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INVESTIGATION OF THE MECHANISMS OF HEAT CONDUCTION IN DIELECTRICS AND METALS ON THE BASIS OF THE MOLECULAR-RADIATION THEORY OF TRANSFER

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The activation mechanisms of transfer of a substance in condensed media are described. Analytical expressions defining the dependences of the electron, photon, and diffusion heat conductivity on the temperature, density, and microscopic characteristics of these media are presented. The temperature dependence of the density of free electrons in conductors was obtained. The results of a comparison of theoretical and experimental data are presented.

Keywords: *electron, photon, and diffusion mechanisms of heat conduction, activation processes, molecular-radiation theory of transfer, density of free electrons.*

Introduction. A characteristic feature of activation processes is an abrupt increase in their intensity with increases in the temperature of a body. This is explained by the fact that, in the case where the temperature of a body increases due to the fluctuation processes, the number of particles in it, which reach an energy level sufficient for the breaking of their bonds with the neighboring particles and for a diffusion jump of them into the environment of other particles, increases rapidly. Until recently, the nature of fluctuation processes has remained unclear.

In the works of the author [1–5] the foundations of the molecular-radiation theory of heat and mass transfer have been developed on the basis of the concept of energy transfer by material carriers emitted continuously and absorbed by particles of a substance. This theory, unlike the classical theory, allows one to obtain both equations of transfer and the transfer parameters expressed in terms of the characteristics of the particles of a body. The author obtained an integro-differential equation of transfer that, in the limit, is transformed into the Fourier heat-conduction equation and the hyperbolic equation and allows one to explain the known disagreement between the classical theory of heat conduction and the experimental data. A formula for the heat conductivity of a multicomponent gel, which correlates well with experimental data and, in the limit, is transformed into the Debye formula, has been derived. The potential of interatomic interaction depending on the energy of particles and the equation of state of condensed media, from which Hooke's law, the law of thermal expansion, and the Grüneisen law follow, have been obtained.

The law for the intensity of spectral radiation of the particles of a body has been obtained within the framework of the molecular-radiation theory [1]. In accordance with this law, the particles of a unit volume of a body, found at the energy level i, radiate at any vibrational frequency ν, an energy $q_{i\nu}$ by quanta in a unit time. The value of this energy is proportional to the energy level i, the quantum energy $h\nu$, and the density of the particles found at the indicated level $n_{i\nu}$, i.e.

$$q_{i\nu} = \varepsilon_\nu i h \nu n_{i\nu} \,. \tag{1}$$

From the Nikitenko law (1) follow [2] the Planck formula for the spectral radiation of a macroscopic black body and the Maxwell–Boltzmann law for the distribution of particles of a body in energy. Law (1) is true for the case where $n_{i\nu} = 1$ and, therefore, is an elementary law. It is impossible to obtain law (1) on the basis of the Planck formula determining the integral characteristic of a macroscopic body.

An expression for the distribution of the particles absorbing and radiating photons of frequency ν in energy in activation processes was obtained on the basis of (1) [2]:

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$$W_{\beta i\nu} = \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]\left[1 - \exp\left(-\frac{(I_{\beta\nu} + 1)\,h\nu}{kT}\right)\right]^{-1} \exp\left(-\frac{E_{i\nu}}{kT}\right), \quad E_{i\nu} = ih\nu\,, \quad i = 0, 1, ..., I_{\beta\nu}\,. \qquad (2)$$

The limiting energy level $I_{\beta\nu}$, at which a particle of the component β can be found in activation processes, is determined from the condition $I_{\beta\nu}h\nu < A_\beta \le (I_{\beta\nu} + 1)h\nu$. After a particle found at the level $I_{\beta\nu}$ absorbs a photon $h\nu$, it activates, liberates an energy $(I_{\beta\nu} + 1)h\nu$, and, in doing so, execute a diffusion jump to the zero energy level in the neighboring cell. At $I_{\beta\nu} \to \infty$, the Nikitenko distribution function (2) is transformed into the Maxwell–Boltzmann distribution law. In [2], the author has obtained, on the basis of (1) and (2), a formula for the mass of particles of the component β per unit volume of a body reaching the activation energy in unit time:

$$G_\beta = \varepsilon_\beta \rho_\beta \left[\exp\left(\frac{A_\beta}{kT}\right) - 1\right]^{-1} \qquad (3)$$

and a formula for the diffusion coefficient of a condensed medium:

$$D_\beta = \frac{1}{3} a_\beta^2 \varepsilon_\beta \left[\exp\left(\frac{A_\beta}{kT}\right) - 1\right]^{-1}\,. \qquad (4)$$

At $A_\beta/RT >> 1$ the Nikitenko formula (4) is transformed into the empirical Arrhenius formula for solid bodies, and at $A_\beta/RT << 1$ it is transformed into the Einstein formula for liquid media. Using (1), the author also obtained formulas for the intensity of evaporation of liquid and solid media depending on the temperature and thickness of the evaporating layer, for the equilibrium pressure of the vapor, and for the equilibrium thickness of the condensed layer of the nonsolid surface [3–5].

At the present time, several mechanisms of energy transfer in condensed media, in particular the electron, phonon, photon, exciton, and resonance ones, have been formulated. It is suggested that the heat-conductivity coefficient of a real body consists of several components that are due to different transfer mechanisms.

It is usually assumed that, in dielectrics, energy is transferred mainly by sound waves, to each of which corresponds a quasiparticle–phonon of definite frequency. If, in the heat-conduction equation $\lambda_g = n_g w_g l_g c_{Vg}/3$ obtained on the basis of the elementary kinetic theory of gases, the velocity of sound w_s is substituted for the gas velocity w_g and the specific heat capacity of a condensed body is substituted for c_{Vg}, an expression for the heat conduction of dielectrics is obtained. However, phonons are not material carriers of energy; therefore, heat conduction by phonons cannot be considered as a fairly reasonable mechanism.

Below, at first, the photon and diffusion mechanisms of heat conduction, determining the intensity of energy transfer in dielectrics, are considered on the basis of the molecular-radiation theory of heat and mass transfer. Then the theory of activation electron heat conduction in conductors, which allows one to determine the change in the density of free electrons in a body with change in its temperature, is presented.

Photon Mechanism of Heat Conduction. This mechanism is realized in both dielectrics and conductors. When the dependence of the coefficient of heat conductivity of a homogeneous isotropic multicomponent body on its temperature and the microscopic characteristics of the particles of this body is determined, it will suffice to consider a plane plate in a stationary nonequilibrium state. Let the x axis be directed along the normal to the boundary surface of the plate, and the y axis be directed along this surface. The temperature field in the plate is defined by the dependence $T = T(x)$. The density of the energy flux q through the surface element ΔS, positioned in the coordinate plane x such that its central point has coordinates (x, $y = 0$), is determined in the following way. Initially the density of the energy flux dq released by the elementary isothermal layer $d\eta$ with coordinate $x + \eta$, positioned at a distance η from the surface element ΔS, is determined. The average energy falling at one degree of freedom of a particle of the component β in the layer $d\eta$, radiating and absorbing photons $h\nu$, is equal to [1] $e_\nu = h\nu\{\exp[h\nu/[kT(x + \eta)] - 1]\}^{-1}$. Let us separate a ring element of radius y, thickness dy, and width $d\eta$ in the layer $d\eta$. The density of the energy flux $d^2q_{\beta\nu}$, which is due to the radiation of photons $h\nu$ by particles of sort β found in the bulk of the element $2\pi y dy d\eta$, through the surface element ΔS comprises

$$d^2 q_{\beta\nu} = -\cos\alpha \, 2\pi y dy d\eta n_{\beta\nu} \varepsilon_{\beta\nu} e_\nu \Phi_\nu (\eta) \, . \tag{5}$$

Here, the cosine of the angle α between the axis x and the radius-vector **r** directed from the center of the surface area ΔS to the point $(x + \eta,\ y)$ of the element being considered is equal to $\cos\alpha = \eta / \sqrt{y^2 + \eta^2}$;

$$\Phi_{\beta\nu} (\eta) = \frac{\xi_{\beta\nu}}{4\pi\eta^2} \exp(-\xi_{\beta\nu} F_\nu \eta) \, , \quad F_\nu = \sum_\beta \sigma_{\beta\nu} n_{\beta\nu} \, . \tag{6}$$

Here, ξ is the coefficient of overlapping of one particles by other particles, $0 < \xi < 1$. For amorphous bodies, $\xi \approx 1$.

Integrating (5) with respect to the variable y over the range of its change $0 < y < \infty$, we find the density of the heat flux $dq_{\beta\nu}$, which is due to the radiation of photons $h\nu$ by particles of sort β found in the layer $d\eta$, through the surface area ΔS:

$$dq_{\beta\nu} = \int_{y=0}^{\infty} d^2 q_{\beta\nu} = -\frac{1}{2} n_{\beta\nu} \varepsilon_{\beta\nu} e_\nu \left[\exp(-\xi_{\beta\nu} F_\nu \eta) + \xi_{\beta\nu} F_\nu \eta \, \mathrm{Ei}(-\xi_{\beta\nu} F_\nu \tau)\right] d\eta \, . \tag{7}$$

The resulting density of the heat flux $q_{\beta\nu}$ is determined as the difference between the energy fluxes passing through the surface element ΔS in the positive and negative directions of the axis x. The value of $q_{\beta\nu}$ is determined by integration of (7) over the thickness of the plate. However, because the exponential function and the integral exponential function Ei entering into (7) decrease fairly rapidly with increase in their argument, instead of integration over the thickness of the plate, integration over a nonlimited interval can be carried out. In this case, we obtain

$$q_{\beta\nu} = \frac{1}{2} c_\nu n_{\beta\nu} \varepsilon_{\beta\nu} \int_0^\infty \left[e_\nu (x + \eta) - e_\nu (x - \eta)\right] \left[\exp(-\xi_{\beta\nu} F_\nu \eta) + \xi_{\beta\nu} F_\nu \eta \, \mathrm{Ei}(-\xi_{\beta\nu} F_\nu \eta)\right] d\eta \, .$$

Taking into account the fact that, in accordance with the Taylor formula $e_\nu(x + \eta) - e_\nu(x - \eta) \approx 2\eta \partial e_\nu(x)/\partial x = 2\eta c_\nu \partial T(x)/\partial x$, where the heat capacity falling at one degree of freedom is

$$c_\nu = \frac{\partial e_\nu (x)}{\partial T} = h\nu \left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-2} \frac{h\nu}{kT^2} \exp\left(\frac{h\nu}{kT}\right), \tag{8}$$

we find

$$q_{\beta\nu} = -\frac{n_{\beta\nu} \varepsilon_{\beta\nu} c_\nu}{\mu_{\beta\nu}^2 F_\nu^2} \frac{\partial T}{\partial x} \int_0^\infty \left[\xi_{\beta\nu} F_\nu \eta \exp(-\xi_{\beta\nu} F_\nu \eta) + (\xi_{\beta\nu} F_\nu \eta)^2 \, \mathrm{Ei}(-\xi_{\beta\nu} F_\nu \eta)\right] d(\xi_{\beta\nu} F_\nu \eta)$$

$$= -\frac{1}{3} \frac{n_{\beta\nu} \varepsilon_{\beta\nu} c_\nu}{\xi_{\beta\nu}^2 F_\nu^2} \frac{\partial T}{\partial x} \, . \tag{9}$$

In the case where the density of the degrees of freedom of the particles of the component β in a body, vibrating with a frequency ν, is equal to [2] $dn_{\beta\nu} = \gamma_\beta 8\pi\nu^2 d\nu / c^3$, the density of the total photon-energy flux through the surface element ΔS is determined by integration of expression (9) over all the frequencies of these particles in the interval $[0, \nu_{\beta\max}]$ and then by summation over all the components of the body:

$$q = \frac{8\pi}{3c^3} \frac{\partial T}{\partial x} \sum_{\beta=1}^{B} \gamma_\beta \int_{\nu=0}^{\nu_{\beta\max}} \frac{\varepsilon_{\beta\nu} \nu^2 c_\nu}{\xi_{\beta\nu}^2 F_\nu^2} d\nu \, . \tag{10}$$

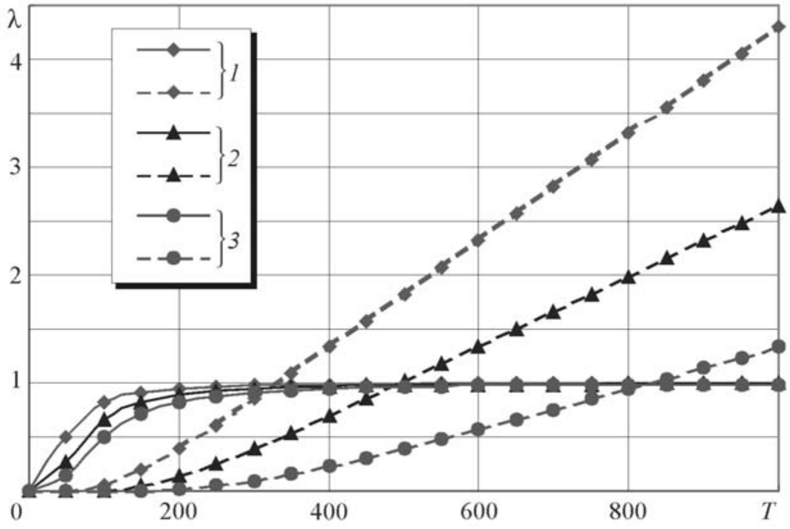

Fig. 1. Dependences of the relative values of the photon λ_{ph} (solid curves) and diffusion λ_D (dashed curves) heat conductivities of a body on its temperature at different values of the characteristic temperature ϑ: ϑ_β = 200 (1), 300 (2), and 400 K (3). *T*. K.

Here, $\gamma_{\beta\nu} = f(\nu)$ is the probable number of degrees of freedom of the atoms of the component β, forming a standing wave with a frequency ν [2], $\gamma_{\beta\nu} = 9n_\beta c^3/(8\pi\nu_{\beta\max})$. Let us substitute the value of γ_β and expression (8) for c_ν into (10), introduce the complex of quantities $\frac{\varepsilon_\beta}{\xi_\beta^2 F^2} = \int\limits_{\nu=0}^{\nu_{\beta\max}} \frac{\varepsilon_{\beta\nu}\nu^2 c_\nu}{\xi_{\beta\nu}^2 F_\nu^2} d\nu \Big/ \int\limits_{\nu=0}^{\nu_{\beta\max}} \nu^2 c_\nu d\nu$ averaged over the frequencies, the new variable $z = \frac{h\nu_{\beta\max}}{kT}$, and the designation $\vartheta_\beta = h\nu_{\beta\max}/k$, and then divide (10) by the temperature gradient $\partial T/\partial x$. As a result, the following formula is obtained for the coefficient of photon heat conductivity:

$$\lambda_{ph} = 3k \sum_{\beta=1}^{B} \frac{\eta_\beta \varepsilon_\beta}{\xi_\beta^2 F^2} \frac{T^3}{\vartheta_\beta^3} \int\limits_0^{\vartheta_\beta/T} \frac{z^4 \exp z\, dz}{(\exp z - 1)^2} = \frac{1}{3} \sum_{\beta=1}^{B} \frac{\varepsilon_\beta c_{V\beta}}{\xi_\beta^2 F^2}. \tag{11}$$

The characteristic temperature ϑ_β of a one-component substance can be assumed to be equal to the Debye temperature.

Figure 1 presents curves characterizing the behavior of the relative coefficient of photon heat conductivity $\bar{\lambda}_{ph} = \lambda_{ph} \Big/ \left[3k \sum_{\beta=1}^{B} n_\beta \varepsilon_\beta / (\xi_\beta^2 F^2) \right]$ of a body in the case where its temperature *T* changes. According to the experimental data of [1], the coefficient of heat conductivity of amorphous bodies changes in proportion to the specific heat capacity. Since $\xi \approx 1$ for amorphous bodies, it follows from (11) that λ_{ph} is proportional to their heat capacity. In crystalline bodies, ξ increases with increase in their temperature and, therefore, at *T* close to ϑ_β (i.e., in the case where the value of the derivative $\partial c_{V\beta}/\partial T$ becomes small), λ_{ph} reaches a maximum. This is in agreement with the experimental data on the heat conduction of dielectrics [6].

Diffusion Mechanisms of Heat Conduction. In the case where particles in a body exchange energy with the help of energy carriers — photons, they are distributed inhomogeneously in energy. This distribution is determined by law (2). The particles that reach the activation energy make a diffusion jump to the environment of other atoms. In the process of this jump, particles transfer the energy accumulated by them earlier. The mass G_β of the particles of the component β from a unit volume, which reach the activation energy in a unit time, is determined by formula (3). The average diffusion velocity of an atom w_β is proportional to the number of jumps G_β/ρ_β executed by this atom in unit time and the average distance a_β traversed by it in one jump, $w_\beta = a_\beta G_\beta/\rho_\beta$. According to the elementary kinetic theory, the density of the energy flux transferred by the atoms of the sort β as a result of their diffusion jumps through the plane z in the positive direction is equal to

$$\overset{+}{q}_\beta(z) = \rho_\beta(z-a_\beta)\, w_\beta(z-a_\beta)\, E_\beta(z-a_\beta)/6 = a_\beta G_\beta(z-a_\beta)\, E_\beta(z-a_\beta)/6\,, \tag{12}$$

and the density of this energy transferred in the negative direction is

$$\overset{-}{q}_\beta(z) = a_\beta G_\beta(z+a_\beta)\, E_\beta(z+a_\beta)/6\,. \tag{13}$$

The average specific internal energy E_β of the component β of a condensed body [1]

$$E_\beta = 9kT^4\,\frac{n_\beta}{\vartheta_\beta^3}\int\limits_0^{\vartheta_\beta/T}\frac{z^3\,dz}{\exp z-1}\,. \tag{14}$$

The resulting density of the heat flux of atoms in the direction z is equal to

$$q_\beta = \overset{+}{q}_\beta - \overset{-}{q}_\beta = -\frac{1}{3}\,a_\beta^2\,\frac{\partial\,(G_\beta E_\beta)}{\partial z} = -\,\lambda_{D\beta}\,\frac{\partial T}{\partial x}\,. \tag{15}$$

It follows herefrom that the diffusion heat conductivity is determined as

$$\lambda_{D\beta} = \frac{1}{3}\,a_\beta^2\,\frac{\partial\,(G_\beta E_\beta)}{\partial T} = \frac{1}{3}\,a_\beta^2\left(G_\beta\,\frac{\partial E_\beta}{\partial T} + E_\beta\,\frac{\partial G_\beta}{\partial T}\right). \tag{16}$$

The specific heat capacity of a unit volume $c_{V\beta}$ and the derivative $\partial G_\beta/\partial T$ are determined as

$$c_{V\beta} = \frac{\partial E_\beta}{\partial T} = 9kn_\beta\left\{4\,\frac{T^3}{\vartheta_\beta^3}\int\limits_0^{\vartheta_\beta/T}\frac{z^3\,dz}{\exp z-1} + \frac{\vartheta_\beta}{T}\left[\exp\left(\frac{\vartheta_\beta}{T}\right)-1\right]^{-1}\right\}, \tag{17}$$

$$\frac{\partial G_\beta}{\partial T} = \varepsilon_\beta\rho_\beta\left[\exp\left(\frac{A_\beta}{kT}\right)-1\right]^{-2}\frac{A_\beta}{kT^2}\exp\left(\frac{A_\beta}{kT}\right). \tag{18}$$

Thus the functional dependence $\lambda_{D\beta} = f(T)$ is completely determined. The diffusion heat conductivity of a multicomponent body λ_D is approximately determined by summation of $\lambda_{D\beta}$ over all its components, i.e., $\lambda_D = \sum\limits_{\beta=1}^{B}\lambda_{D\beta}$.

The difficulty of calculating $\lambda_{D\beta}$ is associated with determination of the diffusion-jump length a_β. The existence of the boundaries of crystals, impurities, dislocations, and mechanical and heat actions decreases the value of a_β because of the scattering of the particles executing a diffusion jump. Therefore, it is assumed that in solid bodies formed by large crystals, the value of a_β increases with decrease in their temperature. This is supported by the fact that at temperatures exceeding ϑ_β, at which the heat capacity c_V is close to $3k$, the conduction of crystalline bodies increases with decreasing temperature. When the temperature of a body is close to ϑ_β, $\lambda_{D\beta}$ reaches a maximum value. As the temperature of the body decreases, a_β increases to the size of a crystal. A further decrease in the temperature does not cause a change in a_β; therefore, at low temperatures, $\lambda_{D\beta}$ changes qualitatively in the same manner as $c_{V\beta}$ changes. An increase in the temperature (in the case where $T > \vartheta_\beta$) leads to a monotonic decrease in a_β to a value of lattice-spacing order. Accordingly, $\lambda_{D\beta}$ asymptotically approaches its minimum value.

If the grains of a crystal, because of their small sizes, approach the sizes of the crystal-lattice cells, which is characteristic of rapidly frozen liquids (amorphous bodies), it can be assumed that the value of a_β is approximately constant. For such bodies, $\lambda_{D\beta}$ changes much like as $c_{V\beta}$ changes.

Figure 1 shows temperature dependences of the relative diffusion heat conductivity of a one-component body in the coordinates T and $\bar{\lambda}_D = \lambda_D/(3kn_\beta\varepsilon_\beta a_\beta^2)$.

Mechanism of Electron Heat Conductivity. The free electrons in a metal make a dominant contribution to their heat conduction. This is true for both solid and liquid conductors. The classical theory of electron conductivity (the Drude theory) is based on the assumption [6, 7] that all the valence electrons, i.e., the electrons located on the outer atomic orbits, are free; they do not interact with the positively charged ions and obey the ideal-gas laws. The following equation of electron heat conductivity was obtained in the approximation of an ideal electron gas on the basis of the elementary kinetic theory: $\lambda_e = w_e n_e l_e c_e/3$. If the kinetic energy of a free electron E_e is equal to the average kinetic energy of the atoms of a gas at the equilibrium state, i.e., $E_e = 3kT/2 = m_e w_e^2/2$, the heat capacity of an electron $c_e = 3k/2$ and then $\lambda_e = w_e n_e l_e k/2$. The Drude equation obtained for λ_e is in satisfactory agreement with the experiment only in certain temperature intervals. Experiments have shown that the heat capacity of free electrons should account for only 1–2% of the above-indicated value of c_e. This is in contradiction to the classical-theory hypothesis, according to which the number of free electrons should not be less than the number of atoms. Moreover, it follows from experiments that the electronic heat capacity is not a constant value.

It is assumed in the quantum theory of electron heat conductivity that all the valence electrons in a gas are free and do not interact with ions and other electrons. To obtain an expression for the coefficients of energy transfer by electrons it is necessary to know the dependences of the velocity and energy of electrons on the wave vector. The determination of these dependences is analogous to the determination of the interaction potential of the gas molecules, even though the former is much more complex. The assumptions used in this case are warranted only for individual types of solid bodies in the limited temperature range.

The heat-conductivity coefficient of pure metals changes depending on their temperature in the following way. When the temperature of a metal increases beginning with $T = 0$ K, at which $\lambda_e = 0$, the rate of change in λ_e depending on T initially increases and then decreases. At $\partial\lambda_e/\partial T = 0$, λ_e reaches the maximum value, which corresponds to the temperature falling within the range 5–40 K for different metals. Then the absolute value of the velocity $\partial\lambda_e/\partial T$ initially increases and then decreases monotonically. In this case, λ_e approaches a constant value.

Neither the Drude theory nor the quantum theory explains the fact that in the region of fairly low temperatures the heat conductivity of metals reaches a maximum that can exceed their heat conductivity at room temperature by an order of magnitude or higher.

A characteristic of activation processes at small temperatures is a sharp increase in λ_e with increase in the temperature of a body. Below, we present the activation mechanism of electron heat conductivity. It will be assumed that at temperatures close to zero on the Kelvin scale all the electrons in a body are bound to atoms and are found at the zero energy level. To a degree of freedom of an atom corresponds one electron. When an energy is supplied to the body, an electromagnetic field arises inside it. In a condensed body, the valence electrons of its particles absorb photons $h\nu$ because of the internal photoeffect and, in doing so, are distributed in energy in accordance with law (2)

$$W_{i\mathrm{ve}} = [1 - \exp(-h\nu/(kT))]\,[1 - \exp(-A_e/(kT))]^{-1} \exp[-ih\nu/(kT)]\,. \tag{19}$$

When an electron reaches an activation energy A_e, it breaks loose from an atom and becomes free.

The activation energy of each electron successively breaking loose from an atom is substantially higher than the activation energy of the previous electron. This is explained by the fact that the negatively charged free electrons and the resulting positive charge of an ion appearing after an electron breaks loose prevent the detechment of bound electrons. Taking into account the fact that g_e depends exponentially on the activation energy A_e, in the determination of the density of free electrons it may be assumed that atoms are monovalent. In this case, the value of n_v is equal to the density of atoms in a metal $n_{met} = \rho_{met}/m_{met}$, and the density of ions n_i is equal to the density of free electrons, i.e.,

$$n_v = n_{met}\,, \quad n_i = n_f\,. \tag{20}$$

Each valence electron can be in the bound or free state. These states alternate in time. The density of the bound valence electrons is equal to

$$n_{\text{b}} = n_{\text{v}} - n_{\text{f}} . \tag{21}$$

In accordance with the laws of conservation of energy and momentum, a free electron cannot absorb a photon. However, electrons that reach the activation energy and, as a result, break loose from atoms of solid bodies are not entirely free. They remain in the field of action of fairly powerful intracrystalline forces and do not lose the ability to initiate a photoeffect [6]. If to each degree of freedom of an atom of a metallic body corresponds one electron, at the instant it breaks loose from the atom its average kinetic energy should be much lower than the average atomic energy. The detachment of an electron reaching the activation energy from an atom can be considered as an internal photoeffect. The kinetic energy of the detached electron is lower than its energy at the instant the detachment begins by the value of the work expended to overcome the intraatomic forces, in part the electrostatic forces.

The electrons that broke loose as a result of the absorption of electromagnetic-field photons in a body at the equilibrium state can reach the average energy of a free particle after a time. If necessary information on the coefficients of radiation and absorption of photons by electrons is available, this time can be determined on the basis of the law for the intensity of spectral radiation of particles (1). The presence of positively charged ions in a metal restricts the time of existence of electrons in the free state and, correspondingly, decreases their average kinetic energy. The time of existence of an electron in the free state decreases as the temperature of the body increases with increase in the density of ions and in the rate of motion of electrons. Further we will assume for simplicity that the average kinetic energy of free motion of an electron is proportional to the kinetic energy of an atom in the gas medium

$$E_{\text{f}} = \zeta\,(T)\,\frac{3}{2}\,kT = \frac{m_{\text{e}} w_{\text{f}}^{2}}{2} , \tag{22}$$

where m_{e} is the electron mass; ζ is the nonequilibrium coefficient accounting for the deviation of the kinetic energy of an electron from the energy of a free neutral particle of the system at the equilibrium state, $0 < \zeta \le 1$. This equation allows one to determine the average velocity w_{f} of free electrons.

Since only n_{f} electrons move with a velocity w_{f} and the other valence electrons are in the bonded state, i.e., are immobile, the average velocity of the valence electrons is determined as

$$w_{\text{v}} = n_{\text{f}} w_{\text{f}} / [n_{\text{f}} + (n_{\text{v}} - n_{\text{f}})] = n_{\text{f}} w_{\text{f}} / n_{\text{v}} . \tag{23}$$

In accordance with (3), the number of valence electrons in a unit volume reaching the activation energy in unit time is determined by the formula

$$g_{\text{e}} = \varepsilon_{\text{e}} n_{\text{b}} \left[\exp\left(\frac{A_{\text{e}}}{kT}\right) - 1 \right]^{-1} . \tag{24}$$

The number of transitions of a bound valence electron to the free state in unit time is

$$\Gamma = \frac{g_{\text{e}}}{n_{\text{v}}} = \varepsilon_{\text{e}} \left(1 - \frac{n_{\text{f}}}{n_{\text{v}}}\right) \left[\exp\left(\frac{A_{\text{e}}}{kT}\right) - 1 \right]^{-1} . \tag{25}$$

Then we will find the average number Γ' of transitions of a free valence electron in a conductor to the bound state as a result of its collisions with positively charged ions in a unit time. An electron traversing a fairly great distance L will collide with all the ions, the centers of which are inside the volume V of a cylinder of length L with a cross section $\sigma_{\text{i.e}}$ equal to the effective absorption cross section of an ion in relation to an electron, $V = \sigma_{\text{i.e}} L$. The number of collisions of an electron in the volume V is $n_{\text{f}} \sigma_{\text{i.e}} L$. The mean path traversed by an electron from the instant it breaks loose from an atom to the instant it is absorbed by an ion is equal to

$$l_e = L/(n_f\sigma_{i.e}L) = 1/(n_f\sigma_{i.e})\,. \tag{26}$$

In unit time, a valence electron traverses a path equal to w_f and, as a result of its collisions with positively charged ions, executes transitions into the bound state, the number of which is

$$\Gamma' = n_f\sigma_{i.e}w_f\,. \tag{27}$$

In the case where the system is at equilibrium, the numbers of transitions of free valence electrons Γ' into the free state and in the opposite direction are equal, i.e., $\Gamma = \Gamma'$. Then from Eqs. (25) and (27) we find

$$\frac{n_f}{n_v} = \frac{1}{1+\varphi}\,, \quad \varphi = \frac{n_v}{\varepsilon_e}\sigma_{i.e}w_f\left[\exp\left(\frac{A_e}{kT}\right) - 1\right]. \tag{28}$$

It follows from (28) that the density of free electrons $n_f \to 0$ at $T \to 0$ and $n_f \to n_v$ at $T \to \infty$. This corresponds to modern views on thermoelectron emission. The density n_f is determined by Eq. (27), and then the value of g_e is determined by Eq. (24).

The time between the two transitions of a valence electron into the free state is equal to

$$t_{tr} = 1/\Gamma = l_e/w_v\,. \tag{29}$$

It consists of the times of existence of a valence electron in the free t_f and bound t_b states, i.e.,

$$t_{tr} = t_f + t_b\,. \tag{30}$$

In the case where the average velocity of movement of a free electron is w_f and the length of its free path is l_e

$$t_f = l_e/w_f\,. \tag{31}$$

It follows from Eqs. (23), (29), and (31) that

$$\frac{w_v}{w_f} = \frac{n_f}{n_v} = \frac{t_f}{t_{tr}}\,. \tag{32}$$

Relations (20)–(31) represent a closed system of equations allowing one to determine the dependence of the quantities n_v, n_b, n_f, n_i, t_{tr}, t_f, t_b, w_v, w_f, l_e, g_e, Γ, Γ', and E_f on the temperature T, the density of atoms in a metal n_{met}, and the parameters A_e, ε_e, ζ, and $\sigma_{i.e}$ involved in these equations. In the case where some of the indicated parameters are unknown, it is necessary to use additional information, e.g., experimental data on the heat conductivity of the metal at definite temperatures, the number of which is equal to the number of unknown parameters of system (20)–(31).

In accordance with the elementary kinetic theory of heat conduction and Eq. (28), the density of the energy flux transferred by free electrons through the plane z in the positive direction of the z axis is determined by the relation

$$q_e^+(z) = \frac{1}{6}n_f(z - l_e)\,w_f(z - l_e)\,E_f(z - l_e)\,, \tag{33}$$

and the density of this energy transferred in the opposite direction is determined as

$$q_e^-(z) = \frac{1}{6}n_f(z + l_e)\,w_f(z + l_e)\,E_f(z + l_e)\,. \tag{34}$$

The resulting density of the heat flux in the z direction is equal to

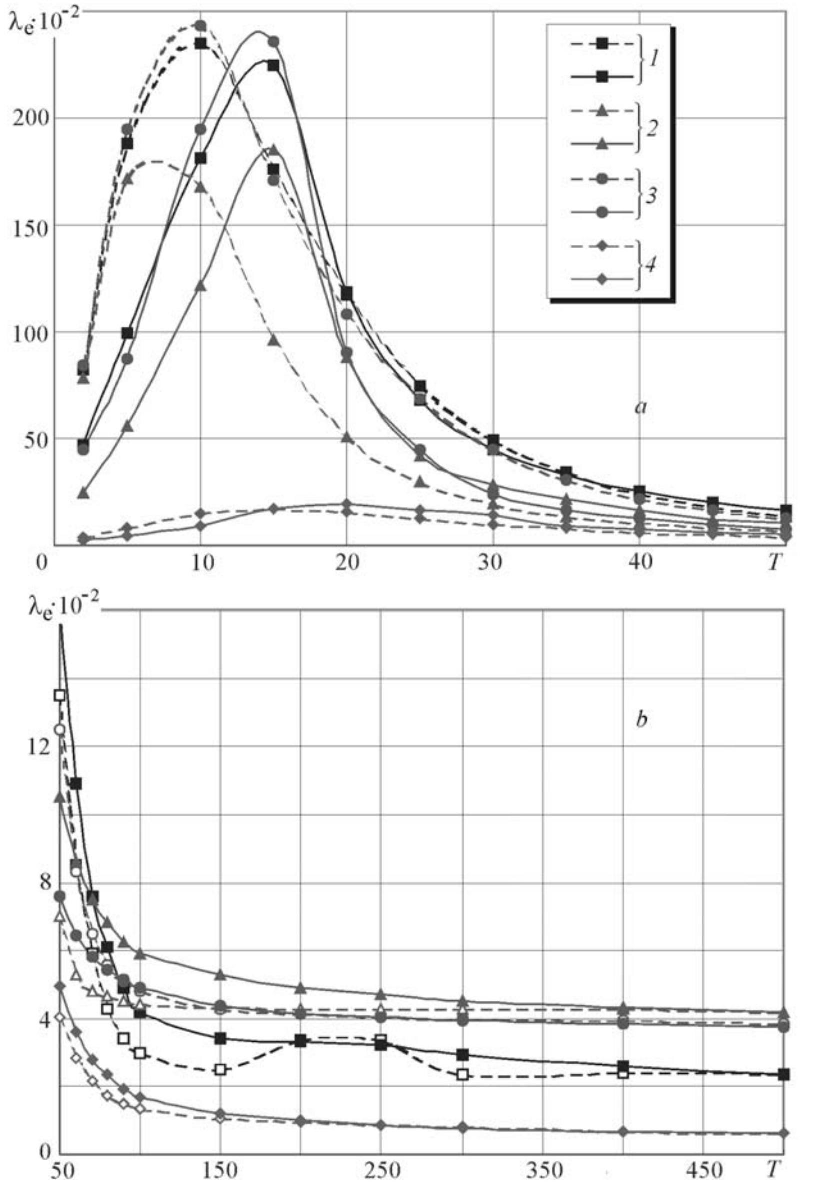

Fig. 2. Dependences of the electron heat conductivity λ_e of a body on its temperature T obtained on the basis of formula (36) (solid curves) and experimentally [8] (dashed curves) within the temperature ranges $0 < T \leq 50$ (a) and $50 < T \leq 500$ K (b) for aluminum (1), silver (2), copper (3), and iron (4). λ_e, W/(m·K); T, K.

$$q_\beta = \overset{+}{q}_\beta - \overset{-}{q}_\beta = -\frac{1}{3} l_e \frac{\partial (n_f w_f E_f)}{\partial z} = -\lambda_e \frac{\partial T}{\partial z} . \tag{35}$$

It follows herefrom that the electron heat conductivity

$$\lambda_e = \frac{1}{3} l_e \frac{\partial (n_f w_f E_f)}{\partial T} . \tag{36}$$

If, in formula (36), $n_f = n_v$, and $\partial(w_f E_f)/dT \approx w_e \partial E_e/dT = 3 w_e k/2$, it is transformed into the formula obtained in the classical Drude theory: $\lambda_e = l_e n_v w_e k/2$.

The results of numerical experiments on comparison of formula (36) with experimental data have shown that the deviation of the velocity of a free electron w_{f} from the average velocity w_{e} of the electron gas at the equilibrium state at different temperatures can be defined by the linear dependence

$$w_{\mathrm{f}} = w_{\mathrm{e}} (1 - \beta_{\mathrm{e}} T) , \quad \beta_{\mathrm{e}} = \mathrm{const} , \quad 0 < \beta_{\mathrm{e}} < 1 . \tag{37}$$

The quantity β_{e} has a value of the order of $1/T_{\mathrm{m}}$, where T_{m} is the melting temperature of the conductor. Substituting expression (37) into (22) we find that $\zeta(T) = (1 - \beta_{\mathrm{e}} T)^2$.

The results of calculations performed on the basis of Eqs. (20)–(37) have shown that the free path of electrons l_{e} increases with decreasing temperature. However, the value of l_{e} is limited by the sizes of the grains of a crystal L_{cr}, and if its temperature further decreases, l_{e} should retain the value of L_{cr}. In Fig. 2, the solid lines present the results of calculation, by formula (26), of the temperature dependences of the electron heat conductivity λ_{e} of different metals — iron, copper, aluminum, and silver. The dashed curves present experimental results [8]. The calculation and experimental data agree qualitatively and quantatively in a wide temperature range, including very low temperatures.

Conclusions. The mechanisms of heat conduction in solid and liquid media were formulated on the basis of molecular-radiation theory of heat and mass transfer. Formulas for the dependences of the electron, photon, and diffusion heat conductivity of dielectrics and metals on their temperature, density, and microscopic characteristics have been obtained. Unlike the known theories of electron heat conductivity, the theory presented allows one to determine the dependence of the density of free electrons on the temperature and properties of a conductor. The results of comparison of the theoretical and experimental data point to the fact that the equations of heat conduction obtained adequately define different mechanisms of energy transfer in condensed media.

NOTATION

A, activation energy, J; a_{β}, average distance transversed by an atom as a result of one jump, m; c, velocity of light, m/sec; c_{β}, mass isobaric heat capacity of the component β, J/(kg·K); c_V, heat capacity per unit volume, J/(m^3·K); D, diffusion coefficient, m^2/sec; e, average energy falling at one degree of freedom of a particle, J; e_{e}, absolute value of the electron charge, C; E, specific internal energy, J/m^3; Ei, integral exponential function; F, effective absorption cross section of the particles of a unit volume, m^{-1}; g, number of particles of a unit volume that reached the activation energy in a unit time, 1/(m^3·sec); G, mass of the particles of a unit volume that reached the activation energy in a unit time, kg/(m^3·sec); h, Planck constant, J·sec; i, ordinal number of an energy level of a particle; $I_{\beta\nu}$, limiting energy level at which a particle of the component β vibrating with a frequency ν can be found in activation processes; j^+, j^-, densities of the diffusion flows of atoms through the plane z in the positive and negative directions of the z axis, kg/(m^2·sec); k, Boltzmann constant, J/K; l_{β}, average length of a diffusion jump of a particle of the component β, m; m_{β}, mass of a particle of the component β, kg; n_{β}, density of the particles of the component β, m^{-3}; q, density of an energy flux, J/(m^2·sec); q^+, q^-, density of the energy fluxes in the positive and negative directions of the z axis, J/(m^2·sec); R, universal gas constant, J/(mole·K); $\mathbf{r}$, radius-vector; t, time, sec; t_{tr}, average time between two transitions of a valence electron into the free state, sec; T, temperature, K; V, volume, m^2; w, velocity, m/sec; $W_{\beta i\nu}$, function of distribution of particles in energy in activation processes; x, y, z, Cartesian coordinates, m; α, angle between the x axis and the radius-vector $\mathbf{r}$; B, number of components in the system; ΔS, element of area, m^2; $\gamma_{\beta\nu}$, number of degrees of freedom of the atoms of the component β forming a standing wave with a frequency ν; Γ, number of transitions of a bound valence electron into the free state in a unit time, 1/sec; Γ', number of transitions of a free valence electron into the bound state in a unit time because of its collisions with positively charged ions, 1/sec; ε_{ν}, coefficient of radiation of photons of frequency ν by a particle; ε_{β}, radiation coefficient averaged over frequencies, sec^{-1}; η, distance of the particles lying in the plane $x + \eta$ from the coordinate plane x, m; ζ, nonequilibrium coefficient; λ_D, λ_{ph}, λ_{e}, coefficients of diffusion, photon, and electron heat conductivity, W/(m·K); ν, frequency of vibrations, sec^{-1}; $\nu_{\beta\max}$, maximum frequency of standing electromagnetic waves arising in a condensed body, sec^{-1}; ξ, coefficient of overlapping of particles; ρ, density, kg/m^3; $\sigma_{\beta\nu}$, effective cross section of absorption of photons of frequency ν by a particle of the component β, m^2; ϑ, characteristic temperature, K; ∇, Hamilton operator. Subscripts: v, valence electron; g, gas, s, sound; i, ion; cr, crystal;

met, metal; m, melting; f, free electron; b, bonded electron; ph, photon; e, electron; β, ordinal number of a component; max, maximum value.

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