The leading odd-order correction to self-consistent theory was incorporated in work by Goldman *et al.*,[9] who retained the convenient MLJ m-6 potential, but used both $m=12$ and $m=13$ with more appropriate potential parameters. The resulting compressibility, in a 12-6 model, is about 10% too large near 0 K but within the limits of experimental error near the triple point. For a 13-6 model, theoretical and experimental values essentially agree near 0 K but the theoretical values for compressibility fall somewhat below the limits of experimental error at temperatures close to the triple point. The comparisons are shown on Fig. 3.

In such calculations the choice of the appropriate potential is still open to some question. Present knowledge of the elastic behavior of solid neon indicates that some further work on the properties of strongly anharmonic fcc crystals is worthwhile.

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Lattice Relaxation and Small-Polaron Hopping Motion[*]

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The three-dimensional analog of Holstein's molecular crystal model is utilized as the basis for a study of the relaxation of the lattice after a small-polaron hop. In particular, it is shown explicitly that the time-dependent activationlike energy arising in the previously developed theory of correlated small-polaron hopping motion is directly related to the actual relaxation of the lattice from the distorted configuration it must assume to facilitate a small-polaron hop. That is, the time dependence of this "activation energy" and the concomitant relaxation of the hop-related lattice displacements are governed by a single entity denoted as the relaxation function. Furthermore it is demonstrated that this function is directly expressible in terms of the transfer of vibrational energy from the initially distorted sites to successive (initially undistorted) neighbor sites. In fact, for the most part, the relaxation of the lattice after a hop is associated with the transfer of vibrational energy to only nearest-neighbor sites, this being essentially a local phenomenon independent of the periodic nature of the lattice. Finally, although the lattice relaxation for our three-dimensional model is found to proceed much faster than in the previously developed one-dimensional model, its effect on small-polaron hopping motion may not be inconsequential. In particular, the small-polaron drift mobility is shown to be significantly affected by lattice relaxation effects when the mean time between small-polaron hops is less than or comparable to the lattice relaxation time; this time being essentially the reciprocal of the optical-phonon bandwidth parameter.

I. INTRODUCTION

The notion of small-polaron hopping motion has been advanced in order to explain the transport properties of excess carriers in a number of low-mobility materials. Specifically, in such materials the electron-lattice interaction is viewed as strong enough so as to make possible the self-trapping of a carrier. That is, the excess carrier distorts the surrounding lattice via the electron-lattice interaction thereby producing a sufficiently deep potential well so that it is bound in its own "induced trap." The unit composed of the carrier, localized with a spacial extent of the order of a lattice constant, and its induced lattice distortion is termed a small polaron.

Fundamental to our understanding of the mechanism which characterizes the hopping motion of a small polaron is the notion of a "coincidence event." Explicitly, it is found that in order for a carrier to be able to jump to an adjacent site the local electronic energy level associated with the bound state of the occupied site must momentarily *coincide* with the local electronic energy level of a neighboring unoccupied site. Such a coincidence event generally requires a substantial local distortion of the lattice. In fact, it is just the minimum potential energy required to produce the distortion concomitant with a coincidence event which is the activation energy characterizing the small-polaron drift mobility in the uncorrelated hopping theories.[1,2] In these calculations, the drift mobility is computed by considering the elementary jump process by which a carrier placed on an initial site hops to one of its neighboring sites. The role of the remainder of the lattice in these considerations is solely to provide a heat bath for the subsystem of the occupied site and its neighbors; the energy associated with the coincidence is transferred to and from this subsystem via the lattice vibrational coupling of the subsystem to the remainder of the material.

As has been stressed previously,[3,4] unless the time required for the lattice to relax from the highly distorted configuration it assumes during a coincidence event is very short compared with the mean time between small-polaron hops, it is not proper to view the hops as independent of one another. If this condition is not fulfilled, the lattice does not generally "forget" one hop before another occurs. In such a situation one views successive small-polaron hops as being correlated with one another.

It was shown that in a one-dimensional model in which the carrier interacts solely with the longitudinal-optical-mode vibrations of the crystal (the usual polaron situation) the lattice relaxation time is $\sim \omega_b^{-1}(2\epsilon_2/kT)^2$, where ω_b is the half-width of the band of longitudinal-optical-mode frequencies, and ϵ_2 is the drift-mobility activation energy calculated in the nonadiabatic hopping theory.[4] It has been argued that the relaxation time in a three-dimensional model would be considerably shorter[3,4] but still sufficiently long in a number of materials so as to require treating the small-polaron hopping motion as highly correlated. Thus, it is of interest to extend the calculation of the one-dimensional model to three dimensions to ascertain the effect of dimensionality on the relaxation of the lattice following a coincidence event.

In the present paper, the three-dimensional molecular crystal model, reviewed in Sec. II, is utilized as a basis for studying the relaxation of the lattice following a hop. The task of Sec. III of this paper is to demonstrate that the activationlike energy which appears in the expression for the probability of two successive nearest-neighbor hops (temporally separated by the time t) is simply the minimum *total* energy required to produce the corresponding two coincidence events. This energy will be shown to be dependent on the time interval (denoted as t) between the two coincidences.

While it is shown in Sec. III that the time dependence of this two-coincidence activation energy is expressed in terms of what is designated as the relaxation function, it is the purpose of Sec. IV to demonstrate explicitly that the time dependence of the actual relaxation of the coincidence distortion is in fact governed by this function.

In the treatment of the relaxation phenomenon that is contained in Refs. 3 and 4, the initial coincidence distortion has been viewed as a wave packet which is composed of a superposition of the optical-mode phonon states; the relaxation of the coincidence distortion is then associated with the decay of the wave packet. In particular, the relaxation function is directly related to fall of the center of such a wave packet. In Sec. V, the relaxation function is studied from another point of view which does not require introducing the normal vibrational modes of the system but rather expresses the relaxation of the coincidence distortion in terms of repeated energy transfers between successive neighbor ions, thereby avoiding the assumption of any long-range order in the system. Thus, in that the periodicity of the lattice does not play an essential role in the relaxation process, it is concluded that one may apply the notion of correlated small-polaron hopping motion to amorphous materials.

The effect of the dimensionality of our model on the relaxation function is demonstrated in Sec. VI in which the relaxation function is calculated for a simple-cubic lattice structure and compared with the results for a linear chain. The more rapid relaxation in the three-dimensional case can readily be seen from Figs. 1–5; these results are found to be in agreement with the previously advanced qualitative arguments of Refs. 3 and 4.

Finally, in Sec. VII, the notion of enhanced jump rates (including jumps both to a previously occupied site as well as to a new site) is employed in calculating the average forward jump rate and, hence, the hopping drift mobility in a simple-cubic lattice. It is explicitly shown, using representative values of the physical parameters of the theory, that for drift mobilities greater than $\sim 10^{-2}$ cm^2/V sec the hopping motion of small polarons is often correlated and characterized by a temperature dependence which does not display the clear activation-type temperature dependence predicted by the uncorrelated hopping theories. This conclusion may provide an explanation for the long-standing difficulty in the theory of electrical transport phenomenon in understanding the temperature dependence of a diverse assortment of materials characterized by drift mobilities lying in the range 10^{-2} to 10 cm^2/

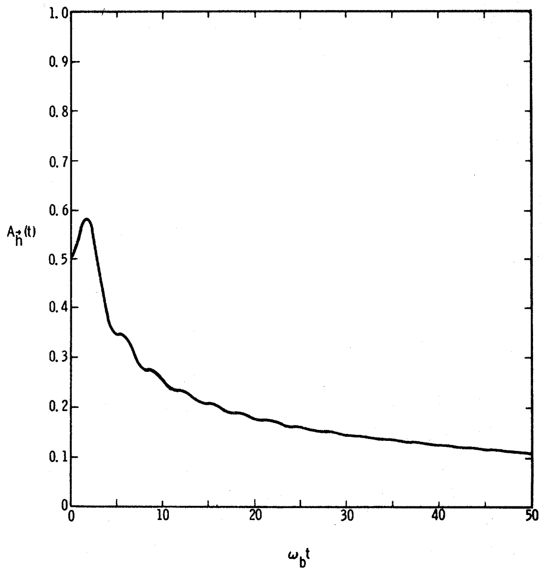

FIG. 1. The relaxation-function amplitude $A_{\vec{h}}(t)$ appropriate to a forward hop in a one-dimensional lattice.

Vsec.[5] In particular, these materials possess drift mobilities which neither manifest the simple thermally activated behavior expected of an elementary hopping theory nor permit consistent application of the notion of occasional scattering of carriers that are described as moving in an energy band.

II. MOLECULAR CRYSTAL MODEL

The molecular crystal model is a theoretical model which was introduced by Holstein[6] to study the small-polaron problem. Explicitly, in this model one considers an excess electron in regular array of N identical diatomic molecules whose orientations are fixed and whose internuclear separations are allowed to vary. The optical-mode vibrations correspond to the oscillations of the internuclear separations of the diatomic molecules. More generally, the x_g's are the local configurational coordinates associated with the optical-mode vibrations. The vibrational part of the Hamiltonian is simply

$$H_L = \sum_{\vec{g}} \left[\frac{1}{2M} \left(\frac{\hbar}{i} \frac{\partial}{\partial x_{\vec{g}}} \right)^2 + \frac{M}{2} \omega_0{}^2 x_{\vec{g}}{}^2 + \frac{M}{2} \sum_{\substack{h \\ \text{neighbors}}} \omega_1{}^2 x_{\vec{g}} x_{\vec{g}+h} \right] , \quad (1)$$

where $x_{\vec{g}}$ is the deviation of the internuclear separation of the gth diatomic molecule from its equilibrium value, M is the reduced mass of a diatomic molecule, and ω_0 is the harmonic oscillator frequency; the final term in the Hamiltonian couples neighboring oscillators and gives rise to the dispersion of the vibrational frequencies. In particular, the dispersion relation gives the relationship between a normal-mode wave vector and its associated frequency

$$\omega_{\vec{k}}{}^2 = \omega_0{}^2 + \tfrac{1}{2}\omega_1{}^2 \textstyle\sum_{\vec{h}} \cos \vec{k}\cdot\vec{h} , \quad (2)$$

where $-\pi \leq \vec{k}\cdot\vec{h} \leq \pi$.

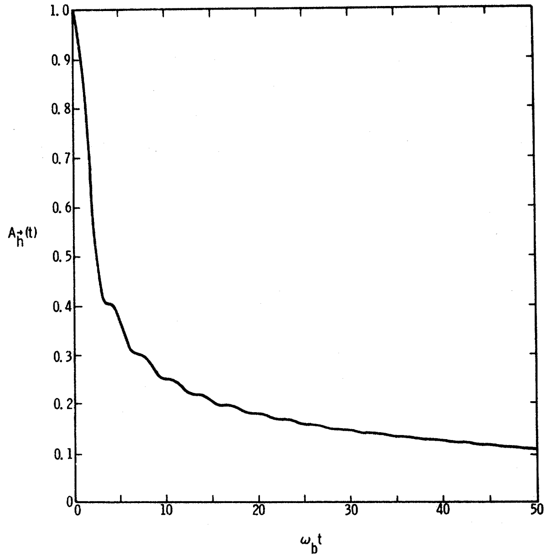

FIG. 2. The relaxation-function amplitude $A_{\vec{h}}(t)$ appropriate to a return hop, calculated for a one-dimensional lattice.

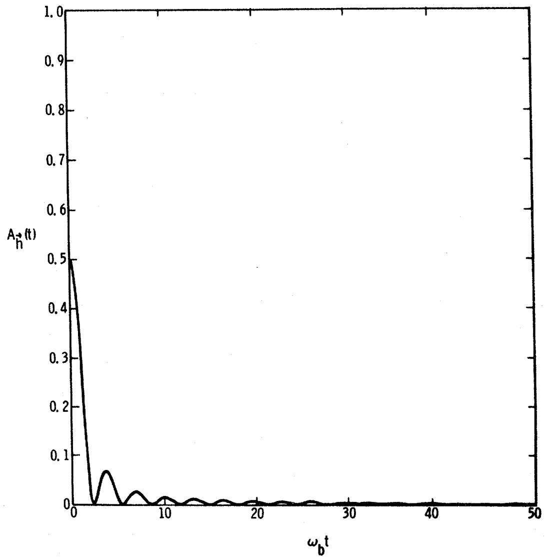

FIG. 3. The three-dimensional relaxation-function amplitude $A_{\vec{h}}(t)$, Eq. (78), corresponding to the second hop being to a third site collinear with the first two.

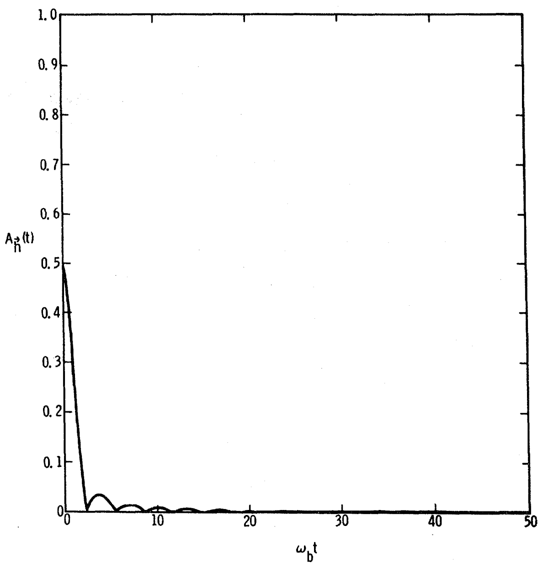

FIG. 4. The relaxation-function amplitude appropriate for the second hop in a simple-cubic crystal being at right angles to the initial hop.

The electronic portion of the Hamiltonian is given by

$$H_e = (1/2m)\,[(\hbar/i)\,\mathrm{grad}_{\vec r}]^2 + \sum_{\vec g} V(\vec r - \vec g, x_{\vec g})\ , \qquad (3)$$

where m and r are, respectively, the electron's mass and position vector, and $V(r-g, x_{\vec g})$ is the contribution of the gth molecule to the electron's potential energy. It is noted that this potential is dependent on the internuclear separation of the gth molecule; this feature introduces the electron-lattice interaction.

The eigenfunction of the system whose Hamiltonian is $H_L + H_e$ is written as a linear superposition of local electronic wave functions, i.e.,

$$\psi(\vec r, \cdots x_{\vec g} \cdots) = \sum_{\vec g} a_{\vec g}(\cdots x_{\vec g} \cdots)\, \phi_{\vec g}(\vec r, x_{\vec g})\ , \qquad (4)$$

where

$$\{(1/2m)\,[(\hbar/i)\,\mathrm{grad}_{\vec r}]^2 + V(\vec r - \vec g, x_{\vec g})\}\, \phi_{\vec g}(\vec r, x_{\vec g}) = E(x_{\vec g})\, \phi_{\vec g}(\vec r, x_{\vec g})\ ; \qquad (5)$$

$E(x_{\vec g})$ is the energy of an electron on an isolated diatomic molecule. The coefficients $a_{\vec g}$ are found, within the standard tight-binding approximations, to be given by the solutions of the coupled equations

$$i\hbar\, \frac{\partial a_{\vec g}}{\partial t} = [H_L + W_{\vec g}(\cdots x_{\vec g} \cdots)]\, a_{\vec g} - J \sum_{\vec h} a_{\vec g + \vec h}\ , \qquad (6)$$

where $W_{\vec g}$ is the electronic energy associated with the excess carrier being on site g, and J is an electronic transfer integral between neighboring sites—for simplicity, it is taken to be independent of the $x_{\vec g}$'s. An additional simplification introduced by Holstein and employed here is to take

$$W_{\vec g} = E(x_{\vec g}) = \mathrm{const} - A x_{\vec g}\ , \qquad (7)$$

where A is a constant associated with the electron-lattice coupling.

For sufficiently small J, the above set of equations may be solved perturbatively in powers of J. In zeroth order $a_{\vec g}$ is the vibrational wave function associated with a carrier at site $\vec g$, the corresponding vibrational Hamiltonian being simply $H_L + W_{\vec g}(\cdots x_{\vec g} \cdots)$.

Furthermore, at sufficiently high temperatures the vibrational motion may be treated classically. In this limit, Holstein's occurrence-probability approach becomes valid for treating small-polaron diffusion. This theory concludes that every time there is a momentary equality of the electronic energy level of the occupied site and its neighboring unoccupied site, there is a finite probability of the carrier hopping to the neighboring site. Such an equality is termed a coincidence event and, within our approximations, is characterized by the equality $x_{\vec g} = x_{\vec g + \vec h}$. The probability that the carrier will avail itself of the opportunity to jump from site $\vec g$ to site $\vec g + \vec h$ given a coincidence between these sites, assuming no correlation between the carrier's response to successive coincidence events (an *electronic* correlation effect), is simply

$$W(\vec g \to \vec g + \vec h) = 2\pi J^2/\hbar A\, |v_{\vec g} - v_{\vec g + \vec h}|\ , \qquad (8)$$

where $v_{\vec g}$ and $v_{\vec g + \vec h}$ are, respectively, the vibrational velocities associated with the internuclear sepa-

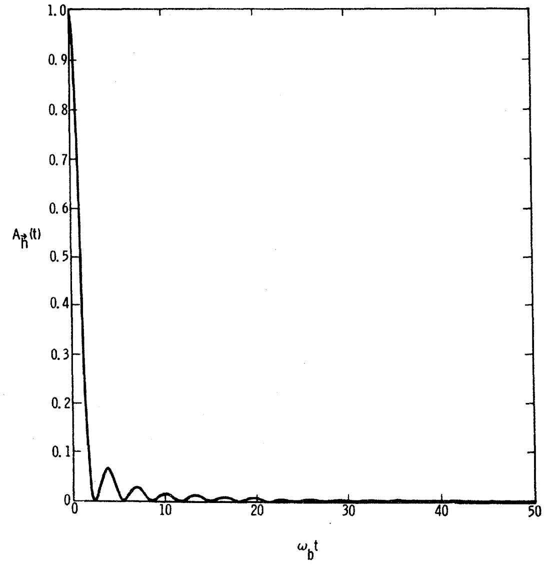

FIG. 5. The relaxation-function amplitude related to a return hop in our three-dimensional cubic model.

rations of sites $\vec{g}$ and $\vec{g}+\vec{h}$ evaluated at the time of coincidence. The above-mentioned *electronic* correlation effect will generally be ignored in the succeeding discussion. The criterion for its neglect is discussed briefly in Sec. VII.

III. TWO-COINCIDENCE ACTIVATION ENERGY

The one-dimensional theory of correlated nonadiabatic small-polaron hopping motion[4] may be readily generalized to three dimensions. One finds [in analogy with Eq. (10) of Ref. 4] that the probability of a small-polaron hop from a particular site $\vec{a}$ to a neighboring site $\vec{b}$ occurring between time zero and time dt_0, being followed by a subsequent hop of the small polaron from site $\vec{b}$ to neighboring site $\vec{b}+\vec{h}$ between times t and $t+dt$, is by $P_{\vec{a},\vec{b};\vec{b},\vec{b}+\vec{h}}(t)\,dt_0\,dt$, where

$$P_{\vec{a},\vec{b};\vec{b},\vec{b}+\vec{h}}(t) \equiv \frac{w_2^{\,2}}{[1-G_{\vec{h}}^{\,2}(t)]^{1/2}} \exp\left[\frac{2\epsilon_2}{\kappa T}\left(\frac{G_{\vec{h}}(t)}{1+G_{\vec{h}}(t)}\right)\right] . \tag{9}$$

In the above equation, w_2 is the uncorrelated nonadiabatic small-polaron jump rate originally calculated by Holstein,[1]

$$w_2 = (J^2/\hbar)\,(\pi/4\kappa T\epsilon_2)^{1/2}\, e^{-\epsilon_2/\kappa T} , \tag{10}$$

where the activation energy of ϵ_2 is

$$\begin{aligned} \epsilon &\equiv \frac{1}{2}\sum_{\vec{k}}\left(\frac{A^2}{4M\omega_{\vec{k}}^{\,2}}\right)(G_{\vec{k}}^{\vec{a},\vec{b}})^2 \\ &= \frac{1}{N}\sum_{\vec{k}}\left(\frac{A^2}{4M\omega_{\vec{k}}^{\,2}}\right)[1-\cos\vec{k}\cdot(\vec{a}-\vec{b})] . \end{aligned} \tag{11}$$

The relaxation function $G_{\vec{h}}(t)$, generally dependent on the location of sites $\vec{a}$, $\vec{b}$, and $\vec{b}+\vec{h}$, is given by the relation

$$G_h(t) = -\sum_{\vec{k}}\left(\frac{1}{\omega_{\vec{k}}^{\,2}}\right) G_{\vec{k}}^{\vec{a},\vec{b}}\, G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}} \cos\omega_{\vec{k}}t \Big/ \sum_{\vec{k}}\left(\frac{1}{\omega_{\vec{k}}}\right)^2 (G_{\vec{k}}^{\vec{a},\vec{b}})^2 , \tag{12}$$

where, as in Ref. 4,

$$G_{\vec{k}}^{\vec{a},\vec{b}} \equiv (2/N)^{1/2}[\sin(\vec{k}\cdot\vec{a}+\tfrac{1}{4}\pi) - \sin(\vec{k}\cdot\vec{b}+\tfrac{1}{4}\pi)] . \tag{13}$$

One might observe that in the limit in which the two hops become independent, i.e., $G_{\vec{h}}(t) \to 0$, the right-hand side of Eq. (9) reduces to $w_2^{\,2}$, the square of the jump rate for uncorrelated hops. It is readily seen from Eqs. (9) and (10) that the nonadiabatic activation energy characterizing two small-polaron hops being separated in time by t is $2\epsilon_2/[1+G_{\vec{h}}(t)]$. While it has been established that the activation energies that appear in the uncorrelated small-polaron hopping theories are the minimum *potential* energies, in excess of the polaron binding energy, required to establish the appropriate coincidence configurations,[7] we shall proceed to demonstrate that this situation is generally *not* the case for the activation energies that occur in the correlated theory. In other words, as distinct from the uncorrelated theory, the activation energies of the correlated hopping theory may *not* generally be represented as the difference in energy between appropriate points on the potential-energy surface $V(\cdots x_{\vec{g}}\cdots) = V_L(\cdots x_{\vec{g}}\cdots) + W_{\vec{g}}(\cdots x_{\vec{g}}\cdots)$. The energy $2\epsilon_2/[1+G_{\vec{h}}(t)]$ is, in fact, the minimum *total* energy, in excess of the polaron binding energy, required to establish two coincidences separated temporally by time t.

To begin, let us describe an arbitrary lattice displacement at site $\vec{g}$, $x_{\vec{g}}$, in terms of the normal (optical vibration) modes of the system[7]:

$$x_{\vec{g}} = (2/N)^{1/2}\sum_{\vec{k}}[Q_{\vec{k}}\cos(\omega_{\vec{k}}t+\delta_{\vec{k}}) + q_{\vec{k}}^{(\vec{b})}] \times \sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) , \tag{14}$$

where $Q_{\vec{k}}$, $\omega_{\vec{k}}$, $\delta_{\vec{k}}$, and $\vec{k}$ are the kth normal-mode amplitude, frequency, phase factor, and wave vector, respectively; the quantity

$$(2/N)^{1/2}\sum_{\vec{k}} q_{\vec{k}}^{(b)} \sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi)$$

is the (nonthermal) distortion of site $\vec{g}$ produced by the carrier occupying the site $\vec{b}$. In Holstein's model,

$$q_{\vec{k}}^{(b)} \equiv (2/N)^{1/2}(A/M\omega_{\vec{k}}^{\,2})\sin(\vec{k}\circ\vec{b}+\tfrac{1}{4}\pi) . \tag{15}$$

Furthermore, the vibrational energy of the system, the energy in excess of the polaron binding energy E_b, may be written as[7]

$$E - E_b = \sum_{\vec{k}} \tfrac{1}{2}M\omega_{\vec{k}}^{\,2}Q_{\vec{k}}^{\,2} . \tag{16}$$

Let us now proceed to calculate the minimum total energy in excess of E_b required to produce a coincidence between sites $\vec{a}$ and $\vec{b}$ at $t=O$ $[x_{\vec{a}}(0) = x_{\vec{b}}(0)]$ and sites $\vec{b}$ and $\vec{b}+\vec{h}$ at some arbitrary time t $[x_{\vec{b}}(t) = x_{\vec{b}+\vec{h}}(t)]$. The conditions for these coincidence events are seen from Eqs. (13) and (14) to be

$$A\sum_{\vec{k}}[Q_{\vec{k}}\cos\delta_{\vec{k}} + q_{\vec{k}}^{(b)}]G_{\vec{k}}^{\vec{a},\vec{b}} = 0 \tag{17}$$

and

$$A\sum_{\vec{k}}[Q_{\vec{k}}\cos(\omega_{\vec{k}}t+\delta_{\vec{k}}) + q_{\vec{k}}^{(b)}]\, G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}} = 0 , \tag{18}$$

respectively, where the coupling constant A has been inserted here for future convenience.

Introducing the Lagrange multipliers α and β and minimizing the quantity $(E-E_b) + \alpha[x_{\vec{a}}(0) - x_{\vec{b}}(0)] + \beta[x_{\vec{b}}(t) - x_{\vec{b}+\vec{h}}(t)]$ with respect to the variables $Q_{\vec{k}}$ and $\delta_{\vec{k}}$, we readily find, after algebraic manipulation, that

$$\tan\delta_{\vec{k}} = \frac{-\beta G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}\sin\omega_{\vec{k}}t}{[\alpha G_{\vec{k}}^{\vec{a},\vec{b}} + \beta G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}\cos\omega_{\vec{k}}t]} \tag{19}$$

and

$$Q_{\vec{k}}=\frac{A}{M\omega_{\vec{k}}^{2}}\left(\frac{\alpha G_{\vec{k}}^{\vec{a},\vec{b}}+\beta G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}\cos\omega_{\vec{k}}t}{\cos\delta_{\vec{k}}}\right)$$

$$=\frac{A}{M\omega_{\vec{k}}^{2}}\left(-\frac{\beta G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}\sin\omega_{\vec{k}}t}{\sin\delta_{\vec{k}}}\right) \quad . \tag{20}$$

Inserting Eqs. (19) and (20) in the conditions (17) and (18), we find that

$$\alpha - G_{\vec{h}}(t)\beta=\tfrac{1}{2} \tag{21}$$

and

$$G_{\vec{h}}(t)\,\alpha-\beta=\tfrac{1}{2} \ , \tag{22}$$

respectively. Solving these simultaneous equations, we have

$$\alpha=-\beta=\tfrac{1}{2}[1+G_{\vec{h}}(t)]^{-1} \ . \tag{23}$$

At this point, we write

$$E-E_{b}=\sum_{\vec{k}}\left(\frac{M}{2}\,\omega_{\vec{k}}^{2}\,Q_{\vec{k}}^{2}\sin^{2}\delta_{\vec{k}}\right)$$

$$+\sum_{\vec{k}}\left(\frac{M}{2}\,\omega_{\vec{k}}^{2}Q_{\vec{k}}^{2}\cos^{2}\delta_{\vec{k}}\right) \ , \tag{24}$$

where it is noted that the first term on the right-hand side of Eq. (24) is the *kinetic energy* $T(0) \equiv \sum_{\vec{g}}(M/2)\dot{x}_{\vec{g}}^{2}$ at $t=0$. Inserting the expressions for $Q_{\vec{k}}$, from Eq. (20), and with the value of α and β determined above, we find

$$E-E_{b}=2\epsilon_{2}/[1+G_{\vec{h}}(t)] \ , \tag{25}$$

QED. Furthermore it is now observed that in the limit of the two coincidence events becoming uncorrelated, i.e., $t\rightarrow\infty$ (assuming, of course, finite dispersion of the optical frequencies), the kinetic-energy contribution to $E-E_{b}$ vanishes:

$$\lim_{t\to\infty}T(0)=\lim_{t\to\infty}\frac{1}{[1+G_{\vec{h}}(t)]^{2}}$$

$$\times\sum_{\vec{k}}\frac{1}{8}\,\frac{A^{2}}{M\omega_{\vec{k}}^{2}}\,(G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}})^{2}\sin^{2}\omega_{\vec{k}}t=0 \ . \tag{26}$$

Finally, several general properties of the relaxation function should be noted. First it is noted that, for finite dispersion of the vibrational frequencies, $\lim_{t\to\infty}G_{\vec{h}}(t)=0$; thus, $E-E_{b}$ equals the activation energy characterizing two independent hops $2\epsilon_{2}$. Second, let us observe at $t=0$ from Eqs. (12) and (25) that $G_{\vec{a}-\vec{b}}(0)=1$ and $E-E_{b}=\epsilon_{2}$; the activation energy is simply ϵ_{2} since only one coincidence need be formed in the circumstance that the second hop is an immediate return jump. However, in the case of $\vec{h}\neq\vec{a}-\vec{b}$, $G_{\vec{h}}(0)$ is such that $E-E_{b}$ is the energy required to form a triple coincidence[8]; in particular, in the limit of vanishing vibrational dispersion $\omega_{1}=0$, $G_{\vec{h}}(0)=\frac{1}{2}$, and $E-E_{b}=\frac{4}{3}\epsilon_{2}\equiv\epsilon_{3}$.

IV. $G_{\vec{h}}(t)$ AND RELAXATION OF LATTICE

While we have related the activation energy chacterizing the hopping of the small polaron to the function $G_{\vec{h}}(t)$, denoted as the *relaxation function*, it is of interest to demonstrate the explicit relationship of the relaxation function to the actual relaxation of the lattice following a coincidence event. To this end we shall investigate the explicit lattice distortion associated with relaxation of the lattice from a coincidence configuration.

We begin by observing from Eq. (14) that the relative displacements associated with the occupied site $\vec{b}$ and a neighboring site $\vec{b}+\vec{h}$ at an arbitrary time t may be written

$$\Delta x_{\vec{h}}(t)=x_{\vec{b}}(t)-x_{\vec{b}+\vec{h}}(t)$$

$$=\sum_{\vec{k}}Q_{\vec{k}}\cos(\omega_{\vec{k}}t+\delta_{\vec{k}})\,G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}+\sum_{\vec{k}}q_{\vec{k}}^{(b)}G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}} \ , \tag{27}$$

where the final term is the (carrier-induced) distortion in a lattice devoid of vibrational excitations, i.e., when $Q_{\vec{k}}=0$ for all $\vec{k}$.[9] Let us now assume, as before, that a coincidence event involving site $\vec{a}$ and site $\vec{b}$ has taken place at $t=0$ and that a second coincidence involving the neighboring sites b and $b+h$ occurs at some time T. Furthermore, let us focus our attention on the particular vibrational trajectory which is characterized as possessing the minimum energy necessary to produce these two coincidence configurations. This is readily done by substituting the values of $Q_{\vec{k}}$ and $\delta_{\vec{k}}$, which were determined in Sec. III, into Eq. (27). This procedure is most expeditiously carried out by noting from Eqs. (20) that

$$Q_{\vec{k}}\cos\delta_{\vec{k}}=(A/2M\omega_{\vec{k}}^{2})\,(G_{\vec{k}}^{\vec{a},\vec{b}}-G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}\cos\omega_{\vec{k}}T)$$

$$\times\,[1+G_{\vec{h}}(T)]^{-1} \tag{28}$$

and

$$Q_{\vec{k}}\sin\delta_{\vec{k}}=(A/2M\omega_{\vec{k}}^{2})\,(G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}\sin\omega_{\vec{k}}T)[1+G_{\vec{h}}(T)]^{-1} \ . \tag{29}$$

We find, making this substitution and performing the indicated summations over $\vec{k}$,[10] that[11]

$$\Delta x_{\vec{h}}(t)=\Delta x_{\vec{h}}(\infty)\left(1-\frac{G_{\vec{h}}(t)+G_{\vec{a}-\vec{b}}(t-T)}{1+G_{\vec{h}}(T)}\right) \ , \tag{30}$$

where

$$\Delta x_{\vec{h}}(\infty)\equiv\sum_{\vec{k}}q_{\vec{k}}^{\vec{b}}\,G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}}$$

$$=(1/N)\sum_{\vec{k}}(A/M\omega_{\vec{k}}^{2})[1-\cos\vec{k}\cdot\vec{h}] \ . \tag{31}$$

Thus it has been shown that the time dependence of the relaxation of the lattice in a two-coincidence situation is governed by the functions $G_{\vec{h}}(t)$ and $G_{\vec{a}-\vec{b}}(t-T)$.

We may, however, proceed further and relate the function $G_{\vec{h}}(t)$ to the relaxation of the relative distortions of sites $\vec{b}$ and $\vec{b}+\vec{h}$ after a coincidence at $t=0$ between sites $\vec{a}$ and $\vec{b}$. In particular, considering the two coincidences to be uncorrelated (that is, going to the limit $T\to\infty$, where t remains finite), the formula becomes particularly simple:

$$\Delta x_{\vec{h}}(t)=\Delta x_{\vec{h}}(\infty)\left[1-G_{\vec{h}}(t)\right] . \tag{32}$$

The above relation provides an explicit physical interpretation of $G_{\vec{h}}(t)$ in terms of the relaxation of the lattice following a coincidence event. Once this physical understanding of the significance of $G_{\vec{h}}(t)$ has been achieved, it is easy to see that the time dependence of $G_{\vec{h}}(t)$ will be generally associated not only with the time which characterizes the relation of the lattice (typically $\sim\omega_0/\omega_1^2$) but with the average vibrational period $(2\pi/\omega_0)$, thereby manifesting the oscillatory nature of the internuclear displacements, the $x_{\vec{g}}$'s.

V. TRANSFER OF VIBRATIONAL ENERGY AND LATTICE RELAXATION

In the preceding discussion, the lattice motion has been analyzed in terms of the normal vibrational modes of the periodic lattice. On the other hand, this procedure, although greatly simplifying the calculations, does not provide a physical picture of how the energy associated with a lattice distortion is dissipated to the remainder of the crystal. Specifically, it is useful to demonstrate the relationship of the relaxation function to detailed energy transfers between lattice sites as the distortions relax. Furthermore, by reexpressing the time dependence of the relaxation function in terms of successive energy transfers from a distorted site first to neighbor sites, then to next-nearest sites, and so forth, the local character of the relaxation process is manifested.[12] Thus, the independence of the principal results of these studies of lattice-relaxation effects on the long-range order of the system will become evident. Let us now observe that the displacement associated with the gth site is in general the sum of two terms, the first being associated with the carrier occupying a particular site (denoted as before as site $\vec{b}$) and the second being associated with the vibrational motion of the lattice. Explicitly, we may (for a linear electron-lattice interaction) write

$$x_{\vec{g}}(t)=D(\vec{g},\vec{b})+X_{\vec{g}}(t) , \tag{33}$$

where, in our case[13] [cf. Eq. (14)],

$$D(\vec{g},\vec{b})=D(\vec{g}-\vec{b})\equiv(2/N)^{1/2}\sum_{\vec{k}}q_{\vec{k}}^{(b)}\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) \tag{34}$$

and

$$X_{\vec{g}}(t)=(2/N)^{1/2}\sum_{\vec{k}}Q_{\vec{k}}\cos(\omega_{\vec{k}}t+\delta_{\vec{k}})\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) . \tag{35}$$

We shall now focus our attention on the vibrational displacements $X_{\vec{g}}(t)$'s. In particular, let us write

$$X_{\vec{g}}(t)\equiv\left[M_{\vec{g}}(t)+M_{\vec{g}}'(t)\right]\cos\omega t+\left[N_{\vec{g}}(t)+N_{\vec{g}}'(t)\right]\sin\omega_0 t , \tag{36}$$

where, as is shown by use of elementary trigonometric identities in Eq. (35),

$$M_g(t)\equiv(2/N)^{1/2}\sum_{\vec{k}}Q_{\vec{k}}\cos\delta_{\vec{k}}\cos[(\omega_{\vec{k}}-\omega_0)t]\times\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) , \tag{37}$$

$$M_g'(t)\equiv-(2/N)^{1/2}\sum_{\vec{k}}Q_{\vec{k}}\sin\delta_{\vec{k}}\sin[(\omega_{\vec{k}}-\omega_0)t]\times\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) , \tag{38}$$

$$N_{\vec{g}}(t)\equiv-(2/N)^{1/2}\sum_{\vec{k}}Q_{\vec{k}}\cos\delta_{\vec{k}}\sin[(\omega_{\vec{k}}-\omega_0)t]\times\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) , \tag{39}$$

and

$$N_{\vec{g}}'(t)\equiv-(2/N)^{1/2}\sum_{\vec{k}}Q_{\vec{k}}\sin\delta_{\vec{k}}\cos[(\omega_{\vec{k}}-\omega_0)t]\times\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) . \tag{40}$$

In order to elucidate the physical significance of these four quantities, let us restrict our attention to the short-time regime $(\omega_{\vec{k}}-\omega_0)t\ll1$, where in the narrow vibrational band limit $\omega_{\vec{k}}-\omega_0\leq3\omega_1^2/2\omega_0$. Thus, we may make the standard approximations

$$\cos[(\omega_{\vec{k}}-\omega_0)t]\approx1-\tfrac{1}{2}(\omega_{\vec{k}}-\omega_0)^2t^2 , \tag{41}$$

$$\sin[(\omega_{\vec{k}}-\omega_0)t]\approx(\omega_{\vec{k}}-\omega_0)t \tag{42}$$

in Eqs. (37)–(40). In order to evaluate the resulting summations, we first recall the eigenvalue equation [equivalent to Eq. (2)]

$$(\omega_{\vec{k}}^2-\omega_0^2)\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4})=\tfrac{1}{2}\omega_1^2\sum_{\vec{h}}\sin[\vec{k}\cdot(\vec{g}+\vec{h})+\tfrac{1}{4}\pi] . \tag{43}$$

In the narrow band limit, $|\omega_{\vec{k}}-\omega_0|\ll\omega_0$, we write $(\omega_{\vec{k}}^2-\omega_0^2)\approx2\omega_0(\omega_{\vec{k}}-\omega_0)$, so that Eq. (43) becomes

$$(\omega_{\vec{k}}-\omega_0)\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi)\approx\tfrac{1}{2}\omega_b\sum_{\vec{h}}\sin[\vec{k}\cdot(\vec{g}+\vec{h})+\tfrac{1}{4}\pi] , \tag{44}$$

where $\omega_b\equiv\omega_1^2/2\omega_0$. Thus, we find, by (i) inserting the approximations (41) and (42) into Eqs. (37)–(40) and by (ii) repeated use of relationships of the form of Eq. (44), that[14]

$$M_{\vec{g}}(t)\approx X_{\vec{g}}(0)-\tfrac{1}{2}(\tfrac{1}{2}\omega_b t)^2\sum_{\vec{h}}\sum_{\vec{h}'}X_{\vec{g}+\vec{h}+\vec{h}'}(0) , \tag{45}$$

$$M_{\vec{g}}'(t)\approx(\tfrac{1}{2}\omega_b t)\Big\{(1/\omega_0)\sum_{\vec{h}}\Big[\dot{X}_{\vec{g}+\vec{h}}(0)+(\omega_b/\omega_0)\sum_{\vec{h}'}\dot{X}_{\vec{g}+\vec{h}+\vec{h}'}(0)\Big]\Big\} , \tag{46}$$

$$N_{\vec{g}}(t)\approx-(\tfrac{1}{2}\omega_b t)\sum_{\vec{h}}X_{\vec{g}+\vec{h}}(0) , \tag{47}$$

$$N_{\vec{g}}'(t)\approx(1/\omega_0)\Big[\dot{X}_{\vec{g}}(0)-(\omega_b/2\omega_0)\sum_{\vec{h}}\dot{X}_{\vec{g}+\vec{h}}(0)+(\omega_b/2\omega_0)^2\sum_{\vec{h}}\sum_{\vec{h}'}\dot{X}_{\vec{g}+\vec{h}+\vec{h}'}(0)\Big]$$

$$-\tfrac{1}{2}(\tfrac{1}{2}\omega_b t)^2(1/\omega_0)\textstyle\sum_{\vec{h}}\sum_{\vec{h}'}\dot{X}_{\vec{g}+\vec{h}+\vec{h}'}(0)\ , \qquad (48)$$

where we have noted from Eq. (35) that

$$X_{\vec{g}}(0)=(2/N)^{1/2}\textstyle\sum_{\vec{k}} Q_{\vec{k}}\cos\delta_{\vec{k}}\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi) \qquad (49)$$

and

$$\dot{X}_{\vec{g}}(0)=-(2/N)^{1/2}\textstyle\sum_{\vec{k}} Q_{\vec{k}}\,\omega_{\vec{k}}\sin\delta_{\vec{k}}\sin(\vec{k}\cdot\vec{g}+\tfrac{1}{4}\pi)\ . \qquad (50)$$

It is clear from the above expressions for $M_{\vec{g}}(t)$, $M_{\vec{g}}'(t)$, $N_{\vec{g}}(t)$, and $N_{\vec{g}}'(t)$, that for sufficiently short times $\omega_b t<1$ the energy-transfer terms are only dependent on the initial distortions and initial vibrational velocities of nearest- and next-nearest-neighbor ions.

In proceeding to apply the above considerations to the calculation of the relaxation function, we consider the situation which is described by the relation (32). Namely, we shall restrict our attention to the circumstance where at $t=0$ all of the vibrational velocities are zero and only the two coincident sites, sites $\vec{a}$ and $\vec{b}$, are distorted. These two sites are taken to possess the deformations appropriate to the minimum energy coincidence configuration (requiring energy ϵ_2)[15]:

$$X_{\vec{g}}(0)=(\delta_{\vec{g},\vec{a}}-\delta_{\vec{g},\vec{b}})\Delta\ , \qquad (51)$$

where

$$\Delta\equiv(1/N)\textstyle\sum_{\vec{k}}(A/2M\omega_{\vec{k}}^2)\{1-\cos[\vec{k}\cdot(\vec{a}-\vec{b})]\}\ . \qquad (52)$$

Applying formulas (45) and (47) to the case of a simple-cubic crystal in which the neighboring sites a and b are coincident at $t=0$, we find

$$M_{\vec{b}}=-M_{\vec{a}}=-\Delta[1-\tfrac{1}{2}z(\tfrac{1}{2}\omega_b t)^2]\ , \qquad (53)$$

$$M_{\vec{b}+\vec{h}}=-\Delta[\tfrac{1}{2}(\tfrac{1}{2}\omega_b t)^2][2-\cos\theta] \quad \text{for } \vec{h}\neq\vec{a}-\vec{b}\ , \qquad (54)$$

and

$$N_{\vec{b}}=-N_{\vec{b}+\vec{h}}=-\Delta(\tfrac{1}{2}\omega_b t)\ , \qquad (55)$$

where z is the number of nearest neighbors, $\cos\theta=\vec{h}\cdot(\vec{b}-\vec{a})/|\vec{h}|\,|\vec{b}-\vec{a}|$, and, as before, $\vec{h}$ is a nearest-neighbor position vector.

We now observe that the relative vibrational induced distortion of sites $\vec{b}$ and $\vec{b}+\vec{h}$ is

$$X_{\vec{b}}-X_{\vec{b}+\vec{h}}=(M_{\vec{b}}-M_{\vec{b}+\vec{h}})\cos\omega_0 t+(N_{\vec{b}}-N_{\vec{b}+\vec{h}})\sin\omega_0 t\ . \qquad (56)$$

Furthermore, it is recalled from Eq. (32) that

$$X_{\vec{b}}-X_{\vec{b}+\vec{h}}=-\Delta X_{\vec{h}}(\infty)\,G_{\vec{h}}(t)\ . \qquad (57)$$

Thus, comparing Eqs. (56) and (57), we have, in general, that

$$G_{\vec{h}}(t)=\frac{M_{\vec{b}+\vec{h}}-M_{\vec{b}}}{2\Delta}\cos\omega_0 t+\frac{N_{\vec{b}+\vec{h}}-N_{\vec{b}}}{2\Delta}\sin\omega_0 t\ , \qquad (58)$$

where it has been noted from Eqs. (31) and (52) that $\Delta X_{\vec{h}}(\infty)=2\Delta$. Thus, we have expressed the relaxation function in terms of functions of time which have been explicitly related to the transfer of energy between sites in the lattice. In fact, we have shown that for sufficiently short times $\omega_b t\lesssim 1$ the relaxation function is dependent only on nearest-neighbor and next-nearest-neighbor energy transfers.

In order to relate the preceding discussion to the previous analysis of the relaxation function,[4] we generalize the notation of the earlier work [cf. Eq. (21) of Ref. 4] and define

$$F_{\text{in}}^{\vec{h}}(\omega_b t)=(M_{\vec{b}+\vec{h}}-M_{\vec{b}})/2\Delta\ , \qquad (59)$$

$$F_{\text{out}}^{\vec{h}}(\omega_b t)=(N_{\vec{b}+\vec{h}}-N_{\vec{b}})/2\Delta\ . \qquad (60)$$

For the one-dimensional system studied in Ref. 4, we find from Eqs. (53)–(55) and the above definitions that

$$F_{\text{in}}^{\vec{h}}(\omega_b t)=\tfrac{1}{2}[1-\tfrac{3}{2}(\tfrac{1}{2}\omega_b t)^2] \quad \text{forward hop}\ , \qquad (61)$$

$$F_{\text{in}}^{\vec{h}}(\omega_b t)=[1-(\tfrac{1}{2}\omega_b t)^2] \quad \text{return hop}\ , \qquad (62)$$

and

$$F_{\text{out}}^{\vec{h}}(\omega_b t)=(\tfrac{1}{2}\omega_b t) \text{ for forward and return hops}\ . \qquad (63)$$

These results are in fact the short-time expansions of the exact results[4]:

$$F_{\text{in}}^{\vec{h}}(\omega_b t)=\tfrac{1}{2}[J_0(\omega_b t)-J_2(\omega_b t)] \quad \text{forward hop}\ , \qquad (64)$$

$$F_{\text{in}}^{\vec{h}}(\omega_b t)=J_0(\omega_b t) \quad \text{return hop}\ , \qquad (65)$$

$$F_{\text{out}}^{\vec{h}}(\omega_b t)=J_1(\omega_b t) \quad \text{forward and return hop}\ , \qquad (66)$$

where the $J_n(\omega_b t)$ are Bessel functions.

At this point, let us observe that $G_{\vec{h}}(t)$ may be regarded as an oscillatory function of time (essentially characterized by a frequency $\sim\omega_0$), the amplitude of which decreases as the lattice relaxes (with the characteristic time ω_b^{-1}); i.e., we may write [cf. Eqs. (26)–(26) of Ref. 4]

$$G_{\vec{h}}(t)=A_{\vec{h}}(t)\cos(\omega_0 t-\phi_{\vec{h}})\ , \qquad (67)$$

where

$$A_{\vec{h}}(t)\equiv\{[F_{\text{in}}^{\vec{h}}(t)]^2+[F_{\text{out}}^{\vec{h}}(t)]^2\}^{1/2} \qquad (68)$$

and

$$\tan\phi_{\vec{h}}=F_{\text{out}}^{\vec{h}}(t)/F_{\text{in}}^{\vec{h}}(t)\ . \qquad (69)$$

Restricting our attention to the coefficient $A_{\vec{h}}(t)$, we find from Eqs. (53)–(55), (59), and (60) that for a forward hop ($\theta=0$ or $\frac{1}{2}\pi$)

$$A_h(t)\approx\tfrac{1}{2}\{1-(\tfrac{1}{2}\omega_b t)^2[z-2-\cos\theta]\}^{1/2}\ . \qquad (70)$$

It is now readily seen that for the one-dimensional model of Ref. 4 ($z=2$ and $\cos\theta=1$), $A_{\vec{h}}(t)$ increases with time [of course, only for sufficiently short times times $\omega_b t \lesssim 1$]. On the other hand, for a simple-cubic structure, $z=6$, $A_{\vec{h}}(t)$ decreases as t increases from zero. Physically, this manifests the fact that, while the number of initially distorted sites which transfer energy to the sites $\vec{b}$ and $\vec{b}+\vec{h}$ is identical in the one-dimensional and three-dimensional cases, the number of sites which receive energy as the initially distorted sites relax is greater in the three-dimensional situation. Thus, for short times ($\omega_b t \lesssim 1$), the net energy involved in the relative vibrational motion of sites $\vec{b}$ and $\vec{b}+\vec{h}$ increases with time for the linear chain but decreases with time for the three-dimensional structure. Thus, the geometrical dependence of the relaxation function has been explicitly demonstrated.

VI. RELAXATION FUNCTION FOR A SIMPLE-CUBIC STRUCTURE

Having noted that the relaxation function will, in general, be significantly affected by the dimensionality of the model being studied, it is of interest to explicitly calculate the relaxation function for a simple-cubic lattice structure and compare the results with those for a linear chain. In particular, we shall write the relaxation function

$$G_{\vec{h}}(t) = F_{\text{in}}^{\vec{h}} \cos\omega_0 t + F_{\text{out}}^{\vec{h}} \sin\omega_0 t \,, \tag{71}$$

where

$$F_{\text{in}}^{\vec{h}}(t) \equiv - \frac{\sum_{\vec{k}} (1/\omega_{\vec{k}}^2)\, G_{\vec{k}}^{\vec{a},\vec{b}} G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}} \cos[(\omega_{\vec{k}} - \omega_0)t]}{\sum_{\vec{k}} (1/\omega_{\vec{k}}^2)\,(G_{\vec{k}}^{\vec{a},\vec{b}})^2} \tag{72}$$

and

$$F_{\text{out}}^{\vec{h}}(t) \equiv \frac{\sum_{\vec{k}} (1/\omega_{\vec{k}}^2)\, G_{\vec{k}}^{\vec{a},\vec{b}} G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}} \sin[(\omega_{\vec{k}} - \omega_0)t]}{\sum_{\vec{k}} (1/\omega_{\vec{k}}^2)(G_{\vec{k}}^{\vec{a},\vec{b}})^2} \,, \tag{73}$$

and concern ourselves with the calculation of $F_{\text{in}}^{\vec{h}}(t)$ and $F_{\text{out}}^{\vec{h}}(t)$.

Restricting our attention, as in Sec. V, to the case of a narrow vibrational band $\omega_b/\omega_0 \ll 1$,

$$\omega_{\vec{k}} = \omega_0 + \omega_b(\cos k_x + \cos k_y + \cos k_z) \,, \tag{74}$$

where $-\pi \le k_x,\ k_y,\ k_z \le \pi$, the above formulas are readily evaluated by (i) transforming the summation over k to an integral, i.e.,

$$\sum_{\vec{k}} \to (2\pi)^{-3} \int_{-\pi}^{\pi} dk_y \int_{-\pi}^{\pi} dk_y \int_{-\pi}^{\pi} dk_z \,,$$

by (ii) utilizing the well-known trigonometric identities for the sine and cosine of the sum of angles, and by (iii) utilizing identities of the form

$$\cos(\theta \cos k_x) = J_0(\theta) + 2 \sum_{h=1}^{\infty} (-1)^n J_{2n}(\theta) \cos(2nk_x) \,, \tag{75}$$

$$\sin(\theta \cos k_x) = 2 \sum_{n=0}^{\infty} (-1)^n J_{2n+1}(\theta) \cos[(2n+1)k_x] \,, \tag{76}$$

where the $J_n(\theta)$'s are Bessel functions. The results of these computations along with the results for the linear-chain calculation are presented in Table I.

It should be noted from Table I that the relaxation function for the sites that are involved in a forward hop is dependent on whether the three sites involved in the two coincidences are collinear or lie at three of the corners of a square. This feature is manifested in the results of Sec. V by the dependence of $M_{\vec{b}+\vec{h}}$ on the angle θ [cf. Eq. (54)]. In addition, it can be readily verified that the expansion of the Bessel functions, for $\omega_b t < 1$, yields results that are identical to the energy-transfer calculation of Sec. V.

The significance of dimensionaltiy on the relaxation function can be most easily seen by writing

$$G_{\vec{h}}(t) = A_{\vec{h}}(t) \cos(\omega_0 t - \phi_{\vec{h}}) \tag{77}$$

and focusing our attention on the amplitude of this oscillatory function:

$$A_{\vec{h}}(t) = \{ [F_{\text{in}}^{\vec{h}}(t)]^2 + [F_{\text{out}}^{\vec{h}}(t)]^2 \}^2 \,. \tag{78}$$

These amplitudes are plotted against $\omega_b t$ in Figs. 1–5; these curves correspond to the correspondingly numbered cases of Table I. It is clear that the relaxation is much more rapid in the three-dimensional model than in the one-dimensional model. In addition, it is seen from Figs. 1, 3, and 4 that the rise of $A_{\vec{h}}(t)$ with time from its initial value in the case of forward hops is only a characteristic of the one-dimensional calculation—the physical origin of this difference having been considered in the discussion of Sec. V.

Finally, it is observed that the asymptotic ($\omega_b t \gg 1$) forms of $A_{\vec{h}}(t)$ for each of the five situations of Table I are, respectively,

TABLE I. The in-phase and out-of-phase amplitudes of the relaxation functions for both linear chain and simple-cubic structures.

Situation	F_{in}	F_{out}
Linear chain		
Forward hop	$\frac{1}{2}[J_0(\omega_b t) - J_2(\omega_b t)]$	$J_1(\omega_b t)$
Return hop	$J_0(\omega_b t)$	$J_1(\omega_b t)$
Simple-cubic structure		
Forward colinear hop	$\frac{1}{2}[J_0(\omega_b t) - J_2(\omega_b t)]J_0^2(\omega_b t)$	$J_1(\omega_b t)J_0^2(\omega_b t)$
Forward right-angle hop	$\frac{1}{2}[J_0^2(\omega_b t) - J_1^2(\omega_b t)]J_0(\omega_b t)$	$J_1(\omega_b t)J_0^2(\omega_b t)$
Return hop	$J_0^3(\omega_b t)$	$J_1(\omega_b t)J_0^2(\omega_b t)$

$$A_{\vec{h}}(t) \sim (2/\pi\omega_b t)^{1/2} , \tag{79}$$

$$A_{\vec{h}}(t) \sim (2/\pi\omega_b t)^{1/2} , \tag{80}$$

$$A_{\vec{h}}(t) \sim (2/\pi\omega_b t)^{3/2} \cos^2(\omega_b t - \tfrac{1}{4}\pi) , \tag{81}$$

$$A_{\vec{h}}(t) \sim (2/\pi\omega_b t)^{3/2} \tfrac{1}{2} \left| \cos(\omega_b t - \tfrac{1}{4}\pi) \right| , \tag{82}$$

$$A_{\vec{h}}(t) \sim (2/\pi\omega_b t)^{3/2} \cos^2(\omega_b t - \tfrac{1}{4}\pi) . \tag{83}$$

These formulas serve as verification of the general arguments previously given in Refs. 3 and 4 concerning the time dependence characterizing the lattice relaxation for long times $\omega_b t \gg 1$.[16]

VII. CORRELATED-HOPPING JUMP RATE

In this section, we shall study the effect of the previously discussed relaxation phenomenon on the small-polaron drift mobility. Rather than utilizing the exact relaxation functions (derived in Sec. VI) in performing a (computer) computation of the drift mobility of a carrier in a cubic lattice, we instead shall carry out a relatively simple calculation which manifests the principal physical effects of the problem.

The starting point of our considerations is the following schematic representation of the essential features of the time-dependent jump rates $R_{\vec{b}+\vec{h}}(t)$ which characterize the subsequent jump of a carrier which hops from site $\vec{a}$ to site $\vec{b}$ at $t=0$. In particular, considering $\vec{b}+\vec{h} \neq \vec{a}$, we have

$$\begin{aligned} R_{\vec{b}+\vec{h}}(t) &= w_2 \alpha \quad \text{for } 0 < t < t_2 , \\ &= w_2 \quad\;\; \text{for } t_2 < t , \end{aligned} \tag{84}$$

and, for $\vec{b}+\vec{h} = \vec{a}$:

$$\begin{aligned} R_{\vec{a}}(t) &= w_2(\alpha+\beta) \quad \text{for } 0 < t < t_1 , \\ &= w_2 \alpha \qquad\quad\; \text{for } t_1 < t < t_2 , \\ &= w_2 \qquad\qquad \text{for } t_2 < t , \end{aligned} \tag{85}$$

where w_2 is the rate characterizing a hop in a relaxed lattice.[17]

It is implied in this simplified model that the "new site" and return jump rates are *enhanced* above their relaxed-lattice value for times less than t_1 and t_2. Specifically, if only the herein-discussed classical relaxation effects are considered and we assume that we may consider only the correlation between successive coincidence events, then $\alpha \approx e^{2\epsilon_2/3\kappa T}$ and $\alpha+\beta \approx e^{\epsilon_2/\kappa T}$. However, it should be commented that there are also quantum-mechanical correlation effects which in general may well play a role in considerations of small-polaron hopping motion. In particular, one may consider two such effects.

The first of these is related to the question of whether (given a coincidence event between sites $\vec{a}$ and $\vec{b}$ at some initial time and a coincidence involving the neighboring sites $\vec{b}$ and $\vec{b}+\vec{h}$ at some time t later) the probability of a carrier availing itself of two opportunities to hop $W(\vec{a} \to \vec{b} \to \vec{b} + \vec{h})$ may be written as the product $W(\vec{a} \to \vec{b})\; W(\vec{b} \to \vec{b} + \vec{h})$. Without going into the details, preliminary considerations[18,19] lead to the conclusion that this replacement is correct for $t > \Delta t \sim \omega_0^{-1}[\hbar\omega_0/(\epsilon_2 \kappa T)^{1/2}]^{1/2}$, where $\omega_0 \Delta t \ll 1$. In that the probability expression Eq. (9) is peaked at intervals of $\sim 2\pi/\omega_0$, with the characteristic width $\omega_0^{-1}[\kappa T/\epsilon_2 A_{\vec{h}}(2\pi n/\omega_0)]^{1/2}$, it can be seen (from the fact that both of these times are taken to be much greater than Δt within the regime of the occurrence-probability approach) that such electronic correlation effects will occur in only rare instances. Furthermore, in the occasional situation when t is very short, $W(\vec{a} \to \vec{b} \to \vec{b} + \vec{h})$ differs from the above-mentioned product by only a numerical factor of order unity. Hence, such correlation effects appear to be of minor importance in the classical limit considered here.

The second quantum-mechanical effect which is of interest to us is associated with dispersion related corrections to Holstein's formula for $W(\vec{b} \to \vec{b} + \vec{h})$, cf. Eq. (8). In particular, it is assumed in deriving Eq. (8) that, given a coincidence, the probability of a hop is related only to that particular coincidence event and is independent of other prior coincidence events; that is, the carrier forgets a coincidence event before another occurs.[20] The validity of this assumption (in a lattice of two or three dimensions[21]) requires satisfying the condition

$$2\pi(\omega_b/\omega_0)\,[(\epsilon_2 \kappa T)^{1/2}/\hbar\omega_0] \gg 1 ; \tag{86}$$

it should be observed that this condition is automatically fulfilled in the classical limit $\hbar \to 0$. A computer calculation by deWit[21] (for a two-dimensional lattice) indicates that the correction to the jump rate associated with the failure to meet the above requirement can be substantial.[22] Furthermore, as may be expected from the fact that the condition (86) is more easily satisfied as the temperature is increased, deWit finds that the fractional augmentation of the jump rate decreases with increasing temperature. Thus, this electronic correlation effect may be thought of as producing a jump-rate enhancement factor which decreases with increasing temperature. We therefore expect that the inclusion of this electronic correlation effect in our theory will yield both an increase in the drift mobility and a further offsetting of the activated temperature-dependent term in the drift-mobility expression.

Finally, it should be stressed that the above discussion is based on preliminary consideration of the quantum-mechanical correlation effects. However, it is felt that a more detailed discussion of these considerations is beyond the scope of the present paper, this paper being principally concerned with classical lattice-relaxation effects. Thus, without further ado, we shall adopt the above schematic model and proceed to compute the average jump rate which is to be related to the drift mobility.

The task of relating the various time-dependent rates to an average forward jump rate has been carried out for a one-dimensional lattice in Sec. V of Ref. 4. The generalization to the case of the three-dimensional model presented above is elementary and yields

$$w=(1+f)^{-1}\int_0^\infty S(t)R^2(t)\,dt\Big/\int_0^\infty S(t)R(t)\,dt\ , \qquad (87)$$

where

$$S(t)\equiv\exp\Big[-\int_0^\infty\textstyle\sum_{\vec h}R_{\vec b+\vec h}(t')\,dt'\Big] \qquad (88)$$

and

$$f\equiv\int_0^\infty S(t)[R_{\vec a}(t)-R_{\vec b+\vec h}(t)]\,dt\ ,\quad b+h\neq a\ . \qquad (89)$$

Inserting the rate expressions, Eqs. (84)–(85), into the above formula we find that

$$w=w_2\frac{\alpha+(\beta/6)e^{-w_2[6\alpha+\beta]t_1}+(1-\alpha)(1+\beta/6\alpha)e^{-6w_2\alpha t_2}e^{-w_2\beta t_1}}{\{1+[(\beta/6\alpha)(1+\beta/6a)^{-1}](1-e^{-w_2(6\alpha+\beta)t_1})\}[1+(\beta/6\alpha)e^{-w_2(6\alpha+\beta)t_1}]}\ . \qquad (90)$$

In examining the above expression, we shall first direct our attention to the limit in which the enhanced-return effect (characterized by the constant β) is nonexistent. In this situation $\beta=0$, and Eq. (90) reduces to

$$w=w_2[\alpha+(1-\alpha)e^{-6w_2t_2}]\ . \qquad (91)$$

The physical content of this expression is readily identified by observing that when the enhanced short-time jump rate characterizing a jump to any of the six neighbors $6w_2\alpha$ multiplied by its characteristic time duration t_2 is much greater than unity, it is most likely that a second hop will occur under the influence of this enhanced rate, $w\rightarrow w_2\alpha$.

In the other extreme, $6w_2\alpha t_2\ll 1$, the enhanced jump rate affects only a small fraction of the hops and hence has little influence on the average rate w, i.e., $w\rightarrow w_2$.

Let us now consider the situation when the probability of the carrier making a hop in the time interval t_1 is substantial; explicitly, let us assume $w_2(6\alpha+\beta)t_1\gg 1$. In this limit we find from Eq. (90) that

$$w=w_2\alpha\left(\frac{1+\beta/6\alpha}{1+\beta/3\alpha}\right)\ . \qquad (92)$$

We can see that the term in parentheses, manifesting the effect of the enhanced-return phenomenon, has only a minor influence on w in that this term always has a value between 0.5 and 1. In particular, in the limit that the enhanced portion of the return jump rate $w_2\beta$ is substantially larger than the total unenhanced rate characterizing a jump to the neighboring sites $6w_2\alpha$, namely $\beta/6\alpha\gg 1$, the term in parentheses is $\frac{1}{2}$. This factor of $\frac{1}{2}$ manifests the fact that in this limit, the carrier having made a hop will tend to jump back and forth repeatedly between the "initial" and "final" sites only effecting a hop in one-half of these instances. Finally, in the complementary limit $\beta/6\alpha\ll 1$, the enhanced-return effect is unimportant and the term in parentheses approaches unity.

It is useful to rewrite the condition $w_2(6\alpha+\beta)t_1\gg 1$ in terms of the mobility in this regime so as to have a self-consistent check on the utilization of the average forward jump rate given in Eq. (92) in determining the drift mobility. In particular, ignoring the term in parentheses in Eq. (92) for simplicity and employing the Einstein relation $\mu=(ea^2/\kappa T)w$ (where a is the lattice constant), we find that

$$w_2\alpha\approx\mu(\kappa T/ea^2)\ .$$

Furthermore, recalling that the enhanced-return jump rate corresponds to a situation in which an "immediate" return hop requires little additional vibrational energy (i.e., characterized by a very small activation energy), we may write

$$w_2(\alpha+\beta)\approx\mu(\kappa T/ea^2)e^{\epsilon_2/3\kappa T}\ .$$

Finally, noting that $t_1\approx\omega_b^{-1}$, we may write the condition for being in this enhanced diffusion regime as

$$\mu(\kappa T/ea^2)(5+e^{\epsilon_2/3\kappa T})\,\omega_b^{-1}>1$$

or

$$\mu>\left(\frac{ea^2}{\hbar}\,\frac{\hbar\omega_0}{\kappa T}\right)\frac{\omega_b}{\omega_0}\,(5+e^{\epsilon_2/3\kappa T})^{-1}\ .$$

Taking $a=6\times10^{-8}$ cm, $\kappa T=\hbar\omega_0$, $\omega_b/\omega_0=0.07$, and $\epsilon_2=5\hbar\omega_0$ as typical parameters[23] we find the condition $\mu>4\times10^{-2}$ cm^2/V sec. Thus, the enhancement effects are expected to be important in such materials as NiO and CoO, where μ is deduced to be between 10^{-1} and 1 cm^2/V sec.[5] A plot of the drift mobility vs reciprocal temperature for the electronic bandwidth parameter $J=\hbar\omega_0=0.04$ eV, with the remaining parameters being given by the values chosen above, is given in Fig. 6.

VIII. SUMMARY AND DISCUSSION

It has been the purpose of this paper to elucidate

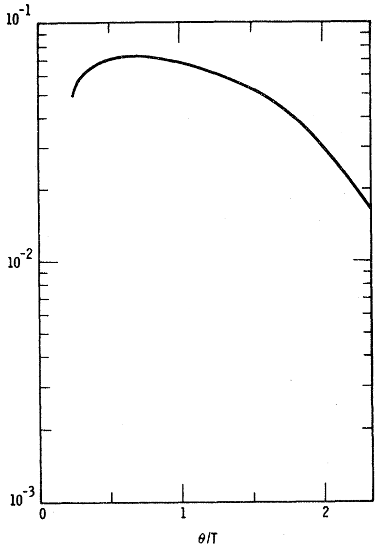

FIG. 6. The drift mobility plotted vs $\hbar\omega_0/\kappa T = \theta/T$ for the values of the physical parameters given in the text.

the nature of the lattice-relaxation effects that arise in the theory of correlated small-polaron hopping motion.[3,4] In particular, in the previously developed theory in which the probability of a small-polaron hop is considered to be influenced only by the immediately preceding small-polaron jump, it is found that the probability of a coincidence between the neighboring sites $\vec{a}$ and $\vec{b}$ at time zero being followed by a coincidence involving the adjacent sites $\vec{b}$ and $\vec{b}+\vec{h}$ at time t is characterized by a t-dependent "activation" energy. It is shown in the present paper that, while the usually encountered activation energies are the minimum potential energies required to produce some specified condition, the time-dependent activation energy encountered here is the minimum *total* energy required to establish the two above-mentioned coincidence events. In the limit in which the two events are uncorrelated, i.e., as $t\rightarrow\infty$, the kinetic-energy contribution to the activation energy is shown to vanish.

The time dependence of the two-coincidence activation energy is expressed in terms of the function $G_{\vec{h}}(t)$, designated as the relaxation function. Furthermore, it is shown that the actual time-dependent relaxation of the lattice distortion associated with both one- and two-coincidence events is determined by the relaxation function. These theorems thereby constitute an explicit demonstration of the relationship of the time-dependent activation energy to the physical relaxation of lattice distortion which accompanies a coincidence event. In the previous works,[3,4] such a relationship was suggested but never proved.

In Sec. V of this paper, the calculation of the relaxation function was recast in terms of repeated transfers of vibrational energy from distorted sites to undistorted sites. In this formulation, the physical significance of the "in-phase" and "out-of-phase" terms in $G_{\vec{h}}(t)$ is manifested, and the previously unproved assertions of Sec. V of Ref. 3 as to their physical meaning are established. Furthermore, it is felt that such a scheme for calculating the relaxation function possesses the advantage of being a more explicit physical description of the relaxation of the lattice than the description of the relaxation phenomenon in terms of the falling of the center of a wave packet (cf. Sec. VIII of Ref. 3). Finally, this approach manifests the feature that except at long times $\omega_b t \gg 1$, the absence or presence of long-range order in the system has little influence on the relaxation phenomenon. Thus, the notion of correlated small-polaron hopping motion may be applied to nonperiodic systems.

It has been anticipated that the relaxation of the lattice in a three-dimensional model would proceed much more rapidly than in a one-dimensional model.[3,4] In Sec. VI, the calculation of the lattice-relaxation function for a simple-cubic structure is outlined and the results presented. In particular, the amplitudes $A_{\vec{h}}(t)$'s of the various lattice-relaxation functions are plotted in Figs. 1–5; the striking effect of dimensionality is readily apparent from these curves. However, in accord with earlier qualitative observations, it is seen that the lattice-relaxation functions are not affected by dimensionality in the short time limit $\omega_b t \ll 1$.

Finally, a schematic model is introduced to facilitate inclusion of lattice-relaxation effects in the calculation of the small-polaron jump rate in a simple-cubic structure. It is shown that for the situation in which the probability of a carrier making a hop before the lattice relaxes is substantial, small-polaron motion is characterized by a diffusion rate that is enhanced above that of the uncorrelated-hopping theory. Furthermore, the small-polaron jump rate in this regime is characterized by an activation energy roughly one-third that associated with the uncorrelated hopping of small polarons.

ACKNOWLEDGMENT

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[8] The triple-coincidence activation energy reduces to that found by Friedman and Holstein (Ref. 7) ($\epsilon_3 = \frac{4}{3}\epsilon_2$) for the situation they consider, namely, that of the three coincident sites being mutual nearest neighbors of one another.

[9] In the limit of vanishing vibrational dispersion $\sum_{\vec{k}} q_{\vec{k}}^{\vec{b}} G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}} = A/M\omega_0^2$.

[10] In carrying out this calculation it is noted that one may replace $(G_{\vec{k}}^{\vec{b},\vec{b}+\vec{h}})^2$ by $(G_{\vec{k}}^{\vec{a},\vec{b}})^2$ in the summations over k.

[11] Recalling that $G_{\vec{h}}(T) = G_{\vec{h}}(-T)$, and that $G_{\vec{a}-\vec{b}}(0) = 1$, one may easily confirm that the conditions (i) $\Delta x_{\vec{a}-\vec{b}}(0) = 0$ and (ii) $\Delta x_{\vec{h}}(T) = 0$ are satisfied by the above expression.

[12] Explicitly, we shall see that for times short compared with $2\omega_0/\omega_1^2$ only the first and second nearest neighbors of the distorted sites are substantially involved in the relaxation process.

[13] If we do not assume the short-range linear electron-lattice interaction of Eq. (7) but a more general linear electron lattice, the constant A in Eq. (15) need only be replaced by the k-dependent coupling function $A_{\vec{k}}$.

[14] In obtaining the square-bracketed terms of Eqs. (46) and (48), we have made use of the expansion $\omega_k^{-1} = \omega_0^{-1} \sum_{n=0}^{\infty} (-1)^n [(\omega_k - \omega_0)/\omega_0]^n$ and have retained terms in these equations to order ω_b^2.

[15] Formulas (51) and (52) are obtained from Eq. (35) by inserting the relation (28) and taking the limit $T \rightarrow \infty$.

[16] Specifically, note Eqs. (80) and (89) of Ref. 4 and the discussion following Eq. (2) of Ref. 3.

[17] While it was noted in Sec. VI that the relaxation-function amplitudes $A_{\vec{b}+\vec{h}}(t)$ associated with subsequent forward and right-angle hops are not strictly equal, their very similar qualitative behavior and near equality in the short-time regime $\omega_b t \lesssim 1$ constitutes the justification of taking them to be identical in this model. In this regard, it is commented that our principal concern is for the situation characterized by most hops occurring in times less than $t_1 \sim \omega_b^{-1}$.

[18] In particular, we have compared the square of the amplitude for a double hop $1 \rightarrow 2 \rightarrow 3$ with the product of the squares of the amplitudes for the hops $1 \rightarrow 2$ and $2 \rightarrow 3$. The ratio of these expressions is given simply, in terms of the quantity E_2 defined in Eq. (3.11c) of Ref. 19, by $[\frac{1}{4} + \frac{1}{2}(E_2^* + E_2) + |E_2|^2]$, where $E_2 = 0$ at $t = 0$ and monotonically increases to the value $\frac{1}{2}$ for $t \gg \Delta t$.

[19] D. Emin, Ann. Phys. (N. Y.) 64, 336 (1971).

[20] As implied in Appendix II of Ref. 1, we may write the amplitude for a hop as the sum of contributions from successive coincidence points. The probability of a hop associated with a particular coincidence event is the sum of the square of the absolute value of the amplitude related to the above-mentioned coincidence event [the expression given by Eq. (8)] and the various cross terms involving the amplitudes for a hop at this coincidence event and at the preceding coincidences. It is the contribution of these cross terms, averaged over the appropriate occurrence-probability function, which must vanish in order to obtain formula (8). Preliminary considerations of the requisite condition for the neglect of these cross terms yields the restriction on the amount of vibrational dispersion given by the requirement (86).

[21] H. J. deWit, Philips Res. Repts. 23, 449 (1968).

[22] It is anticipated that these corrections will be reduced somewhat in a calculation for a three-dimensional model.

[23] The choice $\epsilon_2 - 5\hbar\omega_0$ was used in the earlier small-polaron papers (Refs. 1, 2, 4, 7, and 19). If one assumes that $\omega_b/\omega_0 = \omega_1^2/2\omega_0^2 \approx M_2/4M_1$ (Ref. 21) and takes M_1 and M_2 to be the atomic masses of nickel and oxygen, respectively, then one sees that the choice $\omega_b/\omega_0 = 0.07$ is appropriate to NiO.

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Optical Response of AgCl and AgBr in the Near and Extreme Ultraviolet*

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The extinction coefficients of AgCl and AgBr have been obtained down to liquid-helium temperature by observing the transmission of thin films in the near-uv direct exciton region (3.5–6.7 eV) and in the extreme uv (30–240 eV) using synchrotron radiation. The index of refraction was determined for both materials by a dispersion relation, and the optical constants were then constructed for AgCl in the range 3–240 eV, using all available data. Some interpretation of the exciton and band-to-band spectra is given. An estimate is made of the effective number of electrons which contribute to the absorption over a wide range of photon energies.

I. INTRODUCTION

The characteristic optical absorption of AgCl and AgBr begins in the near ultraviolet at photon energies of approximately 3 eV. Measurements on single crystals indicate that the absorption tails in this region are strongly temperature-dependent according to the so-called Urbach rule.[1,2] Detailed investigations down to liquid-helium temperatures on the pure materials[3] and also on mixed crystals[4]