Alternating-current conductivity of amorphous semiconductors (two-site model of small polarons)

A. G. Petukhov and M. G. Foĭgel'

I. I. Mechnikov State University, Odessa

(Submitted 7 September 1988)
Zh. Eksp. Teor. Fiz. **95**, 1037–1048 (March 1989)

A theory of the dynamic conductivity is developed for amorphous semiconductors containing deep centers with a strong electron–phonon interaction. The frequency dispersion of the complex conductivity at acoustic frequencies is investigated employing a two-site model of small polarons. A distinguishing feature of this model is an exponential dependence of the polarizability of a pair of point defects and of the parameters of a configuration barrier, governing the relaxation time of a dipole, on the distance between the centers. The real part $\sigma_1 \propto \omega^s T^n$ of the complex conductivity is calculated for a wide range of temperatures T and frequencies ω. A classification is provided of the regimes of small-polaron hopping and each of these corresponds to specific temperature and frequency dependences of the power exponents s and n and also of the dielectric loss tangent. A comparison with experimental data for several amorphous and glassy semiconductors demonstrates that the dynamic (ac) conductivity of *a*-Ge and *a*-Ge:H is due to hopping of small polarons.

1. INTRODUCTION

Investigations of the ac conductivity $\sigma(\omega)$ provide important information on the nature of localized electron states in amorphous and glassy semiconductors.[1,2] At acoustic frequencies and low radio frequencies in the range $10^2 < \omega < 10^8$ Hz the real part of the conductivity is a monotonically rising function of the frequency and is described by a dependence of the type[2]

$$\operatorname{Re} \sigma(\omega, T) = \sigma_1(\omega, T) \propto \omega^s T^n, \tag{1}$$

where $s \lesssim 1$ and depends weakly on the frequency, whereas n is usually nonnegative. This dependence is normally interpreted by the Debye model of dielectric losses[3] due to reorientation of dipoles with a wide spectrum of relaxation times τ (Ref. 4). The role of dipoles in a disordered semiconductor or insulator may be played by close pairs of point defects with localized carriers. A periodic external electric field alters the populations of the centers forming a pair, which involves phonon-stimulated jumps of an electron from one center to another. We shall consider this specific relaxation mechanism, which should be distinguished from the resonance mechanism characterized by $s \approx 2$ (Refs. 1 and 5) and active at higher frequencies.

The simplest explanation of the dependence (1) is based on the concept of a sufficiently wide band of one-electron localized states, which is partly filled with electrons.[1,6] In this model the main contribution to $\sigma(\omega,T)$ comes from a pair of defects which correspond to states located on both sides of the Fermi level in a band of width T, much smaller than the width of an impurity band Δ_0. The optimal size of the pairs r_ω that dominate the conductivity at a frequency ω can be found from the condition

$$\omega\tau(r_\omega) = 1, \tag{2}$$

and the characteristic probability (per unit time) of a tunnel jump of an electron from center to center is

$$\nu(r) = \tau^{-1}(r) = \nu_0 \exp(-2r/a), \tag{3}$$

where r is the distance between the centers; a is the localization radius of a carrier; $\nu_0 \approx 10^{10}$–10^{12} s^{-1} is of the order of the frequency of local phonons and depends weakly on r and T (Ref. 1). In this case the dynamic conductivity is described satisfactorily by the familiar Austin–Mott expression[1,6] characterized by the following power exponents

$$s = 1 - 4 \ln^{-1}(\nu_0/\omega), \quad n = 1. \tag{4}$$

We can see that the value of s is independent of temperature and for typical frequencies of $\omega \approx 10^6$ Hz it is close to 0.8.

In the case of amorphous and glassy semiconductors at low (usually helium) temperatures the value of $\sigma_1(\omega)$ is practically independent of temperature, i.e., we have $n \ll 1$, in the index s is close to unity. On increase in temperature the power exponent s decreases somewhat and the value of n rises reaching a few units.[2] Allowance for the Coulomb correlations of the level populations by Éfros[7] modifies the Austin–Mott formula so that if $T < e^2/\varkappa r_\omega$, where $\varkappa$ is the permittivity of the material and e is the electron charge, the power exponents are given by

$$s = 1 - 3 \ln^{-1}(\nu_0/\omega), \quad n = 0, \tag{5}$$

whereas for $T > e^2/\varkappa r_\omega$, we still have Eq. (4). This result in qualitative agreement with the dependences $s(T)$ and $n(T)$ observed experimentally for a number of glassy semiconductors,[2] but it yields $s < 1$ and $n \ll 1$.

These dependences were explained by Elliott[8] by developing the concept of thermally activated electron jumps from one attractive center to another across a Coulomb barrier separating the centers. The height of this barrier is

$$V(r) = V_{max} - 4e^2/\varkappa r, \tag{6}$$

where $V_{\max}$ is the ionization energy of an isolated center, which decreases on the reduction in the distance r between the centers. The probability of a jump

$$\nu(r) = \tau^{-1}(r) = \nu_0 \exp[-V(r)/T] \tag{7}$$

0038-5646/89/030597-07$04.00

then rises exponentially. In processes of this type the barrier height depends on the distance and the barrier is overcome by thermal activation called correlated barrier hopping (CBH).[2,8] In the case of the CBH models, we have[2]

$$s=1-\frac{6T}{V_{max}}\left(1-\frac{V_\omega}{V_{max}}\right)^{-1}, \tag{8}$$

where

$$V_\omega=T\ln(\nu_0/\omega) \tag{9}$$

is the optimal barrier for pairs that dominate the conductivity at a frequency ω. The barrier height is determined from the condition $\omega\tau(V_\omega)=1$. In this case the power exponent n describing the temperature dependence of $\sigma_1(\omega,T)$ in Eq. (1) is

$$n=m+(1-s)\ln(\nu_0/\omega). \tag{10}$$

Here the parameter m has the values 0, 1, or 2, depending on the statistics of the pair occupancy, on the width of the impurity band Δ_0, and on correlations in the spatial distribution of the centers. For example, in the case of an uncorrelated distribution of impurities, forming a fairly wide energy band, it is found that at high temperatures $e^2/\varkappa r_\omega \ll T \ll \Delta_0$, when the Coulomb correlations between the populations of the centers are unimportant, we find that $m=2$ (Ref. 2). At low temperatures such that $T \ll e^2/\varkappa r_\omega$ Δ_0, we have $m=1$. Finally, in the case of a narrow energy band with $\Delta_0 \ll T$, we find that $m=0$. We can demonstrate that the relationship (10) between the power exponents s and n is universal for all models of the CBH type (see Ref. 2) and is indepenent of the actual form of $V(r)$.

According to Eqs. (2), (6), (7), and (9), the optimal size of the pairs contributing to the conductivity at the frequency ω in the Elliott model[8] is

$$r_\omega=\frac{4e^2}{\varkappa V_{max}}\left(1-\frac{V_\omega}{V_{max}}\right)^{-1}. \tag{11}$$

In the case of amorphous and glassy semiconductors, for which the Fermi level is located near the middle of the band gap E_g, we have $V_{\max}\approx E_g/2\approx 1$ eV. This means that $V_\omega \ll V_{\max}$, and $r_\omega \approx 4$–5 Å. The characteristic size of a pair r_ω obtained in this way is of the order of the localization radius a of a carrier at a deep center. Therefore, the Coulomb correlations in the populations of the centers, as well as the quantum-mechanical tunneling effects[7] and the electron–phonon interaction (if the latter is important) play a dominant role in such materials. It seems to us that a better approach is that in which such close pairs of deep centers are described by a two-site model of small polarons,[9,10] especially as electrical and optical properties of amorphous and glassy semiconductors are governed mainly by the large number of deep centers with a strong electron–phonon interaction which are present in these materials.[1]

Our aim will be to analyze the dynamic (ac) conductivity of amorphous semiconductors using such a two-site small-polaron model. We shall consider the approximation of the closest pairs, i.e., those with the shortest internal distance, because it is known that this approximation is valid at sufficiently high frequencies when the size r_ω is definitely less than the characteristic distance between the centers. It should also be noted that the two-site small-polaron model can be generalized in a natural manner to the case of small bipolarons.

2. TWO-SITE SMALL-POLARON MODEL

We shall consider an isolated pair of centers 1 and 2 separated by a distance r. We shall assume that one electron is localized at this pair. The Hamiltonian of such a system considered in the representation of the creation and annihilation operators a_i^+ and a_i of an electron at the sites $i=1$ or 2 is written in the form[9,10]

$$H=\frac{P^2}{2\mu}+\frac{1}{2}\mu\omega_0{}^2Q^2+\frac{1}{2}(\Delta-\lambda Q)(n_1-n_2)$$

$$+J(r)(a_1{}^+a_2+a_2{}^+a_1), \tag{12}$$

where $n_i=a_i^+a_i$ is the occupation number of a site i; μ is the reduced mass of the atoms forming the investigated pair; ω_0 is the frequency of a local phonon corresponding to an asymmetric mode Q interacting with the electron subsystem; $P=-i\hbar\partial/\partial Q$ is the momentum which is conjugate with the configuration coordinate Q; λ is the electron–phonon interaction constant (deformation potential); $J(r)$ is the electron transport (tunneling) integral; $\Delta=\varepsilon_1-\varepsilon_2$ is the difference between the one-electron energies. The energy of the system is measured from $(\varepsilon_1+\varepsilon_2)/2$.

We shall analyze the adiabatic potential $E_r(Q)$ of the ground state of a pair of size r in the symmetric case when $\varepsilon_1=\varepsilon_2$, i.e., $\Delta=0$. We shall demonstrate below that these are the pairs that dominate the contribution to $\sigma(\omega)$. Introducing a dimensionless configuration coordinate $q=Q\mu\omega_0^2/2\lambda$ and diagonalizing the electronic part of the Hamiltonian (12), we obtain (Fig. 1)

$$E_r(q)={}^1/_2W[1+{}^1/_2(q^2-\xi_r{}^2)-(1+q^2-\xi_r{}^2)^{1/2}], \tag{13}$$

where

$$W=\lambda^2/4\mu\omega_0{}^2 \tag{14}$$

is the polaron shift and

$$\xi_r=(1-|J(r)|^2/W^2)^{1/2}. \tag{15}$$

In Eq. (13) the energy $E_r(q)$ is measured from the minimum value of the adiabatic potential, i.e., $E_r^{\min}=0$.

In the case of very large pairs (those with very large internal distances), when $|J(r)|\ll W$, we have $\xi_r\approx 1$ and the adiabatic potential represents two shifted parabolas with minima near the points $q_{\min}=\pm\xi_r\approx\pm 1$ separated by a barrier $V\approx V_{\max}=W/2$. As r is reduced, the tunneling integral in the range $r>a$ rises steeply in accordance with the law[5]

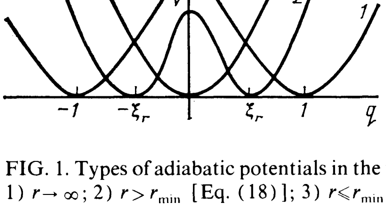

FIG. 1. Types of adiabatic potentials in the two-site small-polaron model: 1) $r\to\infty$; 2) $r>r_{\min}$ [Eq. (18)]; 3) $r\leqslant r_{\min}$.

$$J(r)=J_0\exp(-r/a), \tag{16}$$

where a is the localization radius of an electron at a center. Therefore, the height of a barrier separating minima of the potential located at the points $q_{\min}=\pm\xi_r$ decreases:

$$V(r)={}^1/_2W(1-|J(r)|/W)^2. \tag{17}$$

Finally, if

$$r\leqslant r_{min}=a\ln(|J_0|/W),\quad |J_0|>W, \tag{18}$$

where $r_{\min}$ is part of the condition $\xi(r_{\min})=0$, the barrier between the minima disappears so that the adiabatic potential becomes of the single-well type. (However, if $|J_0|\leqslant W$, then $r_{\min}=0$.)

If $r>r_{\min}$, each of the two minima of the adiabatic potential shown in Fig. 1 corresponds to an asymmetric distribution of the electron density shifted toward one of the centers. This shift can be regarded as the localization of a small radius polaron at a center. According to Holstein,[9] such localization cannot be described by the Hamiltonian (12), but it appears because of the interaction of an impurity quasimolecule with the lattice phonons (thermostat) and this in fact ensures jumps of a polaron from site to site. However, it is important to note that the change in the dipole moment of the system due to small-polaron jumps is

$$p(r)=e|\alpha_1{}^2(r)-\alpha_2{}^2(r)|r=e\xi_r r, \tag{19}$$

where $\alpha_1(r)$ and $\alpha_2(r)$ are the coefficients of the expansion of the wave function of an electron localized on a pair of centers at $q=q_{\min}=\pm\xi_r$, in terms of the wave functions of the centers 1 and 2. Therefore, the quantity $e\xi_r<e$ introduced by Eq. (15) represents the effective transferred charge, which is generally less than the charge of an electron e. The reason for this is a partial sharing of an electron between the centers because of the tunneling effect. Therefore, in particular, pairs of size $r\leqslant r_{\min}$ with the dipole moment $p=\xi_r=0$ make no contribution to the dynamic conductivity.

At high temperatures the jump of a polaron from the center 1 to the center 2 for a symmetric pair of size $r>r_{\min}$ involves thermally activated overcoming of a barrier V described by Eq. (17). Depending on the nonadiabaticity parameter

$$\eta(r)=|J(r)|^2/\hbar\omega_0(VT)^{1/2}, \tag{20}$$

it is usual to distinguish two types of jumps in the small-polaron theory: adiabatic ($\eta\gtrsim1$) and nonadiabatic ($\eta\ll1$) (for details see Refs. 9–12). In the nonadiabatic case when the electron transport integral is very small and can be regarded as a perturbation, the probability of a jump per unit time is

$$w_{12}(r)=w_{21}(r)=w_s(r)=\pi^{1/2}\nu_0\eta(r)\exp(-W/2T). \tag{21}$$

In the adiabatic case, we have

$$w_{12}(r)=w_{21}(r)=w_s(r)=\nu_0\exp[-V(r)/T]. \tag{22}$$

In contrast to Ref. 12, we shall describe the adiabatic case using the exact expression (17) for $V(r)$ and not its limiting value $V_{\max}=W/2$, because in the case of deep intrinsic defects in amorphous semiconductors we have $|J_0|\gtrsim E_g>W$ (we shall discuss this assumption in Sec. 6).

In the case of slightly asymmetric pairs with $\Delta\ll V$, in the calculations we can assume (see Ref. 2)

$$w_{12}(r)=w_s(r)\exp(-\Delta/2T),\quad w_{21}=w_s(r)\exp(\Delta/2T). \tag{23}$$

3. CALCULATION OF $\sigma_1(\omega)$. HIGH TEMPERATURES

The expression for the complex ac conductivity can be obtained in the pair approximation by calculating the polarizability of a pair of centers of size r with a scatter of unrenormalized energies Δ (Ref. 7). After integration with respect to r and Δ, followed by averaging over the pair orientations, we find that

$$\sigma(\omega)=\frac{4\pi i\omega}{3T}\int\limits_{r_{min}}^{\infty}dr\,r^2p^2(r)\int\limits_0^{\infty}\frac{d\Delta\Phi(r,\Delta)}{\mathrm{ch}^2(\Delta/2T)(1+i\omega\tau(r,\Delta)]}, \tag{24}$$

where $p(r)$ is given by Eq. (19). If $T\gg\hbar\omega_0$, the relaxation time calculated using Eq. (23) is

$$\tau(r)=[w_{12}(r)+w_{21}(r)]^{-1}=[2w_s(r)\mathrm{ch}(\Delta/2T)]^{-1}. \tag{25}$$

The function

$$\Phi(r,\Delta)=F(r,\Delta)f(r) \tag{26}$$

is selected so that $4\pi r^2\Phi(r,\Delta)dr d\Delta$ is the number of closest pairs (per unit volume) with sizes between r and $r+dr$ and their scatter of the level energies from Δ to $\Delta+d\Delta$ found on the assumption that only one electron is localized at each pair. The function $f(r)$ in Eq. (26) allows for spatial correlations in the relative positions of the centers. [In the absence of such correlations we have $f(r)=1$.] The function $F(r,\Delta)$ describing the Coulomb correlations of the occupied centers, is calculated in Ref. 7:

$$F(r,\Delta)=g^2(\mu)\begin{cases}\dfrac{\Delta}{\mathrm{th}(\Delta/2T)}, & T>e^2/\varkappa r, \quad (27\mathrm{a})\\ \Delta+e^2/\varkappa r, & T<e^2/\varkappa r, \quad (27\mathrm{b})\end{cases}$$

where $g(\mu)$ is the density of one-electron states at the Fermi level μ. (We shall show later that the characteristic energy of the Coulomb repulsion of electrons localized at the nearest sites is $e^2/\varkappa r_\omega>T$ in the small polaron model.)

We shall consider first the adiabatic hopping regime ($\eta\gtrsim1$). Using Refs. (15)–(17), (22), (23), and (25), we go over in Eq. (24) from integration with respect to r to integration with respect to V:

$$\begin{aligned}&r(V)\equiv r_V=r_{min}-a\ln[1-(2V/W)^{1/2}],\\&\xi^2(V)=(2V/W)^{1/2}[2-(2V/W)^{1/2}].\end{aligned} \tag{28}$$

Here and later we are ignoring the dependence $\tau(\Delta)$ [see Eq. (23)] because the main contribution to the conductivity comes from pairs characterized by $V\gg\Delta\approx T$. Substituting Eq. (28) into Eq. (24), we obtain the following expression for the real part of the conductivity:

$$\sigma_1(\omega)=\mathrm{Re}\,\sigma(\omega)=\frac{2^{3/2}\pi e^2\omega a}{3}\int\limits_0^{V_0'}\frac{dV\,r_V{}^4\xi^2(V)f(r_V)}{V^{1/2}[W^{1/2}-(2V)^{1/2}]}$$

$$\times\frac{\omega\tau(V)}{1+\omega^2\tau^2(V)}\int\limits_0^{\infty}\frac{d\Delta F(\Delta,r_V)}{T\,\mathrm{ch}^2(\Delta/2T)}, \tag{29}$$

where the upper integration limit $V_0' < W/2$ is found from the condition of going over to the nonadiabatic regime: $\eta(V_0') \approx 1$ [see Eq. (20)].

A strong (exponential) dependence $\tau(V)$ of the integral in Eq. (29) is characterized by a sharp maximum at the point $V = V_\omega$ of Eq. (9), which was found from the condition $\omega\tau(V_\omega) = 1$. Consequently, bearing in mind that $d\tau/\tau = dV/T$, we could carry out integration with respect to V. Substituting Eq. (27) into Eq. (29), we can integrate also with respect to Δ. Consequently, allowing for the Coulomb correlations in the populations of the defects, which are important when $T < e^2/\varkappa r_\omega$, we obtain

$$\sigma_1(\omega) = \frac{2\pi^2 e^4 a}{3V_{max}\varkappa} T\omega r_\omega^3 g^2(\mu) f(r_\omega)\left[1 + (1 - y_\omega)^{-1}\right], \quad (30)$$

where

$$y_\omega = (2V_\omega/W)^{1/2} < 1, \quad V_\omega = T\ln(\nu_0/\omega) < W/2,$$

and $r_\omega = r(V_\omega)$ [see Eq. (28)]. It follows from Eq. (30) that in the case of a random distribution of defects ($f = 1$) the power exponent is

$$s = 1 - \frac{y_\omega}{2\ln(\nu_0/\omega)}\left[\left(1 + 3\frac{a}{r_\omega}\right)\frac{1}{1 - y_\omega} - \frac{1}{2 - y_\omega}\right]. \quad (31)$$

The other power exponent n is given by Eq. (10) with $m = 1$. It should be pointed out that the universality of Eq. (10) in fact follows from the temperature and frequency dependences of the optimal barrier given by Eq. (9), which is universal for all the models of the CBH type.

At sufficiently low temperatures such that

$$T \ll T_1(\omega) = W/2\ln(\nu_0/\omega) \quad (32)$$

we have $y_\omega \ll 1$ so that

$$s(T) \approx 1 - \left[\frac{T}{8W\ln(\nu_0/\omega)}\right]^{1/2}\left(1 + 6\ln^{-1}\frac{|J_0|}{W}\right), \quad (33)$$

if, of course the barrier can be overcome by thermal activation at these temperatures.

In the nonadiabatic regime for which η of Eq. (20) is much less than unity, the relaxation time is described by Eq. (25) with w_s of Eq. (21). Integrating Eq. (24) with respect to r and Δ and bearing in mind that $p(r) = er$, we obtain (see also Ref. 2) the following expression for the conductivity if $T < e^2/\varkappa r_\omega$, T_1 in Eq. (32):

$$\sigma_1(\omega) = \frac{\pi^2 e^4 a}{6\varkappa}\omega r_\omega^3 g^2(\mu) f(r_\omega), \quad (34)$$

where

$$r_\omega = \frac{a}{2}\left[\ln\left(\frac{\nu_0'}{\omega}\right) - \frac{W}{2T}\right], \quad \nu_0' = \nu_0\frac{|J_0|^2}{\hbar\omega_0}\left(\frac{2\pi^3}{WT}\right)^{1/2}. \quad (35)$$

In the case of small polaron shifts $\hbar\omega_0 < W < 2T\ln(\nu_0'/\omega)$ if $f = 1$, these expressions reduce to the Éfros formula if we allow for renormalization of the constant ν_0. At very high temperatures we find that the substitution $e^2/\varkappa r_\omega \to \frac{1}{4}\pi^2 T$ yields the familiar Austin–Mott expression.[1,2] We can readily see that

$$s = 1 - 3\left[\ln\left(\frac{\nu_0'}{\omega}\right) - \frac{W}{2T}\right]^{-1}, \quad n = 3\left[\frac{2T}{W}\ln\left(\frac{\nu_0'}{\omega}\right) - 1\right]^{-1}. \quad (36)$$

It follows from Eqs. (17) and (20) that at a fixed frequency ω the adiabatic case characterized by $\eta \gtrsim 1$ applies at temperatures

$$T \lesssim T_1^*(\omega) \approx T_1(\omega)\left[1 - \left(\frac{2\hbar\omega_0}{W}\right)^{1/2}\ln^{-1/4}\frac{\nu_0}{\omega}\right], \quad (37)$$

where $T_1(\omega)$ is described by Eq. (32). However, the nonadiabatic case ($\eta \ll 1$) is known to occur at temperatures $T \gg T_1(\omega)$. Therefore, the transition from the nonadiabatic to the adiabatic case occurs at some temperature of the order of $T_1(\omega) \approx W[2\ln(\nu_0/\omega)]^{-1}$ which increases logarithmically on increase in the frequency ω. We can easily show that in the case of a random distribution of defects the conductivity $\sigma_1(\omega)$ measured at a fixed frequency does not decrease on increase in temperature.

4. CALCULATION OF $\sigma_1(\omega)$. LOW TEMPERATURES

At temperatures T much lower than that corresponding to the energy of a local phonon $\hbar\omega_0$ the jumps of a polaron from site to site involve tunneling under the potential barrier $E_r(q)$ described by Eq. (13). If the height of this barrier is $V \gg \hbar\omega_0$, then in the case of a symmetric pair in the semiclassical approximation the probability of a jump per unit time given by[13]

$$w_{12} = w_{21} = w_s(r) = \nu_0\exp\left[-2S_r(T)/\hbar\right], \quad (38)$$

where

$$S_r(T) = \int_0^{\hbar/2T}\left[\frac{W}{2\omega_0^2}\left(\frac{\partial q}{\partial\tau}\right)^2 + E_r(q)\right]d\tau \quad (39)$$

is the semiclassical effect for a subbarrier transition, and the dependence $q(\tau)$ is found from the Euclidean equation of motion[14]

$$\frac{\partial^2 q}{\partial\tau^2} - \frac{\omega_0^2}{W}\frac{\partial E_r(q)}{\partial q} = 0. \quad (40)$$

Equation (38) applies to the adiabatic case when

$$\eta = |J|^2/\hbar\omega_0 V \gg 1. \quad (41)$$

In the case of slightly asymmetric pairs characterized by $\Delta \ll V$ at temperatures $T \lesssim \hbar\omega_0$, we have

$$w_{12} = w_s\exp(-\Delta/T), \quad w_{21} = w_s, \quad (42)$$

so that the reciprocal of the relaxation time is

$$\tau^{-1}(r) = w_{12} + w_{21} = w_s\left[1 + \exp(-\Delta/T)\right]. \quad (43)$$

In the nonadiabatic case when η of Eq. (41) is much less than unity, Eqs. (38), (42), and (43) should be multiplied by η. At low temperatures the dynamic conductivity is described, as before, by general expressions given by Eqs. (24), (26), and (27).

In the adiabatic case at low temperatures the main contribution to the conductivity comes from pairs with sufficiently low and narrow barriers. This makes it possible to represent the function $E_r(q)$ [Eq. (13)] as a Landau expansion in powers of $|q^2 - \xi_r^2| < 1$. If we confine ourselves to the first term of the series, we obtain

$$E_r(q) = {}^1/_8 W(q^2 - \xi_r^2)^2, \quad (44)$$

where ξ_r is described by Eq. (15). Then, introducing

$x = q/\xi_r$ and $\tau' = \omega_0\tau/\sqrt{2}$, we obtain

$$S_r(T)=\frac{W\xi_r^3}{\omega_0\sqrt{2}}\,g(y), \qquad (45)$$

where $y = \hbar\omega_0\xi_r/2\sqrt{2}\,T$ and

$$g(y)=\int_0^y\left[\frac{1}{2}\left(\frac{\partial x}{\partial\tau'}\right)^2+\frac{1}{4}\,(x^2-1)^2\right]d\tau. \qquad (46)$$

Then, using Eq. (40) we find that at low temperatures in the range

$$T<T_2(\omega)=\xi(\omega)\hbar\omega_0, \qquad (47)$$

where

$$\xi(\omega)=\left[\frac{3\hbar\omega_0}{4W}\ln\left(\frac{\nu_0}{\omega}\right)\right]^{1/3}, \qquad (48)$$

we have

$$S_r(T)\approx S_r(0)=\frac{g(0)\,W\xi_r^3}{\omega_0\sqrt{2}}=\frac{2W\xi_r^3}{3\omega_0}. \qquad (49)$$

Equation (48) for $\xi(\omega)$ is obtained subject to the condition $\omega\tau(r_\omega) = 1$. At high temperatures $T> T_2$ [Eq. (47)] it follows from Eq. (45) that

$$S_r(T)=\hbar W\xi_r^4/16T=\hbar V(r)/2T, \qquad (50)$$

i.e., using the expression for the barrier height $V(r)$ [Eq. (17)] at low values of ξ_r, we again obtain from Eq. (38) the expression (22) for the probability of a subbarrier transition. Therefore, Eqs. (38), (40), (45), and (46) describe hf dynamics of small-polaron jumps at any temperature.

Substituting Eqs. (43) and (27b) into Eq. (24), and integrating with respect to r and Δ, we find with the aid of Eqs. (38), (42), and (49) that at temperatures in the range $T<\hbar\omega_0\xi(\omega)<e^2/\varkappa r_\omega$ and at sufficiently high frequencies satisfying the condition $\xi^2(\omega)\ll 1$, the real part of the conductivity is given by the expression

$$\sigma_1(\omega)\approx\frac{8\pi^2e^4a}{9\varkappa}\left(\frac{3\hbar\omega_0}{W}\right)^{4/3}g^2(\mu)\,r_{min}^3\ln^{1/3}\left(\frac{\nu_0}{\omega}\right)\omega, \qquad (51)$$

where $r_{\min}$ is described by Eq. (18).

Equation (51) corresponds to

$$s=1-\frac{1}{3\ln(\nu_0/\omega)}, \qquad n=0. \qquad (52)$$

We can easily show that in this case, when the barrier is overcome by tunneling, the relationship (10) between s and n is not obeyed.

It should be pointed out that the condition $\xi^2(\omega)\ll 1$ is necessary and sufficient for the use of the adiabatic potential $E_r(q)$ in the form given by Eq. (44), which can be employed in an analytic approximation for an expression for $\sigma_1(\omega)$. We can easily show that the inequality $\xi^2(\omega)\ll 1$ is in fact equivalent to the inequality (41). Therefore, the adiabatic case corresponds to $\xi(\omega) < 1$, i.e., it corresponds to

$$\omega>\omega_1\approx\nu_0\exp(-4W/3\hbar\omega_0). \qquad (53)$$

On the other hand, the condition of validity of the semiclassical description is

$$\hbar\tilde{\omega}_0={}^1/_4\hbar\omega_0\xi(\omega)<V={}^1/_8W\xi^4(\omega), \qquad (54)$$

where $\tilde{\omega}_0$ is the frequency of a local phonon renormalized by the tunneling effect and this phonon corresponds to one of the equilibrium positions $q_{\min} = \pm\xi$. The inequality of Eq. (54) is known to be satisfied when

$$\omega<\omega_2=\nu_0\exp(-{}^8/_3). \qquad (55)$$

We can easily see that in the case of materials with a sufficiently large polaron shift $W> 2\hbar\omega_0$ the frequency integral $\omega_1<\omega<\omega_2$ in which the adiabatic description is valid can be exponentially large.

If $\omega<\omega_1$, we have the nonadiabatic case when the probability of a jump is given by Eq. (3) and the constant is renormalized to[9]

$$\nu_0\to\tilde{\nu}_0=\nu_0\frac{2\pi|J_0|^2}{\hbar\omega_0W}\exp\left(-\frac{2W}{\hbar\omega_0}\,\mathrm{th}\,\frac{\hbar\omega_0}{4T}\right)\times\begin{cases}1, & T<\dfrac{\hbar\omega_0}{4}\\ \left(\dfrac{\pi W}{\hbar\omega_0}\,\mathrm{sh}\,\dfrac{\hbar\omega_0}{2T}\right)^{1/2}, & T>\dfrac{\hbar\omega_0}{4}\end{cases} \qquad (56)$$

Therefore, in this case we can describe $\sigma_1(\omega)$ by means of the Austin–Mott–Éfros formula (34) with the renormalized optimal size of pairs:.

$$r_\omega=(a/2)\ln(\tilde{\nu}_0/\omega). \qquad (57)$$

5. TANGENT OF THE ANGLE OF DIELECTRIC LOSSES

The general expression for the complex conductivity of Eq. (24) makes it possible (see Ref. 2) to find its imaginary path $\sigma_2(\omega, T)$ and to determine the loss-angle tangent:

$$\mathrm{tg}\,\psi=\sigma_2/\sigma_1=\mathrm{Im}\,\sigma/\mathrm{Re}\,\sigma. \qquad (58)$$

In particular, in the adiabatic case at low temperatures $T<T_2$ defined by Eq. (47), we have

$$\mathrm{tg}\,\psi=(3/2\pi)\ln(\nu_0/\omega), \qquad (59)$$

whereas at temperatures $T> T_2$, we find that

$$\mathrm{tg}\,\psi=(2/3\pi)\ln(\nu_0/\omega)\,[5-2s(T)]. \qquad (60)$$

It should be noted that Eq. (60) is derived on the assumption that $T\ll T_1(\omega)$ where the dependence $s(T)$ is described by Eq. (33).

In the nonadiabatic case we have

$$\mathrm{tg}\,\psi=(1/2\pi)\ln(\tilde{\nu}_0/\omega), \qquad (61)$$

where $\tilde{\nu}_0(T)$ is given by Eq. (56).

6. DISCUSSION OF RESULTS AND COMPARISON WITH THE EXPERIMENTAL DATA

We analyzed above the frequency and temperature dependences of the ac conductivity in semiconductors and insulators characterized by a fairly wide band of localized states which is partly filled with small polarons. In other words, we assumed that the Fermi or quasi-Fermi level is inside the polaron energy band. This may occur in high-resistivity crystalline semiconductors compensated by deep impurities with a strong electron–phonon interaction[15,16] and also in p- or n-type samples of amorphous hydrogenated silicon (a-Si:H) and germanium (a-Ge:H). In the latter case the ac conductivity is due to jumps of small polarons between vacant or singly filled states of dangling bonds in Si and Ge, which act as deep-level centers with a positive two-electron correlation energy.[1,2,17] In the case of glassy chalcogenide semiconductors the very strong electron–phonon interaction ensures that the pairing of polarons at one center is preferred from the energy point of view, i.e., that small bipolarons are formed.[1] Therefore, polarons contribute to the ac conductivity mainly at high temperatures or under strong equilibrium conditions, when bipolarons begin to dissociate effectively.[1,2] Consequently, in order to ensure that the results obtained describe the polaron conductivity in glassy chalcogenide semiconductors in the absence of excitation, the expressions for $\sigma(\omega)$ must be multiplied by $\exp(-|U_{\text{eff}}|/2T)$, where $U_{\text{eff}} \approx -1$ eV is a two-electron effective correlation energy.

A typical energy of local phonons $\hbar\omega_0$ in amorphous semiconductors and insulators is of the order of 0.02–0.04 eV and typical values of the polaron shifts are $W \approx 0.1$–0.5 eV (Refs. 1 and 17). Therefore, the semiclassical description of the process of jumps of a carrier from center to center used above is valid provided $\hbar\omega_0/W \ll 1$.

The presence of a high configuration barrier (of the order of $W/2$) reduces strongly the probability of polaron jumps and, therefore, a typical length of a jump. Estimates indicate that at frequencies in the range $\omega \approx 10^3$–10^8 Hz the characteristic dimensions r_ω of pairs governing $\sigma(\omega)$ are of the order of 5–10 Å. It follows that the energy of the Coulomb repulsion between two polarons localized at a pair of defects is given by $e^2/\varkappa r_\omega$ (Ref. 7) and this is of the order of 1 eV, which is many times greater than the value of T. Consequently, in contrast to hopping conduction involving shallow levels,[6,7] the Coulomb correlation effects are important at all temperatures.

The dependences $\sigma_1 \propto \omega^s T^n$ and $\tan\psi(\omega,T) = \sigma_2/\sigma_1$ can be analyzed conveniently by means of the ω–T diagram shown in Fig. 2. [Strictly speaking, the separation into regions shown in this figure is meaningful only for points sufficiently far from the curves. Therefore, these "phase" curves represent in reality bands within which a smooth transition takes place from one case to another.]

At sufficiently high frequencies such that $\omega > \omega_1$ in Eq. (53) and sufficiently low temperatures so that $T < T_2$ in Eq. (47), we have the tunnel adiabatic jumps [see Eqs. (51) and (59)] characterized by $n = 0$ and by $\frac{7}{8} < s < 1 - \hbar\omega_0/4W$ when the latter is very close to unity [Eqs. (52) and (55)]. When temperature is increased, we have the activated adiabatic case when $\sigma_1(\omega,T)$ is described by Eq. (30) and $\tan\psi(\omega,T)$ is described by Eq. (60). Equation (30) is characterized by $n = 1$ and s of Eq. (31), where $s < 1$ and, like $\tan\psi$, it decreases on increase in temperature. A further increase in temperature in the range $T > T_1$ of Eq. (32) results in transition to the activated nonadiabatic case [Eqs. (34) and (61)]. In this case [see Eq. (36)] quantities $s < 1$ and $\tan\psi$ begin to increase with temperature whereas the power exponent n reaches several units and falls with temperature. Therefore, in the hf range defined by $\omega > \omega_1$ the temperature dependence $s(T)$ has a minimum, whereas $n(T)$ has a maximum at $T \approx T_1$ of Eq. (32), both of which shift toward higher temperatures on increase in the frequency.

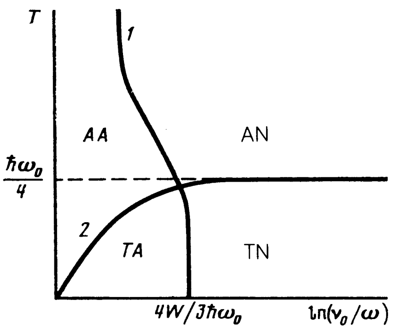

FIG. 2. Schematic form of the temperature–frequency diagram describing the various mechanisms of hopping of small polarons: TA—tunnel adiabatic; AA—activated adiabatic; TN—tunnel nonadiabatic; AN—activated nonadiabatic. Curves 1 and 2 are described, respectively, by $T = T_1(\omega)$ of Eq. (32) and $T = T_2(\omega)$ of Eq. (47).

At low frequencies such that $\omega < \omega_1$ in Eq. 53, the conductivity is described by Eqs. (34) and (57) and $\tan\psi$ is given by Eq. (61). Then Eq. (57) corresponds to

$$s = 1 - 3\ln^{-1}(\tilde{v}_0/\omega), \tag{62}$$

$$n = \frac{3W}{2T\ln(\tilde{v}_0/\omega)\,\mathrm{ch}^2(\hbar\omega_0/4T)}, \tag{63}$$

where $\tilde{v}_0(T)$ is described by Eq. (56). We can see that in the nonadiabatic case the value of $s < 1$ rises on increase in temperature, whereas $n(T) > 0$ behaves nonmonotonically reaching its maximum value for $T \approx \hbar\omega_0$.

The fullest experimental data on the ac conductivity have been obtained for amorphous germanium (a-Ge).[2] We shall now analyze them.

A characteristic feature of amorphous germanium is a nonmonotonic temperature dependence of the power exponent s: at temperatures $T < 40$–100 K and for frequencies $\omega \approx 10^4$–10^5 Hz this quantity falls from 0.88–0.95 to 0.6–0.7 on increase in temperature and then exhibits a tendency to rise but all the time it remains less than unity. The power exponent n is of the order of 4 in the region of the minimum of $s(T)$ and at helium temperatures it approaches zero. At sufficiently high frequencies $\omega > \omega_1$ of Eq. (53) these dependences can be deduced quite satisfactorily from the small polaron model [see Fig. 2 and also Eqs. (52), (31), and (36) listed in the order of increasing temperatures]. Moreover, the presence of a minimum in the functional dependence $s(T)$, reported also for a-Si and a-As in Ref. 2, could not be explained by any other method.1)

The exception to this rule is the model proposed by Long[2] which combines contradictory ideas on large polarons (low temperatures) and small polarons (high temperatures), localized at the same defects. Moreover, this model is used to describe the effects observed in covalent (homopolar) semiconductors (Ge, Si, As) which the existence of polarons with a large radius r_0 is very problematic; the experimental results can be matched to the theory based on this model if we assume an anomalously small value of r_0 (of the order of few angstroms) and it fails to account for the low-temperature saturation of the dependence $s(T)$ which is due to the tunneling in the heavy subsystem (see Sec. 5).

It follows from Eqs. (31), (11), and (36) that particularly in the model of small polarons at sufficiently high temperatures, when jumps are thermally activated, the power exponents n and s depend only on the ratio T/W. This allows us to explain also the universal nature of the dependences

$n(T)$ and $s(T)$ for samples of a-Ge:H with different hydrogen concentrations[2] if we assume that an increase in the hydrogen concentration enhances the polaron shift. The values $W \approx 0.1$ eV obtained in this way agree with the barriers governing the characteristic frequency $\omega_c \sim \exp(-W/2T)$, which corresponds to a peak of dielectric losses $\sigma_1(\omega)/\omega$ (Ref. 2).

The small polaron model also accounts quantitatively for the experimentally determined loss-angle tangent of a-Ge if we assume that at $\omega \approx 10^4$ Hz the hopping is nonadiabatic and it is described by Eqs. (61), (34), and (57) with $W \approx 0.1$ eV, $\hbar\omega_0 \approx 0.01$ eV, and $\nu_0 \approx 10^{13}$ Hz.

We considered the ac conductivity due to small polarons in the case where the preexponential factor $|J_0|$ in the electron tunneling integral is greater than the polaron shift W. The opposite case ($|J_0| < W$) is analyzed in Ref. 12. We can easily show that in the latter case it follows from Ref. 12 that $s \to 0$ when $T \to 0$, and then this power exponent rises monotonically with increase in temperature. However, this behavior of $s(T)$ has not been observed in the case of amorphous and glassy semiconductors.[2]

As pointed out above, the ac conductivity at acoustic and low radio frequencies exhibited by glassy chalcogenide semiconductors[2,3] and clearly also by a-SiO$_2$ (Refs. 18 and 19) is due to the hopping of small bipolarons. Since bipolarons are essentially three-level systems,[20] a quantitative theory of $\sigma(\omega)$ involving bipolarons requires a separate discussion. Clearly, in this case the nonadiabatic hopping is not realized because of the large (of the order of $|U_{\text{eff}}| \approx 1$ eV) unreduced configuration barrier. However, the main features of the behavior of $\sigma(\omega, T)$ due to adiabatic jumps of small polarons, particularly the monotonic fall of $s(T)$ and the rise of $n(T)$ (Ref. 2), can be explained exactly as in the case of the small-polaron model.

The authors are grateful to V. G. Karpov, V. I. Perel', M. I. Klinger, B. I. Shklovskiĭ, and A. L. Éfros for valuable discussions.

[1)] For example, all the models of the CBH type,[2] including the model of Elliott,[8] predict either a monotonic fall of $s < 1$ on increase in temperature or a monotonic rise, but with the value $s > 1$.

---

[1] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed., Clarendon Press, Oxford (1979).

[2] A. R. Long, Adv. Phys. **31**, 553 (1982).

[3] H. Fröhlich, *Theory of Dielectrics*, 2nd ed., Clarendon Press, Oxford (1958).

[4] M. Pollak, Philos. Mag. **23**, 519 (1971).

[5] B. I. Shklovskiĭ and A. L. Éfros, Zh. Eksp. Teor. Fiz. **81**, 406 (1981) [Sov. Phys. JETP **54**, 218 (1981)].

[6] M. Pollak and T. H. Geballe, Phys. Rev. **122**, 1742 (1961).

[7] A. L. Éfros, Philos. Mag. B **43**, 829 (1981).

[8] S. R. Elliott, Philos. Mag. B **36**, 1291 (1977).

[9] T. Holstein, Philos. Mag. B **37**, 49 (1978).

[10] Y. A. Firsov (ed.), *Polarons* [in Russian], Nauka, Moscow (1975.)

[11] V. G. Karpov, Fiz. Tekh. Poluprovodn. **19**, 123 (1985) [Sov. Phys. Semicond. **19**, 74 (1985)].

[12] V. V. Bryksin and A. N. Samukhin, Fiz. Tverd. Tela (Leningrad) **29**, 178 (1987) [Sov. Phys. Solid State **29**, 98 (1987)].

[13] S. V. Meshkov, Zh. Eksp. Teor. Fiz. **89**, 1734 (1985) [Sov. Phys. JETP **62**, 1000 (1985)].

[14] S. Coleman, in: The Whys of Subnuclear Physics (Proc. Fifteenth Intern. School of Subnuclear Physics, Erice, Italy, 1977, ed. by A. Zichichi), Plenum Press, New York (1979), p. 805.

[15] A. G. Milnes, *Deep Impurities in Semiconductors*, Wiley, New York (1973).

[16] V. P. Kalinushkin, D. I. Munin, E. M. Omeljanovsky, *et al.*, Semicond. Sci. Technol. **2**, 379 (1987).

[17] L. A. Balagurov, É. M. Omel'yanovskiĭ, A. G. Petukhov, *et al.*, Fiz. Tekh. Poluprovodn. **21**, 1631 (1987) [Sov. Phys. Semicond. **21**, 987 (1987)].

[18] M. Meaudre and R. Meaudre, Phys. Rev. B **29**, 7014 (1984).

[19] K. Shimakawa and A. Kondo, Phys. Rev. B **29**, 7020 (1984).

[20] A. G. Petukhov, Fiz. Tekh. Poluprovodn. **22**, 527 (1988) [Sov. Phys. Semicond. **22**, 323 (1988)].

Translated by A. Tybulewicz