4. Electrons in Metals

The metallic type of conductivity is known long ago and has been deeply studied but the role of electron dynamics was understood only recently. The models of free electrons explain many properties of metals. In these models, the electrons are supposed to leave their atoms and form the gas of free electrons.

The periodicity of the crystalline lattice is of importance. Indeed, the periodic electrostatic electric field essentially affects the relation between the energy of an electron and its momentum. Consideration of that field leads to a zone theory of solids. The theory made it possible to understand the properties of semiconductors and dielectrics.

The theories of metals are founded on assumption that electrons are independent and follow the Fermi-Dirac statistics.

4.1 Properties of Metals

The theoretical models are founded on well-known experimental results.

1. The Ohm law is true in metals at isothermal condition.

$$\mathbf{J} = \sigma\mathbf{E}, \tag{4.1}$$

σ [$Om^{-1}m^{-1}$] - the specific conductivity; **J** [A/m^2] – the current density; **E** [V/m] – the electric field strength.

2. The metal is an excellent electric conductor. It should be noted that electric conductivity of an insulator is of order 10^{-16} $Om^{-1}m^{-1}$, the electric conductivity of a semiconductor is in the interval from 10^{-4} $Om^{-1}m^{-1}$ up 10^{5} $Om^{-1}m^{-1}$, but the electric conductivity of metals is 10^{6} - 10^{8} $Om^{-1}m^{-1}$ [6].

3. The heat conductivity of a metal (κ) is great. A good heat conductor is a good electric conductor at the same time. In 1853 Wiedemann and Franz found that the ratio of heat conductivity (κ) and electric conductivity (σ) is the same for different metals (the Wiedemann-Franz law). At room temperature, κ does not depend on temperature, but σ does depend on temperature as T^{-1} (Fig.4.1, copper). The ratio

$$L \equiv \kappa / \sigma T \tag{4.2}$$

is called the *Lorenz number* (Table 4.1 [1]).

Table 4.1. Specific electric conductivity and Lorenz number of metals

	T = 100 K		T = 273 K		T = 373 K	
	σ,$Om^{-1}m^{-1}$, $\times 10^{8}$	L, $(W/K)^2$ $\times 10^{-8}$	σ, $Om^{-1}m^{-1}$, $\times 10^{8}$	L, $(W/K)^2$ $\times 10^{-8}$	σ,$Om^{-1}m^{-1}$, $\times 10^{8}$	L, $(W/K)^2$ $\times 10^{-8}$
Au	1.6	2.0	0.5	2.4	0.35	2.43
Al	2.1	1.5	0.4	2.2	0.23	2.21
Cd	4.3	2.1	0.15	2.4	0.1	2.43
Cu	2.9	1.9	0.65	2.3	0.43	2.33
Fe	8.0	3.1	0.11	2.8	0.06	2.85
Pb	0.15	2.0	0.052	2.5	0.036	2.56
W	9.8	2.8	0.21	2.1	0.16	3.20

4. If a metal is cooled below certain temperature (which depends on θ_D), the increasing of κ and σ is observed. For copper (Fig.4.1) and some one-valence metals at the steepest part of the curve, the electric conductivity is proportional to T^{-5}.

5. At certain low temperature, the electric conductivity reaches the state of saturation. It is due to impurities and lattice defects. The *specific electric resistance* ρ (Om·m) of many metals follows the *Matticene rule*. In accordance with that rule, the resistance (caused by impurities and defects) is identical for all metals and does not depend on temperature.

$$\rho = \rho_L(T) + \rho_{def.}, \qquad (4.3)$$

$\rho_L(T)$ - the component of the specific resistance produced by heat oscillation of atomic lattice, $\rho_{def.}$ - the component produced by the scattering of electrons on defects. The contribution of $\rho_{def.}$ is observed at very low temperature because $\rho_L(T)$ tends to zero when $T \to 0$ K.

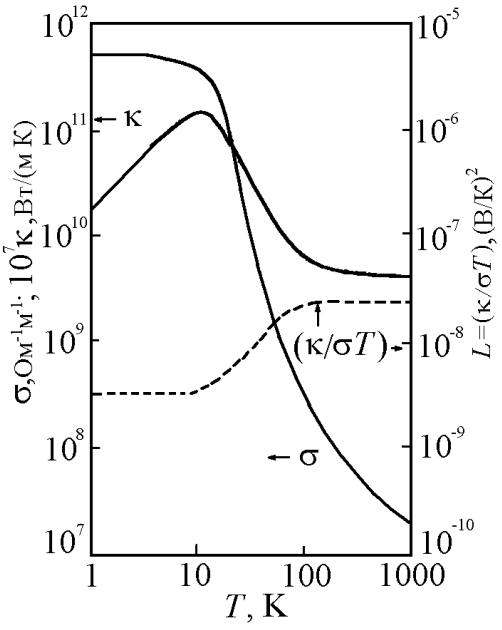

Fig.4.1 The temperature dependence of electric conductivity σ and electron conductivity κ of the copper

6. Magnetic phenomena in ferromagnetic metals and alloys affect the specific electric resistance.

7. About half of metals become the super conductors at low temperature.

8. The specific heat capacity of the free electron gas is small. It is proportional to temperature. The magnetic sensitivity is also small and does not depend on temperature.

9. When there is a combination of electric, magnetic, and temperature fields, a number of thermal, galvanic, and magnetic phenomena are produced (for example, the temperature gradient can generate the electric current or potential difference).

10. In very pure mono-crystals, the strong magnetic fields produce the orientation effects with an oscillation dependence on the magnetic field strength.

4.2. Classic Theory of Free Electrons

The theory is based on the Maxwell-Bolzmann velocity distribution. The motion of electrons is subdivided into two components. The first component describes the chaotic (thermal) motion of electrons. The average thermal velocity is zero. The average heat speed is not a zero. The second component describes the drift motion, which is produced by an electric field or by the gradient of temperature.

4.2.1 The Drude-Lorenz Model of Electric Conduction

In electric field, besides the chaotic motion of electrons there is an oriented motion, which is called the *drift*. Thus, the drift produces the oriented translation of electric charges i.e. the electric current. The average drift velocity $\langle \mathbf{v}_d \rangle$ depends on the electric field strength **E** and on the scattering of electrons by the crystalline lattice. The

influence of a lattice can be interpreted as the resistance force, which is proportional to the electron speed. The density of electric current is:

$$\mathbf{j} = en\langle \mathbf{v}_d \rangle , \tag{4.4}$$

e – elementary charge, n – electron concentration. The field acts upon an electron with a force $e\mathbf{E}$. The scattering of electrons by the lattice is considered as elastic. The mass of an electron is small in comparison with that one of an atom; the fraction of energy lost in a single collision is small too. Assume that the retarding force acting on electron is proportional to the mass and velocity of the particle. Thus, the motion equation can be written as follows:

$$m\frac{d\mathbf{v}}{dt} = e\mathbf{E} - \frac{m\mathbf{v}}{\tau}, \tag{4.5}$$

m – electron mass; $\mathbf{v}$ – electron speed; $e\mathbf{E}$ – the electric force acting upon an electron $\frac{m\mathbf{v}}{\tau}$ - retarding force; dimension of τ is time.

Equation (4.5) is non-uniform equation of the first order. The solution of the uniform equation

$$\frac{d\mathbf{v}}{dt} + \frac{\mathbf{v}}{\tau} = 0 . \tag{4.6}$$

Can be chosen as

$$\mathbf{v}(t) = \mathbf{C}e^{-t/\tau} . \tag{4.7}$$

$\mathbf{C}$ – a vector constant found from the initial condition. The partial solution of equation (4.5) is found easily: $\mathbf{v}_1 = \frac{e\tau\mathbf{E}}{m}$. Thus, the general solution:

$$\mathbf{v}(t) = \mathbf{C}e^{-t/\tau} + \frac{e\tau\mathbf{E}}{m} \tag{4.8}$$

The initial condition is $\mathbf{v}(0) = 0$. Thus, the electric field is switched in at the zero time moment:

$$\mathbf{C} = -\frac{e\tau\mathbf{E}}{m} \tag{4.9}$$

$$\mathbf{v}(t) = \frac{e\tau\mathbf{E}}{m}\left(1 - e^{-t/\tau}\right) \tag{4.10}$$

It follows from (4.10) that at $t >> \tau$, the velocity tends to its limit $e\tau\mathbf{E}/m$. We can write:

$$\mathbf{v}_\mathrm{d} = \mathbf{v}(t)\big|_{t>>\tau} = \frac{e\tau\mathbf{E}}{m} \tag{4.10a}$$

To evaluate the relaxation time (τ), Ohm's law is of use: $\mathbf{j} = en\mathbf{v}_\mathrm{d} = en\frac{e\tau\mathbf{E}}{m} = \frac{e^2 n\tau}{m}\mathbf{E} = \sigma\mathbf{E}$. It leads to:

$$\sigma = \frac{e^2 n\tau}{m} . \tag{4.11}$$

The numerical calculation shows that the relaxation time is about 10^{-13} s.

We remind our readers that the relaxation time is the time interval when the stationary state of electron motion is produced.

If the electric field is switched off at zero moment, the equation (4.5) under condition

$$\mathbf{E}(t) = \begin{cases} \mathbf{E} \; npu \; t < 0 \\ 0 \; npu \; t < 0 \end{cases} \tag{4.12}$$

Can be transformed as follows:

$$m\frac{d\mathbf{v}}{dt} = -\frac{m\mathbf{v}}{\tau}. \tag{4.13}$$

Taking into account the initial condition: $\mathbf{v}(0) = \mathbf{v}_{\mathrm{d}} = \frac{e\tau\mathbf{E}}{m}$ we write the solution as:

$$\mathbf{v}(t) = \frac{e\tau\mathbf{E}}{m}e^{-t/\tau} \tag{4.14}$$

It means that after the electric field **E** is switched in, the average speed of electrons (hence, the electric current density **j**) is changing in accordance with: $\mathbf{j}(t) = \mathbf{j}_0 e^{-t/\tau}$.

The relaxation time is an important characteristic of a conducting substance. According to the Drude theory, the relaxation time and the time of free path are identical.

In order to describe the electric conduction, it is very convenient to introduce a quantity (4.15), which is called the *drift mobility*:

$$\mu = \frac{\mathbf{v}_{\mathrm{d}}}{\mathbf{E}} = \frac{e\tau}{m}. \tag{4.15}$$

Sometime the electric conductivity is expressed in terms of the *average free path* $\lambda = v_{\mathrm{T}}\tau$. That quantity is defined as the distance covered by an electron with a heat speed v_{T} in the time interval of free path. Thus, in the Drude model, the electric conductivity σ is:

$$\sigma = \frac{e^2 n\tau}{m} = \frac{e^2 n\lambda}{mv_{\mathrm{T}}} = \frac{e^2 n\lambda}{(3mk_B T)^{1/2}} = en\frac{e\tau}{m} = en\mu \tag{4.16}$$

We have taken into account that the average kinetic energy of an electron is $\frac{3}{2}k_B T$, and the mean square velocity is $v = (3k_B T/m)^{1/2}$:

In analogue way, the heat capacity:

$$\kappa_e = \frac{2}{3}\tau v^2 C_e \tag{4.17}$$

.

C_e is the volume specific heat of the electron gas $(3/2)k_{\mathrm{B}}n$. Hence:

$$\kappa_e = nk_{\mathrm{B}}\tau v^2 = \frac{3n\tau k_{\mathrm{B}}^2 T}{m} \tag{4.18}$$

Combining the equation (4.18) and (4.16) we get the Lorenz number:

$$L \equiv \frac{\kappa_e}{\sigma T} = \frac{3k_{\mathrm{B}}^2}{e^2} = 2.2\cdot 10^{-8}(\mathrm{V/K})^2 \tag{4.19}$$

That quantity is in a good agreement with the experimental data for metals (Table 4.1).

We can see that the ratio of heat conductivity to electric conductivity at the temperature below 100K does not follow the Wiedemann-Franz law. For many metals at law temperature, the quantity becomes constant again (see the data for copper). The ratio

$\kappa_e/\sigma T$ becomes constant at such low temperature that it can be explained by scattering on impurities and defects. The Drude model can not explain that.

4.2.2. The Lorenz Model

Lorenz (1905) assumed that electrons in metal follow the Maxwell distribution:

$$f_0 \equiv n\left(\frac{m}{2\pi k_0 T}\right)^{3/2} \exp\left[\frac{-m\left(v_x^2+v_y^2+v_z^2\right)}{2k_0 T}\right] \tag{4.20}$$

n – electron concentration. The distribution is spherically symmetric in the velocity space.

You can find the detailed discussion of Lorenz ideas in [6,7,8]. We will try to explain his ideas not using complicated mathematics calculations.

Thus, the equilibrium distribution (4.20) describes the electrons in metals when there are no external force fields. The metal is isotropic and f_0 does not depend on the space coordinates. The electric field applied to metal produces the drift of electrons. The velocity distribution f differs from the equilibrium distribution f_0. Assume that the field **E** is uniform and the space derivative of (f - f_0) is zero. Hence, we can write:

$$\left(\frac{df}{dt}\right) = \left(\frac{df}{dt}\right)_{field} + \left(\frac{df}{dt}\right)_{coll.} \tag{4.21}$$

The first addend describes the action of field; the second addend describes the action of collisions. Taking into account that the momentum of electron is m**v** and acting force e**E,** we can represent the first addend as:

$$\left(\frac{df}{dt}\right)_{field} = \left(\frac{d\mathbf{v}}{dt}\right)\cdot\left(\frac{df}{d\mathbf{v}}\right) = \left(\frac{-e\mathbf{E}}{m}\right)\cdot\left(\frac{df}{d\mathbf{v}}\right). \tag{4.22}$$

Assume that collisions reconstruct the distribution f_0 along the free path and the quantity $(df/dt)_{coll.}$ is proportional to (f_0 - f):

$$\left(\frac{df}{dt}\right)_{coll.} = \frac{(f-f_0)}{\tau_r} \tag{4.23}$$

τ_r – relaxation time. Combining equation (4.22) and (4.23), we can represent equation (4.21) in the form of the *continuity equation*:

$$\left(\frac{df}{dt}\right) + \frac{e\mathbf{E}}{m}\cdot\left(\frac{df}{d\mathbf{v}}\right) + \frac{(f-f_0)}{\tau_r} = 0 \tag{4.24}$$

That is a relation between the equilibrium state distribution function f_0 and the distribution function f, which is produced by the external electric field.

The concurrency between the action of an applied field and the process of scattering affects the new distribution (its position and forms). For not very great fields, the shift of the quantity f produced by the field should be small in comparison with $v_{ср.кв.}$ Thus, the distortion of the distribution is less noticeable than the entire shift.

If the acting time $t >> \tau_r$ the stationary state is produced and the first addend in (4.24) is zero. Then, according to equation (4.2):

$$f = f_0 + \frac{\tau_r e\mathbf{E}}{m} \cdot \left(\frac{df}{d\mathbf{v}} \right) = 0 \quad . \tag{4.25}$$

Integration of that distribution shows that the drift velocity (hence, the electric conductivity) is not a zero.

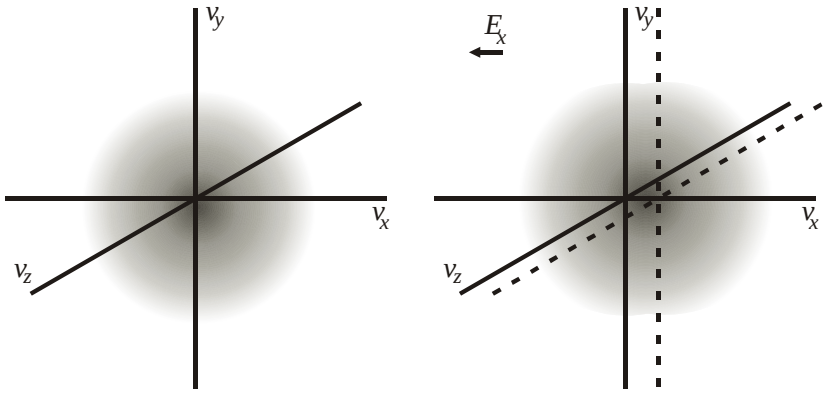

Fig.4.2. The velocity distribution of classic electron gas (left) The velocity distribution of the same gas in the external electric field (right)

If the field (see Fig.4.2) is oriented along x-axis, the current density:

$$j_x = -\int e v_x f dv_x dv_y dv_z \tag{4.26}$$

Taking into account that the integral including f_0 is zero, we get:

$$j_x = \sigma E_x = -\int \left(E_x e^2 / m \right) \tau_r v_x \left(\partial f / \partial \mathbf{v} \right) dv_x dv_y dv_z \tag{4.27}$$

In order to calculate that integral, assume that τ_r depends only on the electron velocity. It is supposed usually that:

$$\tau_r = A v^j \tag{4.28}$$

The power index depends on the scattering mechanism. Assume that in a metal with the atomic residue concentration N and scattering radius R, the free path does not depend on electron speed and is of order

$$\lambda \sim \left(\pi R^2 N \right)^{-1} \tag{4.29}$$

The average time of free path is:

$$\tau = \frac{\lambda}{v} \tag{4.30}$$

$\tau = \lambda / v \, \mathrm{v}$ is a thermal velocity of electron, with which it moves from one scattering center to another. It means that the wavelength λ is equal A [see equation (4.26)] and j = -1, i.e. the mean time of free path as it follows from equation (4.30). When the field mainly acts on the slow electrons, that scattering mechanism is the strongest. Introducing (4.30) into (4.27) we get:

$$\sigma = -\int \left(\lambda e^2 / m v_x \right) \cdot \left(\partial f / \partial v_x \right) dv_x dv_y dv_z \tag{4.31}$$

$v_x^2 = (v^2/3)$

That integral can be transformed into a integral relative the speed v. Taking into account that the mean quantity of and the volume of the spherical layer (radius v and thickness dv) in the velocity space is равен $4\pi v^2 dv$, we transform the integral (4.31) as follows:

$$\sigma = \left(4\pi e^2 / 3m \right) \int_0^\infty \lambda v^2 \left(-\partial f_0 / \partial v \right) dv \tag{4.32}$$

It should be noted that the main contribution in the integral gives the velocity interval in which the module of the derivative of the distribution function relative to speed is maximal. Calculation of the integral (4.32) leads to:

$$\sigma = \frac{4ne^2\lambda}{3(2\pi m k_B T)^{1/2}} \tag{4.33}$$

That expression is of the same form as that one of Drude model (see 4.33). The expression (4.16) and (4.33) differ only by the factor $(3\pi/8)^{1/2} = 1.09$.

From the Lorenz solution of the Boltzmann kinetic equation in the external field some important results follow. In a conductor with a temperature gradient, the electromotive force is produced (Thomson effect).

The other phenomena are produced when the electric, magnetic and temperature fields act simultaneously. The force acting upon an electron in an electromagnetic field (the Lorenz force):

$$\mathbf{F} = -e\left[\mathbf{E} + (\mathbf{v} \times \mathbf{B})\right] \tag{4.34}$$

The factor describing the influence or the field in equation (4.21) is:

$$\left(\partial f / \partial t\right)_{field} = (-e/m)\left[\mathbf{E} + (\mathbf{v} \times \mathbf{B})\right]\left(\partial f / \partial \mathbf{v}\right) \tag{4.35}$$

The first order stationary solution of the Bolzmann kinetic equation:

$$\sigma\mathbf{E} = \mathbf{J} + [\pi e\lambda / 2(2\pi m k_0 T)^{1/2}]\mathbf{J} \times \mathbf{B} = \mathbf{J} - [\sigma R_H]\mathbf{J} \times \mathbf{B}\,. \tag{4.36}$$

σ – electric conductivity [see equation (4.33)]. The quantity R_H is called the Hall constant, which characterizes the magnitude of a transversal electric field produced by the magnetic field (the Hall effect, 1879). The comparison of the equation (4.33) and (4.36) shows that

$$R_H = -\left(3\pi / 8ne\right). \tag{4.37}$$

The first addend in the right part of equation (4.36) shows that the magnetic field perpendicular to electric current should not decrease the electric conductivity along the sample. But, experiments show that the electric conductivity of a metal in a magnetic field decreases (effect of magnetic resistance, 1856). If to solve the Bolzmann equation by decomposition and to take into account higher powers of magnetic field strength, we get that the electric conductivity increases proportional to the square of the magnetic field strength. That fact coincides with experiments.

$$\sigma_B = \frac{J^2\sigma}{J^2 + \left(\sigma R_H\right)^2 \left|\mathbf{J} \times \mathbf{B}\right|^2} \tag{4.38}$$

Thus, the magnetic resistance is maximal when the magnetic field is normal to a current, and in the model of free electrons it should be zero when the current is parallel to the magnetic field. For certain metals, the Hall constant is positive, and it can not be explained by equation (4.37) for the free electrons. It should be noted that the results of Lorenz were great progress in physics.

Thus, we discussed the classical models of Drude and Lorenz in order to be ready to discuss the modern quantum models. The more serious deficiency of classical models is that the specific heat conductivity and magnetic susceptibility is smaller than it should be when the charges are free. In reality, the mean free path is much greater than the inter-atomic distance and decreases with temperature. It does not follow from equation (4.29). Many attempts were made to overcome those difficulties of the classical theory of free electrons. All of them were futile. The quantum mechanics solved these problems.