PHYSICAL REVIEW B VOLUME 43, NUMBER 14 15 MAY 1991-I

Semiclassical small-polaron hopping in a generalized molecular-crystal model

David Emin
Sandia National Laboratories, Albuquerque, New Mexico 87185-5800

(Received 8 November 1990)

The thermally activated rates for high-temperature adiabatic and nonadiabatic small-(bi)polaron hopping are calculated for a generalization of Holstein's molecular-crystal model. In the expanded model a carrier occupying a molecule is coupled to many molecular vibrational modes rather than to just the single vibrational mode envisioned in the original model. This generalization of the molecular-crystal model does not significantly affect the semiclassical small-(bi)polaron jump rates. In particular, for the generalized model the hopping activation energy becomes a sum of contributions associated with each of the vibrational modes to which the carrier is coupled. The vibrational frequency that is the preexponential factor for adiabatic small-(bi)polaron hopping is the square root of the sum of the squares of the vibrational frequencies weighted by their relative contributions to the net hopping activation energy.

I. INTRODUCTION

Phonon-assisted hopping of charge carriers or excitons occurs in many classes of solids. These systems include crystals, glasses, and polymers.[1] There are two distinct types of phonon-assisted hopping: (1) weak-coupling single-phonon hopping and (2) strong-coupling multiphonon hopping. The type of hopping that occurs is generally determined by the spatial extent of the localized states between which the hopping occurs. The size of the electronic states affects the hopping processes because electronic states are only appreciably coupled to phonons that have half-wavelengths that exceed the diameter of the localized states.[2,3] Weak-coupling single-phonon hopping occurs when the localized electronic states between which hopping occurs are both sufficiently large that they are only effectively coupled to the small fraction of phonon states that have sufficiently long wavelengths.[2,3] For example, single-phonon hopping occurs between large-radius impurity centers in semiconductors.[4] By contrast, phonon-assisted hopping between severely localized electronic states is of the multiphonon (small-polaronic) type.

Single-phonon and multiphonon hops are distinguished by their temperature dependences.[2,3] For example, when the thermal energy k_BT exceeds the energy of the phonons involved in the hop, the jump rate for a single-phonon hop (proportional to the density of available phonons) becomes simply proportional to the temperature. By contrast, in this high-temperature regime, a multiphonon (small-polaronic) jump rate is thermally activated with an activation energy that exceeds the energies characterizing the phonons involved in the hop.

Theoretical studies of multiphonon (small-polaronic) hopping[2,3,5] have employed the molecular-crystal model introduced by Holstein.[6] This model envisions a crystal composed of molecules possessing a single deformation parameter: $x_{\mathbf{g}}$ is the deformation parameter for the molecule at site $\mathbf{g}$. Furthermore, in this model the energy of an electron on a molecule is taken to depend linearly on the deformation parameter of that molecule. Explicitly, the energy of a carrier on site $\mathbf{g}$, $\epsilon_{\mathbf{g}}$, is written as $-Ax_{\mathbf{g}}$, where A is a measure of the electron-lattice coupling strength.

For the molecular-crystal model, the elemental jump rate is thermally activated in the high-temperature regime ($k_BT > \hbar\omega_0/3$, where ω_0 is the vibrational frequency of a molecule's deformational parameter).[2] In this high-temperature regime, the molecules' vibratory motion is treated classically, and small-polaronic hopping can be understood in terms of the occurrence of "coincidence events."[1,5,7] Coincidence events occur because the local (molecular) electronic levels change as the molecules' deformation parameters vibrate about their equilibrium values. In particular, a coincidence event occurs when the electronic energy level of the molecule occupied by a carrier "momentarily" equals the electronic energy level of another molecule. At such a transitory degeneracy, the carrier can transfer from the occupied molecule to the molecule that has an electronic energy level coincident with it. The resulting elemental jump rate is

$$R = [(\omega_0/2\pi)\exp(-E_A/k_BT)]\bar{P}(T) \ . \tag{1}$$

Here the activation energy E_A is the minimum net energy required to displace the molecules from their equilibrium configuration so as to produce a coincidence event between an occupied site and an unoccupied site. The square-bracketed factor in Eq. (1) is the rate at which coincidence events occur between the two molecules between which hopping is being considered. $\bar{P}(T)$ is the average of the probability that the carrier will avail itself of the opportunity afforded by the coincidence event and hop between sites.

The physical situation encountered in real solids is generally much more complicated than that envisioned in the molecular-crystal model. In particular, a molecule generally has many more than one vibrational degree of freedom. Furthermore, a carrier on a molecule is generally coupled (to some extent) to all of its vibrational modes. Thus, one might question the applicability of Eq. (1) to real solids. For example, one may wonder what vibrational frequency enters into the expression for the jump rate if the carrier is coupled to many vibrational modes.

In this paper the elemental jump rate in the semiclassical high-temperature regime is calculated for a generalized version of the molecular-crystal model. The form of the jump-rate expression is found to be unaltered from that of the simple molecular-crystal model. The frequency factor that plays the role of ω_0 in Eq. (1) is just found to be a weighted average of the involved vibrational frequencies, Eq. (15b).

Since generalizing the molecular-crystal model produces no qualitative changes in the jump rates, estimates of observable quantities based on the jump rates are also unaffected by this generalization. This result is consistent with experimentally determined small-(bi)polaron dc conductivities and Hall mobilities in varied complex systems being in reasonable agreement with calculations based on the simple molecular-crystal model (e.g., see Refs. 8–12). However, the mobilities deduced from some nondispersive transient photoconductivity measurements differ significantly from the results of calculations for equilibrated carriers within the molecular-crystal model. In particular, the electric-field dependences of the mobilities deduced from these experiments[13] differ from those predicted and observed for equilibrated small polarons. In addition, extrapolating these field-dependent mobilities to their low-field limits yields estimates of the preexponential factor of the mobility in Eq. (1) that are much larger than those expected of equilibrated carriers.[14]

It was suggested in Ref. 14 that a generalization of the molecular-crystal model might yield significantly increased values of the preexponential factor of the mobilities. However, the calculations of this paper indicate that the present expansion of the molecular crystal does not produce this result.

II. GENERALIZED MOLECULAR-CRYSTAL MODEL

Since an elemental hop involves only two sites, here only two molecules are explicitly considered. Each of the two molecules has N vibrational degrees of freedom. In the harmonic approximation, neglecting vibrational dispersion, the vibrational energy of the two molecules is

$$E_{\text{vib}}=\sum_{n=1}^{N}[M_n(\dot{x}_n^2+\dot{y}_n^2)+k_n(x_n^2+y_n^2)]/2\ , \tag{2}$$

where M_n and k_n are the reduced mass and stiffness constant, respectively, of the nth vibrational mode of a molecule. The deformation coordinates of the nth mode at the initial and final sites are x_n and y_n, respectively.

Generalizing the molecular-crystal model so that the electronic states of both initial and final sites depend on all of the N deformation coordinates of each molecule, the local electronic energies of initial and final sites are

$$\epsilon_i=\epsilon_i(0)-\sum_{n=1}^{N}A_n x_n \tag{3a}$$

and

$$\epsilon_f=\epsilon_f(0)-\sum_{n=1}^{N}A_n y_n\ , \tag{3b}$$

where A_n is the electron-lattice coupling constant associated with the nth mode and $\epsilon_f(0)$ and $\epsilon_i(0)$ are the electronic energies of initial and final sites when the configurational coordinates are all at their carrier-free equilibrium values. In the presence of an applied electric field E, $\epsilon_f(0)-\epsilon_i(0)=-q\mathbf{E}\cdot\mathbf{R}_{fi}$, where q is the charge of the carrier and $\mathbf{R}_{fi}$ is the position vector between sites f and i.

With the carrier being permitted to move between initial and final sites with the transfer integral J, the two electronic energy hypersurfaces of the two-site system become

$$W_{\pm}(x_1,\ldots,x_N;y_1,\ldots,y_N)=(\epsilon_f+\epsilon_i)/2\pm[(\epsilon_f-\epsilon_i)^2/4+J^2]^{1/2}\ . \tag{4}$$

When severely confined to the initial site to form a small polaron, $|\epsilon_i|\gg|\epsilon_f|,|J|$. Then the lowest electronic state is $W_-\approx\epsilon_i=-|\epsilon_i|$. However, at a coincidence $\epsilon_i=\epsilon_f$, one has $W_-=\epsilon_i-|J_c|$. The subscript c is placed on the transfer energy at a coincidence to emphasize that since the transfer energy is generally dependent on the atomic configuration, the electronic transfer energy at a coincidence generally differs from that at the equilibrium configuration.

III. SEMICLASSICAL JUMP RATE

The high-temperature small-polaron jump rate in Holstein's semiclassical occurrence probability approach may be written as[1]

$$R=\int_{-\infty}^{\infty}d\dot{E}\,P(\dot{E})|\dot{E}|\langle\delta(\epsilon_f-\epsilon_i)\delta(\dot{\epsilon}_f-\dot{\epsilon}_i-\dot{E})\rangle\ , \tag{5}$$

where

$$\dot{E}=(\dot{\epsilon}_f-\dot{\epsilon}_i)|_{\epsilon_f=\epsilon_i} \tag{6}$$

is the time rate of change of the relative electronic energies of initial and final sites evaluated at the coincidence event. Here $P(\dot{E})$ is the probability that the electronic carrier will negotiate a hop when a coincidence event occurs. The brackets indicate a thermal average over all configurational velocities and positions: $\{\dot{x}_n\}$, $\{\dot{y}_n\}$, $\{x_n\}$, $\{y_n\}$.

If the intersite transfer energy is sufficiently small so that a carrier rarely responds to the opportunity afforded by the occurrence of a coincidence event by executing a hop, the hopping is termed "nonadiabatic."[1,5,7] Then,[5]

$$P(\dot{E})=2\pi J_c^2/\hbar|\dot{E}|\ll 1\ . \tag{7}$$

Alternatively, if the electronic transfer energy at the coincidence J_c is large enough so that the carrier can always follow the atomic motion, the hopping is termed "adiabatic."[1,5,7,15] Then,

$$P(\dot{E})=\begin{cases}1 & \text{for } \dot{E}>0 \qquad (8a)\\ 0 & \text{for } \dot{E}<0\ , \qquad (8b)\end{cases}$$

provided there is sufficient dispersion of the vibrational frequencies so as to preclude an immediate return hop.[5,15]

If the vibrational dispersion is not sufficient to preclude an immediate return hop, the carrier responds to a coincidence by shuttling between initial and final sites. Ultimately the carrier will settle on a site. If it lights on the final site, a hop will have taken place. Thus, for (adiabatic) hopping in which immediate-return hops are likely, a carrier will effect a hop in half of the instances of an appropriate coincidence event:[16]

$$P(\dot{E})=\begin{cases}\frac{1}{2} \text{ for } \dot{E}>0 & \text{(9a)}\\ 0 \text{ for } \dot{E}<0\,. & \text{(9b)}\end{cases}$$

To calculate the jump rate, the averages of the two δ functions in Eq. (5) must be evaluated. To accomplish this task, it is first noted that the linear dependence of the local electronic energies on the local configurational coordinates [cf. Eqs. (3a) and (3b)] permits writing the average of the product of the two δ functions in Eq. (11) as the product of independent averages:

$$\begin{aligned}\langle \delta(\dot{\epsilon}_f-\dot{\epsilon}_i-\dot{E})\delta(\epsilon_f-\epsilon_i)\rangle_{\{\dot{x}_n\}\{\dot{y}_n\}\{x_n\}\{y_n\}}\\ =\langle \delta(\dot{\epsilon}_f-\dot{\epsilon}_i-\dot{E})\rangle_{\{\dot{x}_n\}\{\dot{y}_n\}}\langle \delta(\epsilon_f-\epsilon_i)\rangle_{\{x_n\}\{y_n\}}\,. \qquad (10)\end{aligned}$$

An integral representation of the δ functions is then adopted:

$$\delta(\dot{\epsilon}_f-\dot{\epsilon}_i-\dot{E})=(2\pi)^{-1}\int d\alpha \exp[i\alpha(\dot{\epsilon}_f-\dot{\epsilon}_i-\dot{E})] \qquad (11a)$$

and

$$\delta(\epsilon_f-\epsilon_i)=(2\pi)^{-1}\int d\beta \exp[i\beta(\epsilon_f-\epsilon_i)]\,. \qquad (11b)$$

With Eqs. (10), (11a), and (11b), the thermal average of Eq. (5) is rewritten as

$$\begin{aligned}\langle \delta(\dot{\epsilon}_f-\dot{\epsilon}_i-\dot{E})\delta(\epsilon_f-\epsilon_i)\rangle_{\{\dot{x}_n\}\{\dot{y}_n\}\{x_n\}\{y_n\}}\\ =\exp(|J_c|/k_BT)(2\pi)^{-2}\\ \times\int d\alpha \exp(-i\alpha\dot{E})F(\alpha)\int d\beta\, G(\beta)\,, \qquad (12)\end{aligned}$$

where

$$\begin{aligned}F(\alpha)&=\langle \exp[i\alpha(\dot{\epsilon}_f-\dot{\epsilon}_i)]\rangle\\ &=\prod_n \langle \exp[i\alpha A_n(\dot{x}_n-\dot{y}_n)]\rangle\\ &=\prod_n \frac{\int d\dot{x}_n\int d\dot{y}_n \exp[-M_n(\dot{x}_n^{\,2}+\dot{y}_n^{\,2})/2k_BT+i\alpha A_n(\dot{x}_n-\dot{y}_n)]}{\int d\dot{x}_n\int d\dot{y}_n \exp[-M_n(\dot{x}_n^{\,2}+\dot{y}_n^{\,2})/2k_BT]} \qquad (13a)\end{aligned}$$

and

$$\begin{aligned}G(\beta)&=\langle \exp[i\beta(\epsilon_f-\epsilon_i)]\rangle\\ &=\exp(i\beta\Delta)\prod_n\langle \exp[i\beta A_n(x_n-y_n)]\rangle\\ &=\exp(i\beta\Delta)\prod_n \frac{\int dx_n\int dy_n \exp\{-[k_n(x_n^2+y_n^2)/2-A_nx_n]/k_BT+i\beta A_n(x_n-y_n)\}}{\int dx_n\int dy_n \exp\{-[k_n(x_n^2+y_n^2)/2-A_nx_n]/k_BT\}}\,, \qquad (13b)\end{aligned}$$

where $\Delta=\epsilon_f(0)-\epsilon_i(0)$. In obtaining Eqs. (12) and (13b) it is recalled [see text below Eq. (4)] that the lowest-lying electronic energy level at a coincidence is $W_-=\epsilon_i-|J_c|$, while the lowest-lying electronic level near equilibrium is $W_-=\epsilon_i$.

Completing the squares in the exponentials contained in Eqs. (13a) and (13b) and then carrying out the standard contour integrations over the configuration coordinates and velocities yields

$$\begin{aligned}F(\alpha)&=\prod_n \exp(-\alpha^2A_n^2k_BT/M_n)\\ &=\exp(-4\alpha^2\epsilon_2\Omega^2k_BT) \qquad (14a)\end{aligned}$$

and

$$\begin{aligned}G(\beta)&=\exp(i\beta\Delta)\prod_n \exp[(-\beta^2A_n^2k_BT+i\beta A_n^2)/k_n]\\ &=\exp[-4\beta^2\epsilon_2k_BT+i\beta(4\epsilon_2+\Delta)]\,. \qquad (14b)\end{aligned}$$

In the final equalities of Eqs. (14a) and (14b), definitions of a generalized nonadiabatic small-polaron hopping activation energy ϵ_2 and a weighted average of the squares of local vibrational frequencies $\omega_n^2=k_n/M_n$ are introduced:

$$\epsilon_2=\sum_n (A_n^2/4k_n) \qquad (15a)$$

and

$$\Omega^2=\sum_n \omega_n^2(A_n^2/4k_n)/\epsilon_2\,. \qquad (15b)$$

In Eq. (15a) the electron-lattice interaction-related contribution to the hopping activation energy ϵ_2 is seen to be a sum of contributions from the different modes to which the carrier is coupled. An analogous result was previously derived for a model in which the carrier was coupled to both acoustic and optic phonons.[17] The square of the characteristic frequency that enters into the hopping problem Ω^2 is seen to be an average of the local vibrational frequencies weighted by the contribution of each mode to the net hopping activation energy.

Inserting Eqs. (14a) and (14b) into Eq. (12) and performing the integrations over α and β yields

$$\langle \delta(\dot{\epsilon}_f-\dot{\epsilon}_i-\dot{E})\delta(\epsilon_f-\epsilon_i)\rangle_{\{\dot{x}_n\}\{\dot{y}_n\}\{x_n\}\{y_n\}}=(\Omega/2\pi)\exp\{-[(4\epsilon_2+\Delta)^2/16\epsilon_2-|J_c|]/k_BT\}$$
$$\times(8\epsilon_2k_BT\Omega^2)^{-1}\exp(-\dot{E}^2/16\epsilon_2k_BT\Omega^2)\ . \tag{16}$$

The semiclassical small-polaron jump rate is obtained when Eq. (16) is inserted into Eq. (5):

$$R=(\Omega/2\pi)\exp\{-[(4\epsilon_2+\Delta)^2/16\epsilon_2-|J_c|]/k_BT\}(8\epsilon_2k_BT\Omega^2)^{-1}\int_{-\infty}^{\infty}d\dot{E}\,P(\dot{E})|\dot{E}|\exp(-\dot{E}^2/16\epsilon_2k_BT\Omega^2)\ . \tag{17}$$

In the adiabatic regime with sufficiently strong vibrational dispersion, $P(\dot{E})$ in Eq. (17) is given by Eqs. (8a) and (8b). Then, the integration over $\dot{E}$ is readily carried out, yielding an expression for the adiabatic jump rate that only differs from the analogous molecular-crystal-model result in that ω_0 is replaced by Ω:

$$R=(\Omega/2\pi)\exp\{-[(4\epsilon_2+\Delta)^2/16\epsilon_2-|J_c|]/k_BT\}\ . \tag{18}$$

In the nonadiabatic limit, where $|J_c|\to 0$ and $P(\dot{E})$ is given by Eq. (7), the integration over $\dot{E}$ in Eq. (17) is readily performed to yield

$$R=(J_c^2/\hbar)(\pi/4\epsilon_2k_BT)^{1/2}$$
$$\times\exp[-(4\epsilon_2+\Delta)^2/16\epsilon_2k_BT]\ . \tag{19}$$

Equation (19) is identical to the result obtained for the simple molecular-crystal model.[1,2]

Finally, it is recalled that the electric-field dependence of the hopping mobility depends upon the electric-field dependence of the elemental jump rates.[2] Within the molecular-crystal model, the electric-field dependences of the small-polaron jump rates of Eqs. (18) and (19) are obtained by just replacing Δ by $-q\mathbf{E}\cdot\mathbf{R}_{fi}$ [see the discussion below Eqs. (3a) and (3b)].[2,5] In this approach any additional electric-field dependence of the jump rates arising from the field dependence of the transfer energy J_c is ignored.

IV. CONCLUSIONS

Despite its extreme simplifications, Holstein's molecular-crystal model has provided an excellent framework within which to understand small-polaronic hopping in solids. Furthermore, the measured magnitudes and temperature dependences of the dc conductivities and Hall mobilities where small-polaronic hopping is suspected are even reasonably consistent with the predictions of calculations based on the molecular-crystal model.[8-12] In addition, the dependence of the electrical conductivity at high electric fields on electric-field strength has been understood, or at least rationalized, in terms predictions of the model.[11]

Some results of transient photoconductivity measurements of hopping transport also agree with predictions of the simple molecular-crystal model. For example, for x-ray-generated holes in SiO_2, the magnitude, temperature dependence, and electric-field dependence of the high-field mobility are all in accord with predictions based on the simple molecular-crystal model.[18] Also, time-of-flight mobility measurements on a series of molecularly doped polymers are consistent with the predicted transition from adiabatic to nonadiabatic small-polaron hopping with increasing intersite separation.[14]

Nonetheless, some transient determinations of mobilities manifest significant departures from the predictions for the motion of equilibrated small polarons obtained from studies of Holstein's molecular-crystal model. For example, some magnitudes of the reported preexponential factors of the mobilities are unacceptably large (corresponding to ω_0 in Holstein's model being over 10^{15} $\sec^{-1}$).[14] These observations motivated asking whether the preexponential factor of the mobility calculated for an extension of Holstein's model might be enhanced sufficiently so as to resolve the discrepancies.[13] In particular, would the coupling of a carrier to multiple local vibrational modes increase the rate at which coincidence events and hops occur?

In the present paper, the semiclassical small-polaron jump rate has been calculated for an expanded model in which a carrier on a molecule can interact with N vibrational modes rather than just the single mode envisioned in the original model. The small-polaron jump rate for the extended model is not significantly different from that of the original model. In particular, the vibrational frequency that serves as the preexponential factor of the adiabatic jump rate is just replaced by the square root of an average of the squares of the vibrational frequencies weighted by the vibrational mode's contribution to the hopping activation energy [see Eq. (15b)].

ACKNOWLEDGMENTS

This work has been performed at Sandia National Laboratories with the support of the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

[1] 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.

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

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

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

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

[6] T. Holstein, Ann. Phys. (N.Y.) **8**, 325 (1959).

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

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

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

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

[11] I. G. Austin, in *Linear and Nonlinear Electron Transport in Solids,* edited by J. T. Devreese and V. E. van Doren (Plenum, New York, 1976), pp. 383–408.

[12] P. Nagels, in *Hopping and Related Phenomena,* edited by H. Fritzsche and M. Pollak (World Scientific, Singapore, 1990), pp. 377–392.

[13] L. B. Schein, A. Peled, and D. Glatz, J. Appl. Phys. **66**, 686 (1989).

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

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

[16] D. Emin, Phys. Rev. **3**, 1321 (1971).

[17] E. Gorham-Bergeron and D. Emin, Phys. Rev. B **15**, 3667 (1977).

[18] R. C. Hughes, Phys. Rev. **15**, 2012 (1977).