

Bipolaron ac conductivity in amorphous semiconductors and dielectrics

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We have developed a theory of the alternating-current (ac) relaxation-type conductivity due to small bipolaron (SB) hopping in amorphous semiconductors and insulators that possess deep centers of the dangling-bond type (D centers) with a negative two-electron correlation energy U_{eff} . Unlike small polarons, SB's were treated as essentially three-level systems in the framework of a two-site approximation. To calculate, both numerically and analytically, the real part $\sigma_1 \propto \omega^s T^n$ of the ac hopping conductivity for different temperatures T in a wide range of audio and low radio frequencies ω , the dynamic polarizability, and the SB hopping rates for dangling bond pairs have been determined. When the electron tunneling integral corresponding to the smallest intersite separations is greater than the doubled polaron shift, both the polarizability and the hopping rate strongly depend upon the shape and parameters of the ground-state adiabatic potential of a small-size pair of strongly interacting D centers. This intimate pair can be viewed as a stretched or weakened bond. A classification of possible regimes of relaxation-type SB hopping (adiabatic and nonadiabatic, as well as tunnel and activation) has been proposed. Each of these corresponds to a specific temperature dependence of the exponents s and n . A comparison to experimental data on ac losses in chalcogenide glasses and α -SiO₂ has been made. It demonstrates that, in these materials, a tunneling adiabatic (TA) regime of SB hopping with $s \approx 1$ and $n \ll 1$ has been observed at low temperatures provided that there are (i) strong Coulombic correlations in the intersite occupations and (ii) strong scattering of one-electron energies. As the temperature is increased, the TA regime seems to be replaced by the activation adiabatic regime with $s < 1$ being a decreasing function and $n > 1$ being an increasing function of T . It was found that in the negative- U_{eff} amorphous systems the stretched bonds of size of 3.5–4.5 Å can be responsible for ac losses within the wide frequency range from 10^2 to 10^8 Hz.

I. INTRODUCTION

It is well established that the electronic properties of amorphous semiconductors such as chalcogenide glasses¹ and amorphous dielectrics such as α -SiO₂ (Ref. 2), α -Si₃N₄ (Ref. 3), and WO_{3-x} glasses⁴ are governed by specific structural point defects. These defects, so called D or U centers,¹ have three charge states and are characterized by a negative two-electron correlation energy U_{eff} . This means that the ground state of the system is diamagnetic and can be described as a set of positively and negatively charged D centers. In the absence of dopants, half of these centers (D_+) do not possess nonbonding electrons, whereas the other half corresponds to the two-electron spinless states D_- which can be described as localized small bipolarons (SB's).¹ The ground (diamagnetic) state is separated by the energy gap $|U_{\text{eff}}|$ from the excited (paramagnetic) state corresponding to the neutral one-electron states D_0 which can be considered as localized small polarons (SP's). (The value of $|U_{\text{eff}}|$ can be of the order of 1 eV in chalcogenide glasses.¹)

Effects caused by the intimate pairs of strongly interacting D centers may appear, provided that their con-

centrations are high.⁵ These may be viewed as quite shallow stretched or weakened bonds.⁶ They have one-electron (more accurately, one-polaron) levels belonging to the band tails, and provide the basis for some alternative explanation of electronic properties of amorphous solids.⁷ (The "holelike" bonding states with one electron are close to the valence-band edge, while the antibonding electronlike ones are adjacent to the conduction-band edge. A typical depth Δ_t of the tails is of the order of 0.2 eV [Ref. 1].)

One might connect the high-frequency dynamic conductivity $\sigma(\omega)$ with the D_-D_+ , D_-D_0 , and D_+D_0 pairs possessing a nonzero dipole moment which is able to change when a periodic electric field is applied.⁸ The dipole moment alternation of D_-D_0 and D_+D_0 pairs involves phonon-stimulated jumps of SP's, so that the D_-D_0 pair transforms to the D_0D_- pair and/or the D_0D_+ pair transforms to the D_+D_0 pair, and vice versa. However, due to the existence of the gap $|U_{\text{eff}}|$, both the SP concentration and, therefore, the one-polaron hopping conductivity due to D centers are proportional to $\exp(-|U_{\text{eff}}|/2T)$, and both are frozen out when $T \leq |U_{\text{eff}}|/2$. (In this paper the temperature T is mea-

sured in the energy units $k_B=1$.) In addition, the (bi)polaron ac conductivity due to isolated D centers *per se* is negligibly small because the unreduced potential barriers involved in hopping are of the order of 0.3–1.2 eV. The discussion of properties of isolated D centers with which we began should be considered as a preliminary step toward describing the nature of the stretched bonds. In particular, it will allow us to explain why stretched bonds in negative- U_{eff} materials are unstable with respect to an asymmetric distortion. In other words, such bonds are usually occupied by localized bipolarons and possess nonzero dipole moments. The concentration of occupied one-polaron band-tail states is $\exp[(E_g/2 - \Delta_i)/T] \cong \exp[0.7 \text{ eV}/T]$ times smaller than that of bipolaron. Therefore, the former also do not participate in low-temperature hopping.

Thus the low-temperature ac conductivity in the materials mentioned above might be connected with the bipolaron jumps within stretched bonds with nonzero dipole moments. So far, in the framework of the theory of ac conductivity, these bipolarons have been treated as particles with a charge $2e$ that overcome the Coulombic barrier between centers in a classical manner.^{9,10} Generally speaking, such an approach is contradictory to the concept of SB localization at intimate pairs of D centers (stretched bonds) of a characteristic dimension of several Å.

From our viewpoint, a more consistent approach should incorporate a description of SB jumps in the framework of a two-site model⁶ according to which a SB, unlike a SP, is essentially a three-level system (Fig. 1). For such a system at low temperatures, a configuration barrier separating the initial and the final states, both ioniclike, is overcome by tunneling, whereas at high temperatures activation plays a dominant role.¹¹ However, in both cases the intermediate (covalentlike) state, consequently virtual¹¹ or real, is involved. It should be noted

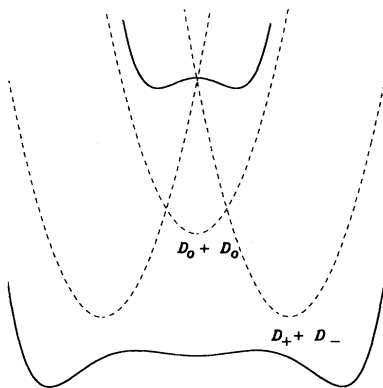


FIG. 1. Origin of multivalley potentials of a small bipolaron localized on an intimate pair of D centers (a stretched bond). The lower (upper) solid line describes the singlet ground (excited) state of the stretched bond. The dashed lines correspond to a pair of isolated centers in different charge states. Note that the ioniclike lateral minima derive mainly from the D_+-D_- and $D--D_+$ states of the isolated-centers' pair, while the covalentlike central minimum resembles the D_0-D_0 state.

that both the shape and size of a potential barrier which governs the characteristic time of the SB jumps, and the polarizability of a stretched bond, may depend exponentially upon its dimension r . It will be shown that it is precisely this fact which causes the main peculiarities of the frequency and temperature dependencies of the ac conductivity in disordered semiconductors and insulators, provided there are no other substantial sources of relaxation-time dispersion, with the exception of the hopping distance r .

The aim of the present paper is to analyze the high-frequency relaxation-type¹² ac hopping conductivity in disordered solids containing centers with a negative two-electron correlation energy. Section II deals with the two-site model of SB. In Sec. III the dynamic polarizability of a three-level stretched bond will be treated. In Sec. IV the general expression for the ac conductivity will be obtained. In Sec. V it will be applied to the investigation of a high-temperature case when the configuration barrier is overcome by activation. This is distinct from the low-temperature case considered in Sec. VI, when the relaxation time is governed by atomic tunneling. Finally, in Sec. VII the temperature and frequency dependencies of the bipolaron hopping conductivity will be discussed with respect to some experimental data, mainly for chalcogenide glassy materials.

II. TWO-SITE MODEL OF SB

We shall consider an isolated pair of D centers separated by a distance r . Suppose that there are two electrons localized at this pair, each of them coupled to a local vibrational mode u_i , where $i=1$ or 2 . Then, according to Anderson¹³ and Holstein,¹⁴ it is convenient to write a complete Hamiltonian of the pair of D centers in the form

$$H = \bar{H} + H + H_{\text{ph}} + H_{e\text{-ph}} \quad (1)$$

Here, the operator

$$\bar{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} \mu \omega_0^2 Q^2, \quad (2)$$

where ω_0 is the local-phonon frequency and μ is the reduced mass of two centers. Note that the operator \bar{H} , which does not contain any electron operators, describes the harmonic oscillator corresponding to a normal symmetric coordinate $Q = u_1 + u_2$.

The operator H describes (i) the oscillator corresponding to a normal asymmetric mode $Q = u_1 - u_2$; (ii) the Coulombic interaction of the localized electrons between themselves and with the mode Q ; and (iii) the tunnel (exchange) interaction between the localized states $|1\rangle$ and $|2\rangle$. In the representation of the operators of the creation ($a_{\sigma i}^\dagger$) and annihilation ($a_{\sigma i}$) of an electron with spin $\sigma = \pm 1/2$ at site $i = 1$ or 2 ,

$$\begin{aligned}
H = & \sum_{i,\sigma} \epsilon_i n_{i\sigma} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} \mu \omega_0^2 Q^2 - \frac{1}{2} \lambda Q \sum_{\sigma} (n_{1\sigma} - n_{2\sigma}) \\
& + J(r) \sum_{i>j,\sigma} (a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma}) \\
& + U \sum_i n_{i\uparrow} n_{i\downarrow} + C(r) \sum_{i>j,\sigma,\sigma'} n_{i\sigma} n_{j\sigma'}, \quad (3)
\end{aligned}$$

where $n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$ is the occupation number of a one-electron state $|i\rangle$, $J(r)$ is the tunneling (hopping) integral, $C(r)$ is the intercenter Coulomb integral, λ is the electron-phonon coupling constant (the deformation potential), U is the Hubbard repulsion energy of two electrons at the same site, and ϵ_i are single-electron energies at the sites $i=1$ and 2.

The last two terms in Eq. (1) describe, respectively, the subsystem of lattice phonons (thermostat) and their interaction with the pair of D centers. This interaction, on one hand, causes the localization of a bipolaron at one of the sites^{15,16} and, on the other hand, determines the intersite (intrabond) bipolaron jump which involves the absorption and the emission of lattice phonons.^{11,16}

The adiabatic potential of the ground (singlet) state which corresponds to the Hamiltonian $\bar{H} + H$ can be written in the form⁶

$$E_s(Q, \bar{Q}) = E_t(Q, \bar{Q}) - E(Q), \quad (4)$$

where

$$E_t(Q, \bar{Q}) = \epsilon_1 + \epsilon_2 + C + \frac{1}{2} \mu \omega_0^2 (Q^2 + \bar{Q}^2) \quad (5)$$

is an adiabatic potential of the excited (triplet) state. A singlet-triplet splitting energy $E(Q)$ satisfies the equation

$$E^3 + 2\bar{U}E^2 + (\bar{U}^2 - 4J^2 + \Delta^2 - \lambda^2 Q^2)E - 4J^2\bar{U} = 0, \quad (6)$$

where $\bar{U} = U - C$ and $\Delta = \epsilon_1 - \epsilon_2$. It is clear that both $E_t(Q, \bar{Q})$ and $E(Q)$ depend parametrically upon the distance r separating the two centers.

It can be shown that for symmetric pairs with $\Delta = \epsilon_1 - \epsilon_2 \ll \epsilon_1 \approx \epsilon_2$ there are three typical energies: (i) the Coulombic energy $\bar{U} = U - C$; (ii) the exchange energy

$$E_{\text{ex}} = (\bar{U}^2/4 + 4J^2)^{1/2} - \bar{U}/2, \quad (7)$$

which is equal to the energy of the singlet-triplet splitting $E_t - E_s = E(Q)$ at $Q=0$; and (iii) the polaron shift

$$W_p = \frac{\lambda^2}{4\mu\omega_0^2}. \quad (8)$$

Depending on the ratio between these values, the ground-state adiabatic potential can have one, two, or three minima (Fig. 2). It is convenient to analyze its behavior in terms of the dimensionless control parameters

$$\gamma = \frac{E_{\text{ex}}}{\bar{U}} + \frac{1}{2}, \quad \kappa = \frac{4W_p}{\bar{U}}. \quad (9)$$

The central minimum (at $Q=\bar{Q}=0$) of the adiabatic potential $E_s(Q, \bar{Q})$ in Figs. 1 and 2 corresponds to a co-

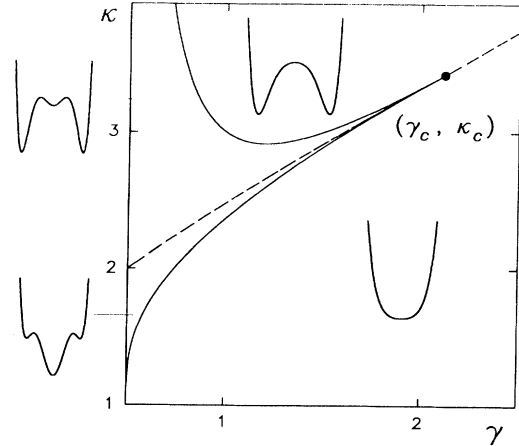


FIG. 2. Phase diagram of the adiabatic potential $E_s(Q, \bar{Q}=0)$ of the SB ground state. The phase curves are given by the following equations (Ref. 6):

$$\kappa = \gamma(2\gamma + 1)/(2\gamma - 1) \quad \text{for } \gamma > 1/2,$$

$$\kappa = \frac{3}{4} + \gamma/2 + (1/2 + \gamma)^{1/2},$$

and

$$\kappa = 1 + 3(\gamma^2 - 1/4)^{1/3}/2 \quad \text{for } 1/2 < \gamma < \gamma_c = 1 + \sqrt{5}/2.$$

valent state of the pair, whereas the lateral minima (at $Q \neq 0$ and $\bar{Q} = 0$) represent ionic (bipolaron) states. The region corresponding to the nonzero dipole moment states that contribute to the ac conductivity is located above the dashed phase line shown in the κ - γ diagram (Fig. 2). Moreover, to participate effectively in the ac conductivity at audio and low-radio frequencies, the localized SBs should overcome very small potential barriers not exceeding a tenth of an eV. It means that the corresponding states are to be close to the dashed line (Fig. 2) which separates the ioniclike stretched bonds, that are likely to be observed in the negative- U_{eff} materials,⁶ from the covalentlike ones.

The electron-tunneling (hopping) integral decreases exponentially with the distance r between the centers (see Refs. 1 and 13):

$$J(r) = J_0 e^{-r/a}, \quad (10)$$

where a is the localization radius of an electron. The Coulomb integral $C(r)$ is of the order of $e^2/\epsilon r$, where ϵ is the dielectric permittivity and e is the electron charge.¹ This means that for $r > a$ the Coulomb energy $\bar{U} = U - C(r) \approx e^2/\epsilon a - e^2/\epsilon r \approx e^2/\epsilon a = U$ does not depend exponentially on r . Therefore, as the distance r between the centers increases, the parameter γ decreases exponentially leaving the parameter κ practically constant [see Eq. (9)]. In other words, one can describe an alternation of r as a shift along a line parallel to the γ axis in the κ - γ diagram. Note that the points on the κ axis correspond to isolated centers ($r \rightarrow \infty$). For those which have $\kappa > 2$, the effective two-electron correlation energy $U_{\text{eff}} = \bar{U} - 2W_p < 0$ (see Ref. 1).

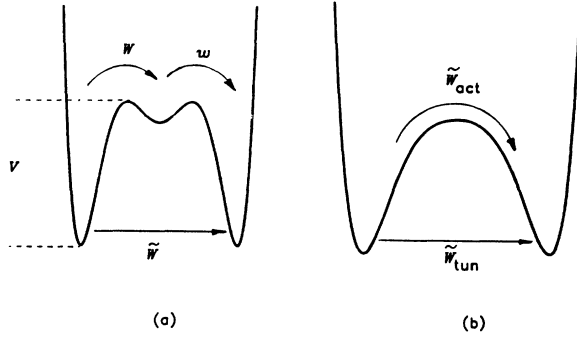


FIG. 3. Bipolaron jumps in the case of (a) intermediate ($\bar{U}/2 < W_p \leq \bar{U}$) and (b) large ($W_p \gg \bar{U}$) polaron shifts W_p . The \bar{W} probabilities describe the direct (elastic) transitions $1 \rightarrow 2$ while the W rates correspond to the two-step (inelastic) transitions $1 \rightarrow 3 \rightarrow 2$ involving the central minima 3.

Depending on the value of $\kappa > 2$, two cases should be considered: (i) $\kappa \gg \kappa_c = (7 + 3\sqrt{5})/4$, and (ii) $2 < \kappa \leq \kappa_c$ (see Fig. 2). The first case corresponds to systems that possess isolated D centers with a polaron shift W_p much greater than a Hubbard repulsion energy \bar{U} . This means that in this case intimate pairs of D centers (stretched bonds) are characterized by the adiabatic potentials $E_s(Q, \bar{Q})$ with quite shallow central minima. The second case describes systems with isolated centers having $\bar{U}/2 < W_p \leq \bar{U}$. It corresponds to intimate pairs characterized by adiabatic potentials with much more profound central minima than in case (i) (see Fig. 3). As a result, for case (ii), a bipolaron executing an activation-type jump from one lateral minimum to another via the central minimum, as a rule, has enough time for thermalization before escaping this intermediate position. Therefore, in this case, the jump can be treated as inelastic (noncoherent), contrary to case (i) when the jumps are presumably elastic (coherent).¹⁷

III. DYNAMIC POLARIZABILITY OF A PAIR

Let us consider a pair of D centers (a stretched bond) with two localized electrons which can exist in one of three states: ionic states ($i = 1$ and 2) with approximately equal energies, or a covalent metastable state ($i = 3$). The latter state is characterized by a quite profound central minimum if $2 < \kappa \leq \kappa_c$. With the occupation probability of the i th state h_i , and the rates (inverse times) of the $i \rightarrow k$ transition W_{ik} [Fig. 3(a)], the corresponding rate equations can be written as

$$\begin{aligned} \dot{h}_1 &= W_{31}h_3 + W_{21}h_2 - (W_{12} + W_{13})h_1, \\ \dot{h}_2 &= W_{32}h_3 + W_{12}h_1 - (W_{21} + W_{23})h_2, \\ \dot{h}_3 &= -(\dot{h}_1 + \dot{h}_2). \end{aligned} \quad (11)$$

It should be noted that W_{12} and W_{21} describe direct (coherent) transitions, activation or tunnel, between the ionic states 1 and 2 without the thermalization within the intermediate covalent state 3 (see Ref. 11). Moreover, ac-

ording to the detailed-balance principle,¹⁸ in equilibrium

$$W_{ik}^0 h_i^0 = W_{ki}^0 h_k^0 \quad (k \neq i). \quad (12)$$

An external electric field $\mathbf{E} = \mathbf{E}_\omega \exp(i\omega t)$ periodically alters the transition rates $W_{ik}(\mathbf{E})$ and, therefore, the occupation probabilities h_i :

$$\begin{aligned} W_{ik}(t) &= W_{ik}^0 + \left[\frac{\partial W_{ik}}{\partial \mathbf{E}} \right]_0 \cdot \mathbf{E}_\omega e^{i\omega t}, \\ h_i(t) &= h_i^0 + \tilde{h}_i e^{i\omega t}, \end{aligned} \quad (13)$$

with $\tilde{h}_i \propto E_\omega$ and $\tilde{h}_1 = -(\tilde{h}_2 + \tilde{h}_3)$. Substituting (13) in (11), collecting the terms proportional to E_ω , and taking into account (12), it is easy to find that

$$\begin{aligned} \tilde{h}_1 &= [(i\omega + A_{22})\mathbf{B}_{12} - A_{12}\mathbf{B}_{21}] \cdot \mathbf{E}_\omega / \delta, \\ \tilde{h}_2 &= [(i\omega + A_{11})\mathbf{B}_{21} - A_{21}\mathbf{B}_{12}] \cdot \mathbf{E}_\omega / \delta, \end{aligned} \quad (14)$$

where

$$\delta = (i\omega + A_{11})(i\omega + A_{22}) - A_{12}A_{21}, \quad (15)$$

$$A_{11} = W_{12}^0 + W_{13}^0 + W_{31}^0, \quad A_{22} = W_{21}^0 + W_{23}^0 + W_{32}^0, \quad (16)$$

$$A_{12} = W_{31}^0 - W_{21}^0, \quad A_{21} = W_{32}^0 - W_{12}^0, \quad (17)$$

$$\mathbf{B}_{12} = \frac{\partial}{\partial \mathbf{E}} [h_3^0 W_{31} + h_2^0 W_{21} - (W_{12} + W_{13})h_1^0]_{\mathbf{E}=0}, \quad (18)$$

$$\mathbf{B}_{21} = \frac{\partial}{\partial \mathbf{E}} [h_3^0 W_{32} + h_1^0 W_{12} - (W_{21} + W_{23})h_2^0]_{\mathbf{E}=0}. \quad (19)$$

Introducing dipole moments of the pair in states 1 and 2 measured with respect to the center of the pair¹⁹

$$\mathbf{p}_i = Z_i(r) e \mathbf{r}_i, \quad \mathbf{r}_2 = -\mathbf{r}_1 = \mathbf{r}/2, \quad (20)$$

where $Z_i(r)e \leq 2e$ is the effective transferred charge⁶ which will be calculated further, and taking into account that

$$\begin{aligned} W_{i3} &= W_{3i} \exp \left[-\frac{\mathbf{p}_i \cdot \mathbf{E} + \Delta_{i3}}{T} \right], \\ W_{12} &= W_{21} \exp \left[-\frac{(\mathbf{p}_1 - \mathbf{p}_2) \cdot \mathbf{E} + \Delta_{12}}{T} \right], \end{aligned} \quad (21)$$

where $\Delta_{ik} = E_s(Q_{\min,i}) - E_s(Q_{\min,k})$ is the energy difference (the energy disparity) between minima i and k , it is possible to rewrite (18) and (19) in the following form:

$$\mathbf{B}_{12} = e\mathbf{r} [h_1^0 W_{13}^0 + h_2^0 W_{21}^0 (Z_1 + Z_2)] / 2T, \quad (18')$$

$$\mathbf{B}_{21} = -e\mathbf{r} [h_2^0 W_{23}^0 + h_1^0 W_{12}^0 (Z_1 + Z_2)] / 2T. \quad (19')$$

By using Eqs. (12)–(19) one can calculate the dynamic dipole moment of the pair:

$$\begin{aligned} \mathbf{d}_\omega &= \mathbf{p}_1 \tilde{h}_1 + \mathbf{p}_2 \tilde{h}_2 \\ &= \mathbf{e} \mathbf{r} (Z_1 \tilde{h}_1 - Z_2 \tilde{h}_2) / 2 \\ &= \frac{e^2 (\mathbf{E} \cdot \mathbf{r}) \mathbf{r}}{4T(\tau_1^{-1} - \tau_2^{-1})} \left[\frac{N_1}{1 + i\omega\tau_1} + \frac{N_2}{1 + i\omega\tau_2} \right], \end{aligned} \quad (22)$$

where

$$\tau_{1,2}^{-1} = \frac{A_{11} + A_{22}}{2} \pm \left[\frac{(A_{11} - A_{22})^2}{4} + A_{12} A_{21} \right]^{1/2}, \quad (23)$$

$$N_{1,2} = \pm F \mp \tau_{1,2} \Psi, \quad (24)$$

$$F = b_{12} + b_{21}, \quad (25a)$$

$$\Psi = b_{12}(Z_1 A_{22} + Z_2 A_{21}) + b_{21}(Z_2 A_{11} + Z_1 A_{12}), \quad (25b)$$

$$b_{12} = [(Z_1 + Z_2) Z_2 W_{12}^0 + Z_1^2 W_{13}^0] h_1^0, \quad (26)$$

$$b_{21} = [(Z_1 + Z_2) Z_1 W_{21}^0 + Z_2^2 W_{23}^0] h_2^0.$$

The equilibrium occupation probabilities²⁰

$$h_i^0 = \frac{g_i}{Z} \exp \left[\frac{n_i F - E_s(Q_{\min,i})}{T} \right], \quad (27)$$

where

$$Z = \sum_i g_i \exp \left[\frac{n_i F - E_s(Q_{\min,i})}{T} \right] \quad (28)$$

is the grand partition function of the pair, F is the Fermi level, g_i is the degree of degeneracy, and n_i is the occupation number of the i th state.

From Eq. (22) it follows that, unlike the two-site small polaron model,⁸ the two-site bipolaron model is characterized by two different relaxation times $\tau_{1,2}$ [see Eq. (23)]. This is a direct consequence of the presence of a profound third (central) minimum in the configuration potential $E_s(Q)$. Let us omit all transition probabilities W_{i3} or W_{3i} in Eq. (23) which involve the central minimum, thus considering only the elastic transitions [Fig. 3(b)]. (This is correct when $\kappa \gg \kappa_c$). Then one of the relaxation times $\tau_2 \rightarrow \infty$, while the second one

$$\tau_1 \rightarrow \tau = \tau_{\text{el}} = (W_{12} + W_{21})^{-1}. \quad (29)$$

As a result, the dynamic dipole moment

$$\mathbf{d}_\omega = \frac{[Z_b(r)e]^2 (\mathbf{E} \cdot \mathbf{r}) \mathbf{r}}{T} \frac{h_1^0 h_2^0}{h_1^0 + h_2^0} \frac{1}{1 + i\omega\tau} \quad (30)$$

is described by almost the same expression as in the SP case.^{8,9} With the exception of the specific character of the relaxation time τ , the only difference is that a one-polaron (or one-electron) charge⁶ is replaced in (30) with the effective transferred bipolaron charge $Z_b(r)e = Z_1 e \approx Z_2 e \leq 2e$. The latter depends on the pair size r and so decreases with it (see Sec. V).

General expression (22) for the dynamic dipole moment can be simplified significantly in the case of the symmetric pair when $E_s(Q) = E_s(-Q)$. Then, setting

$W_{12}^0 = W_{21}^0 = \tilde{W}$, $W_{32}^0 = W_{31}^0 = w$, $W_{13}^0 = W_{23}^0 = W$, $Z_1 = Z_2 = Z_b$, and $h_1^0 = h_2^0 = h_0$ in Eqs. (22)–(28), it is easy to show that

$$\mathbf{d}_\omega = \frac{(Z_b e)^2 (\mathbf{E} \cdot \mathbf{r}) \mathbf{r}}{2T} \frac{h_0}{1 + i\omega\tau}, \quad (31)$$

where

$$\tau = \tau_s = (2\tilde{W} + W)^{-1}. \quad (32)$$

Here, some comments are in order. Though formally there are two finite relaxation times in the symmetric SB case, one of the coefficients N_1 or N_2 in Eq. (22) vanishes, resulting in the appearance of only one relaxation time τ_2 or τ_1 in Eq. (31). In addition, the relaxation time τ_s [see Eq. (32)] that “survives” does not depend on the probability $w = W_{32} = W_{31}$ of escaping the central minimum at all [Fig. 3(a)]. In this case, when the field is applied, the increase in the population of the central minimum, induced by the increased probability flow from one of the lateral minima, is compensated for by a subsequent decrease induced by the increased probability flow from the central minimum to the second lateral minimum.

Moreover, as can be seen from a comparison of Eqs. (29) and (32), the presence of the central minimum leads to a decrease in the relaxation time due not only to an increase of the probability \tilde{W} itself of the direct (elastic) transitions $1 \rightarrow 2$ and $2 \rightarrow 1$ ($D_+ + D_- \rightarrow D_- + D_+$) caused by the lowering of the barrier, but also to the appearance of an additional two-step (inelastic) transition $1 \rightarrow 3 \rightarrow 2$ or $2 \rightarrow 3 \rightarrow 1$ involving the central minimum (Fig. 3). The contribution of the inelastic channel (W) to the total inverse time τ_s^{-1} [see Eq. (32)] contains the factor $\frac{1}{2}$, as compared to the elastic channel ($2\tilde{W}$). The reason is that in the symmetric case, a SB executing the $1 \rightarrow 3 \rightarrow 2$ transition and having been trapped into the central minimum (state 3) with probability $\frac{1}{2}$ can come back ($3 \rightarrow 1$ transition) or move forward ($3 \rightarrow 2$ transition), thus successfully completing the $1 \rightarrow 2$ transition [Fig. 3(a)].

Finally, as the main contribution to the ac conductivity comes from the slightly asymmetric intimate pairs (stretched bonds) characterized by the energy difference $\Delta_{12} \approx T$ (see Refs. 1 and 9), instead of using the overcomplicated general formula (22) for the dynamic dipole moment, we will exploit the simple expression (30) together with the following interpolation formula for the relaxation time:

$$\tau = \begin{cases} (2\tilde{W} + W)^{-1}, & 2 < \kappa \leq \kappa_c \\ (2\tilde{W})^{-1}, & \kappa \gg \kappa_c. \end{cases} \quad (33)$$

The approximate formula (30) allows for asymmetry and obviously matches the correct expression (31) in the symmetric limit. Expression (33) takes into account both elastic and inelastic transitions and seems to describe the central minimum contribution to the SB hopping process (Fig. 3) fairly well, provided that the energy disparity Δ_{ik} is small.

IV. ac CONDUCTIVITY

Now we are in a position to write the expression for the complex ac conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ by using the expression

$$i\omega\mathbf{P}_\omega = \sigma(\omega)\mathbf{E}_\omega \quad (34)$$

for the integral dipole moment \mathbf{P}_ω of a unit volume which is simply equal to the sum of the dipole moments \mathbf{d}_ω of the pairs. Integrating the expression for \mathbf{P}_ω over the angles between \mathbf{r} and \mathbf{E}_ω , and using (30) and (34), one can obtain (see also Refs. 8 and 21)

$$\begin{aligned} \sigma(\omega) &= \frac{i\omega}{2} \int d\mathbf{r} \int d\epsilon_1 \int d\epsilon_2 \rho_e(\epsilon_1)\rho_e(\epsilon_2)\mathbf{d}_\omega \\ &\cong \frac{2\pi e^2 i\omega}{3T} \int_0^\infty dr r^4 Z_b^2(r) \\ &\quad \times \int dE_1 \int dE_2 \frac{h_1^0 h_2^0 \rho_b(E_1)\rho_b(E_2)}{(h_1^0 + h_2^0)(1 + i\omega\tau)}, \end{aligned} \quad (35)$$

where the factor $\frac{1}{2}$ was introduced to avoid double counting of pairs. Here, ρ_e is a one-electron density of states, $\rho_b(E)$ is a bipolaronic density of states, h_i^0 [see Eq. (27)] is the equilibrium occupation probability of the site $i=1$ or 2 having the bipolaron energy $E_i = E_s(Q_{\min,i})$, τ [see Eq. (33)] is the relaxation time, and $Z_b(r)e$ is the effective charge of a bipolaron localized at the D -center pair of dimension r .

If the effective correlation energy $|U_{\text{eff}}|$ is much greater than the characteristic width Δ_0 of the one-electron energy band, then only the D_+ and D_- states with $n_i=0$ or 2 effectively participate in the grand partition function (28). Then, taking into account that the energy of the Coulombic repulsion of two bipolarons localized at a typical pair, which is of order of $e^2/\epsilon r$, is greater than T , one can perform the integration over E_1 and E_2 in Eq. (35) [see Refs. 9 and 21 for details],

$$\begin{aligned} \sigma_1(\omega) &= \text{Re}\sigma(\omega) \\ &= \frac{e^4 \pi \omega^2 \rho_e^2}{6\epsilon} \int_{r_{\min}}^\infty dr r^3 Z_b^2(r) \frac{\tau(r)}{1 + \omega^2 \tau^2(r)}, \end{aligned} \quad (36)$$

where ϵ is the dielectric permittivity, $\rho_e = \rho_e(F - U_{\text{eff}}/2) \approx \rho_b/2$ is the one-electron density of states measured in the center of the one-electron D -state band (F is the Fermi level), and r_{\min} is the minimum size of the pair for which the bipolaron (ionic) state is either a ground state (for $2 < \kappa \leq \kappa_c$) or does not exist at all (for $\kappa \gg \kappa_c$). (The dashed line in Fig. 2 corresponds to the pairs with $r = r_{\min}$). Furthermore, as the relaxation time τ [see Eq. (33)] increases exponentially with the size r of a pair, the integrand in Eq. (36) reaches (at given ω and T) a sharp maximum at point $r_{\omega,T}$ such that

$$\omega\tau(r_{\omega,T}) = 1. \quad (37)$$

Thus the value of $r_{\omega,T} \geq r_{\min}$ describes the optimum size of pairs making the greatest contribution to the ac con-

ductivity at given ω and T . It also allows us to perform the integration over r , giving

$$\sigma_1(\omega, T) = \frac{e^4 \pi^2 \rho_e^2}{12\epsilon} Z_b^2(r_{\omega,T}) \omega r_{\omega,T}^3 \left| \frac{\partial r_{\omega,T}}{\partial \ln \omega} \right| \quad (r_{\omega,T} \geq r_{\min}). \quad (38)$$

Here, the modulus reflects the fact that $\partial r_{\omega,T} / \partial \ln \omega < 0$. Formulas (36)–(38) are valid if the relaxation time τ depends substantially upon the intersite distance r only. (We will discuss this assumption in Sec. V.)

The experimentally measured real part of the ac conductivity is usually presented in the form of a power-law function^{1,9}

$$\sigma_1(\omega, T) \propto \omega^s T^n. \quad (39)$$

Expression (38) allows us to evaluate the power exponents

$$\begin{aligned} s = \frac{\partial \ln \sigma_1}{\partial \ln \omega} &= 1 + \left[\frac{3}{r_{\omega,T}} + 2 \frac{\partial \ln Z_b(r_{\omega,T})}{\partial r_{\omega,T}} \right. \\ &\quad \left. + \frac{\partial^2 r_{\omega,T} / \partial (\ln \omega)^2}{(\partial r_{\omega,T} / \partial \ln \omega)^2} \right] \frac{\partial r_{\omega,T}}{\partial \ln \omega}, \end{aligned} \quad (40)$$

$$\begin{aligned} n = \frac{\partial \ln \sigma_1}{\partial \ln T} &= \left[\frac{3}{r_{\omega,T}} + 2 \frac{\partial \ln Z_b(r_{\omega,T})}{\partial r_{\omega,T}} \right. \\ &\quad \left. + \frac{\partial^2 r_{\omega,T} / \partial \ln \omega \partial \ln T}{(\partial r_{\omega,T} / \partial \ln \omega)(\partial r_{\omega,T} / \partial \ln T)} \right] \frac{\partial r_{\omega,T}}{\partial \ln T}, \end{aligned} \quad (41)$$

where the optimum-pair size $r_{\omega,T} > r_{\min}$ is a solution of the transcendental equation (37).

It immediately follows from Eq. (37) that in the limit of a broad one-electron band ($\Delta_0 \gg T$), if $Z_b=1$ and $\tau(r) = \omega_0^{-1} \exp(2r/a)$, the value of $r_{\omega,T} = (a/2) \ln(\omega_0/\omega)$. Then, in accordance with Ref. 21, expressions (40) and (41) transform to

$$s = 1 - \frac{3}{\ln(\omega_0/\omega)}, \quad n = 0. \quad (42)$$

These describe the low-temperature limit ($T < e^2/\epsilon r_\omega$) of the ac conductivity due to the localized electrons in disordered semiconductors in the presence of strong Coulombic correlations in the level occupation.

V. HIGH TEMPERATURES, ACTIVATION REGIME

To proceed further, both the spatial dependencies of the relaxation time τ and that of the transferred charge Z_b should be specified. These can be evaluated within the framework of the two-site model of SB's (Sec. II). Let us first consider a high-temperature case when the height $V(r)$ of the barrier between ground (ionic) and excited (covalent) states (which, obviously, is equal to the barrier between two ionic states [see Fig. 3(a)]) is overcome by activation. By using (6), it can be shown^{14,22} that, in the standard semiclassical approximation, the probability

(rate) of the $1 \rightarrow 3$ or $2 \rightarrow 3$ process may be written in the form

$$W = \frac{\omega_0}{2\pi} F(\eta) \exp \left[-\frac{V(r)}{T} \right], \quad (43)$$

where

$$F(\eta) = 2 \int_0^\infty dx e^{-x} \frac{1 - \exp(-\pi\eta/2x^{1/2})}{2 - \exp(-\pi\eta/2x^{1/2})}. \quad (44)$$

Here,

$$\eta(r) = \frac{J^2(r)}{\hbar\omega_0(VT)^{1/2}} \quad (45)$$

is the so called nonadiabaticity parameter. Depending upon the value of η , two types of jumps can be accomplished:²² adiabatic ($\eta \geq 1, F \cong 1$) or nonadiabatic ($F \cong \pi^{3/2}\eta \alpha J^2 \ll 1$). In Eq. (45), $J(r)$ is the tunnel integral (10), and ω_0 is the local-phonon frequency. The probability \bar{W} of direct activation hopping $1 \rightarrow 2$ or $2 \rightarrow 1$ between two ionic states is also described by an Eq. (43)-type expression with η proportional to $J^4 \ll J^2 \propto \bar{W}$ (see Ref. 11 for details). This means that, in the high-temperature case, $W > \bar{W}$, and the relaxation time is governed mainly by the inelastic transitions $1 \rightarrow 3 \rightarrow 2$ and $2 \rightarrow 3 \rightarrow 1$:

$$\tau = (2\bar{W} + W)^{-1} \cong W^{-1} \quad (46)$$

provided $2 < \kappa \leq \kappa_c$ and $\eta \ll 1$. For $2 < \kappa \leq \kappa_c$ and $\eta \geq 1$, both elastic and inelastic transitions contribute to

$$\tau \cong (3W)^{-1} \quad (47)$$

because here $\bar{W} = W$. Finally, for $\kappa \gg \kappa_c$, in accordance with Eq. (33) (see also Ref. 11), the transitions are purely elastic ($\bar{W} = 0$), so

$$\tau \cong (2\bar{W})^{-1}. \quad (48)$$

By using Eqs. (4)–(6) one can show that the barrier for the $1 \rightarrow 3$ or $1 \rightarrow 2$ transitions is

$$V(r) = \frac{2}{\sqrt{3}} \bar{U} \frac{(\kappa-1)^2}{\kappa} \sin\varphi(1 - \cos\varphi) \quad (49)$$

if $\kappa > \gamma(2\gamma+1)/(2\gamma-1)$, and

$$V(r) = \bar{U} \left[\kappa \left[1 - \frac{Z_b^2}{8} \right] - \frac{1+\nu+2\gamma}{2} \right] \quad (50)$$

if $\gamma/2 + \frac{3}{4} + (\gamma + \frac{1}{2})^{1/2} \leq \kappa \leq \gamma(2\gamma+1)/(2\gamma-1)$, and $\gamma < \gamma_c$ [see Fig. 2]. This barrier governs the relaxation time [see Eqs. (46)–(48)] that, in any high-temperature case, is proportional to $\exp[V(r)/T]$. The effective bipolaron charge (in units of the electron charge e)

$$Z_b(r) = 2 \left[1 - \nu + \left[\frac{\nu}{2\kappa} \right]^2 (2\kappa - \nu - 1) \right]^{1/2}, \quad (51)$$

where

$$\nu = \frac{4}{3}(\kappa-1) \left[1 - \cos \left[\frac{\pi}{3} - \varphi \right] \right], \quad (52)$$

$$\cos 3\varphi = \frac{27}{2}\alpha - 1, \quad (53)$$

and

$$\alpha(r) = \frac{\gamma^2 - \frac{1}{4}}{2(\kappa-1)^3} = \frac{2\bar{U}J^2(r)}{(4W_p - \bar{U})^3}. \quad (54)$$

The values κ and $\gamma(r)$ are given by formulas (7)–(9). By analyzing the κ - γ diagram (Fig. 2) it is easy to show that the bipolaron state exists if $0 < \alpha < 4/27 \ll 1$. Thus, for $2 < \kappa \leq \kappa_c$,

$$V(r) \cong V_0(1 - 4\alpha^{1/2} + 3\alpha), \quad V_0 = \frac{(4W_p - \bar{U})^2}{8W_p} \quad (55)$$

and

$$Z_b(r) \cong 2[1 - 2(\kappa-1)\alpha]^{1/2}. \quad (56)$$

For $\kappa \gg \kappa_c$, corresponding to $\bar{U} \rightarrow 0$,

$$V(r) \cong 2W_p \left[1 - \frac{J(r)}{2W_p} \right]^2 \quad (57)$$

and

$$Z_b(r) \cong 2 \left[1 - \left[\frac{J(r)}{2W_p} \right]^2 \right]^{1/2}. \quad (58)$$

The latter expressions resemble those of the SP (Ref. 8) case because the central minimum does not play any significant role when $\kappa \gg \kappa_c$. It should be added here that, in the adiabatic case, if $J_0 > 2W_p$, both the barrier height V [see (49) or (50)] and the transferred charge Z_b [see (51)] decrease with the distance r between centers, thus causing a huge decrease in the relaxation time. Contrary to this, in the nonadiabatic case an exponential decrease in τ with decreasing r is totally connected with an increase in the tunnel integral (10), while V and Z_b are constant and equal to their maximum values V_0 and 2, respectively.

So far, we ignored the influence of the intersite energy disparity Δ upon the hopping rate τ^{-1} . In certain cases, it may be justified as follows. According to Emin,²³ at low temperatures the small (bi)polaron hopping rate τ^{-1} is governed by the low-energy acoustic-phonon emission, and, therefore, increases with Δ not faster than Δ^3 . This power-law dependence definitely cannot compete in the nonadiabatic regime, with the exponential dependence of τ^{-1} upon the hopping distance r [see Eqs. (43) and (45)]. It is especially true for the adiabatic regime characterized by the superexponential dependence of $\tau^{-1}(r)$ which takes place when $J_0 > W_p$ (for SP hopping⁸) or $\kappa \gg \kappa_c$ and $J_0 > 2W_p$ (for SB hopping). But if the above-mentioned inequalities do not hold, the barrier V and, therefore, the relaxation time τ do not depend substantially upon r . Then the intersite energy disparity Δ becomes the principal source of the hopping-rate dispersion in disordered systems.²³

Now the $\sigma_1(\omega, T)$ dependence can be calculated for the high-temperature case by using formulas (38) or (39)–(41) together with Eqs. (37) and (43)–(53). Then we are in a

position to discuss some simple cases that can be treated analytically. Let us first consider a nonadiabatic limit $\eta \ll 1$. Then, from Eqs. (37), (46)–(48), (55), and (57), it follows that for

$$T > T_1(\omega) = \frac{V_0}{\ln(\omega'_0/\omega)}, \quad (59)$$

the optimum-pair size

$$r_{\omega,T} = \frac{\xi a}{2} \left[\ln \left[\frac{\omega'_0}{\omega} \right] - \frac{V_0}{T} \right], \quad (60)$$

where $\xi = 1$ and $\omega'_0 \approx J_0^2 \hbar^{-1} (V_0 T)^{1/2}$ for $2 < \kappa \leq \kappa_c$, $\xi = \frac{1}{2}$ and $\omega'_0 \propto J_0^4$ for $\kappa \gg \kappa_c$ (see Ref. 11 for details), and V_0 is given by Eq. (55). Therefore [see Eqs. (56), (58), (40), and (41)],

$$s = 1 - \frac{3}{\ln \left[\frac{\omega'_0}{\omega} \right] - \frac{V_0}{T}}, \quad n = (1-s) \frac{V_0}{T}. \quad (61)$$

For low temperatures $T < T_1$, [see Eq. (59)] such that the optimum-pair size is small enough ($r_{\omega,T} - r_{\min} \leq a$), the adiabatic hopping regime ($\eta \geq 1$) should be considered as long as the relaxation time is still governed by the activation process. The cases of intermediate ($2 < \kappa \leq \kappa_c$) and large ($\kappa \gg \kappa_c$) polaron shifts should then be treated separately. The reason for this might be explained as follows. By substituting $F(\eta) = 1$ into Eq. (43), and using Eqs. (39) and (46) to (48), it is easy to calculate the optimum-pair activation barrier

$$V(r_{\omega,T}) = T \ln(\omega_0/\omega). \quad (62)$$

For $\kappa \gg \kappa_c$, this barrier decreases with temperature tending to zero as $T \rightarrow 0$. (At the same time, $r_{\omega,T} \rightarrow r_{\min}$). Meanwhile, for $2 < \kappa \leq \kappa_c$ and/or $J_0 < 2W_p$ the barrier remains finite as $r_{\omega,T} \rightarrow r_{\min}$, i.e., $T \rightarrow 0$. For this case, this means that the characteristic relaxation time τ increases exponentially as $T \rightarrow 0$, provided it depends only on r . Thus for any small but finite T , one can define

$$\omega_t(T) = \tau^{-1}(r_{\min}) = W(r_{\min}; T), \quad (63)$$

where r_{\min} is obtained from the equation⁶ (see Fig. 2)

$$\kappa = \frac{3}{4} + \frac{1}{2} \gamma(r_{\min}) + \left[\frac{1}{2} + \gamma(r_{\min}) \right]^{1/2}, \quad (64)$$

such that for $\omega > \omega_t$ the product $\omega \tau(r_{\min})$ definitely exceeds unity.²⁴ This results in the cancellation of ω^2 in the numerator and denominator of formula (36) for $\sigma_1(\omega)$. In this case, the dependence of the SB relaxation time upon the intersite energy disparity Δ should be taken into account.²³

Contrary to this, for $\kappa \gg \kappa_c$ and $J_0 > 2W_p$ the intersite separation r plays the major role. Here, at low temperatures, the value of s is close to 1:

$$s \approx 1 - \frac{1}{4} \left[\frac{T}{2W_p \ln(\omega_0/\omega)} \right]^{1/2} \left[1 + 6 \ln^{-1} \frac{J_0}{2W_p} \right]. \quad (65)$$

This expression is valid when $V(r_{\omega,T}) \ll V_0 \approx 2W_p$,

i.e., $T \ll T_1(\omega)$, and strongly resembles that of the SP model.⁸ Moreover, as $\partial r_{\omega,T} / \partial \ln T = -\ln(\omega_0/\omega) \partial r_{\omega,T} / \partial \ln \omega$, the universal relation^{8–10}

$$n = m + (1-s) \ln(\omega_0/\omega), \quad (66)$$

with $m = 0, 1$, or 2 can be obtained for $T < T_1(\omega)$. Such a relation is common for all models of the correlated-barrier-hopping (CBH) type.¹⁰ In particular, for the broadband case ($\Delta_0 \gg T$) considered above, $m = 1$ (see Ref. 9 for details).

VI. LOW TEMPERATURES, TUNNEL REGIME

At temperatures T lower than those corresponding to approximately one-fourth of the energy $\hbar\omega_0$ of a local phonon,¹¹ the jumps of a SB are connected with tunneling under the potential barrier in the (Q, \bar{Q}) configuration space [see Fig. 3(b)]. The shape $E_r(Q)$ of the barrier separating two ionic states of a symmetric pair can be found from Eqs. (4)–(6). In particular, setting $\bar{U} \rightarrow 0$, which corresponds to $\kappa \gg \kappa_c$, and taking into account Eq. (58), one can obtain

$$E_r(q) \cong \frac{W_p}{2} \left[q^2 - \frac{Z_b^2(r)}{4} \right]^2, \quad (67)$$

provided $E_r(q) \ll W_p/2$. Here, $q = \lambda Q / 4W_p = \mu \omega_0^2 Q / \lambda \leq Z_b/2$ is a dimensionless coordinate. The approximate formula (67) describes low and narrow barriers corresponding to pairs which participate in the ac conductivity at very low temperatures.

Then, the probability of the adiabatic $1 \rightarrow 2$ transition²⁵

$$\bar{W} = \omega_0 \exp \left[- \frac{2S_r(T)}{\hbar} \right], \quad (68)$$

where

$$S_r(T) = \int_0^{\hbar/2T} \left[\frac{2W_p}{\omega_0^2} \left[\frac{dq}{d\tau} \right]^2 + E_r(q) \right] d\tau \quad (69)$$

is the semiclassical action for a SB subbarrier transition. The optimum trajectory $q(\tau)$ involved can be found from the least-action principle.²⁶ After introducing $x = 2q/Z_b$ and $\tau' = Z_b \omega_0 \tau / 2$, we have

$$S_r(T) = \frac{W_p Z_b}{8\omega_0} g(y), \quad (70)$$

where $y = \hbar\omega_0 Z_b / 4T$, and

$$g(y) = \int_0^y \left[2 \left[\frac{dx}{d\tau'} \right]^2 + \frac{1}{2}(x^2 - 1)^2 \right] d\tau'. \quad (71)$$

For $T \rightarrow 0$ we obtain

$$S_r(T \rightarrow 0) = S_r(0) \cong \frac{W_p Z_b^3(r_\omega) g(\infty)}{8\omega_0} = \frac{W_p Z_b^3(r_\omega)}{3\omega_0}, \quad (72)$$

where the optimum-pair transferred charge can be found from the condition $\omega \tau(r_\omega) = \omega / \bar{W}(r_\omega) = 1$. For very

small temperatures, this gives [see Eqs. (68) and (70)–(72)]

$$Z_b(r_\omega) = \left[\frac{3\hbar\omega_0}{2W_p} \ln \left(\frac{\omega_0}{\omega} \right) \right]^{1/3}. \quad (73)$$

For the condition $E_r(Q) \ll W_p/2$ to be valid for any small Q , it follows that $Z_b(r_\omega)$ should be much less than unity. This means that to great accuracy $r_{\omega, T \rightarrow 0} \cong r_{\min} = a \ln(J_0/2W_p)$ if, of course, $J_0 > 2W_p$. Therefore, at temperatures less than the renormalized phonon energy,

$$T < T_2(\omega) = \hbar\tilde{\omega}_0 = \frac{1}{2}Z_b(r_\omega)\hbar\omega_0, \quad (74)$$

where tunneling plays a major role, the real part of the conductivity [see (38)]

$$\sigma_1(\omega) \cong \left[\frac{\pi e^2}{12} \right]^2 \frac{a}{\epsilon} \left[\frac{3\hbar\omega_0}{2W_p} \right]^{4/3} \rho_3^2 r_{\min}^3 \omega \ln^{1/3} \left(\frac{\omega_0}{\omega} \right). \quad (75)$$

As in the SP case,⁷ this leads to

$$s = 1 - \frac{1}{3 \ln(\omega_0/\omega)}, \quad n = 0. \quad (76)$$

Equation (76) represents the (bi)polaron low-temperature limit which is specific for the small (bi)polaron problem. It differs significantly from the electron low-temperature limits both in the presence²¹ [see Eq. (42)] and the absence¹ [when the Austin-Mott formula

$$s = 1 - \frac{4}{\ln(\omega_0/\omega)}, \quad n = 1 \quad (77)$$

holds] of Coulomb correlations in the occupation numbers.

For $2 < \kappa \leq \kappa_c$ and/or $J_0 < 2W_p$, the lowest possible barrier, which at low temperatures, is overcome by tunneling, is finite. Therefore, as in the activation regime [see Eq. (56)], the threshold frequency can be defined by means of the condition $\omega_t \tau(r_{\min}) = 1$, such that for all

$$\omega > \omega_t = \omega_0 \exp(-S_{\min}/\hbar), \quad (78)$$

the real part of the ac conductivity is governed by the intersite energy disparity.²³ In (78), $S_{\min} = S_{r \rightarrow r_{\min}}(T \rightarrow 0)$ is the action (69) corresponding to the minimum barrier available with r_{\min} as a solution of Eq. (64).

The approximate formula (67) for the potential barrier, which we have exploited to analyze the low-temperature adiabatic case, is valid if $Z_b(r_\omega) \ll 1$ [see Eq. (73)]. This statement is equivalent to

$$\omega > \omega_1 = \omega_0 \exp \left[-\frac{2W_p}{3\hbar\omega_0} \right], \quad (79)$$

and actually coincides (see Ref. 8) with the applicability of the adiabatic regime ($\eta \geq 1$) [see Eq. (45)]. If $\omega < \omega_1$ and $T < \hbar\omega_0/4$, we have the case of nonadiabatic $1 \rightarrow 2$ tunneling [Fig. 3(b)] which has a probability (see also Ref. 11)

$$\bar{W} = \bar{W}_{\text{tun}} = \frac{4\pi J^4(r)}{(\hbar\omega_0)^2 W_p^2 (1+u)^4} \omega_0 \times \exp \left[-\frac{4W_p}{\hbar\omega_0} (1+u - u \ln u) \right], \quad (80)$$

where $u = 1 - \bar{U}/2W_p$. This leads to expression (38) with

$$r_\omega = \frac{a}{4} \ln \frac{\tilde{\omega}_0}{\omega}. \quad (81)$$

As a result, the power exponents s and n are described by means of the modified Efros²¹ formula (42) with parameter ω_0 interchanged with $\tilde{\omega}_0$, in accordance with Eqs. (80) and (10). [The value of $\tilde{\omega}_0$ can be calculated easily from Eqs. (80), (10), (46), and (37)].

Finally, general expression (35) makes it possible to calculate the imaginary part $\sigma_2(\omega)$ of the ac conductivity and, therefore, to determine the tangent of dielectric losses⁹

$$\tan \Psi = \sigma_2/\sigma_1 = \text{Im} \sigma / \text{Re} \sigma. \quad (82)$$

This can be shown to be nearly the same as in the SP case.⁸

VII. DISCUSSION

Formulas (40) and (41) together with Eqs. (37), (33), and (43)–(54) have been used to calculate numerically the exponents s and n describing the real part (39) of the ac bipolaron hopping conductivity in wide temperature and frequency ranges. Several reasonable values of the polaron shift W_p , the Hubbard repulsion energy \bar{U} , the preexponential factor J_0 in expression (10) for the electron-tunneling integral, and the local-phonon energy $\hbar\omega_0$ have also been treated. The typical results obtained are presented in Figs. 4–6.

It is convenient to summarize them by means of a ω - T phase diagram shown in Figs. 7(a) and 7(b) for the cases of large ($\kappa \gg \kappa_c$) and intermediate ($2 < \kappa \leq \kappa_c$) polaron shifts W_p , respectively.²⁷ The ω - T space in the diagrams is divided into several regions, each of which corresponds to specific temperature and frequency dependencies of the power exponents describing the real part $\sigma_1 \propto \omega^s T^n$ of the complex conductivity. The vertical line [see Figs. 7(a) and 7(b)], which is described by the equation $T = T_1(\omega)$ [see expression (59)], separates the regions of high-frequency adiabatic regimes of SB hopping from those of the low-frequency nonadiabatic ones. The horizontal line, which corresponds to the equation $T = T_2(\omega)$ [see expression (74)], separates the region of the low-temperature tunnel regimes from those of the high-temperature activation ones.²⁸

The main qualitative difference between the two pictures shown in Fig. 7 is the presence of a Δ region in the left part of Fig. 7(b) which represents the case of intermediate polaron shifts $\bar{U}/2 < W_p \leq \bar{U}$, i.e., $2 < \kappa \leq \kappa_c$, and/or $J_0 < 2W_p$. This region corresponds to Emin's²³ energy-disparity-governed Δ regime of SB hopping which dominates at rather high frequencies exceeding some threshold value $\omega_t(T)$ [see Eqs. (63) and (78)]. In the case

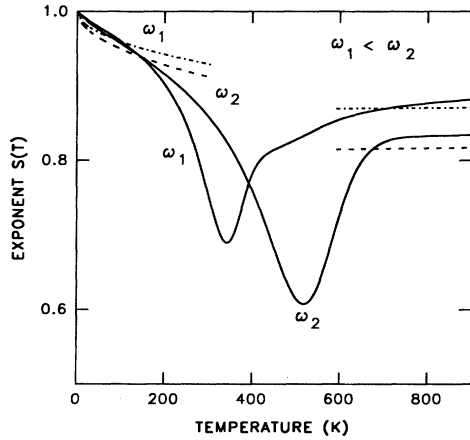


FIG. 4. The temperature dependence of the exponent s in the case of large polaron shift ($W_p = 0.3 \text{ eV} \gg \bar{U} = 0.01 \text{ eV}$) calculated for two different frequencies: (1) $\omega = \omega_1 = 10^5 \text{ Hz}$ and (2) $\omega = \omega_2 = 10^8 \text{ Hz}$ with parameters $J_0 = 2 \text{ eV}$ and $\omega_0 = 10^{13} \text{ Hz}$. The dashed and dash-and-dotted curves are described by the low- (adiabatic) and high-temperature (nonadiabatic) asymptotics (65) and (61), respectively. Note that the approximate expression (59) for the temperature T_1 of the minimum of $s(T)$ gives $T_1(\omega_1) \approx 390 \text{ K}$ and $T_1(\omega_2) \approx 620 \text{ K}$, in fair agreement with the results of the numerical calculations.

of intermediate polaron shifts and/or rather small nearest-neighbor hopping integrals, a transition to the Δ regime is found to be connected to the presence of finite potential barriers separating the ionic (bipolaron) states of the smallest possible pairs that have these states as ground states. This is not a case when polaron shifts are large enough ($W_p \gg \bar{U}$, i.e., $\kappa \gg \kappa_c$), and, therefore, the barriers mentioned are negligibly small (or do not exist) for the intimate pairs of D centers.

A shaded region in Figs. 7(a) and 7(b) corresponds to

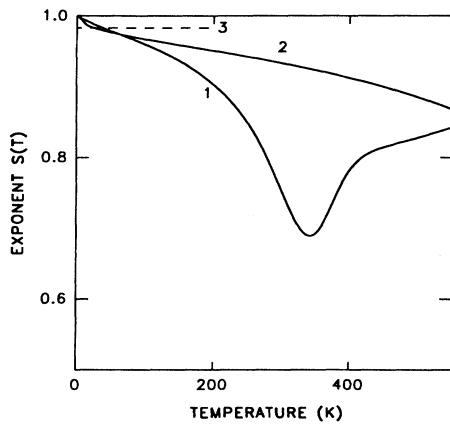


FIG. 5. The same as in Fig. 4 for $\omega = 10^5 \text{ Hz}$, but for two different values of the polaronic shift: (1) $W_p = 0.3 \text{ eV}$ and (2) $W_p = 0.8 \text{ eV}$. The dashed curve (3) corresponds to the low-temperature tunneling adiabatic (TA) regime described by Eq. (76).

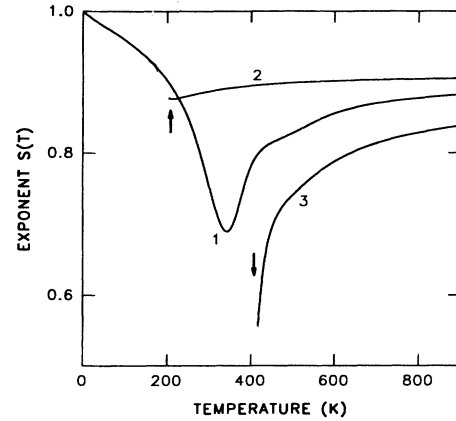


FIG. 6. A comparison of the $s(T)$ dependencies in the case of (1) large polaron shift $W_p = 0.3 \text{ eV} \gg \bar{U} = 0.01 \text{ eV}$, with that of (2) intermediate polaron shift $\bar{U}/2 = 0.2 \text{ eV} < W_p = 0.3 \text{ eV} < \bar{U} = 0.4 \text{ eV}$ for $\omega = 10^5 \text{ Hz}$, $\omega_0 = 10^{13} \text{ Hz}$, and $J_0 = 2 \text{ eV}$. At $T \approx 180 \text{ K}$, curve (2) reveals a transition to the high-frequency energy-disparity-governed Δ regime (Ref. 23) that is marked by an arrow. The same transition also can be seen in curve (3), which corresponds to $W_p = 0.3 \text{ eV} \gg \bar{U} = 0.01 \text{ eV}$, but $J_0 = 0.01 \text{ eV} \ll 2W_p$. At lower temperatures, one can expect the increase of s as temperature is decreased, thus causing s to approach 1, which is typical for the Δ regime (Ref. 23).

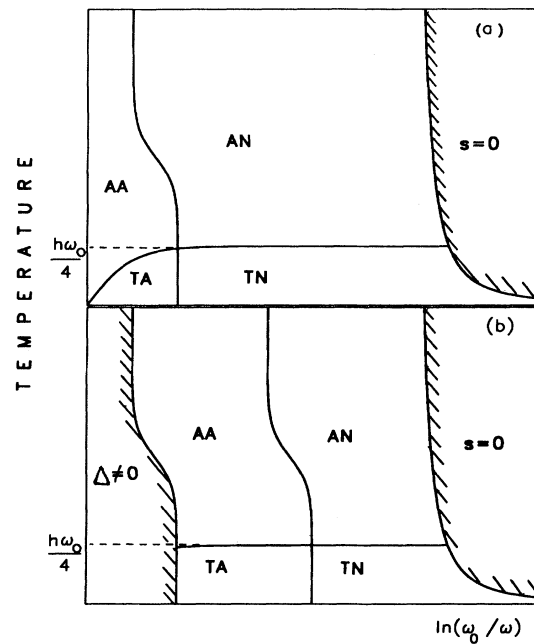


FIG. 7. Temperature-frequency diagram describing different hopping regimes of a SB [AA, activation adiabatic; AN, activation nonadiabatic; TA, tunnel adiabatic; TN, tunnel nonadiabatic; and Δ , energy-disparity-governed adiabatic (Ref. 23)], in the cases of (a) large polaron shifts ($\kappa \gg \kappa_c$) and large hopping integrals ($J_0 > 2W_p$); and (b) intermediate polaron shifts ($2 < \kappa \leq \kappa_c$) and/or small hopping integrals ($J_0 < 2W_p$). The shaded regions correspond to the low-frequency dispersionless multihopping conductivity.

an extremely weak frequency dependence of the real part of the complex conductivity. This appears in the low-frequency limit

$$\omega < \omega_l = \omega'_0 \exp \left[-\frac{\xi \bar{r}(T)}{a} - \frac{\Delta_0 + V_0}{T} \right]. \quad (83)$$

A drastic reduction of $s \ll 1$ occurs because of the contribution of multiple hopping that plays a significant role insofar as the optimal-pair size $r_{\omega, T}$ [see (60) or (81)] begins to compare with the mean distance \bar{r} between D centers, or the Mott's variable-range hopping²⁹ distance $\bar{r}(T) \propto T^{-1/4}$, whichever is longer. (In the last formula, Δ_0 is the width of the one-electron band, V_0 [see Eq. (55)] is the height of a configuration barrier, ξ is a dimensionless coefficient of order of unity that could be calculated in the framework of percolation theory,²⁹ and ω'_0 has been given in the description of Eq. (60).) For such low frequencies, the pair approximation that has been exploited in this paper is no longer valid.

In the case of intermediate polaron shifts and/or small hopping integrals J_0 at sufficiently high frequencies $\omega > \omega_l$ [see Eq. (83)] [though lower than ω_t given by Eq. (79)] and sufficiently low temperatures $T < T_2$ [see Eq. (67)], tunnel adiabatic (TA) SB hopping makes the main contribution to the ac conductivity described by Eq. (75). This means that σ_1 is almost temperature independent ($n \ll 1$), while parameter s given by Eq. (76) is extremely close to 1. It is also true for the Δ regime²³ ($\omega > \omega_t$) if the intersite Coulomb correlations²¹ are taken into account.

When temperature is increased within the range $T_2 < T < T_1$, we have an adiabatic activation (AA) regime [see Eqs. (65) and (66)]. Here, as for any other correlated-barrier hopping mechanism, parameter s , being less than 1, decreases, while n , being greater than 1, rises with temperature.

When temperature T exceeds the value $T_1(\omega)$ given by Eq. (59), a transition to an activation-nonadiabatic (ANA) regime of SB hopping occurs. The reason for such behavior might be explained as follows. As temperature increases, at given ω , the optimum-pair size $r_{\omega, T}$, which is a solution of Eq. (37), decreases because of the decrease in the relaxation time τ . As a result, at a certain temperature T_1 such that $\eta(r_{\omega, T_1}) = 1$, the nonadiabaticity parameter (45) exceeds 1, thus causing the transition to the ANA regime which is described by formulas (38), (60), and (61). Contrary to the AA (activation-adiabatic) regime, s increases with temperature tending to 1 as $T \rightarrow \infty$. Meanwhile, n decreases approaching zero at high temperatures.

Thus parameter s reaches its minimum value (Figs. 4 and 5), whereas parameter n has a maximum at the same temperature approximately equal to $T_1(\omega)$. According to Eq. (59), for both values the point of an extremum shifts toward the higher temperatures as frequency ω increases (Fig. 4).

At low frequencies $\omega < \omega_l$ [see Eq. (74)], such that the optimum-pair size r_{ω} [see Eq. (81)] is small enough to ensure the validity of the condition $\eta(r_{\omega}) < 1$, the nonadiabatic regime of hopping begins from very low tempera-

tures. First, at $T < \hbar\omega_0/4$, this regime possesses a tunnel nonadiabatic (TNA) character which is described by formulas (30) and (43). These lead to expressions (42) for s and n with renormalized parameter $\omega_0 \rightarrow \tilde{\omega}_0$ [see Eq. (80)]. Then, as the temperature exceeds $\hbar\omega_0/4$, a transition to the ANA regime occurs. This has been described by Eq. (61). Thus at low frequencies ($\omega < \omega_l$) the exponent n reaches its maximum at $T \cong \hbar\omega_0/4$, while, contrary to the high-frequency case, s monotonically increases with temperature.

Almost all the above-mentioned characteristics of the SB ac conductivity for $\kappa \gg \kappa_c$ qualitatively resemble those of the SP type.⁸ This is due to the two-well nature of adiabatic potentials describing a two-site SB in the case of large polaron shifts ($W_p \gg \bar{U}$). Of course, relatively deeper polaronic wells produced by two electrons localized on a center lead to much higher characteristic temperatures T_1 and T_2 , when compared to the SP case. This means that the ANA regime of SB hopping would hardly have been observed in reality. The same is true for the dispersionless SB multihopping regime. Both of them will not be observed because of the SP contribution to ac and dc conductivity that usually becomes dominant at lower temperatures.¹

The ac hopping conductivity due to SB's seems to have been observed in some chalcogenide glasses at sufficiently low temperatures $T \leq 100$ K (see Refs. 1 and 9, and references therein). For those materials, typical energies of the polaron shift W_p are of the order of 0.25–0.6 eV, while typical values of the effective two-electron correlation energy $U_{\text{eff}} = \bar{U} - 2W_p \cong -(0.5-1.0)$ eV < 0 (see Ref. 1). This allows us to evaluate the Hubbard repulsive energy \bar{U} to be much smaller than the polaron shift. Therefore, in our classification, chalcogenide glasses should be considered materials with strong polaron shifts ($\kappa \gg \kappa_c$). Moreover, the electron-tunneling integral corresponding to the smallest intersite separations, according to Harrison³⁰ (V_2 in his notations) is

$$J_0 = 2.16 \frac{\hbar^2}{md^2}, \quad (84)$$

where m is the free-electron mass, and d is the nearest-neighbor distance that for chalcogenides is of the order of 2.4 Å. For As_2Se_3 this gives $J_0 \cong 2.8$ eV $> 2W_p \cong 1$ eV, and $\bar{U} \cong 0.2$ eV $< W_p \cong 0.5$ eV (see Refs. 1 and 9).

A characteristic feature of the ac conductivity in chalcogenide glasses, measured within the frequency range from 10^2 to 10^8 Hz, is that the power exponent s is very close to unity ($1-s < 0.05$) up to 50–100 K, then tends to drop a little.¹ At the same time, the second power exponent n is much less than unity. It begins to increase as the temperature approaches 100 K (see Refs. 1 and 8). This behavior strongly agrees with that deduced from the SB model, provided that the TA hopping regime dominates at low temperatures.

For $\omega = 10^5$ Hz and $\omega_0 \approx 10^{13}$ Hz,^{1,9} from Eq. (76) it follows that $1-s = 0.02$ or $s = 0.98$ (Fig. 5), and $n = 0$ is in good agreement with the experimental data. Meanwhile, for the low-temperature electron limit²¹ [see Eq. (42)] it is easy to obtain $1-s = 0.18$ and $n = 0$. [The

Austin-Mott formula (77) gives $1-s=0.24$ and $n=1$.]

As $r_{\omega,T \rightarrow 0}$ is close to $r_{\min} \approx a \ln(J_0/2W_p)$, one can evaluate the typical size of stretched bonds to be responsible for the low-temperature ac losses within the wide frequency range from 10^2 to 10^8 Hz. For instance, in As_2Se_3 it is close to several localization radii $a \cong d \cong 2.4$ Å, and is of the order of (4 ± 0.5) Å (see also Refs. 1, 9, and 10). Equation (74) allows us to make a rough estimation of the characteristic temperature T_2 of the transition from the TA to AA hopping regimes,³¹ in accordance with experimental data,⁹ to be several times smaller than $\hbar\omega_0 \approx 300$ K.

Due to large polaron shifts, the characteristic frequency [Eq. (71)] of the transition from activation adiabatic (AA) to activation-nonadiabatic (ANA) regimes is very small (< 1 Hz). For the same reason, the characteristic temperature T_1 [Eq. (59)] that corresponds to the AA-ANA transition and, therefore, to the minimum in the $s(T)$ dependence, is very high (> 200 K) in chalcogenide glasses. This explains why, to the best of our knowledge,^{1,9,10} neither the ANA mechanism nor the above-mentioned minimum have been observed there.

However, both the minimum in the $s(T)$ dependence and the maximum in the $n(T)$ dependence that are specific for small (bi)polaron hopping seem to be observed in amorphous germanium.^{8,9} This material is characterized by smaller polaron shifts, compared to chalcogenide glasses, and by the positive effective correlation energy U_{eff} that prevents electron coupling.

By means of formula (75) we evaluated the density of localized electronic states ρ_e participating in the low-temperature ac conductivity of $a\text{-As}_2\text{Se}_3$. Setting the localization radius $a \cong d \cong 2.4$ Å, and $J_0 = 2.8$ eV (see Ref. 30), as well as $W_p = 0.5$ eV, $\epsilon = 12$, $\omega_0 = 10^{13}$ Hz, $\omega = 10^4$ Hz, and $\sigma_1 \cong 10^{-12} \Omega^{-1} \text{cm}^{-1}$ (see Ref. 1), we obtained $\rho_e \cong 2 \times 10^{20} \text{cm}^{-3} \text{eV}^{-1}$. Since a typical depth Δ_t of the band-edge tails in chalcogenides is of the order of 0.2 eV (Ref. 1), the above-mentioned value of ρ_e can be used to show that the concentration of stretched bonds is of the order of $4 \times 10^{19} \text{cm}^{-3}$, which is only 0.01% of the overall bond concentration. We believe that this is not unreasonable for amorphous solids.

A comprehensive quantitative comparison of the results obtained in this paper to the experimental data on ac conductivity in As_2Se_3 will be published elsewhere.³² It allows us to conclude that small bipolaron hopping definitely manifests itself in chalcogenide glasses at quite low temperatures.

As in the case of the SP model,⁸ the presence of a high configuration barrier V strongly reduces the probability

(43) of SB hopping, thus reducing the characteristic size of the pairs participating in the ac conductivity up to several Å. This means that the typical energy of the Coulombic repulsion of two SB's, localized at a pair, is much greater than T . Therefore, the intersite Coulombic correlation effects,²¹ in contrast to the ac hopping conductivity involving shallow centers in crystalline semiconductors,^{1,33} play a crucial role in SB hopping at all temperatures, as has been assumed above.

A similar analysis might be made with respect to $a\text{-SiO}_2$ and $a\text{-Si}_3\text{N}_4$, although the detailed comparison needs much more elaborate experimental data. [For instance, in $a\text{-SiO}_2$, in qualitative accordance with the SB model, s also is very close to unity, while $n \ll 1$ (see Refs. 1, 2, and 9).]

Another extremely interesting application of the theory presented in this paper is likely to be connected to the recent experiments on the hopping transport of charged carriers both in molecularly doped polymers (MDP's) (Ref. 34) and crystalline $\text{La}_2\text{CuO}_{4+y}$ (see Ref. 35). (The latter might be viewed as a high- T_c superconducting material below the point of an insulator-to-metal transition.) It is very important that the transition from AA to ANA regimes of SP (or SB) hopping is first directly observed³⁴ in MDP simply by changing the concentration of dopants, which there is equivalent to changing the characteristic hopping length r . These experiments³⁴ also reveal a strong dependence of the (bi)polaron hopping activation energy V upon r that is typical for the AA regime in the case when $J_0 > 2W_p$ or W_p .

If so, then the ac conductivity measurements might also reveal the AA-ANA transition in MDP's by means of the minimum in the $s(T)$ dependence. To observe this minimum, a material with the concentration of dopants slightly lower than that corresponding to the AA-ANA transition observed in the dc experiments³⁴ should be used. For such a material, one could expect to find the intimate pairs with the barriers V strongly dependent upon the ac hopping distance $r_{\omega,T}$, as well as the distant pairs with the constant V effectively participating in hopping at low and high temperatures, respectively.

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