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Low-temperature ac conductivity of adiabatic small-polaronic hopping in disordered systems

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Electronic hopping is commonly treated as occurring between localized states that are so widely separated that the motion is limited by the electronic transfer energy linking the sites. Then, the jump rate is usually assumed to fall exponentially with increasing intersite separation. However, this approach is inappropriate in many situations where the separation between the hopping sites is small enough that electronic carriers *adiabatically* follow the atomic motion. For adiabatic motion, the jump rates are essentially independent of intersite separation. Here the low-temperature ac conductivity for adiabatic small-polaronic hopping between close pairs of sites is calculated presuming a distribution of local site energies. Low-temperature relaxation of each such carrier is assumed to occur primarily through the emission of a very-low-energy acoustic phonon. For small-polaronic hops, low-temperature one-phonon emission rates are extremely slow. Dispersion of the transition rates arises from the dependence of the relaxation rates on the energy separations between the sites. In the low-temperature limit, the polarization conductivity is proportional to both temperature and frequency. Above this low-temperature limit, the severity of this temperature dependence increases with increasing temperature. In this higher-temperature regime, the temperature dependence of the conductivity also decreases as the frequency is increased. These results are in accord with observations in many systems with hopping conduction, including those for which there is explicit evidence of adiabatic small-polaronic hopping (e.g., *p*-type MnO, boron carbides, and many transition-metal-oxide glasses).

I. INTRODUCTION

Phonon-assisted electronic hops may be divided into four categories. These four categories result from the two pairs of complementary regimes that define the electronic and vibrational dynamics associated with a jump. First, a hop is either *small-polaronic* or *nonpolaronic*. Second, a hop is either *adiabatic* or *nonadiabatic*. Taken together these two dichotomous situations define four distinct types of electronic hops: adiabatic or nonadiabatic small-polaronic hops as well as adiabatic or nonadiabatic nonpolaronic hops.

A *small-polaronic* hop is one that involves at least one small-polaronic state, an electronic state with a strong net electron-lattice coupling. Since an electronic state is generally strongly coupled only to vibrational modes with wavelengths that exceed the electronic state's spatial extent,[1-3] a severely localized electronic state has a strong net electron-lattice coupling strength. By contrast a *nonpolaronic* hop involves only nonpolaronic states, states with weak net electron-lattice coupling strengths. Nonpolaronic hops exclusively involve large-radius electronic states, states that encompass very many atoms. The atomic transition-metal-ion states between which hopping occurs in transition-metal-oxide glasses are small polaronic.[4] However, the large-radius shallow donors and acceptors in silicon and germanium are nonpolaronic.[1,3]

The temperature dependences of the hopping mobility at high enough temperatures distinguish small-polaronic hops from nonpolaronic hops. At temperatures above a fraction ($\approx\frac{1}{3}$) of the characteristic phonon temperature, small-polaronic hops predominantly involve the absorption and emission of very many phonons.[2,3,5] Small-polaronic hopping yields thermally activated mobilities with activation energies that typically lie between 0.1 and 1 eV. However, nonpolaronic hops, dominated by the absorption or emission of a single phonon, have jump rates that only increase linearly with temperature in this temperature regime.[1,3] In other words, the "differential activation energy" associated with nonpolaronic hopping rises to a value in this temperature regime that is only the thermal energy $k_B T$, where k_B is the Boltzamnn constant and T is the temperature. Thus, the temperature dependence associated with the hopping mobility, at say room temperature, indicates whether the hopping is small polaronic or nonpolaronic. With this criterion, hopping observed above cryogenic temperatures is typically small-polaronic hopping.[6-8]

As the temperature is lowered below this "semiclassical" thermally activated regime, the temperature dependence of a small-polaronic jump rate becomes progressively milder.[2,3] This "multiphonon freeze-out" phenomenon provides a non-Arrhenius temperature dependence that is qualitatively similar to that often ascribed to variable-range hopping.[9] Generally, the freezing out of multiphonon processes and the percolative aspects of hopping in a disordered material act in tandem and produce similar effects.[2] Frequently, the temperature dependence of the dc conductivity is nearly independent of changes that should affect percolative aspects of hopping (e.g., altered disorder or dimensionality).[10] One then infers that the multiphonon-freeze-out phenomenon is the dominant effect at the temperatures where this behavior is observed.[11]

Adiabatic hops occur between sites between which the electronic transfer energy is sufficiently large that the electron carrier can always follow atomic motions.[4,5,7,8,12–14] Typically for small-polaron hops the electronic transfer energies required for adiabaticity must only exceed a characteristic phonon energy.[5,12] *Nonadiabatic* hops occur between sites for which the electronic transfer energies are much smaller. Thus, nonadiabatic hops must usually transcend large intersite distances.

Several methods permit distinguishing adiabatic from nonadiabatic small-polaronic hopping. Consider small-polaronic hopping at "high temperatures" (> phonon temperature/3), where the mobility is[5,7,12–14]

$$\mu_{\rm dc}=[(q\nu_{\rm phonon}r^2/k_BT)\exp(-E_A/k_BT)]P\ . \qquad (1)$$

In Eq. (1), q is the carrier's charge, $\nu_{\rm phonon}$ is the characteristic phonon frequency, r is the characteristic intersite jump distance, E_A is the mobility's activation energy, and P is the probability that the charge carrier will follow the atomic motion so as to produce a hop. For adiabatic jumps, $P\approx 1$. However, for nonadiabatic hopping $P \ll 1$. As illustrated in Fig. 1, hopping passes from adiabatic to nonadiabatic as the intersite separation is increased. Since the factor $q\nu_{\rm phonon}r^2/k_BT$ is typically 0.1–1.0 cm^2/V s,[6,7] preexponential factors of the mobility Eq. (1) that are measured to be about 0.1–1.0 cm^2/V s imply that $P\approx 1$. That is, in these instances, adiabatic hopping is indicated. Alternatively, values of preexponential factors that are much smaller than 0.1–1.0 cm^2/V s imply nonadiabatic hopping. A second means of determining whether hopping is adiabatic or nonadiabatic is to determine whether there is a strong pressure dependence of the preexponential factor of the mobility. The only very strong pressure dependence of the preexponential factor is that of the factor P when the hopping is nonadiabatic, i.e., when $P \ll 1$. Finally, for hopping between dopants the absence or presence of a strong dependence of P on the average intersite separation indicates adiabatic or nonadiabatic hopping, respectively.

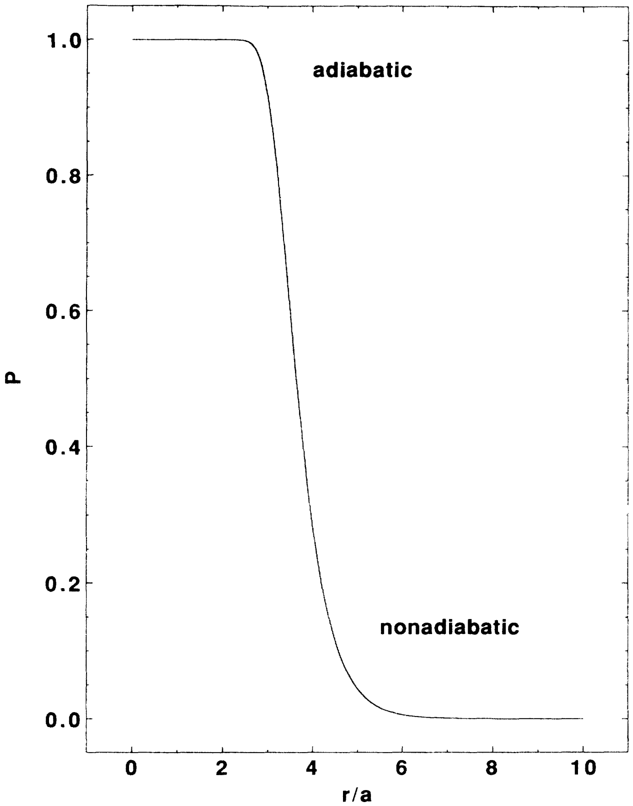


FIG. 1. P, the probability of an electronic hop given a coincidence event, is sketched against the ratio of the intersite separation, r, to the characteristic radii of the two sites involved in a hop, a. For short hops the electron adiabatically follows the atomic motion resulting in P becoming nearly independent of r. For long hops the electronic hopping is nonadiabatic as the electron tunnels too slowly to adiabatically follow the atomic motion. P then depends strongly on r.

These tests of adiabaticity confirm that adiabatic hopping typically predominates. For example, measurements of the conductivity and Hall mobility in boron carbides and in MnO imply that the hopping is adiabatic since P is estimated to be close to unity.[15,16] Evidence of adiabatic hopping in boron carbides also comes from the negligible dependence of P on hydrostatic pressure. This very weak pressure dependence is inferred from the pressure dependence of the dc conductivity.[17] The weak pressure dependence of the transient carrier mobility of some molecular systems also indicates adiabatic hopping.[18] In some molecularly doped polymers, analysis of the dependence of the transient mobility on the average interdopant separation implies adiabatic hopping for average interdopant separations below 35 Å.[19] In boron carbides, adiabatic hopping is also implied by the jump rate being independent of the average separation between the presumed hopping sites, icosahedral carbon atoms.[20,21]

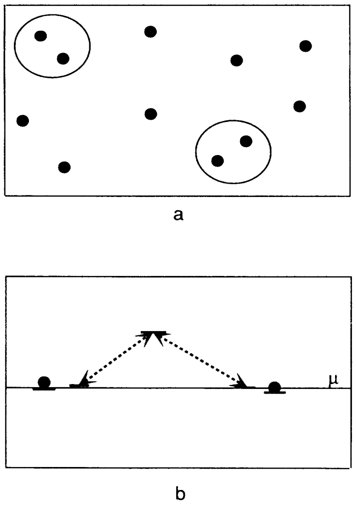
This paper addresses the low-temperature ac adiabatic hopping conductivity in disordered systems. In disordered hopping systems the relatively facile motion of carriers within "polarization centers" provides a source of ac conductivity.[4,22–24] Centers that polarize in response to an applied electric field with rates comparable to that of the applied frequency ω contribute to the ac conductivity at that frequency.[4,22–24] In this sense the ac conductivity measures the density of polarization centers within which carriers respond at a given frequency.

At low temperatures the polarization occurs predominantly via hops that require only (temperature-independent) spontaneous emission of phonons.[4,23] By contrast, the low-temperature dc conductivity is determined by "difficult" hops that require the absorption of vibrational energy to facilitate motion between regions of easy motion. Such hops become progressively slower as the temperature is reduced. For this reason, the ac conductivity rises above the dc conductivity when the temperature is low enough. Thus, the ac conductivity is observed at low temperatures.

Despite the hopping within polarization being faster than that which limits the dc conductivity, at the low frequencies of such measurements (< 10^6 Hz) the relaxation rates for the polarization centers are only $\approx\omega$.[4,22–24] To obtain such small relaxation rates, the predominant hops within polarization centers must be very slow. Such slow *adiabatic* hops can occur if the energy differences between the hopping sites of the polarization center are very small. In particular, low-temperature rates of small-polaronic hops in which few phonons are emitted become extremely small because of their suppression by the small-polaron factor $\exp(-2S)$, with $S \gg 1$, in conventional small-polaron notation.[2,3,5,7,10,13]

Thus, the ac conductivity for adiabatic small-polaronic hopping motion is ascribed to polarization centers formed by charged carriers that move between nearly degenerate localized states. Because sites that are especially close to one another share a common environment, such pairs are especially likely to be nearly degenerate with one another. Figure 2 illustrates polarization centers formed by pairs of sites that occur among a random distribution of localized states. These pairs of sites are considered two-site polarization centers, since the energies of the two sites of these polarization centers are closer to one another than are those of the sites that limit the dc transport. That is, dc transport requires hopping away from these polarization centers. As illustrated in the lower portion of Fig. 2, such hops require the absorption of relatively large amounts of energy. Thus, in this scenario, as the temperature is lowered, phonon absorbing hops are suppressed, freezing out the dc transport. However, since the ac conductivity is not limited by phonon-absorption processes, it survives.

In Sec. II, the contribution to the ac polarization conductivity of a carrier that hops between the two sites of a two-site polarization center is calculated. In Sec. III, a formal expression is found for the net ac conductivity arising from the adiabatic hopping of polarons among sites with a distribution of energy levels. The relaxation rate for low-temperature acoustic-phonon-assisted hopping between pairs of states is determined in Sec. IV. The calculation is completed in Sec. V when the rate derived in Sec. IV is combined with the formal expression found in Sec. III. The calculated ac conductivity rises sublinearly with applied frequency and rises with an increasingly strong temperature dependence as the temperature is raised. These behaviors are similar to those measured in very many systems, including those in which adiabatic small-polaronic hopping has been firmly established. Some examples of systems in which the ac conductivity measured at low temperatures is similar to that calculated here are the transition-metal-oxide glasses and the boron carbides. The physical arguments and results are summarized in Sec. VI.



a

b

FIG. 2. In *a* two two-site polarization centers among a random distribution of sites, depicted as solid dots, are highlighted by being enclosed within circles. In *b* the energy levels of the sites of these two centers and of an intermediate (high-energy) site are shown. The horizontal line depicts the chemical potential μ. The dashed arrows indicate that dc transport requires hopping to an intermediate site with higher energy.

II. MODEL: A TWO-SITE POLARIZATION CENTER

Here, the ac conductivity is modeled as arising from polarization centers comprising two sites between which a carrier adiabatically transfers in response to an ac field. The two-site picture should give at least a qualitative account of the effect of polarization centers on the ac conductivity.

The two sites that share the single carrier are denoted as sites 1 and 2. The local ground-state energies associated with a small polaron occupying either of these sites are ε_1 and ε_2, respectively. With the polaronic transfer energy associated with moving a small polaron between the two sites being denoted as t_p, the two eigenvalues of the eigenstates of the pair are $(\varepsilon_1+\varepsilon_2)/2 \pm \{[(\varepsilon_1-\varepsilon_2)/2]^2 + t_p^2\}^{1/2}$. For adiabatic polaron hopping t_p is independent of the intersite separation. Its adiabatic value is $\approx \sqrt{E_b h \nu_{\text{phonon}}/\pi}\exp(-S)$.[5,25]

In terms of the average energy of the pair $\varepsilon \equiv (\varepsilon_1+\varepsilon_2)/2$ and the energy difference between the two sites $\Delta \equiv \varepsilon_2 - \varepsilon_1$, the eigenvalues of the pair are $\varepsilon \pm \delta/2$, where $\delta/2 \equiv \{[(\varepsilon_1-\varepsilon_2)/2]^2 + t_p^2\}^{1/2}$. The occupation probabilities of these two states p_1 and p_2 are also denoted by the subscripts 1 and 2, since these state occupation probabilities correspond to the site occupation probabilities in the limit of $t_p \to 0$. The master equation for the rate of change of p_1 and p_2 is

$$\begin{aligned}\partial p_1(t)/\partial t &= p_2(t)R(2\to 1) - p_1(t)R(1\to 2)\\ &= R(2\to 1) - p_1(t)[R(1\to 2) + R(2\to 1)]\ , \end{aligned} \tag{2}$$

where $R(2\to 1)$ and $R(1\to 2)$ are the rates for transitions between states 1 and 2. The conservation of probability condition $p_1+p_2=1$ has been used in obtaining the second equality of Eq. (2). This differential equation is readily solved to yield the relaxation from an initial value $p_1(0)$ to the equilibrium value $p_1(\infty)$:

$$p_1(t) = p_1(\infty) + [p_1(0) - p_1(\infty)]\exp(-t/\tau)\ , \tag{3}$$

where

$$1/\tau \equiv R(1\to 2) + R(2\to 1)\ , \tag{4}$$

and the condition of detailed balance in equilibrium $p_1(\infty)R(1\to 2) = p_2(\infty)R(2\to 1)$ has been used.

To calculate the frequency-dependent conductivity, consider the turning on of an electric field parallel to the two sites of the pair at $t=0$. The imposition of the electric field E alters the energy difference between sites 1 and 2 from Δ ($=\varepsilon_2-\varepsilon_1$) to $\Delta+qER$, where R is the separation between sites 1 and 2. The imposition of the small electric field shifts the equilibrium occupation probability for the carrier occupying site 1 from its value without the field (at $t=0$) to that with the field (at $t=\infty$)

$$\begin{aligned} p_1(0)-p_1(\infty) &= -(\partial p_1/\partial\delta)(\partial\delta/\partial\Delta)qER \\ &= \mathrm{sech}^2(\beta\delta/4)(\Delta/\delta)\beta qER/8\ , \end{aligned} \tag{5}$$

where

$$p_1=1/[\exp(\beta\delta/2)+1]\ . \tag{6}$$

Here β is $1/k_BT$ with k_B representing the Boltzmann constant and T representing the absolute temperature.

The polarization current density for motion of a carrier between a pair of sites in the volume V after the field is applied at $t=0$ is

$$\begin{aligned} J(t) &= -(qR/V)\partial p_1(t)/\partial t \\ &= (qR/V\tau)[p_1(0)-p_1(\infty)]\exp(-t/\tau) \\ &= E(\beta q^2R^2/8V\tau)(|\Delta|/\delta)\mathrm{sech}^2(\beta\delta/4)\exp(-t/\tau)\ . \end{aligned} \tag{7}$$

Then, taking the Fourier transform of both the current and the electric field, the real part of the polarization conductivity from a pair of sites is found to be

$$\begin{aligned} \sigma_{\mathrm{pair}}(\omega) &= \mathrm{Re}[J(\omega)/E(\omega)] \\ &= (\beta q^2R^2\omega/8V)(|\Delta|/\delta) \\ &\quad \times \mathrm{sech}^2(\beta\delta/4)\{\omega\tau/[1+(\omega\tau)^2]\}\ . \end{aligned} \tag{8}$$

It is noted that the ac conductivity of the pair Eq. (8) vanishes both when the energy difference Δ vanishes and when Δ, and hence δ, approaches infinity. As noted previously,[4] the first situation occurs because the charge transfer that accompanies a transition between states 1 and 2 is $|\Delta|/\delta$.[26] The polarization conductivity also vanishes as $\beta\delta\rightarrow\infty$, since the ability of the electric field to alter the polarization falls with the extent of the preexisting polarization.

III. ac CONDUCTIVITY

To obtain the net polarization conductivity, the contributions of all polarization centers in the solid must be summed. To begin, the number of polarization centers whose two sites have an average local energy ε lying between ε and $\varepsilon+d\varepsilon$ and an energy difference lying between Δ and $\Delta+d\Delta$ is written as $V\rho_2(\varepsilon,\Delta)d\varepsilon\, d\Delta$. The subscript 2 on $\rho_2(\varepsilon,\Delta)$ is employed to emphasize that this function has the dimensions $(\text{energy})^{-2}(\text{volume})^{-1}$ rather than that of the density of states, $(\text{energy})^{-1}(\text{volume})^{-1}$. For example, if a density of sites n has a Gaussian distribution of energies with a rms spread of W, for any pair of sites one has $\rho_2(\varepsilon,\Delta)=(n/2\pi W^2)\exp\{-[\varepsilon^2+(\Delta/2)^2]/W^2\}$.

A transition between states requires that one of the two states be initially occupied while the other is initially unoccupied. For states labeled as 1 and 2 the probability of one and only one of the two sites of a pair being occupied is given by the occupancy factor, $P_{\mathrm{oc}}=f_1(1-f_2)+f_2(1-f_1)$. The occupancy factors f_1 and f_2 are taken as Fermi functions to ensure that the carriers do not doubly occupy a state. The energies of a carrier in states 1 or 2 are then written as $\varepsilon-\delta/2$ or $\varepsilon+\delta/2$, respectively. After some algebraic manipulations, one obtains

$$\begin{aligned} P_{\mathrm{oc}} &= \cosh(\beta\delta/2)/\{2\cosh[\beta(\varepsilon-\delta/2-\mu)/2] \\ &\quad \times\cosh[\beta(\varepsilon+\delta/2-\mu)/2]\} \\ &= \cosh(\beta\delta/2)/\{\cosh[\beta(\varepsilon-\mu)]+\cosh(\beta\delta/2)\}\ , \end{aligned} \tag{9}$$

where μ is the chemical potential for the carriers. Summing up over all polarization centers the net real part of the polarization conductivity becomes

$$\sigma_{\mathrm{pol}}(\omega)=(q^2\langle R^2\rangle\omega/8)\int d\Delta(|\Delta|/\delta)\frac{\cosh(\beta\delta/2)}{\cosh^2(\beta\delta/4)}\frac{\omega\tau}{[1+(\omega\tau)^2]}\int d(\beta\varepsilon)\rho_2(\varepsilon,\Delta)/\{\cosh[\beta(\varepsilon-\mu)]+\cosh(\beta\delta/2)\}\ . \tag{10}$$

In writing this equation, it is presumed that the relaxation time for charge transfer between the two sites of a center, τ, is not a strong function of their average energy, ε.

To carry out the integrations of Eq. (10), some simplifications are now made. First, it is anticipated that the principal contributions to the $\beta\varepsilon$ integral will occur when ε is close to μ. This presumption is based on the observation that the two energies of the two sites of the pair must straddle μ for only one of the sites to be occupied as $T\rightarrow 0$. Then, presuming $\rho_2(\varepsilon,\Delta)$ to vary slowly with ε when ε is in the vicinity of μ, $\rho_2(\varepsilon,\Delta)$ is replaced by $\rho_2(\mu,\Delta)$ in the integrand. Noting that the integrand falls off exponentially for large values of $|\beta(\varepsilon-\mu)|$, the range of integration of $\beta\varepsilon$ may be extended to be from $-\infty$ to ∞. Carrying out this procedure yields a known integral.[27] Performing the integration and rearranging terms yields a simple result,

$$\begin{aligned} &\int_{-\infty}^{\infty} d(\beta\varepsilon)\rho_2(\varepsilon,\Delta)/\{\cosh[\beta(\varepsilon-\mu)]+\cosh(\beta\delta/2)\} \\ &\quad \approx\rho_2(\mu,\Delta)\int_{-\infty}^{\infty}dx\,[\cosh(x)+\cosh(\beta\delta/2)]^{-1} \\ &\quad =\rho_2(\mu,\Delta)(\beta\delta)\mathrm{csch}(\beta\delta/2)\ . \end{aligned} \tag{11}$$

Inserting Eq. (11) into Eq. (10) and employing identities of hyperbolic functions yields another expression for the polarization conductivity:

$$\sigma_{\text{pol}}(\omega)=(q^2\langle R^2\rangle\omega)\int d\Delta\,\rho_2(\mu,\Delta)\times\frac{\beta|\Delta|\coth(\beta\delta/2)}{16\cosh^2(\beta\delta/4)}\frac{2\omega\tau}{1+(\omega\tau)^2}\,. \tag{12}$$

The occupation probability and polarizability of a given two-site center produce the β-dependent factor in the integrand of the integral in Eq. (12). This factor rises from a value of zero at $\Delta=0$ to a maximum and then falls exponentially within increasing δ as $\exp(-\beta\delta/2)$. The final factor in the integrand of the integral in Eq. (12) is a dynamic factor that describes motion between the two sites. This factor achieves its peak value of unity at the value of Δ for which $\omega\tau=1$. The temperature dependence of $\sigma_{\text{pol}}(\omega)$ arises both, explicitly, from the β-dependent factor and, implicitly, from the dynamic factor through the temperature dependence of τ. With the primary contributions to $\sigma_{\text{pol}}(\omega)$ coming from the vicinity of $\omega\tau=1$, one can interpret the polarization conductivity of Eq. (12) as being the product of the carrier's charge q, its "mobility" when it moves between sites at the frequency $\omega, q\langle R^2\rangle\omega/k_BT$, and the density of polarizable centers at temperature T that can respond at frequency ω:

$$n_{\text{pairs}}(\omega,T)\equiv\int d\Delta\,\rho_2(\mu,\Delta)\frac{|\Delta|\coth(\beta\delta/2)}{16\cosh^2(\beta\delta/4)}\frac{2\omega\tau}{1+(\omega\tau)^2}$$
$$\approx\rho_2(\mu,0)\int d\delta\frac{\delta\coth(\beta\delta/2)}{8\cosh^2(\beta\delta/4)}\frac{2\omega\tau}{1+(\omega\tau)^2}\,. \tag{13}$$

In obtaining the second line of Eq. (13), (1) it is noted that τ is an even function of Δ; (2) it is presumed that $\rho_2(\mu,\Delta)$ depends only weakly on Δ within the regime of principal importance in the integration; and (3) the integration variable is converted from Δ to δ, noting that $\partial\Delta/\partial\delta=\delta/\Delta$. A factor of 2 is introduced with this change of variable because δ is an even function of Δ.

Consider the frequency dependences of $\sigma_{\text{pol}}(\omega)$ of Eq. (12). If the frequency is sufficiently high so that $\omega\tau\gg1$ throughout the region in which the remaining factors of the integrand are appreciable, there is negligible frequency dependence of $\sigma_{\text{pol}}(\omega)$. Alternatively, if the frequency is sufficiently small so that $\omega\tau\ll1$ throughout the region in which the remaining factors of the integrand are appreciable, $\sigma_{\text{pol}}(\omega)$ is both relatively small and proportional to ω^2. These limits, where either $\omega\tau\gg1$ or $\omega\tau\ll1$ throughout the entire integration region, essentially reproduce the limiting results for a single pair, Eq. (8). However, if the domain of integration includes values of $|\Delta|$ for which $\omega\tau\approx1$, an intermediate frequency dependence is obtained.

IV. LOW-TEMPERATURE RELAXATION RATE

To proceed further, an expression for the relaxation time, τ, as a function of δ must now be introduced. As discussed in the introductory section, the low-temperature low-frequency ac conductivity due to adiabatic small-polaronic hopping in disordered materials is dominated by very slow transitions that arise from hops between sites of nearly equal energy. Thus, τ of Eq. (4) is evaluated with transition rates appropriate to low-temperature adiabatic small-polaron transitions for which δ is sufficiently small that the predominant transitions occur with the absorption or emission of only a single acoustic phonon of energy δ.[6]

The relaxation time τ is associated with transitions between states 1 and 2. However, states 1 and 2 , $|1\rangle$ and $|2\rangle$, may be expressed as superpositions of (orthogonalized) localized states associated with the carrier residing on either site 1 or site 2, ϕ_1 and ϕ_2. In particular,

$$|1\rangle=C_1^-\phi_1+C_2^-\phi_2 \tag{14a}$$

and

$$|2\rangle=C_1^+\phi_1+C_2^+\phi_2\,, \tag{14b}$$

where the minus sign corresponds to state 1 and the plus sign to state 2. For this two-site problem, the expansion coefficients are

$$C_1^\pm=\frac{2t_p}{\sqrt{(2t_p)^2+(\delta\pm\Delta)^2}} \tag{15a}$$

and

$$C_2^\pm=\frac{\delta\pm\Delta}{\sqrt{(2t_p)^2+(\delta\pm\Delta)^2}}\,. \tag{15b}$$

Since the dominant phonon-assisted transitions between nearly degenerate states at low temperature involve the emission or absorption of long-wavelength acoustic phonons, the deformation-potential model can be employed. That is, the electron-lattice interaction energy for a carrier at position $\mathbf{r}$ is written as

$$V(\mathbf{r})=iE_D\sqrt{\hbar/2\rho sV}\sum_{\mathbf{q}}\sqrt{|\mathbf{q}|}[b_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r})-\text{c.c.}]\,, \tag{16}$$

where E_D is the deformation-potential energy, ρ in the solid's density, s is the longitudinal sound velocity, V is the solid's volume, and $b_{\mathbf{q}}$ is the annihilation operator for a phonon of wave vector $\mathbf{q}$. The matrix element of $V(\mathbf{r})$ between states 1 and 2 is then evaluated to yield

$$\begin{aligned}\langle 2|V|1\rangle&\approx C_1^+C_1^-\langle\phi_1|V|\phi_1\rangle+C_2^+C_2^-\langle\phi_2|V|\phi_2\rangle\\&=(t_p/\delta)[\langle\phi_1|V|\phi_1\rangle-\langle\phi_2|V|\phi_2\rangle]\\&=(t_p/\delta)\langle\phi_1|V|\phi_1\rangle[1-\exp(i\mathbf{q}\cdot\mathbf{R})]\,.\end{aligned} \tag{17}$$

In the first line of Eq. (17) the customary step of neglecting terms involving matrix elements of the electron-lattice interaction between different localized states is employed.[1,2] In the limit of long-wavelength phonons the orthogonality of the local (Wannier) wave functions ensures that these terms vanish. In obtaining the second line of Eq. (17) the products of the expansion coefficients have been evaluated. In obtaining the last equality, $\mathbf{R}$ is defined as the position vector from the centroid of site 1 to that of site 2. Evaluation of the matrix elements of Eq. (17) is completed by noting that the only factor in the deformation potential that depends on the electron's position is $\exp(i\mathbf{q}\cdot\mathbf{r})$. Matrix elements of this factor are essentially unity when the wavelengths of the involved phonons exceed the radii of the localized states: $\langle\phi_1|\exp(i\mathbf{q}\cdot\mathbf{r})|\phi_1\rangle\approx 1$. This situation prevails for the situation of interest here: hops between nearly degenerate severely localized small-(bi)polaronic states induced by the absorption or emission of very-low-energy acoustic phonons.

Having determined the matrix elements of the deformation potential, the rate for a transition from state 1 to state 2 with the emission of a single acoustic phonon of energy δ can now be obtained from the golden rule. After some algebra one obtains

$$R_{\text{emission}}(\delta)=(t_p^2E_D^2/\pi\rho s^5\hbar^4)\delta[1+N(\delta)]\times\left[1-\frac{\sin(\delta R/\hbar s)}{(\delta R/\hbar s)}\right], \tag{18}$$

where $N(\delta)$ is the number of available phonons of energy δ. With $N(\delta)$ being taken to be the thermally available number of phonons,

$$N(\delta)=\frac{\exp(-\beta\delta/2)}{2\sinh(\beta\delta/2)}\ . \tag{19}$$

The transition rate of Eq. (18) is similar to that obtained by Miller and Abrahams for a hop between shallow impurities induced by the emission of an acoustic phonon.[1] A correspondence can be made to the result of their problem by replacing (1) the adiabatic small-(bi)polaronic transfer energy t_p of Eq. (18) with their electronic transfer energy W; and (2) the energy difference between states 1 and 2, δ by their difference between site energies $|\Delta|$. However, while Miller and Abrahams consider nonadiabatic hopping between widely separated large-radius localized states, the concern of this paper is adiabatic hops between close pairs of severely localized states. Hence, while Miller and Abrahams take $\delta R/\hbar s\gg 1$, the opposite limit is considered here: $\delta R/\hbar s\ll 1$. In this situation, Eq. (18) may be rewritten as

$$R_{\text{emission}}(\delta)=R_0(\delta/\hbar\omega_D)^3\frac{\exp(\beta\delta/2)}{2\sinh(\beta\delta/2)}\ , \tag{20}$$

where $R_0\equiv\omega_D\pi(q_DR)^2[(t_pE_D)^2/Ms^2(\hbar\omega_D)^3]$ and $M=6\pi^2\rho/(q_D)^3$ is the mass of a unit cell in the Debye approximation with q_D being the Debye wave vector. Since $E_b\approx E_D^2/Ms^2$, $S\approx E_b/\hbar\omega_D$, and $t_p^2\approx(\hbar\omega_D)^2Se^{-2S}$, one has $R_0\approx\omega_D(q_DR)^2(Se^{-S})^2$, where $S\gg 1$ for small polarons.

The transition rate for the complementary phonon-assisted process, phonon absorption, may be obtained from the emission rate of Eq. (20) by using the principle of detailed balance: simply multiplying Eq. (20) by the factor $\exp(-\beta\delta)$:

$$R_{\text{absorption}}(\delta)=R_0(\delta/\hbar\omega_D)^3\frac{\exp(-\beta\delta/2)}{2\sinh(\beta\delta/2)}\ . \tag{21}$$

The relaxation rate $1/\tau$, defined in Eq. (4), is the sum of the rates of Eqs. (20) and (21):

$$1/\tau=R_0(\delta/\hbar\omega_D)^3\coth(\beta\delta/2)\ . \tag{22}$$

As expected of hopping processes, the relaxation rate of Eq. (22) rises with increasing temperature. At sufficiently low temperatures, where $\beta\delta/2>1$, $\coth(\beta\delta/2)\approx 1$. Then, the relaxation rate approaches the temperature-independent rate associated with the spontaneous emission of an acoustic phonon. At higher temperatures, where $\beta\delta/2<1$, $\coth(\beta\delta/2)\approx 2k_BT/\delta$. Then, the relaxation rate becomes simply proportional to the temperature as absorption and stimulated emission of low-energy acoustic phonons contribute almost equally to the relaxation rate. Equation (22) also indicates that the relaxation rate becomes progressively slower as the energy disparity δ is reduced. This phenomenon occurs because the density of states of the low-energy acoustic phonons that are capable of facilitating a transition falls as δ is reduced.

V. DENSITY OF POLARIZATION CENTERS: $n_{\text{pairs}}(\omega,T)$

The low-frequency polarization conductivity essentially measures the density of polarization centers that can respond at temperature T to frequency ω, $n_{\text{pairs}}(\omega,T)$. For hopping systems at low temperatures one generally finds that $n_{\text{pairs}}(\omega,T)$ rises with increasing temperature at a rate that falls with increasing frequency.

Proceeding to calculate $n_{\text{pairs}}(\omega,T)$ from Eq. (13), it is first noted that the dynamic factor $2\omega\tau/[1+(\omega\tau)^2]$ is peaked about $\omega\tau=1$ and that τ depends on δ. Therefore, the dynamic factor is peaked about the value of δ corre-

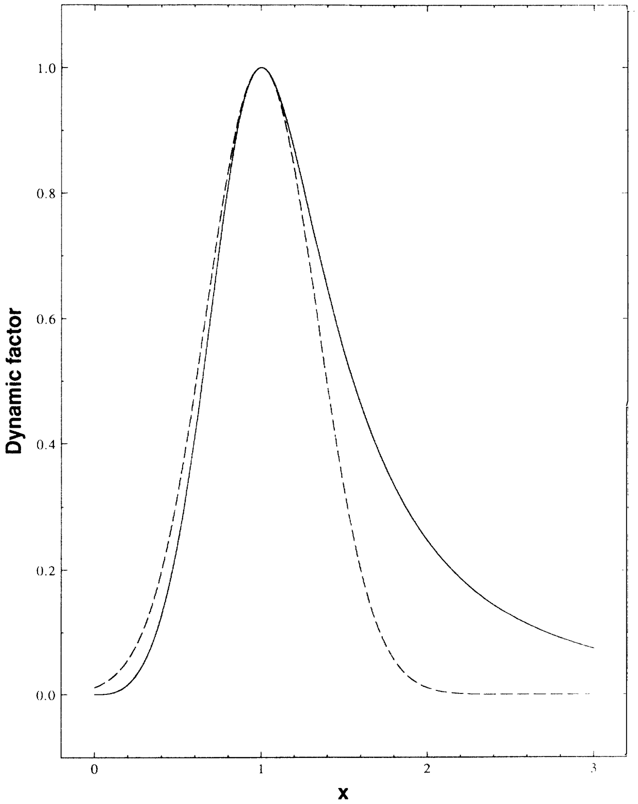


FIG. 3. The Gaussian approximation to the dynamic factor given by Eq. (23) (dashed curve) is compared with the exact result (solid curve) in the low-temperature regime where $\tau^{-1}\propto\delta^3$ and $x\equiv\delta/\delta_0$.

sponding to $\omega\tau=1$, defined as δ_0. Expanding the dynamic factor about its peak value one obtains

$$\frac{2\omega\tau}{1+(\omega\tau)^2}\approx\exp[-f^2(\delta-\delta_0)^2/2]\ , \tag{23}$$

where $f\equiv\partial(\omega\tau)/\partial\delta$ evaluated at $\omega\tau=1$. In general, f may be written as $-n/\delta_0$, where n is a function of temperature and δ_0 is a function of both ω and temperature. In the low- and high-temperature limits of Eq. (22) these functions are very simple. For example, at low temperatures where $\beta\delta_0/2>1$, one readily finds from Eq. (22) that $f\approx-3/\delta_0$ and $\delta_0\propto\omega^{1/3}$. Alternatively, when $\beta\delta_0/2\ll1$ one finds from Eq. (22) that $f\approx-2/\delta_0$ and $\delta_0\propto\omega^{1/2}$. Here, interest will focus on the low-temperature limit, although f shall be written as $-n/\delta_0$ for generality. In Fig. 3, the Gaussian approximation to the dynamic factor, given by Eq. (23), is compared with the exact result in the low-temperature regime where $\tau^{-1}\propto\delta^3$. This approximation is seen to be reasonably good.

The remaining factor of the integrand of Eq. (13) is $(\delta/8)\coth(\beta\delta/2)\mathrm{sech}^2(\beta\delta/4)$. At low temperatures where $\beta\delta/2\gg1$ this factor may be approximated as $(\delta/2)\exp(-\beta\delta/2)$. Presuming that the principal contributions to the integral of Eq. (13) occur at such values of $\beta\delta$, the integral may be approximated as

$$n_{\text{pairs}}(\omega,T)\approx[\rho_2(\mu,0)/2]\times\int_{2t_p}^{\infty}d\delta\,\delta\exp(-\beta\delta/2)\times\exp[-n^2(\delta-\delta_0)^2/2(\delta_0)^2]\ , \tag{24}$$

where it is noted that the minimum value of δ is $2t_p$.

Introducing the change of variable $x\equiv\delta/\delta_0$ transforms Eq. (24) to

$$n_{\text{pairs}}(\omega,T)=[\rho_2(\mu,0)\delta_0^2/2]\times\int_{2t_p/\delta_0}^{\infty}dx\,x\exp(-\beta\delta_0x/2)\times\exp[-n^2(x-1)^2/2]\ . \tag{25}$$

The product of the exponential factors of the integrand of Eq. (25) is peaked at a value of x that shifts from unity to smaller values of x as $\beta\delta_0$ is increased. This effect is evident upon completing the square of the arguments of the exponentials contained within the integrand of Eq. (25):

$$n_{\text{pairs}}(\omega,T)=[\rho_2(\mu,0)\delta_0^2/2]\exp[-(\beta\delta_0/2)+(\beta\delta_0/2)^2/2n^2]\int_{2t_p/\delta_0}^{\infty}dx\,x\exp\{-n^2[x-1+(\beta\delta_0/2n^2)]^2/2]\}\ . \tag{26}$$

The integral of Eq. (26) can be evaluated with changes of variable to z and z^2, where $z\equiv(n/\sqrt{2})[x-1+(\beta\delta_0/2n^2)]$ and $z_0\equiv(n/\sqrt{2})[2t_p/\delta_0-1+(\beta\delta_0/2n^2)]$:

$$\begin{aligned}n_{\text{pairs}}(\omega,T)&=[\rho_2(\mu,0)\delta_0^2/2]\exp[-(\beta\delta_0/2)+(\beta\delta_0/2)^2/2n^2]\\&\quad\times\left\{\int_{z_0}^{\infty}d(z^2/n^2)\exp(-z^2)+[1-(\beta\delta_0/2n^2)](\sqrt{2}/n)\int_{z_0}^{\infty}dz\exp(-z^2)\right\}\\&=[\rho_2(\mu,0)\delta_0^2/2]\exp[-(\beta\delta_0/2)+(\beta\delta_0/2)^2/2n^2]\\&\quad\times\{(1/n^2)\exp[-(z_0)^2]+[1-(\beta\delta_0/2n^2)]\sqrt{\pi/2n^2}\,\mathrm{erfc}(z_0)\}\ .\end{aligned} \tag{27}$$

At low temperatures, with z_0 being large, $z_0\sqrt{\pi}\exp[(z_0)^2]\mathrm{erfc}(z_0)\approx1-1/2(z_0)^2$.[28] Using this relation and the definition of z_0, Eq. (27) becomes

$$\begin{aligned}n_{\text{pairs}}(\omega,T)&=[\rho_2(\mu,0)/2](\delta_0/n)^2\exp[-(z_0)^2-(\beta\delta_0/2)+(\beta\delta_0/2)^2/2n^2]\\&\quad\times\left\{1+\frac{[1-(\beta\delta_0/2n^2)]}{z_0\sqrt{2}/n}[1-1/2(z_0)^2]\right\}\\&=[\rho_2(\mu,0)/2](\delta_0/n)^2\exp\{-(n^2/2)[1-(4t_p/\delta_0)+(2\beta t_p/n^2)-(2t_p/\delta_0)^2]\}\\&\quad\times\frac{1/2(z_0)^2+(2t_p/\delta_0)/[(\beta\delta_0/2n^2)-1]}{1+(2t_p/\delta_0)/[(\beta\delta_0/2n^2)-1]}\ .\end{aligned} \tag{28}$$

Presuming that t_p (generally $<10^{-3}\hbar\omega_D$) is much smaller than any other physical parameter in Eq. (28), Eq. (28) is simplified by letting $t_p\rightarrow0$. Then, Eq. (28) reduces to

$$\begin{aligned}n_{\text{pairs}}(\omega,T)&\approx\rho_2(\mu,0)(\delta_0/nz_0)^2\exp(-n^2/2)/4\\&\approx2\rho_2(\mu,0)\frac{(k_BT)^2}{[1-(2n^2k_BT/\delta_0)]^2}\exp(-n^2/2)\ .\end{aligned} \tag{29}$$

Equation (29) may be obtained more directly from Eq. (25) if its integral is evaluated in a less general and methodical manner. In particular, in this more direct approach, the focus on small values of x is anticipated as $\exp[-n^2(x-1)^2/2]$ is replaced by $\exp(-n^2/2)\times\exp(n^2x)$ in the integral's integrand. In addition, the lower limit of integration of the integral is set equal to zero. Direct integration of the simplified integral then immediately yields Eq. (29).

Multiplying $n_{\rm pairs}(\omega,T)$ contained in Eq. (29) by $q^2\langle R^2\rangle\omega/k_BT$ yields an expression for the low-temperature low-frequency polarization conductivity that may be expressed as

$$\sigma_{\rm pol}(\omega)=\sigma_0\frac{(\omega/\omega_0)(T/T_0)}{[1-(T/T_0)(\omega_0/\omega)^{1/n}]^2}\ , \tag{30}$$

where two constants are introduced:

$$\sigma_0\equiv 2q^2\langle R^2\rangle\rho_2(\mu,0)\omega_0 k_B T_0 \exp(-n^2/2)$$

and

$$(\omega_0)^{1/n}/T_0\equiv 2n^2k_B\omega^{1/n}/\delta_0\ .$$

Here ω_0 and T_0 serve as nonindependent scale factors for the frequency and temperature. Note that δ_0 generally rises with ω. In particular, in the low-temperature regime, $n=3$ and δ_0 is proportional to $\omega^{1/3}$. Thus, the temperature and frequency dependences of the denominator cause $\sigma_{\rm pol}(\omega)$ to manifest a progressively weaker rise with increasing temperature as ω is increased. As the temperature is lowered sufficiently, the conductivity becomes simply proportional to both temperature and frequency. These findings are illustrated in Fig. 4, where $\log_{10}[\sigma_{\rm pol}(\omega)/\sigma_0]$ of Eq. (30) is plotted against T_0/T for four values of ω/ω_0 where n is its low-temperature value, 3. The plots of Fig. 4 are in qualitative agreement with measurements in systems for which there is evidence that adiabatic small-polaron or small-bipolaron hopping occurs.[2,29]

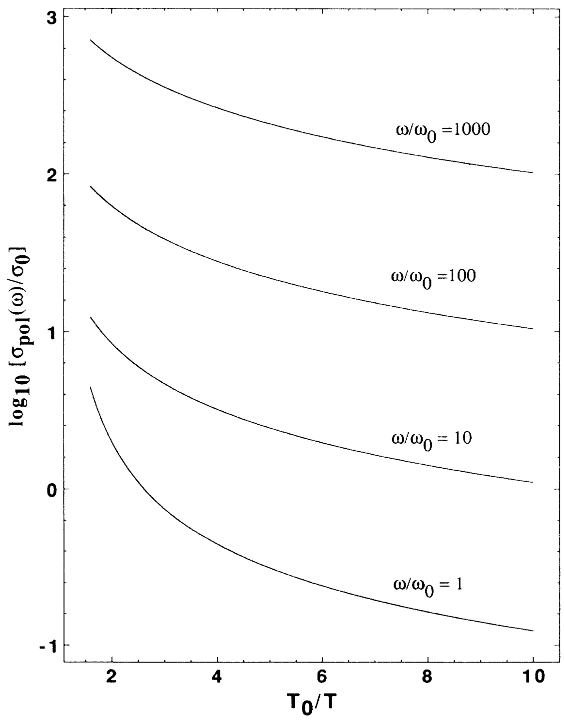


FIG. 4. The normalized polarization conductivity of Eq. (30) with $n=3$ is plotted against the dimensionless reciprocal temperature T_0/T at reduced frequencies of $\omega/\omega_0=1$, 10, 100, and 1000.

VI. SUMMARY

For many, if not most, systems with small-polaronic hopping the intersite separations are sufficiently small that the hopping is adiabatic. In this adiabatic regime, the small-polaronic jump rates are insensitive to intersite separations. As the temperature is lowered, dc conduction in disordered systems with adiabatic polaronic hopping is progressively suppressed as carriers find it increasingly hard to negotiate diffusion-limiting difficult hops that require the absorption of athermal amounts of vibrational energy. However, since ac conduction does not require carriers to perform these difficult hops, the ac conductivity is generally very much larger than the dc conductivity at low temperatures.

In many systems, such as transition-metal-oxide glasses and the boron carbides,[4,29] the low-temperature low-frequency ac conductivity is associated with a very small fraction (e.g., 0.1%) of the carriers that contribute to the dc conductivity. For this reason, the ac conductivity may be viewed as arising from isolated polarization centers. A polarization center is a rare cluster of sites among which carriers can move with relative ease. In particular, the energy differences between a center's sites cannot be much greater than k_BT. That is, the polarization centers are composed of sites whose energy levels are nearly degenerate with one another. Since pairs of sites that are unusually close to one another tend to experience nearly equivalent environments, such pairs of sites naturally form polarization centers.

Since the energy differences between the sites of the polarization centers are much lower than the Debye energy, relaxation can occur with the emission or absorption of only a single acoustic phonon. In fact, for low-temperature small-polaronic hopping between nearly degenerate states, hopping is predominantly due to the emission or absorption of only a single low-energy acoustic phonon.[2]

Since the low-frequency ac conductivity measures the carriers' response at rather low frequencies ($<10^6$ Hz), the carriers of the polarization centers must move between nearly degenerate sites at these very low frequencies. That is, the relaxation rates must be very much lower than vibrational frequencies. For small-polaronic hops, the rates for single-phonon emission *are* especially small. In particular, the rates for low-temperature single-phonon hops of small polaronic carriers are proportional to the factor $\exp(-2S)$, the so-called band-narrowing factor of small-polaron theory.[2,3,5] Typically, S is at least 10. Thus, this factor reduces the low-temperature rate for a small polaron's emission of a single phonon by at least nine orders of magnitude $[\exp(-20)=2.5\times10^{-9}]$ from that associated with hopping between shallow-impurity centers (where $S\rightarrow 0$).[1,2] It is for this reason that the adiabatic hopping of small polarons and small bipolarons can account for the low-frequency ac conductivity observed at low temperatures.

The presence of disorder produces a distribution of energy differences between the sites of polarization centers. This spread of energy differences Δ produces dispersion of the relaxation rates. The polarization conductivity is the sum of contributions that arise from polarization centers with different energy differences. The net polarization conductivity, given by $\sigma_{\text{pol}}(\omega)$ of Eq. (30) and illustrated in Fig. 4, rises with increasing temperature. This temperature dependence also decreases as the frequency is increased. In the low-temperature limit the polarization conductivity is proportional to both temperature and frequency. These results are in accord with observations in many systems with hopping conduction, including those for which there is other evidence of adiabatic small-polaronic hopping.

These findings are obtained with very general considerations. The generality of the theory is compatible with is predictions' consistency with experimental observations of dissimilar systems for which there is evidence of adiabatic small-polaronic hopping.

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[1] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

[2] D. Emin, Phys. Rev. Lett. **32**, 303 (1974).

[3] D. Emin, Adv. Phys. **24**, 305 (1975).

[4] I. G. Austin and N. F. Mott, Adv. Phys. **18**, 41 (1969).

[5] T. Holstein, Ann. Phys. (N.Y.) **8**, 343 (1959).

[6] D. Emin, C. H. Seager, and R. K. Quinn, Phys. Rev. Lett. **28**, 813 (1972).

[7] D. Emin, in *Electronic and Structural Properties of Amorphous Semiconductors,* edited by P. G. LeComber and J. Mort (Academic, New York, 1973), pp. 261–328.

[8] D. Emin, in *Polycrystalline and Amorphous Thin Films and Devices,* edited by L. L. Kazmerski (Academic, New York, 1980), pp. 17–58.

[9] N. F. Mott, Philos. Mag. **19**, 835 (1969).

[10] D. Emin, in *Physics of Structurally Disordered Materials,* edited by S. S. Mitra (Plenum, New York, 1976), pp. 461–506.

[11] L. Zuppiroli and L. Forro, Phys. Lett. A **141**, 181 (1989).

[12] D. Emin and T. Holstein, Ann. Phys. (N.Y.) **53**, 439 (1969).

[13] D. Emin, Phys. Today, **35** (6), 34 (1982).

[14] D. Emin, Phys. Rev. B **43**, 11 720 (1991).

[15] C. Wood and D. Emin, Phys. Rev. B **29**, 4582 (1985).

[16] C. Crevecoeur and H. J. de Wit, J. Phys. Chem Solids **31**, 783 (1970).

[17] G. A. Samara, D. Emin, and C. Wood, Phys. Rev. B **32**, 2315 (1985).

[18] F. K. Dolezalek and W. E. Spear, J. Non-Cryst. Solids **4**, 97 (1970).

[19] L. B. Schein, D. Glatz, and J. C. Scott, Phys. Rev. Lett. **65**, 472 (1990).

[20] D. Emin, in *The Physics and Chemistry of Carbides, Nitrides and Borides,* edited by R. Freer (Kluwer, Amsterdam, 1990), pp. 691–704.

[21] D. Emin, in *Boron-Rich Solids,* edited by D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin, and C. L. Beckel (AIP, New York, 1991), pp. 65–76.

[22] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Solids* (Clarendon, Oxford, 1979).

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

[24] M. Pollak and G. E. Pike, Phys. Rev. Lett. **28**, 1449 (1972).

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

[26] Note that the argument of Ref. 4 leads to a factor of $(|\Delta|/\delta)^2$ rather than to the factor $|\Delta|/\delta$ obtained here.

[27] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1965), Integral 3.513.

[28] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, 1964), Eq. 7.1.23.

[29] G. A. Samara, H. L. Tardy, E. L. Venturini, T. L. Aselage, and D. Emin, in *Boron-Rich Solids* (Ref. 21), pp. 77–84.