JOURNAL OF SOLID STATE CHEMISTRY 12, 246–252 (1975)

Transport Properties of Small Polarons*†

DAVID EMIN

Sandia Laboratories, Albuquerque, New Mexico, 87115

Received July 3, 1974

A qualitative discussion of the essentials of small-polaron motion is presented. After a very brief description of the notion of a small polaron and the situation under which it is formed, the principal physical features and predictions of the theory of small-polaron transport is addressed. Specifically, small-polaron band and hopping motion are both initially considered with the discussion thereafter being restricted to hopping motion. First quantum-mechanical treatments of small-polaron hopping motion are considered. Then the semiclassical approach to the calculation of the high-temperature ($\kappa T \gtrsim \hbar\omega_{\mathrm{Debye}}$) adiabatic and nonadiabatic jump rate is described with the question of correlated hopping motion also being addressed. After this, the high-frequency absorption associated with small-polaron motion is considered. Finally, a review of the Hall-mobility calculations and some comments about the thermoelectric power are presented.

The purpose of this paper is to present some essential features of the theory of small-polaron motion. As will become clear shortly, the insulators to which this discussion may find applicability are those in which the electronic carriers are characterized as having "low-mobilities," i.e., mobilities less than, say, 1 cm^2/V sec.

To begin, let us define what we mean by a polaron, in general, and a small polaron, in particular. If a carrier remains in the vicinity of a particular atomic site over a time interval longer than a typical vibrational period, the atoms in the neighborhood of the excess charge will have sufficient time to assume new equilibrium positions consistent with the presence of the added charge. These atomic displacements will generally produce a potential well for the excess carrier. If this carrier-induced potential well is sufficiently deep, the carrier may occupy a bound state, being unable to move without an alteration of the positions of the surrounding atoms. The unit comprising the bound carrier and its induced lattice deformation is termed a *polaron*. Alternatively, since the potential well resulting from the carrier-induced displacements acts to "trap" the carrier itself, the carrier is often referred to as being *self-trapped*. In addition, the adjective small in the term *small polaron* indicates that the self-trapped carrier is essentially confined to a "small region" which is typically just a single atomic site.

Unfortunately, the term *polaron* is somewhat misleading. The name polaron is derived from early considerations of a model in which the carrier-induced potential well arises solely from the classical (electrostatic) interaction of a carrier with the optical-mode dipoles of a polar material. However, the argument that a stationary carrier will induce deformation, and hence a potential well, which will tend to hold it in place, is quite general and is not at all restricted to a polar system. In fact, the best experimental evidence for the existence of small polarons is found in situations in which the carrier interacts with the atoms via an electron–lattice interaction which is short-range rather than via the long-range (electrostatic) interaction characteristic of the early theoretical discussions. For instance,

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* This work is supported by the U.S. Atomic Energy Commission.

† Invited paper.

small polarons even exist in nonpolar crystals such as orthorhombic sulfur and realgar, As_4S_4 (*1*, *2*). Thus, one should not restrict consideration of small-polaron formation to polar materials in which the classical coupling of an electron to the optical modes of an ionic lattice may be large, in this sense the term *polaron* is a misnomer. It should be remembered that self trapping occurs in both polar and nonpolar materials and may be associated with the carrier's interaction with both acoustic and optical-mode lattice vibrations.

The present discussion is not concerned with the question of determining the conditions under which small polarons are formed, but rather the aim here is to discuss the transport properties of small polarons. Thus, for the present, it will simply be noted that for sufficiently (but not unreasonably) large values of the electron–lattice coupling strength small polarons will be formed. The theory of their formation will be discussed more fully by this author later at this conference.

Let us now consider the energetic situation which prevails in the case of an excess electron forming a small polaron. Namely, as a result of a carrier displacing the atoms surrounding it, its energy is reduced by an amount $2E_b$ while the strain energy of the lattice associated with producing this distortion is increased by an amount E_b. This yields a net reduction of the energy of the system comprising an electron and a deformed lattice, relative to that of an electron in an undeformed lattice, by the amount E_b; this energy is termed the small-polaron binding energy. Furthermore, since the small polaron may equally well reside on any one of the geometrically equivalent sites in the crystal, we may expect the formation of a small-polaron band analogous to an electronic band of a rigid lattice.

Pursuing the analogy with an electronic band, we may proceed as in the standard tight-binding approach to view the wavefunction of the small polaron as the sum of local wavefunctions; in particular, in the case of the small polaron it is appropriate to take the local wavefunction to be a product of the *local electronic* wavefunction and the vibrational wavefunction associated with the concomitant local deformation (*3*). The width of the small-polaron band calculated in this modified tight-binding scheme, is proportional to the product of an electronic transfer integral and a vibrational overlap integral. Each of the two vibrational wavefunctions in the vibrational overlap integral represents a localized lattice deformation with the two deformations and concomitant wavefunctions being related by a simple lattice translation of one lattice spacing. This vibrational overlap factor, related to atomic tunneling, is typically very small. Thus, in a crystal the small-polaron band is usually extremely narrow, its width being very small compared with even vibrational energies. This is because the motion of the carrier requires the concomitant transport of an atomic displacement pattern.

A small polaron in an ideal crystal may move from site to site via two distinct processes. The first involves the tunneling of a small polaron between neighboring sites with no change in the phonon population. These so-called diagonal processes involve simply translating the carrier and its self-induced lattice distortion between adjacent sites without any change in the atomic vibratory motion; this corresponds to band motion. The complementary processes are those in which the phonon population changes with a site-to-site transfer. These processes, termed nondiagonal processes, correspond to the phonon-assisted tunneling of the carrier between adjacent sites. Thus, the small-polaron mobility is a sum of two contributions: one associated with small-polaron band motion and the other with small-polaron hopping motion. In an ideal crystal the small-polaron band mobility will predominate at absolute zero. With rising temperature the band contribution to the mobility will fall, while the hopping component will increase until, at sufficiently high temperatures, small-polaron motion proceeds predominantly via phonon-assisted hopping. The actual temperature of the changeover depends on the details of the model [the details of the coupling of the electron to both the optical and acoustic phonons of the crystal and the model for the "scattering" associated with small-polaron band motion]. However, the extreme narrowness of the small-polaron band leads one to expect that the band motion typically will be washed out by whatever disorder exists in a real crystal. Thus, only small-polaron hopping motion will be discussed. Examples of small-polaron hopping motion appear to be found in the hopping of Ni^{3+} holes around Li^+ impurities in NiO and in the unbound hopping of Mn^{3+} holes in MnO (*4*, *5*). In the first case the observed high-frequency conductivity is associated with small-polaron hopping motion. In the second example the hopping of small-polaron holes give rise to a dc conductivity.

In the following discussion most of our concern will be focussed on calculations in which the electronic transfer integral associated with a small-polaron hop is sufficiently small so as to treat it perturbatively; the phonon-assisted site-to-site jump rate is then proportional to some power of the relevant electronic transfer integral. Physically, this regime corresponds to a situation in which the electron cannot adiabatically follow an alteration of the atomic positions. Thus this is termed nonadiabatic small-polaron motion. The complementary regime, in which the electron can always adjust to the atomic state, is termed the adiabatic regime and will also be discussed here.

The fundamental quantity with which we shall now be concerned is the rate which characterizes a phonon-assisted transition that takes a small-polaron from one site to a neighboring site. If one considers each hop of a carrier to be uncorrelated with its prior hops (or hops of other carriers) then the relevant jump rate is calculated by placing a small polaron on a particular site at some initial time and then computing the rate at which it moves to a neighboring site. The lattice vibrations then act as a thermal bath with which the electron can exchange energy. It is clear that a necessary condition for the lattice vibrations to fulfill this function is that vibrational energy be capable of being transferred from lattice site to lattice site, i.e., there must be adequate dispersion of the vibrational frequencies.

The nonadiabatic jump rate may be calculated exactly (*6*, *7*). In Fig. 1 the phonon-assisted jump rate associated with a small-polaron hop, in units of $2\pi J^2/\hbar^2\omega_0$ [J is the electronic transfer integral and ω_0 is the mean optical-mode frequency], is plotted vs reciprocal temperature, in units of the optical mode temperature, $\theta = \hbar\omega_0/\kappa$, for two values of the phonon-dispersion parameter, ω_b; the width of the optical band is $6\omega_b$. Focusing attention on either one of the two curves of Fig. 1, it is seen that two distinct temperature dependences are manifested. At sufficiently low temperatures, $(2E_b/\hbar\omega_o)\operatorname{csch}(\beta\hbar\omega_o/2) \ll 1$ [in the case of small-polaron hopping $(2E_b/\hbar\omega_o) \gg 1$], multiphonon processes are frozen out and the jump rate is dominated by the phonon-assisted process which involves the absorption of the minimum amount of vibrational energy which results in an energy conserving hop. In the case at hand, a carrier's interaction with only optical phonons, this process is a two phonon process. Namely, a phonon of energy $\sim\hbar\omega_o$ is absorbed and another is emitted. The low-temperature jump rate is concomitantly activated with the activation energy $\hbar\omega_o$ associated with the probability of absorbing a phonon of energy $\hbar\omega_o$. In the complementary high temperature regime multiphonon processes are no longer frozen out. Then the jump rate manifests a thermally activated behavior with the activation energy $\varepsilon_2 = E_b/2$. It should be noted that this high-temperature activation energy is not associated with phonon energies but

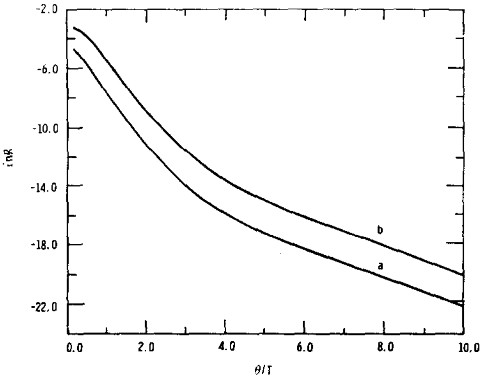

FIG. 1. The natural logarithm of the optical-phonon-assisted jump rate in dimensionless units is plotted against $\theta/T (\theta \equiv \hbar\omega_0/\kappa)$ for $E_b/\hbar\omega_0 = 10$, and (a) $2\pi\omega_b/\omega_0 = 0.5$, and (b) $2\pi\omega_b/\omega_0 = 0.05$.

simply with the electron–lattice coupling strength and the stiffness of the material, the parameters involved in E_b. The fact that the activation energy depends on no quantum-mechanical quantities suggests that a semiclassical interpretation of this high-temperature activation energy is possible. Later, we shall see that this is, in fact, the case. It is interesting to note that in the typical example illustrated in Fig. 1, the transition between the low-temperature and high-temperature regimes occurs over a relatively narrow range of temperature. This is a feature of both the (representative) values of the parameters used in this plot and the fact that the electron–lattice interaction only involves optical phonons.

Finally, some comment should be made about the role of vibrational dispersion in this calculation. The upper curve of the two in Fig. 1 differs from the lower curve solely in that the dispersion in this case is smaller. The dispersion dependence is greater as the temperature is lowered. If one proceeds to the limit of zero vibrational dispersion the rate increases and becomes undefined. Alternatively, as the dispersion is increased, the dispersion dependence of the jump rate becomes less and less. An interesting aspect of the optical phonon-assisted jump rate (which will not be dwelled on here) is that it is undefined for a one-dimensional system: an attempt to calculate it yields a divergent result for all values of the optical bandwidth; Fig. 1 is for a three-dimensional lattice.

If a carrier interacts with the atoms of a lattice via a short-range interaction, such as when a carrier on a transition metal ion displaces adjacent ligands as in, say, MnO (*5*), the interaction between the carrier and the acoustic phonons is, a priori, comparable to that between the carrier and optical phonons. Thus one is led to consider the jump rate in the situation in which the carrier interacts solely with acoustic phonons (*8*). This situation differs from the optical phonon problem in a fundamental manner. Namely, since the acoustic phonons with which a carrier can interact extend from the Debye energy down to zero energy, at no finite temperature are all acoustic phonons frozen out, i.e., $\kappa T > \hbar\omega_{\mathbf{q}}$ from some $\mathbf{q}$. Because there is no special freezing out energy for all the phonons, a thermally activated temperature-dependence of the jump rate will not be observed at low-temperatures. This is illustrated by the curve of Fig. 2, in which the logarithm of the phonon-assisted jump rate, in units of $J^2/\hbar^2\omega_m$, is plotted vs θ_m/T, where θ_m is the temperature corresponding to the energy of the maximum energy phonon with which a carrier can interact, $\hbar\omega_m = K\theta_m$. At low temperatures the jump rate is nonactivated. As in the optical-phonon calculation, when the temperature is raised above the temperature corresponding to the maximum-energy phonon with which the carrier can interact, the jump rate becomes thermally activated. In fact, as in the optical phonon problem, this high-temperature behavior can be understood via a semiclassical picture.

In the main, the remainder of this summary will be devoted to studies of small-polaron hopping motion within this high-temperature semiclassical regime. A fundamental concept characteristic of this regime is the notion of a *coincidence event*. Specifically, taking the *electronic* energy-level associated with a carrier occupying any site in a crystal to be a function of the instantaneous positions of the atoms of the crystal, it may be seen that, since the positions of the atoms are constantly

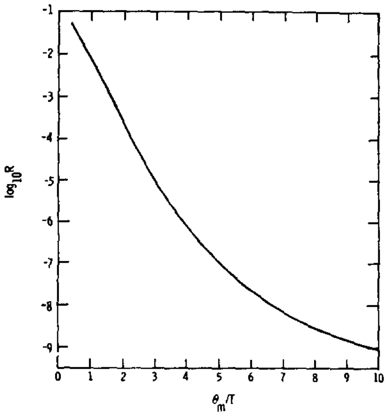

FIG. 2. The logarithm of the acoustic-phonon-assisted jump rate in dimensionless units is plotted against $\theta_m/T(\theta_m \equiv \hbar\omega_m/\kappa)$ for a typical value of the electron–lattice coupling strength.

changing (associated with the vibratory motion of the lattice), the electronic energy associated with a carrier occupying any given site is also changing. Amidst the myriad of distortional configurations which are assumed by the vibratory atoms, occasionally a situation is encountered in which the electronic energy of an electron at a given site "momentarily" equals that which it would have if it occupied an adjacent site. Such an occurrence is termed a *coincidence event* (*3*). While an energy coincidence is viewed as instantaneous in terms of classical physics, in quantum mechanics it has a finite duration. If this time duration is long compared with the time it takes an electron to transfer between coincident sites, $\sim\hbar/J$, then the electron can always "follow the lattice motion" and avail itself of the opportunity to make a hop. This situation is characteristic of the so-called *adiabatic* regime. Alternatively, the time required for an electron to hop may be large compared with the duration of a coincidence. Then an electron will not always follow the lattice motion and hop when a coincidence event presents itself; this is the *nonadiabatic* domain. In this case the jump rate, and hence the drift mobility, is reduced from what it is in the adiabatic regime by a factor P, $P < 1$, where P is the probability that given a coincidence event the carrier will hop (*3*, *6*). Finally, it is noted the minimum energy required to produce a lattice deformation associated with a coincidence event is just the activation energy characteristic of the high-temperature regime of the previously described jump-rate studies.

In thinking about small-polaron hopping motion one typically considers successive hops of a carrier to be uncorrelated with one another. However, the preceding discussion of a semiclassical view of a small-polaron hop is suggestive of a mechanism via which small-polaron motion may be highly correlated. In particular, if a small polaron's hop is to be considered independent of its previous hop then the distortion associated with creating the coincidence event of the first hop must relax, dissipating an amount of energy comparable to the hopping activation-energy away from the involved sites, in a time which is much shorter than the mean time between small-polaron hops (*9*). If the carrier has a substantial probability of hopping (either to a different neighbor or back to the site it occupied previously) before the lattice relaxes then its motion will be highly correlated. In this case the effective activation energy characterizing small-polaron hopping motion will be substantially reduced from that associated with uncorrelated hopping motion since much of the distortion needed to form a coincidence event is present residually from the prior hop. In fact, in the highly correlated situation the carrier can be viewed as frequently hopping back and forth between two coincident sites. In this circumstance a contribution to the net diffusion of the particle occurs when it alters its back and forth jumping motion to hop to a third site. Time is not adequate in the present review to develop a detailed discussion of this phenomenon; for this the reader is referred to the literature (*9–11*). However, as illustrated in Fig. 3, in this type of correlated small-polaron hopping situation the high-temperature small-polaron hopping mobility need not manifest a clear thermally activated behavior. In fact, the mobility in this domain may even fall slowly with increasing temperature. Since correlation effects will only manifest themselves when the jump rate is greater than or

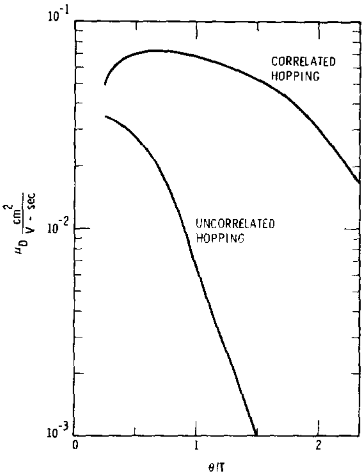

FIG. 3. The semiclassically-calculated small-polaron drift mobility is plotted versus θ/T for $E_b/\hbar\omega_0 = 10$ with correlation effects being included (upper curve) and with them being ignored (lower curve).

comparable to the relaxation rate, typically this restricts consideration of these correlation effects to sufficiently large values of the transfer integral J.

Associated with small-polaron hopping motion is a rather distinctive ac conductivity (*6*, *7*, *12*). Briefly, in the high-temperature semiclassical regime, the ac conductivity is typically peaked at a frequency near $2E_b/\hbar$ with a width $\sim (8\kappa T E_b)^{1/2}/\hbar$. In the low-temperature regime ($\kappa T < \hbar\omega_o$) the details of the absorption spectrum depend on the frequency spectrum of the phonons with which the carrier can interact. If a carrier interacts with a narrow band of optical frequencies, its low-temperature conductivity is made up of a series of peaks the envelope of which is again peaked near $2E_b/\hbar$ but with a smaller width $\sim (8\hbar\omega_o E_b)^{1/2}/\hbar$. While the high-temperature conductivity is characterized by the activation energy $(2E_b - \hbar\omega)^2/8E_b$, in the low-temperature limit the ac conductivity approaches temperature independence. This is because the dominant processes at low temperatures are those in which an electron absorbs a photon and spontaneously emits phonons. It should be stressed that the details of the temperature dependence in the low-temperature regime is an artifact of restricting the electron–lattice interaction to optical phonons. Finally, it is noted that a small-polaron conductivity (absorption) peak may be associated with either small-polaron hopping about a defect or free small-polaron motion.

The problem of understanding the Hall mobility associated with the hopping motion of small-polarons in the high-temperature semiclassical regime is an intricate one which has received considerable attention during the past decade (*9*, *13–15*). The question of how the application of a small static magnetic field will alter the polaron's hopping motion is central to these investigations. Generally speaking the magnetic field only manifests itself when the lattice distorts in such a way as to provide a carrier in a zero field situation with equal probabilities of hopping to any one of several sites. It is in these instances, when the carrier may be said to have a choice of "final" sites, that a magnetic field can effect the hopping motion so as to provide a Hall current. Not surprisingly, the Hall mobility associated with hopping motion differs qualitatively from what results from a free-electron-like picture. For instance, the Hall mobility will generally differ very substantially in both magnitude and temperature dependence from the mobility associated with a conductivity measurement; concomitantly the Hall coefficient does not simply measure the carrier number. In fact, it has been demonstrated that when the drift mobility is low ($\ll 10^{-1}$ cm^2/V sec) and thermally activated, the mobility measured in a Hall experiment can be much higher ($\sim 10^{-1}$ cm^2/V sec) and less activated; it can even be a decreasing function of increasing temperature. Furthermore, although the sign of the Hall effect for free-electron-like behavior by itself determines the sign of the charge carrier, in a hopping situation this is no longer the case (*16*). For instance, the hopping motion of holes will yield a hole-signed Hall effect in a square lattice but not in a hexagonal lattice. Thus unlike the free-electron situation, a Hall effect experiment does not directly measure the carrier's drift mobility.

Finally, a short comment about the thermoelectric power associated with hopping motion is in order. The thermopower measurement is in effect a measurement of the average energy carried by a particle as it moves through a material. In the case of hopping motion the question which arises is how much of the energy which is absorbed in making a hop is carried with the particle. To answer this question we must examine how much vibrational energy is absorbed and/or emitted at the initial and final sites of a jump in the hop process. In the simplest model of small-polaron motion, energy is absorbed and emitted equally at both sites and none of the hopping energy is carried with the particle. However, if as in a classical over-the-barrier hop, the energy to hop is all absorbed at the initial site and emitted at the final site, then the hopping energy is all carried along with the carrier. Alternatively, if, as in the case of correlated small-polaron hopping motion, the energy is absorbed primarily at the final site and emitted at the initial site, then the hopping energy is carried in the direction *opposite* to that of the carrier (*6*).

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