8. FREE ELECTRON THEORY.

Aim: To introduce the free electron model for the physical properties of metals. It is the simplest theory for these materials, but still gives a very good description of many properties of metals which depend on the dynamics of the electrons.

We assume a free electron gas in the metals. The "ions", i.e atomic nuclei with inner electrons (in closed shells) are immersed in a gas of freely moving conduction electrons. This assumption works best for the simple metals, i.e. the alkali metals (Li, Na, K...), but also for the noble metals and Al.

How can the electrons be considered as free? 1. We will see later that matter waves can propagate freely in a periodic structure (lattice). 2. Electron-electron interactions are effectively screened due to the high density of electrons. 3. The Pauli principle also acts to diminish electron-electron scattering.
The most important scattering mechanism for the electrons is instead from the phonons (lattice vibrations).

1. Basics of the free electron model (K p. 134-141).

We assume that the electrons move in a box potential, i.e. the potential in the metal is taken to be zero and ∞ outside of the metal (an infinite barrier at the surface). We also employ the **independent electron approximation**. This means that each electron is considered to move independently of the others. We now proceed as follows:

a) Solve the Schrödinger equation for one electron. From that we find the **orbitals**, which are defined as solutions for a system of one electron.

b) Boundary conditions may be fixed, K p. 134-135 ($\psi=0$ at the surfaces of the metal), but as usual in solid state physics we may choose periodic boundary conditions (K p. 137). From the periodic boundary conditions we obtain the set of k-values that are allowed. The procedure is the same as the one we earlier applied for the lattice vibrations.

The general solution of the free electron Schrödinger equation is a plane wave, $\psi_\mathbf{k}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})$.

c) The components of $\mathbf{k}$, together with the spin quantum number specify the different energy levels. The Pauli principle says that we can only have two electrons, one with each spin, in each energy level. We now fill the obtained energy levels with conduction electrons, starting from the lowest one. At T=0 the energy of the highest filled level is called **the Fermi energy**, ε_F. At higher temperature, the occupancy of the levels is smeared out around the Fermi level, in accordance with **the Fermi-Dirac distribution** (K p. 136-137).

d) Next we compute the energy as a function of k (the dispersion relation of this problem), $\varepsilon(\mathbf{k})$, as well as other basic quantities like the Fermi velocity and Fermi temperature (K p. 138-141). The density of electron states as a function of energy $D(\varepsilon)$, can be obtained by a procedure rather similar to the one used for the Debye model before. It can be expressed either by eq. (20) or eq. (21) in K p. 140-141.

From K eq. (21), we can as a special case obtain the density of states at the Fermi energy as:

$$D(\varepsilon_F) = 3N / 2\varepsilon_F ,$$

where N is the number of electrons. For numerical estimates one may also conveniently express the density of states per atom by replacing N with the number of conduction electrons per atom N_0 and the volume V by the volume per atom, Ω. Hence the electron density can be expressed as $n = N/V = N_0/\Omega$.

Below we illustrate how the distribution in energy of the conduction electrons is obtained from the product of the density of states, $D(\varepsilon)$, and the Fermi-Dirac distribution (adapted from Myers).
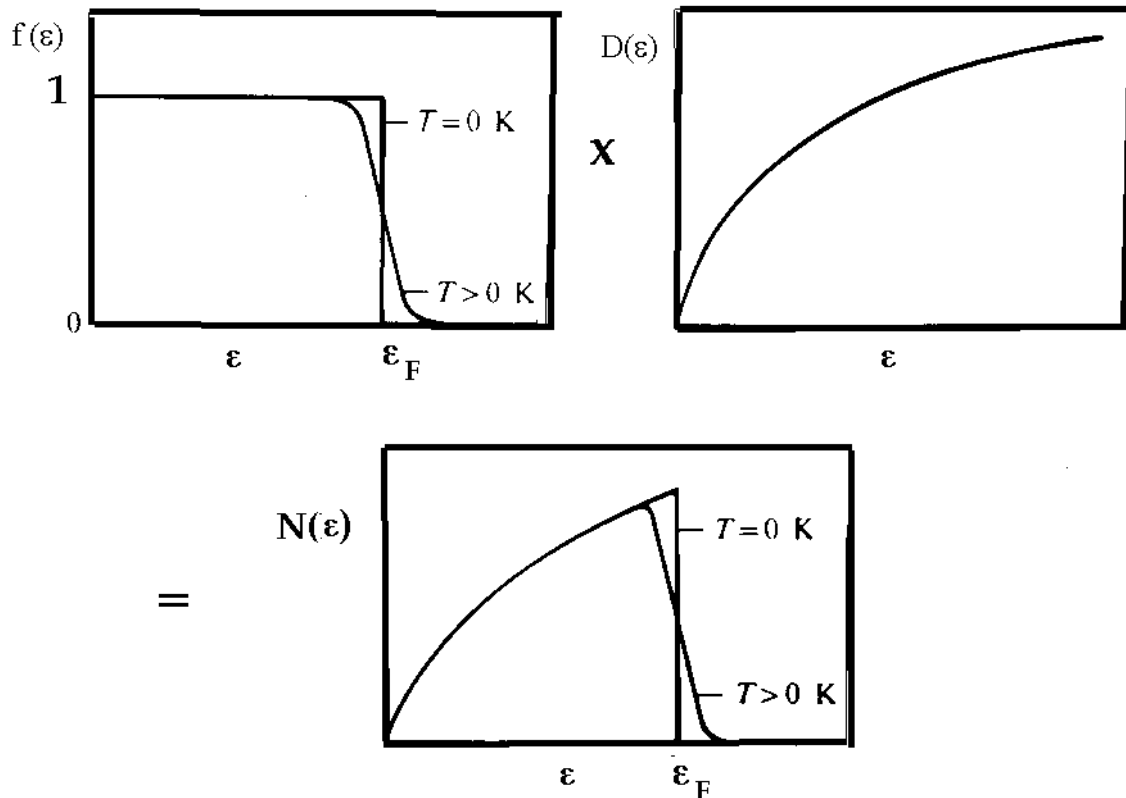
How large is the electron density of states?

Example: Al has three conduction electrons per atom and a Fermi energy of 11.6 eV. The relation above directly gives $D(\varepsilon_F) = 0.39$ eV^{-1} atom^{-1}. On the other hand one mole of Al (a macroscopic solid) has, at the Fermi energy, $2.34 \ 10^{23}$ levels per eV with an average spacing of $4.3 \ 10^{-24}$ eV. Hence the energy levels of a macroscopic metal are so close ("quasicontinuous" and certainly broadened in reality) that they must be viewed as a continuous energy band.

2. Electronic heat capacity (K p. 141-147).

In metals, the free electrons give a contribution to the heat capacity, in addition to that of the lattice vibrations. The total energy of the electron gas is obtained by integrating over the electron energy distribution (see figure above), and the derivative with respect to temperature gives the electronic heat capacity. The contributing electrons are those that can be excited to an empty state at temperature T. They are within an interval $\pm K_B T$ of the Fermi energy. In this interval the density

of states is approximately equal to its value at the Fermi energy and the Fermi-Dirac function is 1/2. Each electron is excited by the thermal energy $3K_BT/2$. The resulting heat capacity becomes

$$C = 3 K_B^2 D(\varepsilon_F) T,$$

which is very close to the result of a more rigorous calculation (K p.142-144).

The figure shows the heat capacity divided by T as a function of the square of T for a typical insulator, KCl, and for a metal, Cu. The insulator has only a contribution from the lattice vibrations; at these low temperatures the Debye T^3-law is obeyed. The metal has an electronic contribution in addition to the one from the lattice vibrations. It is seen from the intersection of the curve with the y-axis. The electronic contribution is linearly dependent on T, as expected.

The proportionality constant, γ, is tabulated on p. 146. The deviation of the experimental values from the free electron ones are taken into account by introducing a **thermal effective mass** of the conduction electrons. Note that $\gamma \sim D(\varepsilon_F) \sim 1/\varepsilon_F \sim m$. The effective mass may be lower or higher than the electron mass depending on if the experimentally observed γ is lower or higher than the free electron value.
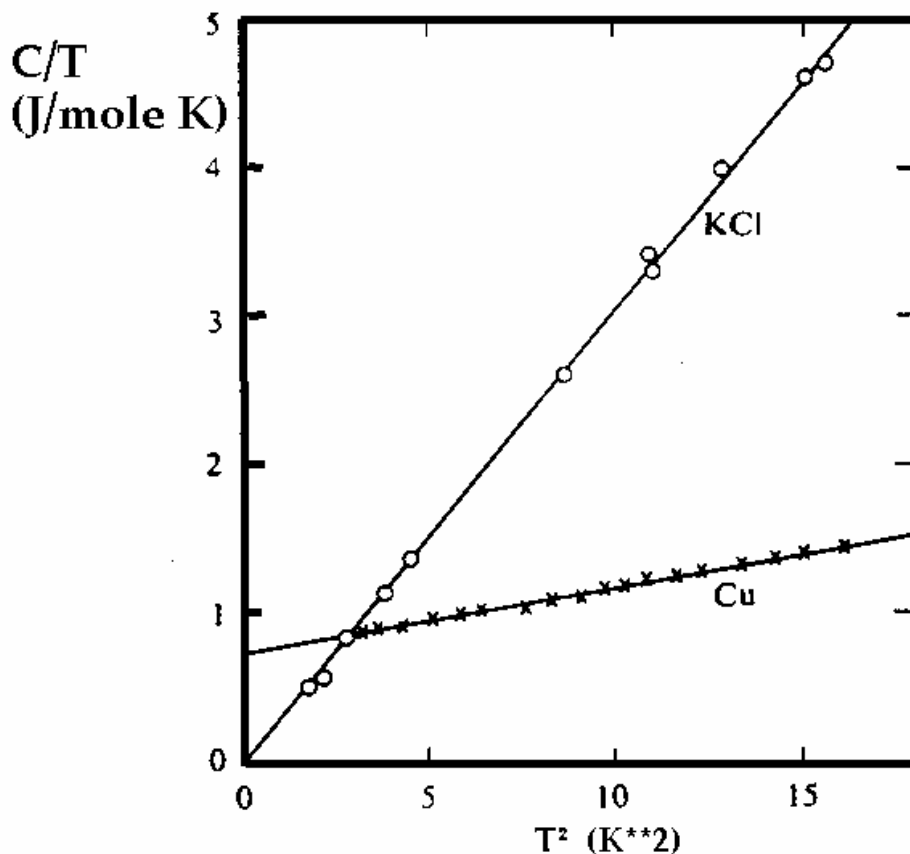
3. Electrical properties (K p. 147-156).

The high electrical conductivity of metals is a direct consequence of the relatively free motion of the electrons.

a) The equation of motion of the free electrons under the force due to applied electric (**E**) and magnetic (**B**) fields can easily be written down, eq (39), p. 147. Restricting ourselves to the case of electrical fields, it is found that the Fermi sphere is moving with constant velocity in k-space. This means that the electron velocity increases indefinitely.

b) This is not possible in reality. It is evident that scattering processes limit the electron velocity and hence the electrical conductivity of metals. The most important ones are collisions of the electrons with phonons, impurities and defects. The scattering is described by a **relaxation time**, τ. The **mean free path** is equal to the Fermi velocity times the relaxation time. A viscous term must be introduced in the equation of motion, which becomes:

$$m\, d\mathbf{v}/dt + m\mathbf{v}/\tau = -e\mathbf{E}.$$

The stationary state in a constant field is obtained by putting the first term equal to zero. The electrical conductivity is obtained from:

$\sigma = -ne\mathbf{v}/\mathbf{E}$, where n is the electron concentration.

c) **Matthiessen's rule** states that the contribution of different scattering processes to the resistivity are additive. The figure below (adapted from Myers) illustrates the general behaviour of the resistivity of metals. At high temperature scattering by phonons dominates. The phonon concentration is approximately proportional to temperature (Planck's law), and hence so is the collision rate, $1/\tau$. This leads to a resistivity proportional to T. At low temperatures the resistivity approaches a constant value. This is due to scattering from impurities, defects etc, whose concentration is independent of temperature. This is illustrated in the right figure for silver with two impurity concentrations.

Potassium (K)

Silver (Ag)

0.5 at% Au

0.02 at% Sn

Ag
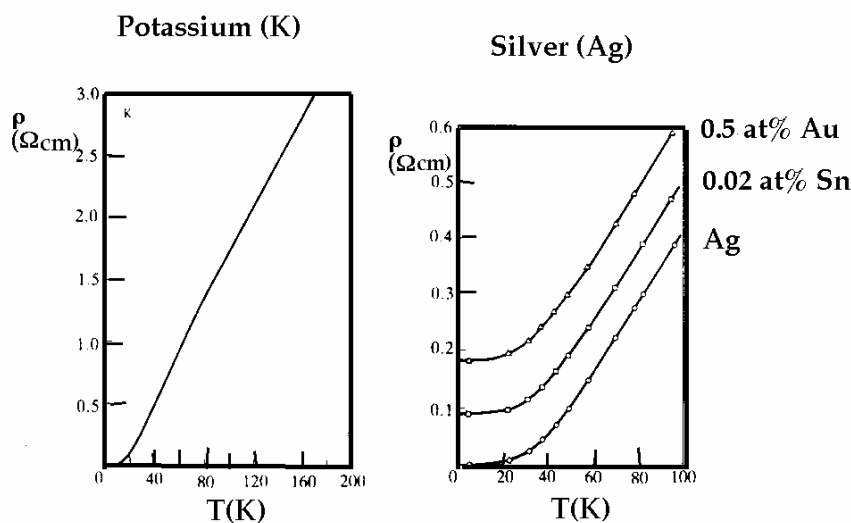
4. Electron motion in magnetic fields (K p. 152-156).

We now have to solve the equation of motion taking into account both applied electric and magnetic fields. As discussed above a collision term also has to be included. We only consider a special case in which the magnetic field is directed along the z-axis. The equation of motion can be separated into one equation for each of the three directions, x, y and z. The movement is circular in the x-y plane with the **cyclotron frequency** $\omega_c = eB/m$. To this is added a linear drift in the direction of the **E**-field.

An application of this theory is the **Hall effect**. In a rod-shaped sample a current (current density J) is flowing in the x-direction and a magnetic field is applied in the z-direction. The charge carriers are forced by the magnetic field to deflect in the (negative) y-direction. The sides of the rod in the y-direction will be oppositely charged and this sets up a transverse **Hall field** in the y-direction. This field is directed in the negative y-direction for negative charge carriers (electrons) and in the positive y-direction in the case of positive charge carriers. The Hall coefficient is given by

$R_H = E_y/J_x B = 1/nq$.

This is hence negative for free electrons, since they have negative charge q=-e. Hall measurements allow one to determine the sign of the charge carriers and their density, n. In Table 4, p. 155, it is seen that the free electron model is good for many simple metals. However, in some cases the Hall coefficient is positive, suggesting positive charge carriers. This is a signal of a breakdown of the free electron model and we need to go into the energy band theory of metals to understand this behaviour.

5. Thermal conductivity of metals (K p. 156-157).

In pure metals the electrons make the dominant contribution to the thermal conductivity. The expression is analogous to that for the phonon contribution and follows from kinetic gas theory. The difference is that we have to use the electronic contribution to the specific heat as well as the Fermi velocity. It is found that the ratio of thermal and electric conductivities is proportional to temperature in the free electron model. This is the **Wiedemann-Franz law.** It is in good agreement with experimental data in a region above the Debye temperature, where the thermal conductivity is almost independent of temperature. This is often at room temperature and above; here the Wiedemann-Franz law is quite good as seen from the Table in K p. 157. The **Lorentz number,** $K/\sigma T$, of many metals is close to this theory at ambient temperatures and above.

The figure below shows a qualitative picture of the temperature dependence of the thermal conductivity of a metal. Just as for the electrical conductivity, phonon scattering of the electrons dominates except at low temperatures. At temperatures above θ_D, the number of phonons is proportional to T, the mean free path $l \sim T^{-1}$, and hence the thermal conductivity of metals becomes constant. At lower temperatures considerably below θ_D, the fraction of excited phonon modes scales as $(T/\theta_D)^3$ (see the Debye sphere), and hence $l \sim T^{-3}$, and $K \sim T^{-2}$. At very low temperatures both the thermal and electrical conductivity are limited by scattering by defects, impurities etc. Here the electrical conductivity is constant, the thermal conductivity is $\sim T$ and the Wiedemann-Franz law is again applicable.

The thermal conductivity of Cu is about 400 W/m K at room temperature and at the maximum at low temperatures of the order 5000 W/m K. Metals have a higher thermal conductivity than most

insulators (not diamond!) at room temperature, but at the low temperature peak in insulators values of the order of 20000 W/m K can be found.