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Electron Scattering from Thermal Vibrations in a Liquid

A. I. GUBANOV
Leningrad Physico-Technical Institute, Academy of Sciences, USSR

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It is shown that the law of conservation of momentum in the electron-phonon system may not necessarily hold in the case of scattering of electrons by the thermal vibrations in a liquid, as a consequence of the absence of strict periodicity in a liquid conductor. Therefore, in addition to the usual scattering of electrons by the phonons in a liquid, there exists an additional phonon-liquid scattering. The electron mean free path length corresponding to this scattering in liquid metals and semiconductors has been computed.

1. INTRODUCTION

QUANTUM-mechanical investigation shows[1] that the behavior of electrons in a liquid is similar to the behavior of electrons in a crystal; in particular, the electrons have a band energy spectrum and move as quasi-free particles. The scattering of electrons as a consequence of the disruption of long range order in liquids was calculated in Ref. 2. But, in addition to this scattering, which is specific to the liquid, there takes place (just as in crystals) a scattering of the electrons by the thermal vibrations which can play a dominant role at a high temperature of fusion. In the present research, we consider the scattering of electrons in the liquid by the thermal vibrations.

It was shown in Ref. 2 that the quasi-Bloch functions of the form

$$\psi_{\mathbf{k}} = G^{-1/2} u_{\mathbf{k}}(\xi)\, e^{i\mathbf{k}\mathbf{r}}, \tag{1}$$

are an excellent zeroth approximation for the description of the electrons in the liquid. Here k is the wave vector of the electron and $u_{\mathbf{k}}(\xi)$ is a function which is almost periodic in the deformed coordinate system ξ in which the self-consistent potential for the electron in the liquid is periodic (see Ref. 1).

Thermal vibrations are considered in the theory of electrical conduction in the approximation of an elastic continuum, and the discreteness of the lattice is taken into account only for the determination of the limiting wave number of the phonons. It is natural that in this approximation there is no difference between crystal and liquid, so that we can use as the phonon, wave functions the same functions as in the theory of solids. Knowing the unperturbed wave functions (1) for the electrons, and making use of the usual functions for the phonons, we can repeat all the calculations for the liquid that have been used for solid conductors.

If we consider the interaction between electrons and phonons as a small perturbation, then the eigenfunction of the unperturbed problem is the product of the electron function and a function of all the oscillators of the lattice, and we can expand the wave function of the perturbed problem in a series of these products:

$$\Psi(t)=\sum c(\mathbf{k},N_{\mathbf{q}j},t)\psi^0_{\mathbf{k}}(r)\prod_{\mathbf{q},j}\psi_{N_{\mathbf{q}j}}(a_{\mathbf{q}j}) \tag{2}$$

$$\times\exp\left\{-\frac{it}{\hbar}\left[E_{\mathbf{k}}+\sum_{\mathbf{q}}\sum_{j}\left(N_{\mathbf{q}j}+\frac{1}{2}\right)\hbar\omega_{\mathbf{q}j}\right]\right\}.$$

As is known from Eq. (34.7) of Ref. 3, the expansion coefficients of c depend on the time and, for small t, satisfy the equation

$$i\hbar\dot{c}(\mathbf{k}',N'_{\mathbf{q}j})=\int\psi^*(\mathbf{k}',N_{\mathbf{q}j})\,U\psi(\mathbf{k},N_{\mathbf{q}j})\,d\tau \tag{3}$$

$$\times\exp\left\{\frac{it}{\hbar}\left[E_{\mathbf{k}'}-E_{\mathbf{k}}+\sum_{\mathbf{q}}\sum_{j}(N'_{\mathbf{q}j}-N_{\mathbf{q}j})\,\hbar\omega_{\mathbf{q}j}\right]\right\}.$$

The symbols here are standard: **k** and **k**′ are the wave vectors of the electron; **q** is the wave vector of the phonon; j is the direction of its polarization; $N_{\mathbf{q}j}$ is the number of phonons with wave vector **q** and polarization direction j; $E_{\mathbf{k}}$ and $E_{\mathbf{k}'}$ are the energies of the electron for the corresponding index values of the wave vector, $\omega_{\mathbf{q}j}$ is the frequency of a phonon with given **q** and j. Integration over $d\tau$ consists of integration both over the radius vector of the electron, **r**, and over the oscillator coordinates $a_{\mathbf{q}j}$.

The perturbation energy U has a different expression in the cases of acoustical and optical thermal vibrations. Initially, we shall consider the scattering by acoustical vibrations---the only vibrations in metals and atomic semiconductors.

2. MEASUREMENT OF THE ELECTRON DISTRIBUTION FUNCTION UNDER THE ACTION OF THERMAL VIBRATIONS

In the deformed-ions approximation the perturbation energy is equal to

$$U=-\mathbf{u}\operatorname{grad}V, \tag{4}$$

where V is the self-consistent potential for the electron and **u** is the displacement of the ions or atoms in the thermal vibrations:

$$\mathbf{u}=G^{-3/2}\sum_{\mathbf{q}}\sum_{j=1}^{3}\mathbf{e}_{\mathbf{q}j}(a_{\mathbf{q}j}\mathbf{e}^{i\mathbf{q}\mathbf{r}}+a^*_{\mathbf{q}j}\mathbf{e}^{-i\mathbf{q}\mathbf{r}}), \tag{5}$$

G^3 is the number of atoms in the elementary cell, $\mathbf{e}_{\mathbf{q}j}$ is the state of polarization of the phonons.

The integral over the electron coordinates in Eq. (3) can, after substitution of Eq. (1) for $\psi_{\mathbf{k}}(r)$ and $\psi_{\mathbf{k}'}(r)$, be represented in the form of a sum of integrals over the G^3 deformed elementary cells:

$$\mathrm{K}^{\pm}=G^{-3}\sum_{\mathbf{n}}e^{i(\mathbf{k}\pm\mathbf{q}-\mathbf{k}')\mathbf{n}}\int e^{i(\mathbf{k}\pm\mathbf{q}-\mathbf{k}')\mathbf{r}'} \tag{6}$$

$$\times\operatorname{grad}V(\mathbf{r}')\,u_{\mathbf{k}}(\mathbf{r}')\,u^*_{\mathbf{k}'}(\mathbf{r}')\,d\tau_0,$$

where **n** is the radius vector of the nth site, $\mathbf{r}'=\mathbf{r}-\mathbf{n}$.

In a crystal, as a consequence of the periodicity of $V(r)$ and $u_{\mathbf{k}}(\mathbf{r})$, the integral over the elementary cell does not depend on the number of cells, but the values of the vector **n** form a regular lattice in space. Therefore, the sum over **n** differs from zero only if

$$\mathbf{k}\pm\mathbf{q}=\mathbf{k}'; \tag{7}$$

the sign (+) refers to K^+ and the sign (−) to K^-. Physically, the condition (7) signifies the law of conservation of momentum in the electron-phonon system, since K^+ describes the absorption of a phonon and K^- the emission of one. Under the condition (7), summation over **n** simply yields the factor G^3.

As noted in Ref. 2, $u_{\mathbf{k}}$ for a liquid, in the isotropic approximation, is a periodic function of the deformed coordinates ξ; therefore, when condition (7) is satisfied, the integral over the deformed elementary cell does not depend on the number of cells, with accuracy up to a small quantity of order ϵ---the degree of disruption of local order, i.e., the relative deformation of the elementary cell. There is no point to keeping a correction of order ϵ, since the perturbation itself is taken to be a small quantity, and these corrections would be of second order of smallness. Thus, when condition (7) is satisfied, the situation in the liquid is no different from that in the crystal.

It is easy to see that all subsequent calculations carried out for crystals will be valid with accuracy to corrections of order ϵ and the same results will be given for liquids. This is purely phonon scattering of the electrons, which is entirely independent of the disruption of long range order in the liquid.

However, if Eq. (7) is not observed, then it is not possible, in the case of a liquid, to prove that the sum over **n** [in Eq. (6)] vanishes. Actually, in the first place, in a liquid, the distant elementary cells are oriented at any angle relative to one another; therefore, the corresponding vectors **r**′ in the different cells make different angles with the constant vector k ± q − k′, i.e., the exponential factors under the integral sign, and the integrals over the elementary cells themselves, depend on the number of cells. Second, the vectors **n** in the liquid no longer form a regular lattice, but are random quantities.

We show that the summation over the G^3 deformed elementary cells gives the factor $G^3\epsilon^2$. In the isotropic approximation, the integral over the elementary cell in Eq. (6) can be taken from under the summation sign; the problem then reduces to the calculation of the sum

$$\sum = \sum_{\mathbf{n}} e^{i\mathbf{q}'\mathbf{n}}, \tag{8}$$

where for brevity we put k ± q − k′ = q′. The vectors **n** in the liquid are random quantities but are not completely independent of one another, since the differences of the vectors **n**, relating to neighboring cells, differ in modulus from the lattice constant only by corrections of order ϵ.

As a preliminary we calculate the analogous sum for a one-dimensional liquid model:

$$\sum\nolimits_1 = \sum_{n=1}^{G} e^{iqx_n}, \tag{9}$$

where

$$qa = 2k\pi/G; \quad x_n = x_{n-1} + a(1 + \varepsilon\gamma_n), \tag{10}$$

a = lattice constant; k = 0, 1, 2, . . . ; G is the number of atoms in the chain; $\epsilon \ll 1$; γ_n are random variables (see Ref. 1). The computation of the sum is similar to the calculation of the length of a polymer molecule with restricted turning of the links (see, for example, Ref. 4, pp. 409-411). We therefore make use of the similar claculations there. We determine the square of the modulus of the sum:

$$\left|\sum\nolimits_1\right|^2 = \sum_{n=1}^{G} e^{iqx_n} \cdot \sum_{m=1}^{G} e^{-iqx_m} \tag{11}$$

$$= G + \sum_{n<m}\sum [e^{iq(x_n - x_m)} + e^{iq(x_m - x_n)}].$$

It follows from (10) that

$$x_n = na + a\varepsilon \sum_{l=1}^{n} \gamma_l; \quad x_m = ma + a\varepsilon \sum_{l=1}^{m} \gamma_l. \tag{12}$$

Substituting (12) in (11), we transform this expression to the form

$$\left|\sum\nolimits_1\right|^2 = G + \sum_{n<m}\sum \Biggl\{ e^{iqa(n-m)} \Biggl[\cos\Biggl(\varepsilon aq \sum_{l=n+1}^{m} \gamma_l\Biggr) - i\sin\Biggl(\varepsilon aq \sum_{l=n+1}^{m} \gamma_l\Biggr)\Biggr] + e^{iqa(m-n)}\Biggl[\cos\Biggl(\varepsilon aq \sum_{l=n+1}^{m} \gamma_l\Biggr) + i\sin\Biggl(\varepsilon aq \sum_{l=n+1}^{m} \gamma_l\Biggr)\Biggr]\Biggr\}. \tag{13}$$

Transforming to mean values, we note that inasmuch as the γ_l take on positive and negative valuse with equal probability, the sines vanish and the average values of the cosine sum will be equal to the products of the mean cosine components. Since the mean square values of all the γ_l are the same, the product reduces to the order of the quantity $\overline{\cos(\epsilon aq\gamma_l)}$. Consequently,

$$\overline{\left|\sum\nolimits_1\right|^2} = G \tag{14}$$

$$+ \sum_{n<m}\sum \overline{[\cos(\varepsilon aq\gamma_l]}^{\,m-n} [e^{iqa(m-n)} + e^{iqa(n-m)}].$$

The summation is carried out without difficulty and yields

$$\overline{\left|\sum\nolimits_1\right|^2} = G + \frac{G\zeta\eta}{1-\zeta\eta} + \frac{G\zeta/\eta}{1-\zeta/\eta} \tag{15}$$

$$- \frac{\zeta\eta\,(1-\zeta^G\eta^G)}{(1-\zeta\eta)^2} - \frac{\zeta}{\eta}\,\frac{(1-\zeta^G/\eta^G)}{(1-\zeta/\eta)^2},$$

where, for brevity, we have put

$$\eta = e^{iqa} = e^{2\pi ik/G}; \quad \zeta = \overline{\cos(\varepsilon aq\gamma_l)}. \tag{16}$$

Discarding the last two terms in Eq. (15), which do not contain the large multiplicative factor G, we get

$$\overline{\left|\sum\nolimits_1\right|^2} \approx G\,\frac{1-\zeta^2}{1-\zeta\eta-(\zeta/\eta)+\zeta^2}. \tag{17}$$

Expanding Eq. (16) in a series, and keeping in mind the smallness of ϵ, and that $\overline{\gamma_l^2} = 1$, we get from Eq. (17), for $q \neq 0$,

$$\overline{\left|\sum\nolimits_1\right|^2} \approx G\varepsilon^2. \tag{18}$$

For $q = 0$, the approximate equation (17) is not suitable, and the more accurate expression (15) yields $\overline{|\Sigma_1|^2} = G^2$, in correspondence with the usual theory.

The three-dimensional case can be reduced to one-dimensional if we direct the x axis along the vector q^1 and the fundamental region of G^3 atoms into G^2 chains of atoms, parallel to the x axis, with G atoms in each. Then we can accomplish summation along the chain as in the one-dimensional case; we get the factor $G\epsilon^2$ in the expression for the mean square modulus of the sum. The summation over the G^2 chains also yields a factor G^2; hence, the sum reduces to multiplication by $G^3\epsilon^2$.

Consequently, scattering of electrons by phonons is possible in a liquid without satisfying the law of conservation of momentum inside the electron-phonon system. This can explain the fact that the lattice, as a consequence of the disruption of long range order in it, can take on additional momentum in the emission or absorption of a phonon by an electron. A similar effect takes place in the case of impurities in crystals.

We call this additional scattering of the electrons "phonon-liquid," since both thermal vibrations and disruption of long range order are essential here in equal degree. At first glance, consideration of phonon-liquid scattering can be regarded as inconsequential, inasmuch as we neglect corrections of order ϵ for the usual phonon scattering in a liquid. However, there were only small corrections to the numerical values of the coefficients in such a case, whereas phonon-liquid scattering is a new physical phenomenon with specific properties and some dependence on the energy of the electron, and therefore (in certain cases) it can play a role in spite of the smallness of ϵ. Let us consider the mean free path length l_{pl} connected with phonon-liquid scattering.

Because of the exponential factor in the integral over the elementary cell, this integral, strictly speaking, depends on $\mathbf{k} + \mathbf{q} - \mathbf{k}'$. However, the factor grad V has a maximum value inside the atomic core, where $\mathbf{r}'$ is small; therefore, the effect of the exponential factor is insignificant (see Ref. 3, p. 227), and we neglect it. Consideration of the exponential factor would only have given rise to a coefficient close to unity.

The summation of G^3 randomly sign-changing quantities gives a factor G^3 in the expression for the square of the modulus of the sum. Integration is carried out over the oscillator coordinates, as in the case of a metal. Integrating Eq. (3) with respect to time, we get, after some transformations (see Ref. 3, pp. 187-190):

$$|c(\mathbf{k}', N_{\mathbf{q}j} - 1, t)|^2 = (2G^{-6}C^2\varepsilon^2/9M\hbar)(\mathbf{k} - \mathbf{k}') \times \mathbf{e}_{\mathbf{q}j} N_{\mathbf{q}j} \Omega(E_{\mathbf{k}'} - E_{\mathbf{k}} - \hbar\omega_{\mathbf{q}j}), \tag{19}$$

$$|c(\mathbf{k}', N_{\mathbf{q}j} + 1, t)|^2 = (2G^{-6}C^2\varepsilon^2/9M\hbar) \times (\mathbf{k} - \mathbf{k}')\mathbf{e}_{\mathbf{q}j}(N_{\mathbf{q}j} + 1)\Omega(E_{\mathbf{k}'} - E_{\mathbf{k}} + \hbar\omega_{\mathbf{q}j}). \tag{20}$$

$$C = \frac{\hbar^2}{2m}\int |\operatorname{grad} u|^2 d\tau_0; \quad \Omega(x) = 2\,\frac{1 - \cos(xt/\hbar)}{(x/\hbar)^2}.$$

Inasmuch as $\mathbf{k} - \mathbf{k}' \neq \pm\mathbf{q}$, the electrons, in contrast to ordinary scattering, interact not only with longitudinal, but also with transverse, waves. Because of the δ-character of the function $\Omega(x)$, the law of energy conservation is satisfied in the electron-photon system. This means that the disrupted lattice, taking on additional momentum, does not absorb additional energy for the photon.

In order to obtain a change in the electron distribution function at the expense of scattering, we must multiply Eq. (19) by the probability for the existence of the initial state, and also by the probability of non-occupation of the final state, and sum over all initial values of the wave vector k of the electron, over all values of the wave vector of the photon q, and over the directions of its polarization j. We emphasize that, in contrast to the ordinary case of phonon scattering, the summation here over k is taken independently of the summation over q. As a result, we obtain:

$$\begin{aligned} f(\mathbf{k}', t) - f(\mathbf{k}', 0) = {} & \frac{2C^2G^{-6}\varepsilon^2}{9M\hbar} \sum_{\mathbf{k},\mathbf{q},j} [(\mathbf{k} - \mathbf{k}')\mathbf{e}_{\mathbf{q}j}]^2 \\ & \times \{\Omega(E_{\mathbf{k}'} - E_{\mathbf{k}} + \hbar\omega_{\mathbf{q}j})[f(\mathbf{k})(1 - f(\mathbf{k}')) \\ & \times (N_{\mathbf{q}j} + 1) - f(\mathbf{k}')(1 - f(\mathbf{k}))N_{\mathbf{q}j}] \\ & + \Omega(E_{\mathbf{k}'} - E_{\mathbf{k}} - \hbar\omega_{\mathbf{q}j})[f(\mathbf{k})(1 - f(\mathbf{k}'))N_{\mathbf{q}j} \\ & - f(\mathbf{k}')(1 - f(\mathbf{k}))(N_{\mathbf{q}j} + 1)]\}. \end{aligned} \tag{21}$$

3. THE MEAN FREE PATH OF THE ELECTRON AS DETERMINED BY PHONON-LIQUID SCATTERING

We introduce the spherical coordinate system k, θ, Φ in the space k, with axis k_x and the coordinates q, ϑ, φ in the space q, with axis along $\mathbf{k}-\mathbf{k}'$, and we replace the summations over k and q by integration, with the help of the formulas

$$\sum_k F(k) = \Omega_0 (G/2\pi)^3 \int k^2 dk \sin\theta \, d\theta \, d\Phi F(k), \tag{22}$$

$$\sum_q F(q) = \Omega_0 (G/2\pi)^3 \int q^2 dq \sin\vartheta \, d\vartheta \, d\varphi F(q),$$

Ω_0 is the volume of the elementary cell. We shall consider that the phonons are in thermal equilibrium, while the electrons have small deviations from thermal equilibrium at the expense of the electric field, or the temperature gradient, which act along the x direction. In this case,

$$N_{\mathbf{q}j} = \frac{1}{\exp\{\hbar\omega_{qj}/kT\} - 1}; \tag{23}$$

$$f = f_0 - k_x \frac{\partial f_0}{\partial E}\chi(E);$$

$$f_0 = [\exp\{(E-\mu)/kT\} + 1]^{-1},$$

$\chi(E)$ is a small correction whose square we shall neglect, μ is the Fermi potential. We shall consider the energy to be dependent only on the modulus of k or k'.

Integration with respect to φ yields the factor 2π, ϑ enters only in the scalar product $(\mathbf{k}-\mathbf{k}')\mathbf{e}_{qj}$. Let $j = 1$ be the longitudinal wave and $j = 2,3$ the transverse, where $\mathbf{e}_{\mathbf{q}2}$ lies in the plane $\mathbf{k}-\mathbf{k}'$, q, and $\mathbf{e}_{\mathbf{q}3}$ are perpendicular to it. Then we easily obtain

$$\int [(\mathbf{k}-\mathbf{k}')\mathbf{e}_{\mathbf{q}1}]^2 \sin\vartheta \, d\vartheta = \frac{2}{3}(\mathbf{k}-\mathbf{k}')^2; \tag{24}$$

$$\int [(\mathbf{k}-\mathbf{k}')\mathbf{e}_{\mathbf{q}2}]^2 \sin\vartheta \, d\vartheta = \frac{4}{3}(\mathbf{k}-\mathbf{k}')^2.$$

In the integration over q, we take into account the δ-character of the function $\Omega(x)$. All the factors save Ω can be removed from the integrand, setting

$$\omega_{\mathbf{q}j} = \pm(E_k - E_{k'})/\hbar; \tag{25}$$

$$q = \omega_{\mathbf{q}j}/u_j = \pm(E_k - E_{k'})/\hbar u_j,$$

where u_1 and u_2 are the velocities of the longitudinal and transverse waves, respectively. The remaining integral gives

$$\int_0^\infty \Omega(E_{k'} - E_k - \hbar\omega_{qj})\, dq \approx 2\pi t / u_j. \tag{26}$$

In the substitution of Eqs. (23) and (25) in (21), all the terms of zeroth order of smallness vanish, leaving only terms with $f_1(E_k)$ and $f_1(E_{k'})$. Further,

$$(\mathbf{k}-\mathbf{k}')^2 = k'^2 + k^2 - 2kk'\cos\vartheta', \tag{27}$$

where ϑ' is the angle between k and k$'$. If we denote by Φ the angle from the plane k$'$, x, then

$$\cos\vartheta' = \cos\theta\cos\theta' + \sin\theta\sin\theta'\sin\Phi. \tag{28}$$

The term in $\sin\Phi$ vanishes upon integration, and all the remaining terms are multiplied by 2π.

The limits of the integration over k are obtained from the condition

$$E(k^j_{\max}) = E_{k'} + \hbar\omega_j, \quad E(k^j_{\min}) = \begin{cases} E_{k'} - \hbar\omega_j & \text{for} \quad E_{k'} \gtrless \hbar\omega_j; \\ 0 \end{cases} \tag{29}$$

ω_1 and ω_2 are the limiting frequencies of the longitudinal and transverse waves.

Carrying out the integration over θ, substituting the value of $(\partial f/\partial s)_{\text{pl}}$ in the kinetic equation for the case in which the electric field E_x acts along the x axis, and setting $k'\cos\theta' = k'_x$, we get the Bloch integral equation for the function $\chi(E)$, which, after several transformations (which make use of the explicit functions for N and f_0), takes the form

$$\sum_{j=1}^{2} \frac{j}{u_j^3} \Big\{ \int_{k'}^{k^j_{\max}} N_{qj} k^2 dk (E_k - E_{k'}) \times \exp\left\{\frac{E_k - E_{k'}}{kT}\right\} \frac{f_0(E_k)}{f_0(E_{k'})} \Big[\frac{2}{3}k^2\chi(E_k) + (k^2 + k'^2)\chi(E_{k'})\Big] dk$$

$$+ \int_{k^j_{\min}}^{k'} N_{qj} k^2 dk (E_{k'} - E_k) \frac{f_0(E_k)}{f_0(E_{k'})} \Big[\frac{2}{3}k^2\chi(E_k) + (k^2 + k'^2)\chi(E_{k'})\Big]\Big\} dk = \frac{27M\pi^3\hbar e E_x}{k'C^2\Omega_0^2\varepsilon^2}\frac{dE}{dk'}. \tag{30}$$

Generalization to the case in which there is a temperature or concentration gradient in addition to the electric field presents no additional difficulties.

For computation of the integral in Eq. (30), it is appropriate to introduce the notation

$$\frac{|E_k - E_{k'}|}{kT} = y, \quad \frac{E_{k'}}{kT} = \eta, \quad \frac{E_{k'} - \mu}{kT} = \zeta, \quad \frac{\hbar\omega_j}{kT} = y_j, \tag{31}$$

$$k' = k(\eta), \quad k = k(\eta \pm y),$$

and transform to integration over y. The left-hand side of Eq. (30) takes the form

$$\frac{(kT)^2 k'^4 \chi(E_{k'})}{dE_{k'}/dk'} \sum_{j=1}^{2} \frac{j}{u_j^3}(I_j' + I_j''), \tag{32}$$

$$I_j' = \int_0^{y_j} \frac{ye^y}{e^y - 1} \frac{e^{\zeta} + 1}{e^{\zeta + y} + 1}\left[\frac{2}{3}\frac{k^2(\eta + y)}{k^2(\eta)}\frac{\chi(\eta + y)}{\chi(\eta)} + \frac{k^2(\eta + y)}{k^2(\eta)} + 1\right]\frac{dk(\eta + y)}{dk(\eta)}\,dy, \tag{33}$$

$$I_j'' = \int_0^{y^*} \frac{y}{e^y - 1} \frac{e^{\zeta} + 1}{e^{\zeta - y} + 1}\left[\frac{2}{3}\frac{k^2(\eta + y)}{k^2(\eta)}\frac{\chi(\eta + y)}{\chi(\eta)} + \frac{k^2(\eta + y)}{k^2(\eta)} + 1\right]\frac{dk(\eta + y)}{dk(\eta)}\,dy,$$

where, in accord with Eq. (19), $y^* = y_j$ for $\eta > y_j$, $y^* = \eta$ for $\eta < y_j$.

The expressions in front of the square brackets in Eq. (33) have a maximum at $y = 0$ and decrease rapidly thereafter. Therefore, we make no great error if we take the values at $y = 0$ for the slowly varying functions $k^2(\eta + y)$, $\chi(\eta + y)$ and $dk(\eta + y)$. This certainly is the case for metals and for semiconductors at high temperatures, since in both cases $\eta \gg y$ for the vast majority of the electrons and these functions vary within relatively narrow limits.

These assumptions are somewhat less valid for semiconductors at low temperatures, but for this case, as we whall see below, phonon-liquid scattering does not play an important role, and a rough estimate suffices .

We note that the assumption $\chi = \text{const}$ also applies in the theory of electrical conductivity in the region of very high temperatures. In our case, the structure of the Bloch integral equation is much more favorable for the assumption mentioned; therefore, it can be extended to any temperature. This means that the mean free path of the electron, connected with the phonon-liquid scattering, exists at any temperature.

As a result of the assumptions we have made, the expressions for I_j' and I_j'' are greatly simplified:

$$I_j' = \frac{8}{3}\int_0^{y_j} \frac{ye^y}{e^y - 1}\frac{e^{\zeta} + 1}{e^{\zeta + y} + 1}\,dy; \tag{34}$$

$$I_j'' = \frac{8}{3}\int_0^{y^*} \frac{y}{e^y - 1}\frac{e^{\zeta} + 1}{e^{\zeta + y} + 1}\,dy.$$

Substituting Eq. (22) in Eq. (20), solving this equation for $\chi(E_{k'})$ and setting $\Omega_0 = a^3$, we obtain the free path length of the electron as determined by the phonon-liquid scattering:

$$l_{\text{pl}} = k'\chi(E_{k'})/eE \tag{35}$$

$$= 27M\pi^3\hbar / k'^4 (kT)^2 C^2 \varepsilon^2 a^6 \sum_{j=1,\,2} j u_j^{-3}(I_j' + I_j'').$$

I_j' is a function of y_j, I_j'' for $\epsilon > y_j$ is also a function of y_j, and for $\epsilon < y_j$ it is a function of ϵ. From Eq. (21), $y_1 = \Theta/T$, where Θ is the Debye temperature. If we assume that for longitudinal and transverse waves there exists just one limiting value of the wave vector q_0, then, evidently, $y_2 = \Theta u_2/Tu_1$; consequently, I_j' and I_j'' are functions of Θ/T. Explicit forms of this function can be obtained in the region of high temperatures ($T \gg \Theta$) and in the region of low temperatures ($T \ll \Theta$).

For $T \gg \Theta$, $y \ll 1$, for most electrons, $y_j < \epsilon$, which means $y^* = y_j$,

$$I_1' = I_1'' = 8\Theta/3T, \quad I_2' = I_2'' = 8\Theta u_2/3Tu_1. \tag{36}$$

Substituting Eq. (36) in Eq. (35), and using the relations

$$u_1 = k\Theta/hq_0, \quad q_0 = (2\pi/a)(^3/_4\,\pi)^{1/3}, \tag{37}$$

we get, after several transformations,

$$l_{\text{pl}} = (9\pi Mak\Theta / 32\beta C^2\varepsilon^2 h^2 (ak')^4) \tag{38}$$

$$\times (\Theta/T)(dE_{k'}/dk')^2.$$

Here β is a number close to unity:

$$\beta = {}^1/_3 + 2u_1^2/3u_2^2. \tag{39}$$

For $T \ll \Theta$ we investigate metals and semiconductors separately. For metals, the electrons in a narrow band around the Fermi level play the important role. Therefore, we set $\zeta = 0$. Further, $\eta > y_j$, $y^* = y_j$, and since $y_j \gg 1$, then the upper limit of integration in both integrals of (34) can be extended to infinity. Then

$$I'_j = I''_j = 2\pi^3/3 \tag{40}$$

(see Ref. 5, pp. 134, 350); I'_j and I''_j do not depend on j. Therefore,

$$l_{\mathrm{pl}} = (9Mak\Theta/8\pi\beta' C^2\varepsilon^2\hbar^2(ak')^4) \times (\Theta/T)^2 (dE_{k'}/dk')^2, \tag{41}$$

$$\beta' = 1/3 + 2u_1^3/3u_2^3. \tag{42}$$

For semiconductors, $\zeta \gg 1$, and we can neglect unity in comparison with e^{ζ}. In the integral for I'_j, we can again extend the integral to infinity. Then

$$I'_j = 4\pi^2/9 \tag{43}$$

(see Ref. 5, pp. 134, 244).

For most electrons in the conduction band of a semiconductor, η has the order of unity for $T \ll \Theta$, $\eta < y$, which means that $y^* = \eta$ and it is easy to see that

$$\text{for } \eta < \pi^2/6 \quad I''_j \leqslant 8\eta/3; \qquad \text{for } \eta > \pi^2/6 \quad I''_j \leqslant 4\pi^2/9, \tag{44}$$

the equality holds: in the first case for $\eta \ll 1$, in the second case for $\eta \gg 1$.

Consequently,

$$l_{\mathrm{pl}} = (27Mak\Theta\alpha(E_{k'})/16\pi\beta' C^2\varepsilon^2\hbar^2(ak')^4) \times (\Theta/T)^2 (dE_{k'}/dk')^2. \tag{45}$$

As $E_{k'}$ increases from zero to infinity, the coefficient $\alpha(E_{k'})$ changes from 1 to ½.

It is of interest to compare the mean free paths obtained here with the value l_{p} which is defined by the usual phonon scattering. In accord with Ref. 3, Eqs. (36.8), (37.15) and (45.16) for metals:

for $T \gg \Theta$

$$l_{\mathrm{p}} = (Mk'^2a^3k\Theta/\pi^3\hbar^2C^2)(\Theta/T)(dE_{k'}/dk')^2, \tag{46}$$

for $T \ll \Theta$

$$l_{\mathrm{p}} = (Mk'^2a^3k\Theta/4\pi^3 124{,}4\hbar^2C^2) \times (\Theta/T)^5 (dE_{k'}/dk')^2. \tag{47}$$

For semiconductors at arbitrary temperature

$$l_{\mathrm{p}} = (9(4\pi/3)^{2/3}Mak\Theta/16\pi\hbar^2C^2(ak')^2) \times (\Theta/T)(dE_{k'}/dk')^2. \tag{48}$$

Consequently, for metals at $T \gg \Theta$,

$$l_{\mathrm{pl}}/l_{\mathrm{p}} \approx 9\pi/(ak')^6\varepsilon^2, \tag{49}$$

and for $T \ll \Theta$,

$$\frac{l_{\mathrm{pl}}}{l_{\mathrm{p}}} \approx \frac{5600}{(ak')^6\varepsilon^2}\left(\frac{T}{\Theta}\right)^3. \tag{50}$$

For semiconductors, for $T \gg \Theta$,

$$l_{\mathrm{pl}}/l_{\mathrm{p}} \approx 2/(ak')^2\varepsilon^2, \tag{51}$$

and for $T \ll \Theta$,

$$l_{\mathrm{pl}}/l_{\mathrm{p}} \approx \Theta/(ak')^2\varepsilon^2 T. \tag{52}$$

In metals close to the filling limit, ak' is approximately equal to π. Therefore, in accord with Eqs. (39) and (40), for $\epsilon \geq 0.1$, and in the region of high and very low temperatures, l_{pl} can be the same order of magnitude as l_{p}; then the phonon-liquid scattering will play a significant role. In semiconductors, $ak' < 1$ for most of the electrons, and is the smaller, the lower the temperature. Therefore, in accord with Eqs. (41) and (42), $l_{\mathrm{pl}} \gg l_{\mathrm{p}}$. In the majority of cases, phonon-liquid scattering can be neglected in semiconductors, and only for high temperatures and comparatively high values of ϵ does it give a small correction to the ordinary thermal scattering.

4. CASE OF OPTICAL SCATTERING

In accord with Fröhlich[6], the perturbation energy in the interaction of the electrons with the optical vibrations of the lattice has the form

$$U = -(4\pi i e^2 / 2a^3 q)(2G^3)^{-1/2} \sum_{\mathbf{q}} (a_{\mathbf{q}} e^{i\mathbf{qr}} - \overset{*}{a}_{\mathbf{q}} e^{-i\mathbf{qr}}), \tag{53}$$

where only the longitudinal optical vibrations interact with the electrons, since dipole polarization arises only for the longitudinal wave.

Subsequent calculation is carried out similar to the case of acoustical vibration; because of lack of space, we will not carry it out and will only note the essential differences and write down the final formulas.

The peculiar features of the calculation with optical vibrations are the following:

1. In the integral over the electron coordinates (6), the factor grad $V(\mathbf{r}')$ is lacking.
2. In the integral over the elementary cell, which is given in Eq. (6), we take from under the integral sign the mean value of the product $u_{\mathbf{k}} u_{\mathbf{k}'}^*$, equal to a^{-3}, taking into account that in most of the elementary cells it is almost constant. This actually takes place in the case of metals (see Ref. 3, p. 79); in the case of ionized matter, such an assumption can be considered as a limiting case.

We compute the remaining integral over an elementary cell in the form of cube with edge a, in which $\mathbf{r}'$ is excluded from the center of the cube. We direct the axes ξ_α along the edge of the cube and for brevity write $\mathbf{k} \pm \mathbf{q} - \mathbf{k}' = \mathbf{q}'$; then,

$$a^{-3} \int e^{i\mathbf{q}'\mathbf{r}'} d\tau_0 = \prod_{\alpha=1}^{3} \frac{\sin(q'_x a/2)}{(q'_\alpha a/2)} \approx 1 - \frac{a^2 q'^2}{24}. \tag{54}$$

The latter expression is obtained by a series expansion in sines and a neglect of powers of aq' above the second. In this case, and also in taking $u_{\mathbf{k}} u_{\mathbf{k}'}^*$ from under the integral sign, we have exaggerated the value of the term which is a correction to the unity term in (54).

3. In Eq. (21) there is lacking a summation over j and in place of the factor $(2C^2/9) \times [(\mathbf{k}-\mathbf{k}')\mathbf{e}_{\mathbf{q}j}]^2$ there is $(e^4/a^6\omega_0)(1-a^2q'^2/12)$, and in place of $\omega_{\mathbf{q}j}$ the frequency of the optical vibration ω_0, which is independent of $\mathbf{q}$:

$$\begin{aligned} q'^2 &= (\mathbf{k} - \mathbf{k}' \pm \mathbf{q})^2 \\ &= (\mathbf{k} - \mathbf{k}')^2 + q^2 \pm 2q\,|\,\mathbf{k} - \mathbf{k}'\,|\cos\vartheta. \end{aligned} \tag{55}$$

4. In the integration over ϑ, the term with $\cos\vartheta$ disappears and the remaining terms are multiplied by 2. Integration with respect to q gives

$$\int_0^{q_0} \left(1 - \frac{a^2 q'^2}{12}\right) dq = q_0 - \frac{a^2 (k - k')^2 q_0}{12} - \frac{a^2 q_0^3}{36}. \tag{56}$$

In semiconductors and for most electrons in the conduction band, $ak \ll 1$; therefore, we can neglect the second term in (46). But in such a case, taking it into account that $q_0 = (2\pi/a)(3/4\pi)^{1/3}$, we get

$$\int_0^{q_0} \left(1 - \frac{a^2 q'^2}{12}\right) dq \approx \left(\frac{0{,}57 \cdot 2\pi}{a}\right)\left(\frac{3}{4\pi}\right)^{1/3}, \tag{57}$$

i.e., consideration of the factor $e^{i\mathbf{qr}}$ in the integral over the elementary cell leads only to the numerical coefficient 0.57. If the work is done more accurately, this coefficient will be close to 1. Integration over Φ gives the factor 2π. In the integration over θ, terms with $k_x = k\cos\theta$ disappear, and the terms with $k'_x = k'\cos\theta'$ are multiplied by 2. In integrating over k, we make use of the δ-character of the function Ω. All the factors save Ωk are removed from under the integral sign. We set $E_k = E_{k'} \pm \hbar\omega_0$, extend the limit of the integration to infinity and take into consideration that in the semiconductor,

$$E_k = \hbar^2 k^2 / 2m^*; \quad E_{k'} = \hbar^2 k'^2 / 2m^*, \tag{58}$$

where m^* is the effective mass of the electron. The integration over k gives

$$\int_{-\infty}^{\infty} \Omega(E_{k'} - E_k \pm \hbar\omega_0)\, k\,dk = \left(\frac{2\pi m^*}{\hbar}\right) t. \tag{59}$$

If we set

$$\begin{aligned} I &= \sqrt{2m^*(E_{k'} + \hbar\omega_0)}\,[N + f_0(E_{k'} + \hbar\omega_0] \\ &\quad + \sqrt{2m^*(E_{k'} - \hbar\omega_0)}\,[1 + N - f_0(E_{k'} - \hbar\omega)], \end{aligned} \tag{60}$$

then, as the result of all the calculations, the mean free path length of the electron as determined by the phonon-liquid scattering on thermal optical vibrations is equal to

$$\begin{aligned} l_{\mathrm{pl}} &= -\frac{k' f_1}{eE_x (df_0/dE)} \\ &= \frac{\pi^2 M \hbar^2 \omega_0 a}{0{,}57\,(3/4\pi)^{1/3} e^4 m^* I \varepsilon^2} \frac{dE_{k'}}{dk'}. \end{aligned} \tag{61}$$

With the help of Eqs. (23), (58), (60) and (61), the length of the free path can be computed in closed form for arbitrary temperature but the quantity is a rather complicated function of the temperature T and the electron energy $E_{k'}$. The expression for l can be greatly simplified in the regions of high and low temperatures, which are separtaed at the Debye temperature

$$\Theta = \hbar\omega_0 / k. \tag{62}$$

For $T \gg \Theta$, $N \approx kT/\hbar\omega_0$; for most electrons, $E_{k'} \gg \hbar\omega_0$, for semiconductors, $f_0 \ll N$:

$$I \approx (2kT / \hbar\omega_0)\, \hbar k'. \tag{63}$$

Substituting (63) in (61), we get, after several transformations,

$$l_{\mathrm{pl}} = \frac{a\pi^2}{0{,}57\,(3/4\pi)^{1/3}\varepsilon^2} \frac{M}{m^*} \left(\frac{\hbar\omega_0}{e^2/a}\right)^2 \frac{E}{kT} \frac{1}{(k'a)^2}. \tag{64}$$

For $T \ll \Theta$,

$$N \approx \exp\{-\hbar\omega_0 / kT\} \ll 1.$$

The second term in Eq. (60) is absent since the energy for most electrons is insufficient to emit a phonon. Consequently,

$$I \approx \exp\{-\hbar\omega_0 / kT\} \sqrt{2m^*\hbar\omega_0} \tag{65}$$

and we get, after some algebra,

$$l/_{\mathrm{pl}} = \frac{2a\pi^2}{0{,}57\,(3/4\pi)^{1/3}\varepsilon^2} \frac{M}{m^*} \frac{\hbar\omega_0 E_{k'}}{(e^2/a)^2} \frac{1}{(k'a)^2} \tag{66}$$

$$\times \exp\{\hbar\omega_0 / kT\} \sqrt{E_{k'} / \hbar\omega_0}.$$

Let us compare the expression obtained for the mean free path with the expressions for the mean free path obtained in the usual phonon scattering. In accord with Davydov and Shmushkevich [Ref. 7, Eqs. (3.97) and (3.98)] we have, for ionic crystals with ionic charge $z = 1$:

for $T \gg \Theta$,

$$l_{\mathrm{p}} = \frac{a}{2\pi} \frac{M}{m^*} \left(\frac{\hbar\omega_0}{e^2/a}\right)^2 \frac{E_{k'}}{kT}, \tag{67}$$

and for $T \ll \Theta$,

$$l_{\mathrm{p}} = \frac{a}{2\pi} \frac{M}{m^*} \left(\frac{\hbar\omega_0}{e^2/a}\right)^2 \exp\{\hbar\omega_0/kT\} \sqrt{\frac{E_{k'}}{\hbar\omega_0}}. \tag{68}$$

Consequently, for $T \gg \Theta$,

$$l_{\mathrm{pl}} / l_{\mathrm{p}} \approx 180\,(k'a\varepsilon)^{-2} \gg 1, \tag{69}$$

and for $G \ll \Theta$,

$$l_{\mathrm{pl}} / l_{\mathrm{p}} \approx 360\,(k'a\varepsilon)^{-2} E_{k'} / \hbar\omega_0 \gg 1. \tag{70}$$

Thus the investigation that we have carried out shows that, with accuracy up to small corrections, the ordinary thermal scattering of the electrons in a liquid can be considered according to the same formulas as in a solid. However, in liquids there also exists an additional phonon-liquid scattering, which can play an important role in liquid metals, while in semiconductors it is only a small correction or is negligibly small.

In conclusion, I take this opportunity to express my gratitude to L. E. Gurevich for his valuable discussions.

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