Hall effect for ultrasmall polarons in hexagonal crystals

V. V. Bryksin

A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences
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A theory is constructed for the Hall effect for ultrasmall polarons, with radius much smaller than the lattice constant and comparable to the amplitude of the thermal vibrations of atoms. It is shown that the Hall mobility μ_H in this model differs radically from the drift mobility. The temperature of μ_H does not have the simple activational form, but rather it has the form $\ln(\mu_H T^{1/2}) \sim kT/\epsilon_H - E_{aH}/kT$, where E_{aH} is three times smaller and ϵ_H is eight times larger than the activation energy of drift mobility. This result makes it possible to reliably identify ultrasmall polarons from measurements of the temperature dependence of the Hall mobility and electric conductivity (under the condition that the current carrier density is constant).

A new model of low mobility was formulated in Ref. 1. It is an extension of the model of small-radius polarons. In this model the effect of the displacements of atoms of the crystal lattice from their equilibrium position as a result of phonon vibrations on the intersite resonance integral, which determines the width of the bare electronic band, is taken into account. This effect is caused by the change produced in the overlapping of the electronic wave functions on neighboring lattice sites due to the change in the interatomic distances accompanying thermal displacements. The possibility that the dependence of the resonant integral on the phonon variables could affect the behavior of small polarons was first pointed out in Ref. 2. However this effect was first specifically discussed in Ref. 3.

1. FORMULATION OF THE PROBLEM

The Hamiltonian in the model of ultrasmall polarons after the polaron canonical transformation was derived in Ref. 1. Neglecting the electron-electron correlations, it has the form

$$H=\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}\left(b_{\mathbf{q}}^{+}b_{\mathbf{q}}+\frac{1}{2}\right)+\sum_{mm'}I_{mm'}a_{m'}^{+}a_{m}\Psi_{mm'}. \tag{1}$$

Here $\omega_{\mathbf{q}}$ is the frequency of a phonon with momentum $\mathbf{q}$ (in order to simplify the notation, here $\mathbf{q}$, generally speaking, also incorporates the number of the phonon branch j), $b_{\mathbf{q}}^{+}$ and $b_{\mathbf{q}}$ are phonon operators, a_m^{+} (a_m) are operators creating (annihilating) electrons at the lattice site m, $I_{mm'}$ is the intersite resonance integral for atoms which are at rest in the position of equilibrium, and $\Psi_{mm'}$ is a multiphonon operator

$$\Psi_{mm'}=\exp\left\{\sum_{\mathbf{q}}\Gamma_{m'm}(\mathbf{q})b_{\mathbf{q}}+\Gamma_{mm'}^{*}(\mathbf{q})b_{\mathbf{q}}^{+}\right\}, \tag{2}$$

$$\Gamma_{mm'}(\mathbf{q})=u_{m'}(\mathbf{q})-u_{m}(\mathbf{q})-v_{mm'}(\mathbf{q}).$$

Here

$$u_m(\mathbf{q})=(2N)^{-1/2}\gamma_{\mathbf{q}}\exp(-i\mathbf{q}\mathbf{R}_m),$$
$$v_{mm'}(\mathbf{q})=(2N)^{-1/2}\delta_{mm'}(\mathbf{q})\{\exp;-i\mathbf{q}\mathbf{R}_m)-\exp(-i\mathbf{q}\mathbf{R}_{m'})\}, \tag{3}$$

$\mathbf{R}_m$ is the radius vector of the mth site, $\gamma_{\mathbf{q}}$ is the electron-phonon coupling constant (in the Froelich Hamiltonian), N is the total number of atoms in the system,

$$\delta_{mm'}(\mathbf{q})=\alpha\left(\frac{\hbar}{M\omega_{\mathbf{q}}}\right)^{1/2}(\mathbf{e}_{\mathbf{q}}(\mathbf{R}_m-\mathbf{R}_{m'}))\,|\mathbf{R}_m-\mathbf{R}_{m'}|^{-1}, \tag{4}$$

$\mathbf{e}_{\mathbf{q}}$ is the characteristic vector of the normal vibrations of the phonon branch, M is the mass of an atom, and α^{-1} is the localization radius of the atomic wave function. The quantity α is determined as follows:

$$I_{mm'}=I_0\exp\{-\alpha|\mathbf{R}_m-\mathbf{R}_{m'}|\}. \tag{5}$$

The effect of thermal displacements on the resonance integral is taken into account through the contribution $v_{mm'}$ in Eq. (2). For $v=0$ the Hamiltonian (2) corresponds to the standard model of small-radius polarons.

The hopping contribution to the mobility μ_h for the model of ultrasmall polarons was calculated in Ref. 1 from the Hamiltonian (1). The result is the expression

$$\mu_h=u_0\frac{z\pi^{1/2}}{8}\frac{I^2}{kT(E_a'kT)^{1/2}}\exp\left(-\frac{E_a}{kT}+\frac{kT}{\epsilon}\right), \tag{6}$$

which we shall require below. Here a is the lattice constant, $I\equiv I_{g0}$ is the resonance integral (5) between the nearest neighbors, $\mathbf{R}_{m'}-\mathbf{R}_m=\mathbf{g}$ is a vector drawn to the site of the nearest neighbor, T is the temperature, and the quantity $u_0=ea^2/\hbar$ has the dimensions of mobility;

$$E_a=\frac{1}{4N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}|\gamma_{\mathbf{q}}|^2(1-\cos\mathbf{q}\mathbf{g}),$$
$$E_a'=E_a+\frac{1}{4N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}|\delta_{\mathbf{q}}|^2(1-\cos\mathbf{q}\mathbf{g}). \tag{7}$$

Here $\delta_{\mathbf{q}}\equiv\delta_{g0}(\mathbf{q})$ [see Eq. (4)], and

$$\epsilon^{-1}=\sum_{\mathbf{q}}\frac{4}{N\hbar\omega_{\mathbf{q}}}|\delta_{\mathbf{q}}|^2(1-\cos\mathbf{q}\mathbf{g}). \tag{8}$$

In Eq. (6) the quantity z is the number of nearest neighbors. We note that in Ref. 1 the expression for μ_h was obtained only for the case of a square lattice ($z=4$). However this result can be easily extended to the case of a hexagonal structure ($z=6$). It should also be noted that in Ref. 1 the expres-

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sion for ϵ^{-1}, as compared with Eq. (8), has an additional term $-\Delta_g^2/E'_a$, where

$$\Delta_g=\frac{1}{N}\sum_q(1-\cos qg)\delta_q^*\gamma_q.$$

However this contribution vanishes for lattices without a preferred direction. In the present paper we neglect contributions of this type. Here we also note that for lattices with $\Delta_g=0$ the expressions obtained in Ref. 4 for the absorption coefficient for light and the I-V-characteristic in the model of ultrasmall polarons simplify significantly.

For a wide range of materials with low mobility the mobility exhibits a temperature dependence which is not of the standard activational type, but rather is described by a relation of the form (6) (see Ref. 3).

It is considered that the radical difference of the Hall mobility μ_H from the drift mobility, both in order of magnitude and with respect to the temperature dependence, is a strong argument in favor of the mechanism of current transport by small polarons. In particular, the calculation performed in Ref. 5 showed that for small polarons in hexagonal crystals we have $\mu_h\sim\exp(-E_a/kT)$, but $\mu_H\sim\exp(-E_a/3kT)$, i.e., the activation energy is three times lower for the Hall mobility than for the drift mobility. The significantly more complicated calculation performed later for square lattices[6,7] showed that, generally speaking, for these structures the activation energy does not decrease exactly by a factor of 3, but even here the Hall and drift mobilities differ radically.

We underscore the fact that here and below we are talking only about quite high temperatures, when transport proceeds by means of hops between lattice sites. At ultralow temperatures, however, transport acquires an ininerant character and the Hall effect can be studied with the help of a Boltzmann-type transport equation.[8] At intermediate temperatures transport proceeds by means of intersite electron tunneling, and the force exerted by the magnetic field is not the Lorentz force.[9]

The present paper is devoted to developing a theory of the Hall effect in the ultrasmall-polaron model in the high-temperature region of hopping transport. The calculation is based on the Hamiltonian (1) using the diagrammatic technique, which was formulated in Ref. 4 and is an extension of the diagrammatic technique of the theory of small polarons.[10,11] In this model the Hall mobility, similarly to the drift mobility, also does not have a purely activational character. For this reason, the measurement of μ_H could serve as an important tool for determining the character of current transport in the material of interest. In the present paper the calculation is performed for the very simple case of a hexagonal lattice, when the probability of intersite transitions in a magnetic field can be calculated in the lowest, three-site approximation.

2. HALL CURRENT IN THE THREE-SITE APPROXIMATION

We shall study the hexagonal configuration shown in Fig. 1. The hopping contribution to the current **j** in the approximation of nearest-neighbor hops can be written in the form[10,11]

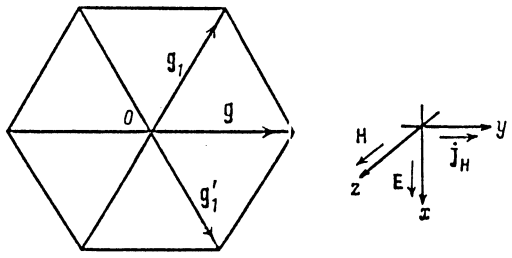

FIG. 1. Planar hexagonal structure. The magnetic field is oriented perpendicular to the plane of the figure.

$$\mathbf{j}=en\sum_{\mathbf{g}}\mathbf{g}W_{0\mathbf{g}}(\mathbf{E},\mathbf{H}), \tag{9}$$

where n is the current-carrier density, **g** is a vector drawn to the site of the nearest neighbor (**g** takes on six values), and $W_{0\mathbf{g}}(\mathbf{E},\mathbf{H})$ is the probability of a hop between the sites 0 and **g** and depends on the electric field **E** and magnetic field **H**. The Hall mobility is most conveniently calculated starting from the assumption that **E** and **H** are arbitrary in magnitude and then linearizing with respect to these fields at the end of the calculation.

The Hamiltonian (1) can be extended as follows to the case when a magnetic field is present.[5] The intersite resonance integral $I_{mm'}$ acquires an additional phase factor which depends on the vector potential **A**. For the gauge $\mathbf{A}=[\mathbf{H}\times\mathbf{r}]/2$ the effect of the magnetic field reduces to replacing

$$I_{mm'}\to\tilde{I}_{mm'}=I_{mm'}\exp\left\{\frac{ie}{2\hbar c}(\mathbf{H}[\mathbf{R}_m\mathbf{R}_{m'}])\right\} \tag{10}$$

in Eq. (1). As for the electric field, taking it into account leads to the appearance of an additional term

$$-e\mathbf{E}\sum_m\mathbf{R}_m a_m^+ a_m$$

in Eq. (1). The appearance of this term in the diagrammatic technique described in Ref. 4 requires associating with each interaction point the additional factor

$$\exp\left\{\frac{i}{\hbar}e\mathbf{E}(\mathbf{R}_{m_i}-\mathbf{R}_{m'_i})t_i\right\},$$

where t_i is the time associated to the interaction point i and $m_i(m'_i)$ is the site index of the electron line entering (leaving) this point. These extensions of the diagrammatic technique in the presence of finite **E** and **H** are entirely analogous to those which are made in the standard theory of small polarons in the presence of external fields.[10,11]

We now calculate the probability $W_{0\mathbf{g}}(\mathbf{E},\mathbf{H})$. In the lowest (second) order in the interaction the magnetic field drops out of the expression for $W_{0\mathbf{g}}$. This is connected with the fact that in this approximation $W_{mm'}\sim I_{mm'}I_{m'm}$, and according to Eq. (10) the phase factors of the resonance integrals mutually cancel (see also Refs. 5, 10, and 11). For this reason the transition probability for the Hall effect must be calculated in the next order of perturbation theory. The corresponding diagrams for hexagonal structures are shown in Fig. 2. The diagram in Fig. 2b is the complex conjugate of the diagram in Fig. 2a. According to the rules formulated in Ref. 4 the probability $W_{0\mathbf{g}}$ has the form

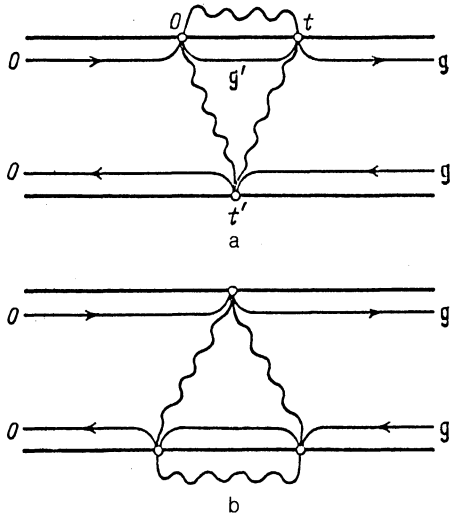

FIG. 2. Diagrams describing the probability of intersite hops which give the first nonvanishing contribution to the Hall current for hexagonal lattices.

$$W_{0g}(\mathbf{E},\mathbf{H})=2\,\mathrm{Re}\sum_{g'}\frac{1}{i\hbar^3}I_{0g}I_{gg'}I_{g'0}\exp(-S_{0g}-S_{gg'}-S_{g'0})$$
$$\times\int_{-\infty}^{\infty}dt'\int_{0}^{\infty}dt\exp\left\{\frac{i}{\hbar}e\mathbf{E}[(\mathbf{g}'-\mathbf{g})t+\mathbf{g}t']+\sum_{q}\frac{1}{4N\,\mathrm{sh}\,\beta\omega_q}\right.$$
$$\times[(1-e^{i\mathbf{qg}})(e^{-i\mathbf{qg}'}-e^{-i\mathbf{qg}})(\gamma_q^*+\delta_{g0}^*)(\gamma_q+\delta_{gg'})$$
$$\times\exp\{i\omega_q(t-t'+i\beta)\}$$
$$+(1-e^{-i\mathbf{qg}})(e^{i\mathbf{qg}'}-e^{i\mathbf{qg}})(\gamma_q+\delta_{0g})(\gamma_q^*+\delta_{g'g}^*)$$
$$\times\exp\{-i\omega_q(t-t'+i\beta)\}$$
$$+(1-e^{-i\mathbf{qg}'})(e^{i\mathbf{qg}}-e^{i\mathbf{qg}'})(\gamma_q^*+\delta_{g'g}^*)(\gamma_q+\delta_{g'0})$$
$$\times\exp\{i\omega_q(t+i\beta)\}$$
$$+(1-e^{i\mathbf{qg}'})(e^{-i\mathbf{qg}}-e^{-i\mathbf{qg}'})(\gamma_q+\delta_{gg'})(\gamma_q^*+\delta_{0g'}^*)$$
$$\times\exp\{-i\omega_q(t+i\beta)\}$$
$$+(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})(\gamma_q^*+\delta_{g0}^*)(\gamma_q+\delta_{g'0})$$
$$\times\exp\{i\omega_q(t'+i\beta)\}$$
$$+(1-e^{-i\mathbf{qg}})(1-e^{i\mathbf{qg}'})(\gamma_q+\delta_{0g})(\gamma_q^*+\delta_{0g'}^*)$$
$$\left.\times\exp\{-i\omega_q(t'+i\beta)\}.\right. \qquad (11)$$

Here the summation over g' includes for given g two values (in Fig. 1, $\mathbf{g}=\mathbf{g}_1$ and $\mathbf{g}'_1$)

$$S_{mm'}=\frac{1}{2N}\sum_{q}[1-\cos\mathbf{q}(\mathbf{R}_m-\mathbf{R}_{m'})](|\gamma_q|^2-|\delta_{mm'}|^2)\,\mathrm{cth}\,\beta\omega_q, \qquad (12)$$

with $\beta=\hbar/2kT$, and γ and δ are defined in Eqs. (3) and (4). The following symmetry relations follow from the condition that the atomic displacements are real:

$$\gamma_q=\gamma_{-q}^*, \qquad \delta_{mm'}(\mathbf{q})=\delta_{m'm}^*(-\mathbf{q}). \qquad (13)$$

Taking these conditions into account and making the substitution of variables $t'\to t'+t$ we transform the relation (11) into the form

$$W_{0g}(\mathbf{E},\mathbf{H})=2\,\mathrm{Re}\sum_{g'}\frac{1}{i\hbar^3}I_{0g}I_{gg'}I_{g'0}\exp(-S_{0g}-S_{gg'}-S_{g'0})$$
$$\times\int_{-\infty}^{\infty}dt'\int_{0}^{\infty}dt\exp\left\{\frac{i}{\hbar}e\mathbf{E}(\mathbf{g}t'+\mathbf{g}'t)+\sum_{q}\frac{1}{4N\,\mathrm{sh}\,\beta\omega_q}\right.$$
$$\times[(1-e^{i\mathbf{qg}})(e^{-i\mathbf{qg}'}-e^{-i\mathbf{qg}})[(\gamma^*+\delta_g^*)(\gamma+\delta_{g-g'})\exp\{i\omega_q(t'+i\beta)\}$$
$$+(\gamma^*-\delta_g^*)(\gamma-\delta_{g-g'})\exp\{-i\omega_q(t'+i\beta)\}]$$
$$+(1-e^{-i\mathbf{qg}'})(e^{i\mathbf{qg}}-e^{i\mathbf{qg}'})[(\gamma^*+\delta_{g'-g}^*)(\gamma+\delta_{g'})\exp\{i\omega_q(t+i\beta)\}$$
$$+(\gamma^*-\delta_{g'-g}^*)(\gamma-\delta_{g'})\exp\{-i\omega_q(t+i\beta)\}]$$
$$+(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})[(\gamma^*+\delta_g^*)(\gamma+\delta_{g'})\exp\{i\omega_q(t+t'+i\beta)\}$$
$$\left.+(\gamma^*-\delta_g^*)(\gamma-\delta_{g'})\exp\{-i\omega_q(t+t'+i\beta)\}]\right\}. \qquad (14)$$

Here we take into account the fact that, according to Eq. (4), $\delta_{mm'}\equiv\delta_{m-m'}=-\delta_{m'-m}$. In Eq. (14) the indices q in the quantities γ and δ have been suppressed.

The expressions for the probabilities (11) and (14) were written out neglecting the divergence-cancelling terms at long times t and t'. These counterterms represent diagrams divided in all possible ways by phonon (wavy) lines. The procedure for summing these counterterms gives the nonhopping contribution to the conductivity, which predominates at low temperatures and is not discussed in the present paper (see Refs. 5, 10, and 11 for a more detailed discussion).

In the subsequent calculations we assume that the symmetry of the lattice imposes some symmetry relations on the phonon spectra. First, we require that all cross terms proportional to the product $\gamma\delta$ in Eq. (14) vanish:

$$\sum_q f(\omega_q)(1-e^{i\mathbf{qg}})(e^{-i\mathbf{qg}'}-e^{-i\mathbf{qg}})(\gamma^*\delta_{g-g'}+\gamma\delta_g^*)$$
$$=\sum_q f(\omega_q)(1-e^{-i\mathbf{qg}'})(e^{i\mathbf{qg}}-e^{i\mathbf{qg}'})(\gamma^*\delta_{g'}+\gamma\delta_{g'-g}^*)$$
$$=\sum_q f(\omega_q)(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})(\gamma^*\delta_{g'}+\gamma\delta_g^*)=0. \qquad (15)$$

In order to verify this we study, for example, the quantity

$$\sum_q f(\omega_q)(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})\gamma\delta_g^*=(\mathbf{Ag}).$$

According to Eq. (4) the vector $\mathbf{A}$ can be represented in the form

$$\mathbf{A}=\sum_q \mathbf{a}_q(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'}),$$

where

$$\mathbf{a}_q=f(\omega_q)\alpha\left(\frac{\hbar}{M\omega_q}\right)^{1/2}\frac{1}{a}\gamma_q\mathbf{e}_q^*.$$

The quantity $\mathbf{a}_q$ does not depend on the vectors of the nearest neighbors.

The vector $\mathbf{A}$ can be represented in the form $\mathbf{A}=\mathbf{A}_1+i\mathbf{A}_2$, where

$$\mathbf{A}_1=\sum_q \mathbf{a}_q[1+\cos\mathbf{q}(\mathbf{g}-\mathbf{g}')-\cos\mathbf{qg}-\cos\mathbf{qg}'],$$

$$\mathbf{A}_2=\sum_q \mathbf{a}_q[\sin\mathbf{qg}'-\cos\mathbf{qg}+\sin\mathbf{q}(\mathbf{g}-\mathbf{g}')].$$

It is obvious that for lattices without a distinguished direction the vector $\Sigma_{\mathbf{q}} \mathbf{a}_{\mathbf{q}} \cos \mathbf{qg}$ can be directed only along $\mathbf{g}$. On the other hand, it does not change when $\mathbf{g}$ is replaced by $-\mathbf{g}$, and for this reason it is equal to 0. Hence it follows that we have $\mathbf{A}_1 = 0$.

Similarly, for such lattices

$$\sum_{\mathbf{q}} \mathbf{a}_{\mathbf{q}} \sin \mathbf{qg} = c\mathbf{g},$$

where c is a scalar that does not depend on $\mathbf{g}$. For this reason

$$\mathbf{A}_2 = c(\mathbf{g}' - \mathbf{g} + \mathbf{g} - \mathbf{g}') = 0.$$

The remaining terms in Eq. (14) can be analyzed similarly and it can be proved that this relation is true.

Second, we assume that

$$\begin{aligned}
&\sum_{\mathbf{q}} f(\omega_{\mathbf{q}})\,(1-e^{i\mathbf{qg}})\,(e^{-i\mathbf{qg}'}-e^{-i\mathbf{qg}})\,(|\gamma|^2+\delta_{\mathbf{g}}^{*}\delta_{\mathbf{g}-\mathbf{g}'}) \\
&= \sum_{\mathbf{q}} f(\omega_{\mathbf{q}})\,(1-e^{-i\mathbf{qg}'})\,(e^{i\mathbf{qg}}-e^{i\mathbf{qg}'})\,(|\gamma|^2+\delta_{\mathbf{g}'-\mathbf{g}}^{*}\delta_{\mathbf{g}'}) \\
&= \sum_{\mathbf{q}} f(\omega_{\mathbf{q}})\,(1-e^{i\mathbf{qg}})\,(1-e^{-i\mathbf{qg}'})\,(|\gamma|^2+\delta_{\mathbf{g}}^{*}\delta_{\mathbf{g}'}). \qquad (16)
\end{aligned}$$

The meaning of this relation can be understood from the fact that these three sums differ from one another only by an interchange of the vectors $\mathbf{g}$, $\mathbf{g}-\mathbf{g}' \to \mathbf{g}'-\mathbf{g}$ and $\mathbf{g}' \to \mathbf{g}'$, $\mathbf{g}$. Each pair of these vectors represents the side of a triangle, formed by a triplet of nearest neighbors of the hexagonal structure (see Fig. 1). This proves Eq. (16) for lattices without a preferred direction. We note that by assumption only the centers of localization form a hexagonal structure. In principle, however, the symmetry of the full crystalline structure, determining the phonon spectra, can be lower.

The relations (15) and (16) greatly simplify the expression for the transition probability, which assumes the form

$$\begin{aligned}
W_{0\mathbf{g}} = 2\,\mathrm{Re} \sum_{\mathbf{g}'} \left(-\frac{i}{\hbar}\right)^3 & I_{0\mathbf{g}} I_{\mathbf{gg}'} I_{\mathbf{g}'0} \exp(-S_{\mathbf{g}} - S_{\mathbf{g}'-\mathbf{g}} - S_{\mathbf{g}'}) \\
&\times \int_{-\infty}^{\infty} dt' \int_{0}^{\infty} dt \exp\left\{\frac{i}{\hbar} e\mathbf{E}(\mathbf{g}t' + \mathbf{g}'t)\right\} \\
&\times \exp\left\{\sum_{\mathbf{q}} A_{\mathbf{q}} [\cos \omega_{\mathbf{q}}(t+i\beta) + \cos \omega_{\mathbf{q}}(t'+i\beta)\right. \\
&\left. + \cos \omega_{\mathbf{q}}(t+t'+i\beta)]\right\}, \qquad (17)
\end{aligned}$$

where

$$A_{\mathbf{q}} = \frac{1}{2N \operatorname{sh} \beta\omega_{\mathbf{q}}} (1-e^{i\mathbf{qg}})\,(1-e^{-i\mathbf{qg}'})\,(|\gamma|^2+\delta_{\mathbf{g}}^{*}\delta_{\mathbf{g}'}). \qquad (18)$$

The expression for W can be further simplified by linearizing it with respect to the magnetic field. In this approximation we must make in Eq. (17) the substitution

$$I_{0\mathbf{g}} I_{\mathbf{gg}'} I_{\mathbf{g}'0} \to I^3 \frac{ie}{\hbar c} (\mathbf{H}[\mathbf{gg}']),$$

where

$$I \equiv I_{0\mathbf{g}} = I_{\mathbf{gg}'} = I_{\mathbf{g}'0}$$

[see Eq. (10)]. We are not interested in the contribution which is zeroth order in the magnetic field. Substituting now the linearized expression for $W_{0\mathbf{g}}$ into Eq. (9) we obtain for the Hall current $\mathbf{j}_H$, directed along the y-axis (see Fig. 1),

$$\mathbf{j}_H = \frac{e^2 n}{2\hbar^4 c} I^3 e^{-3s} \sum_{\mathbf{g},\mathbf{g}'} \mathbf{g}(\mathbf{H}[\mathbf{gg}'])K_{\mathbf{gg}'}, \qquad (19)$$

where

$$\begin{aligned}
K_{\mathbf{gg}'} = &\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \exp\left\{\frac{i}{\hbar} e\mathbf{E}(\mathbf{g}t' + \mathbf{g}'t)\right\} \\
&\times \exp\left\{\sum_{\mathbf{q}} A_{\mathbf{q}} [\cos \omega_{\mathbf{q}}(t+i\beta) + \cos \omega_{\mathbf{q}}(t'+i\beta)\right. \\
&\left. + \cos \omega_{\mathbf{q}}(t+t'+i\beta)]\right\}. \qquad (20)
\end{aligned}$$

In deriving Eq. (20) we used the fact that we are interested only in the real part of the integrals over t and t'. This made it possible to make the following substitution, taking into account the symmetry of the integrand:

$$2\mathrm{Re} \int_{-\infty}^{\infty} dt' \int_{0}^{\infty} dt \to \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt.$$

We also took into account the fact that

$$S_{\mathbf{g}} = S_{\mathbf{g}-\mathbf{g}'} = S_{\mathbf{g}'} \equiv S.$$

3. TEMPERATURE DEPENDENCE OF THE HALL MOBILITY

We perform the double integration in Eq. (20) with the help of the identity

$$\begin{aligned}
&\int_{-\infty}^{\infty} dt\, dt' f(t, t', t+t') \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega \int_{-\infty}^{\infty} dt\, dt'\, dt'' f(t, t', t'') \exp\{i\Omega(t''-t-t')\}.
\end{aligned}$$

Using this relation and displacing t, t', and t'' by $i\beta$ we transform Eq. (20) into the form

$$\begin{aligned}
K_{\mathbf{gg}'} = &\frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega \exp\left\{\beta\left[\frac{e\mathbf{E}}{\hbar}(\mathbf{g}+\mathbf{g}') - \Omega\right]\right\} \\
&\times F(\Omega) F\left(\Omega - \frac{e\mathbf{E}\mathbf{g}}{\hbar}\right) F\left(\Omega - \frac{e\mathbf{E}\mathbf{g}'}{\hbar}\right), \qquad (21)
\end{aligned}$$

where

$$F(\Omega) = \int_{-\infty}^{\infty} dt \exp\left\{i\Omega t + \sum_{\mathbf{q}} A_{\mathbf{q}} \cos \omega_{\mathbf{q}} t\right\}. \qquad (22)$$

The integration in Eq. (22) is performed by the saddle-point method customarily employed in the theory of small polarons (see, for example, Refs. 4 and 11). The first saddle-point t_0 lies on the imaginary axis, $t_0 = i\eta$, and η satisfies the equation

$$\Omega = \sum_{\mathbf{q}} A_{\mathbf{q}} \omega_{\mathbf{q}} \operatorname{sh} \omega_{\mathbf{q}} \eta. \qquad (23)$$

Expanding the exponential in a series in powers of t around

the point $t = i\eta$ up to quadratic terms and performing the integration we obtain

$$F(\Omega)=\left(\frac{2\pi}{\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2 \operatorname{ch}\omega_{\mathbf{q}}\eta}\right)^{1/2} \times\exp\left\{-\eta\Omega+\sum_{\mathbf{q}} A_{\mathbf{q}}\operatorname{ch}\omega_{\mathbf{q}}\eta\right\}. \tag{24}$$

In this case, for $\hbar\omega_{\mathbf{q}}/\sigma kT \ll 1$ and $A_{\mathbf{q}} \gg 1$ it is easy to verify that the characteristic value Ω in the integral (21) is quite small, so that we have $\omega_{\mathbf{q}}\eta \ll 1$. Then we obtain from Eq. (3) the following explicit expression for η:

$$\eta \approx \frac{\Omega}{\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2}. \tag{25}$$

Now, expanding in Eq. (24) the exponential in a series in powers of $\omega_{\mathbf{q}}\eta$ up to quadratic terms, taking into account Eq. (25), we have

$$F(\Omega)=\left(\frac{2\pi}{\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2}\right)^{1/2}\exp\left\{\sum_{\mathbf{q}} A_{\mathbf{q}}-\frac{\Omega^2}{2\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2}\right\}. \tag{26}$$

We now substitute Eq. (26) into Eq. (21). After an elementary integration over Ω we have

$$K_{\mathbf{gg}'}=\frac{2\pi}{3^{1/2}\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2} \times\exp\left\{3\sum_{\mathbf{q}} A_{\mathbf{q}}+\frac{1}{\hbar}\beta e\mathbf{E}(\mathbf{g}+\mathbf{g}')+\frac{1}{6}\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2\left[\beta-\frac{e\mathbf{E}(\mathbf{g}+\mathbf{g}')}{\hbar\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2}\right]^2\right\}. \tag{27}$$

Now we can find an expression for the Hall current $\mathbf{j}_H$, substituting Eq. (27) into Eq. (19) and confining ourselves to the linear approximation in the electric field $\mathbf{E}$:

$$\mathbf{j}_H=\frac{2\pi}{3^{1/2}}\frac{e^3 n\beta I^3}{c\hbar^5\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2} \times\exp\left\{-3S+3\sum_{\mathbf{q}} A_{\mathbf{q}}+\frac{1}{6}\beta^2\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2\right\} \times\sum_{\mathbf{g},\mathbf{g}'} \mathbf{g}(\mathbf{H}[\mathbf{gg}'])(\mathbf{E}(\mathbf{g}+\mathbf{g}')). \tag{28}$$

Now we can perform the summation over the nearest neighbors $\mathbf{g}$ and $\mathbf{g}'$ taking into account the geometry of the problem, shown in Fig. 1. The result is

$$\mathbf{j}_H=3^{1/2}\pi\frac{e^3 n\beta I^3 a^4}{c\hbar^5\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2}[\mathbf{EH}] \times\exp\left\{-3S+3\sum_{\mathbf{q}} A_{\mathbf{q}}+\frac{1}{6}\beta^2\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2\right\}, \tag{29}$$

where $a = |\mathbf{g}|$ is the lattice constant.

Now we pass in Eq. (29) to the high-temperature classical limit $\hbar\omega_{\mathbf{q}} < kT$ of interest to us. According to Eq. (18), in this temperature range

$$\sum_{\mathbf{q}} A_{\mathbf{q}}\omega_{\mathbf{q}}^2=\frac{4kT}{\hbar^2}E_a'', \qquad E_a''=E_a+{}^1/_4\varepsilon, \tag{30}$$

where E_a is the polaron activation energy (17),

$$\varepsilon=\frac{1}{N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})\delta_{\mathbf{g}}^*\delta_{\mathbf{g}'}.$$

Using the explicit expression for $\delta_{\mathbf{g}}$ (4) we have

$$\varepsilon=\frac{\hbar^2\alpha^2}{NMa^2}\sum_{\mathbf{q}}(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})(\mathbf{e}_{\mathbf{g}}^*\mathbf{g})(\mathbf{e}_{\mathbf{q}}\mathbf{g}').$$

Now we take into account the fact that the eigenvectors of the phonon oscillations satisfy the sum rule

$$\sum_j e_{\mathbf{q}\alpha}^* e_{\mathbf{q}\beta}=\delta_{\alpha\beta}.$$

We recall that summation over the indices j of the phonon branches, as we have already noted above, is implied in all summations over q. Here α and β are the projections on the coordinate axes. When we take this identity into account, the expression for ε assumes the form

$$\varepsilon=\frac{\hbar^2\alpha^2}{Ma^2N}(\mathbf{gg}')\sum_{\mathbf{q}}(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})=\frac{\hbar^2\alpha^2}{2M}. \tag{31}$$

We note here also that the energy E_a' (7) appearing in the expression for the drift mobility (6) is related to ε:

$$E_a'=E_a+{}^1/_2\varepsilon. \tag{32}$$

In order of magnitude, with $\alpha^{-1}\approx 1$ Å and $m\approx 10^{-22}$ g, the energy ε is equal to 10^{-4} eV, i.e., it is much less than kT. For this reason the quantities E_a' and E_a'' are virtually identical to E_a. We also note that the ratio ε/kT is the squared ratio of the de Broglie wavelength to the localization length.

Now we study the quantity $3(\Sigma_{\mathbf{q}}A_{\mathbf{q}} - S)$ in the temperature range $kT > \hbar\omega_{\mathbf{q}}$. This combination appears in the argument of the exponential in Eq. (29). When this expression is expanded in a series in powers of the small parameter, the first term of the expansion is proportional to T. The most important property of such an expansion is the fact that the terms proportional to the squared electron-phonon coupling constant $|\gamma|^2$ cancel in the first term of the expansion. Only terms proportional to δ^2 remain. This remaining contribution has the form

$$\frac{3kT}{N}\sum_{\mathbf{q}}\frac{1}{\hbar\omega_{\mathbf{q}}}\{(1-\cos\mathbf{qg})|\delta_{\mathbf{g}}|^2+(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})\delta_{\mathbf{g}}^*\delta_{\mathbf{g}'}\} = kT\left(\frac{1}{\epsilon}+\frac{1}{\epsilon_H}\right),$$

where ϵ^{-1} is determined in Eq. (8), and

$$\epsilon_H^{-1}=\frac{1}{N}\sum_{\mathbf{q}}\frac{1}{\hbar\omega_{\mathbf{q}}}\{3(1-e^{i\mathbf{qg}})(1-e^{-i\mathbf{qg}'})\delta_{\mathbf{g}}^*\delta_{\mathbf{g}'} -(1-\cos\mathbf{qg})|\delta_{\mathbf{g}}|^2\}. \tag{33}$$

As concerns the next term, proportional to T^{-1}, in the expansion of the quantity $3(\Sigma_q A_q - S)$, we include in it only the contribution proportional to $|\gamma|^2$. This contribution is equal to $-3E_a/2kT$ with E_a determined in Eq. (7). Taking this term into account, the expression for σ_{xy} ($j_H = \sigma_{xy}E$) in Eq. (29) assumes the form

$$\sigma_{xy}=enu_0\frac{u_0H}{c}\frac{3^{1/2}\pi}{8}\frac{I^3}{E_a(kT)^2}\times\exp\left\{-\frac{4}{3}\frac{E_a}{kT}+kT\left(\frac{1}{\epsilon}+\frac{1}{\epsilon_H}\right)\right\}. \quad (34)$$

Here we have neglected the difference between E_a'' and E_a [see Eq. (30)]. The quantity $u_0 = ea^2/\hbar$ has the dimension of mobility.

We can now find the Hall mobility

$$\mu_H=\frac{c}{H}\frac{\sigma_{xy}}{\sigma_{xx}}=\frac{c}{H}\frac{\sigma_{xy}}{en\mu_h}.$$

The drift mobility μ_h is determined in Eq. (6). For the case of hexagonal crystals, which we are studying, in this formula we set $z = 6$. From Eqs. (43) and (6) we have

$$\mu_H=u_0\left(\frac{\pi}{12}\right)^{1/2}\frac{I}{(E_akT)^{1/2}}\exp\left\{-\frac{1}{3}\frac{E_a}{kT}+\frac{kT}{\epsilon_H}\right\}. \quad (35)$$

At the same time we determine the Hall constant $R = \mu_h/c\sigma_{xx}$:

$$R=\frac{1}{enc}\frac{2}{3^{3/2}}\frac{kT}{I}\exp\left\{\frac{2}{3}\frac{E_a}{kT}-kT\left(\frac{1}{\epsilon}-\frac{1}{\epsilon_H}\right)\right\}. \quad (36)$$

For $\epsilon^{-1} = \epsilon_H^{-1} = 0$ the expressions (35) and (36) transform, of course, into the results of the standard theory of small polarons (see Ref. 11).

We now note that the quantities ϵ^{-1} and ϵ_H^{-1}, introduced above, can be expressed in terms of the mean-square displacements of the atoms. For this we introduce ρ_m—the displacement of an atom from its equilibrium position:

$$\rho_m=\sum_q\left(\frac{\hbar}{2NM\omega_q}\right)^{1/2}e_q\exp(-iqR_m)(b_q+b_{-q}^+).$$

The mean-square displacement in the high-temperature limit has the form

$$\langle\rho_{m\alpha}\rho_{m'\beta}\rangle=\sum_q\frac{\hbar}{2NM\omega_q}e_{q\alpha}e_{q\beta}^*\exp[iq(R_{m'}-R_m)]\operatorname{cth}\frac{\hbar\omega_q}{2kT}\approx\frac{kT}{N}\sum_q\frac{1}{M\omega_q^2}e_{q\alpha}e_{q\beta}^*\exp[iq(R_{m'}-R_m)].$$

Hence it follows that

$$\frac{kT}{\epsilon}=2\alpha^2\langle[(\rho_0-\rho_g)g]^2\rangle,$$

$$\frac{kT}{\epsilon_H}=3\alpha^2\langle[(\rho_0-\rho_g)g][(\rho_0-\rho_{g'})g']\rangle-\frac{kT}{4\epsilon}.$$

In the short-range approximation, when $\langle\rho_{0\alpha}\rho_{g\beta}\rangle = 0$ holds, we thus obtain

$$\frac{kT}{\epsilon}=4\alpha^2\langle(\rho_0g)^2\rangle,$$

$$\frac{kT}{\epsilon_H}=3\alpha^2\langle(\rho_0g)(\rho_0g')\rangle-\frac{kT}{4\epsilon}=\frac{3}{2}\alpha^2\langle(\rho_0g)^2\rangle-\frac{kT}{4\epsilon}=\frac{kT}{8\epsilon}.$$

Hence we obtain the following relation between ϵ and ϵ_H in the short-range approximation for a hexagonal crystal:

$$\epsilon_H=8\epsilon. \quad (37)$$

Thus if for hexagonal crystals the Hall mobility activation energy is three times lower than the drift activation energy, the characteristic energy ϵ_H is eight times greater than ϵ. If, however, the first assertion is not based on model considerations concerning the phonon spectra, then the second ratio is valid only for short-range interactions.

The temperature dependence of the drift mobility μ_h (6) and Hall mobility μ_H (35) is illustrated in Fig. 3. In the region of not too high temperatures these curves become straight lines as functions of $1/T$. As the temperature increases the temperature dependence of both μ_h and μ_H becomes stronger. For the drift mobility this transition occurs at the temperature $kT_h = (\epsilon E_a)^{1/2}$. For the Hall mobility this transition occurs at a higher temperature:

$$kT_H=(8\epsilon E_a/3)^{1/2}=1{,}63kT_h.$$

In this high-temperature region the functions f defined in the caption to Fig. 3 become straight lines as a function of T.

It should be noted that in practice, when measurements are peformed over a temperature range which is not too wide, the dependence shown in Fig. 3 can look like an activational dependence for which the activation energy changes at $T\sim T_h$ and T_H for μ_h and μ_H, respectively. For this reason, in order to make a more reliable comparison between theory and experiment the temperature dependence of f must be constructed both as a function of both T and T^{-1}, and it must be verified that these functions do indeed become linear at high temperatures (on the T-scale) and at low temperatures (on the $1/T$-scale). This procedure makes it possible to reconstruct both parameters E_a and ϵ of the theory. Such an analysis of the experimental data was performed in

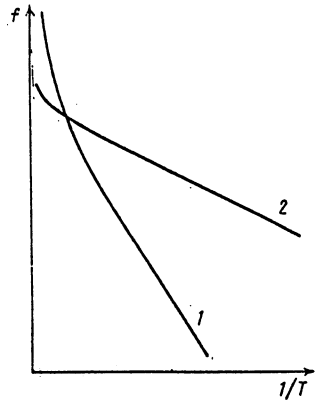

FIG. 3. Drift mobility (curve 1, $f=\ln(\mu_h T^{1/2})$) and Hall mobility (curve 2, $f=\ln(\mu_H T^{1/2})$) as functions of $1/T$.

Ref. 3 for the temperature dependence of the electric conductivity of a large number of materials.

Measuring the Hall and drift mobilities simultaneously and comparing the experimental results with the functions (6) and (35) makes it possible to judge, with a high degree of reliability, whether or not ultrasmall polarons are present in the material under study. We also note that the Hall coefficient in this model (35) differs radically from the quantity 1/enc, which is obtained (to within a numerical factor) in the theory of current transport on the basis of the classical Boltzmann equation. In addition, the quantity Renc not only differs radically from unity, but it also depends strongly on the temperature:

$$\ln \frac{Renc}{T} \propto \frac{2}{3}\frac{E_a}{kT} - \frac{7}{8}\frac{kT}{\epsilon} + A, \qquad (38)$$

where A does not depend on the temperature. The relation (38) was written taking into account Eq. (37), i.e., it is valid only for the short-range model.

In conclusion we emphasize once again that the specific results obtained in the present paper are valid only for hexagonal structures. For square lattices the theory is much more complicated, but the qualitative results of the theory can hardly differ radically from those obtained above, as in the case of the standard theory of small case of the standard theory of small polarons. The only radical difference for the Hall effect in lattices of these two types is the existence of a p-n anomaly in the Hall effect for hexagonal structures. This anomaly consists of the fact that the sign of the Hall emf does not change at the transition from electronic to hole conductivity. In cubic crystals, where a four-site model (and not a three-site model, as for hexagonal structures) must be studied in order to calculate the Hall effect, the p-n anomaly does not occur (see Refs. 11 and 12, as well as Refs. 13 and 14).

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