10. Disordered Materials

The physics of non-crystalline structure is very popular nowadays. A great number of substances are non-ordered. In them there is no a distant order but there is a close order of atoms. Those substances are called **amorphous** substances.

The non-crystalline substances with the shear viscosity coefficient more then 10^{13} - 10^{14} $N \cdot c/m^2$, are called **amorphous solids**. The can be of dielectric, semiconductor, and metal properties.

The structure of metals, semiconductors, and dielectrics are justified by the distant order. Discovery of the fact those amorphous substances have the like properties that crystalline ones lead to reevaluation of periodicity. In 1960 Ioffe and Regel assumed that the electric characteristics of amorphous semiconductors depended on not the close but distant order. The theory of non-ordered structures was developed, which explained many experimental data.

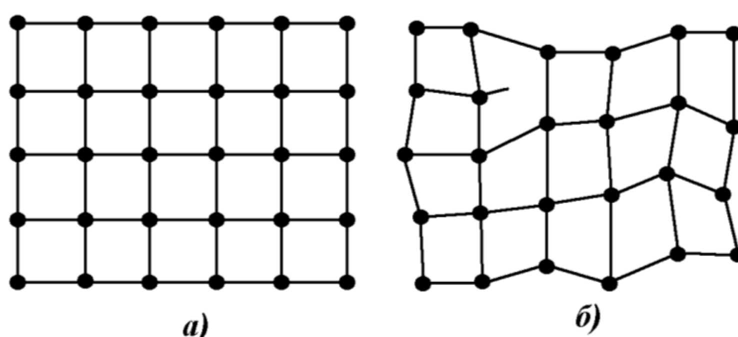

Fig.10.1.The crystalline structure (a); non-ordered substances (b).

10.1 The Structure of Non-ordered Substances

The ideas concerning the structure of amorphous substances are usually deduced from X-ray and electron diffraction experiments. It was shown that in a non-ordered structure, the first coordination sphere limits the strict close order.

Indeed, the first coordination spheres of amorphous and crystalline silicon are practically identical. The second coordination sphere of amorphous silicon is not as distinct as in a crystal one. In the amorphous silicon, the third coordination maximum of the radial distribution of atoms totally vanishes. Thus we can stay that the structure of amorphous silicon is characterize by the close order (as the structure of crystal) dut the close order region is restricted by the first coordination sphere.

We can assume that atoms of an amorphous solid are arranged in a three dimensional **continuos net,** which is like the lattice of a crystal. That lattice (opposite to crystal) is a little deformed.

The accidental distortions of bonds and angles accumulate and lead to complete diminishing of the distant order. The distortions can be also due to fluctuations of chemical composition. Fig.10.1 shows the structure of an crystalline and amorphous body.

10.2 Electrons in a Non-crystalline Medium

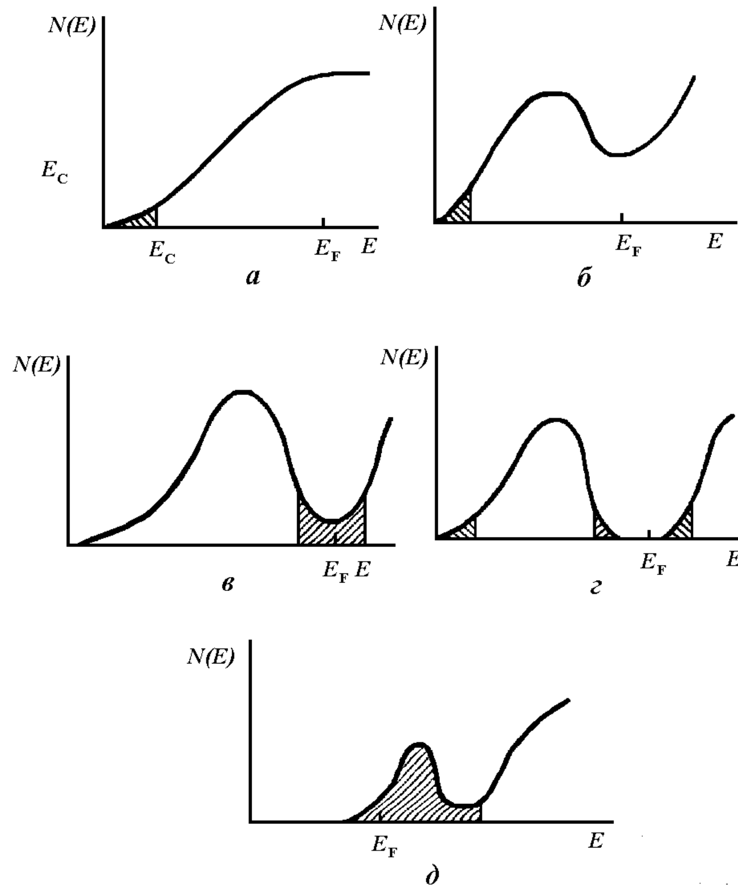

Fig.10.2. The density of states in non-crystalline substances..
E_F – the Fermi level at zero temperature; the localized states are dashed; *а* – liquid or amorphous metal; *б* – semimetals; *в* – semimetals with a deep pseudo slit; *г* – intrinsic dielectric; *∂* – the impurity zone in a strongly compensated electron semiconductor.

The zone theory can be applied with success while investigating the amorphous bodies. Unfortunately the concepts of the Fermi surface and Brillouin zone can be of use.

We are going to discuss only the main aspects of the theory in order to understand the peculiarities of the electron energy spectrum.

In a non-ordered system the distant (sometime even close) order is violated. The charge current carriers are in accidental electric fields.

Dependence between the carrier concentration and density state distribution *N(E)* is shown in Fig.10.2.

$$n = \int_E N(E) f(E) dE \qquad (10.1)$$

f(*E*) – the Fermi distribution function.

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \qquad (10.2)$$

The function $N(E)$ depends on approach we make.

Assume that electron scattering by an atom is small and electrons are characterized by the wave functions with a definite wave number k. The free path L is great and with accordance that $L\Delta k \sim 1$, $\Delta k/k << 1$. In first approximation: $E = \frac{\hbar^2 k^2}{2m}$. The Fermi surface is a sphere and:

$$N(E) = \frac{4\pi k^2}{8\pi^3}\frac{dE}{dk} = \frac{km}{2\pi^2\hbar^2} \tag{10.2}$$

That condition is true in liquid metals. The quantity m is not necessary the mass of a free electron.

Assume that the interaction is strong: $\Delta k/k \sim 1$, the free path is small ($kL \sim 1$). The probability of the state localization is appreciable (Fig.10.2). When $\Delta k/k \sim 1$ there can be strong deviation from the free electron model. The situation denoted by *б, в*,and *г* correspond to $\Delta k/k \sim 1$.

10.2.1 Localized States

The density of states at the zone edges diminishes sharply to zero (Fig.10.2*г*). The zone states are localized. The impurity states are localized. In amorphous bodies, the local states are of importance. They violate the periodicity.

In any case, we are to solve the Schrödinger equation:

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{10.3}$$

In the strong bond approximation, the potential wells of a crystal produce the narrow band of levels (Fig.10.3). They are produced for example in d-zone of transit metal or donor, which form the metallic impurity zone in a semiconductor. Assume that the wells are far from each other and the intersection of the atomic wave functions $\varphi(r)$ is small. The Bloch wave function of an electron is a superposition of wave functions of separate wells:

$$\psi_k(x, y, z) = \sum_n \exp(ik \cdot R_n)\varphi(\mathbf{r} - \mathbf{R}_n) \tag{10.4}$$

Assume that the functions φ are spherically symmetric (s-function). Let the quantity W_0 be the energy of an electron in an isolated well. The energy of an electron in a simple cubic lattice can be written as follows:

$$E = W_0 + W_k, \tag{10.5}$$

$$W_k = -2I(\cos k_x a + \cos k_y a + \cos k_z a). \tag{10.6}$$

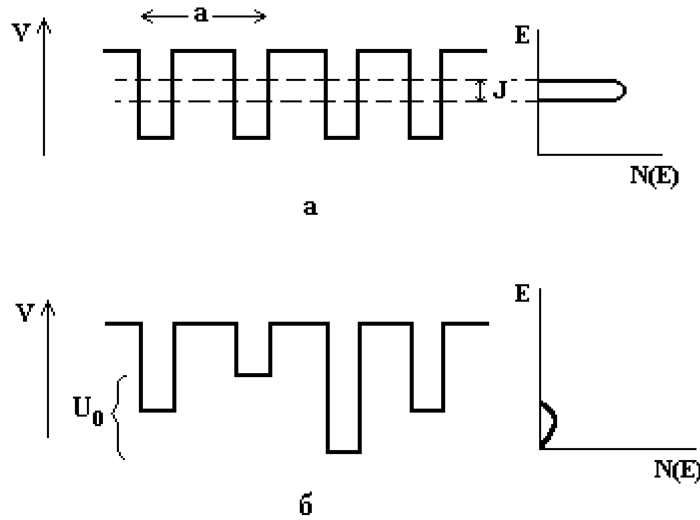

Fig.10.3

The quantity I is called the superposition integral:

$$I = \int \varphi^*(r - a_n)\hat{H}\varphi(r - a_{n+1})d^3x, \qquad (10.7)$$

$\hat{H}$ is the Hamilton operator. Assume that the intergral can be represented as follows:

$$I = Ie^{-\alpha R} \qquad (10.8)$$

$$I_0 \approx \alpha^3 v_0 D_0, \quad \alpha = \sqrt{2m_0W_0}/\hbar;$$

The quantity D_0 is the depth of the well, R – the distance between the wells ($R = a$ for a simple cubic lattice). The effective mass m^* at the zone bottom:

$$m^* = \frac{\hbar^2}{2Ia^2} \qquad (10.9)$$

The zone width:

$$J = 2zI, \qquad (10.10)$$

Z is the coordination number.

Let us discuss the transformation of an energy zone if the potential becomes non-periodical. Such potential can be produced by two ways.

We can displace each center at an accidental distance. The energy of an electron would be $\frac{1}{2}U_0$.

We can add the accidental energy to potential energy of each well. The enegy of an electron would transform: $W_0 + \frac{1}{2}U_0$.

Assume:

$$\langle U^2 \rangle = U_0^2,$$

The potential energy V is shown in Fig.10.3б (the Anderson potential).

If the potential U_0 is small its action leads to the free path L. That quantity can be evaluated from:

$$\frac{1}{L} = \frac{2\pi}{\hbar}\left(\tfrac{1}{2}U_0\right)^2 \frac{a^3N(E)}{u}, \qquad (10.11)$$

The quantity E and u are at Fermi level; a^3 is an atomic volume.

Introducing (10.2) into (10.11) we arrive at:

$$\frac{1}{L} = 4\pi\left(\frac{m}{2\pi\hbar^2}\right)^2 a^3\left(\tfrac{1}{2}U_0\right)^2, \tag{10.12}$$

$$\frac{a}{L} = \frac{(U_0/I)^2}{16\pi}. \tag{10.12a}$$

We remind our readers that if $kL < 1$, the concept f the free mean path is of no use. At the middle of a zone $ka \sim 1$; and parameter a is the minimal free path. The sing of the wave function changes chaotically from well to well. In accordance with (10.12) it can be if: $(U_0/I) \sim 7$, i.e. $(U_0/I) \approx 7/12$ at $z = 6$.

Assume that at zero moment an electron is located in a well. What happens later? Anderson found that if $(U_0/I) > 5$ (z=6), there is no diffusion. Thus all the states are localized. The dependence of the critical quantity (U_0/I) on the coordination number is weak. If the ratio (U_0/I) is less then the critical one, delocalizated states would appear in the cener of a zone (Fig.10.4). Experimental data confirm it.

The localized states discussed are due to the energy fluctuation. Indeed, if defects are distributed accidentally and their concentration is small the energy levels in the forbidden zone depend only on the properties of defects. The δ-form maximums would appear on the function *N(E)*.

The situation would change if the concentration of defects becomes great. The collective properties of the field would be produced. The discrete energy levels generated are called the **fluctuation levels.** The probability of great fluctuation is small. Thus the density of states decreases rapidly with the distance from the allowed zone boundary. Function *N(E)* is uninterrupted. The states are localized (in certain energy interval).

Two situations are possible: there is a distinct boundary between levels E_c and E_v, discrete levels fill entire region between Ec and Ev, which are the borders of conduction and valence zone. The last situation takes place for amorphous substances when there are distinct borders between localized and non-localized states.

The density of states as the function of energy for amorphous semiconductors is shown in Fig.10.4. The slit of mobility (E_c-E_v) is shown in Fig.10.4,a and б. A rather peculiar form is shown in Fig.10.4в.

The “tails” of localized states are rather long and can overlap near the middle of mobility slit. If there is a Fermi level in the overlap region, the electrons can freely pass from the ceiling of valence zone into the bottom of conduction zone.

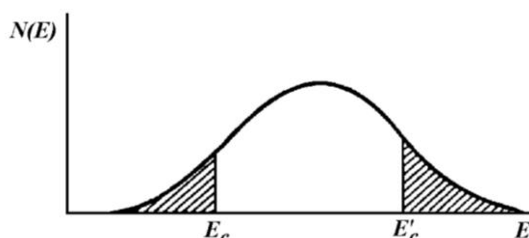

Fig.10.4. The density of states in the Anderson model. The dashed area – the localized states

Besides the fluctuation levels in non-ordered system, there can be defects, which are the centers of localization of the free charge carriers. Those defects produce the narrow peaks, which can be widen when there are accidental fields.

For situation *а*, *б* and *г* the concept of forbidden zone is valid, i.e. there is a region where the density of states is zero. Fig.10.4г represents the situation when discrete levels fill entire energy interval. The localized electrons transport the electric charge only by ‘over-jumps”.

The region populated by discrete levels is called “ **the mobility slit”** (E_c - E_v) (Fig.10.4, б).

We remind our readers that if the Fermi level is in the region of non-located states, the substance is a metal. If the Fermi level is in the region of localized states, the substance is semiconductor or dielectric.

Two types of conductivity are possible:

a) The carrier transport along non-localized states;
b) Jumps between the localized states.

10.2.1 Amorphous Substances

There are three types of amorphous semiconductors.

1. Compounds $A^{III}B^{V}$, which in an amorphous modification are manufactured as thin films by precipitation.
2. The glasses containing the atoms of sulfur, selenium, and tellurium produced by cooling of melting material.
3. The glasses composed of the elements of the fifth group.

The main features of amorphous substances can be listed as follows.

Conductivity for energy $E > E_c$ is of a usual zone type. When $E < E_c$, the ‘jumps’ between the localized states generate the conductivity.

There are three mechanisms of conductivity.

a) Conduction by the excited in a non-localized state carriers ($E>E_c$). When the current is due to the holes, we get (see Fig.10.4):

$$\sigma = \sigma_o \exp\left[-\frac{(E_C - E_F)}{kT}\right] \qquad (10.13)$$

When the energy of a carrier reaches the critical one, the mobility changes by the factor of 1000. In the jump conductivity region, the temperature dependence of mobility is: $\mu \sim \exp(-E/kT)$.

1. Conductivity through the de-localized states. The holes produce the electric current in many amorphous semiconductors.

$$\sigma = \sigma_o \exp\left[-\frac{(E_F - E_v)}{kT}\right] \qquad (10.14)$$

The quantity σ_o of many materials is in the interval of 100 - 500 ohm^{-1}cm^{-1} and can be written as follows: $\sigma_o = eN(E_C)kT\mu_o$. If the quantity σ_o does not depend on temperature, $\mu \sim T^{1}$. The dependence between lgσ and inverse temperature is linear.

2.Conductivity through the localized states with energy closes to E_A or E_B.

$$\sigma = \sigma_o \exp\left[-\frac{(E_F - E_B + \Delta E)}{kT}\right] \qquad (10.15)$$

ΔE – the activation energy of jumps, E_B – energy of the zone edge.

3. Conductivity through the localized states with energy close to the Fermy level. The charge transportation is performed by jumps through the localized states (Fig.10.5). The process is like the conductivity through impurities of strongly alloyed semiconductors. If the states are localized an electron can move only by jumps from one state to another exchanging the energy with phonons.

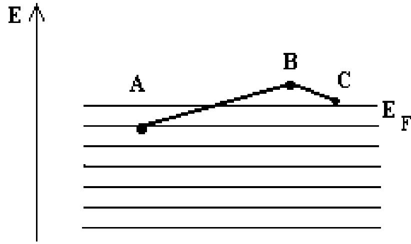

Fig.10.5. The jump mechanism of conductivity

There are two types of electron conductivity: the current depends on electron mobility (the energy is near the Fermi level), the conductivity ($E \sim E_F$) is small in comparison with that one of electrons of conduction zone. In the first situation if the states are localized, the conductivity:

$$\sigma \approx e^2 pR^2 N(E_F)kT. \qquad (10.16)$$

$p = \nu_{фон} e^{-2\alpha R - E_S/kT}$ is the probability of a over-jump, R is the length of a jump, the factor $\nu_{фон}$ depends on phonon spectrum (10^{12}-$10^{13}c^{-1}$), E_S is the jump activation energy. When localization is strong, an electron approaches the closest neighbor:

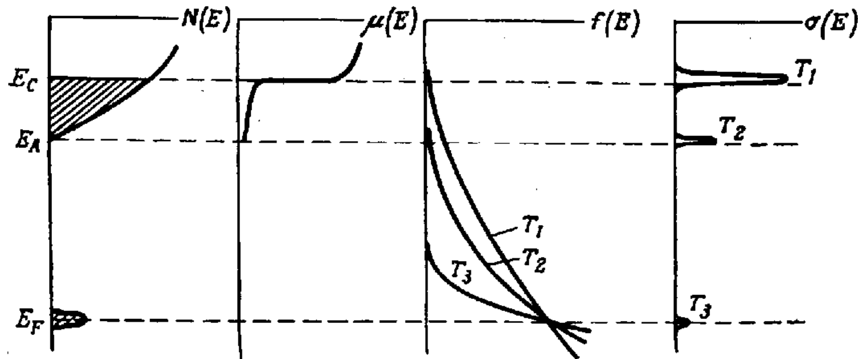

Fig.10.6. The temperature dependence of conductivity
σ (*E*) = *e N* (*E*) μ (*E*) *f* (*E*); $T_1 > T_2 > T_3$.

$$E_S \approx \frac{1}{R^3 N(E)} \qquad (10.17)$$

The activation energy is small only when the factor $e^{-\alpha R}$ is also small to make the electron jump to the nearest center. It can be at high temperature. In Anderson model, the quantity E_S is of the zone width order. At low temperature, the jump conductivity is defined by: $\sigma = \sigma_o \exp\left[\left(-\frac{T_0}{T}\right)^{1/4}\right]$, (10.18)

Thus:

$$\sigma = e\int N(E)\mu(E)f(E)dE, \qquad (10.19)$$

$f(E)$-the energy distribution function..

The functions $N(E)$, $\mu(E)$, $f(\mathrm{E})$, and $\sigma(E)$ are shown in Fig.10.6..

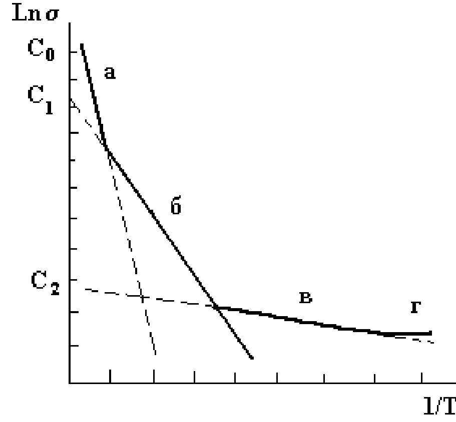

Fig.10.7. The temperature dependence of conductivity according the model of the density of states shown in Fig.10.6

The function $\ln\sigma = f\left(T^{-1}\right)$ for all mechanisms discussed is shown in Fig.10.7. Rgioin *a* represents transportation through non-localized states, region *б* represents transportation through the zone tail states, region *в* and *г* represents transportation through localized states near the Fermi level. The Mott law is true in the last region.

If the density of states produced by defects is great, there would not be the temperature interval where the process *б* dominates and the region *a* smoothly transforms into region *в*. The experimental data confirms it.

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In the de-localized state region of amorphous semiconductors, the charge mobility:

$$\mu = e\tau/m, \tag{10.20}$$

τ - the relaxation time. We can represent (10.20) as follows:

$$\mu = el/m\bar{v}. \tag{10.21}$$

The quantity l is the free path, $\bar{v}$ - the mean speed of an electron. When $E > E_c$ the motion of carriers follows the Boltzmann equation.

The electron density:

$$n = N(E)k_B T \exp\left[-\left(E_c - E_F/k_B T\right)\right]. \tag{10.22}$$

The conductivity:

$$\sigma = \sigma_o \exp\left[-\frac{\left(E_c - E_F\right)}{k_B T}\right] \tag{10.23}$$

The mobility

$$\mu_c = \frac{\sigma_o}{eN\left(E_c\right)k_B T}. \tag{10.24}$$

$\sigma_0 \sim 350$ ohm^{-1}cm^{-1}, $\mu_c \approx 12$ cm^2·V^{-1}·c^{-1}.

We can formally use the concept of mobility in the region $E < E_c$, where the charge transportation is performed by jumps. If the conductivity is described by the equation like (10.16):

$$\mu_{прыжк} = \frac{1}{6}\bar{v}\frac{eR^2}{k_B T}\exp\left(-\frac{\Delta E}{k_B T}\right). \tag{10.25}$$

We neglected the factor $e^{-2\alpha R}$, that can be done at great degree of localization. Usually $\bar{\nu} \approx 10^{12}$ c^{-1}. Near E_c , $\Delta E \le k_B T$. Thus, when the energy approaches $E = E_c$ (or E_v in valence zone), the mobility increases by the factor of about 10^3 (Fig.10.8).

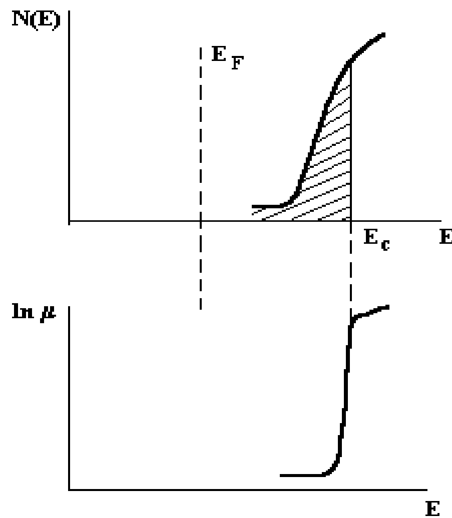

Fig.10.8. A mobility threshold

Amorphous semiconductors (opposite to crystalline ones) are almost insensible to alloying.

Besides amorphous semiconductors, there are amorphous dielectrics, which are widely used in microelectronics. The conductivity is performed by the charge carrier jumps from one localized state to the other. The activation energy of the process is considerably lower then the activation energy of impurity conductivity of crystalline dielectrics.

The density of amorphous dielectrics is lower then that one of crystals. Hence its dielectric susceptibility is also lower.

The energy losses of amorphous dielectrics strongly depend on the width of the mobility slit. If the mobility slit is small, the losses are due mainly to the jump conductivity.

In the last years, a new type of materials amorphous metals (metallic glasses) is of great interest. The amorphous state f metals was observed long ago while depositing from electrolytes and pulverizing upon a cool base. An effective and high productive technology is developed to produce amorphous metals. The technology is based upon fast cooling (more then 10^6 K/c) of a thin stream of melting metal. It was shown that impurities promote the formation of amorphous layers.

Investigations show that in amorphous metals there are no grain borders and point defects. The chaotic continuous distribution of spherical particles with tight packing is supposed to be in metallic glasses.

While heating the metallic glasses are being crystallize. That peculiarity is due to the metallic type of a bond.

The metallic glasses are very stabile. The critical strain of metallic glasses is greater then that of a steal.

The metallic amorphous alloys are rust-durable.

The specific resistance of amorphous metals $[(1 - 2)\cdot 10^{-4}$ ohm·cm] is 2—3 times more then that one of crystalline alloys that is due to the small free path.