Solids

Electrons in crystal lattices

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

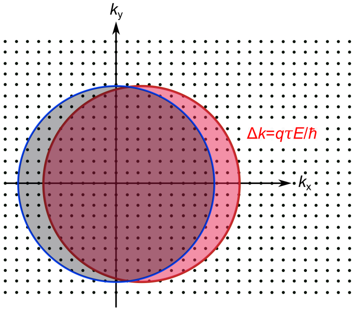
Electric conductivity

Sommerfeld model

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

Electric conductivity 1

drift velocity: $\vec{v} = \mu \vec{E}$ $\rightarrow$ shift of the Fermi sphere $\Delta \vec{k} = \frac{m\vec{v}}{\hbar} = \frac{m\mu}{\hbar}\vec{E}$



estimate of the shift:

$\mu = 4.4 \cdot 10^{-3}\,\mathrm{m^2V^{-1}s^{-1}}$ for copper and
$E = 100\,\mathrm{V/m}$

$$\Delta k = \frac{2\pi\,500 \cdot 10^3\,\mathrm{eV}\,4.4 \cdot 10^{-3}\,\mathrm{m^2V^{-1}s^{-1}}}{4.14 \cdot 10^{-15}\,\mathrm{eVs}\,(3 \cdot 10^8\,\mathrm{ms^{-1}})^2} 100\,\mathrm{V/m}$$
$$= 3710\,\mathrm{m^{-1}} <<<< k_\mathrm{F} \approx 10^{10}\,\mathrm{m^{-1}}$$

(electron mass $m \approx 500\,\mathrm{keV}/c^2$)

Electric conductivity 1 Comment 1

When an electric field is applied to a conductor, the charge carriers begin to drift along the direction of the electric field.

The drift velocity shifts the Fermi sphere somewhat along the direction of the electric field.

The sketch shows, greatly exaggerated, the displacement of the Fermi sphere when the electric field is applied in the x direction.

In the figure, the black dots denote the *k* states.

The blue circle indicates the Fermi sphere when no electric field is applied.

The red circle indicates the Fermi sphere when an electric field is applied.

Electric conductivity 1 Comment 2

Most electron waves have a counter wave and only a small part of the occupied k states near the Fermi surface on the right side of the Fermi sphere can contribute to the transport of the electric charge.

The drift velocity can be calculated from the electrical mobility μ and the electric field strength E.

The displacement of the Fermi sphere in k space can be calculated with the momentum mv.

The calculation shows the estimate based on the mobility μ of copper and a field strength of 100 V/m.

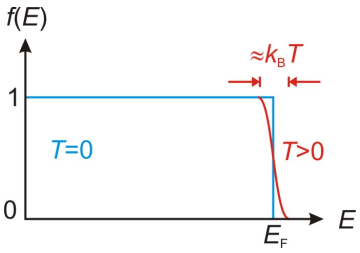
For the calculation it is assumed that the mass of the charge carriers corresponds to the mass of a free electron, i.e. $500\,\mathrm{eV}/\mathrm{c}^2$.

Electric conductivity 1 Comment 3

This assumption is only approximately fulfilled for copper, but this has no influence on the result of the estimate.

The displacement of the Fermi sphere due to the drift speed of the electrons in an electric field is about 6 orders of magnitude smaller than the Fermi wave number k_F.

Electric conductivity 2



Thermal softening of the Fermi surface

$$E = \hbar^2 k^2/2m \quad \rightarrow \quad \frac{\Delta E}{E} = 2\frac{\Delta k}{k}$$

with $\Delta E = k_B T$, $T = 300\,\mathrm{K}$, $E = E_\mathrm{F} = 7\,\mathrm{eV}$ (copper) and $k = k_F$

$$\begin{aligned}\Delta k_F &= k_F \frac{1}{2}\frac{k_B T}{E_F}\\ &= k_F \frac{8.62 \cdot 10^{-5}\,\mathrm{eVK^{-1}} \cdot 300\,\mathrm{K}}{2 \cdot 7\,\mathrm{eV}}\\ &= k_F \cdot 1.85 \cdot 10^{-3}\end{aligned}$$

$$\Delta k_F = 1.36 \cdot 10^{10}\,\mathrm{m^{-1}} \cdot 1.85 \cdot 10^{-3} \approx 2.5 \cdot 10^{7}\,\mathrm{m^{-1}} >> \Delta k \approx 3.7 \cdot 10^{3}\,\mathrm{m^{-1}}$$

Electric conductivity 2 Comment

The figure shows once again the influence of temperature on the Fermi distribution function, greatly exaggerated.

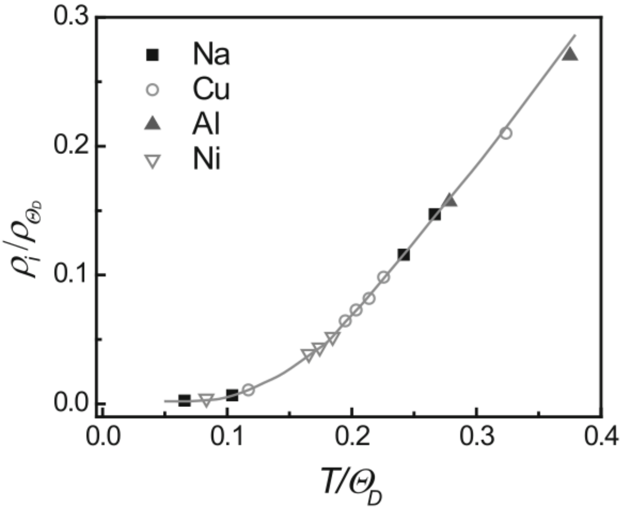
In the case of Fermi energy, the step of the distribution function softens in an energy range that corresponds to thermal energy.

In this way, the softening of the Fermi surface in the wavenumber space can also be estimated.

Since the thermal energy at room temperature is about a thousandth of the Fermi energy, the surface of the Fermi sphere is also smeared in this order of magnitude in the wavenumber space.

The estimate for copper shows that the displacement of the Fermi sphere by an electric field is generally much smaller than the thermal smearing of the Fermi surface.

Electric conductivity 3



Electric conductivity 3 Comment

The temperature dependence of the specific resistance of the metals follows a universal curve if the temperature is normalized to the Debye temperature Θ_D and the specific resistance to a suitable value.

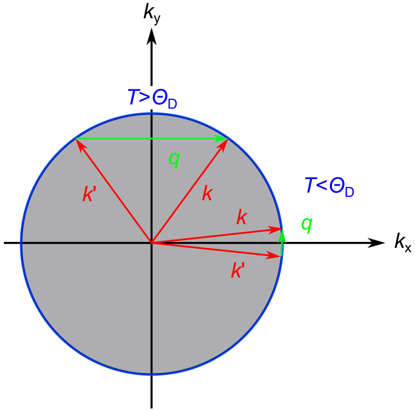
The temperature dependence is essentially determined by the fact that the conduction electrons can absorb and emit phonons.

In addition, there is a temperature-independent component that arises from the scattering of the conduction electrons at imperfections, i.e. impurity atoms and other lattice defects.

This contribution determines the temperature-independent resistance at low temperatures, which is subtracted in the figure.

Electric conductivity 4

electron-phonon scattering $\vec{k} = \vec{k}' \pm \vec{q}$ and $E(\vec{k}) = E(\vec{k}') \pm \hbar\omega(\vec{q})$



- Only electrons in the range of the Fermi surface participate in the scattering
- $E(\vec{k}), E(\vec{k}') >>> \hbar\omega(\vec{q})$, i.e. quasi elastic scattering
- the scattering rate is proportional to the phonon number

$$\bar{n} = \frac{1}{\exp(\hbar\omega(\vec{q})/k_B T) - 1}$$

Electric conductivity 4 Comment 1

The temperature dependence of the electric resistance is due to electron-phonon scattering

In the first line the law of momentum and energy conservation for the emission (+) and absorption (-) of a phonon by a conduction electron is formulated.

Only electrons can take part in the scattering processes whose wave vectors $\vec{k}$ lie in the thermally softened area around the Fermi surface.

The energy of the phonon is always very much smaller than the Fermi energy of the electrons.

Therefore, the electron-phonon scattering is quasi-elastic.

The influence of electron-phonon scattering on the electrical resistance depends on the number of phonons.

Electric conductivity 4 Comment 2

Therefore, it can be expected that the electrical resistance decreases with decreasing temperature.

The figure outlines two scattering processes.

In one scattering process there is a large angle between the wave vectors of the electrons, in the other scattering process the angle is small.

If the temperature is higher than the Debye temperature, then all phonon modes within the 1^{st} Brillouin zone are excited.

Since the dimensions of the Fermi sphere roughly correspond to the dimensions of the 1^{st} Brillouin zone, the scattering with phonons at the edge of the 1^{st} Brillouin zone can lead to large scattering angles.

Electric conductivity 4 Comment 3

Such scattering processes hinder effectively the charge transport and increase the electrical resistance.

For $k_B T >> \hbar_{\max}$, i.e. $T > \Theta_D$, $\bar{n}$ is proportional to temperature, which explains the linear increase in electrical resistance with temperature, i.e. $\rho \propto T$.

If the temperature is much lower than the Debye temperature, only acoustic phonons in the vicinity of the Γ point can be excited.

These phonons have a small momentum and therefore cannot change the direction of propagation of the electron wave significantly.

For this reason, the influence of the electron-phonon scattering on the electrical resistance becomes very small when the temperature is much lower than the Debye temperature and vanishes for $T \to 0$.

Electric conductivity 4 Comment 4

Remark on the temperature dependence of the electrical resistance at low temperatures.

The temperature dependence of the heat capacity of the crystal lattices is simply proportional to the number of phonons at low temperatures, i.e $\propto T^3$.

The temperature dependence of electrical resistance is quite complicated at low temperatures.

At low temperatures only small-angle scattering is possible and the number of phonons is proportional to q^2. Compare the figure: It is not the phonons inside a sphere with the radius q that contribute, only phonons on a circular disk with the radius q contribute because of energy and momentum conservation.

The electron-phonon coupling is proportional to q for small q-values. Electrons can more easily excite lattice vibrations with short than with long wavelengths.

Electric conductivity 4 Comment 5

The scattering theory shows that the influence of forward scattering is proportional to q^2

Since $q_{\text{max}} \propto T$ one expects a low temperature dependence $\propto T^5$.

Density of states

Sommerfeld model 3

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

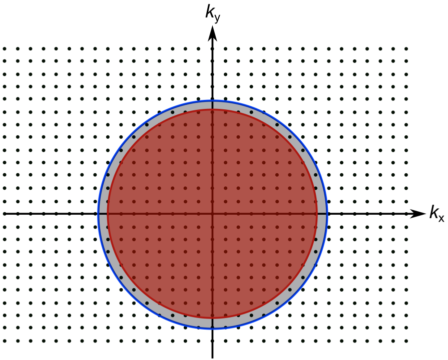
Density of states 1

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

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

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

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

Density of states 2 Comment

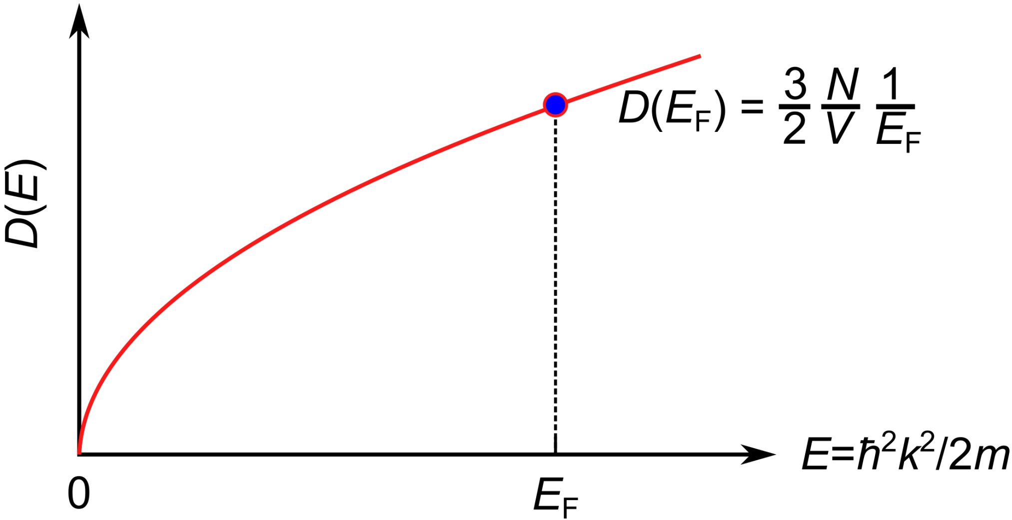
The density of states can easily be calculated for the Fermi sphere of the Sommerfeld model.

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



$$D(E_F) = \frac{3}{2}\frac{N}{V}\frac{1}{E_F}$$

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 $D(E_F)$ is proportional to the density of the conduction electrons and inversely proportional to the Fermi energy.

Heat capacity of the electron gas

Sommerfeld model 4

- 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 o 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.

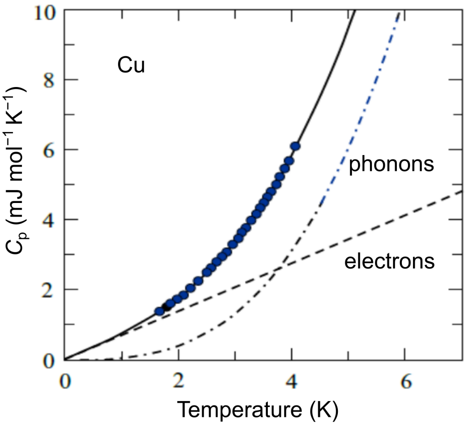
The constant of proportionality between the heat capacity of the electron gas and the temperature is denoted by γ.

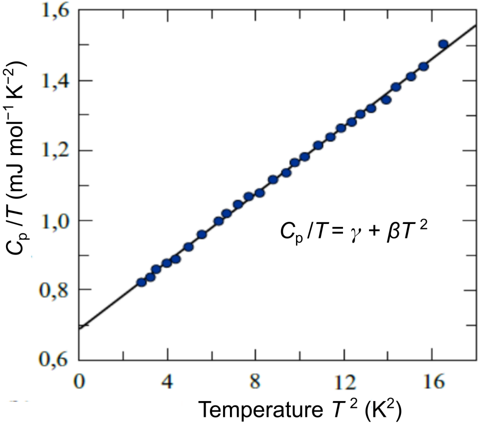
The second equation outlined in red gives the heat capacity of a metal at low temperatures.

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 the last lecture.

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.

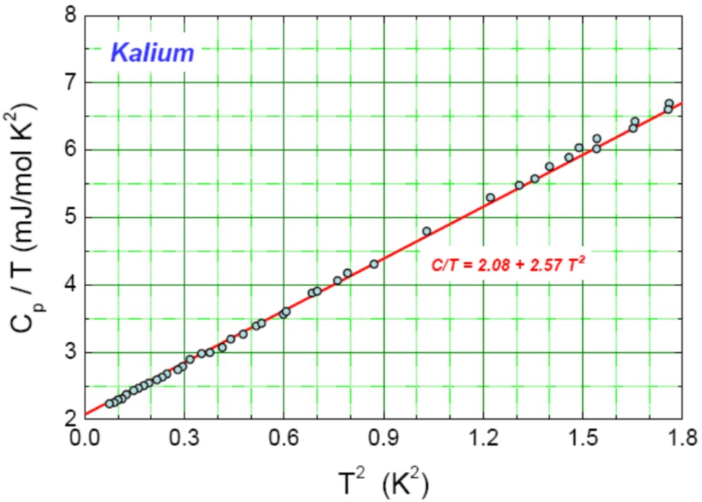
Heat capacity of the electron gas 3 Comment 3

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 $C = Nk_\mathrm{B}\frac{12\pi^4}{5}(\frac{T}{\Theta_\mathrm{D}})^3$ 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

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

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

$$\gamma = 6\cdot 10^{-23}\,\mathrm{mol}^{-1}\frac{\pi^2}{2}\frac{(8.617\cdot 10^{-5})^2\,\mathrm{eV\,K^{-2}}}{7\,\mathrm{eV}}1.6\cdot 10^{-19}\,\mathrm{AsV} = \underline{0.5\,\mathrm{mJ\,mol^{-1}\,K^{-2}}}$$

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

$$\gamma = 6\cdot 10^{-23}\,\mathrm{mol}^{-1}\frac{\pi^2}{2}\frac{(8.617\cdot 10^{-5})^2\,\mathrm{eV\,K^{-2}}}{2.12\,\mathrm{eV}}1.6\cdot 10^{-19}\,\mathrm{AsV} = \underline{1.66\,\mathrm{mJ\,mol^{-1}\,K^{-2}}}$$

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 thermal electron mass m^*

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

	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 systematically underestimates the value of γ.

The measurements show that the density of states in the Fermi energy is greater for all substances than can be expected from the Sommerfeld model.

Since the density of states according to the Sommerfeld model is proportional to the mass of the charge carriers, instead of the mass of a free electron m_e, an effective mass m^* is introduced, which describes the increased γ values.

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 electron mass m_e.

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 value of γ is remarkably large.

Since electrons are fermions and electrons have to be involved in some way in transporting the charge, substances like $CeAl_3$ called heavy fermion compounds.

Heat capacity of the electron gas 6 — Comment 3

The reason for the increased density of states at the Fermi energy lies in the interaction of the conduction electrons with the crystal lattice.

The interaction between the conduction electrons and the crystal lattice is neglected in the Sommerfeld model.

The effects of the interaction of the conduction electrons with the (static) crystal lattice were explained in 1929 by Rudolf Peierls in collaboration with Heisenberg, Sommerfeld and Pauli.

The theory is so fundamental that it is simply referred to as the semiclassical model of electron dynamics.

Revision

Summary in Questions

1. Why is the Debye temperature a characteristic temperature for the electrical resistance of a metal?
2. What is the displacement of the Fermi sphere when an electric field strength of 1000 V/m is applied to a metal?
3. How is the density of states of an electron gas defined?
4. Calculate the density of states at the Fermi energy of copper.
5. Explain why the heat capacity of an electron gas is proportional to temperature.