Optical and electrical properties of supersmall polarons

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Frequency dependences of the indices of light absorption and refraction for supersmall polarons are obtained. The model considered differs from the small-polaron one in that the effect of thermal displacements on the resonance integral is taken into account. Such an effect is important only when the localization radius is smaller than the rms atomic displacements. Therefore the corresponding electron-phonon formations are called supersmall polarons. The optical properties of supersmall polarons are described by a two-oscillator model, i.e., the frequency dependence of the light absorption has two peaks. The current-voltage characteristic has an exponential form with a non-traditional temperature dependence of the exponent.

1. INTRODUCTION AND PROBLEM FORMULATION

For small radius polarons we use a Fröhlich-type Hamiltonian describing the electron-phonon interaction[1,2]

$$H=H_{ph}+\sum_{mm'} J_{mm'}a_{m'}^{+}a_m+\sum_{\mathbf{q}m}\hbar\omega_{\mathbf{q}}a_m^{+}a_m[u_m(\mathbf{q})b_{\mathbf{q}}+u_m^{*}(\mathbf{q})b_{\mathbf{q}}^{+}]. \quad (1)$$

Here H_{ph} is the Hamiltonian of the phonon field

$$H_{ph}=\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}(b_{\mathbf{q}}^{+}b_{\mathbf{q}}+{}^1/_2), \quad (2)$$

$\omega_{\mathbf{q}}$ is the frequency of a phonon with momentum $\mathbf{q}$ belonging to a jth phonon branch (below we omit the index j, implying that $\mathbf{q}$ denotes the set $\{\mathbf{q}j\}$); $J_{mm'}$ is the resonance integral between the lattice sites m and m', a_m and $b_{\mathbf{q}}$ are the electron and phonon operators, respectively, and

$$u_m(\mathbf{q})=\gamma_{\mathbf{q}}\exp(-i\mathbf{q}\mathbf{R}_m)/(2N)^{1/2}, \quad (3)$$

where $\gamma_{\mathbf{q}}$ is the constant of the electron-phonon coupling, $\mathbf{R}_m$ is the radius-vector of the site m, and N is the total number of the atoms in the system.

The small-polaron model in the high temperature region, where the current transport is by hopping, leads to an activational dependence of mobility: $\ln\mu_h \propto -E_a/kT$.

However, it has been noted in Ref. 3 that, generally speaking, the resonance integral depends on phonon variables. In particular, if we assume that $J_{mm'}$ exponentially depends on the difference between instantaneous (nonequilibrium) distances between the sites

$$J_{mm'}=J_0\exp\{-\alpha|\mathbf{R}_m-\mathbf{R}_{m'}|\}, \quad (4)$$

then, assuming that $\mathscr{R}_m=\mathbf{R}_m+\boldsymbol{\rho}_m$, where $\boldsymbol{\rho}_m$ is the thermal atomic displacement ($\boldsymbol{\rho}_m \ll \mathbf{R}_m-\mathbf{R}_{m'}$) and going on to second quantization with respect to the phonon variables ρ_m, we have

$$J_{mm'}=I_{mm'}\exp\Big\{-\sum_{\mathbf{q}}[v_{mm'}(\mathbf{q})b_{\mathbf{q}}+v_{mm'}^{*}(\mathbf{q})b_{\mathbf{q}}^{+}]\Big\}. \quad (5)$$

Here

$$I_{mm'}=J_0\exp(-\alpha|\mathbf{R}_m-\mathbf{R}_{m'}|),$$
$$v_{mm'}(\mathbf{q})=(2N)^{-1/2}\delta_{mm'}(\mathbf{q})[\exp(-i\mathbf{q}\mathbf{R}_m)-\exp(-i\mathbf{q}\mathbf{R}_{m'})], \quad (6)$$

$$\delta_{mm'}(\mathbf{q})=\alpha\left(\frac{\hbar}{M\omega_{\mathbf{q}}}\right)^{1/2}\mathbf{e}_{\mathbf{q}}(\mathbf{R}_m-\mathbf{R}_{m'})/|\mathbf{R}_m-\mathbf{R}_{m'}|, \quad (7)$$

where $\mathbf{e}_{\mathbf{q}}$ is the eigenvector of the phonon branch, and M is the atomic mass.

The small-polaron theory, taking into account the effect of phonon displacements on the resonance integral, is developed in Ref. 4. It is shown there that, after the polaron canonical transformation in the one-electron approximation, such a modification of the small-polaron model leads to a Hamiltonian of the form

$$\tilde{H}=H_{ph}+\sum_{mm'}I_{mm'}a_{m'}^{+}a_m\Psi_{mm'},$$
$$\Psi_{mm'}=\exp\Big\{\sum_{\mathbf{q}}[\Gamma_{m'm}(\mathbf{q})b_{\mathbf{q}}+\Gamma_{mm'}^{*}(\mathbf{q})b_{\mathbf{q}}^{+}]\Big\}, \quad (8)$$
$$\Gamma_{m'm}(\mathbf{q})=u_m(\mathbf{q})-u_{m'}(\mathbf{q})-v_{m'm}(\mathbf{q}).$$

For $v=0$, of course, the Hamiltonian (8) reduces to the standard Hamiltonian of the small-polaron theory.

The main difference between the considered model and the small-polaron one lies in a more complex temperature dependence of the hopping mobility, which has the form $\ln\mu_h \propto AT-E_a/kT$ (see Ref. 4). Note that such a temperature dependence has been apparently obtained for the first time in Ref. 5. Having analyzed there numerous experimental data, the authors have shown that a temperature dependence of this type is typical for a large number of materials (see also Ref. 6). It should be stressed that a nontrivial contribution AT to $\ln\mu_h$ is important only if the parameter $\alpha^2\overline{\rho^2}\gtrsim 1$, where $\overline{\rho^2}$ is the rms value of the thermal atomic displacement, and α^{-1} is the radius of the localized state [see (4)]. In other words, the model becomes nontrivial only for very small localization radii α^{-1}. Therefore the electron-phonon formation in question is called below a supersmall polaron.

The important feature of the small-polaron model is the presence of the Gaussian peak of the light absorption at the frequency $\hbar\omega=4E_a$ (Refs. 7,8). This is one of the basic, if not the most important, features in the analysis of experimental data in specific materials, when one is to confirm or reject the concept of current transport by small polarons. Therefore, in this paper, we have performed calculations of optical properties of supersmall polarons. Their basic result

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is that the optical properties of supersmall polarons are described by the two-oscillator model, whereas the standard small polarons are described by the single-oscillator model.

Using the formal analogy between the expressions for light absorption and current-voltage characteristics in the hopping regime, we have calculated the latter for supersmall polarons. In the range of moderate fields (up to the dissociation of the polaron state) the field dependence of the current has the form $\ln j \propto E/E_0$, as in the case of small polarons. However E_0 is not simply proportional to T, as in the standard theory, but has a more complex temperature dependence.

2. GENERAL EXPRESSIONS FOR THE TEMPERATURE DEPENDENCE OF THE ELECTRIC CONDUCTIVITY

The optical properties of a substance are fully described by the frequency dependence of the complex dielectric constant $\varepsilon(\omega)$, which can be written in the form $\varepsilon(\omega) = \tilde{\varepsilon}(\omega) + 4\pi i\sigma(\omega)/\omega$, where $\sigma(\omega)$ is the frequency dependent electric conductivity, and $\tilde{\varepsilon}(\omega)$ describes the contributions of other mechanisms (e.g., interaction with phonons). In the frequency range considered we assume that $\tilde{\varepsilon}$ is independent of ω and is real. Assuming also that the absorption is weak ($\varepsilon''/\varepsilon' \ll 1$), we can find a simple relation between the indices of light absorption $\alpha(\omega)$ and refraction $n(\omega)$, and the imaginary σ'' and real σ' parts of the electroconductivity: $\alpha(\omega) = 2\pi\sigma'(\omega)/n_0\omega$, $n(\omega) = n_0 - 2\pi\sigma''(\omega)/n_0\omega$, where $n_0 = \sqrt{\tilde{\varepsilon}}$. Thus, the frequency dependence of $\sigma(\omega)$ fully determines the optical properties of a substance.[1]

The hopping contribution to $\sigma(\omega)$ can be calculated straightforwardly, using the Kubo formula to the lowest (second) order in $I_{mm'}$ [see Eq. (8)]. Such calculations, in the framework of the standard small-polaron theory, have been performed in Ref. 10 (see also Ref. 2). Since the transformed Hamiltonian $\tilde{H}$ for supersmall polarons given by Eq. (8) very much resembles the simple polaron one, the corresponding calculations are identical. The technique of calculating matrix elements of many-phonon operators is given in Ref. 4. The final result is

$$\sigma(\omega)=\frac{e^2}{2kTV}f(1-f)\sum_{mm'}(\mathbf{R}_m-\mathbf{R}_{m'})_x^2 W_{mm'}(\omega). \tag{9}$$

Here V is the system volume, the index x denotes the projection on the direction of the electric field, $f = (\exp\mu + 1)^{-1}$ is the probability of site occupation, and μ is the chemical potential. Note that, contrary to Ref. 4, the occupation probability f is not considered small.

The probability $W_{mm'}$ of the transition between the sites m and m' is given by the expression

$$W_{mm'}=\frac{2}{\hbar^2}I_{mm'}^2\exp(-2S_{mm'})\int_0^\infty dt e^{-i\omega t}$$
$$\times\int_{-1/2}^{1/2}d\lambda\left\{\exp\left[\sum_{\mathbf{q}}\frac{1-\cos\mathbf{q}(\mathbf{R}_m-\mathbf{R}_{m'})}{2N\,\mathrm{sh}(\hbar\omega_{\mathbf{q}}/2kT)}\left[(\gamma_{\mathbf{q}}+\delta_{mm'}(\mathbf{q}))^2\right.\right.\right.$$
$$\times\exp\left(i\omega_{\mathbf{q}}\left(t+\frac{i\hbar\lambda}{kT}\right)\right)+(\gamma_{\mathbf{q}}-\delta_{mm'}(\mathbf{q}))^2$$
$$\left.\left.\left.\exp\left(-i\omega_{\mathbf{q}}\left(t+\frac{i\hbar\lambda}{kT}\right)\right)\right]\right]-1\right\}. \tag{10}$$

The dimensionless quantities $\gamma_{\mathbf{q}}$ and $\delta(\mathbf{q})$ are defined by Eqs. (3) and (7),

$$S_{mm'}=\frac{1}{2N}\sum_{\mathbf{q}}[1-\cos\mathbf{q}(\mathbf{R}_m-\mathbf{R}_{m'})][\gamma_{\mathbf{q}}^2-\delta_{mm'}^2(\mathbf{q})]\mathrm{cth}\frac{\hbar\omega_{\mathbf{q}}}{2kT}. \tag{11}$$

In what follows we restrict ourselves to the approximation of hops between the nearest neighbors, i.e., $\mathbf{R}_m - \mathbf{R}_{m'} = \mathbf{g}$, where $\mathbf{g}$ is the radius-vector of the nearest neighbor. Then (9) acquires the form

$$\sigma(\omega)=\frac{e^2a^2}{2kT}n(1-f)[W_{\mathbf{g}}(\omega)+W_{-\mathbf{g}}(\omega)], \tag{12}$$

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

$$W_{\mathbf{g}}(\omega)=\frac{2}{\hbar^2}I^2e^{-2S}\int_0^\infty dt e^{-i\omega t}\int_{-1/2}^{1/2}d\lambda$$
$$\times\left\{\exp\left[\sum_{\mathbf{q}}\Lambda_{\mathbf{q}}\left[(\gamma_{\mathbf{q}}+\delta_{\mathbf{g}}(\mathbf{q}))^2\exp\left(i\omega_{\mathbf{q}}\left(t+\frac{i\hbar\lambda}{kT}\right)\right)\right.\right.\right.$$
$$\left.\left.\left.+(\gamma_{\mathbf{q}}-\delta_{\mathbf{g}}(\mathbf{q}))^2\exp\left(-i\omega_{\mathbf{q}}\left(t+\frac{i\hbar\lambda}{kT}\right)\right)\right]\right]-1\right\},$$
$$\Lambda_{\mathbf{q}}=(1-\cos\mathbf{qg})/2N\,\mathrm{sh}(\hbar\omega_{\mathbf{q}}/2kT). \tag{12a}$$

Here $I\equiv I_{\mathbf{g}0}$, $S\equiv S_{\mathbf{g}0}$, $\delta_{\mathbf{g}}\equiv\delta_{\mathbf{g}0}$. For a cubic lattice, S and I do not depend on $\mathbf{g}$, whereas $\delta_{\mathbf{g}} = -\delta_{-\mathbf{g}}$, see (7). The last relation, as seen from (12a), gives rise to the symmetry $W_{-\mathbf{g}}(\omega) = W_{\mathbf{g}}(-\omega)$.

Let us recall also that the subtraction of unity from the exponential in the braces in Eqs. (12a) and (10) corresponds to the subtraction procedure and ladder summation of the subtracted contributions. As a result, the expression in the braces vanishes as $t\to\infty$. Such a ladder summation eventually gives rise to a tunnel contribution to the conductivity, which is added to the hopping contribution and which dominates in the low temperature range.[1,2] In this temperature range the frequency dependence $\sigma(\omega)$ for supersmall polarons (and for small polarons as well) most probably has the Drude-Lorentz form $\sigma'(\omega) = \sigma(0)/(1+\omega^2\tau^2)$.

Now we can go on to specific calculations of the frequency dependence of the electric conductivity.

3. LIGHT ABSORPTION COEFFICIENT

In the expression for the real part of $W_{\mathbf{g}}'(\omega)$ one can integrate over t from $-\infty$ to ∞. After shifting t by $-i\hbar\lambda/kT$, the integration over t becomes trivial. As a result, Eq. (12a) yields

$$W_{\mathbf{g}}'(\omega)=\frac{I^2}{\hbar^2}e^{-2S}\frac{\mathrm{sh}(\hbar\omega/2kT)}{\hbar\omega/2kT}\int_{-\infty}^{\infty}dt e^{-i\omega t}$$
$$\times\left\{\exp\left[\sum_{\mathbf{q}}\Lambda_{\mathbf{q}}[(\gamma_{\mathbf{q}}+\delta_{\mathbf{g}}(\mathbf{q}))^2\exp(i\omega_{\mathbf{q}}t)\right.\right.$$
$$\left.\left.+(\gamma_{\mathbf{q}}-\delta_{\mathbf{g}}(\mathbf{q}))^2\exp(-i\omega_{\mathbf{q}}t)]\right]-1\right\}. \tag{13}$$

As $\omega\to 0$, this expression reduces to the one for the probability of intersite hopping obtained in Ref. 4. Integration over t will be performed using the saddle point method. The first saddle point $t_0 = i\tau$ is on the imaginary axis of the complex time, and τ obeys the equation

$$\omega = \sum_{\mathbf{q}} \Lambda_{\mathbf{q}}\omega_{\mathbf{q}}\{[\gamma_{\mathbf{q}}+\delta_{\mathbf{g}}(\mathbf{q})]^2\exp(-\omega_{\mathbf{q}}\tau) - [\gamma_{\mathbf{q}}-\delta_{\mathbf{g}}(\mathbf{q})]^2\exp(\omega_{\mathbf{q}}\tau)\}. \qquad (14)$$

As for the next saddle points having nonvanishing real parts their contribution is small due to phonon dispersion, and they are not taken into account in the theory of small polarons.[1-3]

Expanding the exponent in (13) in a power series in t in the vicinity of the saddle point $t = i\tau$ accurate to quadratic terms and integrating over t, we find

$$W_{\mathbf{g}}'(\omega) = I^2 e^{-2S}(2\pi)^{1/2}\frac{\operatorname{sh}(\hbar\omega/2kT)}{\hbar^3\omega/2kT} \times \exp\left\{\omega\tau + \sum_{\mathbf{q}}\Lambda_{\mathbf{q}}[(\gamma_{\mathbf{q}}+\delta_{\mathbf{g}})^2\exp(-\omega_{\mathbf{q}}\tau) + (\gamma_{\mathbf{q}}-\delta_{\mathbf{g}})^2\exp(\omega_{\mathbf{q}}\tau)]\right\} \Big/ \left\{\sum_{\mathbf{q}}\Lambda_{\mathbf{q}}\omega_{\mathbf{q}}^2[(\gamma_{\mathbf{q}}+\delta_{\mathbf{g}})^2 \times\exp(-\omega_{\mathbf{q}}\tau)+(\gamma_{\mathbf{q}}-\delta_{\mathbf{g}})^2\exp(\omega_{\mathbf{q}}\tau)]\right\}^{1/2}. \qquad (15)$$

To obtain a simple analytic dependence of $W_{\mathbf{g}}'$ on ω and T, consider only the case $\omega_{\mathbf{q}}\tau \ll 1$. In this limit we find an explicit expression for τ from Eq. (14):

$$\tau = \left\{2\sum_{\mathbf{q}}\Lambda_{\mathbf{q}}\omega_{\mathbf{q}}\gamma_{\mathbf{q}}\delta_{\mathbf{g}}(\mathbf{q}) - \frac{\omega}{2}\right\} \Big/ \sum_{\mathbf{q}}\Lambda_{\mathbf{q}}\omega_{\mathbf{q}}^2[\gamma_{\mathbf{q}}^2+\delta_{\mathbf{g}}^2(\mathbf{q})]. \qquad (16)$$

Expanding now the exponent in (15) in a power series in τ accurate to τ^2 and setting τ equal to zero in the factor preceding the exponential, we find

$$W_{\mathbf{g}}'(\omega) = \pi^{1/2}\frac{I^2}{\hbar^2}e^{-2S}\frac{\operatorname{sh}(\hbar\omega/2kT)}{\hbar\omega/2kT} \times \exp\left\{\sum_{\mathbf{q}}\Lambda_{\mathbf{q}}[\gamma_{\mathbf{q}}^2+\delta_{\mathbf{g}}^2(\mathbf{q})](2-\omega_{\mathbf{q}}^2\tau^2)\right\} \times\left\{\sum_{\mathbf{q}}\Lambda_{\mathbf{q}}\omega_{\mathbf{q}}^2[\gamma_{\mathbf{q}}^2+\delta_{\mathbf{g}}^2(\mathbf{q})]\right\}^{-1/2}. \qquad (17)$$

Consider, finally, the most interesting high-temperature limit $2kT > \hbar\omega_{\mathbf{q}}$. This limit is the most interesting one because only in the range of sufficiently high temperatures can the effect of phonon displacements on the resonance integral be noticeable. In this temperature range we get from (11)

$$W_{\mathbf{g}}'(\omega) = W(0)\frac{\operatorname{sh}(\hbar\omega/2kT)}{\hbar\omega/2kT}\exp\left(\frac{\hbar\omega}{2E_a'}\Delta_{\mathbf{g}} - \frac{\hbar^2\omega^2}{16E_a'kT}\right), \qquad (18)$$

where $W(0)$ is the intersite hopping probability governing the hopping static conductivity[4]

$$W(0) = \frac{I^2\pi^{1/2}}{\hbar(4E_a'kT)^{1/2}}\exp\left[-\frac{E_a}{kT}+\frac{kT}{\epsilon}\right]. \qquad (19)$$

The following quantities, having the dimension of energy, are introduced here:

$$E_a = \frac{1}{4N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}\gamma_{\mathbf{q}}^2(1-\cos\mathbf{qg}),$$
$$E_a' = \frac{1}{4N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}[\gamma_{\mathbf{q}}^2+\delta_{\mathbf{g}}^2(\mathbf{q})](1-\cos\mathbf{qg}), \qquad (20)$$
$$\epsilon^{-1} = \frac{4}{N}\sum_{\mathbf{q}}\frac{1}{\hbar\omega_{\mathbf{q}}}\delta_{\mathbf{g}}^2(\mathbf{q})(1-\cos\mathbf{qg}) - \frac{\Delta_{\mathbf{g}}^2}{E_a'}.$$

The dimensionless parameter $\Delta_{\mathbf{g}}$ is defined as

$$\Delta_{\mathbf{g}} = \frac{1}{N}\sum_{\mathbf{q}}\gamma_{\mathbf{q}}\delta_{\mathbf{g}}(\mathbf{q})(1-\cos\mathbf{qg}) = -\Delta_{-\mathbf{g}}. \qquad (21)$$

E_a is the activation energy for the intersite hopping in the standard small-polaron theory. The probability $W(0)$ in the form (19) has been found in Ref. 4, and it gives rise to the aforementioned temperature dependence of the hopping mobility of the type $\ln\mu_h \propto AT - E_a/kT$ $(A = k/\epsilon)$.

Substituting now the expression (18) for $W_{\mathbf{g}}'(\omega)$ into the formula (12) for $\sigma'(\omega)$ we get the final expression for the real part of the conductivity, giving the frequency and temperature dependences of the light absorption

$$\sigma'(\omega) = \sigma_h\frac{\operatorname{sh}(\hbar\omega/2kT)}{\hbar\omega/2kT}\operatorname{ch}\frac{\hbar\omega\Delta}{2E_a'}\exp\left(-\frac{\hbar^2\omega^2}{16E_a'kT}\right), \qquad (22)$$

where

$$\sigma_h = \frac{e^2a^2}{kT}n(1-f)W(0) \qquad (23)$$

is the static hopping conductivity. The subscript g of Δ is omitted in (22), since this expression does not change when $-\Delta$ is substituted for Δ.

The obtained frequency dependence (22) of σ' reduces to the well-known expression for the real part of the electric conductivity of small polarons for $\delta_{\mathbf{g}} = 0$, i.e., $\Delta = 0$, $E_a' = E_a$, which constitutes Gaussian peak of width $4\sqrt{E_akT}$ and with a maximum at $\hbar\omega = 4E_a$. For supersmall polarons, however, as follows from (22), this dependence is formed by superposition of two Gaussian peaks of equal width $4\sqrt{E_a'kT}$ [it is larger than in the case of small polarons, since, according to (20), $E_a' \geqslant E_a$]. The maximums of these peaks correspond to the frequencies

$$\hbar\omega_{1,2} = 4(E_a' \pm |\Delta|kT). \qquad (24)$$

Therefore the pair of peaks mentioned above is resolved in experiment only if $\Delta^2 > E_a'/4kT$. It is assumed that $E_a' > |\Delta|kT$, so that the frequency $\omega_2 > 0$ [see (24)].

Thus, in the theory of supersmall polarons, as in the case of small polarons, the frequency dependence of the light absorption conveys important information about the character of the current transfer, especially when compared to the temperature dependence of the static electric conductivity.

Note, in conclusion, that the light absorption maximum is preserved also in the limit of weak coupling with phonons, when $\gamma_{\mathbf{q}} \to 0$, i.e., $\Delta = 0$, $E_a = 0$,

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

In this limit two peaks merge into one Gaussian at frequency $\hbar\omega = 4E_a'$. The temperature dependence of the static electric conductivity in this limit has the form $\ln\mu_h \propto AT$.

4. REFRACTIVE INDEX OF LIGHT

As noted above, the refractive index of light is determined by the frequency dependence of the imaginary part of the electric conductivity, σ'', [i.e., by $W''_g(\omega)$]. The calculations of $\sigma''(\omega)$ may be performed with the help of formulas (12) and (12a). However, a simpler way is to use the dispersion relations. According to (12a), the function $W_g(\omega)$ [and, consequently, $\sigma(\omega)$] is analytic in the lower half of the complex plane ω. Hence $\sigma'(\omega)$ and $\sigma''(\omega)$ are related by the expression

$$\sigma''(\omega)=\frac{2\omega}{\pi}\int_0^\infty\frac{\sigma'(z)\,dz}{z^2-\omega^2}, \qquad (25)$$

where the integral is taken in the sense of the principal value. Substituting expression (22) for $\sigma'(\omega)$ into (25), we get

$$\sigma''(\omega)=\sigma_h\frac{2\hbar\omega kT}{\pi}\int_0^\infty\frac{dz}{z}\,\mathrm{sh}\left(\frac{z}{2kT}\right)\mathrm{ch}\left(\frac{\Delta z}{2E_a'}\right)\times\frac{\exp(-z^2/16E_a'kT)}{z^2-\hbar^2\omega^2}. \qquad (26)$$

As noted above, the integrand is a superposition of two Gaussian curves with the maxima at $z=\hbar\omega_{1,2}$, where the frequencies $\omega_{1,2}$ are given by Eq. (24). In the frequency range lying at a distance exceeding the peak width $4\sqrt{E'_a kT}$ from the resonant frequencies $\omega=\omega_{1,2}$ one can integrate over z in (26) as follows: 1) substitute $\exp(z/2kT)/2$ for $\sinh(z/2kT)$; 2) integrate over z from $-\infty$ to ∞; 3) discard the factor $\{z(z^2-\hbar^2\omega^2)\}^{-1}$ from the integrand at the points $z=\hbar\omega_{1,2}$. After such operations the integration over z is carried out without difficulty. As a result, we have

$$\sigma''(\omega)=\sigma_h\frac{(kT)^{3/2}E_a'^{1/2}\omega}{2\hbar^2\pi^{1/2}}\sum_{i=1}^{2}\frac{\exp(\hbar^2\omega_i^2/16E_a'kT)}{\omega_i(\omega_i^2-\omega^2)}. \qquad (27)$$

Note that the transition to the small-polaron model in (27) by the substitutions $E'_a\to E_a$ and $\omega_1=\omega_2=4E_a/\hbar$ yields a result consistent with the well-known one.[2]

Thus, the optical properties of supersmall polarons are described by the two-oscillator model with resonant frequencies $\omega=\omega_{1,2}$ and the lifetime for both oscillators is equal to $\hbar/4\sqrt{E'_a kT}$. However, the optical properties of small polarons are described by the one-oscillator model. This fact shows, in principle, how to identify small and supersmall polarons in experiment. Near the resonance points $\omega=\omega_{1,2}$ the function $\sigma''(\omega)$, as usual, reverses sign. The divergencies of $\sigma''(\omega)$ at $\omega=\omega_{1,2}$ in Eq. (27) reflect the presence of two peaks of finite amplitude in the exact formula (26) and a drastic change of $\sigma''(\omega)$, with reversal of the sign in the vicinity of the resonances in the interval $\hbar\Delta\omega\sim4\sqrt{E'_a kT}$. In these vicinities the simple analytical expression (27) is not valid, and one has to use the exact expression (26). Note that the double reversal of the sign of the function $\sigma''(\omega)$ in the vicinity of the resonances (as ω grows the signs alternate as $+,-,+,-$) occurs only under the condition of good resolution of the two absorption peaks, when $\Delta^2>E'_a/kT$ (see Sec. 3). If this inequality does not hold, the pair of oscillators is strongly coupled, and the sign of $\sigma''(\omega)$ changes only once, as in the small-polaron theory.[2]

5. CURRENT-VOLTAGE CHARACTERISTIC FOR SUPERSMALL POLARONS

The calculations of the frequency dependence of the electroconductivity performed above allows, practically without any extra calculations, to write the result for the field dependence of the current for supersmall polarons in the hopping regime. To do that, it is necessary to use the formal analogy between the expressions for the current in the hopping regime in an arbitrary field and for the real part of the electric conductivity as a function of frequency.

The current j in the hopping regime can be written as

$$\mathbf{j}=en\sum_m\mathbf{R}_m W_{m0}(\mathbf{E}), \qquad (28)$$

where $W_{m0}(\mathbf{E})$ is the probability of hopping from the site 0 to the site m in an external electric field $\mathbf{E}$. Inclusion of the electron-field interaction

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

in the zeroth Hamiltonian does not change this contribution under the polaron canonical transformation, since the density operator $a_m^+a_m$ is invariant under this transformation.

If the interaction with the field is included into the Hamiltonian, then, in the diagram technique,[1,2,4] each interaction point i should be associated with an extra factor

$$\exp[ie\mathbf{E}(\mathbf{R}_{m_i}-\mathbf{R}_{m_i'})t_i/\hbar],$$

where m_i (m_i') is the index of the electron line terminating at or leaving the point i (cf. the algorithm for taking into account the diagonal disorder in Ref. 4, when the role of random energy ε_m at a site is played by the external-field potential $-e\mathbf{E}\mathbf{R}_m$). Such an algorithm makes the probability $W_{g0}(\mathbf{E})$ of hopping between the nearest neighbors in the electric field formally equal to the real part of $W'_{g0}(\omega)$ given by Eq. (13) with the substitution $\hbar\omega\to e\mathbf{E}g$. Comparing expression (28) for the current with expression (12) for $\sigma(\omega)$, we get the formal equality

$$\mathbf{j}(\mathbf{E})=\sigma'(\omega)\,|_{\hbar\omega=eEa}\mathbf{E},$$

where a is the lattice constant. Substituting here $\sigma'(\omega)$ in the form (22) yields the following current-voltage characteristic for supersmall polarons:

$$j=\frac{2kT}{ea}\sigma_h\,\mathrm{sh}\frac{eEa}{2kT}\,\mathrm{ch}\left(\frac{eEa}{2E_a'}\Delta\right)\exp\left[-\frac{(eEa)^2}{16E_a'kT}\right]. \qquad (29)$$

For $\Delta=0$ and $E_a=E'_a$ this expression reduces to the well-known current-voltage characteristic for small polarons[11] (see also Refs. 1 and 2). As in the small-polaron theory,[12] the expression (29) is apparently valid only in the region where the current increases with the field, i.e., for $eEa<\hbar\omega_{1,2}$. As the analysis of the two-site model in the electric field shows,[2] for small polarons and for fields $eEa\geqslant4E_a$ the potential barrier for intersite hopping vanishes, resulting most likely in dissociation of the polaron state (the electron is detached in the field from the polaron cloud).

In the range of moderate fields, when $eEa<4\sqrt{E'_a kT}$, but $eEa>2kT$, $2E'_a/\Delta$, the current-voltage characteristic (29) acquires a particularly simple exponential form

$$\ln j=\ln j_0+E/E_0, \qquad (30)$$

where

$$j_0=\frac{kT}{2ea}\sigma_h,\quad E_0=\frac{2kTE_a'}{ea(\Delta kT+E_a')}. \qquad (31)$$

Thus, in the supersmall-polaron model in the range of sufficiently strong electric fields the current-voltage characteristic increases exponentially, as in the case of small polarons. However in the range of weaker fields the current-voltage characteristics for supersmall polarons are more diverse. When considering possible forms of the $j(E)$ curve in weaker fields one has to discern two cases.

1) $\Delta kT>E_a'$. In this case, as seen from (24), $\omega_2<0$, i.e., the absorption frequency dependence (22) has only one peak with the maximum at $\omega=\omega_1$. For these parameters there is a field range $kT>eEa/2>E_a'/\Delta$, in which the current-voltage characteristic also has the exponential form (30), but with other constants:

$$j_0={}^1/_2\sigma_h E,\quad E_0=2E_a'/ea\Delta, \qquad (32)$$

so that the characteristic field E_0 does not depend on temperature at all. As the field increases, for $eEa\gtrsim 2kT$, a transition to characteristics with the parameters j_0 and E_0 given by Eq. (31) occurs, with E_0 decreasing and becoming temperature-dependent.

2) $\Delta kT<E_a'$. In this case, as described above, the optical properties of supersmall polarons are given by the two-oscillator model. Under these conditions there is a range of fields $kT<eEa/2<E_a'/\Delta$, in which the current-voltage characteristic is again given by Eq. (30), but j_0 and E_0 have the following form

$$j_0=\frac{kT}{ea}\sigma_h,\quad E_0=2kT/ea. \qquad (33)$$

For these parameters, in this range of fields, the characteristic field E_0 is proportional to the temperature, as it is in the standard theories of hopping transport, small polarons included. Note here that in the case of weak coupling with phonons, when $\Delta\to 0$, the current-voltage characteristic in the whole range of fields (in the nonlinear region) corresponds to a simple exponential growth with E, with j_0 and E_0 given by Eqs. (33).

Such a correlation between optical and electric properties of supersmall polarons may, in principle, become an effective test for the verification of the presence of supersmall polarons in a system. However the current-voltage characteristics in the polaron models in crystalline substances become nonlinear in sufficiently strong fields, when $E\sim 2kT/ea\sim 10^3$–$10^4 T$ (here T is the absolute temperature in K, and E is in V/cm). In such strong fields break-downs and electrodissociation of the polaron state may occur in real materials. Also the Frenkel-Pool effect and other parasitic effects may become important, so that the observation of the current-voltage characteristics in the form (30) becomes impossible. In this respect, natural and artificial superstructures having a large lattice constant a may be more promising for experiments in strong electric fields.

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