Theory of particle transfer in extremely narrow bands

Yu. Kagan and L. A. Maksimov

I. V. Kurchatov Institute of Atomic Energy

(Submitted December 29, 1972)
Zh. Eksp. Teor. Fiz. **65**, 622–632 (August 1973)

Quantum diffusion of particles is investigated in narrow bands whose width Δ is small compared with the characteristic vibrational spectrum frequency. Interaction with phonons in this case leads to dynamic destruction of the band which is exhibited in an appreciable time-fluctuating level shift at neighboring sites. The incoherent width γ which arises as a consequence is defined by intersite interaction and hence its magnitude does not depend on the overlap intergral and may be arbitrary in the Δ scale. A solution is obtained within the formalism of the density matrix kinetic equation, which is valid throughout the whole temperature range and for an arbitrary relation between Δ and γ. A special analysis is made of the role of defects, which may be particularly important in the case of narrow bands.

1. INTRODUCTION

The present paper is devoted to the transport problem in crystals in the case of extremely narrow bands. We have in mind bands whose width Δ is small in comparison with the characteristic frequencies ω_0 of the phonon spectrum, and is arbitrary with respect to the particle interaction with the phonons. Much interest has been evinced in this problem recently, especially in connection with the problem of quantum diffusion of heavy particles, the theory of semiconductors with low mobility, and a few general aspects of the problem of a conductor-dielectric junction.

Of greatest physical interest is that of particle transport under conditions of dynamic decay of the band. If the interaction of the particles with the lattice vibrations V is large in comparison with the width of the band, then short-wave phonon excitations lead to a large (in the scale of Δ) relative shift of the levels at the neighboring sites. This results in a "trapping" of the particles, similar to that occurring in the case of a large statistical scatter of the levels (see, for example,[1]). In our case, however, there is a fundamental difference, in that for each fixed pair of sites the level shift fluctuates in time about a zero value. This predetermines the presence of a coherent activationless transport for a perfectly arbitrary relation between V and Δ.

The problem can be expressed in an alternate purely kinetic formulation. Indeed, the interaction of the particle with the phonons leads to an intra-site scattering and accordingly to an incoherent level width γ. The amplitude of such scattering does not contain Δ, so that γ can have an arbitrary value with respect to the coherent width Δ. The coherent transport is connected with the ratio Δ/γ and decreases with decrease of the latter. Within the framework of such a picture, however, it is clear that the dependence on the parameter Δ/γ should remain monotonic in principle, down to arbitrarily small values.

It is important that when $\Delta/\gamma \ll 1$ the effective mean free path of the particles is small in comparison with the interatomic distance a. It is clear therefore that it is necessary to develop a theory that holds true in a region where the standard kinetic theory is usually not applicable.

We note that the dynamic decay of the band has so far apparently not been taken into account in the theory of low-mobility electrons, where primary consideration was given to intersite phonon scattering (see, for example,[2,3]). In the case of sufficiently narrow bands, however, the amplitude of this scattering is always small in comparison with the amplitude of intersite scattering, which can play the decisive role in the band mechanism of transport.

We employ a formalism based on the use of a kinetic equation for the density matrix. For the sake of simplicity it is assumed that the particle-phonon interaction is small enough to be able to neglect the polaron effect, and the particle energy renormalization $\delta\epsilon$ is assumed to be small in comparison with ω_0. At the same time, the relation between $\delta\epsilon$ and Δ is arbitrary and, in particular, it is possible to have $\omega_0 \gg \delta\epsilon \gg \Delta$.

Within the framework of these assumptions, we have obtained a unified solution which is valid in the entire temperature range and for an arbitrary ratio of Δ to γ. We analyze also the influence exerted on quantum diffusion by defects, the role of which is particularly strong in the case of very narrow bands.

We assume that the particle density is low, and consider consequently only the single-particle problem. By the same token, we disregard correlation effects which, in the case of narrow bands, can in principle assume a role at even relatively low particle density.

2. KINETIC EQUATION FOR THE DENSITY MATRIX

The Hamiltonian of a system consisting of a particle in a crystal can be written in the form

$$H = H^0 + V, \tag{2.1}$$

where

$$H^0 = H_1 + H_2, \quad H_1 = H_1^0 + \langle H' \rangle, \quad V = H' - \langle H' \rangle. \tag{2.2}$$

Here H_1^0 is the Hamiltonian of the particle in a periodic potential, H_2 is the Hamiltonian of the phonon subsystem, and H' is the Hamiltonian of the interaction of the particle with the phonons; the angle brackets denote averaging over the equilibrium phonon distribution.

We use the usual equation for the density matrix of the system (henceforth $\hbar = 1$)

$$i\partial\rho / \partial t = [H, \rho] \tag{2.3}$$

and take the traces over the phonon variables in both halves of the equation.

We introduce the particle density matrix

$$\rho_1 = \mathrm{Sp}_2\, \rho. \tag{2.4}$$

Then

$$i\partial\rho_1/\partial t=[H_1,\rho_1]+\mathrm{Sp}_2[V,\rho]. \qquad (2.5)$$

The equation for the total density matrix (2.3) can be rewritten in integral form

$$\rho(t)=e^{-iH^0t}\rho(0)e^{iH^0t}-i\int_0^t e^{-iH^0\tau}[V,\rho(t-\tau)]e^{iH^0\tau}\,d\tau.$$

Here $\rho(0)=\rho_1(0)\rho_2^{(0)}$, where $\rho_1(0)$ is the initial particle density matrix and $\rho_2^{(0)}$ is the equilibrium density matrix of the phonon system.

Introducing this representation into the right-hand side of (2.5) we get

$$\frac{\partial\rho_1}{\partial t}+i[H_1,\rho_1]=\mathrm{Sp}_2\int_0^t[e^{-iH^0\tau}[V,\rho(t-\tau)]e^{iH^0\tau},V]\,d\tau. \qquad (2.6)$$

The system density matrix in the right-hand side of (2.6) is connected with ρ at the instant of time t by the relation

$$\rho(t-\tau)=S^+(\tau)e^{iH^0\tau}\rho(t)e^{-iH^0\tau}S(\tau), \qquad (2.7)$$

where $S(\tau)$ is the usual S matrix.

We shall henceforth assume that the interaction of the particle with the phonons is weak enough for the renormalization of the particle energy $\delta\epsilon$, which characterizes the scale of this interaction, to be small in comparison with the characteristic phonon frequency ω_0, and at the same time it is arbitrary with respect to the width of the band

$$\omega_0\gg\delta\varepsilon>\Delta. \qquad (2.8)$$

In addition, we assume for simplicity that other levels of the particle in an isolated well (or other bands) lie sufficiently far to be able to neglect their role.

In view of the foregoing we confine ourselves in the right-hand side of (2.6) to an approximation quadratic in the operator V. Then the total density matrix in the right-hand side of (2.6) can be replaced by

$$\rho(t)=\rho_2^{(0)}\rho_1(t), \qquad (2.9)$$

When (2.7) is substituted in (2.6), we need retain only the diagonal part of the operator $S(\tau)$. The latter can be calculated directly under condition (2.8).

If we recognize that in the case of narrow bands the damping of the diagonal S-matrix elements is determined by two-phonon interaction, or by single-phonon interaction in second-order perturbation theory, then we can use, for example, the results of[4]. The corresponding calculations, with allowance for (2.8), yield

$$(S(\tau))_{pp}{}^{\alpha\alpha}=\exp\{-{}^1/{}_2\gamma_p\tau-i\delta\varepsilon_p\tau\}, \qquad (2.10)$$

where

$$\gamma_p=2\pi\sum_{p'\beta}\langle|V_{p'p}^{\beta\alpha}|^2\delta(\varepsilon_p-\varepsilon_{p'}+E_\alpha-E_\beta)\rangle. \qquad (2.11)$$

In these expressions, the subscript p characterizes the state of the particle with energy ϵ_p, and the index α characterizes the state of the phonon system with energy E_α.

In the case of a continuous phonon spectrum, taking the diagonal matrix element is equivalent to averaging over the thermodynamic equilibrium. Therefore γ_p and $\delta\epsilon_p$ in (2.10) are independent of the index α, and the angle brackets are introduced in (2.11) in explicit form.

It is easily understood that when (2.8) is satisfied the renormalization $\delta\epsilon_p$ is practically independent of the index p. It turns out, however, that γ_p of (2.11) is likewise independent of p. Indeed, when $T\gg\Delta$ we certainly can neglect $\epsilon_p-\epsilon_{p'}$ in the argument of the δ-function. On the other hand, when $T\gg\Delta$, if we consider two-phonon interaction, only long-wave phonons with energy on the order of Δ can contribute to γ_p. But the momentum conservation law in scattering, together with the condition that the group velocity of the particles be small in comparison with the velocity of sound, a condition that follows from (2.8), leads to the inequality $|\epsilon_p-\epsilon_{p'}|\ll|E_\alpha-E_\beta|$.

The fact that the argument of the δ-function in (2.11) is independent of p and p′ implies directly, under the assumptions made here, that γ_p is independent of p. Thus, the matrix element (2.10) is independent of both indices.

Finally, we recognize that the characteristic time within which the density matrix changes is large in comparison with all the characteristic interaction times and replace the upper limit of integration in the right-hand side of (2.6) by infinity. Then, substituting relations (2.7), (2.9), and (2.10) in (2.6) and taking the foregoing considerations into account, we obtain an equation for the density matrix in the form

$$\partial\rho_1/\partial t+i[H_1,\rho_1]=\mathrm{Sp}_2\int_0^\infty[e^{-iH^0\tau}[V,\rho_2^{(0)}e^{iH^0\tau}\rho_1(t)e^{-iH^0\tau}]e^{iH^0\tau}V]e^{-\gamma\tau}\,d\tau. \qquad (2.12)$$

If this equation is rewritten in terms of the eigenfunctions of the Hamiltonian H_1, then it is easy to verify that the integration with respect to τ in the right-hand side leads to the appearance of expressions of the form $\delta_\gamma(E_\alpha-E_\beta+\epsilon_p-\epsilon_{p'})$, where

$$\delta_\gamma(x)=\frac{1}{\pi}\frac{\gamma}{x^2+\gamma^2}.$$

If we use the condition (2.8), then the same reasoning as in the analysis of γ [Eq. (2.11)] enables us to neglect $\epsilon_p-\epsilon_{p'}$ in comparison with $E_\alpha-E_\beta$ in the argument of the function δ_γ. The fact that the argument of δ_γ becomes independent of the state of the particle makes it very convenient to change over to a site representation which makes it possible, as will be shown later on, to obtain all the results in a physically lucid form. Within the framework of this representation, Eq. (2.12) can be represented in the form

$$\frac{\partial\rho_{1mn}}{\partial t}+i[H_1,\rho_1]_{mn}=-I_{mn}, \qquad (2.13)$$

$$I_{mn}=\pi\sum\rho_{2\alpha}^{(0)}\delta_\gamma(E_\alpha-E_\beta)\{V_{ms}{}^{\alpha\beta}V_{sl}{}^{\beta\alpha}\rho_{1ln}+V_{ls}{}^{\alpha\beta}V_{sn}{}^{\beta\alpha}\rho_{1ml}-2V_{ms}{}^{\alpha\beta}V_{ln}{}^{\beta\alpha}\rho_{1sl}\}. \qquad (2.14)$$

We recognize that the matrix element of V which is not diagonal in the site number certainly contains, in comparison with the diagonal element, a small parameter proportional to the overlap integral or to the ratio of Δ to the depth of the intrasite well (with the same dependence on the phonon variables). In the zeroth approximation in the overlap, retaining in (2.14) only the matrix elements of V which are diagonal in the sites, we have

$$I_{mn}^{(0)}=\Omega_{mn}\rho_{1mn},$$
$$\Omega_{mn}=\pi\sum\rho_{2\alpha}^{(0)}\delta_\gamma(E_\alpha-E_\beta)\{V_{mm}{}^{\alpha\beta}V_{mm}{}^{\beta\alpha}+V_{nn}{}^{\alpha\beta}V_{nn}{}^{\beta\alpha}-2V_{mm}{}^{\alpha\beta}V_{nn}{}^{\beta\alpha}\}. \qquad (2.15)$$

From (2.15) it follows, in particular, that

$$\Omega_{mm}=0. \qquad (2.16)$$

Thus, the off-diagonal elements of the density matrix attenuate with frequency Ω_{mn}, the value of which is determined only by the intrasite scattering and does not contain a small overlap parameter. In general, however, the collision integral in the equation for the diagonal elements of the density matrix vanishes in the considered approximation.

We consider the I_{mm} term that is linear in the overlap integral. From (2.14) it follows directly that

$$I_{mm}^{(1)} = \pi \sum \rho_{2\alpha}^{(0)} \delta_\gamma (E_\alpha - E_\beta) \{\rho_{1ms} (V_{ss}{}^{\alpha\beta} V_{sm}{}^{\beta\alpha} - V_{mm}{}^{\alpha\beta} V_{sm}{}^{\beta\alpha}) + \rho_{1sm} (V_{ms}{}^{\alpha\beta} V_{ss}{}^{\beta\alpha} - V_{ms}{}^{\alpha\beta} V_{mm}{}^{\beta\alpha})\}.$$

It is easy to show that, for the most general form of the operator of the particle-phonon interaction in a regular crystal, the expression in the round brackets vanishes after summation over the phonon variables.

Thus, a nonzero contribution to the collision integral appears for the diagonal elements of the density matrix only in the approximation $I^{(2)}$. Retaining in the collision integral only the diagonal elements of ρ_1 (the off-diagonal elements are certainly small in comparison with the diagonal ones, see the next section for details) we obtain ultimately

$$I_{mm}^{(2)} = 2\pi \sum \rho_{2\alpha}^{(0)} \delta_\gamma (E_\alpha - E_\beta) |V_{ms}{}^{\alpha\beta}|^2 (\rho_{1mm} - \rho_{1ss}). \tag{2.17}$$

We shall henceforth return in the collision integrals only the first nonvanishing terms in the overlap (2.15) and (2.17).

3. PARTICLE TRANSPORT IN THE CASE OF EXTREMELY NARROW LINES

When considering narrow lines, it can be assumed that the only nonvanishing matrix elements of the operator H_1 are those corresponding to transitions between the nearest sites. We denote this element by h (cubic symmetry is assumed). Then equation (2.13), with allowance for (2.15), can be rewritten in the form (we omit the subscript 1 of the density matrix)

$$\frac{\partial \rho_{mn}}{\partial t} + ih \sum_{g} (\rho_{m+g,n} - \rho_{m,n+g}) = -\Omega_{mn} \rho_{mn}. \tag{3.1}$$

The vector g runs here through values corresponding to the nearest coordination sphere.

Regarding ρ as a function of the variables m and n, we change over to new variables m and $l = m - n$ and we take the Fourier transform with respect to the variable m. Recognizing that Ω_{mn} depends only on the difference $m - n$, we obtain (the distance to the nearest site is taken to be unity)

$$\dot{\rho}_l(\mathbf{k}) + ih \sum_{g} \rho_{l+g}(\mathbf{k}) [e^{i\mathbf{kg}} - 1] = -\Omega_l \rho_l(\mathbf{k}). \tag{3.2}$$

We have obtained an equation in a mixed representation which in some sense is the inverse of the Wigner representation and is very convenient for our problem.

At the minimal value of l, corresponding to a shift to the nearest coordination sphere, we have

$$\dot{\rho}_g(\mathbf{k}) + ih\rho_0(\mathbf{k}) [e^{-i\mathbf{kg}} - 1] + ih \sum_{g' \neq g} \rho_{g+g'}(\mathbf{k}) [e^{i\mathbf{kg}} - 1] = -\Omega_g \rho_g. \tag{3.3}$$

Let

$$h |e^{-i\mathbf{kg}} - 1| / \Omega_g \ll 1. \tag{3.4}$$

When considering transport in a macroscopic system, we are interested in the characteristic evolution times t_0 of the distribution of particles for which $t_0 \gg 1/\Omega_g$. A quasistationary connection is then established between the off-diagonal elements of the density matrix ($l \neq 0$) and the diagonal elements ($l = 0$), and from (3.3) we obtain in first approximation

$$\rho_g(\mathbf{k}) = -ih \frac{(e^{-i\mathbf{kg}} - 1)}{\Omega_g} \rho_0(\mathbf{k}). \tag{3.5}$$

It is easy to show that more remote off-diagonal elements of the density matrix contain progressively higher powers of the small parameter (3.4), in particular

$$|\rho_{g+g'}(\mathbf{k})| - (h / \Omega_g)^2 |e^{-i\mathbf{kg}} - 1|^2 \rho_0(\mathbf{k}) \quad (\mathbf{g} + \mathbf{g}' \neq 0).$$

Therefore it suffices to retain the approximation (3.5) in the case of condition (3.4).

In the mixed representation, the equation for the diagonal matrix elements takes the form (3.2) with $l = 0$, but it is necessary in this case to introduce in the right-hand side the Fourier component of (2.17) ($\Omega_0 = 0$ by virtue of (2.16)). This component is equal to

$$I_0^{(2)}(\mathbf{k}) = 2\pi \sum \rho_{2\alpha}^{(0)} \delta(E_\alpha - E_\beta) |V_{mm+g}^{\alpha\beta}|^2 (1 - e^{i\mathbf{kg}}) \rho_0(\mathbf{k}) \equiv \eta(\mathbf{k}) \rho_0(\mathbf{k}). \tag{3.6}$$

We introduce relation (3.5) into the left-hand side of (3.2) with $l = 0$. As a result we obtain ($\Omega_g \equiv \Omega_1$)

$$\dot{\rho}_0(\mathbf{k}) + \frac{4h^2}{\Omega_1} \sum_{g} \left(\sin \frac{\mathbf{kg}}{2} \right)^2 \rho_0(\mathbf{k}) = -\eta(\mathbf{k}) \rho_0(\mathbf{k}). \tag{3.7}$$

Solution of this equation yields

$$\rho_0(\mathbf{k}, t) = \rho_0(\mathbf{k}, 0) e^{-\xi_{\mathbf{k}} t}, \quad \xi_{\mathbf{k}} = \frac{4h^2}{\Omega_1} \sum_{g} \sin^2 \frac{\mathbf{kg}}{2} + \eta(\mathbf{k}). \tag{3.8}$$

The solution (3.8) was obtained under assumption (3.4). One might think that this limits significantly the relation between the band width $\Delta \sim h$ and Ω_1. This is not so, however. The point is that in any real problem we are interested in the spatial distribution of the density of particles having a characteristic linear dimension $L \gg a$. But the function $\rho_0(k, t)$ is precisely the spatial Fourier component of the density. It is clear therefore that an important role is played in the transport problem by the solution (3.8) corresponding to small $k \sim 1/L$. Under this condition (3.4) takes the form

$$hka / \Omega_1 \sim ha / \Omega_1 L \ll 1. \tag{3.4$'$}$$

It is clear that it is valid also when the bandwidth is large in comparison with the frequency Ω_1. At $ka \ll 1$, the expression for (3.8) becomes equal to (we introduce the interatomic distance a in explicit form)

$$\xi_{\mathbf{k}} = k^2 D, \quad D = D_{coh} + D_{in\,coh}, \tag{3.9}$$

$$D_{coh} = \frac{h^2 a^2 Z}{3\Omega_1}, \quad D_{in\,coh} = \frac{\pi Z a^2}{3} \sum \rho_{2\alpha}^{(0)} |V_{mm+g}^{\alpha\beta}| \delta(E_\alpha - E_\beta). \tag{3.10}$$

By comparing (3.8) and (3.9) with the relation

$$\dot{n}(\mathbf{k}) = -Dk^2 n(\mathbf{k}),$$

which follows from the diffusion equation, we find that D in (3.9) is the summary diffusion coefficient. Thus, the relations (3.10) together with Ω_1 from (2.15) actually determine the solution of the problem.

We note that the assumed condition $1/t_0\Omega_1 \ll 1$ reduces, if account is taken of the relation $t_0 \approx L^2/D$ and of the result (3.9), to the same inequality (3.4).

Greatest interest attaches here to the coherent function to which the coefficient D_{coh} in (3.9) and (3.10) corresponds. It stems from the coherent tunneling of the particles and is limited by the correlation-breaking frequency or, equivalently, by the attenuation frequency of the density matrix elements Ω_1 that are not diagonal in the sites. This density matrix is determined by expression (2.15), from which it follows that the correlation breaking is due to intrasite scattering by phonons.

We introduce the effective two-phonon interaction in the second-quantization representation, in the form

$$V=\frac{1}{2}\sum_{q_1q_2}\frac{B(q_1,q_2)}{(\omega_{q_1}\omega_{q_2})^{1/2}}A_{q_1}A_{q_2},\quad A_q=a_q+a_{-q}^+. \tag{3.11}$$

Here a^+ and $\underline{a}$ are the phonon creation and absorption operators. The index q = (q, n) defines simultaneously the wave vector q of the phonon and the number of the branch, and B depends on the particle coordinate r.

The interaction (3.11) differs from zero only to the extent of the change in the relative position of the ions making up the lattice. Therefore at small $|\mathbf{q}_1|$ or $|\mathbf{q}_2|$ we have

$$B(q_1,q_2)\sim|\mathbf{q}_1|,\ |\mathbf{q}_2|. \tag{3.12}$$

It is easy to show that in the general case the B matrix element diagonal in the site functions is given by

$$(B(q_1,q_2))_{\mathbf{mm}}=B_{00}(q_1,q_2)e^{i(\mathbf{q}_1+\mathbf{q}_2)\mathbf{m}}. \tag{3.13}$$

Using (3.11) and (3.13) for (2.15) we obtain directly

$$\Omega_1=2\pi\sum_{q_1q_2}\frac{|B_{00}(q_1,q_2)|^2}{\omega_{q_1}\omega_{q_2}}n_{q_1}(n_{q_2}+1)[1-e^{i(\mathbf{q}_1-\mathbf{q}_2)\mathbf{l}}], \tag{3.14}$$

where n_q is the equilibrium Planck distribution of the phonons. If we omit the exponential from the square brackets of this expression, then this expression practically coincides with the value of γ in (2.11). It is easy to conclude from (3.14) that at high temperatures we have $\gamma \ll \omega_0$ by virtue of (2.8), and that at low temperatures, taking (3.12) into account, we have $\gamma \sim T^7$. By virtue of this, we neglect in (3.14) the difference between $\delta\gamma$ and the usual δ-function.

It is important that Ω_1 does not contain an overlap integral. Therefore the relation between Ω_1 and h, at least at room temperature, can be quite arbitrary. In particular, the inequality $\Omega_1 \gg h$ is possible. On the other hand, at low temperatures we have

$$\Omega_1\sim T^9 \tag{3.15}$$

and by changing the temperature one can arrive at the opposite inequality $\Omega_1 \ll h$.

We emphasize that expression (3.12) for D_{coh} is valid for an arbitrary ratio h/Ω_1. It is interesting that if it is recognized that the group velocity is equal to

$$u_{gr}\sim ha,$$

then we obtain formally from (3.10) for the equivalent mean free path

$$\lambda\sim ah/\Omega_1. \tag{3.16}$$

Thus, the expression for D_{coh} (3.10) is valid also under the condition $\lambda \ll a$, which is obtained in the case of strong dynamic destruction of the band ($h \ll \Omega_1$).

An additive contribution to the summary particle transport is made also by incoherent diffusion (D_{incoh} in (3.9)), which is a tunnel jump to the neighboring site with simultaneous excitation of the phonon system. D_{incoh} of (3.10) is determined now by the intersite scattering. It is interesting that this transport takes place also in the absence of the polaron effect, within the framework of which its analog is well known (see, for example,[2,3]).

Using (3.11), we obtain directly

$$D_{in\,coh}=\frac{4\pi Za^2}{3}\sum_{q_1q_2}\frac{|B_{01}(q_1,q_2)|^2}{\omega_{q_1}\omega_{q_2}}n_{q_1}(n_{q_2}+1)\delta(\omega_{q_1}-\omega_{q_2}). \tag{3.17}$$

The matrix element B_{01} contains, naturally, the overlap integral. As a consequence, the incoherent-diffusion coefficient is proportional to the square of the overlap integral and in this sense it is of the same order of smallness as $D_{coh} \sim h^2$.

At low temperatures, taking (3.12) into account, we have

$$D_{in\,coh}\sim T^7. \tag{3.18}$$

Bearing in mind that in this region we have

$$D_{coh}\sim 1/T^9, \tag{3.19}$$

we can state that at low temperatures the transport is determined in practice by coherent diffusion only.

At high temperatures we have for both diffusion coefficients, in order of magnitude

$$D_{coh}\sim J^2a^2\frac{\varepsilon^2}{\omega_0}\left(\frac{\omega_0}{T}\right)^2,\quad D_{in\,coh}\sim J^2a^2\omega_0\left(\frac{T}{\omega_0}\right)^2, \tag{3.20}$$

where ϵ is the characteristic energy for the intrasite motion of the particles ($h \sim J\epsilon$). It can be concluded from (3.20) that for electrons we have at all temperatures

$$D_{coh}\gg D_{in\,coh}.$$

For ions at $T > \omega_0$ the coefficient D_{incoh} can become comparable with D_{coh}. In the limiting case, the summary diffusion coefficient can then even go through a minimum.

4. ROLE OF DEFECTS

So far we have considered particle transport in an ideal vibrating lattice. It is of interest to understand how the results obtained above are altered in the presence of impurities or any structure violation.

In the case of extremely narrow bands, the principal role of the impurities reduces to a static collapse of the levels, which exceeds Δ in a relatively large vicinity around the defect, a region that becomes by the same token inaccessible to coherent motion of the particles.

We are interested only in the region of low temperatures. If the defect causes a lowering of the energy levels, which is equivalent to attraction, then inelastic scattering with energy transfer to the phonons can lead to a capture of the particle in this region. In the opposite case, when the levels around the defect shift upward, a large region actually inaccessible to the particles is produced for both elastic and inelastic interaction. We consider below only the latter case and, bearing in mind sufficiently low temperatures, take only elastic scattering into account.

We consider sufficiently low impurity concentrations c, when the summary volume of the inaccessibility regions is small in comparison with the volume of the crystal. In this case, a theory linear in the concentration can be constructed in the momentum representation in standard fashion, on the basis of the value of the operator t for scattering of a particle by an individual region of this kind (see, for example,[5]). It is therefore convenient to consider, for the impurity problem proper, an equation for the density matrix in the momentum representation, or more accurately in the representation of Bloch functions corresponding to the Hamiltonian H_1 (2.2). However, with an aim at taking simultaneous account of the interaction of the particles both with defects and with phonons, we change over from the momentum representation to the site representation, which, as seen from the foregoing, is physically more representative of the problem in the case of narrow bands.

The presence of impurities leads to the appearance of an additional term $I^{(Im)}$ in the right-hand side of the equation for the density matrix (2.6), (2.12). We are interested in the matrix element of this operator in the momentum representation, $I^{(im)}_{p,p+k}$, corresponding to small $k \sim L^{-1}$, where L is a dimension characterizing the spatial distribution of the particle density (see the preceding section). If we neglect k in comparison with p in the scattering-amplitude matrix elements, then we have for a medium having a random impurity distribution

$$I^{(im)}_{\mathbf{p},\mathbf{p}-\mathbf{k}} = \sum_{\mathbf{q}} W_{\mathbf{pq}}(\rho_{\mathbf{p},\mathbf{p}-\mathbf{k}} - \rho_{\mathbf{q},\mathbf{q}-\mathbf{k}}), \qquad (4.1)$$
$$W_{\mathbf{pq}} = 2\pi c|t_{\mathbf{qp}}|^2\delta(\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{q}}).$$

We change over to the mixed representation (l, k) used in the preceding section:

$$I_{\mathbf{l}}^{(im)}(\mathbf{k}) = \sum_{\mathbf{p}} I^{(im)}_{\mathbf{p}\mathbf{p}-\mathbf{k}} e^{i(\mathbf{p}-\mathbf{k})\mathbf{l}}$$
$$= \frac{1}{N}\sum_{l'}\rho_{\mathbf{l}'}(\mathbf{k})e^{i\mathbf{k}(\mathbf{l}'-\mathbf{l})}\sum_{\mathbf{pq}} W_{\mathbf{pq}}e^{i\mathbf{pl}}(e^{-i\mathbf{pl}'} - e^{-i\mathbf{ql}'}). \qquad (4.2)$$

It is seen directly from this expression that the nonzero contribution is due only to density-matrix elements that are not diagonal in the sites ($l' \neq 0$), and the collision integral itself has a nonzero value only at $I \neq 0$.

The equation for the density matrix takes in this representation the form (3.2), where the collision integral (4.2) must be additionally introduced into the right-hand side. Repeating, on going from the off-diagonal equation for the density matrix to the diagonal equation, the same arguments as in the preceding section, we should consider only the equation with $l = g$ and retain in the sum in the right-hand side of (4.2) only terms with $l' = g'$.

It is easy to verify that the quasistationary solution of (3.3) with the collision integral (4.2) added is

$$\rho_{\mathbf{g}}(\mathbf{k}) = (\mathbf{gk})f(k^2).$$

Taking this into consideration, we obtain directly

$$I_{\mathbf{g}}^{(im)}(\mathbf{k}) = -\Omega_{\mathbf{g}}^{(im)}\rho_{\mathbf{g}}(k), \qquad (4.3)$$
$$\Omega_{\mathbf{g}}^{(im)} = -\frac{1}{N}\sum_{\mathbf{g}'}(\mathbf{gg}')\sum_{\mathbf{pq}} W_{\mathbf{pq}}e^{i\mathbf{pq}}[e^{-i\mathbf{pg}'} - e^{-i\mathbf{qg}'}].$$

From this it follows immediately that in the presence of defects the expression (3.10) for D_{coh} retains the same form in our case, except that Ω_1 is replaced by

$$\Omega = \Omega_1 + \Omega_1^{(im)}. \qquad (4.4)$$

From (4.3) and (4.1) we can easily obtain an estimate for $\Omega_1^{(im)}$. It can be easily verified here that to observe a sharp growth in the diffusion coefficient with decreasing temperature it is necessary to have extremely low defect concentrations.

If the matrix elements of the scattering operator t are expanded in terms of k, then the correction to (4.1) and (4.2) yields a value that no longer vanishes at $l = 0$. This introduces a correction for D_{incoh} of (3.10), but this correction is proportional to the concentration and is therefore negligibly small.

5. CONCLUDING REMARKS

The expressions (3.9), (3.10), (4.4), and (4.3) obtained above determine the diffusion coefficient in the entire temperature interval from extremely low temperatures, when $T, \Omega_1 < \Delta$ and the usual band mechanism of transport should operate, up to $T > \omega_D$, when $T, \Omega_1 \gg \Delta$, $\Omega_1^{(im)}$ and the equivalent mean free path is smaller than the interatomic distance. It is interesting that in practically the entire temperature region the decisive role is played by the coherent mechanism of diffusion and the finite character of λ is determined by the dynamic collapse of the band with a characteristic relaxation frequency Ω_1 (3.14) (or Ω (4.4)). As seen from (3.1), this frequency determines the damping decrement of the density-matrix elements that are not diagonal in the sites. It plays a rather general role in kinetic phenomena in narrow bands and determines, in particular, the damping of the Bloch states in a crystal when the overlap tends to zero. Indeed, assume that at the instant $t = 0$ the state of the particle is specified by means of a Bloch wave function ψ_p. Then

$$\rho_{\mathbf{mn}}{}^0 = N^{-1}\exp\{i\mathbf{p}(\mathbf{m}-\mathbf{n})\}.$$

As $h \to 0$, the frequency $\Omega^{(im)} \to 0$ and we have from (3.1)

$$\rho_{\mathbf{mn}}(t) = \rho_{\mathbf{mn}}(0)\exp\{-\Omega_{\mathbf{m}-\mathbf{n}}t\}.$$

It follows therefore that decay of a state that is coherent over the entire crystal takes place after a time on the order of $1/\Omega_1$. In the final stationary state there are no longer any correlations between the individual sites, and this state is completely described by a density matrix ρ_{mm} which is diagonal in the sites.

---

[1] P. Anderson, Phys. Rev., 109, 1492 (1958).

[2] M. J. Klinger, Rep. Progr. Phys., 30, 225 (1968).

[3] J. Appel, Sol. St. Phys., 21, 193 (1968).

[4] Yu. Kagan, Zh. Eksp. Teor. Fiz. 47, 366 (1964) [Sov. Phys.-JETP 20, 243 (1965)].

[5] J. M. Luttinger and W. Kohn, Phys. Rev., 109, 1892 (1958).

Translated by J. G. Adashko
64