 7 Comment 1

If there is a magnetic field but no electric field, the time dependence of the *k*-vector is determined by the Lorentz force.

$\dot{\vec{k}}$ is perpendicular to the energy gradient and perpendicular to the direction of the magnetic field.

The energy of the electron (quasiparticle) does not change on its orbit.

Likewise, the component of the *k*-vector parallel to the magnetic field $\vec{k}_{||}$ does not change.

The electron moves in a plane of constant energy characterized by the parallel component of the *k*-vector, i.e. in a plane perpendicular to the magnetic field that intersects the Fermi surface.

The energy of the quasiparticles is close to of the Fermi energy.

Semiclassical electron dynamics 7 Comment 2

The figure shows the Fermi surface of copper in the periodic zone scheme.

Depending on the direction of the applied magnetic field, the quasiparticles follow closed or open orbits.

Semiclassical electron dynamics 8

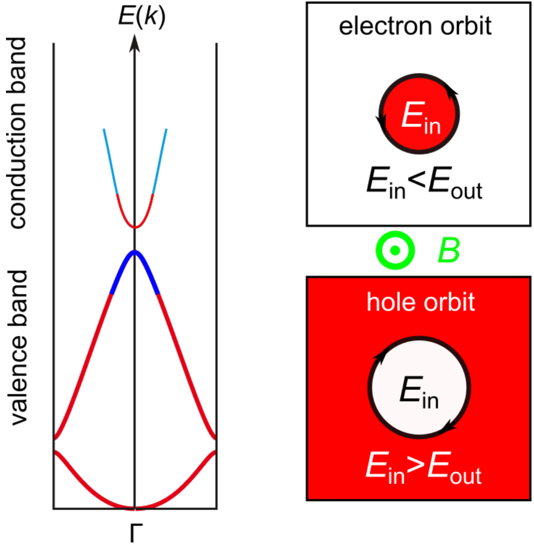
$$\boxed{\hbar\dot{\vec{k}} = \vec{F} = q\vec{v}\times\vec{B}}$$

with

$$\vec{v} = \frac{1}{\hbar}\frac{\partial E(\vec{k})}{\partial\vec{k}}$$

and

$$q = -e$$



Semiclassical electron dynamics 8 Comment 1

The left side shows the equation of motion of quasiparticles in a homogeneous magnetic field.

The figure shows a schematic band structure.

The occupied *k* states are shown by red lines and the unoccupied *k* states are shown by blue lines.

There are energy gaps between the bands.

The *k* states at the top of the second band have a negative effective mass and correspond to positively charged electron holes.

The conductivity of the band is described by the positively charged quasiparticles of the unoccupied *k* states.

Semiclassical electron dynamics 8 Comment 2

The third band is occupied by electrons that are excited across the band gap.

They occupy *k* states have a positive effective mass and the conductivity is based on negatively charged quasiparticles (they are commonly referred to as electrons).

In a semiconductor, the second band is called the valence band and the third band is called the conduction band.

The figure on the right shows a schematic 1st Brillouin zone in a plane perpendicular to the applied magnetic field.

The occupied *k* states are shown in red and the unoccupied *k* states are shown in white.

For the 3rd band, the quasiparticle orbit in the magnetic field surrounds the occupied *k*-states.

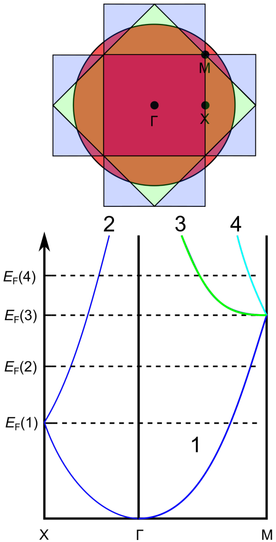
Semiclassical electron dynamics 8 Comment 3

For the 2nd band, the quasiparticle orbit encloses the unoccupied k states.

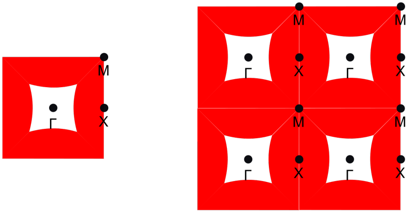
Depending on the direction of the energy gradient $\frac{\partial E(\vec{k})}{\partial \vec{k}}$ the orbits are traversed clockwise or counterclock wise.

If the orbit encloses the occupied k states, it is called an electron orbit, while if the orbit encloses the unoccupied k states, it is called a hole orbit.

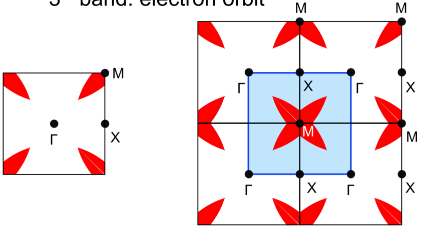
Semiclassical electron dynamics 9: 4 free electrons in sc lattice



2nd band: hole orbit



3rd band: electron orbit



Semiclassical electron dynamics 9 Comment

The figure shows again the situation of four quasi-free electrons in the primitive cell of an sc lattice.

First the Brillouin zones in the Γ-X-M plane, secondly the band structure in the Γ-X and the Γ-M directions and on the right the 2nd Brillouin zone and 3rd Brillouin zone for the 2nd and 3rd energy band.

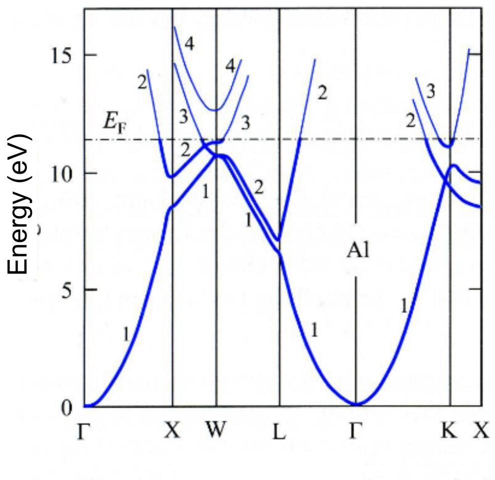
It is obvious that there are hole orbits on the Fermi surface of the 2nd Brillouin zone and electron orbits on the Fermi surface of the 3rd Brillouin zone.

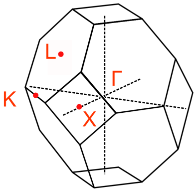
It is not shown, but is easy to see, that there are also electron orbits on the Fermi surface of the 4th Brillouin zone.

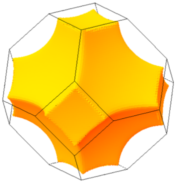
It is amazing that hole orbits exist even though only free electrons are taken into account.

Semiclassical electron dynamics 10

Hall effect of aluminum: electron configuration [Ne] $3s^2 3p^1$







Fermi surface
second band

Semiclassical electron dynamics 10 Comment 1

Aluminum has valence 3. The valence electrons occupy the 3s and 3p orbitals.

The three valence electrons can move almost freely.

Aluminum crystallizes in an fcc lattice.

The left figure shows the band structure of aluminum, which agrees very well with the band structure of free electrons.

The periodic potential energy induces only small energy gaps.

The 1st Brillouin zone of the fcc lattice is shown on the right. The letter W denotes the corners of the the square face.

Semiclassical electron dynamics 10 Comment 2

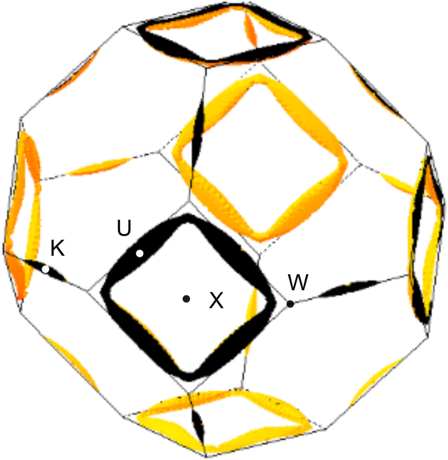
The first energy band with the lowest energy is completely occupied by electrons and cannot contribute to conductivity.

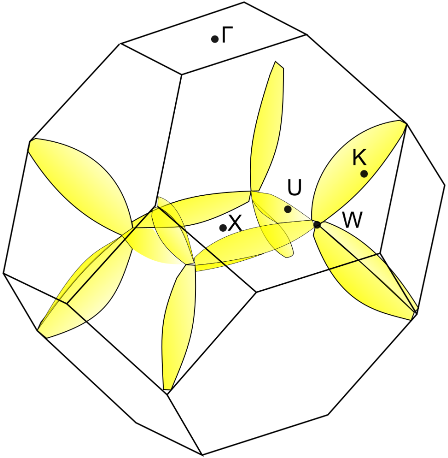
The conductivity is caused by the electrons in the 2nd and 3rd energy band.

The Fermi surface of the 2nd energy band is shown at the bottom right.

As for the electrons in a simple cubic lattice, the Fermi surface encloses unoccupied *k* states.

Semiclassical electron dynamics 11: Fermi surface of the 3rd band





Semiclassical electron dynamics 11 Comment

The figures show the Fermi surface of the 3rd energy band of aluminum.

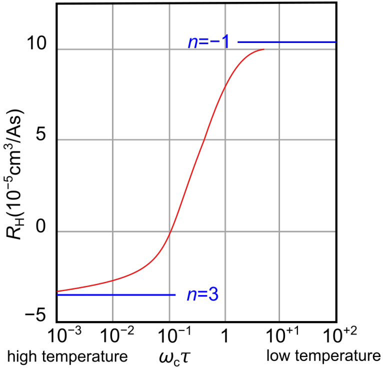
On the left side the result of a calculation and on the right side the quasi-free-electron approximation.

As for the electrons in a simple cubic lattice, the Fermi surface of the 3rd energy band encloses occupied *k*-states.

To show the closed Fermi surface, the center of the primitive cell is shifted from the Γ point to the X point.

Semiclassical electron dynamics 12

Hall coefficient of Aluminum



Drude model

$$\boxed{R_H = \frac{\rho_{xy}}{B} = \frac{1}{-enN_{Al}/V}}$$

- N_{Al}: number of aluminum atoms
- n number of charge carriers per aluminum atom
- $\omega_c\tau \to 0$: $n = 3$ electrons per Al atom
- $\omega_c\tau \to \infty$: $n = -1$, i.e. one electron hole per Al atom

Semiclassical electron dynamics 12 Comment 1

The figure shows the Hall coefficient as a function of $\omega_c\tau$ measured by R. Lück 1966.

The abscissa $\omega_c\tau$ needs a comment.

In the free electron theory the product of the magnetic field and the conductivity is $B\sigma = B\frac{q^2}{m}\frac{N}{V}\tau = q\frac{N}{V}\omega_c\tau$ with $\omega_c = Bq/m$.

In the experiment, the conductivity σ and the magnetic field B were measured.

$\omega_c\tau$ is obtained by dividing $B\sigma$ by the electron density of aluminum of three valence electrons per aluminum atom.

$\omega_c\tau$ measures the cycles that a quasiparticle (electron or hole) can go through in a magnetic field.

Semiclassical electron dynamics 12 Comment 2

For aluminum there are three valence electrons and the charge carrier density is $n \cdot N_{\mathrm{Al}}$. Here n denotes the number of valence electrons per aluminum atom and N_{Al} the number of aluminum atoms.

At high temperature and low magnetic field strength, i.e. $\omega_c\tau \to 0$, the Hall coefficient corresponds to three valence electrons.

At low temperature and high magnetic field strength, i.e. $\omega_c\tau \to \infty$, the Hall coefficient corresponds to one positive charge carrier per aluminum atom.

At high temperatures, the mean collision time is short and the mean free path of the electrons is very short.

So it doesn’t matter that the Fermi surface is intersected by Bragg planes.

The reflection at the Bragg planes does not affect the average electron dynamics and the quasi-free electron behavior is obtained.

Semiclassical electron dynamics 12 Comment 3

It is worth noting that the Hall coefficient crosses the zero line at $\omega_c\tau \approx 10^{-1}$.

In the free-electron model, this result would indicate that the carrier density diverges, i.e. $q\frac{N}{V} \to \infty$.

That is certainly not true. The dramatic variation of the Hall coefficient shows that the electron dynamics are strongly influenced by the Bragg planes when the quasiparticles can complete cycles in the magnetic field.

Semiclassical electron dynamics 13

transport theory (I.M. Lifshitz 1956)

$$B \to \infty \quad \underline{\sigma_{xy} = -e(n_e - n_h)\frac{N_{\mathrm{Al}}}{V}\frac{1}{B} = \rho_{xy}^{-1}}$$

$$\boxed{R_{\mathrm{H}} = \frac{1}{-e(n_e - n_h)N_{\mathrm{Al}}/V}}$$

- number of electrons in the 1st band: $n_1 = 2 \cdot N_{\mathrm{Al}}$
- number of electrons in the 2nd band: $n_2 = (2 - n_h) \cdot N_{\mathrm{Al}}$
- number of electrons in the 3rd band: $n_3 = n_e \cdot N_{\mathrm{Al}}$

$$n_1 + n_2 + n_3 = 3 \cdot N_{\mathrm{Al}} = (2 + 2 - n_h + n_e) \cdot N_{\mathrm{Al}} \quad \to \quad \underline{n_e - n_h = -1}$$

Semiclassical electron dynamics 13 Comment 1

Unfortunately, there is no heuristic way to see what happens as the mean collision times get longer and the magnetic fields get stronger.

In 1956, I. M. Lifshitz et al. obtained an important theoretical result for the case $\omega_c\tau \to \infty$.

Based on the semi-classical electron dynamics, I. M. Lifshitz et al. calculated the red underlined formula for the transverse conductivity σ_{xy} for $\omega_c\tau \to \infty$.

Here, $n_e \cdot N_{\mathrm{Al}}$ is the number of occupied k states enclosed by Fermi surfaces and $n_h \cdot N_{\mathrm{Al}}$ the number of unoccupied k states enclosed by Fermi surfaces.

The theory is only valid if there are only closed quasiparticle orbits.

Semiclassical electron dynamics 13 Comment 2

For a strong magnetic field, it also follows that the transverse conductivity is the reciprocal of the transverse resistivity, i.e. $\sigma_{xy} = \rho_{xy}^{-1}$.

With this theoretical result, the simple formula for the Hall coefficient, outlined in red, follows.

This formula appears to be a generalization of the formula in the quasi-free electron approximation.

But this is not true: there is no interpolation between the $\omega_c\tau \to 0$ case and the high field/low temperature $\omega_c\tau \to \infty$ case.

Between the two cases $R_H \to 0$ which is not possible either with the free-electron approximation or with the high-field/low-temperature result.

Semiclassical electron dynamics 13 Comment 3

This formula holds as long as the number of occupied k-states and unoccupied k states enclosed by Fermi surfaces are not equal.

The number $n_e - n_h$ is easy to calculate for aluminum.

The number of k states in 1st Brillouin zone is equal to the number of aluminum atoms N_{Al}.

The first band is completely occupied with 2 electrons per k states.

The second band is partially occupied and $n_h \cdot N_{\mathrm{Al}}$ k states are unoccupied.

The third band is occupied with $n_e \cdot N_{\mathrm{Al}}$ electrons.

Semiclassical electron dynamics 13 Comment 4

Since there are three valence electrons per aluminum atom, the number $n_e - n_h = -1$ agrees with the experimental result.

The Hall effect of aluminum confirms the validity of semiclassical electron dynamics.

The discussion also shows that understanding the Hall effect is usually quite difficult.

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?