Solids

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

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

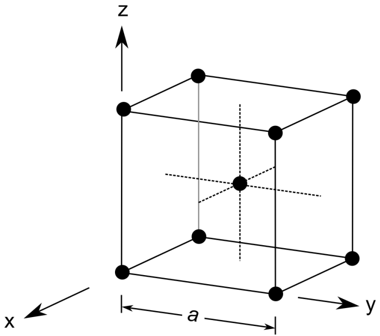
Sodium

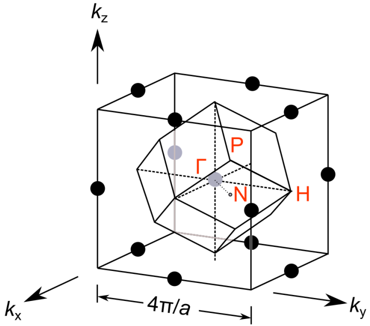
Energy bands and Fermi surfaces 2

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

Sodium 1

- Sodium atoms form a bcc lattice (and the reciprocal lattice is an fcc lattice)





- The shortest distance between the center and the boundaries of the 1st Brillouin zone is between the Γ and the N point with $\frac{1}{2}\sqrt{2}\frac{2\pi}{a} = \frac{4.44}{a}$

Sodium 1 Comment

Metallic sodium is considered as the first realistic example.

Sodium crystallizes in a bcc lattice.

The left figure shows the cubic unit cell.

The right figure shows the 1st Brillouin zone.

The reciprocal lattice of sodium is an fcc lattice.

The shortest distance between the Γ point and the surface of the 1st Brillouin zone is the distance Γ-N with about $4.44/a$.

Sodium 2

- The electron configuration of the free sodium atom is $[\mathrm{Ne}]3\mathrm{s}^1$
- The periodic variation of the potential energy of the 3s electron is small
- Since the cubic cell of the bcc lattice contains 2 sodium atoms, the electron density is $2/a^3$ and the Fermi wave number is

$$k_\mathrm{F}^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 \frac{2}{a^3} \rightarrow k_\mathrm{F} = \frac{3.9}{a} < \frac{4.44}{a}$$

- The Fermi sphere of the 3s electrons is well enclosed in the 1st Brillouin zone

Sodium 2

Comment

The 3s electron of the sodium atom is the conduction electron.

The variation in the potential energy of the 3s electron is small and the quasi-free electron approximation is not that bad.

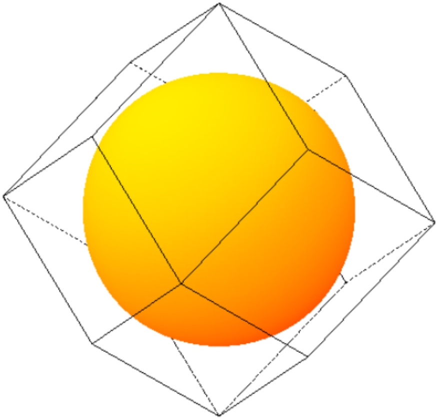
The Fermi wave number can be calculated with the electron density.

The Fermi sphere is enclosed by the 1st Brillouin zone.

The following figure shows the Fermi sphere within the 1st Brillouin zone of sodium.

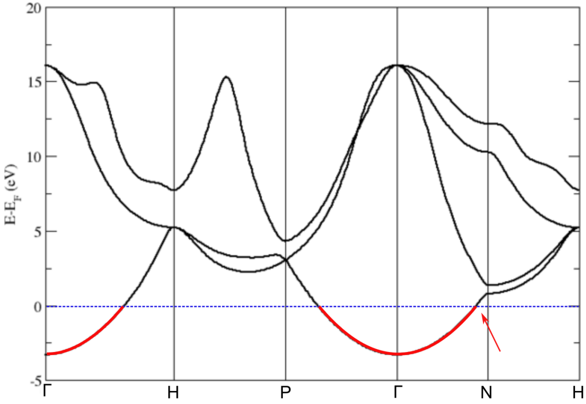
Sodium 3

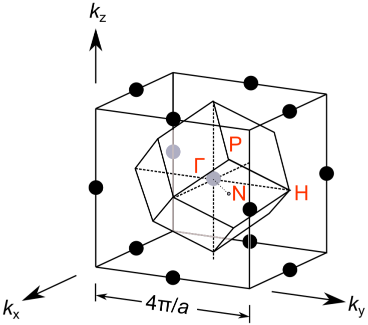
Fermi sphere and 1st Brillouin zone of sodium



Sodium 4

band structure of metallic sodium





Sodium 4

Comment 1

The figure on the left shows the band structure of metallic sodium along the indicated directions within the 1st Brillouin zone.

The right figure shows the 1st Brillouin zone of the bcc lattice with the symmetry points.

The band structure of sodium is very close to the band structure of the quasi-free electron approximation.

The figure shows that even the free electron approximation in three dimensions leads to an astonishingly complex band structure, although it results from the parabolas of the kinetic energy of a quasi-free electron.

The properties of metallic sodium are determined by the electrons on the Fermi surface.

Sodium 4 Comment 2

The thermal energy at room temperature (300 K) is only $k_B T \approx 26$ mK and is much smaller than the Fermi energy.

The red lines indicate the occupied k states.

The occupied k states with the highest energy determine the Fermi surface, which is a sphere to a good approximation.

As expected, the N point of the 1st Brillouin zone has the smallest distance to the Fermi surface (indicated by the small arrow).

Copper

Energy bands and Fermi surfaces 3

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

Copper 1

band structure of Copper

- The electron configuration of metallic copper is $[\mathrm{Ar}]4\mathrm{s}^1 3\mathrm{d}^{10}$
- The energy levels of the 4s and 3d electrons are close to each other
- The 4s electron is the conduction electron
- Since the cubic cell of the fcc lattice contains 4 copper atoms, the density of the 4s electrons is $4/a^3$ and the Fermi wave number is

$$k_\mathrm{F}^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 \frac{4}{a^3} \rightarrow k_\mathrm{F} = \frac{4.9}{a}$$

Copper 1

Comment

The periodic table shows that the 4s orbital is first occupied by two electrons before the 3d orbitals of the transition metals are filled with electrons.

However, if it is possible to use the 4s electrons to create a half or fully filled 3d shell, then 4s electrons will end up in the 3d orbitals.

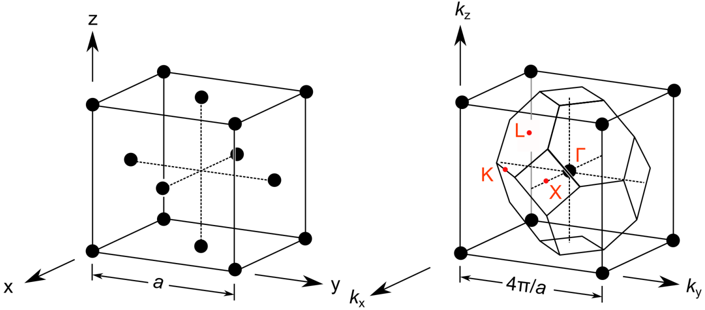
The energies of the 4s orbital and the 3d orbital are close to each other.

In the case of copper, this results in the $[\mathrm{Ar}]4\mathrm{s}^1 3\mathrm{d}^{10}$ configuration.

The 4s electron is the conduction electron for which the Fermi wave number $k_\mathrm{F} = 4.9/a$ results.

Copper 2

cubic unit cell and 1st Brillouin zone of copper



- The distance between the Γ point and X is $2\pi/a \approx 6.2/a$
- The distance between the Γ point and L is $\frac{1}{2}\frac{2\pi}{a}\sqrt{3} \approx 5.4/a$
- The Fermi sphere of the 4s electrons is enclosed by the 1st Brillouin zone

Copper 2

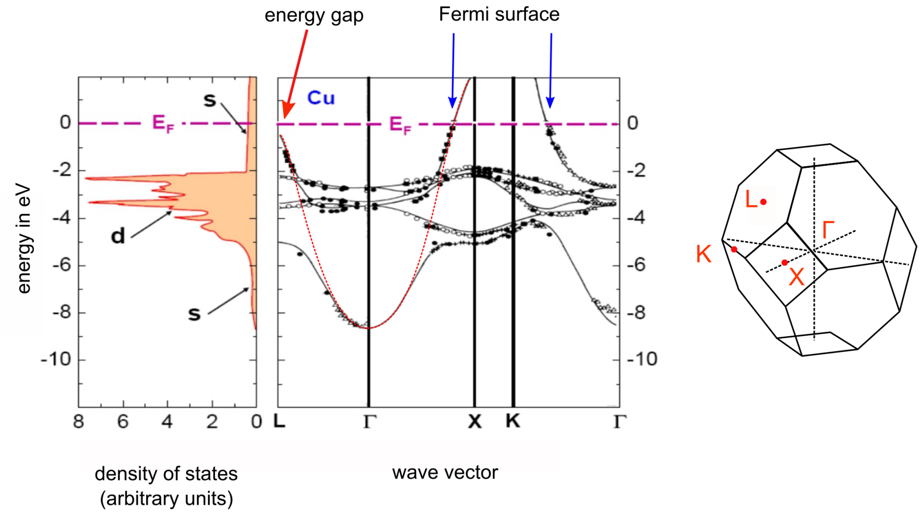
Comment

The left figure shows the cubic fcc unit cell of copper and the right figure the 1st Brillouin zone.

The distance between the L point on the hexagonal surface of the 1st Brillouin zone and the Γ point is with $5.4/a$ the smallest between the surface of the 1st Brillouin zone and the Γ point.

The Fermi sphere of the 4s electrons lies within the 1st Brillouin zone.

Copper 3


energy gap
Fermi surface
Cu
s
E_F
E_F
d
s
energy in eV
0
-2
-4
-6
-8
-10
8
6
4
2
0
L
Γ
X
K
Γ
density of states
(arbitrary units)
wave vector
L
Γ
K
X

Copper 3

Comment 1

The left part of the figure shows the density of states of the electrons that occupy the 3d orbitals and the 4s orbital.

The electrons of the 4s and the 3d orbitals share the same energy range.

The middle part of the figure shows the band structure of copper.

The 1st Brillouin zone is sketched on the right to show the directions in which the band structure was measured and calculated.

The 4s electrons show roughly the behavior of the free electrons.

For comparison I have drawn a red dotted parabola for the kinetic energy of the quasi-free 4s electrons.

Compared to the band of 4s electrons, the bands of 3d electrons are narrow.

Copper 3

Comment 2

This suggests that the mobility of the 3d electrons is rather low.

Although the 3d electrons are not bound to the copper atoms, they cannot contribute to the conductivity of copper.

The energy of the 3d electrons is well below the Fermi energy of the 4s electrons.

There are five 3d bands and ten 3d electrons per copper atom.

All k states are therefore occupied by two 3d electrons, so that the 3d bands cannot contribute to the conductivity of copper.

Since there are five comparatively narrow 3d bands, the density of states of the 3d electrons is concentrated in a small energy range and therefore large compared to the density of states of the 4s electrons.

Copper 3

Comment 3

The energy band of the 4s electrons must pass through the area of the 3d energy bands.

This leads to avoided level crossings and there are no electron states on the idealized parabola in this energy range.

The 4s electrons with the highest energy define the Fermi surface.

The occupied *k* states reach the Fermi energy near the X and K points

I have marked these points in the band structure with blue arrows.

Copper 3

Comment 4

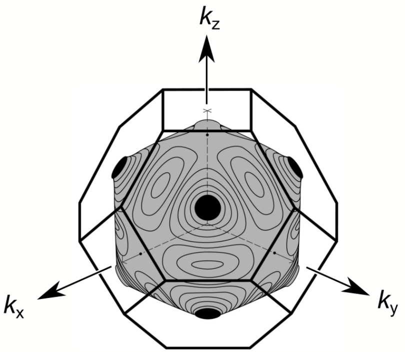
The Fermi surface is slightly closer to the X point than to the K point. (The distance Γ-K is $\frac{3\pi}{\sqrt{2}a} \approx 6.66/a$)

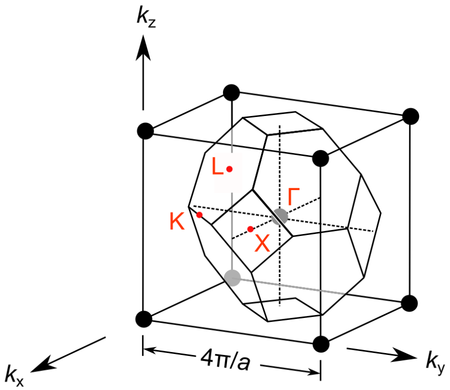
The band structure in the area of the L point is remarkable.

The energy of the *k* states of the 4s electron is smaller than the Fermi energy, i.e. there is no Fermi surface in the area of the L point.

(Remember that the Fermi surface is defined by the occupied *k* states with the Fermi energy. Only electrons that occupy these *k* states can easily be excited thermally or by an external electric field.)

Copper 4





Copper 4

Comment 1

The left figure shows the Fermi surface of copper and the right figure again the 1^{st} Brillouin zone of the fcc lattice.

The Fermi surface is almost spherical with the remarkable deviations at the L points.

The energy of the *k* states within the black circles at the L points is smaller than the Fermi energy.

Only at the edge of the black circles does the energy of the *k* states reach the Fermi energy.

The Fermi surface is shown in gray.

Copper 4

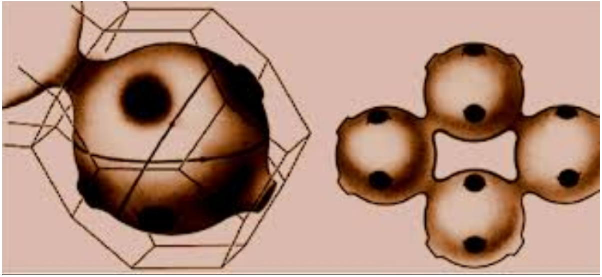
Comment 2

The contour lines around the L point indicate that the Fermi surface rises above the level of a spherical Fermi surface.

The contour lines in the area of the K point indicate that the Fermi surface is slightly below the level of a spherical Fermi surface.

Copper 5

Fermi surface of copper in the reduced (left) and the periodic zone scheme (right)



Copper 5

Comment

The figure on the left shows the Fermi surface in a reduced zone scheme.

The figure on the right shows the Fermi surface in the periodic zone scheme.

The lines with the arrows in the figure on the left cannot be explained with the current status of the discussion.

They indicate closed electron orbits in a magnetic field.

The periodic zone scheme shows that there can also be open electron orbits in copper that pass the boundaries of the 1st Brillouin zone.

What electron orbits are is explained in the Electron Dynamics section.

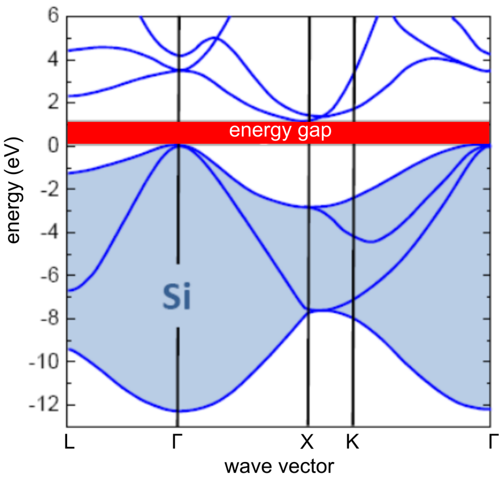
Silicon

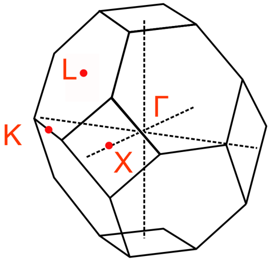
Energy bands and Fermi surfaces 4

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

Silicon

band structure of Silicon





Silicon

Comment 1

The figure shows the band structure of Silicon.

The diamond structure of Silicon is due to the $3sp^3$ hybrid orbitals.

The crystal structure is an fcc lattice with two silicon atoms inside the primitive unit cell.

The 1st Brillouin zone of the fcc lattice is shown on the right.

The band structure shows the quasi-free electron parabolas, i. e. the electrons of the $3sp^3$ hybrid orbitals are not localized at all but are very mobile.

Because the number of valence electrons within the primitive unit cell is even, silicon is not a metal (electron configuration of silicon [Ne] $3s^2$, $3p^2$).

The shaded energy bands are fully occupied.

Silicon

Comment 2

All k states of the energy bands with in the 1^{st} Brillouin zone are occupied with two electrons (spin up and down).

The bottom of the next excited unoccupied energy band is separated by an energy gap of approximately 1 eV from the top of the highest occupied energy band.

The energy gap correspond to a temperature of about 11600 K ($1\,\text{eV} = k_\text{B}T$).

Consequently only a very small number of electrons can be excited over the energy gap at room temperature.

Silicon is known as a semiconductor, i.e. it is not a very good insulator but certainly a very bad conductor.

Silicon

Comment 3

Electrons from the top of the highest occupied energy band at the Γ point have to gain momentum in addition to energy in order to reach the bottom of the first excited band in the range of the X point of the 1st Brillouin zone.

Therefore Silicon is called an indirect semiconductor.

In a direct semiconductor the bottom of the lowest excited energy band can be reached from the top of the highest occupied energy band without an additional momentum.

Electron dynamics

Electrons in crystal lattices

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

Electron dynamics

up to now: time independent Schrödinger equation

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

Solution: Bloch waves

$$\varphi_{\vec{k}}(\vec{r}) = u(\vec{r})\exp(i\vec{k}\vec{r}) \quad \text{with} \quad u(\vec{r}) = u(\vec{r}+\vec{R})$$

and

$$\boxed{E(\vec{k}) = E(\vec{k}+\vec{K})} \quad \text{and} \quad \boxed{\varphi_{\vec{k}}(\vec{r}) = \varphi_{\vec{k}+\vec{K}}(\vec{r})}$$

Electron dynamics

Comment 1

So far only the idealized Hamiltonian of the electrons in a perfect periodic crystal lattice has been considered.

The electrons were assumed to move independently in a mean potential formed by all other electrons and the atomic nuclei.

The Schrödinger equation can be solved using Bloch waves, which can be determined with great accuracy.

Nevertheless, the Bloch wave does not describe the real conditions in a crystalline solid.

The electron waves are scattered by lattice vibrations, impurities, and other lattice defects, and the electron waves respond to applied electric and magnetic fields or to bombardment with photons, electrons, or other particles.

Electron dynamics

Comment 2

The first steps in describing the response of electrons in a crystal to external fields were taken by Rudolf Peierls in 1929.

Leaving aside all the complicated theoretical considerations, the result of his work can be summarized as follows:

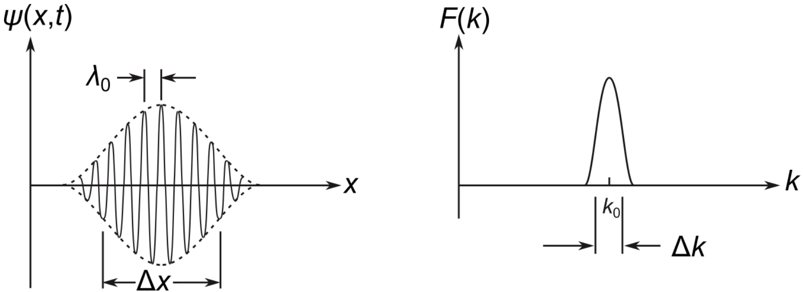
Electrons are described by wave packets formed by the Bloch waves.

Neither the energy nor the momentum of the electrons are precisely defined in the sense that they are eigenvalues of the Hamiltonian or the momentum operator.

But both the energy and the momentum are reasonably well determined by the wave packets.

Electron dynamics 1

wave packets



wave packets move with the group velocity

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

Electron dynamics 1

Comment 1

Although the formation of wave packets from Bloch waves is a mathematically well-defined procedure, it is nevertheless very demanding.

Within the framework of Peierl’s theory, however, it turns out that only properties of wave packets that are already known from classical wave physics are important.

The figure shows a classic wave packet in position and momentum space.

The wave packets are created by the superimposition of many waves with slightly different wave vectors.

The figure on the left shows a wave packet in position space and the figure on the right shows the amplitude function $F(k)$ of the waves contributing to the superposition.

Electron dynamics 1

Comment 2

Most important is the fact that wave packets propagate with the group velocity.

The equation outlined in red gives the formula used to calculate the group velocity.

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

The frequency $\omega(\vec{k})$ can be replaced by the band energy $E(\vec{k})$ of the Bloch wave.

It is not the phase velocity of the Bloch waves that is important for electron dynamics, but the group velocity of the wave packets.

The speed of the band electrons is determined by differentiating the band energy $E(\vec{k})$ according to the components of the wave vector.

Electron dynamics 1

Comment 3

If the energy is constant, i.e. independent of the wave vector, the group velocity is zero and the electrons are localized.

The greater the derivative of the band energy with respect to the components of the wave vector, the greater the speed of the wave packets.

Electron dynamics 2

equation of motion of a wave packet

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

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

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

Electron dynamics 2

Comment 1

A truly 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 semi-classical 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.

Electron dynamics 2

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.

Electron dynamics 2

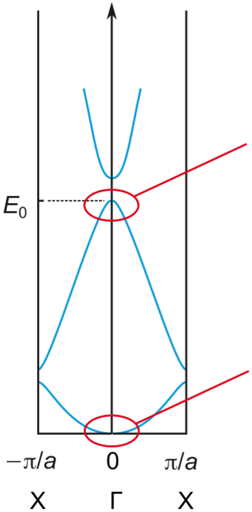
Comment 3

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.

Electron dynamics 3



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

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

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

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

Electron dynamics 3 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:

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

Electron dynamics 3 Comment 2

This changes the sign of the charge.

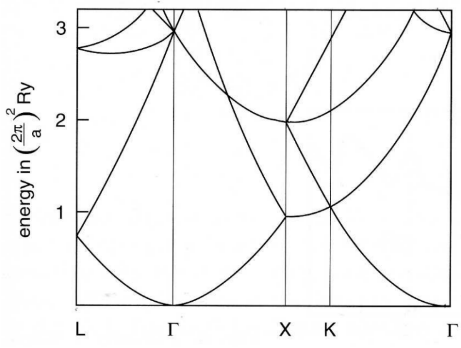
The wave packets at the top of the second band respond to the force of an applied electric or magnetic field with a negative mass, or alternatively with a positive charge.

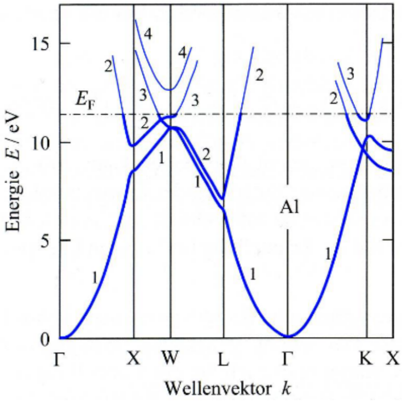
The fact that positive charge carriers can be detected when measuring the Hall effect has a simple explanation in the context of semi-classical electron dynamics.

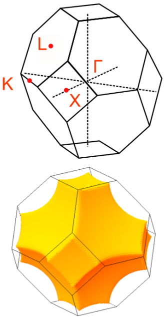
Electron dynamics 4

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

free electron parabola fcc lattice







Fermi surface second band

Electron dynamics 4

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 kinetic energy parabolas of free electrons along the symmetry directions of the fcc lattice.

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

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

The periodic potential energy induces small energy gaps.

Electron dynamics 4 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 third energy band has electron character, while a detailed investigation shows that the second energy band has hole character, i.e. the second derivative $E(\vec{k})$ is negative in the range of the Fermi energy.

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

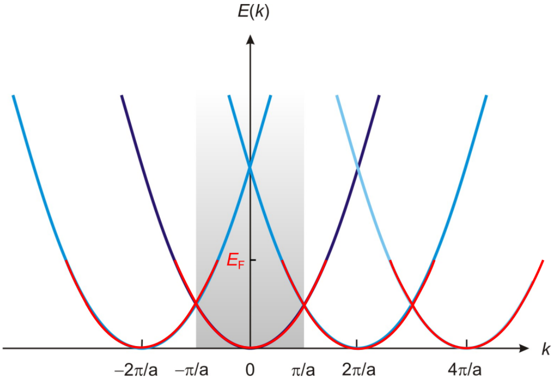
The effective mass of the electrons on this Fermi surface is negative.

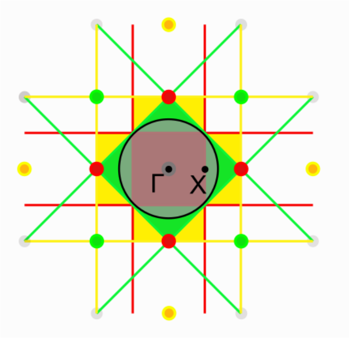
The conductivity of aluminum is dominated by the positive charges of the 2nd energy band.

Electron dynamics 5

three electrons per primitive unit cell of a simple cubic lattice

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





Electron dynamics 5 Comment 1

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 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.

Electron dynamics 5

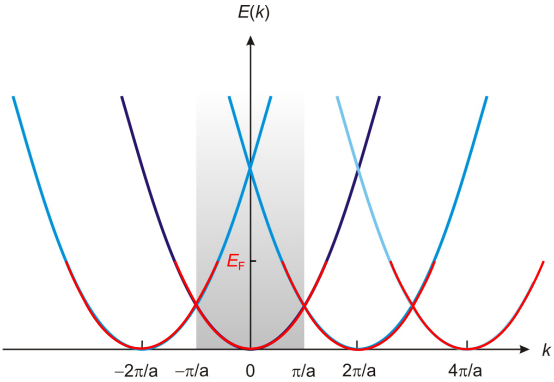
Comment 2

The figure on the left shows the energy bands in the periodic zone scheme in the Γ-X direction.

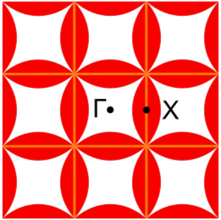
The occupied *k* states are marked in red.

As long as the influence of a periodic potential energy is not taken into account, the second derivative of $E(\vec{k})$ is always positive and all bands have electron character in the range of the Fermi energy.

Electron dynamics 6



periodic zone scheme 2^{nd} band



Electron dynamics 6 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 2nd energy band marked in red in the periodic zone scheme.

The red areas enclose white areas of unoccupied *k* states.

The unoccupied *s*tates are usually called electron-hole states.

The Fermi surface of the 2nd energy band of aluminum resembles the white area of the unoccupied states *k* states in the simple cubic lattice.

The Fermi surface of the 2nd energy band of aluminum encloses the electron-hole states that dominate electrical conductivity.

Electron dynamics 7: “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

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

Electron dynamics 7

Comment 1

The current density is defined as the charge carrier density multiplied by the charge carrier velocity: i.e. $j = \rho v$.

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. $-2e$.

To get the current density, the sum of the velocities must be divided by the volume of the crystal.

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

Electron dynamics 7 Comment 2

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

If a band is not completely occupied by electrons, then 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

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

Electron dynamics 7

Comment 3

When integrating over the period of the 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 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.

Electron dynamics 7

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 second derivative of the energy $E(\vec{k})$ turns out to be negative due to the influence of the periodic potential, the electrons can be assigned a positive charge, so it is convenient to consider the unoccupied electron hole states instead of the occupied one electron states to calculate the electric current.

For this reason, the 2nd energy band of aluminum can also be called the electron-hole band and the Fermi surface encloses the unoccupied k states of the electron holes.

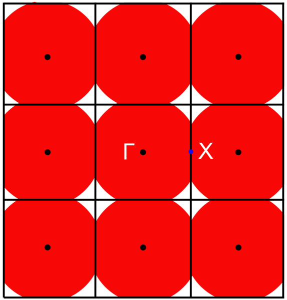
Electron dynamics 8

Electron configuration of zinc: [Ar]$4s^2 3d^{10}$

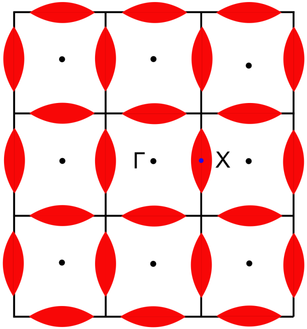
According to the Hall-effect, zinc is a metal with positive charge carriers

two nearly free conduction electrons in a simple cubic lattice

first band



second band



Electron dynamics 8 Comment

In the table with the hall constants in the 23rd lecture, zinc also has a positive hall constant.

Zinc is next to copper on the periodic table.

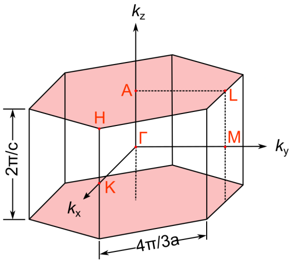
The 3d orbitals are fully occupied by 10 electrons and also the 4s orbital is fully occupied by 2 electrons.

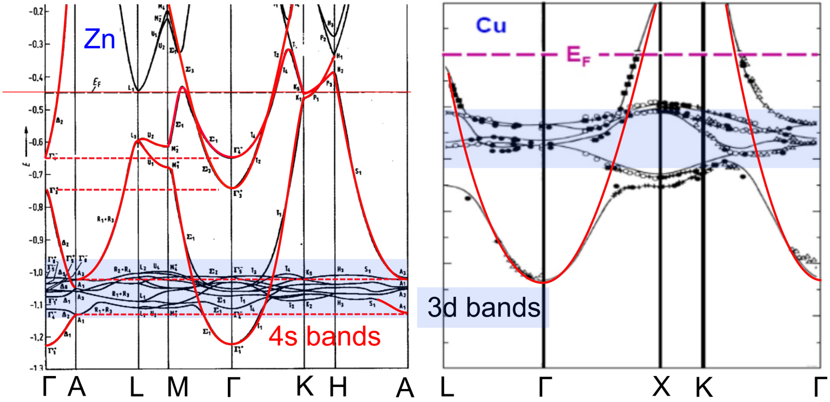
According to the number of electrons, all occupied energy bands in the 1st Brillouin zone can be completely occupied by electrons.

If that were true, zinc would be an insulator, which is not the case.

Comparison with the simple cubic lattice shows that this need not be the case if the bands are not fully occupied.

Electron dynamics 9





Electron dynamics 9

Comment 1

Zinc crystallizes in an hcp lattice that is slightly stretched along the c axis compared to the hexagonal closest packing and there are two zinc atoms per primitive unit cell.

The figure on the left shows the 1st Brillouin zone of the hexagonal lattice.

$a = 0.266\,\text{nm}$ and $c = 0.495\,\text{nm}$ denote the lattice constants.

The middle panel shows the band structure of zinc.

For comparison, the figure on the right shows the band structure of copper again.

In contrast to copper, zinc has an extra electron.

Electron dynamics 9 Comment 2

In both band structures, the narrow 3d bands crossing the 4s band can be seen at low energies.

The parabolic segments of the kinetic energy of the 4s electrons are marked in red ($E_{kin} = \frac{\hbar^2 \vec{k}^2}{2m}$).

For copper, the kinetic energy of the 4s electrons reaches the Fermi energy just above the energy of the 3d bands.

For zinc, the Fermi energy is well above the energy of the 3d bands and the band structure is relatively complicated, although the behavior of quasi-free electrons can still be clearly seen.

The 1st Brillouin zone shows that the Bragg planes have smaller distances along the z-direction than in the directions perpendicular to it.

Electron dynamics 9 Comment 3

As a result, the 4s band is split into three sub-bands along the path Γ-A in the energy range under consideration.

The first bandgap at the A point is in the energy range of the 3d bands, which is confusing because of the interaction between the 4s and 3d electrons.

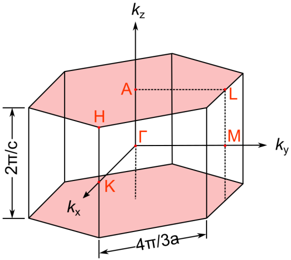
The second band gap at the Γ point can be clearly seen.

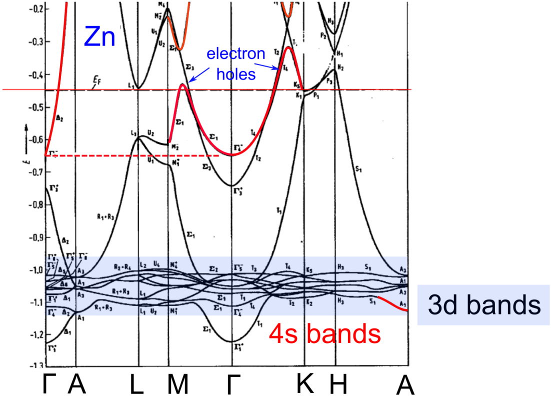
Perpendicular to the z-direction, the Bragg planes have larger distances, so that the energy between the band gaps is larger (remember again $E_{kin} = \frac{\hbar^2 \vec{k}^2}{2m}$).

This circumstance introduces a new feature of the band structure that has not occurred before.

In addition to the energy splittings at the Γ point and the Bragg planes, there are now avoided level crossing within the 1st Brillouin zone.

Electron dynamics 10





Electron dynamics 10

Comment

The energy bands marked in red between the symmetry points Γ-M and Γ-K show that level-anticrossings can occur not only on the Bragg planes, but also within the 1st Brillouin zone.

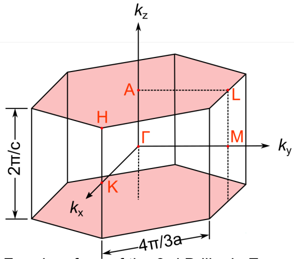
The band peaks between Γ-M and Γ-K can be approximated by parabolas with negative B values.

Therefore, these bands correspond to electrons that have negative effective masses or positive charges.

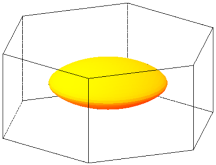
There are also energy bands that correspond to a positive mass and whose charge carriers can therefore be assigned a negative charge.

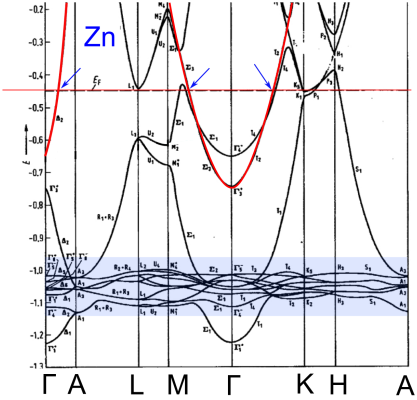
The electron band between the symmetry points Γ-A is marked in red as an example.

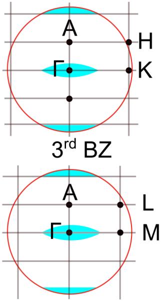
Electron dynamics 11



Fermi surface of the 3rd Brillouin Zone







Electron dynamics 11 Comment

The left side of the figure shows the 1st Brillouin zone of the hexagonal lattice and below it the Fermi surface of the 3rd Brillouin zone, which has been shifted back into the 1st Brillouin zone.

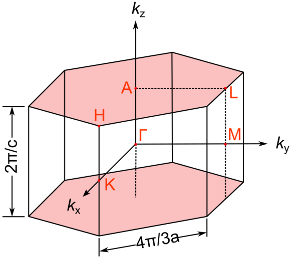
The right side shows the construction of the Fermi surface.

The radius of the Fermi sphere takes into account that there are four 4s electrons in the primitive unit cell of zinc (There are two zinc atoms per primitive unit cell of the quasi hcp-lattice).

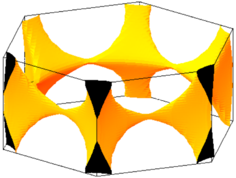
The energy bands that contribute to the Fermi surface are marked in red.

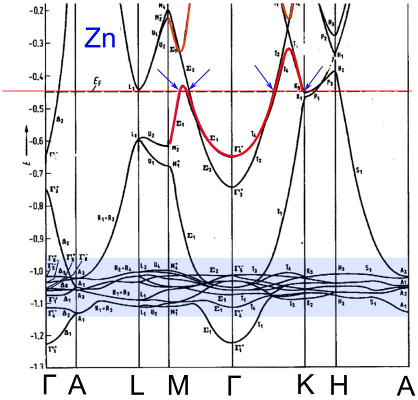
The Fermi energies of these bands are marked with blue arrows and the Fermi surface envelops occupied electron states.

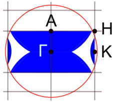
Electron dynamics 12

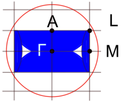


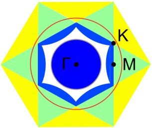
Fermi surface of the 2nd BZ











Electron dynamics 12

Comment 1

The figures on the left show the 1st Brillouin zone of a hexagonal crystal lattice at the top and below the Fermi surface of the second energy band.

The Fermi surface envelops the unoccupied electron states.

This Fermi surface results when the areas of the Fermi sphere that are in the 2nd Brillouin zone are shifted into the 1st Brillouin zone.

These operations are shown in the figures on the right.

The top figure shows the A-Γ-K plane.

The blue areas denote the occupied electronic states.

Electron dynamics 12

Comment 2

The white areas in the 1st Brillouin zone are the unoccupied electron states.

The displacements take place along the Γ-A-direction (large sections of the Fermi sphere) and along the Γ-K-direction (small sections of the Fermi sphere).

The middle figure shows the A-Γ-M plane.

Since the distance Γ-M is smaller than the distance Γ-K, the segments of the Fermi sphere shifted in the Γ-M direction are larger than in the A-Γ-K plane.

Therefore, the areas of unoccupied electron states in the A- Γ-M plane are smaller than in the A -Γ-K plane (Compare the spatial representation of the Fermi surface on the left.).

Electron dynamics 12 Comment 3

The bottom figure shows the K-Γ-M plane, which is perpendicular to the hexagonal axis of the crystal lattice.

The blue circular area in the middle of the 1st Brillouin zone results from the displacements of the 2nd Brillouin zone into the 1st Brillouin zone along the Γ-A direction.

The blue segments at the edge of the 1st Brillouin zone arise when the areas of the Fermi sphere that lie in the areas of the 2nd Brillouin zone (marked in green) are shifted into the 1st Brillouin zone.

The electron-hole bands in the Γ-M and Γ-K directions are marked in red in the middle figure.

The blue arrows mark the points where the band energy equals the Fermi energy.

Electron dynamics 12

Comment 4

With these simple constructions one can visualize, at least qualitatively, how the complicated Fermi surface of the electron-hole band comes about in a hexagonal crystal lattice.

In addition to the two Fermi surfaces just discussed, there are other Fermi surfaces that enclose smaller areas of the reciprocal lattice.

Revision

Summary in Questions

1. Sketch the band structure of quasi-free electrons in a simple cubic crystal lattice for the path Γ-X-M-Γ for the 1st and 2nd energy bands.
2. Compare your sketch to the band structure of sodium for the path Γ-H-P-Γ.
3. Sodium crystallizes in bcc lattice. Calculate the distance between P and Γ of the 1st Brillouin zone ($\frac{1}{2}\sqrt{3}\frac{2\pi}{a}$).
4. How is a wave packet formed?
5. With what speed does a wave packet move?
6. What experimental evidence suggests that band electrons travel in wave packets?
7. How do electric and magnetic fields determine the movement of band electrons?
8. Why do band electrons sometimes behave like positive charge carriers?