

## Theory of electronic transport in molecular crystals. III. Diffusion coefficient incorporating nonlocal linear electron–phonon coupling

R. W. Munn and R. Silbey

Citation: *J. Chem. Phys.* **83**, 1854 (1985); doi: 10.1063/1.449373

View online: <http://dx.doi.org/10.1063/1.449373>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v83/i4>

Published by the [American Institute of Physics](#).

---

### Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



**AIP Advances**

Special Topic Section:  
**PHYSICS OF CANCER**

Why cancer? Why physics? [View Articles Now](#)

# Theory of electronic transport in molecular crystals. III. Diffusion coefficient incorporating nonlocal linear electron-phonon coupling

R. W. Munn<sup>a)</sup>

Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

R. Silbey

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 3 January 1985; accepted 28 February 1985)

Electronic transport in molecular crystals is studied for simultaneous local and nonlocal linear electron-phonon coupling using a generalized polaron Hamiltonian derived previously. Nonlocal coupling increases the scattering, giving lower band contributions and higher hopping contributions. It also gives a phonon-assisted term which dominates at high temperature, leading eventually to a constant diffusion coefficient whose magnitude depends on the ratio of the nonlocal to local coupling and is independent of transfer integral. Incorporating nonlocal coupling thus mainly increases the magnitude of the diffusion coefficient and decreases its temperature dependence.

## I. INTRODUCTION

This series of papers seeks to develop a theory of electronic transport in molecular crystals valid for arbitrary electronic and phonon bandwidths and for arbitrary linear electron-phonon coupling strength. In Paper I,<sup>1(a)</sup> the case of local (in site) coupling was treated and general results given. In Paper II,<sup>1(b)</sup> the problem of nonlocal coupling was tackled; this turns out to be more difficult in general than the local case, which is perhaps the reason that it has not been extensively treated before. In the general case, nonlocal effects surely play a role, but these have been largely neglected. In Paper II,<sup>1(b)</sup> a nonlocal polaron transformation of the model Hamiltonian was given and its effects on band shapes studied. In the present paper, we study transport in this model. Recently, the field of exciton transport and exciton-phonon coupling has been extensively reviewed by Kenkre and Rein-eker.<sup>2</sup>

Given that the transformation leaves only a weak residual interaction, the method for deriving the diffusion coefficient  $D$  has been established.<sup>1,3-5</sup> To a good approximation,

$$D = a^2 \langle \langle v_k^2 / \Gamma_{kk} + \gamma_{kk} \rangle \rangle, \quad (1.1)$$

where  $a$  is the nearest-neighbor distance and  $\mathbf{k}/a$  is the wave vector; the double angle brackets denote a thermal average over polaron states of energy  $E_k$ , and  $v_k$  is  $\nabla_k E_k$ . The quantities  $\Gamma_{kk}$  and  $\gamma_{kk}$ , referred to as scattering and hopping rates, are given by

$$\Gamma_{k'k'} = \sum_k' W_{kk;k'k'}, \quad (1.2)$$

$$\gamma_{k'k'} = \frac{1}{2} \nabla_q^2 \sum_k \text{Re} \times \left( \frac{1}{2} W_{kk;k'+q,k'+q} - W_{k,k+q;k',k'+q} \right) \Big|_{q=0}, \quad (1.3)$$

where the primed sum excludes  $\mathbf{k} = \mathbf{k}'$ . Finally, the quantities  $W$  are given by

<sup>a)</sup> Visiting Fellow. Permanent address: Department of Chemistry, UMIST, Manchester, M60 100, U. K.

$$W_{k,k+q;k',k'+q} = \int_0^\infty dt \{ \langle V_{k'+q,k+q} V_{kk'}(t) \rangle \times \exp[i(E_{k'+q} - E_{k+q})t] + \langle V_{k'+q,k+q}(t) V_{kk'} \rangle \exp[-i(E_k - E_{k'})t] \}. \quad (1.4)$$

Here  $V_{kk'}(t)$  is a coefficient in the residual interaction expressed in the Heisenberg representation with respect to the zeroth-order phonon Hamiltonian, and the single angle brackets denote an average over phonon states.

Thus the evaluation of  $D$  is automatic, at least in principle. In practice, each stage presents difficulties. As in Papers I and II, we treat these difficulties by making approximations which allow results to be obtained in algebraic form. In this way the behavior of the model is obtained in broad outline and can readily be explored analytically and numerically.

In Sec. II we present the Hamiltonian with some modifications helpful in treating transport. In Appendix A we evaluate the correlation functions  $\langle VV(t) \rangle$  and in Appendix B we use these to obtain the scattering and hopping rates. These results are combined in Sec. III where an expression for the diffusion coefficient is derived and its behavior is studied. Finally, Sec. IV consists of a discussion, with particular reference to the new features which arise when nonlocal coupling is incorporated in electronic theory.

## II. HAMILTONIAN

The transformed Hamiltonian is<sup>1(b)</sup>

$$\tilde{H} = H_{\text{ex}} + H_{\text{ph}} + V, \quad (2.1)$$

where  $H_{\text{ex}}$  is the excitation or polaron Hamiltonian,  $H_{\text{ph}}$  is the phonon Hamiltonian, and  $V$  is the residual interaction. Here

$$H_{\text{ex}} = \sum_k E_k a_k^+ a_k, \quad (2.2)$$

$$E_k = \epsilon + \bar{J}_k - N^{-1} \sum_q \omega_q |A_k^q|^2, \quad (2.3)$$

where  $q_k^+$  and  $a_k$  are polaron creation and annihilation oper-

ators,  $\epsilon$  is the bare excitation energy,  $\tilde{J}_k$  is the renormalized transfer integral, and  $A_k^q$  is a parameter of the generalized polaron transformation; the last term in  $E_k$  corresponds to the polaron binding energy, with  $\omega_q$  a phonon frequency. The renormalized transfer integral is related to its bare analog  $J_k$  in the untransformed Hamiltonian by

$$\tilde{J}_k = \sum_{k'} J_{kk'} \langle \theta_{k'k}^+ \theta_{kk'} \rangle, \tag{2.4}$$

where

$$\theta_{kk'} = [\exp - \mathbf{S}]_{kk'}, \tag{2.5}$$

$$\theta_{kk'}^+ = [\exp \mathbf{S}]_{k'k}, \tag{2.6}$$

$$S_{kk'} = N^{-1/2} A_{-k}^{k-k'} (b_{k'k}^+ - b_{k-k'}). \tag{2.7}$$

The phonon Hamiltonian retains the usual form

$$H_{ph} = \sum_q \omega_q (b_q^+ b_q + \frac{1}{2}), \tag{2.8}$$

with  $b_q^+$  and  $b_q$  the phonon creation and annihilation operators.

The transformation parameters are chosen to be related to the nonlocal electron-phonon coupling parameters  $f_k^q$  in the untransformed Hamiltonian by<sup>1(b)</sup>

$$A_{-k}^q = \sum_{k'} f_{-q}^q \langle \theta_{k'+q,k+k}^+ \theta_{k'k} \rangle. \tag{2.9}$$

The interaction then takes the form  $\sum_{kk'} V_{kk'} a_k^+ a_{k'}$ , where

$$V_{kk'} = \sum_k \{ J_{\kappa} T_{\kappa k; \kappa k'} - N^{1/2} \sum_Q \omega_Q f_{-Q}^Q \times [ 2N^{-1/2} A_{-k}^{-Q} T_{\kappa+Q, k; \kappa, k'-Q} - T_{\kappa+Q, k; \kappa k'} \psi_Q ] \}, \tag{2.10}$$

with  $\psi_0 = b_0 + b_0^+$  the phonon displacement operator. The operators  $T$  are defined as

$$T_{kk'; qq'} = \theta_{kk'}^+ \theta_{qq'} - \langle \theta_{kk'}^+ \theta_{qq'} \rangle, \tag{2.11}$$

their exponential form helping to ensure that matrix elements of  $V^2$  are never large, whatever the strength of the electron-phonon coupling. In Eq. (2.10) the second and third terms are Hermitian only when taken together, whereas for use in this paper it proves convenient to rewrite  $V_{kk}$ ; so that its terms are individually Hermitian:

$$V_{kk'} = \sum_k \left\{ J_{\kappa} T_{\kappa k; \kappa k'} - N^{-1/2} \sum_Q \omega_Q f_{-Q}^Q \times [ N^{-1/2} (A_{-k}^{-Q} T_{\kappa+Q, k; \kappa, k'-Q} + A_{-k}^{Q*} T_{\kappa+Q, k+Q; \kappa k'}) - \frac{1}{2} (T_{\kappa+Q, k; \kappa k'} \psi_Q + \psi_Q T_{\kappa+Q, k; \kappa k'}) ] \right\}. \tag{2.12}$$

This form corresponds to one used previously in which nonlocal coupling changes the transfer integral through the displacements in the polaron state.<sup>6</sup>

Evaluation of the thermal averages in  $\tilde{J}_k$  and  $A_k^q$  yields<sup>1(b),7-9</sup>

$$\tilde{J}_k = \sum_{k'} \langle \theta_k \rangle^2 [\exp E^0]_{kk'} J_{k'}, \tag{2.13}$$

$$A_k^q = \sum_{k'} \langle \theta_k \rangle \langle \theta_{k-q} \rangle [\exp E^q]_{kk'} f_{k'}^q, \tag{2.14}$$

where

$$\langle \theta_k \rangle = \exp \left( -\frac{1}{2} \sum_{k'} E_{kk'}^0 \right), \tag{2.15}$$

$$E_{kk'}^q = N^{-1} (2n_{k-k'} + 1) (A_{k-k'}^{k-k'})^* A_{k-k'}, \tag{2.16}$$

and  $n_q$  is the thermal equilibrium number of phonons in mode  $q$  of frequency  $\omega_q$ :

$$n_q = n(\omega_q) = (e^{\beta \omega_q} - 1)^{-1}, \tag{2.17}$$

with  $\beta = 1/k_B T$ . In order to solve the implicit Eq. (2.14) for the transformation parameters, approximations are made.

At least for optic modes it is plausible to take (see Paper II)

$$f_k^q \approx g - i(\phi_k - \phi_{k-q}), \tag{2.18}$$

where  $g$  is the local coupling parameter and the  $\phi_k$  which describe the nonlocal coupling are odd in  $k$ . The real part of  $A_k^q$  is then just  $g$ , and its imaginary part as assumed to be proportional to that of  $f_k^q$ :

$$A_k^q = g - i\eta(\phi_k - \phi_{k-q}). \tag{2.19}$$

The imaginary part of Eq. (2.14) is thereby evaluated, and the scaling parameter  $\eta$  can be obtained independent of wave vector as assumed, after some simplifications which include replacing the exponent in Eq. (2.15) by its average over  $k$ . Such simplifications are not necessary in evaluating  $\tilde{J}_k$  from Eq. (2.13), but for the more difficult analysis in the present paper, it proves convenient to make them nonetheless. This will normally have only a minor effect on the band, which is, in any case, given a simple model form.

We take  $J_k$  and  $\phi_k$  in the nearest-neighbor forms,

$$J_k = J \cos k, \tag{2.20}$$

$$\phi_k = \phi \sin k. \tag{2.21}$$

Numerical solutions<sup>1(b)</sup> show that  $\eta$  never rises above unity but falls significantly with increasing  $\phi, g$ , and  $T$ , though the product  $\eta\phi$  always increases as  $\phi$  increases for fixed  $g$  and  $T$ . The algebraic and numerical behavior of  $\eta$  shows that an adequate representation well suited for present purposes is

$$\eta \approx \exp [ - (2n + 1) (g^2 + \eta^2 \phi^2) ], \tag{2.22}$$

which is exact as  $\phi \rightarrow 0$  and also for  $g = 0$  and  $(2n + 1) \phi^2 \rightarrow \infty$ . With previous assumptions, the energies become

$$E_k = \epsilon' + \tilde{J} \cos k - C \sin^2 k, \tag{2.23}$$

where

$$\epsilon' = \epsilon - \omega (g^2 + \frac{1}{2} \eta^2 \phi^2), \tag{2.24}$$

$$\tilde{J} = \eta J, \tag{2.25}$$

$$C = \omega \eta^2 \phi^2 \tag{2.26}$$

while  $\omega$  is the mean phonon frequency and  $n = n(\omega)$ . The last term in  $E_k$  distorts the band and complicates its density of states function (see Sec. IV); if  $C$  is large enough compared with  $\tilde{J}$ , the band may acquire an additional extremum between the center and the boundary of the Brillouin zone, so becoming wider than  $2\tilde{J}$ . Since the scaling parameter  $\eta$  now renormalizes  $J$  and is independent of wave vector, the average  $\langle \theta^+ \theta \rangle$  has the same structure as for local coupling, corresponding to

$$\langle \theta_{kk'}^+ \theta_{qq'} \rangle = [\eta \delta_{kk'} + N^{-1}(1 - \eta)] \delta_{k+q, k'+q'} \quad (2.27)$$

This correctly yields Eq. (2.25) and (2.19) from Eqs. (2.4) and (2.9), respectively.

### III. DIFFUSION COEFFICIENT

#### A. Thermal averaging

Using the results of Appendix A and B, we may evaluate the thermal average over the states in Eq. (1.1). For a function  $F(E)$  we use

$$\langle \langle F(E) \rangle \rangle = Q^{-1} \int_{-\infty}^{\infty} dE e^{-\beta E} N(E) F(E), \quad (3.1)$$

$$Q = \int_{-\infty}^{\infty} dE e^{-\beta E} N(E), \quad (3.2)$$

where  $N(E)$  is the density of states (see Appendix B). The scattering rate  $\Gamma_{kk}$  is given as a function of energy in Eq. (B14), but for  $v_k^2/\Gamma_{kk}$  and part of  $\gamma_{kk}$  we need the velocity as a function of  $E$ .

The velocity is biggest in regions where the density of states  $N(E)$  is largest, and hence should contain two Gaussians like those in  $N(E)$ . From Eq. (2.23) the mean-square velocity is  $\frac{1}{2}(J^2 + C^2)$ . Then a suitable approximate form which gives this result is

$$v(E)^2 N(E) = [J^2 G(E; 2^{-1/2} B) + C^2 G(E + \frac{1}{2} C; 2^{-1/2} C)] / 2\pi^{1/2}, \quad (3.3)$$

where  $G(x; b)$  is defined in Eq. (B2). Combining  $v$  with  $N(E)$  in this way gives the product required for the averaging in a much neater form than writing a separate expression for  $v(E)^2$  yielding complications from cross terms between different Gaussians.

In performing the thermal averaging and simplifying the results, products and ratios of Gaussians occur. Some can be treated exactly, but not all. Examination of the products and ratios shows, however, that unless  $B$  and  $C$  are very close in size, one Gaussian of each pair is dominant. We therefore approximate each combination of Gaussians as the sum of the dominant contributions for  $B$  large and for  $C$  large. This should provide an adequate interpolation through the region where  $B$  and  $C$  are comparable in size.

The partition function  $Q$  is found to be

$$Q = [B \exp(\beta^2 B^2/4) + C \exp(\beta C/2) \times \exp(\beta^2 C^2/4)] / (B + C). \quad (3.4)$$

The band contribution to the diffusion coefficient reduces to

$$D_b/a^2 = [(B + C)/2\Gamma_0(2\pi)^{1/2}] \times \left\{ \frac{B^2 + \Gamma^2}{4(B^2 + 2\Gamma^2)^{1/2}} \exp[-\beta^2 \Gamma^2 B^2/4(B^2 + 2\Gamma^2)] + \frac{C^2 + \Gamma^2}{(C^2 + 2\Gamma^2)^{1/2}} \exp[-\beta^2 \Gamma^2 C^2/4(C^2 + 2\Gamma^2)] \right\}. \quad (3.5)$$

Here the exponents never exceed  $\beta^2 \Gamma^2/4$  in magnitude, and since we assume  $\beta \Gamma \ll 1$ , the exponentials can be set to unity, leaving

$$D_b/a^2 = \frac{B + C}{2(2\pi)^{1/2} \Gamma_0} \left[ \frac{B^2 + \Gamma^2}{4(B^2 + 2\Gamma^2)^{1/2}} + \frac{C^2 + \Gamma^2}{(C^2 + 2\Gamma^2)^{1/2}} \right]. \quad (3.6)$$

The factor 1/4 in the first term in square brackets occurs because the maximum contribution to the velocity from the transfer integral is  $\tilde{J}$ , i.e., only half the corresponding contribution  $B$  to the bandwidth, whereas the maximum contribution to the velocity from the nonlocal coupling is equal to the whole contribution  $C$  to the bandwidth.

The part of the hopping contribution independent of the polaron velocities reduces to

$$D_h/a^2 = \frac{1}{2} \Gamma_0 \left\{ \frac{B}{(2B^2 + \Gamma^2)^{1/2}} \times \exp[-\beta^2 B^4/4(2B^2 + \Gamma^2)] + \frac{C}{(2C^2 + \Gamma^2)^{1/2}} \exp[-\beta^2 C^4/4(2C^2 + \Gamma^2)] \right\}, \quad (3.7)$$

and the other part reduces to

$$D'_h/a^2 = \frac{1}{2} \Gamma_0 (B + C) \left\{ \frac{B^2/(B^2 + \Gamma^2)}{4(3B^2 + 2\Gamma^2)^{1/2}} \times \exp\left[-\frac{1}{4} \beta^2 B^2 \left(\frac{2B^2 + \Gamma^2}{3B^2 + 2\Gamma^2}\right)\right] + \frac{C^2/(C^2 + \Gamma^2)}{4(3C^2 + 2\Gamma^2)^{1/2}} \exp\left[-\frac{1}{4} \beta^2 C^2 \left(\frac{2C^2 + \Gamma^2}{3C^2 + 2\Gamma^2}\right)\right] \right\}. \quad (3.8)$$

The velocity dependence of  $D'_h$  again leads to a factor 1/4 in the term depending on  $B$ .

#### B. Algebraic behavior

The contributions [Eqs. (3.6)–(3.8)] to the diffusion coefficient each consist of  $B$  and  $C$ . These terms have essentially the forms obtained for local coupling in Paper I except that  $D'_h$  was not derived there. Compared with  $D_h$ ,  $D'_h$  is negligible if  $\Gamma$  is much greater than  $B$  and  $C$ , and has no important qualitative effect if  $\Gamma$  is much less than  $B$  and  $C$ . Minor differences from Paper I occur in numerical factors arising from the corrected form of  $\gamma_{kk}$  and the more carefully derived form of  $v(E)$  constrained to give the correct mean-square velocity.

Nonlocal coupling affects the diffusion coefficient first by modifying the transfer integral, which is changed by the displacements on polaron formation.<sup>6</sup> It is this feature which affects the energies, density of states, and velocities. It also leads to the pairs of terms in the contributions to the diffusion coefficient, cross terms being zero in our treatment, although nonlocal coupling does affect  $B$  and  $\Gamma$ . These effects from modifying the transfer integral are largely quantitative, producing no new types of behavior.

The other way in which nonlocal coupling affects the diffusion coefficient is by introducing a new type of term in the interaction  $V$ . This term involving  $U$  represents phonon-induced fluctuations in the transfer integral. The mean-square fluctuations are nonzero, giving rise to the term proportional to  $I_1(y)$  in  $\Gamma_0$ , Eq. (B13). This corresponds to the

phonon-assisted current.<sup>10,11</sup> By increasing the scattering, it decreases  $D_b$  and increases  $D_h$  and  $D'_h$ .

At sufficiently high temperatures, both  $I_0(y)$  and  $I_1(y)$  tend to the same asymptotic value  $e^y(2\pi y)^{1/2}$ , and the term in  $[n(n+1)]^{1/2}$  dominates  $\Gamma_0$ . In this limit  $\Gamma = y^{1/2}\Delta$  is much greater than  $B$  and  $C$ , so that  $D'_h$  can be neglected compared with  $D_h$ , which reduces to

$$D_h/a^2 = (B + C)\Gamma_0/2\Gamma. \quad (3.9)$$

Substituting for  $\Gamma_0$  and  $\Gamma$ , we find

$$D_h/a^2 = [\omega C/8^{1/2}\Delta (g^2 + \eta^2\phi^2)]e^y. \quad (3.10)$$

If further  $g = 0$  (or  $g \ll \phi$  and the temperature is not too high: see below) so that nonlocal coupling dominates, substitution for  $C$ ,  $n$ , and  $y$  yields

$$D_h/a^2 = (\omega^2/8^{1/2}\Delta) \exp(2\eta^2\phi^2/\sinh \frac{1}{2}\beta\omega), \quad (3.11)$$

which for  $\beta\omega \gg 1$  becomes

$$D_h/a^2 = (\omega^2/8^{1/2}\Delta) \exp(4\eta^2\phi^2/\beta\omega). \quad (3.12)$$

The high-temperature hopping diffusion coefficient for pure local coupling<sup>1</sup> follows similarly as

$$D_h/a^2 = (J^2\beta\omega/128^{1/2}\Delta) \exp(-\frac{1}{2}g^2\beta\omega). \quad (3.13)$$

Comparing Eqs. (3.12) and (3.13) we see that for pure nonlocal coupling  $D_h$  lacks the factor  $\beta\omega$  compared with pure local coupling, because nonlocal coupling introduces the extra factor  $[n(n+1)]^{1/2}$  in  $\Gamma_0$  which cancels that in  $y$ . Nonlocal coupling therefore gives a constant preexponential factor rather than one which decreases with increasing temperature as for local coupling. Since in this limit  $\beta\omega \ll 1$ , nonlocal coupling will also tend to give a larger preexponential factor. This tendency may be enhanced by the dependence on  $\omega^2$  rather than  $J^2$  and by the lack of dependence on coupling strength compared with the inverse dependence for local coupling.

The exponentials differ markedly in form, though both increase with increasing temperature. For local coupling the renormalization factor  $\eta^2$  from  $J^2$  in the transfer rate combines with  $e^y$ , leaving an exponential which becomes constant at high temperature so that  $D_h$  eventually decreases through the preexponential factor  $\beta\omega$ . For pure nonlocal coupling the renormalization factor  $\eta^2$  from  $\omega C$  in the transfer rate cancels with a corresponding factor in the scattering rate, leaving the factor  $e^y$  intact. Here the decrease in  $\eta^2$  with increasing temperature offsets the increase in  $1/\beta$  until at the highest temperatures this exponential also becomes constant, and  $D_h$  with it.

In practice, local and nonlocal coupling must occur simultaneously: there is no general mechanism or symmetry constraint which can force either to be zero, whether for excess charge carriers or for singlet or triplet excitons. Then at high temperatures the nonzero  $g$  will always reduce  $\eta$  until eventually  $g^2 \gg \eta^2\phi^2$ . This yields a hopping diffusion coefficient from Eq. (3.10) which has features of both Eqs. (3.12) and (3.13), with nonlocal coupling determining the transfer rate but local coupling the scattering rate and the exponential:

$$D_h/a^2 = (\omega^2\phi^2/8^{1/2}g^2\Delta) \exp(-\frac{1}{2}g^2\beta\omega). \quad (3.14)$$

Hence, this limit yields simple activated behavior. The con-

stant preexponential factor displays the competitive effects of nonlocal coupling in promoting and of local coupling in hindering transport, while the activation energy  $\frac{1}{2}g^2\omega$  is half the local polaron binding energy. Equations (3.13) and (3.14) correspond to the expressions for the mobility contributions  $\mu_1$  and  $\mu_2$  given by Sumi<sup>12</sup> for a Gaussian density of states, except that his preexponential factors each differ from those here because they refer to the most strongly coupled limit<sup>6</sup> of small polaron theory.<sup>13</sup>

### C. Numerical behavior

Numerical calculations of the total diffusion coefficient  $D = D_b + D_h + D'_h$  obtained from Eqs. (3.6)–(3.8) are presented in Figs. 1–6. Each figure shows  $D$  as a function of  $T$  for various values of  $\phi^2$  and a fixed value of  $g^2$ , which increases in successive figures. All these figures refer to the same values of  $\Delta = 0.1\omega$  and  $J = 0.5\omega$ . This value of  $J$  is the largest compatible with our neglect of multiphonon contributions to  $\mathcal{W}$  in Eqs. (B2) and (B3) at all temperatures, so that the figures actually give the smallest relative contributions from nonlocal coupling. Temperatures below  $1/\beta\omega = 0.2$  are excluded by our approximations and those above  $1/\beta\omega = 5$  are likely to exceed typical crystal melting temperatures for plausible optical mode frequencies  $\omega$ .

Figure 1 shows the results for pure nonlocal coupling. Stronger coupling means stronger scattering and hence lower band mobilities and higher hopping mobilities, these contributions dominating at low and high temperatures, respectively. Thus we see that increasing the coupling strength decreases  $D$  at low temperatures and increases it at high temperatures, so that the curves for different coupling strengths cross at intermediate temperatures. (The crossings for  $\phi^2 = 3$  and 10 are omitted for clarity.) The curves go through a minimum and for the stronger couplings show a point of inflection before increasing again. This feature is associated with the hopping contribution  $D'_h$ . As the temperature increases,  $\Gamma$  increases through the factor  $y^{1/2}$  and  $D'_h$  falls relative to  $D_h$ , until eventually  $D$  increases through

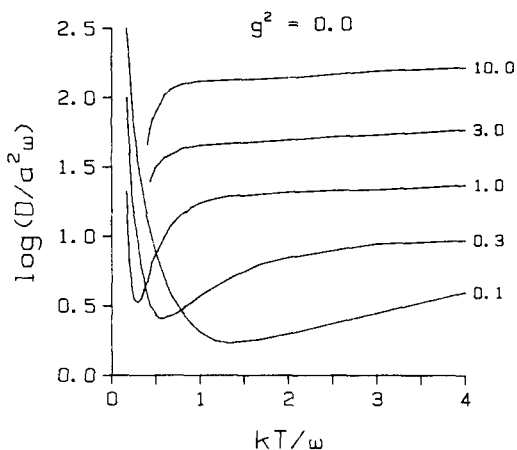


FIG. 1. The reduced diffusion coefficient  $D/\omega a^2$  as a function of the reduced temperature  $1/\beta\omega$  for different values of the nonlocal electron-phonon coupling. The local electron-phonon coupling is given by  $g^2 = 0$  (i.e., the coupling is entirely nonlocal), the transfer integral by  $J/\omega = 0.1$ . Each curve is marked with the value of  $\phi^2$  determining the nonlocal electron-phonon coupling.

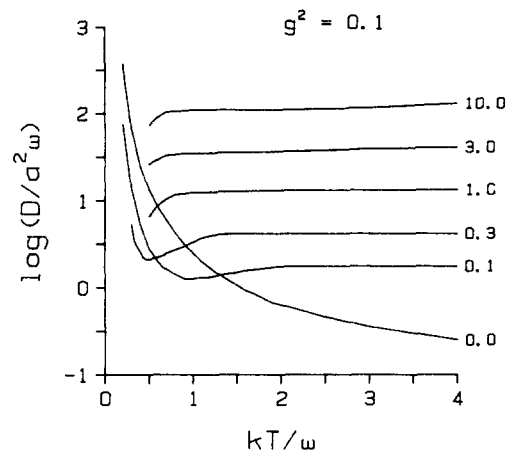


FIG. 2. Same as Fig. 1, but with  $g^2 = 0.1$ . Since  $g$  is nonzero,  $\phi$  can now be zero.

the phonon-assisted contribution.

Once the local coupling is nonzero, we can compare diffusion coefficients with and without nonlocal coupling. Figures 2–6 show this for successively stronger local coupling, with most crossings omitted for clarity. The stronger the local coupling, the more similar the curves in general shape, though this comparison is complicated by the change in the shape of the curves with  $g^2$  for pure local coupling. At high temperatures the curves for large  $g^2$  are well described by Eq. (3.14), with  $D \propto \phi^2$  except for the lowest values of  $\phi^2$  including zero.

Calculations for lower values of  $J$  show more marked effects of nonlocal coupling, because the band and hopping contributions depending on  $B$  are reduced compared with those depending on  $C$ . The curves therefore show deeper minima, which for  $\phi^2 = 0$  may disappear completely. All diffusion coefficients are reduced by similar amounts, so that proportionately larger changes are seen for smaller values of  $\phi^2$ . The subsidiary maxima seen at intermediate temperatures for the larger values of  $\phi^2$  and smaller values of  $g^2$  are weakened or eliminated. Finally the curves incorporating nonlocal coupling diverge more rapidly from those with  $\phi^2 = 0$  at high temperatures, in accordance with the factor  $\phi^2/J^2$  in the ratio of Eqs. (3.14) and (3.13).

Reducing the phonon bandwidth  $\Delta$  increases the diffu-

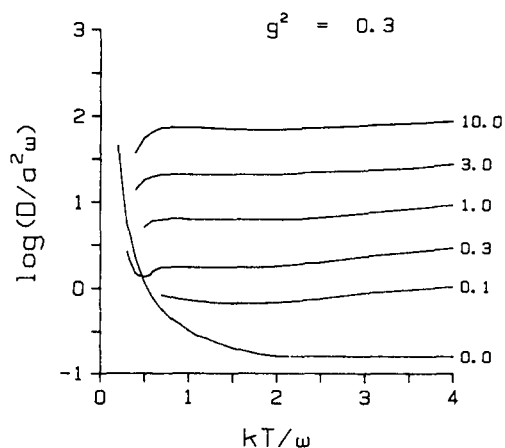


FIG. 3. Same as Fig. 1, but with  $g^2 = 0.3$ .

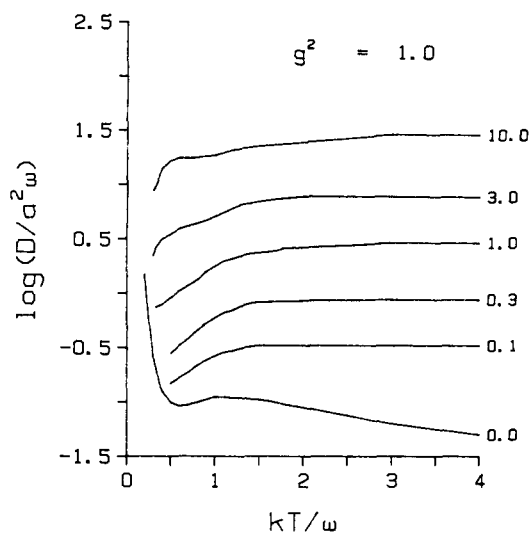


FIG. 4. Same as Fig. 1, but with  $g^2 = 1$ .

sion coefficient at most temperatures of interest. For narrow bands, weak coupling, and intermediate temperatures the increase comes mainly through  $D'_h \sim 1/\Gamma^2 \sim 1/\Delta^2$ , but at higher coupling strengths and temperatures  $D_h$  dominates and the increase varies as  $1/\Delta$ , from Eqs. (3.13) and (3.14). Thus  $D$  may go through a quite marked maximum as  $T$  increases, as Fig. 7 shows.

#### IV. DISCUSSION

##### A. Review of results

The results in the present paper constitute a theory of electronic transport in molecular crystals more general than hitherto available. Although only linear electron-phonon coupling is treated, it may comprise local or nonlocal interactions or both, and neither type of interaction is restricted in magnitude. The transfer integral is not restricted in magnitude, either, although for simplicity of presentation we have taken  $B < \omega$  as in Paper I and  $C < \omega$ . Polaron band narrowing ensures that these conditions are readily fulfilled ex-

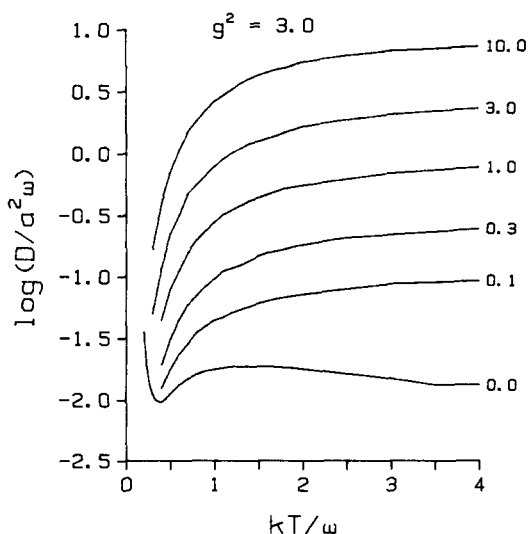


FIG. 5. Same as Fig. 1, but with  $g^2 = 3$ .

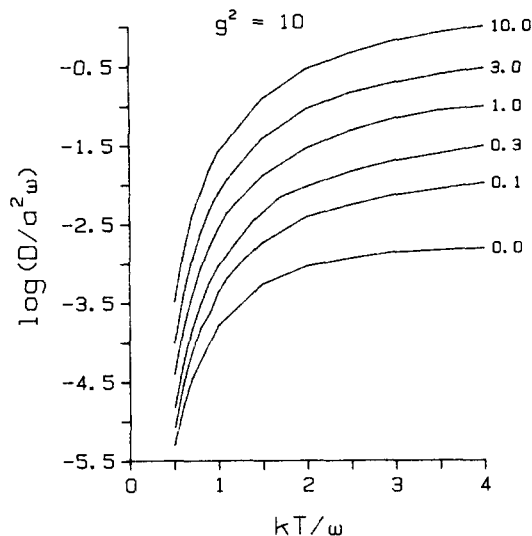


FIG. 6. Same as Fig. 1, but with  $g^2 = 10$ .

cept for wide bands, weak coupling, and low temperatures, conditions when our treatment is least suitable and least necessary. We have assumed Gaussian densities of states for the polaron and phonon bands; these analytically convenient forms provide reasonable representations of densities of states in three dimensions. A number of approximations have also been made for convenience, as indicated at various points in the text. None is expected to have major qualitative effects, and all could be avoided in numerical work.

As expected, nonlocal coupling has the biggest effect on the diffusion coefficient when it is largest compared with the local coupling. The additional nonlocal coupling tends to decrease the diffusion coefficient at low temperatures and increase it at high temperatures, until eventually the phonon-assisted term [Eq. (3.14)] dominates. Qualitatively speaking, the strength of the nonlocal coupling affects the magnitude of the diffusion coefficient for given values of the other parameters, but not the temperature dependence. The shapes of the curves change more between different Figs. 1–7 than within a given figure.

Nonlocal coupling has been treated previously in a number of ways.<sup>6,10–12,14–18</sup> These treatments do not use the

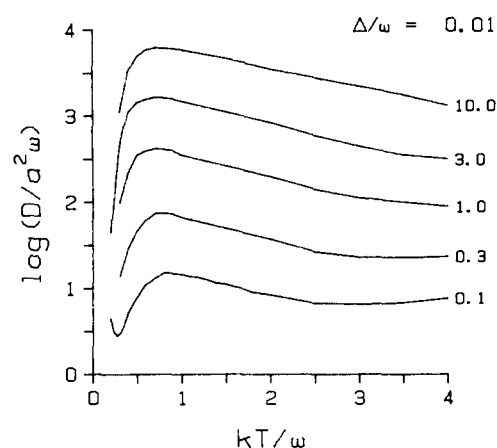


FIG. 7. Same as Fig. 1, but with  $g^2 = 0.3$  but  $\Delta/\omega = 0.01$  and  $J/\omega = 0.1$ .

nonlocal polaron transformation as done here, but this omission is less serious than it might seem, provided the local transformation or some equivalent technique<sup>6</sup> is used. This reduces the nonlocal term in the residual interaction  $V$  by a factor  $\exp[-(2n+1)g^2]$ . Provided the temperature is high enough and  $g^2$  is large enough, the nonlocal term is small enough for a perturbative treatment to apply.

## B. Temperature-independent mobilities

Recent interest in nonlocal coupling has been stimulated by the possibility that it might explain the almost temperature-independent charge-carrier drift mobilities observed in some crystallographic directions for certain crystals.<sup>19</sup> Since the mobility  $\mu$  is related to the diffusion coefficient by the Einstein relation  $\mu = e\beta D$ , any contribution to  $D$  which is proportional to  $T$  at high temperatures will eventually yield a constant mobility. Contributions varying like  $n$ ,  $[n(n+1)]^{1/2}$ , etc., will have this effect. However, most theories yield contributions which ultimately become constant or decrease with increasing  $T$ , so that  $\mu \sim T^{-n}$  with  $n > 1$ .<sup>20</sup> Such is the case with the present treatment, which yields mobilities independent of temperatures over significant ranges of temperature only for special sets of parameter values. Ultimately the present results yield  $\mu \sim 1/T$ , while in the extreme strong coupling limit<sup>6</sup>  $g^2[n(n+1)]^{1/2} \gg \omega/\Delta > 1$  the method of steepest descents<sup>13</sup> yields  $\mu \sim 1/T^{1/2}$ , as noted by Sumi.<sup>12</sup>

In fact, temperature-independent mobilities are not commonly observed, as far as the rather limited data available are concerned. Where they are observed, a layer-like structure perpendicular to the transport direction appears to be a necessary concomitant, and this structural feature ought, therefore, to play an essential role in explaining such mobilities. It would imply weak transfer interactions between layers, greatly enhanced by vibrations changing the distance between layers, vibrations which would tend to be of low frequency. This implies an important contribution from nonlocal coupling, with its tendency to increase the magnitude of  $D$  and reduce its rate of fall with temperature. The other important qualitative effect of a layer structure would be to make the polaron density of states rectangular rather than the Gaussian assumed here. It is this effect which produces a constant mobility in Sumi's theory,<sup>12</sup> whereas a Gaussian form gives results consistent with those here, as we have seen. We also note that the mobilities within the layers tend to decrease more rapidly than in the present theory (except for special parameter sets), so that the average temperature dependence resembles that here.

It has been suggested<sup>21</sup> that constant mobilities may be common because hopping rates are generally proportional to  $n$ . This is true, but only for weak coupling (both local and nonlocal), and then hopping will not be predominant. Once coupling becomes strong, polaron effects complicate the temperature dependence, including that of the phonon-assisted part with its additional factor  $[n(n+1)]^{1/2}$ . It then requires some special feature such as wide phonon and narrow carrier bands, or the rectangular density of states in two dimensions to yield a constant mobility.<sup>6</sup> Temperature-independent mobilities are striking precisely because they are

unusual, and as such they require special explanation rather than the general theory presented here.

### C. Comparison of local and nonlocal coupling

As already argued, both types of coupling must occur in general, although their relative strengths will depend on the phonon modes concerned. For example, molecular modes may be expected to have much more effect on the local site energy than on the transfer integrals. The strength of the nonlocal coupling will also correlate with the size of the transfer integrals to some extent. When these are accidentally zero by cancellation of terms, vibrations can only make them larger, but as the transfer integrals become larger through strong overlap, vibrations will have relatively less effect, until the Frenkel exciton or tight-binding limit is superseded by the Wannier exciton or delocalized limit and nonlocal coupling becomes zero.

Nonlocal coupling can be anisotropic whereas local coupling cannot. This property was implicitly invoked above in explaining the constant mobility in layer structures. An analogous property could explain the anisotropy in charge-carrier trap depths for transport within and between layers in anthracene,<sup>22</sup> if one accepts the idea<sup>23</sup> that static disorder in imperfect crystals (rather than dynamic disorder due to phonons in perfect crystals) can cause trapping through changes in transfer integrals as well as through changes in site energies.

Although both nonlocal and local coupling conserve crystal momentum, strong local coupling and polaron formation can be regarded as symmetry breaking.<sup>24</sup> One could perhaps view this as the reason why local coupling ultimately leads to a decreasing diffusion coefficient at high temperatures whereas nonlocal coupling leads to a constant diffusion coefficient. This in turn is why the nonlocal coupling eventually dominates.

Only linear coupling has been treated here. Quadratic local coupling associated with frequency changes in lattice or molecular phonon modes is known to be significant in some cases. If weak, it can be treated by methods like those here,<sup>25</sup> but if strong it is difficult to treat because bound states can form. For nonlocal coupling, the roughly exponential dependence of molecular overlap on molecular separation and perhaps orientation implies an important role for quadratic and higher terms.<sup>17,18</sup> However, bound-state formation is not a problem, and it has proved possible to treat transport for an exponential dependence of transfer integral on the phonon displacement operator.<sup>18</sup>

It may also be remarked that the approximate form [Eq. (2.18)] for the electron-phonon coupling coefficients yields zero nonlocal coupling at the zone center  $q = 0$ . This form might thus seem more suited to acoustic modes. However, our treatment implies only one molecule per unit cell. In this case, the optic modes at  $q = 0$  correspond to all molecules rotating in phase, and the *linear* electron-phonon coupling vanishes. The effects of having more than one molecule in the unit cell have been little explored in the context of transport theory, except in band structure calculations.

### D. CONCLUSIONS

Nonlocal electron-phonon coupling decreases diffusion coefficients at low temperatures and increases them at high enough temperatures through a phonon-assisted contribution which becomes constant. The present results complement and extend previous work on nonlocal coupling. By not yielding a constant mobility at high temperatures, they support the idea that such behavior requires special explanation associated with a layer-like structure in which nonlocal coupling is important.

Extensions of the present work to include different phonon branches with different couplings in a realistic structure are possible. The problem is that such extensions would be very complicated without some indication of the dominant interactions. This argues the need for further fundamental work on electron-phonon coupling now that there are theories to incorporate it. Further systematic study of exciton diffusion coefficients and charge-carrier mobilities would also define better the range of behavior theory must explain.

### ACKNOWLEDGMENTS

This work was supported by NATO Grant No. 1054 and by a grant to RS from the National Science Foundation. RWM is grateful to Professor D. P. Craig for extending him the hospitality of his group while the work was done.

### APPENDIX A: CORRELATION FUNCTIONS

#### 1. Structure

The correlation functions depend on thermal averages involving  $T$  defined by Eq. (2.11) and  $u$  defined by

$$u = \frac{1}{2}(T\psi + \psi T) \quad (\text{A1})$$

as in Eq. (2.12). We write  $T = F - \langle F \rangle$ , where

$$F = \theta^+ \theta = \exp(\lambda b^+ + \mu b) \equiv \exp Z, \quad (\text{A2})$$

and similarly

$$G = \frac{1}{2}(\psi F + F\psi). \quad (\text{A3})$$

The required averages are then

$$\langle T_1 T_2 \rangle = \langle F_1 F_2 \rangle - \langle F_1 \rangle \langle F_2 \rangle, \quad (\text{A4})$$

$$\langle T_1 u_2 \rangle = \langle F_1 G_2 \rangle - \langle F_1 \psi_2 \rangle \langle F_2 \rangle - \langle F_1 \rangle \langle G_2 \rangle, \quad (\text{A5})$$

$$\langle u_1 T_2 \rangle = \langle G_1 F_2 \rangle - \langle F_1 \rangle \langle \psi_1 F_2 \rangle - \langle G_1 \rangle \langle F_2 \rangle, \quad (\text{A6})$$

$$\langle u_1 u_2 \rangle = \langle G_1 G_2 \rangle - \langle F_1 \rangle \langle \psi_1 G_2 \rangle - \langle G_1 \psi_2 \rangle \langle F_2 \rangle + \langle F_1 \rangle \langle F_2 \rangle \langle \psi_1 \rangle \langle \psi_2 \rangle, \quad (\text{A7})$$

where  $\langle \psi \rangle = 0$  has been used.

We use the result<sup>7</sup> that for exponents  $Z_1$  and  $Z_2$  which commute with their commutator:

$$e^{Z_1} e^{Z_2} = e^{Z_1 + Z_2} e^{(1/2)[Z_1, Z_2]}. \quad (\text{A8})$$

We also have<sup>7,8</sup>

$$\langle F \rangle = \exp[ \frac{1}{2}(2n + 1)\lambda\mu ], \quad (\text{A9})$$

which with Eq. (A8) yields

$$\langle F_1 F_2 \rangle = \exp[ \frac{1}{2}(2n + 1)(\lambda_1 + \lambda_2)(\mu_1 + \mu_2) + \frac{1}{2}(\lambda_2 \mu_1 - \lambda_1 \mu_2) ]. \quad (\text{A10})$$



The averages involving  $\psi$  are obtained by applying Eq. (3.8) to Eq. (3.2) to show that

$$\partial F / \partial \lambda = (b^+ + \frac{1}{2} \mu) F = F(b^+ - \frac{1}{2} \mu), \quad (\text{A11})$$

$$\partial F / \partial \mu = (b - \frac{1}{2} \lambda) F = F(b + \frac{1}{2} \lambda) \quad (\text{A12})$$

so that in particular

$$G = \partial F / \partial \lambda + \partial F / \partial \mu. \quad (\text{A13})$$

Then differentiation of Eqs. (A9) and (A10) gives the results

$$\langle G \rangle = \langle \frac{1}{2} (Z\psi + \psi Z) \rangle \langle F \rangle \equiv \langle R \rangle \langle F \rangle, \quad (\text{A14})$$

$$\langle F_1 \psi_2 \rangle = \langle Z_1 \psi_2 \rangle \langle F_1 \rangle, \quad (\text{A15})$$

$$\langle F_1 G_2 \rangle = [\langle Z_1 \psi_2 \rangle + \langle R_2 \rangle] \langle F_1 F_2 \rangle, \quad (\text{A16})$$

$$\langle \psi_1 F_2 \rangle = \langle \psi_1 Z_2 \rangle \langle F_2 \rangle, \quad (\text{A17})$$

$$\langle G_1 F_2 \rangle = [\langle R_1 \rangle + \langle \psi_1 Z_2 \rangle] \langle F_1 F_2 \rangle, \quad (\text{A18})$$

$$\langle F_1 G_2 \rangle = \{ [\langle Z_1 \psi_2 \rangle + \langle R_2 \rangle] \langle R_1 \rangle + \langle \psi_1 Z_2 \rangle + \langle \psi_1 \psi_2 \rangle \} \langle F_1 F_2 \rangle. \quad (\text{A19})$$

Substitution in Eqs. (A4)–(A7) yields the various thermal averages. Now the form of  $V$  in Sec. II uses the result that because  $Z$  is anti-Hermitian, the contribution of  $\langle G \rangle$  is zero, as it must be to make  $\langle V \rangle$  zero. Then the thermal averages simplify to

$$\langle T_1 u_2 \rangle = \langle Z_1 \psi_2 \rangle \langle T_1 T_2 \rangle, \quad (\text{A20})$$

$$\langle u_1 T_2 \rangle = \langle \psi_1 Z_2 \rangle \langle T_1 T_2 \rangle, \quad (\text{A21})$$

$$\langle u_1 u_2 \rangle = [\langle Z_1 \psi_2 \rangle \langle \psi_1 Z_2 \rangle + \langle \psi_1 \psi_2 \rangle] \langle T_1 T_2 \rangle. \quad (\text{A22})$$

## 2. Detailed evaluation of averages

We now take account of the matrix nature of  $Z$  and the time dependence of  $F_2$  and  $\psi_2$  obtained by replacing  $b^+$  by  $b^+ e^{i\omega t}$  everywhere. The average of the phonon displacement operators is thus

$$\langle \psi_Q \psi_Q(t) \rangle = [n_Q e^{-i\omega_Q t} + (n_Q + 1) e^{i\omega_Q t}] \delta_{Q', -Q} \quad (\text{A23})$$

$$\equiv P_Q(t) \delta_{Q', -Q}, \quad (\text{A24})$$

so that  $P_Q(0) = 2n_Q + 1$ .

The remaining average  $\langle F_1 F_2 \rangle$  is evaluated from Eq. (A10) using the techniques developed in Paper II (but with a slightly different notation). The exponent  $S$  which appears in each factor  $\theta^+$  or  $\theta$  is written in turn as  $T^+ - T$ ,  $U^+ - U$ ,  $X^+ - X$ , and  $Y^+ - Y$ , so that  $Z_1 = T^+ + U^+ - T - U$  and  $Z_2 = X^+ + Y^+ - X - Y$ . The different symbols allow different matrix elements to be assigned. The terms in  $\lambda_1 \mu_1$  and  $\lambda_2 \mu_2$  from Eq. (A10) contribute factors  $\langle \theta^+ \theta \rangle$  which form matrix products with other contributions arising from the cross terms between  $Z_1$  and  $Z_2$ :

$$\begin{aligned} & \langle \theta_{k_1 k_2}^+ \theta_{k_3 k_4} \theta_{q_1 q_2}^+(t) \theta_{q_3 q_4}(t) \rangle \\ &= \sum_{p_1 \dots p_8} \langle \theta_{p_1 k_2}^+ \theta_{k_3 p_2} \rangle [\exp - \langle T^+ X + T X^+ \rangle]_{p_1 p_3; q_3 p_4} \\ & \quad \times [\exp \langle T^+ Y + T Y^+ \rangle]_{p_3 k_1; q_3 p_5} \\ & \quad \times [\exp \langle U^+ X + U X^+ \rangle]_{p_2 p_6; p_4 p_7} \\ & \quad \times [\exp - \langle U^+ Y + U Y^+ \rangle]_{p_6 k_4; p_5 p_8} \langle \theta_{q_1 p_7}^+ \theta_{p_8 q_4} \rangle. \end{aligned} \quad (\text{A25})$$

The exponentials are given by, for example,

$$\begin{aligned} & [\exp - \langle T^+ X + T X^+ \rangle]_{k_1 k_2; q_1 q_2} \\ &= [\exp - E^{k_2 - q_1}(t)]_{-q_2; -q_1} \delta_{k_1 + q_1; k_2 + q_2}, \end{aligned} \quad (\text{A26})$$

where

$$E_{k_1 k_2}^q(t) = N^{-1} P_{k_1 - k_2}(t) (A_{k_1 - q}^{k_1 - k_2})^* A_{k_1}^{k_1 - k_2}, \quad (\text{A27})$$

which reduces to  $E_{k_1 k_2}^q$  of Eq. (2.16) for  $t = 0$ .

Exponents containing factors  $P(t)$  are characteristic of correlation functions for linear electron-phonon coupling.<sup>1,9</sup> Substitution of Eq. (A26) in Eq. (A25), making use of the momentum conservation required by Eq. (2.27) for  $\langle \theta^+ \theta \rangle$ , yields

$$\begin{aligned} & \langle \theta_{k_1 k_2}^+ \theta_{k_3 k_4} \theta_{q_1 q_2}^+(t) \theta_{q_3 q_4}(t) \rangle \\ &= \sum_{r_1 r_2 r_3} \langle \theta_{k_2 + r_1; k_2}^+ \theta_{k_3; k_3 - r_1} \rangle \langle \theta_{q_2 + r_2; q_2}^+ \theta_{q_3; q_3 - r_2} \rangle \\ & \quad \times [\exp - E^{k_1 + q_4 + r_3 - q_2 - q_3}(t)]_{k_3 + r_3 - q_1 - k_4 - r_1; -q_2 - r_2} \\ & \quad \times [\exp E^{k_1 + r_2 - q_3}(t)]_{-q_4 - r_3; r_2 - q_3} \\ & \quad \times [\exp E^{k_3 - q_1 - r_1}(t)]_{-q_1; k_3 + r_3 - q_1 - k_4 - r_1} \\ & \quad \times [\exp - E^{k_4 - q_4 - r_3}(t)]_{-q_4; -q_4 - r_3} \\ & \quad \times \delta_{k_1 + q_1 + k_4 + q_4; k_2 + q_2 + k_3 + q_3}. \end{aligned} \quad (\text{A28})$$

In Paper II, an expression was derived relating  $\langle \theta^+ \theta \rangle$  to  $\exp E^q$ . With the simplified form [Eq. (2.27)] for  $\langle \theta^+ \theta \rangle$ , this expression yields

$$[\exp E^q]_{-k_1; -k_2} = \delta_{k_1 k_2} + N^{-1} (\eta^{-1} - 1). \quad (\text{A29})$$

The corresponding expression for  $\exp E^q(t)$  is derived by replacing  $2n_Q + 1 = P_Q(0)$  in  $\eta$  by  $P_Q(t)$ , while  $\exp E^q(t)$  is obtained by matrix inversion. For proper decaying correlations, previous results<sup>1,9</sup> show that  $N^{-1} \sum_Q P_Q(t)$  should be replaced by  $P(t) A(t)$ , where  $P(t)$  refers to the mean frequency  $\omega$  and  $A(t)$  is the Fourier transform of the phonon density of states. Then it is found that

$$[\exp \pm E^q(t)]_{k_1 k_2} = \delta_{k_1 k_2} + N^{-1} (H^{\pm 1} - 1), \quad (\text{A30})$$

where

$$H = \exp[(g^2 + \eta^2 \phi^2) P(t) A(t)]. \quad (\text{A31})$$

As  $t \rightarrow \infty$ ,  $A(t) \rightarrow 0$  and  $H \rightarrow 1$ , so that the exponentials in Eq. (A28) reduce to Kronecker deltas. The average then breaks up into the product of the separate averages  $\langle \theta_{k_1 k_2}^+ \theta_{k_3 k_4} \rangle$  and  $\langle \theta_{q_1 q_2}^+ \theta_{q_3 q_4} \rangle$ , making  $\langle T_1 T_2 \rangle$  zero as required at long times for irreversibility.

Using Eq. (A30) in Eq. (A28) with Eq. (2.27) leads eventually to

$$\begin{aligned} & \langle T_{k_1 k_2; k_3 k_4} T_{q_1 q_2; q_3 q_4}(t) \rangle \\ &= N^{-2} \eta^2 [(H - 1)^2 D_{k_1 + q_4; k_2 + q_3} \\ & \quad + (H^{-1} - 1) D_{k_1 + q_1; k_2 + q_2}] \\ & \quad + N(H - 1) (D_{k_1 k_2} D_{q_3 q_4} + D_{k_3 k_4} D_{q_1 q_2}) \\ & \quad + N(H^{-1} - 1) (D_{k_1 k_2} D_{q_1 q_2} + D_{k_3 k_4} D_{q_3 q_4}) \\ & \quad \times \delta_{k_1 + q_1 + k_4 + q_4; k_2 + q_2 + k_3 + q_3}, \end{aligned} \quad (\text{A32})$$

where

$$D_{k_1 k_2} = \delta_{k_1 k_2} - N^{-1}. \quad (\text{A33})$$

This expression for the correlation function agrees with that

for local coupling in Paper I, with  $H^2 - 1$  corresponding to  $\gamma_1$ ,  $H - 1$  to  $\gamma_2$ ,  $H^{-1} - 1$  to  $\gamma_3$ , and  $H^{-2} - 1$  to  $\gamma_4$ .

As before, we take for  $A(t)$  the Gaussian form

$$A(t) = \exp(-\Delta^2 t^2/4), \quad (\text{A34})$$

where  $\Delta$  is the phonon bandwidth, assumed much less than  $\omega$ . Then by analogy with Paper I we obtain

$$H^r - 1 \approx \exp(-\Gamma^2 t^2/4) \sum_{m=-\infty}^{\infty} e^{(1/2)m\beta\omega} e^{im\omega t} [I_m(\frac{1}{2}r y) - \delta_{m0}], \quad (\text{A35})$$

where

$$y = 4(g^2 + \eta^2 \phi^2)[n(n+1)]^{1/2} \quad (\text{A36})$$

and

$$\Gamma = \Delta (\frac{1}{2}|r| y \leq 1) \quad (\text{A37})$$

$$= [\Delta (\frac{1}{2}|r| y)^{1/2}] (\frac{1}{2}|r| y > 1) \quad (\text{A38})$$

with  $I_m(Z)$  the modified Bessel function of order  $m$ . Except for small  $y$  (low temperature and both local and nonlocal coupling weak),  $\gamma_2$  and  $\gamma_3$  with  $r = \pm 1$  are much smaller than  $\gamma_1$  and  $\gamma_4$  with  $r = \pm 2$ , and will be neglected as previously.

### 3. Evaluation of sums

The interaction  $V$  consists of three types of term, in  $\mathcal{J}\Gamma$ ,  $\omega f\Gamma$  and  $\omega f u$ . These give rise to six types of cross term in  $\langle V_{k'+q, kq} V_{kk'}(t) \rangle$ . We consider these in turn.

First we get

$$N^{-2} \left[ \gamma_1 \sum_{\kappa} \tilde{J}_{\kappa} \tilde{J}_{\kappa-q} + \gamma_4 \sum_{\kappa} \tilde{J}_{\kappa} \tilde{J}_{\kappa-r} \right] = \frac{1}{2} N^{-1} J^2 (\gamma_1 \cos q + \gamma_4 \cos r), \quad (\text{A39})$$

where  $r = k + k' + q$  recurs frequently. This term is as for local coupling except that the renormalization now depends on  $\phi$  as well as  $g$ .

Next we get

$$-N^{-3} \sum_{\kappa Q} \omega_Q \eta^2 \tilde{J}_{\kappa} [(h_{-\kappa}^{\kappa} - h_{-\kappa}^{\kappa}) (\gamma_1 h_{-\kappa+q}^{\kappa} + \gamma_4 h_{\kappa-r}^{\kappa}) + (h_{-\kappa'}^{\kappa} - h_{-\kappa}^{\kappa}) (\gamma_1 h_{-\kappa-q}^{\kappa} + \gamma_4 h_{\kappa-r}^{\kappa})] \quad (\text{A40})$$

where  $h_{\kappa}^{\kappa} = f_{\kappa}^{\kappa} - g$ . The real parts  $g$  are removed by the term  $-N^{-1}$  in  $D_{k_1, k_2}$  and by the occurrence of differences such as  $A_{\kappa}^{\kappa} - A_{\kappa}^{\kappa}$ . Performing the summations yields

$$-\frac{1}{4} N^{-1} \tilde{J} C \{ (\gamma_1 + \gamma_4) [\cos k + \cos k'] + \cos(k+q) + \cos(k'+q) + 2(\gamma_1 \sin q + \gamma_4 \sin r) [\sin(k+q) + \sin(k'+q)] + 2(\gamma_1 \sin q - \gamma_4 \sin r) [\sin k + \sin k'] \}, \quad (\text{A41})$$

where from Eq. (2.26)  $C = \omega \eta \phi^2$ .

The remaining term not involving  $u$  is

$$N^{-4} \sum_{\kappa Q Q'} \omega_Q \omega_{Q'} \eta^4 (h_{-\kappa}^{\kappa} - h_{-\kappa'}^{\kappa}) (h_{-\kappa'}^{\kappa} - h_{-\kappa}^{\kappa}) \times (\gamma_1 h_{-\kappa}^{\kappa} h_{-\kappa+q}^{\kappa} + \gamma_4 h_{-\kappa}^{\kappa} h_{\kappa-r}^{\kappa}), \quad (\text{A42})$$

where terms involving  $g$  cancel as before. This leads to

$$\frac{1}{4} N^{-1} C^2 \{ (\gamma_1 + \gamma_4) \{ 1 + \cos(k-k') + (\sin k + \sin k')^2 + [\sin(k+q) + \sin(k'+q)]^2 \Delta \} + 2(\gamma_1 \cos q - \gamma_4 \cos r) (\sin k + \sin k') \times [\sin(k+q) + \sin(k'+q)] \}. \quad (\text{A43})$$

The term in  $\langle \psi \psi(t) \rangle$  is

$$N^{-3} \omega^2 \eta^2 \sum_{\kappa Q} P_Q(t) h_{-\kappa}^{\kappa} (\gamma_1 h_{-\kappa-q}^{\kappa} + \gamma_4 h_{\kappa-r}^{\kappa}) = N^{-2} \omega C \sum_Q P_Q(t) (1 - \cos Q) (\gamma_1 \cos q + \gamma_4 \cos r). \quad (\text{A44})$$

To be consistent with the earlier derivation of  $H$ , we should take  $N^{-1} \sum_Q P_Q(t)$  as  $P(t) A(t)$ . However, including  $A(t)$  here is no longer physically necessary to ensure decaying correlations, these being already ensured by its inclusion in  $\gamma_1$  and  $\gamma_4$ , and is mathematically inconvenient as it yields terms decaying at a rate  $\Gamma/2^{1/2}$  in addition to those decaying at a rate  $\Gamma/2$ . We therefore set  $P_Q(t) \approx P(t)$  to obtain this term as

$$N^{-1} \omega C P(t) (\gamma_1 \cos q + \gamma_4 \cos r). \quad (\text{A45})$$

The terms involving combinations of  $\Gamma$  with  $u$  all depend on the quantity

$$D_Q(t) = (n_Q + 1) e^{i\omega_Q t} - n_Q e^{-i\omega_Q t}, \quad (\text{A46})$$

while those involving  $u$  combined with  $u$  depend on  $D_Q(t)$ . Although these terms are nonzero, their contribution to  $W$  vanishes as we explain later, and they will not be treated in detail.

## APPENDIX B: SCATTERING AND HOPPING RATES

### 1. Calculation of $W$

Only the real part of Eq. (1.4) for  $W$  is required, and this can be calculated essentially as in Paper I. The contributions of Eqs. (A39), (A41), and (A43) to  $\langle VV(t) \rangle$  are of the form  $\rho \gamma_1 + \sigma \gamma_4$ , where the prefactors  $\rho$  and  $\sigma$  do not depend on  $t$ . These yield contributions to  $W$  of the form

$$\pi^{1/2} \sum_{m=-\infty}^{\infty} [\rho + (-1)^m \sigma] e^{m\beta\omega/2} [I_m(y) - \delta_{m0}] \times [G(E_{k'+q} - E_{k+q} + m\omega; \Gamma) + G(E_{k'} - E_k + m\omega; \Gamma)], \quad (\text{B1})$$

where

$$G(x; b) = b^{-1} \exp(-x^2/b^2). \quad (\text{B2})$$

The contribution (A45) to  $\langle VV(t) \rangle$  is of the form  $(\rho \gamma_1 + \sigma \gamma_4) P(t)$ , and yields a contribution to  $W$  of the form

$$\pi^{1/2} \sum_{m=-\infty}^{\infty} [\rho + (-1)^m \sigma] e^{m\beta\omega/2} [I_m(y) - \delta_{m0}] \times \{ (n+1) \{ G[E_{k'+q} - E_{k+q} + (m+1)\omega; \Gamma] + G[E_{k'} - E_k + (m+1)\omega; \Gamma] \} + n \{ G[E_{k'+q} - E_{k+q} + (m-1)\omega; \Gamma] + G[E_{k'} - E_k + (m-1)\omega; \Gamma] \} \}. \quad (\text{B3})$$

Since  $\Gamma \sim \Delta \ll \omega$ , the dominant contributions to the sums in (B1) and (B3) occur when the energy numerators in the Gaussian exponents are small compared with  $\omega$ . For narrow

polaron bands where  $2\bar{J}$  and  $C$  fall well below  $\omega$ , the dominant contributions occur when the energy numerators contain zero multiples of  $\omega$ . Then the dominant contribution from  $\rho\gamma_1 + \sigma\gamma_4$  is

$$\pi^{1/2}(\rho + \sigma)[I_0(y) - 1] \times \{G(E_{k'+q} - E_{k+q}; \Gamma) + G(E_{k'} - E_k; \Gamma)\} \quad (\text{B4})$$

and that from  $(\rho\gamma_1 + \sigma\gamma_4)P(t)$  is

$$\pi^{1/2}(\rho - \sigma)2[n(n+1)]^{1/2}I_1(y) \times \{G(E_{k'+q} - E_{k+q}; \Gamma) + G(E_{k'} - E_k; \Gamma)\}. \quad (\text{B5})$$

Other contributions will henceforth be neglected.

In Eq. (B5) the factor  $[n(n+1)]^{1/2}$  is the value common to the quantities  $ne^{\beta\omega/2}$  and  $(n+1)e^{-(1/2)\beta\omega}$ . This is why the contribution from  $D_Q(t)$  vanishes: it leads to the difference between these quantities. The same reasoning applies to the contribution from  $D_Q(t)D_{Q'}(t)$ , except for  $Q = Q'$  when it is nonzero but a factor  $N^{-1}$  smaller than the others and hence negligible. It also happens that the  $q$  dependence of terms depending on  $D(t)$  would ultimately give zero contribution to  $\Gamma_{kk}$  and  $\gamma_{kk}$  anyway.

The factors denoted  $\rho$  and  $\sigma$  above are complicated factors of  $k, k'$ , and  $q$ . They can be carried farther through the analysis which follows, at the cost of much algebra and complexity, but eventually approximations prove necessary. It is therefore convenient to make at this stage the simplifying assumption that the prefactors can be replaced by their averages over  $k$  and  $k'$ . This is in the spirit of the approximations previously used<sup>2</sup> in deriving  $\eta$ , and yields results which reduce to those in Paper I for  $C = 0$ . With this assumption we obtain

$$W_{k,k+q;k',k'+q} = (\pi^{1/2}/N) \{ [\frac{1}{2}\bar{J}^2 \cos q + \frac{1}{2}C^2(4 + \cos^2 q)] \times [I_0(y) - 1] + 2\omega C \cos q [n(n+1)]^{1/2}I_1(y) \} \times \{G(E_{k'+q} - E_{k+q}; \Gamma) + G(E_{k'} - E_k; \Gamma)\}. \quad (\text{B6})$$

## 2. Sum over states

We now have to sum (B6) over states  $k$ . This is done by transforming to an integral over the density of states, as in Paper I. Because of the nonlocal coupling, the energies now contain two  $k$ -dependent terms. We therefore represent the density of states  $N(E)$  at energy  $\epsilon' + E$  by the sum of two Gaussians, one for each term:

$$N(E) = [BG(E; B) + CG(E + \frac{1}{2}C; C)]/\pi^{1/2}(B + C). \quad (\text{B7})$$

Here  $B$  is that part of the bandwidth due to the transfer integral, which can be taken as  $2\bar{J}$  (this corresponds to  $\bar{B}$  in Paper I). The second term in  $N(E)$ , centered at  $E = -\frac{1}{2}C$ , represents the increased density of states at the bottom of the band and the eventual increase in bandwidth above  $B$  as  $C$  increases for fixed  $J$ . Although our formalism is essentially one dimensional, the use of Gaussians in the density of states simulates the form expected in a three-dimensional crystal without marked anisotropy.

Using Eq. (B7) with (B6), we obtain

$$\sum_k W_{k,k+q;k',k'+q} = [\pi^{1/2}/(B + C)] \times \{ [\frac{1}{2}\bar{J}^2 \cos q + \frac{1}{2}C^2(4 + \cos^2 q)] [I_0(y) - 1] + 2\omega C \cos q [n(n+1)]^{1/2}I_1(y) \} \times \{ BG [E_{k'}; (B + \Gamma^2)^{1/2}] + BG [E_{k'+q}; (B^2 + \Gamma^2)^{1/2}] + CG [E_{k'} + \frac{1}{2}C; (C^2 + \Gamma^2)^{1/2}] + CG [E_{k'+q} + \frac{1}{2}C; (C^2 + \Gamma^2)^{1/2}] \}. \quad (\text{B8})$$

For the scattering rate  $\Gamma_{k'k'}$ , the term  $k = k'$  is to be excluded from the sum over  $k$  [see Eq. (1.2)] but is of order  $1/N$  and hence negligible.

## 3. Scattering and hopping rates

The scattering rate is obtained by setting  $q = 0$  in (B8):

$$\Gamma_{k'k'} = \{ (\bar{J}^2 + 5C^2) [I_0(y) - 1] + 4\omega C [n(n+1)]^{1/2}I_1(y) \} \times [\pi^{1/2}/(B + C)] \{ BG [E_{k'}; (B^2 + \Gamma^2)^{1/2}] + CG [E_{k'} + \frac{1}{2}C; (C^2 + \Gamma^2)^{1/2}] \}. \quad (\text{B9})$$

From Eq. (1.3), the first part of the hopping rate can be obtained by differentiating  $\Gamma_{k'k'}$  twice with respect to  $k'$ , and the second part can be obtained by differentiating Eq. (B8) twice with respect to  $q$  and setting  $q \rightarrow 0$ . Now the first derivative of  $G(x; b)$  with respect to  $x$  is proportional to  $x$ , and the second derivative consists of terms proportional to  $x^2$  and  $x$  plus a term independent of  $x$ . Since  $G(x; b)$  is largest where  $x$  is zero, the terms in  $x$  and  $x^2$  can be neglected to a first approximation; their contribution was similarly neglected in Paper I. Hence we take

$$\nabla_q G(x; b) \approx 0, \quad (\text{B10})$$

$$\nabla_q^2 G(x; b) \approx -(2/b^2)(dx/dq)^2 G(x; b). \quad (\text{B11})$$

The hopping rate is then found to be

$$\gamma_{k'k'} = \{ [J^2(1+z) + C^2(2+5z)] [I_0(y) - 1] + 4\omega C(1+z)[n(n+1)]^{1/2}I_1(y) \} [\pi^{1/2}/2(B + C)] \times \{ BG [E_{k'}; (B^2 + \Gamma^2)^{1/2}] + CG [E_{k'} + \frac{1}{2}C; (C^2 + \Gamma^2)^{1/2}] \}, \quad (\text{B12})$$

where  $z = v_k^2/(B^2 + \Gamma^2)$ .

As in Paper I we find that  $\gamma_{k'k'}$  is roughly proportional to  $\Gamma_{k'k'}$ , the part proportional to  $z$  being exactly  $\frac{1}{2}z\Gamma_{k'k'}$  because of the approximations (B10) and (B11). (Note that compared with Paper I we have extracted a factor  $a^2$  to give each rate the same dimensions and have inserted a factor  $1/2$  previously omitted). Since the numerical coefficients depend on our previous approximations, it is convenient to force total proportionality by taking

$$\gamma_{k'k'} = \frac{1}{2}(1+z)\Gamma_{k'k'}. \quad (\text{B13})$$

The only factors not so related are the coefficients of  $C^2$  multiplying  $I_0(y) - 1$ , which we replace by the value 4 intermediate between the 5 in  $\Gamma_{k'k'}$  and the 2 in  $\gamma_{k'k'}$ :

$$\begin{aligned} \Gamma_{k'k'} &= \Gamma_0 \{ BG [E_{k'}; (B^2 + \Gamma^2)^{1/2}] \\ &\quad + CG [E_{k'} + \frac{1}{2}C; (C^2 + \Gamma^2)^{1/2}] \} \\ \Gamma_0 &= \pi^{1/2} \{ (\tilde{J}^2 + 4C^2) [I_0(y) - 1] \\ &\quad + 4\omega C [n(n+1)]^{1/2} I_1(y) \} / (B + C). \quad (\text{B14}) \end{aligned}$$

A factor smaller than 5 in  $\Gamma_{k'k'}$  is also compatible with the results obtained if the prefactors  $\rho$  and  $\sigma$  are not averaged as in Eq. (B6), though the rate remains positive as expected.

<sup>1</sup>(a)R. Silbey and R. W. Munn, *J. Chem. Phys.* **72**, 2763 (1980); (b) R. W. Munn and R. Silbey, *ibid.* **82**, 1843 (1985).

<sup>2</sup>Y. Kenkre and P. Reineker, *Exciton Dynamics in Molecular Crystals and Aggregates*, Springer Tracts in Physics (Springer, New York, 1982).

<sup>3</sup>D. Yarkony and R. Silbey, *J. Chem. Phys.* **67**, 5818 (1977).

<sup>4</sup>R. W. Munn and R. Silbey, *Mol. Cryst. Liq. Cryst.* **57**, 131 (1980).

<sup>5</sup>V. Capek and R. W. Munn, *J. Chem. Phys.* **76**, 4674 (1982).

<sup>6</sup>V. Capek and R. W. Munn, *Phys. Status Solidi B* **108**, 521 (1982); **109**, 245 (1982).

<sup>7</sup>R. M. Wilcox, *J. Math. Phys.* **8**, 962 (1967).

<sup>8</sup>M. Grover and R. Silbey, *J. Chem. Phys.* **52**, 2099 (1970).

<sup>9</sup>M. Grover and R. Silbey, *J. Chem. Phys.* **54**, 4834 (1971).

<sup>10</sup>P. Gosar and S. -I. Choi, *Phys. Rev.* **150**, 529 (1966).

<sup>11</sup>P. Gosar and I. Vilfan, *Mol. Phys.* **18**, 49 (1970).

<sup>12</sup>H. Sumi, *J. Chem. Phys.* **70**, 3775 (1979).

<sup>13</sup>T. Holstein, *Ann. Phys. (NY)* **8**, 343 (1959).

<sup>14</sup>L. Friedman, *Phys. Rev.* **140**, A1649 (1965).

<sup>15</sup>M. I. Klinger, *Phys. Status Solidi*, 1062 (1962); *Problems of Linear Electron (Polaron) Transport Theory in Semiconductors* (Pergamon, Oxford, 1979).

<sup>16</sup>M. Umehara, *J. Phys. Soc. Jpn.* **47**, 852 (1979).

<sup>17</sup>I. Vilfan, *Lecture Notes in Physics* (Springer, Heidelberg, 1977), Vol. 65, p. 629.

<sup>18</sup>P. Gosar, *Recent Developments in Condensed Matter Physics*, edited by J. T. Devreese (Plenum, New York, 1981), Vol. 1, p. 593.

<sup>19</sup>L. B. Schein, *Chem. Phys. Lett.* **48**, 571 (1977); L. B. Schein, C. B. Duke, and A. R. McGhie, *Phys. Rev. Lett.* **40**, 197 (1978); L. B. Schein and A. R. McGhie, *Phys. Rev. B* **20**, 1631 (1979).

<sup>20</sup>L. B. Schein, *Phys. Rev. B* **15**, 1024 (1977).

<sup>21</sup>P. Reineker, V. M. Kenkre, and R. Kühne, *Phys. Lett. A* **84**, 294 (1981).

<sup>22</sup>K. H. Probst and N. Karl, *Phys. Status Solidi A* **27**, 499 (1975); A. Samoć, M. Samoć, J. Sworakowski, J. M. Thomas, and J. O. Williams, *ibid.* **37**, 271 (1976).

<sup>23</sup>P. Petelenz, *Mater. Sci.* **7**, 285 (1981).

<sup>24</sup>P. Gosar, *Phys. Scr.* **22**, 314 (1980); D. P. Craig and L. A. Dissado, *Chem. Phys. Lett.* **44**, 419 (1976).

<sup>25</sup>R. W. Munn and R. Silbey, *J. Chem. Phys.* **68**, 2439 (1978).