

4.2 Quantum Theory of Free Electrons in Metals

In accordance with the model of free electrons, the valence electrons of a metal can move freely inside it. They cause the electric conduction and are called the *conduction electrons*. Assume that the form of a sample is a cube with the edge L . Taking into account that the potential energy is zero (electrons are free), the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) \quad (4.39)$$

The solution can be chosen as follows:

$$\psi(\mathbf{r}) = Ce^{i\mathbf{k}\cdot\mathbf{r}}, \quad (4.40)$$

$\mathbf{k} = \mathbf{p}/\hbar$ is a wave vector related to energy by the expression (1.4). The normalization condition:

$$\int \psi\psi^* dV = CC^* \int dV = C^*CL^3 = 1, \quad (4.41)$$

Integration is made through entire volume of a sample. Thus, $C = 1/L^{3/2}$ and:

$$\psi(\mathbf{r}) = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (4.42)$$

The wave function follows the border condition:

$$\psi(x+L, y, z) = \psi(x, y, z) \quad (4.43)$$

It leads to:

$$\left. \begin{aligned} k_x &= (2\pi n_x/L) \\ k_y &= (2\pi n_y/L) \\ k_z &= (2\pi n_z/L) \end{aligned} \right\}, \quad (4.44)$$

n_x, n_y и n_z – positive or negative integers. Components of \mathbf{k} are the quantum numbers. Introducing quantity (4.44) into equation (4.42) leads to:

$$\psi = \frac{1}{L^{3/2}} \exp\left[i \frac{2\pi}{L} (n_x x + n_y y + n_z z) \right]. \quad (4.45)$$

Thus, the wave vector is quantified. Hence, the energy of the conduction electrons is quantified too. Introducing equation (4.44) into formula (1.4) we get allowed energies of the proper states with the wave vector \mathbf{k} .

$$E_k = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \quad (4.46)$$

The wave vector \mathbf{k} and the spin number $s = \pm 1/2$ characterize the state of a conduction electron. Hence, the state is characterized by four quantum numbers: n_x, n_y, n_z , and s . The sum of squares of the quantum numbers n_i determines the electron energy. A number of combination of quantum numbers (except when $n_x = n_y = n_z = 0$) may correspond to the same energy. That number is called the *degeneration degree* and the energy levels are called the *degenerated levels*. The degeneration degree increases with energy. Analogously to the wave vector space introduce the space of quantum numbers, which axes correspond to the numbers n_x, n_y, n_z . In that space every point correspond to a pair of states (differing by spin). The surface of equal energy is a sphere of the radius

$n^* = \sqrt{n_x^2 + n_y^2 + n_z^2}$. The number of states (ν_E) with the energy less than E [equation (4.46)] is twice greater than the number of points inside the sphere of the radius n^* . The point density is a unit. Thus:

$$\nu_E = 2 \cdot \frac{4}{3} \pi n^{*3} = \frac{8}{3} (n_x^2 + n_y^2 + n_z^2)^{3/2}. \quad (4.47)$$

Combining equation (4.46) and (4.47) we get:

$$\nu_E = \frac{8}{3} \pi \left(\frac{2m}{\hbar^2} \right)^{3/2} \left(\frac{L}{2\pi} \right)^3 E^{3/2} = \frac{8}{3} \pi V \frac{(2m)^{3/2}}{(2\pi\hbar)^3} E^{3/2}. \quad (4.48)$$

It follows from equation (4.48):

$$d\nu_E = 4\pi V \frac{(2m)^{3/2}}{(2\pi\hbar)^3} E^{1/2} dE. \quad (4.49)$$

$d\nu_E$ is a quantity of states inside the energy interval from E up to $E + dE$.

Hence, the density of states $g(E) = d\nu/dE$, i.e. the number of states per the unique energy interval:

$$g(E) = 4\pi V \frac{(2m)^{3/2}}{(2\pi\hbar)^3} E^{1/2}. \quad (4.50)$$

Let n be the number of free electrons per unit volume, then nV is the total number of electrons. According to exclusive principle at zero temperature, all the lowest levels with energy $E_F(0)$ would be filled, the levels with $E \gg E_F(0)$ would be vacant. The quantity $E_F(0)$ is called the *Fermi energy* at zero temperature. The Fermi level (E_F) is a parameter in electron distribution. It weakly depends on temperature. Parameter Fermi is an energy at which the probability for an electron to be in the given state is one half. A quantity $E_F(0)$ is the magnitude of E_F at $T = 0\text{K}$.

The state of conduction electron is characterized by the wave number \mathbf{k} and spin quantum number $s = \pm 1/2$. Hence, the state is characterized by four quantum numbers: n_x, n_y, n_z , and s . The energy of an electron depends on the sum of the squares of quantum numbers n_i . A number of combinations of quantum numbers correspond to the single sum of their squares. Hence, the levels are degenerated. The degree of degeneration increases with energy.

The surface of the same energy E_F in k -space (or p -space) is called the *Fermi surface*. For free electrons, that surface is described by equation:

$$E_F = \frac{\hbar^2 k^2}{2m} \quad (4.51)$$

Thus, the Fermi surface (4.51) is a sphere. At zero temperature, the Fermi surface is a border between the occupied and vacant levels.

The quantity $E_F(0)$ can be evaluated. Introduce $\nu_E = nV$ in formula (4.48):

$$\nu_E = \frac{8}{3} \pi V \frac{(2m)^{3/2}}{(2\pi\hbar)^3} [E_F(0)]^{3/2}. \quad (4.52)$$

Hence:

$$E_F(0) = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}. \quad (4.53)$$

The conduction electron concentration is 10^{22} - 10^{23} cm^{-3} , thus $E_F(0) = 5\text{eV}$.

Let us find the mean energy of electrons at the temperature of absolute zero. The energy of electrons, which fill the states in the energy interval from E up to $E+dE$ is:

$$Edv_E = Eg(E)dE. \quad (4.54)$$

The total energy of all conduction electrons can be estimated as follows:

$$\int Edv_E = \int_0^{E_F(0)} Eg(E)dE. \quad (4.55)$$

Dividing that quantity by the entire number of electrons $\int g(E)dE$, we get the mean energy of an electron:

$$\langle E \rangle = \frac{\int_0^{E_F(0)} Eg(E)dE}{\int_0^{E_F(0)} g(E)dE}. \quad (4.56)$$

Taking into account the expression $g(E)$ (4.12):

$$\langle E \rangle = \frac{\int_0^{E_F(0)} E^{3/2} dE}{\int_0^{E_F(0)} E^{1/2} dE} = \frac{3}{5} E_F(0). \quad (4.57)$$

When the quantity $E_F(0)$ is about 5eV, the average energy of conduction electrons at the temperature of absolute zero is about 3eV. It is rather a great magnitude. The temperature of a classical electron gas with such energy should be about 25 thousands of degrees.

It is clear why the heat capacity of an electron gas at room temperatures is small. The mean energy of an electron at the room temperature is 0.025eV. The quantum of that energy can excite only electrons of the highest levels close to Fermi level. The main part of electrons of the deep levels remains in initial states and would absorb energy while heating.

Thus, only small part of conduction electrons participates in heat process, and that is the reason why the heat capacity of electrons in metal is small.

In Fig.4.3 the function (4.50) is shown. The dashed area corresponds to the number of states filled at the absolute zero. The heating is accompanied by transition of electrons from the levels close to Fermi level on the higher levels [higher than $E_F(0)$].

As a result, the edge of the dashed figure is not sharp. The dashed

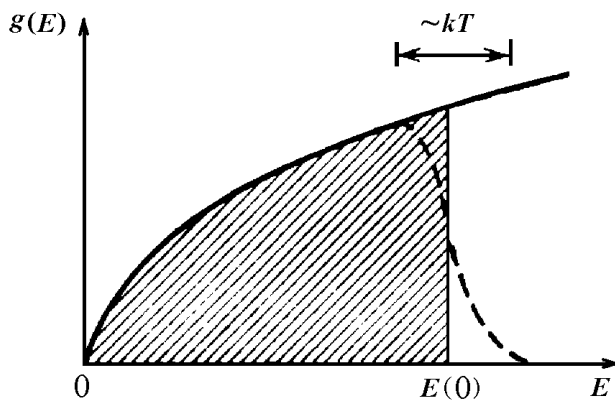


Fig.4.3. The electron state density as function of energy in model of free electrons. The dashed curve corresponds

the distribution curve. The area down that curve is identical with the

initial one at the absolute zero (the area is nV). The width of that region is about kT . Thus, a fraction of electrons of order of T/T_F takes part in a heat process.

$$T = \frac{E_F(0)}{k} \quad (4.58)$$

That quantity is called the *Fermi temperature*. As a result, the electron heat capacity is:

$$C_{el} \approx C_{class} \frac{T}{T_F} \quad (4.59)$$

At room temperature, that quantum quantity is about 100 times smaller than the classical one ($T \approx 300\text{K}$, $T_F \approx 25\,000\text{K}$).

4.4 Fermi-Dirac Statistics

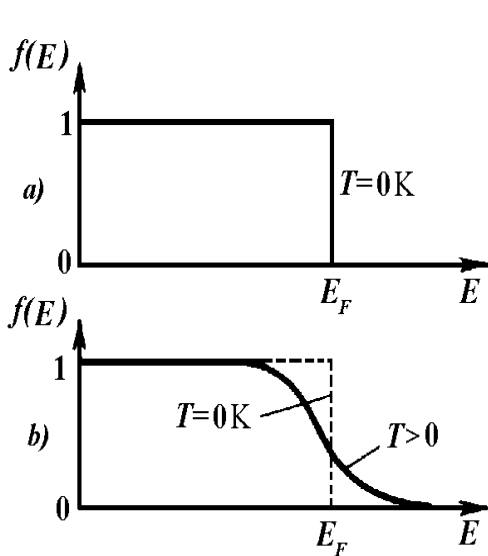


Fig.4.4. Fermi distribution.

At absolute zero in each state with $E_F(0)$ there is an electron. There are no electrons in the states with $E > E_F(0)$. Hence, at an absolute zero, the energy distribution is of the form shown in Fig. 4.4a. Let us find the distribution function at a temperature, which is not zero. In order to do it, discuss the non-elastic collisions of electrons with the impurity atom introduced inside a crystalline metallic lattice. The two possible energy states designate by the indices 0 and ε . Assume that an electron transmits from the state \mathbf{k} with energy E into the state \mathbf{k}' with energy $E + \varepsilon$. The impurity

atom transits from the state ε to the zero level. The probability $P_{\mathbf{k}\mathbf{k}'}$ of the transition $\mathbf{k}(E) \rightarrow \mathbf{k}'(E + \varepsilon)$ is proportional: 1) probability $f(E)$ that the electron occupies the state $\mathbf{k}(E)$, 2) probability $[1 - f(E + \varepsilon)]$ that the state $\mathbf{k}'(E + \varepsilon)$ is free 3) probability $p(\varepsilon)$ that the atom is in the state ε . Thus:

$$P_{\mathbf{k}\mathbf{k}'} \sim f(E)[1 - f(E + \varepsilon)]p(\varepsilon) \quad (4.60)$$

The probability $P_{\mathbf{k}'\mathbf{k}}$ of the inverse process is proportional to:

$$P_{\mathbf{k}'\mathbf{k}} \sim f(E + \varepsilon)[1 - f(E)]p(0) \quad (4.61)$$

$p(0)$ is the probability that the impurity atom is in zero state.

In accordance with the principle of detailed balancing, the proportionality coefficient in equation (4.60) and (4.61) is identical. In an equilibrium state, the probability of transitions $\mathbf{k} \rightarrow \mathbf{k}'$ and $\mathbf{k}' \rightarrow \mathbf{k}$ is the same:

$$f(E)[1 - f(E + \varepsilon)]p(\varepsilon) = f(E + \varepsilon)[1 - f(E)]p(0), \quad (4.62)$$

Hence:

$$\frac{f(E + \varepsilon)}{1 - f(E + \varepsilon)} \cdot \frac{1 - f(E)}{f(E)} = \frac{p(\varepsilon)}{p(0)} = e^{-\varepsilon/k_B T}, \quad (4.63)$$

We assumed that the probabilities for an impurity atom to be on the level 0 and ε follows the Boltzmann distribution.

The functional equation (4.63) holds at any temperature if

$$\frac{1-f(E)}{f(E)} = e^{(E-\mu)/k_B T}, \quad (4.64)$$

The parameter μ does not depend on E . Hence:

$$\frac{f(E+\varepsilon)}{1-f(E+\varepsilon)} = e^{-[(E+\varepsilon)-\mu]/k_B T}, \quad (4.65)$$

The product of these two equations at any temperature equals $e^{-\varepsilon/k_B T}$.
The solution of (4.68) lads to:

$$f(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1}, \quad (4.66)$$

That function is called the *FermiDirac distribution*. Parameter μ is called the *chemical potential*. The quantity $f(E_i)$ represents the average number of electrons $\langle n_i \rangle$ in the state with energy E_i . Equation (4.66) can be written as follows:

$$\langle n_i \rangle = \frac{1}{\exp\left(\frac{E_i - \mu}{k_B T}\right) + 1}. \quad (4.67)$$

The distribution (4.67) is the basic one of Fermi-Dirac statistics. The particles, which follow that statistics, are called *fermions*. Their spin is half integer. They obey the exclusion principle.

Parameter μ and E_F are identical, and are called the *Fermi level* or the *Fermi energy*. We can write:

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}. \quad (4.68)$$

From formula (4.68) it follows that at absolute zero:

$$f(E) = 1, \quad \text{если } E < E_F,$$

$$f(E) = 0, \quad \text{если } E > E_F.$$

Thus, at 0 K the Fermi level E_F is the upper occupied level $E_F(0)$ (see Fig.4.4a).

When $E = E_F$ function $f(E) = 1/2$, i.e. the probability of occupation of Fermi level is 50%.

In a unit crystalline volume the electron density can be given as follows:

$$n = \int_0^{\infty} g(E)f(E)dE. \quad (4.69)$$

Apparently it is a normalization condition for a function $f(E)$. Introducing (4.50) and (4.68) into (4.60) we get:

$$n = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\infty} \frac{E^{1/2} dE}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \quad (4.70)$$

Thus, E_F as function of T and n can be found. If all states below the Fermi level $E_F(0)$, can be considered to be occupied then we write:

$$n = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F(0) \int_0^{E_F(0)} E^{1/2} dE = \frac{1}{2\pi^2} \left(\frac{2mE_F(0)}{\hbar^2} \right)^{3/2}, \quad (4.71)$$

Numerically:

$$n = 4.55 \cdot 10^{27} (E_F(0))^{3/2} \text{ m}^{-3}, \quad (4.72)$$

The energy expressed in electron volts. In a metal there are about 10^{28} free electrons per 1 m^3 , thus the Fermi energy in accordance with (4.5) is several electron volts.

The integral (4.70) is of the type of Fermi-Dirac integrals.

$$F_j(y_0) = \int_0^\infty \frac{y^j dy}{1 + \exp(y - y_0)}. \quad (4.73)$$

Those integrals can not be expressed in terms of elementary functions for an arbitrary y_0 , but there are their asymptotic representations for great negative and great positive y_0 . Besides, those integrals are tabulated.

The Fermi energies at arbitrary and zero temperature are related by:

$$E_F \approx E_F(0) \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F(0)} \right)^2 \right]. \quad (4.74)$$

Inspection of equation (4,74) shows that at low temperature, the Fermi levels practically do not depend on temperature. Thus in many applications we can assume that $E_F = E_F(0)$. It should be noted that for thermoelectric phenomena, the dependence E_F on T is principal.

The function (4.30) is shown in Fig.4.4b. A glance at equation (4.30) shows that when $E = E_F$, $f_F(E) = 1/2$, i.e. the occupation probability is 50%. If $E > E_F$ then $f_F(E) < 1/2$, and if $E < E_F$, then $f_F(E) > 1/2$.

When the temperature is increasing the 'step' of function $f_F(E)$ becomes more sloping (Fig.4.4b). Let us make a comparison between the quantum distribution $f_F(E)$ and the classic distribution:

$$f_{M-B}(E, T) = A e^{-E/k_B T}, \quad (4.75)$$

Assume that $E - E_F \gg k_B T$. Not taking into account the unit in the denominator of the equation (4.69) we get:

$$f(E) \Big|_{E-E_F \gg k_B T} \approx \text{const.} \cdot e^{-\frac{E-E_F}{k_B T}} \quad (4.76)$$

Comparison of formula (4.79) and (4.80) leads to the conclusion that if $E - E_F \gg k_B T$ the classic distribution function can be used.

The behavior of an electron gas depends on the ratio between the temperature of a crystal and the Fermi temperature E_F/k_B . Two situations are distinguished.

1. $E_F \gg k_B T$. A gas is called the *degenerated gas*. 2. $E_F \ll k_B T$. The gas is called *non-degenerated*.

The Fermi temperature is about several scores of thousands degrees. Hence even at melting temperature ($\sim 10^3 \text{ K}$), the electron gas should be considered as degenerated. In semiconductors, the free electron density is appreciably less than in metals. Hence, the

quantity E_F is small (E_F is approximately proportional $n^{2/3}$). Thus, at room temperature, the electron gas in semiconductors is not degenerated and follows the classical statistics.

4.5 Sommerfeld Model

Sommerfeld applied the quantum equations for the density states (4.50) and distribution function (4.68). Only electrons with the energy close to the Fermi level were supposed to produce conductivity. The Boltzmann kinetic equation was the basis of the theory. The main result was as follows [compare with (4.32)].

$$\sigma = \frac{-4\pi e^2}{3m} \int_0^\infty \lambda v^2 \left(\frac{\partial f_0}{\partial v} \right) dv = \frac{-8\pi e^2}{3m^2} \int_0^\infty \lambda E \left(\frac{\partial f_0}{\partial E} \right) dE \quad (4.77)$$

The distribution function is normalized in the way analogue equation (4.20).

$$f_0 = \frac{2(m/2\pi\hbar)^3}{1 + \exp\left(\frac{mv^2 - 2E_F}{2k_B T}\right)} = 2(m/2\pi\hbar)^3 f(E), \quad (4.78)$$

$f(E)$ – the occupation probability (4.68). Introducing (4.78) into (4.77), we can write the electric conductivity as follows:

$$\sigma = \frac{-2e^2 m}{3\pi^2 \hbar^3} \int_0^\infty \lambda E \left(\frac{\partial f(E)}{\partial E} \right) dE = \frac{-ne^2}{mv(E_F)} \int_0^\infty \frac{\lambda E}{E_F} \left(\frac{\partial f(E)}{\partial E} \right) dE \quad (4.79)$$

That equation is got using equation (4.77) and expression for the electron velocity when the energy of the last is the Fermi energy: $v(E_F) = (2E_F/m)^{1/2}$.

The quantity df/dE for small and great energy is zero. Thus, the integrand is not a zero only in the interval of several quantities $k_B T$ near the Fermi level E_F . The function $f(E)$ and its derivative are shown in Fig.4.5. The maximal magnitude of the derivative is $(-1/4k_B T)$ when $E = E_F$. Taking into account that the function (df/dE) can be considered as delta-function, we can assume that for an arbitrary not too fast function $\beta(E)$:

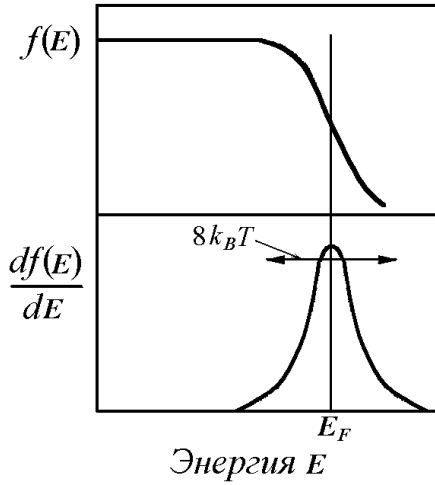


Fig.4.5 The energy dependence of the Fermi-Dirac distribution

$$-\int_0^{\infty} \beta(E) \left(\frac{\partial f(E)}{\partial E} \right) dE = \beta(E) \quad (4.80)$$

Hence, the equation

$$-\int_0^{\infty} \frac{\lambda E}{E_F} \left(\frac{\partial f(E)}{\partial E} \right) dE = \lambda(E_F) \quad (4.81)$$

is the mean path of an electron with the Fermi energy. Introducing equation (4.81) into (4.79), we get:

$$\sigma = \frac{-ne^2 \lambda(E_F)}{mv(E_F)} \quad (4.82)$$

It is convenient to use the time of free path between two subsequent collisions. For electrons moving with the speed corresponding the Fermi energy:

$$\tau = \lambda(E_F)/v(E_F) \quad (4.83)$$

The electric conductivity:

$$\sigma = \frac{-ne^2 \tau}{m}, \quad (4.84)$$

The expression (4.84) coincides with that one gotten by Drude.

At the assumption that there are no collisions, the external electric field displaces uniformly all points of the Fermi sphere in \mathbf{k} -space. The electrons can collide with impurities, defects, and phonons but the Fermi sphere holds its displaced position in the external field (Fig.4.6).

The external electric field diminishes the population of the thin curved region of the \mathbf{k} -space and populates the mirror symmetric zone on the opposite side of the occupied part of the Fermi sphere.

All states with the changing population correspond to the energies close to the Fermi energy. Thus according to Sommerfeld, not all-free electrons produce the electric conductivity. The number of *conducting electrons* with the energy close to the Fermi level is essentially less. The Sommerfeld approximation leads to electron heat conductivity and the Lorenz number $(\pi^2 k_B^2 / 3e^2)$, which are in good agreement with experimental data. In analogue way, Sommerfeld got the solution of the Boltzmann equation for magnetic resistance, galvanic magnetic and thermal electric phenomena in strongly degenerated electron gas. These solutions are available for simple and complex metallic crystals.

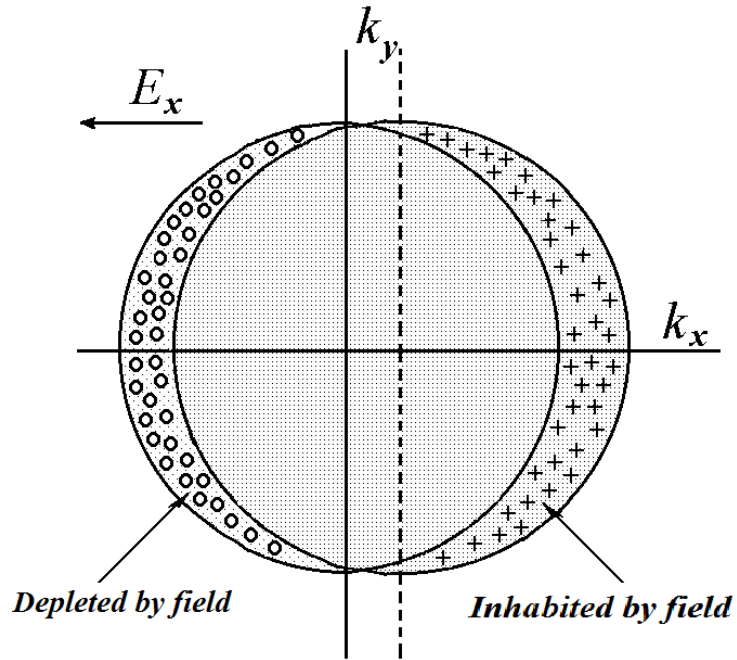


Fig.4.6. An electric field displaces the occupied region in the wave vector space. When there is no field, the occupied region is a sphere. Its center is located at the origin of coordinate frame. That sphere is called the Fermi sphere. The electric field transmits the Fermi sphere as a whole at a distance, which depends on $\lambda(E_F)$. There can be other forms of the Fermi surface.