Small-polaron theory with allowance for the influence of lattice vibrations on the resonance integral

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(Submitted 18 April 1991)
Zh. Eksp. Teor. Fiz. **100**, 1556–1566 (November 1991)

A small-radius polaron theory is proposed with allowance for the influence of phonon displacements on the interstitial resonance integral. After a canonical transformation, the Hamiltonian of such a model is similar to the Hamiltonian of the standard small-polaron theory, some generalizations of which permit the use of the methods of the proposed theory. The specific results differ radically from the well-known conclusions of the small-polaron theory if the rms phonon displacement of the atoms is of the order or larger than the polaron radius. In particular, the width of the polaron band increases exponentially with temperature, and the hopping conductivity ceases to be of the simple activation type.

Standard small-radius polaron theory[1-3] is based on the use of the Fröhlich Hamiltonian, assuming strong coupling of the electrons with the polarization optical phonons. The most important fundamental results is here the deduced hopping character of the conduction in the low-temperature region and the concomitant low mobility μ_h. The temperature dependence of the mobility has an activation character, $\ln \mu_h \propto -E_a/kT$. On the other hand, a dependence of the type $\ln \mu_h \propto AT$ has been observed in many low-mobility materials in a larger temperature interval,[4] contrary to small-polaron theory. In Ref. 4 (see also Ref. 5) it was shown that a dependence of this type can be obtained if account is taken of the effect of lattice displacements on the interstitial tunneling, since the overlap of the wave functions on neighboring lattice sites depends on the positions of the nuclei.

The present paper is devoted to a small-radius-polaron theory in which this effect is taken into account. Such a generalization of the theory has made it possible to show that if the dimensionless parameter $\alpha^2 \overline{\rho^2}$ is not too small (α^{-1} is the radius of the localized state and $\overline{\rho^2}$ is the rms thermal displacement) the small-polaron model leads to hopping-conduction temperature dependence of the type $\ln \mu_h \propto AT - E_a/kT$, which is observed in experiment in a very large number of materials.[4] This dependence of the mobility is accompanied by feasibility of an exponential growth of the polaron-band width with temperature, like $\exp(BT)$, with $B > 0$, in the region above the Debye temperature. In standard small-polaron theory, on the contrary, the polaron bandwidth decreases exponentially in this temperature region, in which $B < 0$.

1. INITIAL HAMILTONIAN AND CANONICAL TRANSFORMATION

To describe an electron–phonon system with account taken of the influence of the lattice vibrations on the quantum-mechanical percolation from site to site, we use the Fröhlich Hamiltonian

$$H = \sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j}(b_{\mathbf{q}j}^{+}b_{\mathbf{q}j}+{}^{1}/_{2}) + \sum_{m,m'} J_{mm'}a_{m'}^{+}a_{m} + \sum_{\mathbf{q}j,m} \hbar\omega_{\mathbf{q}j}a_{m}^{+}a_{m}[u_{m}(\mathbf{q}j)b_{\mathbf{q}j} + u_{m}^{*}(\mathbf{q}j)b_{\mathbf{q}j}^{+}], \quad (1)$$

where ω_{qj} is the frequency of the phonon branch j with momentum q, a_m^+ [a_m is a photon creation (annihilation) operator on the site m],

$$u_m(\mathbf{q}j) = \gamma(\mathbf{q}j)\exp(-i\mathbf{q}\mathbf{R}_m)/(2N)^{1/2},$$

$\gamma(qj)$ is the electron–phonon coupling constant, N is the total number of sites in the crystal, R_m is the radius vector of the site m, and $J_{mm'}$ is the resonance integral of the sites m and m'. A Hamiltonian in the form (1) is used in small-polaron theory.[2,3] To take the influence of the lattice vibrations on the tunneling into account we introduce the dependence of $J_{mm'}$ on the atomic displacements. To this end we assume an exponential dependence of the resonance integral on the distance between sites (generally nonequilibrium):

$$J_{mm'} = J_{mm'}^{(0)}\exp(-\alpha|\mathbf{U}_m - \mathbf{U}_{m'}|),$$

where α is the reciprocal radius of the electron state on the site, and U_m is the radius vector of the instantaneous atom position. We put next $U_m = R_m + \rho_m$, where ρ_m is the thermal deviation of the atom from the equilibrium position R_m. Assuming ρ_m to be a small quantity, we obtain the following form of the resonance integral

$$J_{mm'} = I_{mm'}\exp\left[-\alpha\frac{(\mathbf{R}_m-\mathbf{R}_{m'})(\boldsymbol{\rho}_m-\boldsymbol{\rho}_{m'})}{|\mathbf{R}_m-\mathbf{R}_{m'}|}\right] \quad (2)$$

where $I_{mm'} = J_{mm'}^{(0)}\exp\{-\alpha|R_m - R_{m'}|\}$.

We now express the phonon displacements in terms of the phonon second-quantization operators (see, e.g., Ref. 6):

$$\boldsymbol{\rho}_{mk} = \sum_{\mathbf{q}j}\left(\frac{\hbar}{2NM_k\omega_{\mathbf{q}j}}\right)^{1/2}\mathbf{e}(k|\mathbf{q}j)(b_{\mathbf{q}j}+b_{\mathbf{q}j}^{+})\exp(-i\mathbf{q}\mathbf{R}_m), \quad (3)$$

where k is the number of the atom in the unit cell, M_k is the mass of this atom, and $\mathbf{e}$ is the eigenvector of the phonon branch. Since we shall consider below electron transitions between only one species of atoms (within one sublattice), we shall omit for brevity the subscript k (it corresponds to the investigated sublattice). We simultaneously omit also the subscript j numbering the phonon mode, assuming that the set $\mathbf{q}$ includes both the phonon vector and the mode index.

Substituting (3) into (2) we obtain an expression for

 0038-5646/91/110861-06$03.00

the resonance integral with allowance for phonon displacements:

$$J_{mm'} = I_{mm'} \exp\Big[-\sum_{\mathbf{q}} (v^{*}_{mm'}(\mathbf{q})\, b_{\mathbf{q}}^{+} + v_{mm'}(\mathbf{q})\, b_{\mathbf{q}})\Big], \quad (4)$$

where

$$v_{mm'}(\mathbf{q}) = (2N)^{-1/2}\delta_{mm'}(\mathbf{q})\,[\exp(-i\mathbf{q}\mathbf{R}_m) - \exp(-i\mathbf{q}\mathbf{R}_{m'})], \quad (5)$$

$$\delta_{mm'}(\mathbf{q}) = \alpha\Big(\frac{\hbar}{M\omega_{\mathbf{q}}}\Big)^{1/2} \mathbf{e}_{\mathbf{q}}(\mathbf{R}_m - \mathbf{R}_{m'})/|\mathbf{R}_m - \mathbf{R}_{m'}|. \quad (6)$$

We call attention to important symmetry relations for v

$$v_{mm'}(\mathbf{q}) = v_{m'm}(\mathbf{q}), \quad v_{mm'}(\mathbf{q}) = v^{*}_{mm'}(-\mathbf{q}), \quad (7)$$

which follow from the relation

$$\delta_{mm'}(\mathbf{q}) = -\delta_{mm'}(\mathbf{q}), \quad \delta_{mm'}(\mathbf{q}) = \delta^{*}_{mm'}(-\mathbf{q}). \quad (8)$$

The initial Hamiltonian of the model considered is thus the Fröhlich Hamiltonian (1) with a resonance integral that depends on the phonon variables in the form (4), i.e., a multiphonon operator. Note also that the form (4) does not depend on the actually chosen simple exponential dependence of the resonance integral on the distance between sites. In particular, if

$$J_{mm'} = J^{(0)}_{mm'} \exp\{-f(|\mathbf{U}_m - \mathbf{U}_{m'}|)\},$$

where $f(x)$ is some function, the form (2) [and hence also (4)] is conserved under the substitution $\alpha \to df/dx$ at $x = |\mathbf{R}_m - \mathbf{R}_{m'}|$.

It is now convenient to apply to this Hamiltonian the polaron canonical transformation[2,3]

$$\tilde{H} = e^{-S} H e^{S}, \quad S = \sum_{m,\mathbf{q}} a_m^{+} a_m [b_{\mathbf{q}}^{+} u_m^{*}(\mathbf{q}) - b_{\mathbf{q}} u_m(\mathbf{q})],$$

$$\tilde{a}_m = a_m \exp\Big[\sum_{\mathbf{q}} (b_{\mathbf{q}} u_m(\mathbf{q}) - b_{\mathbf{q}}^{+} u_m^{*}(\mathbf{q})\Big],$$

$$\tilde{b}_{\mathbf{q}} = b_{\mathbf{q}} - \sum_{m} u_m^{*}(\mathbf{q})\, a_m^{+} a_m.$$

The result is

$$\tilde{H} = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}}(b_{\mathbf{q}}^{+} b_{\mathbf{q}} + 1/2) - \sum_{m,\mathbf{q}} a_m^{+} a_m \hbar\omega_{\mathbf{q}} |u_m(\mathbf{q})|^2 - \sum_{\mathbf{q}, m \neq m'} a_m^{+} a_m a_{m'}^{+} a_{m'} \hbar\omega_{\mathbf{q}} u_m^{*}(\mathbf{q})\, u_{m'}(\mathbf{q}) + H'. \quad (9)$$

The second term of the right-hand side of (9) describes the polaron shift (the energy gain due to the polaron effect), and the third the attraction between polarons on account of virtual phonon exchange. This term plays the decisive role in the formation of a bound polaron state[7,8] and in the description of bipolaron superconductivity.[9]

The contribution H' in small-polaron theory serves as a perturbation, and takes in the model considered the form

$$H' = \sum_{m,m'} I_{mm'} a_{m'}^{+} a_m \exp\Big(\sum_{m_1} V_{mm',m_1} a_{m_1}^{+} a_{m_1}\Big) \times \exp\Big\{\sum_{\mathbf{q}} [b_{\mathbf{q}}(u_m - u_{m'}) - b_{\mathbf{q}}^{+}(u_m^{*} - u_{m'}^{*})]\Big\} \times \exp\Big[-\sum_{\mathbf{q}} (v^{*}_{mm'} b_{\mathbf{q}}^{+} + v_{mm'} b_{\mathbf{q}})\Big] \quad (10)$$

where

$$V_{mm',m_1} = \sum_{\mathbf{q}} [v^{*}_{mm'}(\mathbf{q})\, u_{m_1}(\mathbf{q}) + v_{m'm}(\mathbf{q})\, u^{*}_{m_1}(\mathbf{q})].$$

We separate now from the sum over m_1 the terms with $m_1 = m$ and $m = m'$, and consider the operator

$$a_{m'}^{+} a_m \exp(V_{nm',m} a_m^{+} a_m + V_{mm',m'} a_{m'}^{+} a_{m'}) = a_{m'}^{+} a_m [(1 - a_m^{+} a_m) + a_m^{+} a_m \exp V_{mm',m}][(1 - a_{m'}^{+} a_{m'}) + a_{m'}^{+} a_{m'} \exp V_{mm',m'}] = a_{m'}^{+} a_m \exp V_{mm',m}.$$

We have used here the identities $a_{m'}^{+} a_m a_m^{+} a_m = a_{m'}^{+} a_m$ and $a_{m'}^{+} a_m a_{m'}^{+} a_{m'} = 0$. Equation (10) takes then the form

$$H' = \sum_{mm'} \tilde{I}_{mm'} a_{m'}^{+} a_m \exp\Big\{V_{mm',m} - \sum_{\mathbf{q}} [b_{\mathbf{q}}^{+}(u_m^{*} - u_{m'}^{*}) - b_{\mathbf{q}}(u_m - u_{m'})]\Big\} \times \exp\Big[-\sum_{\mathbf{q}} (v^{*}_{mm'} b_{\mathbf{q}}^{+} + v_{m'm} b_{\mathbf{q}})\Big], \quad (10a)$$

where

$$\tilde{I}_{mm'} = I_{mm'} \exp\Big(\sum_{m_1 \neq m,m'} a_{m_1}^{+} a_{m_1} V_{mm',m_1}\Big). \quad (11)$$

Since the phonon operators in last two exponentials of (10a) commute to a c-number, we can use the operator identity

$$\exp \hat{A} \cdot \exp \hat{B} = \exp(\hat{A} + \hat{B}) \cdot \exp(c/2),$$

where $c = [\hat{A}, \hat{B}]$ is a number. As a result we get the relation

$$\exp\Big\{-\sum_{\mathbf{q}} [b_{\mathbf{q}}^{+}(u_m^{*} - u_{m'}^{*}) - b_{\mathbf{q}}(u_m - u_{m'})]\Big\} \times \exp\Big[-\sum_{\mathbf{q}} (v^{*}_{mm'} b_{\mathbf{q}}^{+} + v_{m'm} b_{\mathbf{q}})\Big] = \exp\Big\{\frac{1}{2}(V_{mm',m'} - V_{mm',m}) + \sum_{\mathbf{q}} [\Gamma^{*}_{mm'}(\mathbf{q})\, b_{\mathbf{q}}^{+} + \Gamma_{m'm}(\mathbf{q})\, b_{\mathbf{q}}]\Big\},$$

where

$$\Gamma_{m'm}(\mathbf{q}) = -u_{m'}(\mathbf{q}) + u_m(\mathbf{q}) - v_{m'm}(\mathbf{q}). \quad (12)$$

As a result, the Hamiltonian H' (10a) is reducible to the form

$$H' = \sum_{mm'} \tilde{I}_{mm'} a_{m'}^{+} a_m \exp\Big[\frac{1}{2}(V_{mm',m} + V_{mm',m'}) + \sum_{\mathbf{q}} (\Gamma^{*}_{mm'} b_{\mathbf{q}}^{+} + \Gamma_{m'm} b_{\mathbf{q}})\Big]. \quad (13)$$

Using the expressions (5) for u and v we get

$$\frac{1}{2}(V_{mm',m} + V_{mm',m'}) = \frac{i}{2N} \sum_{\mathbf{q}} [\gamma_{\mathbf{q}} \delta^{*}_{mm'}(\mathbf{q}) - \gamma_{\mathbf{q}}^{*} \delta_{mm'}(\mathbf{q})] \times \sin \mathbf{q}(\mathbf{R}_m - \mathbf{R}_{m'}).$$

This quantity is symmetric with respect to the interchange $m \rightleftarrows m'$ and is positive. When it does not vanish as a result of lattice symmetry (γ and δ are complex quantities), we shall assume that

$$I_{mm'} \to I_{mm'} \exp[{}^1/_2(V_{mm',m}+V_{mm',m'})],$$

and the factor $\exp[\frac{1}{2}(V_{mm',m}+V_{mm',m'})]$ will therefore be omitted below.[1)]

We change over now in the canonically transformed Hamiltonian $\tilde{H}$ [Eqs. (9) and (13)] to the one-electron approximation, leaving out all the electron–electron correlations. In this approximation we can, first, leave out of (9) the interpolaron attraction (third term of the right-hand side). Second, there is no need to take into account the $I_{mm'}$ renormalization (11), i.e., we can replace $\tilde{I}_{mm'}$ by $I_{mm'}$. In addition, by shifting the energy origin we can set equal to zero the contribution from the polaron shift in (9) (second term of the right-hand side). After these simplifications the Hamiltonian $\tilde{H}$ takes the form

$$\tilde{H} = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}}(b_{\mathbf{q}}^{+}b_{\mathbf{q}}+{}^1/_2) + \sum_{mm'} I_{mm'} a_{m'}^{+} a_m \Psi_{mm'},$$
$$\Psi_{mm'} = \exp\left[\sum_{\mathbf{q}} \Gamma_{mm'}^{*}(\mathbf{q})\, b_{\mathbf{q}}^{+} + \Gamma_{m'm}(\mathbf{q})\, b_{\mathbf{q}}\right]. \tag{14}$$

The Hamiltonian (14) is outwardly similar to the Hamiltonian in small-polaron theory if the substitution $\Gamma_{mm'} \to u_{m'} - u_m$ is made. The main difference, due to allowance for the influence of the phonon displacements on the resonance integral ($v \neq 0$) is that in this model we have, in contrast to the standard theory, $\Gamma_{mm'} \neq \Gamma_{m'm}$, which leads to far-reaching consequences and requires a review of all the results.

To conclude this section, we note that the Hamiltonian (14) can be used not only for crystalline materials but also for disordered systems. Three circumstances must be borne in mind here. First, the presence of off-diagonal disorder makes the resonance integral a random quantity. Second, the onset of diagonal disorder is described by the additional contribution

$$\sum_m \varepsilon_m a_m^{+} a_m, \tag{15}$$

to the Hamiltonian, where ε_m is the electron energy at the site (a random quantity). This contribution is invariant to the polaron canonical transformation, and can therefore be added both to H (1) and to $\tilde{H}$ (14). Third and final, if disorder in the phonon subsystem must be taken into account, all the summations over $\mathbf{q}$ and j must be replaced by summation over the quantum numbers of the normal oscillations of the phonon subsystem.[3]

2. TEMPERATURE DEPENDENCE OF THE POLARON BAND

The matrix element of the operator $\Psi_{mm'}$ in (12), which is diagonal with respect to the phonons, describes the phonon renormalization of an unrenormalized electron band[1-3]

$$E(\mathbf{k}) = \sum_m I_{mm'} \langle \Psi_{mm'} \rangle \exp[i\mathbf{k}(\mathbf{R}_m - \mathbf{R}_{m'})]. \tag{16}$$

Using the known equality[2,3]

$$\langle \exp(\alpha b^{+} + \beta b) \rangle = \exp[\alpha\beta(\mathcal{N}+{}^1/_2)], \tag{17}$$

where $\mathcal{N} = (\exp(\hbar\omega/kT) - 1)^{-1}$ is the Planck function, we obtain

$$\langle \Psi_{mm'} \rangle = \exp(-S_{mm'}),$$
$$S_{mm'} = \frac{1}{2}\sum_{\mathbf{q}} \operatorname{cth}\frac{\hbar\omega_{\mathbf{q}}}{2kT}[|u_m - u_{m'}|^2 - |v_{mm'}|^2 - 2i\,\mathrm{Im}(u_{m'} - u_m)v_{mm'}^{*}].$$

The pure imaginary contribution to $S_{mm'}$ describes the phase factor of the effective band and vanishes if

$$\gamma_{\mathbf{q}}^{*}\mathbf{e}_{\mathbf{q}} - \gamma_{\mathbf{q}}\mathbf{e}_{\mathbf{q}}^{*} = \gamma_{-\mathbf{q}}\mathbf{e}_{\mathbf{q}} - \gamma_{\mathbf{q}}\mathbf{e}_{-\mathbf{q}} = 0.$$

We assume hereafter that this condition is met. Substituting now the explicit expressions for u_m and $v_{mm'}$, we get

$$S_{mm'} = \frac{1}{2N}\sum_{\mathbf{q}} [1 - \cos\mathbf{q}(\mathbf{R}_m - \mathbf{R}_{m'})] \operatorname{cth}\frac{\hbar\omega_{\mathbf{q}}}{2kT}[\gamma_{\mathbf{q}}^2 - \delta_{mm'}^2(\mathbf{q})]. \tag{18}$$

The temperature-dependent phonon renormalization of the band consists thus of two contributions of opposite sign. The positive contribution to $S_{mm'}$ ($\propto \gamma^2$) is due to the polaron-induced increase of the particle mass and is part of the standard theory of small polarons. The second (negative) contribution is due to the increase of the probability of interstitial tunneling with increase of the phonon-oscillation amplitude.[4] In fact, it is easily seen that this contribution is equal to $-\alpha^2\rho_{mm'}^2/2$, where $\rho_{mm'}^2$ is the rms displacement of the atoms,

$$\overline{\rho_{mm'}^2} = \left\langle \frac{[(\mathbf{R}_m - \mathbf{R}_{m'})(\boldsymbol{\rho}_m - \boldsymbol{\rho}_{m'})]^2}{(\mathbf{R}_m - \mathbf{R}_{m'})^2} \right\rangle.$$

To prove this relation we must use Eq. (3). This fact means that the effects considered in the investigated model are significant only when the rms thermal displacements of the atoms are comparable with or are larger than the localization radius of an electronic state on a site ($\alpha^2\rho^2 \gtrsim 1$).[10] On the one hand, this limits strongly the number of materials for which the generalization considered here is vital, and on the other it makes them substantial mainly at high temperatures, when $\hbar\omega_q < 2kT$, and the phonon oscillations acquire a purely classical character. In this temperature region we have

$$\overline{\rho_{mm'}^2} = \frac{2kT}{N}\sum_{\mathbf{q}} \frac{1 - \cos\mathbf{q}(\mathbf{R}_m - \mathbf{R}_{m'})}{M\omega_{\mathbf{q}}^2} \frac{[(\mathbf{R}_m - \mathbf{R}_{m'})\mathbf{e}_{\mathbf{q}}]^2}{(\mathbf{R}_m - \mathbf{R}_{m'})^2}.$$

Thus, according to (18), at not too large a coupling constant γ, the width of the polaron band at $\hbar\omega_q < 2kT$ increases exponentially with temperature like $\exp(BT)$, where

$$B = \frac{k}{N}\sum_{\mathbf{q}} \frac{1 - \cos\mathbf{q}(\mathbf{R}_m - \mathbf{R}_{m'})}{\hbar\omega_{\mathbf{q}}}[\delta_{mm'}^2(\mathbf{q}) - \gamma_{\mathbf{q}}^2].$$

This band broadening is due to the increases of the tunneling probability with increase of the atom oscillation amplitude.[4] If, however, $\gamma^2 > \delta^2$, then $B < 0$ and the polaron band narrows down with temperature, meaning a heavier polaron jacket.

3. DIAGRAM TECHNIQUE

Since the Hamiltonian (14) of the model considered is quite similar to the Hamiltonian of the standard small-polaron theory, a diagram technique can be obtained by a relatively simple generalization of the small-polaron technique

in the site representation.[2,3] We shall not repeat here the rather cumbersome derivation, and state only the final result.

The diagram consists of n interaction points located on a contour in the complex-time plane (see Fig. 1). In the one-electron approximation all the points are joined successively by electron lines that carry a site index m. The interaction points are next joined in all possible manners by phonon (wavy) lines. Each point i is set in correspondence with a factor

$$(\pm i/\hbar) I_{m_i m_i'} \exp(-S_{m_i m_i'}),$$

where m_i' (m_i) is the index of the outgoing (incoming) electron line at the point, and $S_{mm'}$ is defined by Eq. (18). The sign $+$ ($-$) is chosen for the lower (upper) part of the contour. The phonon bundle joining the points i and k (the point k precedes the point i on the contour, see Fig. 1) is set in correspondence with the factor

$$\exp\left\{\sum_{\mathbf{q}} \frac{1}{2\,\mathrm{sh}\,(\hbar\omega_{\mathbf{q}}/2kT)} \left[\Gamma^*_{m_i' m_i} \Gamma_{m_k m_k'} \exp\left(i\omega_{\mathbf{q}}\left(t_i - t_k + \frac{i\hbar}{2kT}\right)\right)\right.\right.$$
$$\left.\left. + \Gamma^*_{m_k' m_k} \Gamma_{m_i m_i'} \exp\left(-i\omega_{\mathbf{q}}\left(t_i - t_k + \frac{i\hbar}{2kT}\right)\right)\right]\right\}$$
$$= \exp\left\{\sum_{\mathbf{q}} \frac{[\exp(i\mathbf{q}\mathbf{R}_{m_i'}) - \exp(i\mathbf{q}\mathbf{R}_{m_i})]\,[\exp(-i\mathbf{q}\mathbf{R}_{m_k}) - \exp(-i\mathbf{q}\mathbf{R}_{m_k'})]}{4N\,\mathrm{sh}\,(\hbar\omega_{\mathbf{q}}/2kT)}\right.$$
$$\times\left[(\gamma_{\mathbf{q}} + \delta_{m_i m_i'})(\gamma_{\mathbf{q}} + \delta_{m_k' m_k}) \exp\left(i\omega_{\mathbf{q}}\left(t_i - t_k + \frac{i\hbar}{2kT}\right)\right)\right.$$
$$\left.\left. + (\gamma_q - \delta_{m_i m_i'})(\gamma_{\mathbf{q}} - \delta_{m_k' m_k}) \exp\left(-i\omega_{\mathbf{q}}\left(t_i - t_k + \frac{i\hbar}{2kT}\right)\right)\right]\right\}. \tag{19}$$

It can be verified that the diagrams expressed in this form diverge at long times.[1] Their convergence is restored by a subtraction procedure[2,3,11] that makes it necessary to eliminate from the diagram with all possible phonon bundles the diagrams with phonon lines broken in all possible manners. When dispersion is taken into account, this procedure restores the convergence. On the other hand, ladder-type summation of the subtracted diagrams lead to a transport equation and, in the upshot, to the appearance of a band contribution to the electric conductivity. The main diagram, however, makes a noise contribution to the mobility.

The procedure described here naturally coincides at $\delta = 0$ with the diagram technique of the standard theory of small polarons.

In the presence of a diagonal disorder (15) in the system, each point i must be set in correspondence to an additional factor

$$\exp\left[\frac{i}{\hbar}(\varepsilon_{m_i'} - \varepsilon_{m_i}) t_i\right],$$

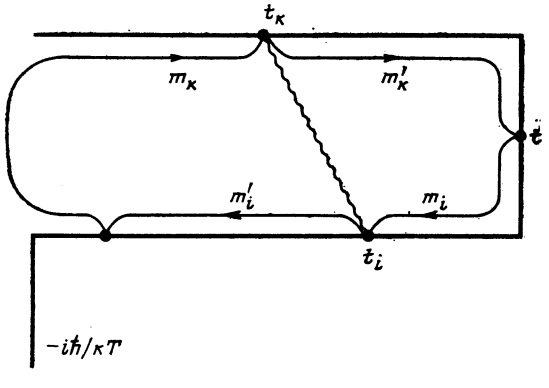

FIG. 1. Integration contour in complex-variable plane and example of a diagram in the site approximation. Only one of three phonon bunches is shown in the figure.

where m_i' (m_i) is the index of the electron line outgoing (incoming) from the point; see also Ref. 3.

4. HOPPING CONDUCTIVITY

We use now the obtained general relations and diagram recipes to calculate the hopping contribution to the electric conductivity. According to general electric conduction theory in the site representation[2,3] the hopping contribution μ_h to the mobility can be expressed as

$$\mu_h = \frac{e}{2kT} \sum_m X_m^2 W_{0m}, \tag{20}$$

where X_m is the component along the x axis (the electric-field direction) of the site radius vector $\mathbf{R}_m$, and W_{0m} is the probability of hopping over from site zero to site m. Relation (20) can be easily understood by writing the corresponding expression for the diffusion coefficient and using the Einstein relation.

In the lowest (second) order with respect to the resonant integral, the hopping probability is described by the two diagrams of Fig. 2. Figure 2a corresponds to the analytic expression

$$\frac{I_{m0}^2}{\hbar^2} \exp(-2S_{m0}) \int_0^\infty dt$$
$$\times \exp\left\{\sum_{\mathbf{q}} \frac{1-\cos \mathbf{q}\mathbf{R}_m}{2N\,\mathrm{sh}\,(\hbar\omega_{\mathbf{q}}/2kT)}\left[(\gamma_{\mathbf{q}} + \delta_{m0}(\mathbf{q}))^2 \right.\right.$$
$$\times \exp\left(i\omega_{\mathbf{q}}\left(t + \frac{i\hbar}{2kT}\right)\right)$$
$$\left.\left. + (\gamma_{\mathbf{q}} - \delta_{m0}(\mathbf{q}))^2 \exp\left(-i\omega_{\mathbf{q}}\left(t + \frac{i\hbar}{2kT}\right)\right)\right]\right\}.$$

The complex-conjugate diagram 2b differs in that limits of integration over t are $-\infty$ and 0. We assume below for simplicity that the constants γ and δ are real.

Confining ourselves to hops between nearest neighbors

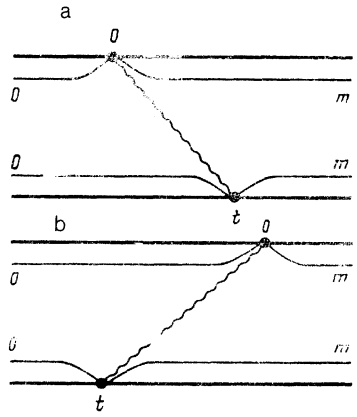

FIG. 2. Two diagrams describing the polaron hopping probability W_{0m} from the zeroth site to the mth. Diagram 2b is the complex conjugate of 2a.

($\mathbf{R}_m = \mathbf{g}$, where $\mathbf{g}$ is the nearest-neighbor vector), we obtain from (20)

$$\mu_h = \frac{ea^2}{kT} W, \tag{21}$$

where $a = |\mathbf{g}|$ is the lattice constant, and W is the probability of hopping between nearest neighbors, given by

$$W = \frac{I^2}{\hbar^2} e^{-2S} \int_{-\infty}^{\infty} dt \Big\{ \exp\Big[\sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{2N \operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} \times [(\gamma_{\mathbf{q}}+\delta_{\mathbf{q}})^2 \exp(i\omega_{\mathbf{q}}t) + (\gamma_{\mathbf{q}}-\delta_{\mathbf{q}})^2 \exp(-i\omega_{\mathbf{q}}t)] \Big] - 1 \Big\}. \tag{22}$$

Here $I \equiv I_{\mathbf{g}0}$ is the resonance integral between nearest neighbors, $S \equiv S_{\mathbf{g}0}$, and $\delta_{\mathbf{q}} \equiv \delta_{\mathbf{g}0}(\mathbf{q})$. It should be noted here that the substitution $\mathbf{g} \to -\mathbf{g}$ reverses the sign of $\delta_{\mathbf{g}0}$, the probability W is not changed by the substitution $\delta \to -\delta$, so that the subscript g of δ can be omitted. Equation (22) is also the result of the integration-variable change $t + i\hbar/2kT \to t$. The appearance of the counterterm -1 in the curly brackets of (22) is due to the subtraction procedure described above, i.e, the subtraction from Fig. 2 of diagrams with omitted phonon bundle.

The integration over t in (22), as is customary in small-polaron theory, is by the saddle-point method. The first saddle point t_0 is located on the imaginary axis, $t_0 = i\tau$, with τ defined by the equation

$$\sum_{\mathbf{q}} \frac{(1-\cos \mathbf{qg})\,\omega_{\mathbf{q}}}{N \operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} [(\gamma_{\mathbf{q}}+\delta_{\mathbf{q}})^2 \exp(-\omega_{\mathbf{q}}\tau) - (\gamma_{\mathbf{q}}-\delta_{\mathbf{q}})^2 \exp(\omega_{\mathbf{q}}\tau)] = 0. \tag{23}$$

Recall that contributions from other saddle points, for which $\mathrm{Re}\, t_0 \neq 0$, are small to the extent that phonon dispersion is present.[2,3,11] Expanding in powers of t in the exponential near the point $t = i\tau$ accurate to $(t - i\tau)^2$ and integrating, we get

$$W = \frac{I^2 e^{-2S} (2\pi)^{1/2}}{\hbar^2} \exp\Big\{ \sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{2N \operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} \times [(\gamma_{\mathbf{q}}+\delta_{\mathbf{q}})^2 \exp(-\omega_{\mathbf{q}}\tau) + (\gamma_{\mathbf{q}}-\delta_{\mathbf{q}})^2 \exp(\omega_{\mathbf{q}}\tau)] \Big\} \Big/ \Big\{ \sum_{\mathbf{q}} \frac{(1-\cos \mathbf{qg})\,\omega_{\mathbf{q}}^2}{2N \operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} \times [(\gamma_{\mathbf{q}}+\delta_{\mathbf{q}})^2 \exp(-\omega_{\mathbf{q}}\tau) + (\gamma_{\mathbf{q}}-\delta_{\mathbf{q}})^2 \exp(\omega_{\mathbf{q}}\tau)] \Big\}^{1/2}. \tag{24}$$

To obtain a simple temperature dependence of W we confine ourselves to the case $\omega_q \tau \ll 1$, which is the case when $2\gamma\delta \ll \gamma^2 + \delta^2$, i.e., either $\gamma \gg \delta$ or $\delta \gg \gamma$. In this limit we have from (23)

$$\tau = 2 \sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{N \operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} \omega_{\mathbf{q}}\gamma_{\mathbf{q}}\delta_{\mathbf{q}} \Big/ \sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{N \operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} \omega_{\mathbf{q}}^2 (\gamma_{\mathbf{q}}^2 + \delta_{\mathbf{q}}^2). \tag{25}$$

Expanding the argument of the exponential in (24) in powers of τ up to τ^2 (we put $\tau = 0$ in the pre-exponential factor) and taking (25) and (18) into account, we get

$$W = \frac{I^2 (2\pi)^{1/2}}{\hbar^2} \exp\Big\{ \sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{N} \Big[\delta_{\mathbf{q}}^2 \operatorname{cth} \frac{\hbar\omega_{\mathbf{q}}}{4kT} - \gamma_{\mathbf{q}}^2 \operatorname{th} \frac{\hbar\omega_{\mathbf{q}}}{4kT} - \frac{\tau\omega_{\mathbf{q}}\gamma_{\mathbf{q}}\delta_{\mathbf{q}}}{\operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} \Big] \Big\} \Big/ \Big\{ \sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{N \operatorname{sh}(\hbar\omega_{\mathbf{q}}/2kT)} \omega_{\mathbf{q}}^2 (\gamma_{\mathbf{q}}^2 + \delta_{\mathbf{q}}^2) \Big\}^{1/2}. \tag{26}$$

In the high-temperature limit $\hbar\omega_q < 2kT$, the temperature dependence of W takes the form

$$W = \pi^{1/2} \frac{I^2}{\hbar (4E_a' kT)^{1/2}} \exp\Big(-\frac{E_a}{kT} + \frac{kT}{\epsilon} \Big), \tag{27}$$

where

$$E_a = \sum_{\mathbf{q}} \frac{\hbar\omega_{\mathbf{q}}}{4N} (1-\cos \mathbf{qg}) \gamma_{\mathbf{q}}^2,$$

$$E_a' = \sum_{\mathbf{q}} \frac{\hbar\omega_{\mathbf{q}}}{4N} (1-\cos \mathbf{qg}) (\gamma_{\mathbf{q}}^2 + \delta_{\mathbf{q}}^2),$$

$$\epsilon^{-1} = 4 \sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{N\hbar\omega_{\mathbf{q}}} \delta_{\mathbf{q}}^2 - \frac{1}{E_a'} \Big\{ \sum_{\mathbf{q}} \frac{1-\cos \mathbf{qg}}{N} \delta_{\mathbf{q}}\gamma_{\mathbf{q}} \Big\}^2 > 0. \tag{28}$$

Without allowance for the influence of the phonon oscillation on the resonance integral, when $\delta_q = 0$, we obtain $\varepsilon^{-1} = 0$, $E_a' = E_a$, and relation (27) goes over into the known results for hopping conductivity of small polarons.[1-3] In the other limiting case of weak coupling to the phonons, when $\gamma_q \to 0$, we obtain $E_a = 0$ and $\ln W \propto kT/\varepsilon$.

Equation (27) is the central actual result of the present paper. With account taken of (21) and with a current-carrier density independent of temperature, this relation shows that the temperature dependence of the hopping conductiv-

ity σ is given by

$$\ln(T^{n}\sigma) = A - \frac{E_a}{kT} + \frac{kT}{\epsilon}, \tag{29}$$

where A is the independent of temperature. An exponential dependence of this type was obtained semiphenomenologically in Ref. 4, where experimental data for a large number of materials were analyzed and compared with a relation of type (29). That relation, to be sure, was not written for $\ln(T^{3/2}\sigma)$ but for $\ln(T\sigma)$. It was observed as a result that (29) describes well the experiments for CdS with In, for GaAs with Cr, for As_2Te_3 and for several other glasses, for VO_2, and also for many other compounds at $E_a = 0$ (i.e., in the absence of a polaron well). Equation (29) with $E_a \neq 0$ can be used for Ti_nO_{2n-1} and V_nO_{2n-1}. Good agreement with (29) was recently observed[12] with the temperature dependence of σ in the solid solutions $Ti_{1-x}Nb_xO_2$.

The most complicated in the comparison of theory with experiment is the question of the localized-state radius which, as already noted, should be very small, not larger than the rms displacement $\overline{\rho^2}$ of the atoms in thermal oscillations, see Sec. 2. The values of the state radius α^{-1} for different materials were deduced in Ref. 4 for different materials from the experimental data on $\sigma(T)$, using a relation similar to (29). The resultant values of α^{-1} range from 0.58 Å for Ti_7O_{13} to 3.4 Å for SiO_2. It was assumed in these calculations that $\varepsilon^{-1} = 2\alpha^2/M\omega^2$, where ω is the characteristic phonon frequency (chosen equal to $10^{12}\,s^{-1}$). This estimate is rather arbitrary. In particular, these estimates are assumed in Ref. 10 to be patently too high. In the proposed theory, according to (26) we obtain for weak coupling with the phonons, $\gamma_q \to 0$,

$$\begin{aligned}\epsilon^{-1} &= \frac{1}{kT}\sum_{\mathbf{q}}\frac{1-\cos \mathbf{qg}}{N}\delta_{\mathbf{q}}^2 \operatorname{cth}(\hbar\omega_{\mathbf{q}}/4kT)\\ &\approx 4\alpha^2\sum_{\mathbf{q}}\frac{1-\cos \mathbf{qg}}{NM\omega_{\mathbf{q}}^2}\frac{(\mathbf{e_q g})^2}{a^2}\\ &= \frac{4\alpha^2}{3}\sum_{\mathbf{q}}\frac{1-\cos \mathbf{qg}}{NM\omega_{\mathbf{q}}^2}e_{\mathbf{q}}^2.\end{aligned} \tag{30}$$

The second (approximate) equality in this chain was written for the quasiclassical high-temperature limit $\hbar\omega_{\mathbf{q}} < 2kT$, and the last equality for a cubic lattice. In the particular case of a Bravais lattice we have $e_{\mathbf{q}}^2 = 1$. Note that in the general case ϵ^{-1} cannot be expressed in terms of the rms displacement ρ^2, since (3) contains the factor $\coth(\hbar\omega_{\mathbf{q}}/4kT)$ and $\coth(\hbar\omega_{\mathbf{q}}/2kT) = 2\mathcal{N} + 1$. In the high-temperature limit, however, we have $kT/\epsilon = 2\alpha^2\overline{\rho^2}$, where $\overline{\rho^2} = \overline{\rho^2_{mm'}}$ for $\mathbf{R}_m - \mathbf{R}_{m'} = \mathbf{g}$ (see Sec. 2).

Notwithstanding the good agreement of (29) with the experimental data for a large group of materials, the character of electron transport in them can be reliably described only after theory is compared with experiment for other kinetic coefficients. These include the temperature dependence of σ at low temperatures, where a transition from hopping current transport to band transport can be expected for crystalline substances[1-3,13] or to hops over level near the Fermi surface for disordered materials (to Mott's law); the frequency dependence of light absorption, which is characterized in the small-polaron model by the presence of a Gaussian peak; the temperature dependence of the Hall mobility which differs radically from that of the drift mobility; the frequency dependence of σ in the rf band for disordered materials; and the temperature dependence of the thermoelectric power. All these kinetic coefficients can be calculated by the procedure proposed in the present paper, using procedures developed in standard small-radius-polaron theory.

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Translated by J. G. Adashko