Solids

Preliminary remarks 1

When we think of conduction electrons, we imagine little balls bouncing back and forth between the atoms of the material.

This picture is just as wrong as the idea that electrons move around atomic nuclei like planets.

Nothing can be explained with these ideas, since the electrons are quantum particles that are described by wave functions.

The Sommerfeld model is based on plane electron waves and we accept that we cannot localize the electrons. Nevertheless, we assume that the electrons collide with atoms, although we do not know where this happens. However we think, this does not matter because the number of conduction electrons is incredibly large.

Preliminary remarks 2

The electron picture is supported by the kinetic energy of the electrons $E_{\text{kin}} = \hbar^2 \vec{k}^2/2m$ in the Sommerfeld model.

We automatically assume that this describes the kinetic energy of the elementary particle and that the mass m is the mass of the free electron.

But all of these ideas are wrong and misleading.

The success of the Sommerfeld model is based on the fact that the real wave functions of electrons in a crystal lattice can be developed into plane waves, i.e. the Sommerfeld model examines the Fourier components from the solution of the Schrödinger equation and can thus correctly describe important aspects of the conduction electrons.

If we think of conduction electrons, we assume that they are all the same.

Preliminary remarks 3

However, this is incorrect because the properties of conduction electrons are determined by the atomic orbital from which they delocalize.

For example, in nickel the electrons delocalize from the five 3d orbitals and in copper they also delocalize from the 4s orbital.

The striking difference between the 3d electrons and the 4s becomes apparent when we compare nickel and copper. Nickel is a ferromagnetic metal, while copper is not magnetic. (In most cases the effects are not that dramatic.)

The Schrödinger describes the wave functions and the energy $E_n(\vec{k})$ of the conduction electrons (n stands for the quantum numbers of the atomic orbitals).

The function $E_n(\vec{k})$ can be developed in a Taylor series expansion, which in most cases begins with the quadratic term $E_n(\vec{k}) \propto \vec{k}^2$.

Preliminary remarks 4

Again, the Sommerfeld model captures this important point correctly, but it is obvious that the mass m in $E_{\text{kin}} = \hbar^2\vec{k}^2/2m$ does not is the mass of a free electron, but a parameter that describes $E_n(\vec{k})$ for small values of k.

For many substances, m does not differ much from the mass of the free electron and again the image of small balls that jump back and forth between the atoms comes in our minds.

To make progress, we must adhere to quantum mechanics and must be particularly careful if we believe we can describe effects of conduction electrons in the particle image.

In this lecture I will describe the solution of the Schrödinger equation for conduction electrons. In the next lecture these results will be applied to real substances.

Sommerfeld model

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

Density of states

Sommerfeld model

- Fermi sphere
- Fermi distribution function
- Electric conductivity
- Density of states
- Heat capacity of the electron gas

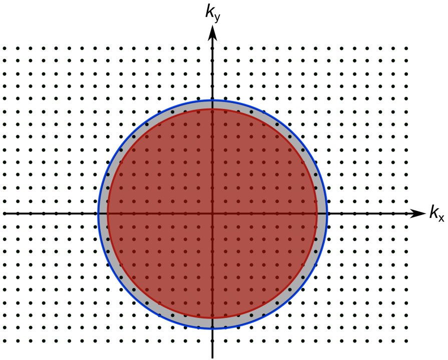
Density of states 1

definition of the density of states (DOS)

$$\boxed{D(E) = \frac{1}{V}\frac{dN}{dE}}$$

DOS

number of *electron states dN* in an energy interval *dE* around the energy *E*



Density of states 1 Comment

The equation outlined in red gives the definition of the density of states.

The density of states gives the number of electron states in an energy interval dE around the energy E.

The figure illustrates the situation for the Fermi sphere.

All k states that are in the blue ring contribute to the density of states at the energy E in the interval dE.

The density of states for the Fermi energy $D(E_F)$ is particularly important because it indicates the number of electrons that can be excited and take part in scattering events.

Density of states 2

number of *k* states in a spherical shell with the thickness *dk* and the radius *k* is

$$\frac{4\pi k^2 \mathrm{d}k}{\frac{(2\pi)^3}{V}}$$

the number of electron states within the shell is

$$\underline{\mathrm{d}N = 2\frac{4\pi k^2 \mathrm{d}k}{\frac{(2\pi)^3}{V}} = V\frac{k}{\pi^2}k\mathrm{d}k}$$

with $E = \hbar^2 k^2 / 2m$ and $dE = \hbar^2 k dk / m$

$$\boxed{D(E) = \frac{1}{V}\frac{dN}{dE} = \frac{\sqrt{2m^3}}{\pi^2 \hbar^3}\sqrt{E}}$$

Density of states 2

Comment

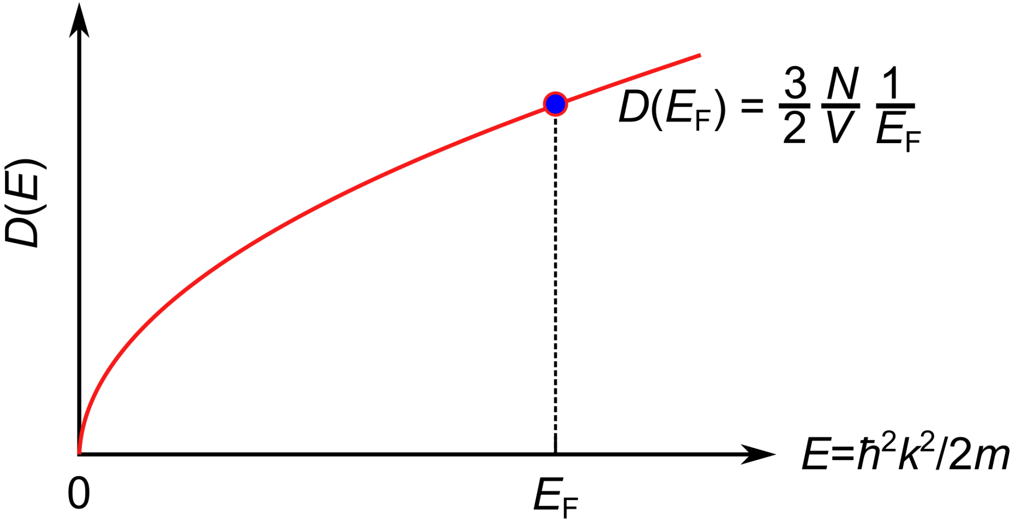
The density of states can easily be calculated for the Fermi sphere of the Sommerfeld model.

The number of k states results when the volume of a spherical shell $4\pi k^2 \mathrm{d}k$ is divided by the volume of a k state $2\pi^3/V$.

A factor of 2 must be taken into account for the number of electron states, since every k state can be occupied by two electrons.

From the kinetic energy of a quasi free electron and the differential of the kinetic energy it follows that the density of states is proportional to the square root of the energy of the electron.

Density of states 3



Density of states 3

Comment

The figure shows the square root behavior of the density of states of quasi free electrons.

The density of states is particularly important for the Fermi energy E_F.

A little calculation shows that $D(E_\mathrm{F})$ is proportional to the density of the conduction electrons and inversely proportional to the Fermi energy.

Heat capacity of the electron gas

Sommerfeld model

- Fermi sphere
- Fermi distribution function
- Electric conductivity
- Density of states
- Heat capacity of the electron gas

Heat capacity of the electron gas 1

the definition of the heat capacity is

$$C = \frac{\partial E}{\partial T}$$

the number of electrons in an energy interval $\Delta E = k_B T$ at the Fermi energy is with the definition of the density of states $D(E) = V^{-1} dN/dE$

$$\underline{\Delta N \propto V D(E_F) k_B T}$$

the additional energy due to an excitation with the energy $k_B T$ is

$$\boxed{\Delta E \propto V D(E_F) (k_B T)^2}$$

Heat capacity of the electron gas 1 Comment

If one neglects the thermodynamic details, such as measurements at constant pressure or constant volume, then the heat capacity is given simply by the change in the energy of the conduction electrons with temperature, as indicated in the formula in the first line.

The number of thermally excitable conduction electrons is determined by the density of states at the Fermi energy.

The number of excitable electrons can be estimated with $\Delta E = k_B T$ and the density of states $D(E_\mathrm{F})$.

The equation underlined in red gives the number of these electrons.

Since the mean excitation energy is also given by $k_\mathrm{B} T$, the equation outlined in red results for the change in energy due to thermal excitations.

Heat capacity of the electron gas 2

the exact result of the Sommerfeld theory for the energy of an electron gas is

$$\underline{E(T) = E(T=0) + V\frac{\pi^2}{6}D(E_F)(k_B T)^2}$$

the heat capacity of an electron gas is

$$\boxed{C = V\frac{\pi^2}{3}D(E_F)k_B^2 T} = Nk_B\frac{\pi^2}{2}\underline{\frac{k_B T}{E_F}} = \gamma T$$

heat capacity of metals at low temperatures

$$\boxed{C = \gamma T + \beta T^3}$$

Heat capacity of the electron gas 2 Comment 1

The equation underlined in red gives the exact temperature dependence of the energy of an electron gas in the Sommerfeld model.

This formula confirms the estimate on the previous page.

The first equation outlined in red gives the heat capacity of the conduction electrons in the Sommerfeld model.

The heat capacity is proportional to the temperature and proportional to the density of states for the Fermi energy.

This formula applies in general and also applies if the restrictions of the Sommerfeld model are relaxed.

Heat capacity of the electron gas 2

Comment 2

The following formula results when the density of states of the Sommerfeld model is used.

The heat capacity of the electron gas is proportional to the ratio between the thermal energy $k_B T$ and the Fermi energy E_F.

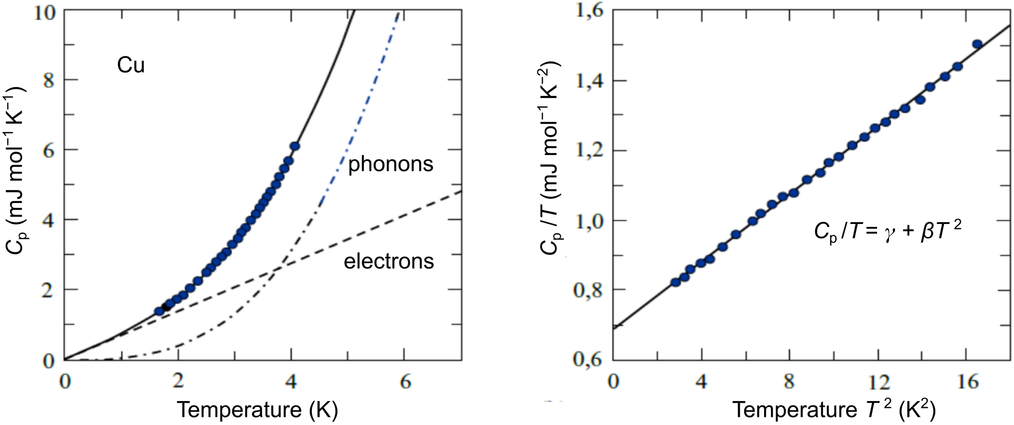
The constant of proportionality between the heat capacity of the electron gas and the temperature is denoted by γ.

The second equation outlined in red gives the heat capacity of a metal at low temperatures.

The heat capacity is composed of the contribution of the conduction electrons, which is proportional to the temperature, and the contribution of the phonons, which is proportional to T^3.

Heat capacity of the electron gas 3

low temperature heat capacity of Copper



Heat capacity of the electron gas 3 Comment 1

The left figure shows the heat capacity of Copper between 2 and 4 K.

The right figure shows the same experimental data.

Now C_p/T is plotted over T^2.

The result is a straight line.

The slop of the straight line determines the contribution of the phonons β.

The intersection of the straight line with the C_p/T-axis results in the contribution of the conduction electrons $\gamma \approx 0.7\, mJ\, mol^{-1} K^{-2}$.

Heat capacity of the electron gas 3 Comment 2

It is worthwhile to compare these low-temperature measurements of the specific heat capacity of copper with the measurements of the specific heat capacity shown in lecture 22.

The high-temperature Dulong-Petit limit case of the specific heat capacity is about 25 $\mathrm{Jmol^{-1}K^{-1}}$ and there is a factor of about 1000 between the measurement at low and high temperatures.

The contribution of the conduction electrons to the specific heat capacity at a temperature of 100 K is in the range of 0.07 $\mathrm{Jmol^{-1}K^{-1}}$.

This is very small compared to the specific heat capacity of 25 $\mathrm{Jmol^{-1}K^{-1}}$ that is reached at high temperatures.

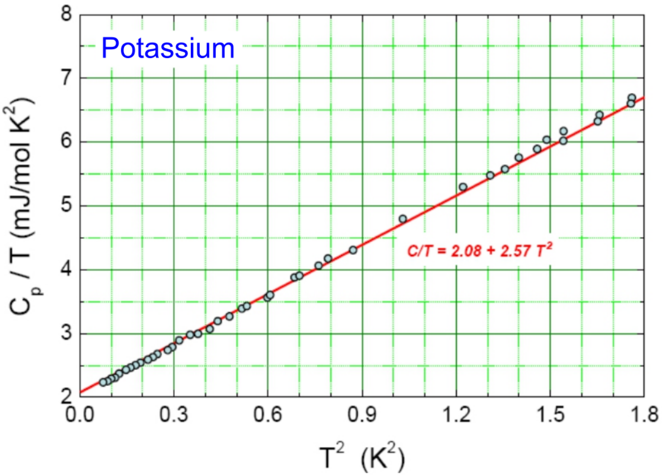
Heat capacity of the electron gas 3 Comment 3

The value $\beta = 0.05\,\mathrm{mJ\,mol^{-1}K^{-4}}$ for the parameter β can be determined from the slope of the straight line in the picture on the right.

With the formula $C = Nk_{\mathrm{B}}\frac{12\pi^4}{5}\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3$ the Debye temperature of copper $\Theta_{\mathrm{D}} = 340$ K results.

Heat capacity of the electron gas 4

$$C/T = \gamma + \beta T^2$$



Heat capacity of the electron gas 4

Comment

As a second example, the figure shows the diagram $C_\mathrm{p}\,/T$ over T^2 for potassium.

The intersection of the straight line with the C_p/T-axis results in the contribution of the conduction electrons $\gamma \approx 2.08\,\mathrm{mJ\,mol^{-1}K^{-2}}$.

Heat capacity of the electron gas 5

Sommerfeld model

$$C = V\frac{\pi^2}{3}D(E_F)k_B^2T = Nk_B\frac{\pi^2}{2}\frac{k_BT}{E_F} \quad \rightarrow \quad \boxed{\gamma = Nk_B\frac{\pi^2}{2}\frac{k_B}{E_F}}$$

e.g. copper $E_\mathrm{F} = 7$ eV

$$\gamma = 6\cdot10^{-23}\,\mathrm{mol}^{-1}\frac{\pi^2}{2}\frac{(8.617\cdot10^{-5})^2\,\mathrm{eV\,K^{-2}}}{7\,\mathrm{eV}}1.6\cdot10^{-19}\,\mathrm{AsV} = \underline{0.5\,\mathrm{mJ\,mol^{-1}\,K^{-2}}}$$

e.g. potassium $E_\mathrm{F} = 2.12$ eV

$$\gamma = 6\cdot10^{-23}\,\mathrm{mol}^{-1}\frac{\pi^2}{2}\frac{(8.617\cdot10^{-5})^2\,\mathrm{eV\,K^{-2}}}{2.12\,\mathrm{eV}}1.6\cdot10^{-19}\,\mathrm{AsV} = \underline{1.66\,\mathrm{mJ\,mol^{-1}\,K^{-2}}}$$

Heat capacity of the electron gas 5 Comment

The numerical value of γ can easily be calculated using the Sommerfeld model.

The calculation gives the value $\gamma = 0.5\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ for copper and $\gamma = 1.66\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ for potassium.

For both examples, the Sommerfeld model yields smaller numbers for γ than those found in the experiment ($\gamma = 0.7\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ for copper and $\gamma = 2.08\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ for potassium).

Heat capacity of the electron gas 6

effective electron mass m^*

since $\gamma = Nk_B \frac{\pi^2}{2} \frac{k_B}{E_F} = Nk_B \pi^2 \frac{\underline{m_e}}{\hbar^2 k_F^2} \quad \rightarrow \quad \underline{\gamma^* = \gamma \frac{m^*}{m_e}}$

	γ^* [mJ mol^{-1} K^{-2}]	$\frac{m^*}{m_e}$
K	2.08	1.2
Cu	0.69	1.4
Fe	4.98	10
$CeAl_3$	1500	200

Heat capacity of the electron gas 6 Comment 1

The Sommerfeld model assumes that the energy of the electrons increases according to $E_{\text{kin}} = \hbar^2 \vec{k}^2 / 2m_e$ when the momentum $\vec{p} = \hbar\vec{k}$ of the electrons increases. Thereby the mass of free electron is used.

In a crystal lattice the energy variation of the conduction electrons depends on the overlap of the atomic orbitals.

If the energy increases proportionally to $\vec{k}^2$ as the momentum increases (this could be the leading contribution of a Taylor expansion of $E(\vec{k})$), an effective mass can be used to describe the energy variation (i.e. $E_{\text{kin}} = \hbar^2 \vec{k}^2 / 2m^*$).

The table shows the experimentally determined γ values for some elements and an intermetallic compound.

The last column shows the ratio between the effective mass m^* and the mass m_e of a free electron.

Heat capacity of the electron gas 6 Comment 2

The numbers for potassium and copper can be checked directly from the measurements and calculations on the previous pages.

Especially for the intermetallic compound $CeAl_3$ the numerical values of γ and the related effective mass m^* are remarkably large.

Since electrons are fermions, substances like $CeAl_3$ are called heavy fermion compounds.

The heat capacity measurements confirm what we know without calculation, that the influence of the crystal lattice on the electrons is important.

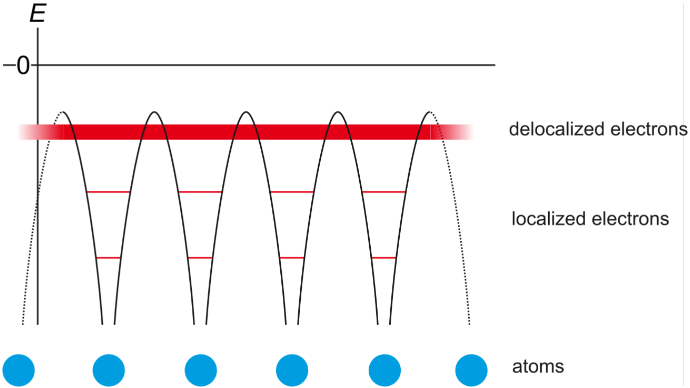
Bloch waves

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

Bloch waves 1

- each electron moves in a cloud of charge that is formed by other electrons in the solid
- the potential energy of each electrons has the periodicity of the crystal lattice



Bloch waves 1 Comment

The Sommerfeld model assumes that the potential energy of each conduction electron is completely independent of the position.

The next step in the approximation is to assume that each electron can move independently of the other electrons in a cloud of charge formed by the other electrons.

This charge cloud has the periodicity of the crystal lattice.

The independent electron approximation has already been used successfully to determine the orbitals of atoms and is also successful in the case of a crystal lattice.

Bloch waves 2

time independent Schrödinger equation

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

and

$$E_{pot}(\vec{r}) = E_{pot}(\vec{r}+\vec{R})$$

with

$$\underline{\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3}$$

Bloch waves 2

Comment

The equation outlined in red shows the Schrödinger equation for an electron with kinetic and potential energy in a crystal lattice.

The potential energy of the electron is determined by the positive nuclei and the negative charge cloud of the other electrons of the crystal. As before, the vectors R denote the vectors of the Bravais lattice.

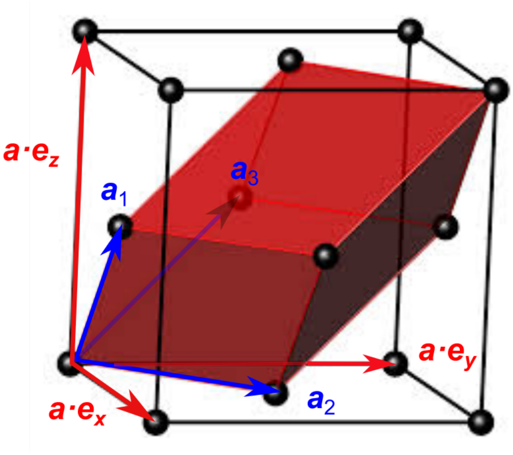
The potential energy depends on the electron in question.

The electrons are characterized by the type of atom and the particular orbital in which they reside.

To determine the charge cloud, all electrons of the atoms must be taken into account.

Bloch waves3

cubic unit cell and a primitive unit cell (red rhombohedron) of the fcc lattice



$$\vec{a}_1 = \frac{a}{2}\left(\vec{e}_x + \vec{e}_z\right)$$
$$\vec{a}_2 = \frac{a}{2}\left(\vec{e}_y + \vec{e}_x\right)$$
$$\vec{a}_3 = \frac{a}{2}\left(\vec{e}_z + \vec{e}_y\right)$$

Bloch waves 3

Comment

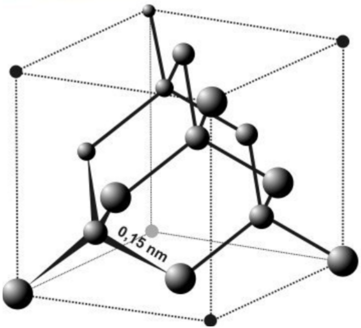
Copper is used as an example below to illustrate the results.

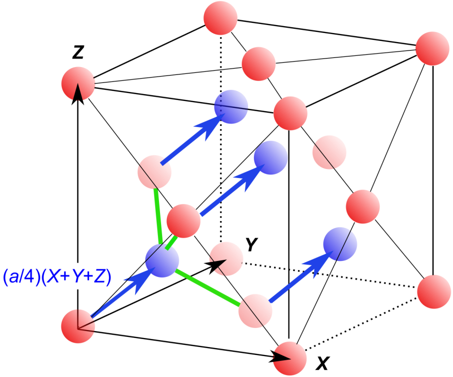
The crystal lattice of copper is an fcc lattice.

The figure shows the cubic and a primitive unit cell of the fcc lattice.

Bloch waves 4

cubic unit cell of the diamond structure
(fcc lattice with two atoms in the primitive unit cell)





Bloch waves 4

Comment

To illustrate the results, silicon and germanium, which crystallize in the diamond structure, are discussed below.

The sketches show the cubic unit cell of the diamond structure, which is an fcc lattice with a diatomic base.

In the sketch on the right, the two types of atoms are marked in red and blue.

A primitive unit cell of the fcc lattice (e.g. the rhombohedron of the previous slide) contains one atom marked in red and one in blue.

Bloch waves 5

Solution of the Schrödinger equation

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

in principle: sum over plane waves

$$\varphi(\vec{r}) = \sum_{\vec{k}} a_{\vec{k}} \exp(i\vec{k}\vec{r})$$

better idea: Bloch waves (Felix Bloch 1928)

$$\boxed{\varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) \exp(i\vec{k}\vec{r})}$$

with

$$\underline{u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})}$$

Bloch waves 5

Comment 1

In principle it is possible to develop the solution of the Schrödinger equation in plane waves.

But since the atomic orbitals of the electrons are still important, this is not a good idea.

The first step towards solving the problem of the wave function in a crystal lattice was taken by Felix Bloch in 1928.

He proposed modulated plane waves to solve the Schrödinger equation.

His approach is so fundamental that the waves have been named after him ever since.

The equation outlined in red shows a general Bloch wave.

Bloch waves 5

Comment 2

The Bloch wave is a plane wave that is multiplied by an amplitude function $u(\vec{r})$.

The amplitude function $u_{\vec{k}}(\vec{r})$ has the periodicity of the crystal lattice.

The amplitude function $u_{\vec{k}}(\vec{r})$ makes it possible to establish the relationship between the localized atomic orbitals on the one hand and the propagating wave function of the crystal lattice on the other.

A strategy for determining the function $u_{\vec{k}}(\vec{r})$ was proposed in 1937 by J.C. Slater with the augmented plane wave method.

In the augmented plane wave method, the crystal volume is divided into spherical areas around the atoms.

Bloch waves 5

Comment 3

The localized atomic orbitals are calculated in the spheres, which are then connected by plane waves in the volume between the spheres.

The mathematical problems of the augmented plane wave method are great and have been solved over time by the work of many scientists.

As soon as one has useful wave functions, the same procedure is used to solve the Schrödinger equation that is used for solving a single atom.

The charge densities in the crystal are calculated using the wave functions.

With the charge densities, the potential energy of the selected electron can be calculated.

Bloch waves 5

Comment 4

The wave function of the selected electron is characterized by the quantum numbers of the atomic orbital and by the wave vector of the Bloch wave.

The Schrödinger equation for the selected electron can be solved with the potential energy.

These calculations have to be done for all orbitals occupied by electrons.

E.g. in the case of copper for the electrons of the 1s to 4s orbitals.

These calculations give an improved set of wave functions that reduce the total energy of the electrons.

The process is repeated iteratively with the refined wave functions until the minimum of the total energy is found.

Bloch waves 5

Comment 5

In solid state physics, this is known as the band structure calculation.

The mathematical details are complicated, but fortunately only relevant for real calculations of the wave functions in a crystal lattice.

The theoretical and numerical details of band structure calculations do not need to be known in order to understand the essential electronic properties of solids.

The most important properties are already determined by the symmetry of the Bloch waves.

Bloch waves 6

the probability density to find an electron is $\varphi^*_{\vec{k}} \cdot \varphi_{\vec{k}}$

with

$$\varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}} \quad \text{and} \quad \boxed{u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})}$$

is

$$\underline{|\varphi_{\vec{k}}(\vec{r})|^2 = |u_{\vec{k}}(\vec{r})|^2 = |\varphi_{\vec{k}}(\vec{r}+\vec{R})|^2}$$

and the probability density is periodic in the crystal lattice

the solutions of the Schrödinger equation in a crystal lattice have the form of Bloch waves

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

Bloch waves 6 Comment

The probability of finding an electron is given by the square of the wave function.

Only the amplitude function contributes to the calculation of the probability density, since the exponential functions do not contribute to the square of the absolute value.

Since the probability density has to show the periodicity of the potential energy, the amplitude function has to be a periodic function in the crystal lattice.

The solutions of the Schrödinger equation in a crystal lattice have the form of Bloch waves and the energy eigenvalues depend on the wave vector of the Bloch wave.

There are also other quantum numbers that characterize the energy and the wave function, e.g. the quantum numbers of the atomic orbitals, which are included in the amplitude function.

For the sake of simplicity, I leave out these additional quantum numbers.

Bloch waves 7

definition of the reciprocal lattice

$$\boxed{\vec{K}\vec{R} = 2\pi n}$$

vectors of the Bravais lattice $\underline{\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3}$

vectors of the reciprocal lattice $\underline{\vec{K} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3}$

$$\boxed{\begin{aligned} \vec{b}_1 &= \frac{2\pi}{V_{\text{cell}}}(\vec{a}_2 \times \vec{a}_3) \\ \vec{b}_2 &= \frac{2\pi}{V_{\text{cell}}}(\vec{a}_3 \times \vec{a}_1) \\ \vec{b}_3 &= \frac{2\pi}{V_{\text{cell}}}(\vec{a}_1 \times \vec{a}_2) \end{aligned}}$$

V_{cell} denotes the volume of the primitive unit cell $V_{\text{cell}} = \vec{a}_1(\vec{a}_2 \times \vec{a}_3)$

Bloch waves 7

Comment

Now it is necessary to recall the definition of the reciprocal lattice.

The scalar product of a reciprocal lattice vector with a vector of the Bravais lattice is equal to a multiple of 2π.

The basis vectors of the reciprocal lattice can easily be calculated with the basis vectors of the Bravais lattice and vice versa.

Bloch waves 8

Bloch waves are periodic in the reciprocal lattice

$$\begin{aligned}\varphi_{\vec{k}}(\vec{r}) &= u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}}\\ &= u_{\vec{k}}(\vec{r})e^{-i\vec{K}\vec{r}}e^{i\vec{k}\vec{r}}e^{+i\vec{K}\vec{r}}\\ &= u'_{\vec{k}}(\vec{r})e^{i(\vec{k}+\vec{K})\vec{r}} \quad \text{with} \quad u'_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{-i\vec{K}\vec{r}}\end{aligned}$$

small auxiliary calculation

$$\begin{aligned}\underline{u'_{\vec{k}}(\vec{r})} &= u_{\vec{k}}(\vec{r})e^{-i\vec{K}\vec{r}} \quad \text{with} \quad u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})\\ &= u_{\vec{k}}(\vec{r}+\vec{R})e^{-i\vec{K}\vec{r}} \quad \text{with} \quad \vec{K}\vec{R} = 2\pi n\\ &= u_{\vec{k}}(\vec{r}+\vec{R})e^{-i\vec{K}(\vec{r}+\vec{R})} = \underline{u'_{\vec{k}}(\vec{r}+\vec{R})} \quad \text{and with} \quad u'_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{-i\vec{K}\vec{r}} := u_{\vec{k}+\vec{K}}(\vec{r})\end{aligned}$$

therefore

$$\boxed{\varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}+\vec{K}}(\vec{r})e^{i(\vec{k}+\vec{K})\vec{r}} = \varphi_{\vec{k}+\vec{K}}(\vec{r})}$$

Bloch waves 8 Comment 1

A very important property of Bloch waves is that they are periodic in the reciprocal lattice.

It is always possible to add a vector of the reciprocal lattice $\vec{K}$ to the wave vector of a Bloch wave.

This shows a small calculation.

The Bloch wave of the first line is multiplied by one in the second line, i.e. $1 = e^{-i\vec{K}\vec{r}}e^{+i\vec{K}\vec{r}}$.

In the third line the function $u_{\vec{k}}(\vec{r})e^{-i\vec{K}\vec{r}}$ is denoted by $u'_{\vec{k}}(\vec{r})$.

The little auxiliary calculation shows that $u'_{\vec{k}}(\vec{r})$ is also a periodic function in the crystal lattice, i.e. $u'_{\vec{k}}(\vec{r}) = u'_{\vec{k}}(\vec{r} + \vec{R})$.

Bloch waves 8

Comment 2

So the function $\varphi_{\vec{k}+\vec{K}}(\vec{r}) = u'_{\vec{k}}(\vec{r})e^{i(\vec{k}+\vec{K})\vec{r}}$ is also a Bloch wave according to the definition but now for the wave vector $\vec{k}+\vec{K}$.

This can be emphasized using the notation $u'_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{-i\vec{K}\vec{r}} := u_{\vec{k}+\vec{K}}(\vec{r})$ and the formula outlined in red.

The Bloch wave for the wave vector $\vec{k}+\vec{K}$ is identical to the Bloch wave for the wave vector $\vec{k}$, since this Bloch wave was simply multiplied by the number one, i.e. $1 = e^{-i\vec{K}\vec{r}}e^{+i\vec{K}\vec{r}}$.

Bloch waves are periodic functions in the reciprocal lattice.

But neither the vectors $\vec{k}$ nor the functions $u(\vec{r})$ are unique, i.e. $\vec{k} \to \vec{k}+\vec{K}$ and $u_{\vec{k}}(\vec{r}) \to u_{\vec{k}+\vec{K}}(\vec{r})$.

Bloch waves 9

Bloch waves are periodic functions in the reciprocal lattice

$$\underline{\varphi_{\vec{k}}(\vec{r}) = \varphi_{\vec{k}+\vec{K}}(\vec{r})}$$

the energy eigenvalues of the Schrödinger equation are therefore also periodic in the reciprocal lattice

$$\boxed{E(\vec{k}) = E(\vec{k}+\vec{K})}$$

the functions $E(\vec{k})$ are called energy bands and as with the phonons

$\hbar\vec{k}$ is a crystal-momentum

Bloch waves 9

Comment 1

The first underlined equation formulates the periodicity of the Bloch waves in the reciprocal lattice.

Due to the periodicity of the wave function in the reciprocal lattice, the energy eigenvalues of the Schrödinger equation in the reciprocal lattice are also periodic functions.

The functions of the energy eigenvalues $E(\vec{k})$ are called energy bands.

The $\vec{k}$ vectors that are necessary to describe electron waves in a crystal lattice can be restricted to a primitive unit cell of the reciprocal lattice.

Bloch waves 9

Comment 2

The wave vector $\vec{k}$ characterize the translation properties of the Bloch wave:

$$\varphi_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r}+\vec{R})e^{i\vec{k}(\vec{r}+\vec{R})} = u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{R}}e^{i\vec{k}\vec{r}} = e^{i\vec{k}\vec{R}}\varphi_{\vec{k}}(\vec{r}).$$

Because of $\vec{K}\vec{R} = n2\pi$ the proportionality factor $e^{i\vec{k}\vec{R}}$ characterizing the translation is the same for all vectors $\vec{k}+\vec{K}$.

As with the phonons, $\hbar\vec{k}$ of an electron in a crystal lattice is a crystal momentum. A vector of the reciprocal lattice can always be added without changing the energy and wave function of the electron.

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
- Hall effect of Aluminum
- Semiconductors
- Ferromagnetism
- Superconductivity

Quasi-free electrons in the sc-lattice

Energy bands and Fermi surfaces 1

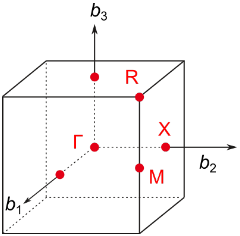
- Quasi-free electrons in the sc-lattice
- Sodium
- Copper
- Silicon

Quasi-free electrons in the sc-lattice 1

Consider an electron in a simple cubic lattice with nearly negligible potential energy

1st Brillouin zone of the sc lattice: $\vec{a}_1 = a\vec{e}_x,\ \vec{a}_2 = a\vec{e}_y,\ \vec{a}_3 = a\vec{e}_z$

and $\vec{b}_1 = \frac{2\pi}{V_{\text{cell}}}(\vec{a}_2 \times \vec{a}_3), \quad \vec{b}_2 = \frac{2\pi}{V_{\text{cell}}}(\vec{a}_3 \times \vec{a}_1), \quad \vec{b}_3 = \frac{2\pi}{V_{\text{cell}}}(\vec{a}_1 \times \vec{a}_2)$



$$\vec{b}_1 = \frac{2\pi}{a^3}(a\vec{e}_y \times a\vec{e}_z) = \frac{2\pi}{a}\vec{e}_x$$

$$\vec{b}_2 = \frac{2\pi}{a}\vec{e}_y$$

$$\vec{b}_3 = \frac{2\pi}{a}\vec{e}_z$$

Quasi-free electrons in the sc-lattice 1 Comment

As an example, consider an electron in a simple cubic lattice.

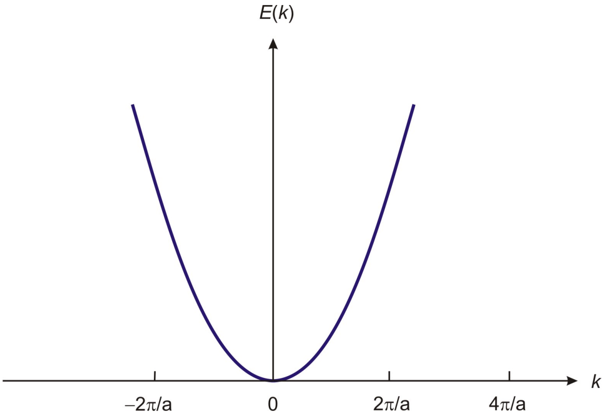
The figure shows the 1st Brillouin zone of a simple cubic lattice.

The basis vectors $\vec{b}_i$ of the reciprocal lattice are parallel to the basis vectors of the Bravais lattice $\vec{a}_i$.

The Bragg planes which enclose the 1st Brillouin zone intersect the basis vectors of the reciprocal lattice in the middle over a length of π/a away from the Γ point

Quasi-free electrons in the sc-lattice 2

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

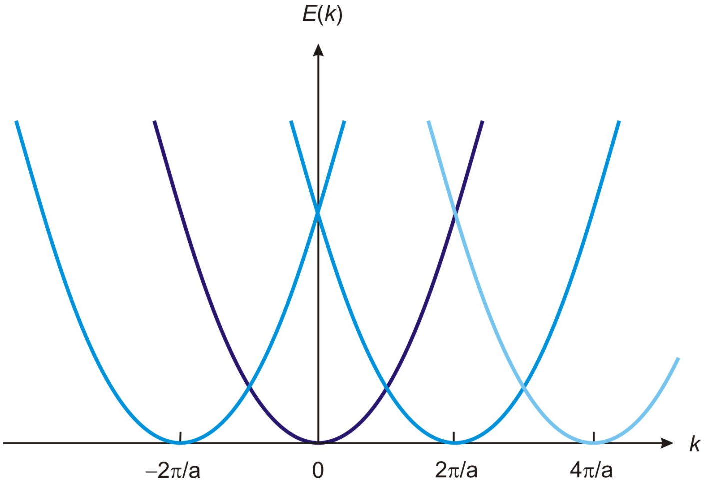


Quasi-free electrons in the sc-lattice 2 Comment

The figure shows the parabola of the kinetic energy of the free electrons e.g. along the *x*, *y*, or *z*-axis of the simple cubic lattice, when the influence of the crystal lattice can be completely neglected.

This is the situation of the Sommerfeld model.

Quasi-free electrons in the sc-lattice 3: periodic zone scheme



$\vec{k} \parallel \vec{b}_{1,2,\text{ or } 3}$

Quasi-free electrons in the sc-lattice 3 Comment

If the modulation of the potential energy is still small, but no longer completely negligible, the solution of the Schrödinger equation in a periodic potential must be considered.

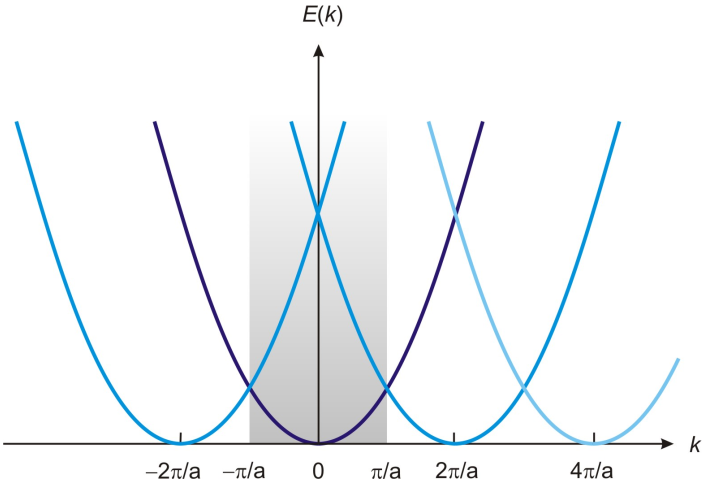
The energy is periodic in the reciprocal lattice, i.e. $E(\vec{k}) = E(\vec{k} + \vec{K})$.

The figure shows the resulting band structure if the k-vector is parallel to one of the basis vectors of the reciprocal lattice $\vec{b}_{1,2,3}$.

By adding reciprocal lattice vectors, the parabola of the kinetic energy is shifted.

This representation of the band structure is called the periodic zone scheme.

Quasi-free electrons in the sc-lattice 4: reduced zone scheme



Quasi-free electrons in the sc-lattice 4 Comment

The shaded area in the picture shows the band structure within the 1st Brillouin zone.

This section of the band structure is sufficient because the entire band structure results from the translation of the 1st Brillouin zone.

The representation of the band structure within the 1st Brillouin zone is called the reduced zone scheme.

Quasi-free electrons in the sc-lattice 5

periodic boundary conditions:

volume of a single *k* state

$$\frac{(2\pi)^3}{V}$$

volume of the 1st Brillouin zone is

$$\frac{(2\pi)^3}{V_{\text{Cell}}}$$

V_{Cell} volume of the primitive elementary cell of the Bravais lattice

- The number of *k* states in the 1st Brillouin zone equals the number of primitive unit cells of the crystal lattice

$$\frac{(2\pi)^3/V_{\text{Cell}}}{(2\pi^3)/V} = V/V_{\text{Cell}} = N$$

Quasi-free electrons in the sc-lattice 5 Comment 1

Since finite crystal lattices are always considered, periodic boundary conditions must also be used for the Bloch waves.

This works like with plane waves. Only the notation becomes complicated because coordinates adapted to the primitive unit cell have to be used.

The first formula underlined in red indicates the volume in k space that a wave vector can occupy.

V denotes the volume of the crystal.

The second formula underlined in red gives the volume of the 1st Brillouin zone.

For a simple cubic lattice, the formula $(2\pi)^3/a^3$ results.

Quasi-free electrons in the sc-lattice 5

Comment 2

Similar to the lattice vibrations, with the Bloch waves the total number of different wave vectors in the 1st Brillouin zone is equal to the number of primitive unit cells in the crystal lattice.

Due to the Pauli principle, each Bloch wave can be occupied by up to two electrons.

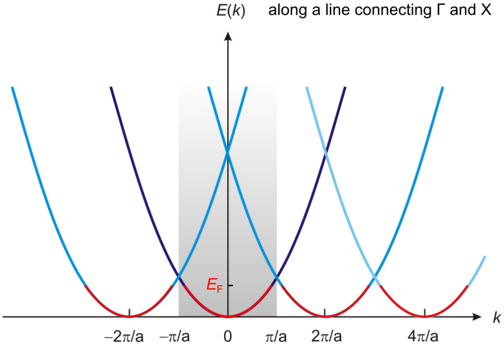
For example, if there is one atom per primitive unit cell and one electron is delocalized, half of the *k* states of the 1st Brillouin zone are occupied with electrons.

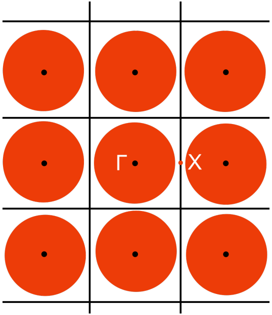
If two electrons are delocalized, all *k* states of the 1st Brillouin zone can be occupied by electrons.

Quasi-free electrons in the sc-lattice 6

one quasi-free electron per primitive unit cell of a simple cubic lattice

$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} = \frac{(3\pi^2)^{\frac{1}{3}}}{a} = \frac{3.09}{a} < \frac{\pi}{a}$$





Quasi-free electrons in the sc-lattice 6 Comment 1

If the influence of the periodicity of the potential energy is very small, the kinetic energy of the electrons $E(\vec{k}) = \hbar^2\vec{k}^2/2m$ remains almost unchanged.

As in the Sommerfeld model, the occupied k states at $T = 0$ are enclosed by the Fermi sphere.

The formula calculates the radius of the Fermi sphere for the case that there is one electron in a primitive cubic unit cell with the lattice parameter a.

The left figure shows the band structure of the Bloch waves for quasi-free electrons in the periodic zone scheme.

The wave vector $\vec{k}$ lies parallel to the connecting line between the Γ point and the X point of the 1st Brillouin zone.

Quasi-free electrons in the sc-lattice 6

Comment 2

The red marked area of the parabolas shows the occupied k states at $T = 0$.

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

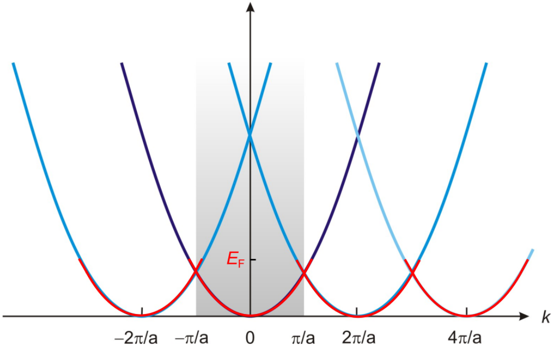
The red circular areas indicate the k states that are occupied at $T = 0$.

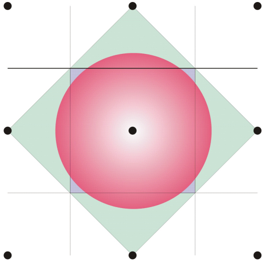
Quasi-free electrons in the sc-lattice 7

two electrons per primitive unit cell of a simple cubic lattice

$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} = \frac{(3\pi^2 \cdot 2)^{\frac{1}{3}}}{a} = \frac{3.9}{a} > \frac{\pi}{a}$$

$E(k)$ along a line connecting Γ and X





Quasi-free electrons in the sc-lattice 7 Comment

Now consider the case where there are two conduction electrons in the primitive unit cell of a simple cubic crystal lattice.

The formula calculates the radius of the Fermi sphere.

The left figure shows the band structure for quasi-free electrons in the periodic zone scheme.

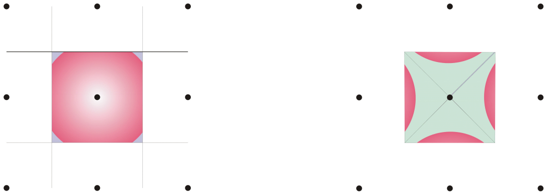
The wave vector $\vec{k}$ lies parallel to the connecting line between the Γ point and the X point of the 1st Brillouin zone.

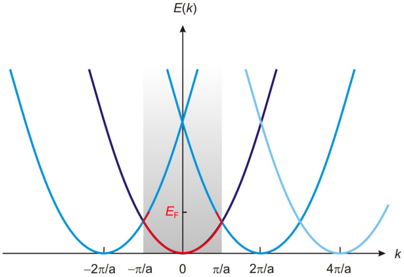
The parabolas drawn in red denote the occupied k states at $T = 0$.

The right figure now shows the Fermi sphere, which is partly in the 1st Brillouin zone and partly in the 2nd Brillouin zone.

Quasi-free electrons in the sc-lattice 8

the reduced zone scheme for two electrons per primitive unit cell of a simple cubic lattice





Quasi-free electrons in the sc-lattice 8

Comment 1

In the reduced zone scheme, only the 1st Brillouin zone is taken into account.

The left figure shows the part of the Fermi sphere that lies in the 1st Brillouin zone.

The middle figure shows the part of the Fermi sphere that lies in the 2nd Brillouin zone.

By adding a vector of the reciprocal lattice, the spherical segments are shifted into the 1st Brillouin zone.

The right figure shows the energy bands when the *k* vector points from the Γ point of the 1st Brillouin zone to the X point.

In the reduced zone scheme, only the area highlighted in gray is considered.

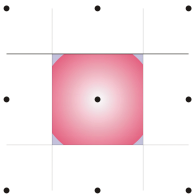
Quasi-free electrons in the sc-lattice 8 Comment 2

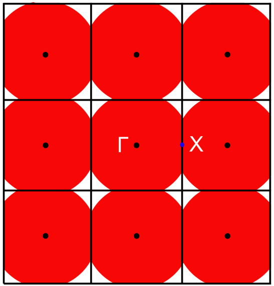
The occupied states are marked in red.

There is an energy band for the *k* states originally located in 1^{st} Brillouin zone and a second energy band for the *k* states shifted in 1^{st} Brillouin zone.

Quasi-free electrons in the sc-lattice 9

Fermi surfaces for two electrons per primitive unit cell of a simple cubic lattice





The occupied k states of the 1^{st} energy band in the reduced zone scheme (left) and the periodic zone scheme (right)

Quasi-free electrons in the sc-lattice 9 Comment

The left figure shows in the reduced zone scheme the occupied *k* states of the lowest energy band.

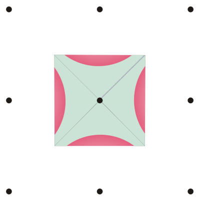
The right figure shows in the periodic zone scheme the occupied *k* states of the lowest energy band.

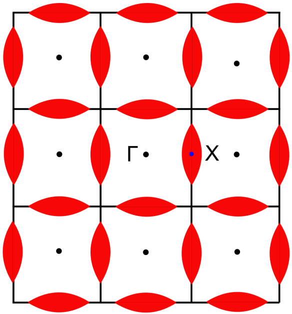
In the periodic zone scheme, the Fermi surface of the lowest energy band becomes visible.

The Fermi surface encloses the almost square white areas in which the *k* are unoccupied.

Quasi-free electrons in the sc-lattice 10

Fermi surfaces for two electrons per primitive unit cell of a simple cubic lattice





The occupied *k* states of the 2nd electron band in the reduced zone scheme (left) and the periodic zone scheme (right)

Quasi-free electrons in the sc-lattice 10 Comment

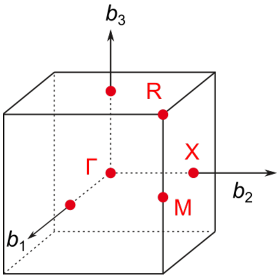
The left figure shows the occupied *k* states of the second energy band in the reduced zone scheme.

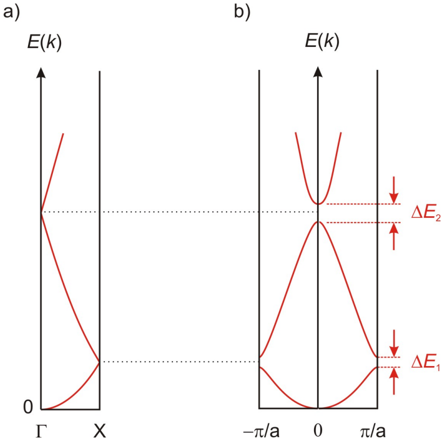
The right figure shows the occupied *k* states for this band in the periodic zone scheme.

The Fermi surface for this band encloses the surfaces drawn in red, which in three-dimensional space have the shape of a discus.

Quasi-free electrons in the sc-lattice 11

- energy gaps open at the intersection points of the energy bands
  $\rightarrow$ “avoided level crossing”





Quasi-free electrons in the sc-lattice 11 Comment 1

Energy gaps open when the periodicity of the potential energy is no longer negligibly small.

The figure on the left side shows the 1st Brillouin zone of the simple cubic lattice.

Figure a) on the right shows the band structure between the Γ point and X when the periodicity of the potential energy is negligibly small.

Figure b) shows what happens when the periodicity of the potential energy can no longer be neglected.

Energy gaps open at the intersection of the energy bands.

Energy bands and Fermi surfaces 11 Comment 2

It is a common feature of quantum mechanics that energy levels avoid crossing points.

The energy gaps increase with increasing periodic variation of the potential energy.

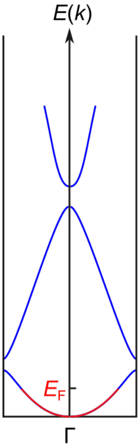
The energy gaps get bigger and the energy bands get narrower.

The stronger the periodic variation of the potential energy, the better the electrons are localized on their atoms and the narrower the energy bands are.

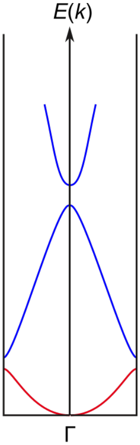
The width of an energy band indicates the mobility of the electrons.

The narrower a band, the better the electrons are localized on their atoms.

Quasi-free electrons in the sc-lattice 12



metal



insulator or semiconductor

Quasi-free electrons in the sc-lattice 12 Comment 1

The left figure illustrates the situation of a metal.

Not all *k* states of an energy band are occupied by two electrons.

Only a small amount of energy is required to excite electrons.

When an electric field is applied to the solid, an electric current flows and the solid is a metal.

The figure on the right shows the situation of an insulator.

If all *k* states of an energy band are occupied by two electrons, the excitation energy is determined by the smallest energy gap to the next higher energy band.

Quasi-free electrons in the sc-lattice 12 Comment 2

If this energy gap is much larger than the thermal energy at room temperature, no electric current can be induced by an applied electric field.

All electrons are blocked in their *k* states and the solid is an insulator.

The transition between an insulator and a semiconductor is gradual.

If the energy gap is small enough that electrons can be thermally excited at room temperature via the energy gap, one speaks of a semiconductor or semi-metal if the energy gap is even smaller.

When the temperature is lowered, the conductivity of these materials becomes lower because the number of excited electrons also becomes smaller.

Quasi-free electrons in the sc-lattice 12 Comment 3

This is in contrast to metals, where the electrical resistance is determined by electron-phonon scattering.

The conductivity of metals increases with decreasing temperature, as electron-phonon scattering freezes out.

The requirement that all *k* states of an energy band must be occupied for an insulator, however, applies to the entire 1st Brillouin zone.

In the cubic model system with two conduction electrons within the primitive unit cell considered at the beginning, the lowest band is metallic, since there are unoccupied states for this band in the 1st Brillouin zone.

Usually there is an energy gap between the bands, which can cause the electrons of the 2nd band to migrate to the lowest band and fill the free *k* states.

Quasi-free electrons in the sc-lattice 12

Comment 4

If the number of conduction electrons in the primitive unit cell is even, all *k* states of the occupied energy bands can be completely occupied by electrons and there is a good chance that the solid is an insulator.

Revision

Summary in Questions

1. How is the density of states of an electron gas defined?
2. Calculate the density of states at the Fermi energy of copper.
3. Explain why the heat capacity of an electron gas is proportional to temperature.
4. Give the definition of a Bloch wave.
5. The k-vector of a Bloch wave is sometimes called a crystal- or quasi-momentum. Why?
6. How many different wave k-vectors are there within the 1st Brillouin zone.
7. 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.
8. Calculate the Fermi wave number k_F when 3 electrons are in the primitive unit cell of the simple cubic lattice.
9. Sketch the Fermi surfaces for the 2nd and 3rd energy band in the reduced and periodic zone scheme.