PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Electron-Phonon Interaction in Organic Molecular Crystals

LIONEL FRIEDMAN
RCA Laboratories, Princeton, New Jersey

(Received 7 July 1965)

A theory of acoustic-mode scattering has been formulated within the tight-binding approximation of band theory, and has been applied to narrow-band semiconduction in organic molecular crystals. The latter problem has been treated previously only in terms of phenomenological scattering parameters. The interaction constants are obtained explicitly as gradients of the characteristic overlap integrals. In addition, the wave-vector dependence of the matrix elements is taken into account. To first order in the (relative) displacements, the matrix elements include scattering by short-wavelength phonons, an essential feature of the narrow-band case not treated by conventional deformation-potential theory. The matrix elements physically represent variations of the band width and band centroid with relative displacement; in addition small (drag) terms proportional to the local lattice velocities are obtained. The theory is first applied to a one-dimensional band model, for the case of both elastic and inelastic scattering. It is then applied to the base-centered-monoclinic structure, for which numerical estimates of the interaction constants have been made available by LeBlanc for anthracene.

I. INTRODUCTION

IN spite of the current interest in the transport properties of organic semiconductors, calculations to date have not taken proper account of the electron-phonon interaction in these systems. Let us begin by reviewing the relevant literature. The energy-band structure[1] of crystalline anthracene was first calculated by LeBlanc,[2] neglecting the intramolecular vibrations and using as molecular basis functions (Hückel) linear combinations of single Slater carbon-atom orbitals. This calculation led to bandwidths of the order of k_0T at room temperature. These calculations were later improved by Katz, Rice, and co-workers.[3] They employed self-consistent-field (SCF) atomic orbitals which more properly describe the molecular wave functions in the regions of configuration space which make the dominant contribution to the intermolecular overlap. They obtained bandwidths an order of magnitude or so larger. Most recently, the additional degrees of freedom associated with the intramolecular vibrations have been taken into account.[4] For a given lowest electronic state, this leads to a series of vibronic sub-bands (or weakly coupled polaron bands) separated by the intramolecular quantum $\hbar\omega_0$. With this and other modifications, the revised bandwidths are of the order of those originally computed by LeBlanc. In view of the smallness of k_0T with respect to $\hbar\omega_0$ ($\sim$0.2 eV), it is evident that carriers move predominantly in the ground-state vibronic level corresponding to the lowest occupied electronic molecular orbital (or highest occupied molecular orbital in the case of hole conduction). In this connection, it is important to distinguish the role of these intramolecular optical modes from that of the intermolecular modes (the acoustic modes, in particular). The former give rise to the previously mentioned vibronic sub-bands. In addition, there is an interaction of the excess charge carrier with these modes. However, because of the small interaction of electrons in the delocalized orbitals of large aromatic molecules with the nonpolar optical modes, and the largeness of the optical quantum, the coupling is expected to be quite weak. Under these circumstances, the sole effect of this interaction is simply to multiply the electronic bandwidth by a vibrational overlap factor less than, but of the order of, unity, and essentially independent of temperature. Since this is an essentially static effect, we shall assume that the carrier propagates in the lowest vibronic band whose width is modified by the above factor. *The interaction of the charge carrier in such a band with the low-frequency intermolecular (in particular the acoustic) modes is the principle subject of the present paper.* Hence, the internal molecular vibrations, thought important in describing the class of materials considered in the present paper, do not play an essential role; our results are equally applicable to the *atomic* tight-binding case.

In any case, given a carrier in such a tight-binding band, the general procedure[2–4] has been to determine the mobility anisotropy assuming a constant time of relaxation or mean free path. The agreement with experiment has been favorable. Galvanomagnetic and thermoelectric effects, with attendant anomalies, have also been calculated within this same approximation.[5]

The thesis of the present paper is that the relaxation-time approximation, while appropriate for these initial investigations, is seriously deficient in several respects. First of all, it cannot predict absolute values of the transport coefficients, but only mobility ratios. Secondly, it cannot give the temperature dependence of the

---

[1] The experimental evidence is that band motion, rather than thermally activated site-jump transitions, is the predominant conduction mechanism in organic crystals of the anthracene type. This is the assumption of the present paper. See Refs. 2 and 5 among others, for further discussion of this point.

[2] O. H. LeBlanc, Jr., J. Chem. Phys. **35**, 1275 (1960).

[3] J. L. Katz, S. A. Rice, S. I. Choi, and J. Jortner, J. Chem. Phys. **39**, 1683 (1963).

[4] R. Silbey, J. Jortner, S. A. Rice, and M. T. Vala, J. Chem. Phys. 42, 733 (1965).

[5] L. Friedman, Phys. Rev. **133**, A1668 (1964).

transport properties. Thirdly, it cannot take into account the anisotropy of the scattering, in addition to the anisotropy of the band structure itself. Lastly, it cannot treat the case of inelastic scattering ($k_0\Theta\lesssim$bandwidth) for which a general time of relaxation does not exist. In the present paper we propose a formulation[6] of the interaction of an excess charge carrier with the intermolecular vibrations, in which the above features are taken into account. The results are applied to acoustic mode scattering in particular. The formulation is made within the tight-binding approximation of band theory, and, as mentioned previously, is applicable to any system (atomic or molecular) which can be described by this approximation.

The method which immediately suggests itself for treating acoustic-mode scattering in nonpolar semiconductors is the familiar deformation-potential approximation of Bardeen and Shockley.[7] As is well known, this approach is valid only for the scattering of carriers in the vicinity of a band edge point by long-wavelength acoustic phonons. While this restriction is well satisfied in conventional, wide-band semiconductors, it is clearly inapplicable to narrow band materials whose bandwidths are $\sim k_0T$ at room temperature. In the latter case, it is necessary to consider scattering transitions between arbitrary points within the Brillouin zone, including, in general, transitions due to short-wavelength phonons. Another well-known feature of deformation-potential theory is that the interaction is expressed in terms of a deformation-potential constant which can be inferred from homogeneous strain experiments, but is often left as an undetermined parameter fitted to the measured mobility.

To avoid the first limitation, we present an alternate formulation of the electron-phonon interaction within the tight-binding approximation of band theory. To first order in relative displacements, the principal matrix elements [cf. (2.25)] are expressed as explicit functions of the initial- and final-electron wave vectors $(\mathbf{k},\mathbf{k}')$ *throughout* the energy band, and not simply in the vicinity of a band-edge point. The anisotropy of the scattering is thereby taken into account. Also, the dependence of this anisotropy on crystallographic structure is explicitly exhibited in the basic form of the matrix elements via the sum over nearest-neighbor site vectors $\mathbf{h}$. In addition, it is found that the interaction constants can be expressed as gradients of the characteristic overlap integrals [cf. (2.13)] which, in turn, can be calculated[8] from the energy-band structure; this avoids the use of a phenomenological deformation-potential constant.

It is evident that in the limit of tight binding, the local wave functions, as well as the local potentials, should be allowed to follow their lattice displacements. The standard Bloch representation does not allow for this possibility. As pointed out by Herring[9] in this connection, the use of Bloch representation results in a very large contribution to the scattering from the interaction term bilinear in the displacements, this contribution being largely cancelled by second order, interband contributions of the linear term. Herring interpreted this as being due to just this inability of the local states to follow the displacements of their local potentials. He furthermore suggested that this large cancellation could be avoided (and bona fide two-phonon processes distinguished) by making a transformation to a representation which deforms locally with the lattice. Such a transformation has been carried out by Blount,[10] and a systematic theory of this type has been presented by Whitfield.[11] In such a representation, the perturbing Hamiltonian is expressed directly in terms of relative displacements or strains, in principal a more physically correct description.

The relevance of these considerations to the present work is as follows. As shown in Appendix A, in the Bloch representation the above-mentioned spurious, second-order scattering terms are indeed obtained. Since the present paper is not concerned with second-order processes, this difficulty is a matter of principal, but leads to no practical difficulties. More serious for the present applications is the fact that the corresponding first-order matrix elements take into account only variations of the local potentials, while the wave functions are constrained at their lattice sites [cf. (A6)]. As previously pointed out, this is physically unreasonable in the tight-binding limit. In Sec. II, a more satisfactory set of matrix elements are derived which allow the local wave functions to follow their displacements rigidly. These are obtained by a systematic development in time-dependent perturbation theory in such a way that the

---

[6] S. Glarum, J. Phys. Chem. Solids **24**, 1577 (1964) has recently formulated the electron-phonon interaction in organic crystals from a similar point of view. The present treatment is felt to be more complete, however, for the following reasons: (a) In addition to the dominant matrix elements associated with variations in the bandwidth with relative displacement, contributions are also obtained which are proportional to variations of the band centroid and to the local lattice velocities; (b) the former is not characterized by an isotropic exponential dependence, but is expressed generally and is obtained directly from the band-structure calculations; (c) the explicit wave-vector dependence of the matrix elements is retained; (d) inelasticity of the collisions is taken into account.

[7] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

[8] These gradients have been calculated by Dr. O. H. LeBlanc, Jr., for anthracene using Hückel combinations of Slater orbitals with an $\alpha=3.08$ Å, as in Ref. 2. The author is indebted to Dr. LeBlanc for these estimates.

[9] C. Herring, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 60.

[10] E. Blount, Phys. Rev. **114**, 418 (1959).

[11] G. Whitfield, Phys. Rev. **121**, 720 (1961). This theory is based on the use of orthogonalized-deformed-Bloch (O.D.B.) representation in which the local displacements are built into the basic states from the very start. This leads to a generalized deformation potential theorem which, in principal, is applicable to the present case. However, in view of the applicability of tight binding to the present case, it is more expedient to formulate the theory within this approximation. In this way, the interaction constants are directly calculable from the tight-binding band structure, while for the O.D.B. method their calculation would be considerably more difficult.

zeroth-order states are the conventional (tight-binding) *Bloch states*[12] [cf. (2.18)].

The transition matrix elements represent three physical sources of the scattering: (a) variations of the transfer integrals, or, roughly speaking, the bandwidth, with relative displacement [cf. (2.25)]; (b) variations of the "Coulomb integrals" or band centroid with relative displacement [cf. (2.26)]; (c) terms proportional to the local lattice velocities which arise from the fact that the moving lattice tends to drag the electron with it [cf. (2.27)]. Even though (c) is a maximum in the tight-binding limit, on the basis of estimates presented in Sec. IV it is concluded that (c) and also (b) are small in comparison to (a). Restricting ourselves only to the matrix elements (a) above, mobility calculations have been carried out for the following cases.

A one-dimensional energy band and Debye phonon spectrum are first investigated in Sec. III in order to see the essential features of the problem. Assuming first that the entire vibronic band is almost uniformly populated with carriers ($\Delta E \equiv$ bandwidth $\ll k_0T$), it is shown that the umklapp processes limit the mobility as much as the normal processes. This is first carried out for the case of elastic scattering. A wave-vector-dependent relaxation time is easily derived for this case [cf. (3.12)]. This readily yields the temperature dependence of the mobility and its explicit dependence on electronic and lattice parameters. We next look at the case $\Delta E \lesssim k_0T$, for which variations of the Boltzmann factor must be considered. The effect of this feature on the temperature dependence of μ is readily taken into account.

Since the Debye temperature[13] need not be vanishingly small compared with the bandwidth, the conductivity is evaluated for the case of inelastic scattering by means of the variational method of transport theory.[14] This yields corrections to the elastic case which depend on $(k_0\Theta/\Delta E)$, and which properly vanish in the elastic limit ($\Theta \sim v_s \to 0$) [cf. (3.33)].

The second case investigated is of greater practical interest: namely, mobility in the *ab* plane of the base-centered-monoclinic structure. The numerical estimates [cf. (4.12)–(4.14) and Table III] are made for anthracene, since the required parameters have been calculated for this material by LeBlanc[8]; however, (4.12)–(4.14) are generally applicable to this crystal structure. Only elastic scattering is considered, and umklapp processes are neglected. Further, in order to keep the transport integrals tractable for numerical evaluation, we have made a few reasonable approximations consistent with the inequalities $k_0T \gg \Delta E \gg k_0\Theta$: namely, the replacement of the Boltzmann population factor by unity, and the replacement of the Planck phonon factor by its high-temperature approximation.[15] A more serious approximation is the replacement of the real phonon spectrum by a two-dimensional, isotropic, longitudinal Debye spectrum. The real phonon spectrum is undoubtedly highly complex, and virtually no data are available on it, as far as is known to the present author. Having presented the general formalism, our point of view is that the previously described approximations are adequate for these initial investigations. When more data are available, and more detailed comparison with experiment is warranted, these various features can be incorporated.

II. BASIC FORMULATION AND DERIVATION OF SCATTERING MATRIX ELEMENTS

In the present section we derive the basic matrix elements which describe the scattering of an excess charge carrier by the intermolecular (center-of-mass) motions of the constituent molecules. In real molecular crystals, the (high-frequency) internal molecular vibrations give rise to a series of vibornic sub-bands. However, in the present section, we shall assume that the molecules are internally rigid. The justification for this is twofold: First, and most important, this effect produces only a static narrowing of the energy bands and does not therefore alter any of the basic features of the electron-phonon interaction. Secondly, the inclusion of the intramolecular coordinates into the Hamiltonian would complicate the treatment without adding any essential physical features. For the sake of completeness, however, the internal vibrations are treated in Appendix C where the correspondence with the treatment of the present section is established.

With this understanding, the total wave function of the electron-phonon system obeys the wave equation

$$i\hbar\frac{\partial\Psi(\mathbf{r},\cdots\mathbf{R}_g\cdots)}{\partial t} = [H_e(\cdots\mathbf{R}_g\cdots)+H_L(\cdots\mathbf{R}_g\cdots)]\Psi, \quad (2.1)$$

where

$$H_e(\cdots\mathbf{R}_g\cdots) = -\frac{\hbar^2}{2m}\nabla_r^2 + \sum_g U(\mathbf{r}-\mathbf{R}_g)$$

is the electronic Hamiltonian[16] corresponding to some general configuration in which the molecules are displaced by amounts $\mathbf{u}_g$ from their vector lattice positions $\mathbf{R}_g^0$, i.e.,

$$\mathbf{R}_g = \mathbf{R}_g^0 + \mathbf{u}_g.$$

---

[12] It is to be emphasized that these zeroth-order states are Bloch states and are not the tight-binding analogs of O.D.B. states. The expansion is in displacements, not strains. See Sec. II for details.

[13] Debye temperatures of the order of 100°K have been reported for naphthalene and anthracene by D. W. J. Cruickshank, Rev. Mod. Phys. **30**, 163 (1958) and M. L. Canut and J. L. Amoros, J. Phys. Chem. Solids **21**, 146 (1961).

[14] See, for example, J. M. Ziman, *Electrons and Phonons* (Cambridge University Press, New York, 1960). A brief summary of the variational method used in the present paper is presented in Appendix B.

[15] In the elastic approximation ($\Theta \to 0$), this replacement is of course exact.

[16] This part of the total Hamiltonian implicitly includes the electron-phonon interaction by virtue of its dependence on the lattice displacements.

Also,

$$H_L(\cdots\mathbf{R}_g\cdots)=-\frac{\hbar^2}{2M}\sum_m \nabla_{\mathbf{u}_m}{}^2+V_L$$

is the lattice Hamiltonian, M being the molecular mass and V_L being the lattice potential energy in the harmonic approximation.

The ground-state local molecular wave functions φ obey the set of equations

$$\left[-\frac{\hbar^2}{2m}\nabla_r{}^2+U(\mathbf{r}-\mathbf{R}_g)\right]\varphi(\mathbf{r}-\mathbf{R}_g)=\epsilon\varphi(\mathbf{r}-\mathbf{R}_g)\,, \quad (2.2)$$

where the U's are the molecular potentials, and ϵ their common eigenvalue. This equation expresses the fact that the wave functions are assumed to follow their center-of-mass displacements rigidly.

The basic procedure is to expand the total wave functions in the basis of the instantaneous, local wave functions

$$\Psi(\mathbf{r},\cdots\mathbf{R}_g\cdots)=\sum_{g'} C_{g'}(\cdots\mathbf{R}_g\cdots)\varphi(\mathbf{r}-\mathbf{R}_{g'})\,. \quad (2.3)$$

Substituting (2.3) into (2.1), taking into account (2.2), multiplying to the left by $\varphi^*(\mathbf{r}-\mathbf{R}_g)$ and integrating over $\mathbf{r}$, we get

$$\sum_{g'} i\hbar\frac{\partial C_{g'}}{\partial t}T_{gg'}=\sum_{g'}\Bigg\{[\epsilon C_{g'}T_{gg'}+\sum_{g''\neq g} U_{g''}+H_L]C_{g'}\varphi_{g'}$$
$$-\frac{\hbar^2}{2M}\sum_m\left(2\boldsymbol{\nabla}_m C_{g'}\cdot\int d^3r\,\varphi_g{}^*\boldsymbol{\nabla}_m\varphi_{g'}+C_{g'}\int d^3r\,\varphi_g{}^*\boldsymbol{\nabla}_m{}^2\varphi_{g'}\right)\Bigg\}\,, \quad (2.4)$$

where

$$\varphi_{g'}\equiv\varphi(\mathbf{r}-\mathbf{R}_{g'})\,,\quad U_{g''}\equiv U(\mathbf{r}-\mathbf{R}_{g''})\,.$$

Also,

$$T_{gg'}=\int d^3r\,\varphi^*(\mathbf{r}-\mathbf{R}_g)\varphi(\mathbf{r}-\mathbf{R}_{g'})=\delta_{gg'}+S_{gg'}\,,$$

where $S_{gg'}$ are the nonorthogonality integrals,[17] different from zero only for nearest neighbors and small compared with unity.[18] The second term on the right-hand side of (2.4) is the well-known coupling terms which arise from the operation of the lattice kinetic energy term on (2.3).

We next multiply (2.4) by the matrix inverse to T,

$$T_{lg}{}^{-1}=\delta_{lg}-S_{lg}\,,$$

correct to first order in S. Summing over g, we get

$$i\hbar\frac{\partial C_l}{\partial t}-\epsilon C_l-H_LC_l=\sum_{g',g''\neq g} C_{g'}\int d^3r\,\varphi_l{}^*U_{g''}\varphi_{g'}-\sum_{g,g',g''\neq g} S_{lg}C_{g'}\int d^3r\,\varphi_g{}^*U_{g''}\varphi_g$$
$$-\frac{\hbar^2}{2M}\sum_{g'}\left[2\boldsymbol{\nabla}_{g'}C_{g'}\cdot\int d^3r\,\varphi_l{}^*\boldsymbol{\nabla}_{g'}\varphi_{g'}+C_{g'}\int d^3r\,\varphi_l{}^*\boldsymbol{\nabla}_{g'}{}^2\varphi_{g'}\right]$$
$$+\frac{\hbar^2}{2M}\sum_g S_{lg}\sum_{g'}\left[2\boldsymbol{\nabla}_{g'}C_{g'}\cdot\int d^3r\,\varphi_g{}^*\boldsymbol{\nabla}_{g'}\varphi_{g'}+C_{g'}\int d^3r\,\varphi_g{}^*\boldsymbol{\nabla}_{g'}{}^2\varphi_{g'}\right].$$

As usual, only terms to first order in the overlap are retained. The S-proportional terms are of at least second order in the overlap and are therefore neglected. Additional simplification follows from the fact that the φ's are assumed to be nondegenerate, and hence, real. These simplifications give the equation of motion

$$i\hbar\frac{\partial C_l}{\partial t}-\epsilon C_l-H_LC_l=W_lC_l+\sum_{g'} J_{lg'}C_{g'}-\frac{\hbar^2}{2M}\sum_{g'}\left[2\boldsymbol{\nabla}_{g'}C_{g'}\cdot\int d^3r\,\varphi_l\boldsymbol{\nabla}_{g'}\varphi_{g'}+C_{g'}\int d^3r\,\varphi_l\boldsymbol{\nabla}_{g'}\varphi_{g'}{}^2\right]$$
$$+\frac{\hbar^2}{2M}\sum_g S_{lg}\sum_{g'} C_{g'}\int d^3r\,\varphi_g\boldsymbol{\nabla}_{g'}{}^2\varphi_{g'}\,, \quad (2.5)$$

---

[17] As usual, the development is carried to first order in the overlap, so that these quantities must be retained in the basic formulation.

[18] It is assumed that the relative displacements are sufficiently small that this applies to the displaced configuration as well as to the perfect crystal.

where

$$W_l \equiv \int d^3r\,|\varphi(\mathbf{r}-\mathbf{R}_l)|^2 \sum_{g''\neq l} U(\mathbf{r}-\mathbf{R}_{g''}), \tag{2.6}$$

$$J_{lg} \equiv \int d^3r\,\varphi(\mathbf{r}-\mathbf{R}_l)U(\mathbf{r}-\mathbf{R}_l)\varphi(\mathbf{r}-\mathbf{R}_{g'}). \tag{2.7}$$

Introducing the nearest-neighbor site vector $\mathbf{R}_h=\mathbf{R}_{g'}-\mathbf{R}_l$, and expanding (2.6) and (2.7) about their lattice positions to first order, we get

$$W_l = W^0 - \sum_{h\neq 0} (\mathbf{u}_{l+h}-\mathbf{u}_l)\cdot(\boldsymbol{\nabla}_h w_h)_0, \tag{2.8}$$

$$J_{lg} = J_h{}^0 - (\mathbf{u}_{l+h}-\mathbf{u}_l)\cdot(\boldsymbol{\nabla}_h J_h)_0, \tag{2.9}$$

where

$$W^0 = \int d^3r\,|\varphi(\mathbf{r})|^2 \sum_{h\neq 0} U(\mathbf{r}-\mathbf{R}_h{}^0), \tag{2.10}$$

$$(\boldsymbol{\nabla}_h w_h)_0 = \left[\boldsymbol{\nabla}_{\mathbf{u}_h} \int d^3r\,|\varphi(\mathbf{r})|^2 U(\mathbf{r}-\mathbf{R}_h)\right]_{\mathbf{u}_h=0}, \tag{2.11}$$

$$J_h{}^0 = \int d^3r\,\varphi(\mathbf{r})U(\mathbf{r})\varphi(\mathbf{r}-\mathbf{R}_h{}^0), \tag{2.12}$$

$$(\boldsymbol{\nabla}_h J_h)_0 = \left[\boldsymbol{\nabla}_{\mathbf{u}_h} \int d^3r\,\varphi(\mathbf{r})U(\mathbf{r})\varphi(\mathbf{r}-\mathbf{R}_h)\right]_{\mathbf{u}_h=0}, \tag{2.13}$$

where advantage has been taken of the translational invariance.

The basic equation of motion (2.5) then becomes

$$\left(i\hbar\frac{\partial}{\partial t}-\epsilon-W^0-H_L\right)C_l-\sum_h J_h{}^0 C_{l+h} = -\sum_h(\mathbf{u}_{l+h}-\mathbf{u}_l)\cdot(\boldsymbol{\nabla}_h J_h)_0 C_{l+h} - C_l\sum_h(\mathbf{u}_{l+h}-\mathbf{u}_l)\cdot(\boldsymbol{\nabla}_h w_h)_0$$
$$-\frac{\hbar^2}{2M}\sum_h\left[2\boldsymbol{\nabla}_{l+h}C_{l+h}\cdot\mathbf{I}_h{}^{(1)}+C_{l+h}I_h{}^{(2)}\right]-\frac{\hbar^2}{2M}I_0{}^{(2)}\left[C_l-\sum_g S_{lg}C_g\right], \tag{2.14}$$

with the further definitions

$$I_h{}^{(1)} = \int d^3r\,\varphi(\mathbf{r})\boldsymbol{\nabla}_h\varphi(\mathbf{r}-\mathbf{R}_h{}^0) = -\int d^3r\,\varphi(\mathbf{r})\boldsymbol{\nabla}_r\varphi(\mathbf{r}-\mathbf{R}_h{}^0),$$
$$I_h{}^{(2)} = \int d^3r\,\varphi(\mathbf{r})\nabla_h{}^2\varphi(\mathbf{r}-\mathbf{R}_h{}^0) = \int d^3r\,\varphi(\mathbf{r})\nabla_r{}^2\varphi(\mathbf{r}-\mathbf{R}_h{}^0), \tag{2.15}$$
$$I_0{}^{(2)} = \int d^3r\,\varphi(\mathbf{r})\nabla_r{}^2\varphi(\mathbf{r}),$$

again using translational invariance and the fact that

$$\boldsymbol{\nabla}_h\varphi(\mathbf{r}-\mathbf{R}_h) = -\boldsymbol{\nabla}_r\varphi(\mathbf{r}-\mathbf{R}_h).$$

The zeroth-order equation obeyed by the C's is obtained by setting all lattice displacements and lattice velocities equal to zero, i.e., all $\mathbf{u}_l=0$, $(\hbar/iM)\boldsymbol{\nabla}_l=0$. The right-hand side of (2.14) then vanishes. The zeroth-order solutions are

$$C_l{}^{k\{N\}} = \mathfrak{N}^{-1/2}e^{i\mathbf{k}\cdot\mathbf{R}_l{}^0}\chi_{\{N\}}, \tag{2.16}$$

with eigenvalues

$$E^{k\{N\}} = \epsilon+W^0+\sum_h J_h{}^0 e^{i\mathbf{k}\cdot\mathbf{R}_h{}^0}+E_{\{N\}}. \tag{2.17}$$

Here, $\mathfrak{N}$ is the total number of unit cells, $\{N\}$ denotes the totality of vibrational quantum numbers, $\chi_{\{N\}}$ is the standard state of the harmonic crystal expressed as a product of normal-mode harmonic oscillator solutions, and $E_{\{N\}}$ is the corresponding phonon energy. The first three terms of (2.17) represent just the energy-band structure of conventional tight-binding theory. Going back to (2.3), the complete zeroth-order solutions are the usual product solutions in the Bloch representation:

$$\Psi^0 = \chi_{\{N\}}\mathfrak{N}^{-1/2}\sum_g e^{i\mathbf{k}\cdot\mathbf{R}_g{}^0}\varphi(\mathbf{r}-\mathbf{R}_g{}^0). \tag{2.18}$$

The solutions of the complete equation of motion (2.14) are expanded in the zeroth-order solutions (2.16):

$$C_l = \sum_{k'\{N'\}} a_{k'\{N'\}}C_l{}^{k'\{N'\}}\exp\{-iE_{k'\{N'\}}t/\hbar\}. \tag{2.19}$$

Equation (2.19) is substituted into (2.14). The resulting equation is then multiplied to the left by $(C_l{}^{k\{N\}})^*$ and summed over l and the vibrational coordinates. After introducing an additional transformation in the interaction picture to eliminate the diagonal $I^{(2)}$ proportional terms of (2.14), we get

$$i\hbar\frac{\partial a_{k\{N\}}}{\partial t} = \sum_{k'\{N'\}} a_{k'\{N'\}}\exp\left\{-\frac{it}{\hbar}(E_{k'\{N'\}}-E_{k\{N\}})\right\}$$
$$\times\langle k\{N\}|V|k'\{N'\}\rangle, \tag{2.20}$$

where the matrix elements of the perturbation describe single-phonon transitions and are written as a sum of terms

$$\langle k\{N\}|V|k'\{N'\}\rangle = \langle k\{N\}|V|k'\{N'\}\rangle_1 + \langle k\{N\}|V|k'\{N'\}\rangle_2 + \langle k\{N\}|V|k'\{N'\}\rangle_3 , \tag{2.21}$$

where

$$\langle k\{N\}|V|k'\{N'\}\rangle_1 = -\mathcal{N}^{-1}\sum_l e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_l^0}\sum_h e^{i\mathbf{k}'\cdot\mathbf{R}_h^0}\langle\{N\}|(\mathbf{u}_{l+h}-\mathbf{u}_l)|\{N'\}\rangle\cdot(\boldsymbol{\nabla}_h J_h)_0 , \tag{2.22}$$

$$\langle k\{N\}|V|k'\{N'\}\rangle_2 = -\mathcal{N}^{-1}\sum_l e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_l^0}\sum_h \langle\{N\}|(\mathbf{u}_{l+h}-\mathbf{u}_l)|\{N'\}\rangle\cdot(\boldsymbol{\nabla}_h w_h)_0 , \tag{2.23}$$

and

$$\langle k\{N\}|V|k'\{N'\}\rangle_3 = -\frac{\hbar^2}{M}\mathcal{N}^{-1}\sum_l e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_l^0}\sum_h e^{i\mathbf{k}'\cdot\mathbf{R}_l^0}\langle\{N\}|\boldsymbol{\nabla}_{l+h}|\{N'\}\rangle\cdot\mathbf{I}_h^{(1)} . \tag{2.24}$$

The lattice displacements and conjugate momenta are expanded in creation and annihilation operators in the usual way[19]:

$$\mathbf{u}_l = \sum_{qj}\left(\frac{\hbar}{2M\mathcal{N}\omega_{qj}}\right)^{1/2}\hat{\epsilon}_{qj}[\alpha_{qj}e^{i\mathbf{q}\cdot\mathbf{l}}+\alpha_{qj}^{\dagger}e^{-i\mathbf{q}\cdot\mathbf{l}}] , \quad \boldsymbol{\nabla}_l = \sum_{qj}\left(\frac{M\omega_{qj}}{2\hbar\mathcal{N}}\right)^{1/2}\hat{\epsilon}_{qj}[\alpha_{qj}e^{i\mathbf{q}\cdot\mathbf{l}}-\alpha_{qj}^{\dagger}e^{-i\mathbf{q}\cdot\mathbf{l}}] ,$$

where ω_{qj}, $\hat{\epsilon}_{qj}$, α_{qj}, and $\alpha_{qj}^{\dagger}$ are respectively the frequency, polarization, and creation and annihilation operators of the mode $(\mathbf{q},j)$. These expansions are substituted into (2.22), (2.23), and (2.24). We make use of the well-known raising and lowering properties of the creation and annihilation operators. Combining[20] terms of $\pm h$ for which $\boldsymbol{\nabla}_h J_{-h} = -\boldsymbol{\nabla}_h J_h$, etc., and carrying out the sum over l to obtain crystal momentum conservation, the matrix elements take the form

$$\langle k\{N\}|V|k'\{N'\}\rangle_1 = -2i\sum_{qj,\pm}\left(\frac{\hbar}{2M\mathcal{N}\omega_{qj}}\right)^{1/2}\delta_{\mathbf{k},\mathbf{k}'\pm\mathbf{q}+\mathbf{K}}\delta_{N_{qj},N_{qj}'\mp 1} \times(N_{qj}'+\tfrac{1}{2}\mp\tfrac{1}{2})^{1/2}\sum_{\mathbf{h}}\hat{\epsilon}_{qj}\cdot(\boldsymbol{\nabla}_h J_h)_0[\sin(\mathbf{k}\cdot\mathbf{R}_h^0)-\sin(\mathbf{k}'\cdot\mathbf{R}_h^0)] , \tag{2.25}$$

$$\langle k\{N\}|V|k'\{N'\}\rangle_2 = -2i\sum_{qj,(\pm)}\left(\frac{\hbar}{2M\mathcal{N}\omega_{qj}}\right)^{1/2}\delta_{\mathbf{k},\mathbf{k}'\pm\mathbf{q}+\mathbf{K}}\delta_{N_{qj},N_{qj}'\pm 1} \times(N_{qj}'+\tfrac{1}{2}\mp\tfrac{1}{2})^{1/2}\sum_{\mathbf{h}}\hat{\epsilon}_{qj}\cdot(\boldsymbol{\nabla}_h w_h)_0\sin[(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_h^0] , \tag{2.26}$$

$$\langle k\{N\}|V|k'\{N'\}\rangle_3 = -2i\sum_{qj,(\pm)}\frac{\hbar^2}{M}\left(\frac{M\omega_{qj}}{2\hbar\mathcal{N}}\right)^{1/2}\delta_{\mathbf{k},\mathbf{k}'\pm\mathbf{q}+\mathbf{K}}\delta_{N_{qj},N_{qj}'\pm 1}(N_{qj}'+\tfrac{1}{2}\mp\tfrac{1}{2})^{1/2}\sum_{\mathbf{h}}(\hat{\epsilon}_{qj}\cdot\mathbf{I}_h^{(1)})\sin(\mathbf{k}\cdot\mathbf{R}_h^0) . \tag{2.27}$$

These matrix elements are the basis for the treatment of the present paper; their application to cases of physical interest will be presented in the following sections. It is to be noted that the wave-vector dependences of the matrix elements are explicit functions of the crystallographic structure, just as is the conventional energy-band structure (2.17) itself. The matrix elements (2.25) and (2.26) are deformation-potential-like, in the sense that they are proportional to $\mathbf{k}-\mathbf{k}'=\mathbf{q}$ in the limit $\mathbf{k}\rightarrow\mathbf{k}'$. The first describes transitions due to variations in the transfer integrals (in effect, the bandwidth) with relative displacement; the second describes variations of the "Coulomb" integrals (in effect, the band centroid) with displacement. Finally, (2.27) is not deformation-potential-like in the above described sense, but rather is proportional to the local lattice velocities, $(-i\hbar/M)\boldsymbol{\nabla}_h$; it physically describes the tendency of the moving lattice to drag the electron with it.[11]

III. APPLICATION TO ONE-DIMENSIONAL MODELS

The matrix elements derived in the previous section are here applied to a one-dimensional band model and a Debye-type phonon spectrum. This model exhibits the basic features of the problem, while avoiding the complications of anisotropy characteristic of the real two- and three-dimensional cases. In this connection, it gives

---

[19] This expansion is valid only for a primitive lattice (one molecule per unit cell). It is adequate for treating the one-dimensional case and the single acoustical mode assumed in Sec. IV. To treat the intermolecular vibrations of the real crystal (two molecules per unit cell) would require a separate expansion for each molecule in the basis. See J. M. Ziman, *Electrons and Phonons* (Cambridge University Press, New York, 1960), Chap. 1.

[20] Here, advantage is taken of inversional symmetry, which is satisfied in the present case.

some feeling for the effects of the inelasticity of the collisions and umklapp processes, features which can be incorporated into the real problem only with considerable complication. Only the conventional single-phonon processes are considered. Two-phonon processes would have to be considered if $\Delta E < k_0 \Theta$. However,[13] it is very unlikely that the bands are this narrow.[2–4]

In the next section, we argue that the matrix elements (2.26) and (2.27) are small in comparison with (2.25); therefore, we consider only the latter in the present model calculations. The starting point is the transition rate due to absorption or emission $(+, -)$ of a single phonon of mode $\lambda = (\mathbf{q}, j)$. We first calculate this in general, and later particularize to one dimension. By standard time-dependent perturbation theory, we get

$$W_{(\pm)}{}^{(\lambda)}(\mathbf{k}, N_\lambda \to \mathbf{k}', N_\lambda \mp 1) = (N_\lambda + \tfrac{1}{2} \mp \tfrac{1}{2}) W_{(\mp)}{}^{(\lambda)}(\mathbf{k} \to \mathbf{k}'),$$

where

$$W_{(\pm)}{}^{(\lambda)}(\mathbf{k} \to \mathbf{k}') = \frac{2\pi}{\hbar} \frac{\hbar}{2MN\omega_\lambda} \times 4\Big[\sum_{h>0} \hat{\epsilon}_\lambda \cdot (\nabla_h J)_0 (\sin(\mathbf{k} \cdot \mathbf{R}_h{}^0) - \sin(\mathbf{k}' \cdot \mathbf{R}_h{}^0))\Big]^2 \times \delta_{\mathbf{k}', \mathbf{k} \pm \mathbf{q} + \mathbf{K}} \delta(E_{\mathbf{k}} - E_{\mathbf{k}'} \pm \hbar\omega_\lambda). \quad (3.1)$$

The collision term of the Boltzmann equation, for the case of classical statistics, reads

$$-\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_{\text{coll}} = \sum_{\mathbf{k}', \lambda, (\pm)} \{ f(\mathbf{k}) W_{(\pm)}{}^{(\lambda)}(\mathbf{k} \to \mathbf{k}')(N_\lambda + \tfrac{1}{2} \mp \tfrac{1}{2}) - f(\mathbf{k}') W_{(\pm)}{}^{(\lambda)}(\mathbf{k}' \to \mathbf{k})(N_\lambda + \tfrac{1}{2} \mp \tfrac{1}{2}) \}. \quad (3.2)$$

It is convenient to rearrange the sum so as to combine the first term with its time-reversed process, giving

$$-\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_{\text{coll}} = \sum_{\mathbf{k}', \lambda, (\pm)} \{ f(\mathbf{k}) W_{(\pm)}{}^{(\lambda)}(\mathbf{k} \to \mathbf{k}')(N_\lambda + \tfrac{1}{2} \mp \tfrac{1}{2}) - f(\mathbf{k}') W_{(\mp)}{}^{(\lambda)}(\mathbf{k}' \to \mathbf{k})(N_\lambda + \tfrac{1}{2} \pm \tfrac{1}{2}) \}. \quad (3.3)$$

Making use of microscopic reversibility

$$W_{(\pm)}{}^{(\lambda)}(\mathbf{k} \to \mathbf{k}') = W_{(\mp)}{}^{(\lambda)}(\mathbf{k}' \to \mathbf{k}),$$

which can be explicitly verified from (3.1), one gets

$$-\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_{\text{coll}} = \sum_{\mathbf{k}', \lambda, (\pm)} W_{(\pm)}{}^{(\lambda)}(\mathbf{k} \to \mathbf{k}') \times \{ f(\mathbf{k})(N_\lambda + \tfrac{1}{2} \mp \tfrac{1}{2}) - f(\mathbf{k}')(N_\lambda + \tfrac{1}{2} \pm \tfrac{1}{2}) \}. \quad (3.4)$$

We now consider a one-dimensional model characterized by the simple band structure

$$E_k = -J \cos(ka), \quad (3.5)$$

and Debye phonon spectrum

$$\omega_q = v_s |q|, \quad (3.6)$$

where v_s is the speed to sound in the continuum limit.

In the standard way, the distribution function $f(\mathbf{k})$ is written

$$f(\mathbf{k}) = f^0(\mathbf{k}) + g(\mathbf{k}), \quad (3.7)$$

where $f^0(\mathbf{k})$ is the equilibrium Boltzmann distribution and $g(\mathbf{k})$ is the deviation from equilibrium. Equation (3.4) then takes the form

$$-\left(\frac{\partial f(k)}{\partial t}\right)_{\text{coll}} = \sum_{q, (\pm)} W_{(\pm)}{}^{q}(k \to k') \times \{ g(k)(N_q + \tfrac{1}{2} \mp \tfrac{1}{2}) - g(k')(N_q + \tfrac{1}{2} \pm \tfrac{1}{2}) \}, \quad (3.8)$$

where

$$W_{(\pm)}{}^{q}(k \to k') = \frac{2\pi}{\hbar} \frac{\hbar}{2M\mathfrak{N}\omega_q} 4(J')^2 [\sin(ka) - \sin(ka')]^2 \times \delta_{k', k \pm q + K} \delta(E_k - E_{k'} \pm \hbar\omega_q), \quad (3.9)$$

where

$$J' \equiv (dJ/da)_0.$$

Elastic Scattering

We first consider the case of elastic scattering, obtained by letting $\hbar\omega_q \to 0$ in the energy delta function. It then follows from (3.5) that the energy conserving transitions are those for which[21]

$$k' = -k.$$

For an impressed external electric field, we then have that

$$g(k') = g(-k) = -g(k). \quad (3.10)$$

Using this property to eliminate $g(k')$ in (3.8) establishes the existence of a relaxation time,

$$-(\partial f(k)/\partial t)_{\text{coll}} = g(k)/\tau(k),$$

where

$$\frac{1}{\tau(k)} = \sum_{k', q, (\pm)} W_{(\pm)}{}^{(q)}(k \to k')(2N_q + 1). \quad (3.11)$$

The various possible elastic processes are the horizontal transitions indicated in Fig. 1.

Here, A and E refer to absorption and emission, while N and U refer to normal and Umklapp processes. These are considered in turn.

N, *E*

The initial wave vector k lies in the range $0 < k < \pi/2a$. For the phonon population factor, we get

$$(2N_q + 1) = \coth(\hbar v_s q / k_0 T).$$

---

[21] This feature is characteristic of elastic scattering in only one dimension, of course, and facilitates the definition of a relaxation time. In the two-dimensional case considered in the next section, transitions occur over a constant energy contour in two-dimensional **k** space. For this reason, the mobility is calculated directly from the variational expression, thereby bypassing the calculation of a relaxation time for that case.

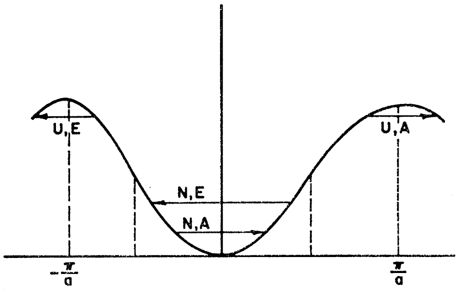

FIG. 1. Normal and umklapp processes for elastic, one-dimensional scattering.

Now in the elastic limit which we are considering in the present section, $\hbar v_s q_{\max}=k\Theta$ is taken to be vanishingly small, as previously discussed. The above Planck factor can then be replaced by its high-temperature limit without approximation:

$$(2N_q+1)=\coth\left(\frac{\hbar v_s q}{k_0 T}\right)\rightarrow\frac{kT}{\hbar v_s q}.$$

In view of the Kronecker delta, for a given (k,k'), the sum over q picks out the single term for which

$$q=k-k'=2k.$$

Finally, the sum over k' is carried out as follows:

$$\sum_{k'}(\cdots)=\frac{L}{2\pi}\int_{-\pi/2a}^{0}dk'(\cdots)$$

$$=\frac{L}{2\pi}\int_{0}^{J}d(\cos k'a)\frac{1}{-a\sin k'a}(\cdots).$$

This sequence of steps straightforwardly gives

$$\frac{1}{\tau(k)}=\frac{1}{2\hbar}\frac{a^2}{Mv_s^2}\frac{\sin(ka)}{(ka)^2}\frac{(J')^2}{J}(k_0T),\quad 0<k<\frac{\pi}{2a}.\qquad(3.12)$$

N, A

Here, $-\pi/2a<k<0$. With the substitution $k=-|k|$, $k'=-|k'|$, the integral becomes identical with that of the previous case and gives the same result.

U, E

With k in the range $-\pi/2a<k<-\pi/a$, it is clear from Fig. 1 that a normal scattering is not possible, since one must have $|q|<\pi/a$. Rather, such a phonon can be emitted, and an umklapp transition (involving the smallest reciprocal lattice vector) made to a final k' within the first zone:

$$k'=k-q+2\pi/a.$$

After summing over q, it is evident that the terms remaining in the sum over k' are invariant to a simple shift by one period,

$$k'\rightarrow k-2\pi/a.$$

Hence, the final result is identical with that of the (N,E) processes.

U, A

By identical arguments, this contribution can be shown to be identical with that of (N,A).

In summary, the four regimes indicated in Fig. 1 make identical contributions to $\tau(k)$, which is therefore seen to be symmetrical about the midpoint of the band. First neglecting the variation of the Boltzmann factor over the band, the drift mobility is four times the quantity

$$(e/k_0T)\langle v_k^2\tau(k)\rangle,$$

where $\tau(k)$ is given by (3.11), and $v_k=(Ja/\hbar)\sin ka$. The integration over k is easily carried out. The final result is

$$\mu^{\text{el}}=\frac{16}{\pi}(\pi-2)\frac{e}{(k_0T)^2}\frac{J^3}{(J')^2}\frac{Mv_s^2}{\hbar}.\qquad(3.13)$$

This result is based on the assumption that the variation of the Boltzmann factor over the band can be neglected. As emphasized by the calculations of Katz and co-workers,[3] however, this assumption *may* not be realized in practice. It is straightforward to take this feature into account in these one-dimensional model calculations. (It is to be recalled that the replacement of the Planck factor by its high-temperature value is still exact in the elastic limit.) We simply find that

$$\mu=\frac{e}{(k_0T)^2}\frac{4}{\pi}\frac{J^3}{(J')^2}\frac{Mv_s^2}{\hbar}\int_0^{\pi/2}d(ka)(ka)^2\sin(ka)$$

$$\times\left\{\exp\left[\frac{2J\cos(ka)}{k_0T}\right]+\exp\left[-\frac{2J\cos(ka)}{k_0T}\right]\right\},$$

where the first exponent in the curly brackets comes from the N processes and the second term from the U processes. Introducing the variables

$$\rho=\frac{kT}{2J},\quad \mu'=\frac{Mv_s^2}{\hbar}\frac{2}{\pi}\frac{J}{(J')^2},$$

we obtain

$$\frac{\mu}{\mu'}=\frac{1}{\rho^2}\int_0^{\pi/2}dx\,x^2\sin x\cosh\left(\frac{1}{\rho}\cos x\right).$$

In Fig. 2, the above equation is plotted as a function of ρ. It is seen that departures from the T^{-2} dependence occur for $k_0T\lesssim 2J$ as expected; the mobility is predicted to decrease more rapidly than T^{-2} with increasing temperature in this range. For $2J=0.1$ eV, the magnitude of the deviation is roughly a factor of 2 at room tem-

TABLE I. Intermolecular transfer integrals and their spatial derivatives (Ref. 8).

	Electron	Hole
E_b	$+16\times10^{-4}$ eV	-21
$(\partial E_b/\partial a)_0$	$-\ 4\times10^{-4}$ eV/Å	$+\ 4$
$(\partial E_b/\partial b)_0$	-50	$+60$
E_α	-24	-19
$(\partial E_\alpha/\partial a)_0$	$+90$	$+50$
$(\partial E_\alpha/\partial b)_0$	$+25$	-10

perature. This feature will not be investigated at the present time for the real base-centered-monoclinic (BCM) structure considered in the next section, because of the complexity of the transport integrals.

Next, we make a numerical estimate of the relaxation time τ, given by (3.12). In this connection, it is important to check the self-consistency of the theory by verifying that τ is not so small as to clearly invalidate the use of band theory in the first place. Equation (3.12) is written

$$\tau(k)=\tau_0\frac{(ka)^2}{\sin(ka)},$$

where

$$\tau_0=2\hbar\frac{Mv_s^2}{a^2}\frac{J}{(J')^2}\frac{1}{k_0T}.$$

We focus on the evaluation of τ_0: For J and J', we choose values corresponding to hole propagation along the b axis of anthracene as given in Table I (i.e., $J=E_b$, $J'=\partial E_b/\partial b$). The latter quantity is particularly large for this case, and so should give a particularly small estimate of τ_0. The values of the various parameters are taken as follows:

$$M=3.3\times10^5 m_e,$$
$$v_s=2\times10^5\ \mathrm{cm|sec},$$
$$a=6\ \text{Å},$$
$$|J|=20\times10^{-4}\ \mathrm{eV},$$
$$|J'|=60\times10^{-4}\ \mathrm{eV/Å},$$
$$T=300°\mathrm{K}.$$

From these we compute

$$\tau_0=5.6\times10^{-13}\ \mathrm{sec}.$$

The energy uncertainty

$$(\hbar/\tau_0)=0.001\ \mathrm{eV}$$

is then to be compared with the assumed value of the bandwidth

$$2J=0.004\ \mathrm{eV}$$

indicating that the energy bands are not "washed out."

Another quantity of interest is the mean free path

$$l(k)=v(k)\tau(k),$$

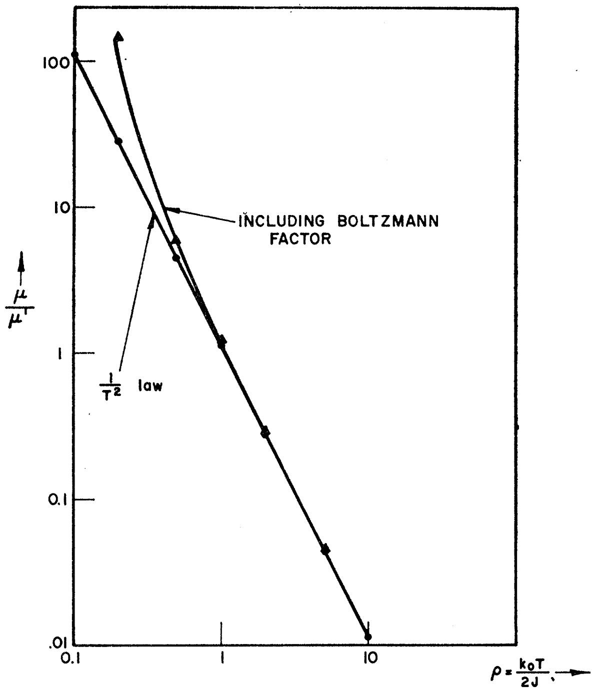

FIG. 2. Temperature dependence of the mobility for one-dimensional, elastic scattering.

where

$$v(k)=(Ja/\hbar)\sin(ka).$$

We get

$$l(k)=\tau_0(Ja/\hbar)(ka)^2.$$

We calculate

$$\tau_0(Ja/\hbar)\approx 11\ \text{Å},$$

which at least is not $<a=6$ Å.

The above estimates exclude the small range of k values near $k=0$, since we are interested only in order of magnitude estimates. These wave-vector dependences, moreover, are felt to be particular to the one-dimensional case. Unfortunately, a $\tau(\mathbf{k})$ is not easily obtained for the two-dimensional elastic scattering considered in the next section. The present estimates based on the one-dimensional model will therefore have to suffice for the present.

Finally, we make a numerical estimate of the mobility given by (3.13). For the same values of the parameters used in the previous estimate of the relaxation time, we obtain

$$\mu^{\mathrm{el}}\cong 2.5\ \mathrm{cm^2/V\text{-}sec},$$

which is to the order of the observed mobilities.[2-4]

Inelastic Scattering

In this subsection, we calculate the mobility for the case in which the Debye temperature is some finite fraction of the bandwidth. Thus, the scattering is inelastic, and the relaxation-time approximation of the previous section cannot be made. To this end we use the variational method of transport theory,[14] suitably modified to the case of nondegenerate statistics.

The starting point of the present calculation is the collision term (3.3), in which the population term has been replaced by its time-reversed process. Again we make the substitution (3.7) and take[22]

$$g(k)=f^0(E_k)\phi(k).$$

Substituting this into (3.3), we obtain

$$-\left(\frac{\partial f(k)}{\partial t}\right)_{\text{coll}}=\sum_{k',\lambda,(\pm)}\{\phi(k)f^0(E_k)W_{(\pm)}{}^{(\lambda)}(k\rightarrow k')(N_\lambda+\tfrac{1}{2}\mp\tfrac{1}{2})$$
$$-\phi(k')f^0(E_k{}')W_{(\mp)}{}^{(\lambda)}(k\rightarrow k')(N_\lambda+\tfrac{1}{2}\pm\tfrac{1}{2})\}. \quad (3.14)$$

In equilibrium, detailed balancing gives the condition

$$f^0(E_k)W_{(\pm)}{}^{(\lambda)}(k\rightarrow k')(N_\lambda+\tfrac{1}{2}\mp\tfrac{1}{2})$$
$$=f^0(E_{k'})W_{(\mp)}{}^{(\lambda)}(k'\rightarrow k)(N_\lambda+\tfrac{1}{2}\pm\tfrac{1}{2}), \quad (3.15)$$

as a consequence of which (3.14) can be written in the form

$$-\left(\frac{\partial f(k)}{\partial t}\right)_{\text{coll}}=\sum_{k',\lambda,(\pm)}L_{(\pm)}{}^{(\lambda)}(k\rightarrow k')[\phi(k)-\phi(k')], \quad (3.16)$$

where the scattering kernel is given by

$$L_{(\pm)}{}^{(\lambda)}(k\rightarrow k')$$
$$=f^0(E_k)W_{(\pm)}{}^{(\lambda)}(k\rightarrow k')(N_\lambda+\tfrac{1}{2}\mp\tfrac{1}{2}). \quad (3.17)$$

By (3.15), $L_{(\pm)}{}^{(\lambda)}(k\rightarrow k')$ is explicitly symmetric in the sense that

$$L_{(\pm)}{}^{(\lambda)}(k\rightarrow k')=L_{(\mp)}{}^{(\lambda)}(k'\rightarrow k), \quad (3.18)$$

Equation (3.16) can more simply be written

$$-\left(\frac{\partial f(k)}{\partial t}\right)_{\text{coll}}=\sum_{k'}L(k,k')[\phi(k')-\phi(k)], \quad (3.19)$$

where

$$L(k,k')=\sum_{\lambda,(\pm)}L_{(\pm)}{}^{(\lambda)}(k\rightarrow k'). \quad (3.20)$$

From (3.18), $L(k,k')$ can be shown to be symmetric in k and k',

$$L(k,k')=L(k',k). \quad (3.21)$$

As is well known, the symmetry of the scattering kernel is essential to the applicability of the variational technique. Given the Boltzmann equation in the form (3.19) with the symmetric kernel (3.21), the development of a maximum variational expression for the electrical conductivity is well known. For the sake of completeness, this is briefly reviewed in Appendix B. For Maxwellian statistics, the result is

$$\sigma_{\text{var}}=(e^2/k_0T)(N/D), \quad (3.22)$$

where

$$N=[\sum_k v_k\phi(k)f^0(E_k)]^2 \quad (3.23)$$

and

$$D=\tfrac{1}{2}\sum_{k,k'}L(k,k')[\phi(k)-\phi(k')]^2. \quad (3.24)$$

This is a maximum variational principal in the sense that

$$\sigma[\phi_{\text{var}}]\leq\sigma[\phi_{\text{exact}}].$$

The form (3.22) has the further convenience of being independent of the normalization of the trial distribution function, ϕ. For the case of electrical conduction, we choose the familiar trial solution (appropriate to one dimension)

$$\phi(k)=v_k. \quad (3.25)$$

For the one-dimensional band (3.5), neglecting variation of the Boltzmann factor $f^0(E_k)$, the numerator N is easily found to be

$$N=(Ja/\hbar)^4(L/a)^4. \quad (3.26)$$

The calculation of the denominator D, Eq. (3.24), is more involved, and is the key part of the present calculation. Substituting (3.21), (3.17), (3.9), and (3.25) into (3.24), we obtain

$$D=\tfrac{1}{2}\sum_{k,k',q,(\pm),K}f^0(E_k)\frac{2\pi}{\hbar}\frac{\hbar}{2M\mathfrak{N}v_s|q|}4(J')^2\left(\frac{Ja}{\hbar}\right)^2$$
$$\times[\sin(ka)-\sin(k'a)]^4(N_q+\tfrac{1}{2}\mp\tfrac{1}{2})$$
$$\times\delta_{k',k\pm q+K}\delta(E_k-E_{k'}\pm\hbar v_s|q|). \quad (3.27)$$

As for the case of elastic scattering, the various possible processes are considered in turn.

N, A

An inelastic (N,A) scattering would be given described by a line such as designated (N,A) on Fig. 1, except that its slope would be finite and positive, rather than zero. For this case, (3.27) is written

$$D^{(N,A)}=\frac{1}{2}\frac{2\pi}{\hbar}\frac{\hbar}{2M\mathfrak{N}v_s}4(J')^2\left(\frac{Ja}{\hbar}\right)^2S, \quad (3.28)$$

where

$$S=\sum_{k,k',q}f^0(E_k)[\sin(ka)-\sin(k'a)]^4\frac{N_q}{q}$$
$$\times\delta_{k',k+q}\delta(E_k-E_{k'}+\hbar v_sq). \quad (3.29)$$

---

[22] In view of the fact that $f^0(1-f^0)=-(k_0T)(\partial f^0/\partial E)$, it is seen that this form is equivalent to the usual form in Fermi statistics, but with the neglect of the exclusion factor.

The sum over k and k' is more simply carried out in terms of relative and center-of-mass coordinates

$$k_r=k'-k\,,\quad k_{cm}=(k'+k)/2\,.$$

The velocity differences and energy differences appearing in (3.29) are readily expressed in terms of these variables by standard trigonometric identities. The Kronecker delta takes the form $\delta_{k_r,q}$, so that the sum over k_r picks out the single term for which $k_r=q$. This leaves the sums over q and k_{cm}:

$$S=2^4\frac{L^2}{(2\pi)^2}\int_0^{\pi/a}dq\,\sin^4\!\left(\frac{qa}{2}\right)\frac{N_q}{q}\int dk_{cm}\cos^4(k_{cm}a)\times\delta\left[-2J\sin(k_{cm}a)\sin\!\left(\frac{qa}{2}\right)+\hbar v_sq\right].\quad(3.30)$$

Again, the Boltzmann factor has been set equal to unity by virtue of the assumption that

$$2J<k_0T\,.$$

The last integral on the right-hand side of (3.30) is easily recast in the form

$$\int d[\sin(k_{cm}a)]\frac{\cos^3(k_{cm}a)}{a}\frac{1}{2J\sin(qa/2)}\times\delta\left[\sin(k_{cm}a)-\frac{\hbar v_sq}{2J\sin(qa/2)}\right].$$

The Dirac delta function picks out the single contribution

$$\sin(k_{cm}a)=\frac{\hbar v_sq}{2J\sin(qa/2)}\geqslant0\,.\quad(3.31)$$

The equality sign holds in the elastic limit $v_s=0$ for which $k_{cm}=0$ and $k'=-k$, in agreement with the results of the elastic scattering case. Next substituting (3.31) into the factor

$$\cos^3(k_{cm}a)=[1-\sin^2(k_{cm}a)]^{3/2}\,,$$

the above integral becomes

$$\frac{1}{a}\left[1-\left(\frac{k_0\Theta_D}{\Delta E}\right)^2\frac{1}{\pi^2}\frac{(qa)^2}{\sin^2(qa/2)}\right]^{3/2}\frac{1}{2J\sin(qa/2)}\,,$$

where

$$k_0\Theta_D\equiv\hbar v_s(\pi/a)\,,$$

and

$$\Delta E\equiv2J\,.$$

By virtue of the inequality $k_0\Theta_D\lesssim\Delta E$ characteristic of the inelastic-scattering regime, the quantity in square brackets is expanded in a Taylor's series, to second order. The remaining integration over q appearing in (3.30) is

$$S=2^4\frac{L^2}{(2\pi)^2}\int_0^{\pi/a}dq\,\sin^3\!\left(\frac{qa}{2}\right)\frac{N_q}{q}\frac{1}{2Ja}\times\left\{1-\frac{3}{2}\left(\frac{k_0\Theta_D}{\Delta E}\right)^2\frac{1}{\pi^2}\frac{(qa)^2}{\sin^2(qa/2)}+\frac{3}{8}\left(\frac{k_0\Theta_D}{\Delta E}\right)^4\frac{1}{\pi^4}\frac{(qa)^4}{\sin^4(qa/2)}+\cdots\right\}.\quad(3.32)$$

Since $k_0T\gg\Delta E\gtrsim k_0\Theta_D$, it follows that N_q can be replaced by its high-temperature limit[15]

$$N_q\to k_0T/\hbar v_sq\,.$$

The latter is substituted into (3.32), the integration over q is performed term by term, and the result is substituted into (3.28). Finally inserting (3.28) and (3.23) into (3.22) and expanding the power series in the denominator, we get

$$\sigma^{(N,A)}=\left(\frac{L}{a}\right)\frac{e^2}{(k_0T)^2}\frac{J^3}{(J')^2}\left(\frac{\pi}{16I_0}\right)\times\left\{1-\left(\frac{k_0\Theta_D}{\Delta E}\right)^2\frac{I_2}{I_0}-\left(\frac{k_0\Theta_D}{\Delta E}\right)^4\frac{I_4}{I_0}\right\},$$

where

$$I_0=\frac{1}{2}\int_0^{\pi/2}dy\frac{\sin^3y}{y^2}=0.345\,,$$

$$I_2=-\frac{3}{\pi^2}\int_0^{\pi/2}dy\,\sin y=-\frac{3}{\pi^2}=-0.305\,,$$

$$I_4=\frac{3}{\pi^4}\int_0^{\pi/2}dy\frac{y^2}{\sin y}=0.047\,.$$

As in the elastic-scattering case, the remaining scattering processes (N,E), and (N,A), (N,E) give contributions identical to the above. The drift mobility is given by

$$\mu^{(\mathrm{inel})}=\sigma^{(\mathrm{inel})}/ne\,,$$

where the carrier density

$$n=\textstyle\sum_k f^0(E_k)$$

is evaluated taking into account our assumption that $k_0T\gg\Delta E$. The final result for the drift mobility is

$$\mu^{\mathrm{inel}}\cong(2.3)\frac{e}{(k_0T)^2}\frac{J^3}{(J')^2}\frac{Mv_s^2}{\hbar}\times\left\{1+0.89\left(\frac{k_0\Theta}{\Delta E}\right)^2-0.14\left(\frac{k_0\Theta}{\Delta E}\right)^4+\cdots\right\},\quad(3.33)$$

which, aside from the different numerical factor arising from the variational method and the correction terms $\sim(k_0\Theta/\Delta E)$, is of the same form as the elastic result (3.13). As pointed out previously, these correction terms explicitly represent the inelasticity of the collisions, and properly vanish in the elastic limit $\Theta\sim v_s \to 0$. These corrections might be expected to be temperature-dependent for the case $k_0T\sim\Delta E$; however, this case has not been investigated.

IV. APPLICATION TO BASE-CENTERED-MONOCLINIC STRUCTURE

In the present section, the model of the previous sections is applied to an approximate calculation of the real problem; namely, the mobility in the *ab* plane of the anthracene crystal. It is felt that the present calculation, to a good approximation, takes into account the anisotropy of the scattering as well as that of the energy-band structure. However, in order to keep the problem tractable for numerical computation, a few simplifying assumptions have been made. We point these out at the outset:

(1) Neglect of the variation of the Boltzmann factor over the energy band. This is a good approximation using LeBlanc's band-structure parameters.[2] These were used, rather than the more recent (and comparable) estimate of Silbey,[4] in order to be consistent with the use of scattering parameters calculated by LeBlanc.[8]

(2) Elastic scattering. As in the one-dimensional case, the Planck factor can then be replaced by its high-temperature form without approximation.

(3) Neglect of umklapp processes. On the basis of the one-dimensional calculations, these would be expected to make a contribution of the same order as the normal processes.

(4) The replacement of the real acoustic phonon spectrum by a single, longitudinal-acoustic, two-dimensional Debye spectrum. This is perhaps the most serious approximation, since the phonon spectrum would be expected to exhibit anisotropy comparable with that of the electronic band structure. However, in the absence of neutron diffraction data or a calculation of the spectrum from first principles, we consider this approximation appropriate for these initial investigations. The phonon anisotropy superimposes an added degree of complication which should more properly be considered in a separate investigation.

Having pointed out these features, we now proceed with the calculation. In order to use only the matrix elements (2.25) as in the one-dimensional case, we now argue that the matrix elements (2.26) and (2.27) are negligible in comparison. We first consider (2.26). As previously noted, this physically represents the variation with relative displacement of the expectation value of energy at a given site due to all other molecular potentials (it is sufficient to consider only nearest neighbors). These derivatives, as well as the quantity W^0 itself, Eq. (2.10), have been estimated by LeBlanc on the basis of the same wave functions and potentials used in his paper.[1] He finds W^0 [Eq. (II.12)] $\sim$50 to 100 smaller that $J_h{}^0$ [Eq. (2.12)] at the intermolecular distances of interest, and that the former decrease only somewhat more rapidly than the latter, by about a factor of 2. This would imply that the over-all change in W is one to two orders of magnitude smaller than that of J_h for a given displacement; hence, (2.26) is discarded.

Next, the order of magnitude of the velocity-dependent contribution (2.27) is compared with (2.25). For a given mode, the ratio of the former to the latter is

$$\frac{\langle k\{N\}|V|k'\{N'\}\rangle_3}{\langle k\{N\}|V|k'\{N'\}\rangle_1}\sim\hbar\omega\frac{|\mathbf{I}^{(1)}|}{(\boldsymbol{\nabla}_h J_h)_0}\lesssim\frac{k_0\Theta}{J}S, \qquad (4.1)$$

where it has been assumed that both $I^{(1)}$ and J_h decrease at the same rate with displacement, both paralleling the decrease of the molecular wave function. The quantity S is a typical nonorthogonality integral

$$S=\int d^3r\,\phi(\mathbf{r})\varphi(\mathbf{r}-\mathbf{R}_h{}^0).$$

It is seen that the ratio (4.1) is entirely negligible for elastic scattering. For inelastic scattering, it is small by the above nonorthogonality integral, and would appear to perhaps contribute as much as the inelastic correction terms of (3.33). In summary, then, only the matrix elements (2.25) are retained for the present calculations.

In the coordinate system defined by the mutually perpendicular **a** and **b** axes of the base-centered-monoclinic structure, the approximate two-dimensional band structure[2-4] is written

$$E_{\mathbf{k}}=4E_\alpha\cos\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right)+2E_b\cos(\mathbf{k}\cdot\mathbf{b}). \qquad (4.2)$$

In treating elastic transitions between points on the constant energy surfaces defined by (4.2), one cannot, of course, make the simple assumption (3.10) used to facilitate the definition of a relaxation time for the one-dimensional case. In fact, attempts to calculate a relaxation time $\tau(\mathbf{k})$ are bypassed, and the conductivity is calculated directly by the variational method. The formalism of the previous section is easily generalized to more than one dimension. The (variational) conductivity is again written in the form

$$\sigma_{\text{var}}=(e^2/k_0T)(N/D),$$

where now

$$N=\Big[\sum_{\mathbf{k}}(\mathbf{v}_{\mathbf{k}})_\epsilon f^0(E_{\mathbf{k}})\Big]^2, \qquad (4.3)$$

$$D=\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}'}L(\mathbf{k},\mathbf{k}')[(\mathbf{v}_{\mathbf{k}})_\epsilon-(\mathbf{v}_{\mathbf{k}'})_\epsilon]^2. \qquad (4.4)$$

In these formulas

$$\phi(\mathbf{k})=\boldsymbol{\varepsilon}\cdot\mathbf{v}_{\mathbf{k}}\equiv|\boldsymbol{\varepsilon}|(\mathbf{v}_{\mathbf{k}})_{\epsilon},$$

and

$$L(\mathbf{k},\mathbf{k}')=\sum_{\lambda,(\pm)}L_{(\pm)}{}^{(\lambda)}(\mathbf{k},\mathbf{k}'),\tag{4.5}$$

where

$$L_{(\pm)}{}^{(\lambda)}(\mathbf{k},\mathbf{k}')=f^0(E_{\mathbf{k}})(N_\lambda+\tfrac{1}{2}\mp\tfrac{1}{2})W_{(\pm)}{}^{(\lambda)}(\mathbf{k}\rightarrow\mathbf{k}').\tag{4.6}$$

Here, $W_{(\pm)}{}^{(\lambda)}(\mathbf{k}\rightarrow\mathbf{k}')$ is given by (3.1) with $\hbar\omega_\lambda=0$ in the Dirac delta function, corresponding to assumption (2) of elastic scattering.

We next invoke assumption (4) that the real phonon spectrum can be replaced by a single, longitudinal-acoustic mode. Hence, in the sum over $\lambda=(\mathbf{q},j)$, the sum over j reduces to the single term $j=l$ (longitudinal). Also, the phonon polarization vector may be written

$$\hat{\mathbf{e}}_{\mathbf{q}l}=\mathbf{q}/|\mathbf{q}|.$$

Writing down the sum over nearest neighbors $h=(\alpha,\beta,b)$ appearing in the absolute square of (3.1), we have

$$\left\{\left[\left(\frac{q_a}{|\mathbf{q}|}\right)\left(\frac{\partial E_\alpha}{\partial a}\right)_0+\left(\frac{q_b}{|\mathbf{q}|}\right)\left(\frac{\partial E_\alpha}{\partial b}\right)_0\right](\sin(\mathbf{k}'\cdot\alpha)-\sin(\mathbf{k}\cdot\alpha))+\left[\left(\frac{q_a}{|\mathbf{q}|}\right)\left(\frac{\partial E_\beta}{\partial a}\right)_0+\left(\frac{q_b}{|\mathbf{q}|}\right)\left(\frac{\partial E_\beta}{\partial b}\right)_0\right](\sin(\mathbf{k}'\cdot\mathbf{b})-\sin(\mathbf{k}\cdot\beta))\right.$$
$$\left.+\left[\left(\frac{q_a}{|\mathbf{q}|}\right)\left(\frac{\partial E_b}{\partial a}\right)_0+\left(\frac{q_b}{|\mathbf{q}|}\right)\left(\frac{\partial E_b}{\partial b}\right)_0\right](\sin(\mathbf{k}'\cdot\mathbf{b})-\sin(\mathbf{k}\cdot\mathbf{b}))\right\}^2.\tag{4.7}$$

The above derivatives of overlap integrals have been calculated by LeBlanc[8,23] using Hückel combinations of Slater orbitals with $\alpha=3.08$ Å^{-1}, and are presented[24] in Table I.

From the relative magnitudes of these quantities, $(\partial E_b/\partial a)_0$ is neglected with respect to $(\partial E_b/\partial b)_0$, and $(\partial E_\alpha/\partial b)_0$ is nelgected with respect to $(\partial E_\alpha/\partial a)$. Further noting that

$$(\partial E_\beta/\partial a)_0=-(\partial E_\alpha/\partial a)_0,$$

and combining the sine functions by appropriate trigonometric identities, (4.7) reduces to

$$\left\{\left(\frac{q_a}{|\mathbf{q}|}\right)\left(\frac{\partial E_\alpha}{\partial a}\right)_0 2\left(\sin\left(\frac{\mathbf{k}'\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}'\cdot\mathbf{b}}{2}\right)-\sin\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right)\right)+\left(\frac{q_b}{|\mathbf{q}|}\right)\left(\frac{\partial E_b}{\partial b}\right)_0(\sin(\mathbf{k}'\cdot\mathbf{b})-\sin(\mathbf{k}\cdot\mathbf{b}))\right\}^2.$$

This expression is inserted into (3.1) for the transition rate. The latter is then substituted into (4.6), which, in turn, is put into (4.5) to get the scattering kernel. Recalling assumption (3), the neglect of umklapp processes, the sum over $\mathbf{q}$ [recall that $\lambda=(\mathbf{q},l)$] is easily carried out. In addition, by the assumption (2) of elastic scattering, the Planck factor is replaced by its high-temperature form $k_0T/\hbar v_s|\mathbf{q}|$. The sum over absorption and emission (±) introduces an additional factor of 2. The result reads

$$L(\mathbf{k},\mathbf{k}')=8\frac{k_0T}{\hbar}\frac{2\pi}{\hbar}\frac{\hbar}{2M\mathfrak{N}}\frac{1}{v_s{}^2}\frac{1}{|\mathbf{k}'-\mathbf{k}|^2}\left\{\left|\frac{k_a'-k_a}{\mathbf{k}'-\mathbf{k}}\right|\left(\frac{\partial E_\alpha}{\partial a}\right)_0 2\left(\sin\left(\frac{\mathbf{k}'\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}'\cdot\mathbf{b}}{2}\right)-\sin\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right)\right)\right.$$
$$\left.+\left|\frac{k_b'-k_b}{\mathbf{k}'-\mathbf{k}}\right|\left(\frac{\partial E_b}{\partial b}\right)_0(\sin(\mathbf{k}'\cdot\mathbf{b})-\sin(\mathbf{k}\cdot\mathbf{b}))\right\}^2\delta(E_{\mathbf{k}}-E_{\mathbf{k}'}).\tag{4.8}$$

This kernel is then inserted into (4.4) for the denominator of the variational conductivity. At this state, the direction of the external electric field has to be selected; it is sufficiently general to take it along the **a** and **b** crystallographic directions. For these two orientations,

$$(\mathbf{v}_{\mathbf{k}})_a=\left(\frac{2E_\alpha a}{\hbar}\right)\sin\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right),$$

and

$$(\mathbf{v}_{\mathbf{k}})_b=\left(\frac{2E_\alpha b}{\hbar}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\sin\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right)+\left(\frac{2E_b b}{\hbar}\right)\sin(\mathbf{k}\cdot\mathbf{b}).$$

---

[23] The choice of wave functions described in footnotes 2 and 8 underestimates the resonance integrals and overestimates their derivatives, thereby predicting a mobility which is likely to be too small. A more accurate set of parameters would be obtained from the calculations of Sibley *et al.*, Ref. 4.

[24] The large values of some of these derivatives together with an estimate of the amplitude of thermal vibrations (0.06–0.1 Å) raises some question as to the validity of a linear approximation [c.f. (2.9)]; however, we do not consider it appropriate to go beyond this approximation at the present stage. As noted in footnote 23, more accurate estimates may lead to smaller values of these derivatives.

It is then a matter of straightforward algebra to express D_{ab} as a sum of quadratures. They are conveniently expressed in terms of the following dimensionless ratios (obtained from Ref. 1 and Table I):

$$\alpha=a/b=1.41\,,\quad s=\frac{E_\alpha}{E_b}=\begin{cases}-1.61\,, & \text{electrons}\\ +0.935\,, & \text{holes}\end{cases},\ r=\frac{(\partial E_\alpha/\partial a)_0}{(\partial E_b/\partial b)_0}=\begin{cases}-1.8\,, & \text{electrons}\\ +0.835\,, & \text{holes.}\end{cases}\tag{4.9}$$

We obtain

$$D_{ab}=2\frac{k_0T}{\hbar}\frac{2\pi}{\hbar}\frac{\hbar}{2M\mathfrak{N}}\frac{1}{v_s^2}\frac{1}{E_b}\left(\frac{\partial E_b}{\partial b}\right)^2\frac{1}{b^2}\left(\frac{L}{2\pi}\right)^4\{\alpha^2 I_{ab}^{(1)}+4r^2 I_{ab}^{(2)}+4r\alpha I_{ab}^{(3)}\}\,,\tag{4.10}$$

where

$$I_{ab}^{(1)}=\int\!\!\int\!\!\int\!\!\int dxdx'dydy'\,\delta\left[\cos y+2s\cos\left(\frac{x}{2}\right)\cos\left(\frac{y}{2}\right)-\cos y'-2s\cos\left(\frac{x'}{2}\right)\cos\left(\frac{y'}{2}\right)\right]$$
$$\times\frac{(y'-y)^2}{[(x'-x)^2+\alpha^2(y'-y)^2]^2}(\sin y'-\sin y)^2 f_{ab}(x,y,x',y')\,,$$

$$I_{ab}^{(2)}=\int\!\!\int\!\!\int\!\!\int dxdx'dydy'\,\delta\left[\cos y+2s\cos\left(\frac{x}{2}\right)\cos\left(\frac{y}{2}\right)-\cos y'-2s\cos\left(\frac{x'}{2}\right)\cos\left(\frac{y'}{2}\right)\right]$$
$$\times\frac{(x'-x)^2}{[(x'-x)^2+\alpha^2(y'-y)^2]^2}\left(\sin\left(\frac{x'}{2}\right)\cos\left(\frac{y'}{2}\right)-\sin\left(\frac{x}{2}\right)\cos\left(\frac{y}{2}\right)\right)^2 f_{ab}(x,y,x',y')\,,$$

$$I_{ab}^{(3)}=\int\!\!\int\!\!\int\!\!\int dxdx'dydy'\,\delta\left[\cos y+2s\cos\left(\frac{x}{2}\right)\cos\left(\frac{y}{2}\right)-\cos y'-2s\cos\left(\frac{x'}{2}\right)\cos\left(\frac{y'}{2}\right)\right]$$
$$\times\frac{(x'-x)(y'-y)}{[(x'-x)^2+\alpha^2(y'-y)^2]^2}(\sin y'-\sin y)\left(\sin\frac{x'}{2}\cos\frac{y'}{2}-\sin\frac{x}{2}\cos\frac{y}{2}\right)f_{ab}\,,$$

where the factors f_{ab} depend on the choice of field direction, and are given by

$$f_a(x',y',x,y)=\left(\frac{2E_\alpha a}{\hbar}\right)^2\left(\sin\left(\frac{x'}{2}\right)\cos\left(\frac{y'}{2}\right)-\sin\left(\frac{x}{2}\right)\cos\left(\frac{y}{2}\right)\right)^2,$$

and

$$f_b(x',y',x,y)=\left(\frac{2E_\alpha b}{\hbar}\right)^2\left[\sin\left(\frac{y'}{2}\right)\left(s\cos\left(\frac{x'}{2}\right)+2\cos\left(\frac{y'}{2}\right)\right)-\sin\left(\frac{y}{2}\right)\left(s\cos\left(\frac{x}{2}\right)+2\cos\left(\frac{y}{2}\right)\right)\right].$$

For the values of the parameters given in Table I and (4.9), the quadratures were performed on a digital computer. The results are presented in Table II.

The numerators, Eq. (4.3), can be evaluated analytically for the two-field directions (as usual, replacing the Boltzmann factor by unity). The results are

$$N_a=\frac{(2\pi)^4}{a^2b^2}\left(\frac{L}{2\pi}\right)^4\left(\frac{2E_b a}{\hbar}\right)^4 s^4,\quad N_b=\frac{(2\pi)^4}{a^2b^2}\left(\frac{L}{2\pi}\right)^4\left(\frac{2E_b a}{\hbar}\right)^4(2+s^2)^2.\tag{4.11}$$

Equations (4.10) and (4.11) are substituted into the variational expression for the conductivity. The mobility is then obtained by division by ne, where the carrier density n is given by

$$n\cong\frac{L}{(2\pi)^2}\int_{-2\pi/a}^{2\pi/a}dk_a\int_{-2\pi/b}^{2\pi/b}dk_b\,.$$

The final results read

$$\mu_{aa}=8\pi^3\frac{e}{(k_0T)^2}\frac{Mv_s^2}{\hbar}\frac{E_b^3}{(\partial E_b/\partial b)^2}\frac{s^2}{\{\alpha^2 I_a^{(1)}+4r^2 I_a^{(2)}+4r\alpha I_a^{(3)}\}}\,,\tag{4.12}$$

$$\mu_{bb}=8\pi^3\frac{e}{(k_0T)^2}\,\frac{Mv_s^2}{\hbar}\,\frac{E_b^3}{(\partial E_b/\partial b)^2}\,\frac{1}{\alpha^2}\,\frac{(2+s^2)^2}{\{\alpha^2 I_b^{(1)}+4r^2 I_b^{(2)}+4r\alpha I_b^{(3)}\}}\,, \tag{4.13}$$

$$\left(\frac{\mu_{aa}}{\mu_{bb}}\right)=\frac{s^2}{(2+s^2)^2}\alpha^2\left\{\frac{\alpha^2 I_b^{(1)}+4r^2 I_b^{(2)}+4r\alpha I_b^{(3)}}{\alpha^2 I_a^{(1)}+4r^2 I_a^{(2)}+4r\alpha I_a^{(3)}}\right\}. \tag{4.14}$$

The mobility expressions using a constant τ cannot predict absolute magnitudes[3]; however, they can predict the mobility ratio. In the notation of the present paper we get, instead of (4.14),

$$\left(\frac{\mu_{aa}}{\mu_{bb}}\right)=\frac{s^2}{(2+s^2)}\alpha^2, \quad (\text{constant } \tau).$$

Substituting the numerical values of the transport integrals given in Table II, we obtain the comparison with experiment shown in Table III. It is first noted that the magnitudes of the calculated mobilities are of the order of unity, in agreement with experiment. In view of the approximate values taken for some of the parameters (the speed of sound, in particular), the agreement may be somewhat fortuitous, but is encouraging and suggests that acoustic mode scattering is a principal scttering mechanism. Secondly, we note that there is only a slight improvement in the predicted mobility anisotropy. This may be attributed to the neglect of some of the smaller interaction constants in evaluating the matrix elements [cf. (4.7) et seq.] and to the assumption of an isotropic phonon spectrum. The small value of the calculated hole mobility is not understood.

V. CONCLUSIONS AND FURTHER DISCUSSION

The complexity of the lattice vibrational spectra and local molecular wave functions makes a complete treatment of the electron-phonon interaction in organic molecular crystals difficult. It is felt that the present treatment is an improvement on the essentially phenomenological treatments to date. It is capable of treating the interaction of the excess carrier with the intermolecular lattice vibrations in general, taking into account the scattering anisotropy and temperature dependence due to these modes. The theory has been applied only to acoustic-mode scattering. In this connection, improved estimates of the transfer integrals and interaction constants would be useful, as would data on phonon dispersion relations and Debye temperatures.

TABLE II. Numerical values of transport integrals.

	$I_a^{(1)}$	$I_a^{(2)}$	$I_a^{(3)}$	$I_b^{(1)}$	$I_b^{(2)}$	$I_b^{(3)}$
Electron	22.3	33.0	27.9	132.3	37.4	−24.7
Hole	32.1	48.9	3.9	178.5	39.3	35.9

TABLE III. Magnitudes and anisotropy of drift mobility. Comparison between theory and experiment.

	μ_{aa}	μ_{bb}	μ_{aa}/μ_{bb}
Electron	cm²/V sec		
Calculated (constant τ)	...	...	1.13
Calculated (present paper)	...	0.85	1.33
Experimental[a]	1.7	1.0	1.7
Hole			
Calculated (constant τ)	...	...	0.61
Calculated (present paper)	...	0.72	0.61
Experimental[a]	1.0	2.0	0.5

[a] R. G. Kepler, in *Organic Semiconductor Conference*, edited by J. J. Brophy and J. W. Buttrey (Macmillan and Company, New York, 1962).

The numerical estimates of mobility of the order of unity suggest that acoustic-mode scattering is important. However, due to uncertainties in the calculation, scattering by other modes of the phonon spectrum cannot be excluded. Indeed, as will be discussed below, some of these should be at least equally important. The quanta of such modes would have to be less than the bandwidth in order to give rise to single-phonon transitions. There are three general classes:

The first are the intermolecular, translational, optical modes. The present formalism can treat these provided their dispersion relations (ω_{qj}) are known.

The second class are the low-frequency ($\hbar\omega_0<$bandwidth) intramolecular optical modes. The high frequency intramolecular modes discussed in the text give rise to the vibronic structure, but do not scatter in lowest order. The low-frequency modes, on the other hand, can scatter within the ground-state vibronic band. The matrix elements due to this mechanism have been derived, but will not be presented in the present paper for the sake of brevity. The essential physical picture here is that the inequality $\hbar\omega_0<\Delta E$ is simultaneously the condition that the molecule not have time to adjust to the presence of the carrier, but continue to execute motion about its neutral equilibrium configuration. The matrix elements then arise from: (1) variations of the local electronic energies $E(x_g)$ and (2) variations of the overlap integrals due to changes of the local wave functions with internal displacement. The low-lying excitations here would likely be the bending modes of the organic molecule; hence, this would probably be a difficult problem to treat in practice.

The third class of phonons are the optical rotational or torsional modes, involving rotations of the molecule about its principal moments of inertia. Numerical estimates[8] of the variation of the transfer integrals with infinitesimal rotation indeed suggest that this mechanism may be as important as that considered in the text.

Impurity or defect scattering in narrow bands would, of course, require a separate treatment. Finally, as the principal scattering mechanisms become better defined, the calculations can be extended to the Hall effect and other transport phenomena of interest.

ACKNOWLEDGMENTS

The author is indebted to Dr. O. H. LeBlanc for the numerical estimates of the scattering parameters used in the present paper. He would also like to acknowledge helpful discussions with G. D. Whitfield.

APPENDIX A: DIFFICULTIES ASSOCIATED WITH MATRIX ELEMENTS IN THE BLOCH REPRESENTATION

Rather than the approach used in the text, it might appear that a more straightforward procedure would be to simply take matrix elements of the perturbed Hamiltonian between the usual tight-binding Bloch states. In this Appendix, we show that this approach has certain difficulties. First of all, it gives a spurious contribution to the scattering due to the fact that only the local potentials, but not their associated wave functions, are allowed to follow the local displacements; the first such contribution occurs in second order in the displacements. More serious for the present applications, the first-order matrix elements have the unphysical aspect that gradients are taken only with respect to the potentials, while the wave functions are held fixed. For these reasons and in view of what is discussed below, the approach of the text is to be preferred.

These difficulties have been discussed more generally by Herring,[9] who points out that the above second-order contribution is largely cancelled by second-order processes involving interband matrix elements of the linear term.[25] Herring interprets this difficulty as being due to the inability of the wave functions to follow their displacements, and suggests that this could be rectified by using a basis which deforms locally with the lattice.[10,11]

We now exhibit the difficulties associated with the straightforward taking of Bloch matrix elements. The total Hamiltonian is

$$H_T = H_e + H_L\,,$$

where

$$H_e = -\frac{\hbar^2}{2m}\nabla_r^2 + \sum_n U(\mathbf{r}-\mathbf{R}_n) \qquad \text{(A1)}$$

is the electronic Hamiltonian, and H_L is the usual lattice Hamiltonian in the harmonic approximation. In what follows, it will prove convenient to decompose (A1) as follows:

$$H_e = H_e^{(m)} + \sum_{n\neq m} U(\mathbf{r}-\mathbf{R}_n{}^0) + \sum_n [U(\mathbf{r}-\mathbf{R}_n) - U(\mathbf{r}-\mathbf{R}_n{}^0)]\,, \qquad \text{(A2)}$$

where

$$H_e^{(m)} = -(\hbar^2/2m)\nabla_r^2 + U(\mathbf{r}-\mathbf{R}_m{}^0)$$

is the electronic Hamiltonian of the mth molecule at its lattice site, and satisfies the local wave equation

$$H_e^{(m)}\phi(\mathbf{r}-\mathbf{R}_m{}^0) = \epsilon\phi(\mathbf{r}-\mathbf{R}_m{}^0)\,.$$

We wish to calculate the matrix elements

$$\frac{\langle\mathbf{k}',\chi'|H_T|\mathbf{k},\chi\rangle}{\langle\mathbf{k}',\chi'|\mathbf{k},\chi\rangle}\,, \qquad \text{(A3)}$$

where

$$|\mathbf{k},\chi\rangle = |\mathbf{k}\rangle\cdot|\chi\rangle\,,$$

in which

$$|\mathbf{k}\rangle = \mathfrak{N}^{-1/2}\sum_m e^{i\mathbf{k}\cdot\mathbf{R}_m{}^0}\phi(\mathbf{r}-\mathbf{R}_m{}^0) \qquad \text{(A4)}$$

is a conventional Bloch function, and $|\chi\rangle$ is the usual product of harmonic-oscillator states. Clearly, in using (A4), there is no possibility of obtaining coupling terms of the kind found in the text. Nonorthogonality of the local states is again taken into account by writing

$$\int d^3r\phi(\mathbf{r}-\mathbf{R}_l{}^0)\phi(\mathbf{r}-\mathbf{R}_m{}^0) = T_{lm} = \delta_{lm} + S_{lm}\,.$$

Calculating (A3), we obtain

$$\frac{(\epsilon+E_{\{N\}})(1+\sum_h e^{i\mathbf{k}\cdot\mathbf{R}_h{}^0}S_{0h}) + (W^0+\sum_h e^{i\mathbf{k}\cdot\mathbf{R}_h{}^0}J_h{}^0)}{(1+\sum_h e^{i\mathbf{k}\cdot\mathbf{R}_h{}^0}S_{0h})} + \frac{\langle\chi'|\sum_{l,m,n} e^{-i\mathbf{k}'\cdot\mathbf{R}_l{}^0+i\mathbf{k}\cdot\mathbf{R}_m{}^0}\int d^3r\phi(\mathbf{r}-\mathbf{R}_l{}^0)[U(\mathbf{r}-\mathbf{R}_m)-U(\mathbf{r}-\mathbf{R}_m{}^0)]\phi(\mathbf{r}-\mathbf{R}_m{}^0|\chi\rangle}{(1+\sum_h e^{i\mathbf{k}\cdot\mathbf{R}_h{}^0}S_{0h})}\,. \qquad \text{(A5)}$$

The first term of (A5) is diagonal in $\mathbf{k}$ and $\{N\}$, and gives the usual band structure. The nonorthogonality integrals S can be neglected here, as can be seen by expanding the denominator and noting that all additional terms are at least of second order in S.

Turning next to the second term which describes the scattering, we see that there are four possibilities for the indices (l,m,n) which give terms up to first order in the overlap: namely, the case in which all indices refer to the

---

[25] The present tight-binding approach refers to a single band constructed by a single, nondegenerate molecular orbital, so that this cancellation cannot be investigated.

same site, and the three cases in which two refer to a given site and the third to a nearest-neighbor site. Only for the first must the S-proportional term be retained. These terms take the following form:

$$\mathfrak{N}^{-1}\langle\chi'|\sum_n e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_n{}^0}\int d^3r|\phi(\mathbf{r}-\mathbf{R}_n{}^0)|^2\left[\mathbf{u}_n\cdot\boldsymbol{\nabla}_n U(\mathbf{r}-\mathbf{R}_n)_0+\tfrac{1}{2}\sum_{\alpha\beta}u_n{}^\alpha u_n{}^\beta\frac{\partial^2 U}{\partial u_n{}^\alpha\partial u_n{}^\beta}\right]|\chi\rangle(1-\sum_h e^{i\mathbf{k}\cdot\mathbf{R}_h{}^0}S_{0h})$$

$$+\mathfrak{N}^{-1}\langle\chi'|\sum_{n,h} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_n{}^0}e^{i\mathbf{k}\cdot\mathbf{R}_h{}^0}\int d^3r\phi(\mathbf{r}-\mathbf{R}_n{}^0)\mathbf{u}_n\cdot\boldsymbol{\nabla}_n U(\mathbf{r}-\mathbf{R}_n)_0\phi(\mathbf{r}-\mathbf{R}_{n+h}{}^0)|\chi\rangle$$

$$+\mathfrak{N}^{-1}\langle\chi'|\sum_{n,h} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_n{}^0}e^{-i\mathbf{k}'\cdot\mathbf{R}_h{}^0}\int d^3r\phi(\mathbf{r}-\mathbf{R}_{n+h}{}^0)\mathbf{u}_n\cdot\boldsymbol{\nabla}_n U(\mathbf{r}-\mathbf{R}_n)_0\phi(\mathbf{r}-\mathbf{R}_n{}^0)|\chi\rangle$$

$$+\mathfrak{N}^{-1}\langle\chi'|\sum_{n,h} e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_{n+h}{}^0}\int d^3r|\phi(\mathbf{r}-\mathbf{R}_{n+h}{}^0)|^2\mathbf{u}_n\cdot\boldsymbol{\nabla}_n U(\mathbf{r}-\mathbf{R}_n)_0|\chi\rangle. \quad \text{(A6)}$$

In the first term above, the difference $[U(\mathbf{r}-\mathbf{R}_n)-U(\mathbf{r}-\mathbf{R}_n{}^0)]$ has been expanded to second order in the displacements, while for the last three terms it has been expanded to first order. The entire first term of (A6) represents the spurious contribution previously referred to. It is associated with displacing the potential of the nth site while the wave function $\phi(\mathbf{r}-\mathbf{R}_n{}^0)$ is constrained at its lattice position. The linear term clearly vanishes by symmetry arguments; the first nonvanishing contribution is the bilinear term, as pointed out by Herring.[9] The second and third terms of (A6) clearly correspond to variations in J, while the last corresponds to variations in W. However, these also do not allow for the fact that the wave functions should follow their local displacements. These arguments then illustrate the aforementioned difficulties, and provide the motivation for the alternate formulation presented in the text.

APPENDIX B: SUMMARY OF THE VARIATIONAL PROCEDURE

In this Appendix, a brief review of the variational method of transport theory is presented, as it applies to the treatment of the present paper. In particular, we indicate the derivation of the text equations (3.22), (3.23), (3.24), (4.3), and (4.4).

With the collision term written as in (3.19), the Boltzmann equation reads

$$D(\mathbf{k})+\sum_{\mathbf{k}'}L(\mathbf{k},\mathbf{k}')[\phi(\mathbf{k}')-\phi(\mathbf{k})]=0, \quad \text{(B1)}$$

where the driving term is

$$D(\mathbf{k})=e\boldsymbol{\mathcal{E}}\cdot\mathbf{v}_k\frac{\partial f^0(E_k)}{\partial E_k}=-\frac{e}{k_0T}\boldsymbol{\mathcal{E}}\cdot\mathbf{v}_kf^0(E_k), \quad \text{(B2)}$$

for the case of Boltzmann statistics.

We define a functional of the distribution function as follows:

$$\begin{aligned}\mathcal{J}[\phi]&\equiv 2\sum_{\mathbf{k}}D(\mathbf{k})\phi(\mathbf{k})+\sum_{\mathbf{k},\mathbf{k}'}\phi(\mathbf{k})L(\mathbf{k},\mathbf{k}')[\phi(\mathbf{k}')-\phi(\mathbf{k})]\\&=2\sum_{\mathbf{k}}D(\mathbf{k})\phi(\mathbf{k})\\&\qquad-\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}'}L(\mathbf{k},\mathbf{k}')[\phi(\mathbf{k}')-\phi(\mathbf{k})]^2,\end{aligned} \quad \text{(B3)}$$

where the second line follows from (B1). The quantity $\mathcal{J}$ has the properties:

(1) $\delta\mathcal{J}=0$ with respect to variations in ϕ, when $\phi=\phi^{(e)}$ is the (exact) solution of (B1), and

(2) $\mathcal{J}[\phi]\leq\mathcal{J}[\phi^e]$.

From (B3) and (B1), it is seen that

$$\begin{aligned}\mathcal{J}[\phi^{(e)}]&=\sum_{\mathbf{k}}D(\mathbf{k})\phi^{(e)}(\mathbf{k})\\&=-\frac{e\boldsymbol{\mathcal{E}}}{k_0T}\cdot\sum_{\mathbf{k}}[\mathbf{v}_kf^0(E_k)]\phi^{(e)}(\mathbf{k})\\&=-\frac{e\boldsymbol{\mathcal{E}}}{k_0T}\cdot\sum_{\mathbf{k}}\mathbf{v}_kg^{(e)}(\mathbf{k})\\&=\boldsymbol{\mathcal{E}}\cdot\mathbf{j}^{(e)}/k_0T\\&=\sigma^{(e)}\mathcal{E}^2/k_0T.\end{aligned}$$

Hence,

$$\sigma^{(e)}=\frac{k_0T}{\mathcal{E}^2}\mathcal{J}[\phi^{(e)}]\geqslant\frac{k_0T}{\mathcal{E}^2}\mathcal{J}[\phi]=\sigma, \quad \text{(B5)}$$

by (B4).

The form (B3) is not homogeneous in ϕ. In order to get a form which is, we set

$$\phi=C\phi_C. \quad \text{(B6)}$$

Substituting (B6) into (B3), the parameter C may be obtained in terms of the two sums of (B3) by requiring that

$$\partial\mathcal{J}(C)/\partial C=0.$$

The value of C so obtained gives

$$\mathcal{J}(C)=\frac{[\sum_{\mathbf{k}} D(\mathbf{k})\phi(\mathbf{k})]^2}{\frac{1}{2}\sum_{\mathbf{k},\mathbf{k}} L(\mathbf{k},\mathbf{k}')[\phi(\mathbf{k})-\phi(\mathbf{k}')]^2},$$

and finally

$$\sigma=\frac{k_0T}{\mathcal{E}^2}\mathcal{J}=\frac{e^2}{k_0T}\frac{[\sum_k(v_k)\,\varepsilon\phi(\mathbf{k})f^0(E_k)]^2}{\frac{1}{2}\sum_{\mathbf{k},\mathbf{k}'} L(\mathbf{k},\mathbf{k}')[\phi(\mathbf{k})-\phi(\mathbf{k}')]^2}.$$

APPENDIX C: INCLUSION OF INTRAMOLECULAR VIBRATIONS

In this Appendix, the Hamiltonian (2.1) is augmented by the inclusion of the high-frequency ($\hbar\omega_0\sim 0.2$ eV), internal vibrations of the constituent molecules. On account of the high frequencies involved, the temporary molecule ion is able to adjust quickly to the presence of the excess carrier. However, the coupling is weak because of the small interaction of the delocalized carrier on a large, nonpolar, aromatic molecule, and also because of the largeness of the optical quantum $\hbar\omega_0$. Consequently, as we shall see, the vibrational overlap (the overlap of vibrational wave functions corresponding to the carrier being on nearest-neighbor sites) is only somewhat less than unity, and essentially independent of temperature. This is the static modification of the treatment of Sec. II to which we referred previously.

Instead of (2.1), the wave equation of the system now reads

$$i\hbar\frac{\partial\Psi(\mathbf{r},\cdots\mathbf{R}_g\cdots,\cdots x_g\cdots)}{\partial t}=[H_e(\cdots\mathbf{R}_g\cdots)+H_L(\cdots\mathbf{R}_g\cdots)+H_L(\cdots x_g\cdots)]\Psi,\quad\text{(C1)}$$

where, in addition to the quantities defined at the beginning of Sec. II, the $(\cdots x_g\cdots)$ represent the internal molecular coordinates, and

$$H_L(\cdots x_g\cdots)\qquad\text{(C2)}$$

is the sum of the kinetic and potential energies of the intramolecular vibrations in the harmonic approximation.

Instead of (2.3), the system wave function is expanded as

$$\Psi(\mathbf{r},\cdots\mathbf{R}_g\cdots,\cdots x_g\cdots)=\sum_{g'} C_{g'}(\cdots\mathbf{R}_g\cdots)\varphi(\mathbf{r}-\mathbf{R}_{g'})\chi_{g'}{}^0(\cdots x_g\cdots),\quad\text{(C3)}$$

where $\chi_{g'}{}^0$ is a ground state vibronic wave function which will be determined later.

We also assume that the local wave functions and potentials are independent of their internal coordinates:

$$\varphi(\mathbf{r}-\mathbf{R}_g;x_g)\cong\varphi(\mathbf{r}-\mathbf{R}_g),$$
$$U(\mathbf{r}-\mathbf{R}_g;x_g)\cong U(\mathbf{r}-\mathbf{R}_g).$$

Substituting (C3) into (C1), we get

$$\sum_{g'}\varphi_{g'}x_{g'}{}^0 i\hbar\frac{\partial C_{g'}}{\partial t}=\sum_{g'}\left\{\left[\epsilon(x_{g'})+\sum_{g''\neq g}U_{g''}+H_L(\cdots\mathbf{R}_g\cdots)+H_L(\cdots x_g\cdots)\right]C_{g'}\varphi_{g'}x_{g'}{}^0-\frac{\hbar^2}{2M}(2\boldsymbol{\nabla}_{g'}C_{g'}\cdot\boldsymbol{\nabla}_{g'}\varphi_{g'}+C_{g'}\nabla_{g'}{}^2\varphi_{g'})x_{g'}{}^0\right\}.$$

We write

$$\epsilon(x_{g'})=\epsilon_0+\Delta\epsilon(x_{g'}),$$

where, in the spirit of our physical picture, $\Delta\epsilon(x_{g'})$ is taken to be linear in $x_{g'}$. This quantity then adds to $H_L(\cdots x_g\cdots)$ to give a Hamiltonian in which the (g')th oscillator vibrates about a displaced position, while the remaining oscillators remain at equilibrium, i.e.,

$$H_L(\cdots x_g\cdots)+\Delta\epsilon(x_{g'})=H_L{}^{g'}(\cdots x_g\cdots).$$

Multiplying to the left by $\varphi_g\chi_g{}^0$ and integrating over $\mathbf{r}$ and the x_g, we obtain, in place of (2.4),

$$\sum_{g'}T_{gg'}\langle\chi_g{}^0|\chi_{g'}{}^0\rangle i\hbar\frac{\partial C_{g'}}{\partial t}=\sum_{g'}\left\{[\epsilon_0C_{g'}T_{gg'}\langle\chi_g{}^0|\chi_{g'}{}^0\rangle]+\sum_{g''\neq g}\left(\int d^3r\,\varphi_gU_{g''}\varphi_{g'}\right)\cdot C_{g'}\langle\chi_g{}^0|\chi_{g'}{}^0\rangle+C_{g'}T_{gg'}\langle\chi_g{}^0|H_L{}^{g'}|\chi_{g'}{}^0\rangle\right\}-\frac{\hbar^2}{2M}\sum_{g'}\left[2\boldsymbol{\nabla}_{g'}C_{g'}\cdot\int d^3r\,\varphi_g\boldsymbol{\nabla}_{g'}\varphi_{g'}+C_{g'}\int d^3r\,\varphi_g\nabla_{g'}{}^2\varphi_{g'}\right]\langle\chi_g{}^0|\chi_{g'}{}^0\rangle.\quad\text{(C4)}$$

The $\chi_g{}^0$ are taken to be the displaced oscillator eigenfunctions of $H_L{}^g$, i.e.,

$$H_L{}^g\chi_g{}^0=E_0\chi_g{}^0,$$

where E_0 is the sum of the zero-point energy and binding energy.

Proceeding as in the text by multiplying to the left by $T_{lg}{}^{-1}$ and summing over g, it is easily seen that we obtain the normalization integral

$$\langle\chi_g{}^0|\chi_g{}^0\rangle=1$$

except for the overlap terms: Those proportional to

$(-\hbar^2/2M)$ are negligible as discussed in the text. For the second term on the right-hand side of (C4), the term $g'=g$ gives unity. However, the term $g''=g$ gives the contribution

$$J_{l,l+h}\langle\chi_l^0|\chi_{l+h}^0\rangle C_{l+h}, \tag{C5}$$

which is the only essential modification of (2.5). The vibrational overlap integral is essentially of the form[26]

$$\langle\chi_l^0|\chi_{l+h}^0\rangle=\exp\{-(E_b/\hbar\omega_0)\},$$

where E_b is the binding energy. Since one would expect that

$$E_b\lesssim\hbar\omega_0$$

the above factor is less than, but of the order of, unity. Had the analysis been carried out at finite temperatures, the above factor would essentially get replaced by[26]

$$\exp\{-(E_b/\hbar\omega_0)(1+2\bar{N})\},$$

where, however,

$$\bar{N}=(e^{\hbar\omega_0/k_0T}-1)^{-1},$$

the average number of phonons at temperature T is exponentially small. These arguments, it is felt, verify the conclusions drawn in the text.

---

[26] T. Holstein, Ann. Phys. (N. Y.) **8**, 343 (1959), Eqs. (27), (28), (33), and (37).

PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Time-Decay Characteristics of a Deep-Donor–Shallow-Acceptor Pair Band in Gallium Phosphide

D. F. NELSON AND K. F. RODGERS
Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

(Received 9 July 1965)

Characteristics of the photoluminescent time decay of a red band at 1.82 eV (20°K) in GaP crystals doped with varying amounts of the shallow acceptor Zn and the deep donor O were studied. The red-band decay is nonexponential in time, shortens with increasing zinc concentration (the concentrated dopant), is nearly independent of the oxygen concentration (the dilute dopant), is essentially constant in shape and magnitude at low temperatures, shifts to lower frequencies during decay, and is not dependent on photoconductivity during decay. These observations are in accord with the model of pair-band decay and so support the interpretation of Gershenzon *et al.* that the red band at 1.82 eV (20°K) is a Zn-O pair band.

INTRODUCTION

A NUMBER of years ago it was proposed that radiative recombination would occur between electrons trapped on donor atoms and holes trapped on acceptor atoms.[1–4] More recently, such radiation has been positively identified in GaP for shallow-donor–shallow-acceptor pairs.[5–7] The identification resulted from the observation of scores of sharp emission lines in the green which were found to obey

$$h\nu_i=E_G-E_D-E_A+e^2/\epsilon r_i, \tag{1}$$

where $h\nu_i$ is the photon energy of the ith donor-acceptor pair emission line, E_G the band gap energy, E_D and E_A the donor and acceptor binding energies, and $e^2/\epsilon r_i$ the Coulombic interaction energy of the ith pair. Since lattice sites have discrete separations, the pair separation r_i is "quantized" and so yields the many discrete emission lines. For separations greater than 40 Å the discrete lines merge into a broad band.[6]

The decay of this broad band in GaP has been studied[8–10] and found to be nonexponential in time. This has been explained by Thomas, Hopfield, *et al.*[8,9] assuming that the donors and acceptors are distributed randomly in the crystal and that the probability of radiative decay of a pair depends on the separation r as $\exp(-r/R)$, where R is comparable to half the Bohr radius of the more weakly bound one of the pair. This model is essentially the same as that proposed by Hoogenstratten[2] to explain the slow decay in ZnS. Specific predictions[8,9] of the time decay of the entire pair band have been made for the conditions of all donors and acceptors initially neutral, extreme dilution of either the donor or acceptor, and no mobility of captured electrons or holes. These predictions are that the shape and height of the decay curves will be inde-

---

[1] J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956); J. Electrochem. Soc. **103**, 342 (1956).

[2] W. Hoogenstratten, Philips Res. Rept. **13**, 515 (1958) (see Chap. 3, Secs. 11 and 12).

[3] E. F. Apple and F. E. Williams, J. Electrochem. Soc. **106**, 224 (1959).

[4] F. E. Williams, J. Phys. Chem. Solids **12**, 265 (1960).

[5] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).

[6] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).

[7] F. A. Trumbore and D. G. Thomas, Phys. Rev. **137**, A1030 (1965).

[8] D. G. Thomas, J. J. Hopfield, and K. Colbow, Symposium on Radiative Recombination, Paris, 1964 (unpublished).

[9] D. G. Thomas, J. J. Hopfield, and W. W. Augustyniak, Phys. Rev. **140**, A202 (1965).

[10] Konrad Colbow, Phys. Rev. **139**, A274 (1965).