Transport Properties of Organic Semiconductors

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(Received 8 October 1963)

Electrical and thermal transport coefficients of a large class of organic crystals are calculated from a Boltzmann equation treatment of narrow-band semiconduction. The latter, in turn, is based on the known tight-binding band structure of these crystals, and on an assumed relaxation time τ. Specifically, assuming bandwidths $\lesssim k_0 T$, explicit expressions are obtained for the electrical conductivity, Hall constant, magneto-conductivity, thermoelectric power, and thermal conductivity. These are expressed in terms of the relevant intermolecular transfer integrals and τ, for various crystallographic directions. In most cases, the results are carried out to the first order in (bandwidth/$k_0 T$). The calculated anisotropy of the electrical conductivity agrees satisfactorily with experiment. The Hall constant is found to be anomalous both in magnitude and sign. Finally, it is pointed out that the anisotropy of the thermoelectric power and magnetoconductivity can, in principle, provide information about the band structure.

I. INTRODUCTION

IN recent years, there has been considerable interest in the electrical-transport properties of organic molecular crystals. This interest derives from the fact that the nature of the charge transport in these materials is different in many important respects from that of conventional elemental and compound semiconductors. The principal distinguishing feature of these crystals is their narrow bandwidths; specifically, bandwidths[1] $\lesssim k_0 T_r$, where T_r=room temperature. As a consequence of the small overlaps, it is not evident, *a priori*, that a conventional energy-band model and Boltzmann equation treatment are applicable in describing their transport properties. In fact, it has been shown[2] that in semiconductors of sufficiently narrow bandwidth, for which the electron-lattice interaction is sufficiently strong,[3] the latter must, in effect, be taken into account before the periodic potential, giving rise to the so-called small polaron mechanism of charge transport. For this case, at sufficiently[3] high temperatures, a band model is found not to apply. Rather, the transport mechanism is a thermally activated[4] hopping motion of the charge carrier between neighboring lattice sites in which the interaction of the carrier with the lattice plays an essential role.

It is therefore somewhat surprising that there is no experimental evidence of the above mechanism in the commonly studied[5] organic crystals. Thus, although the electrical conductivity follows the standard law of semiconduction, $\sigma = \sigma_0 e^{-E_a/k_0 T}$, the temperature dependence of the mobility, as deduced from transit time[6] and Hall[7] measurements, varies typically like $\mu \sim T^{-n}$, with $3 \gtrsim n \gtrsim 1$. In particular, there is no evidence that the mobilities have an activation-type temperature dependence. The absence of self-trapping and the alternate applicability of band motion is due to the fact that the bandwidths, though $\lesssim k_0 T_r$, are not small compared to the binding energy of the excess carrier on the organic molecule-ion due to the associated lattice deformation.[2] This question is considered in Appendix A, where a numerical estimate for anthracene verifies the above conclusion.

In addition to the above two mechanisms, alternate models have been proposed[8] in which the carrier is assumed to tunnel between the potential wells of adjacent molecules. As pointed out be Keller and Rast,[8] such a model is really in the spirit of the band approximation. However, it is difficult to see how it can account for the anisotropy and relative values of the electron and hole mobilities; these features are, however, adequately accounted for by the energy-band structure. In addition, the temperature dependence of the mobility is assumed to arise due to thermal vibrations of the barrier width. As pointed out by Tredgold,[8] however, such a mechanism should lead to a mobility which is always an increasing function of temperature (though not of an activated form). This is physically reasonable, since higher temperatures should more heavily weight larger amplitude vibrations of the barrier width, thereby increasing the tunneling probability and, hence, the

[1] As will be noted later in the paper, there are variations of the calculated bandwidths to be found in the literature, some of which indicate that this inequality is weakly violated (i.e., $W \gtrsim k_0 T_r$). This point will be discussed in Ref. 23 in connection with the actual calculations.

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

[3] The meaning of these inequalities will be discussed in the next paragraph and in Appendix A.

[4] Such a mechanism may explain the thermally activated mobilities of excess holes in the transition metal oxides. See F. J. Morin, Phys. Rev. 93, 1199 (1954); and R. R. Heikes and W. D. Johnston, J. Chem. Phys. 26, 582 (1957).

[5] The most extensively studied organic semiconductor is anthracene which serves as a prototype for the present paper. Also included are a large class of related organic crystals noted in Refs. 7, 10, 11, and 30. These all share the base-centered monoclinic crystal structure. No claim is made that the band model and the methods used in the present paper will be found to apply universally to transport in organic semiconductors.

[6] R. G. Kepler, in *Organic Semiconductor Conference*, edited by J. J. Brophy and J. W. Buttrey (The Macmillan Company, New York, 1962), p. 1; O. H. Le Blanc, J. Chem. Phys. 33, 626 (1960); R. G. Kepler, Phys. Rev. 119, 1226 (1960).

[7] G. Heilmeier, G. Warfield, and S. Harrison, Phys. Rev. Letters 8, 8 (1962); temperature dependences are given for measurements on Cu-Phthalocyanine, Phys. Rev. (to be published).

[8] R. A. Keller and H. E. Rast, Jr., J. Chem. Phys. 36, 2640 (1962); and R. H. Tredgold, Proc. Phys. Soc. (London) 80, 807 (1962).

mobility. Such a temperature dependence, however, is at variance with experiment.[6] In summary, then, the present work follows the initial investigations of Le Blanc,[9] Thaxton et $al.,$[10] and Katz et $al.$[11] in assuming that the transport properties of these crystals can be explained in terms of band theory.

Intermolecular overlap[12] integrals for anthracene were first calculated by Murrell.[13] The tight-binding band structure of this material, however, was first determined by Le Blanc[8] in order to estimate the anisotropy of the drift mobility. Later calculations of this type were provided by Thaxton[9] and Katz[10] for anthracene and related organic crystals, all of which share the base-centered monoclinic crystal structure. Except for variations in the estimates of the intermolecular transfer integrals (see Ref. 1) among the above authors, this aspect of the problem is relatively straightforward due to the simplicity of the tight-binding approximation.

The more difficult problem within the band approximation is a proper treatment of the scattering. In the present paper, we follow the above-mentioned authors in assuming the existence of a constant relaxation time[14] τ. This assumption is often qualified by noting that τ may depend on $\mathbf{k}$, the electron wave vector. We must go even farther in pointing out that it is likely that, under some circumstances, the relaxation time assumption may be entirely unjustified, and that, due to the narrow bandwidths, the scattering may not be amenable to a standard, one-phonon deformation potential treatment. In this connection, it must also be shown why the anisotropy of the scattering does not have to be invoked in order to explain the drift mobility anisotropy. This problem will be considered in a future paper.

There are two important respects in which the narrow bandwidths must be taken into account. The first relates to the validity of the band picture. With the mobility μ given by[15]

$$\mu = (e/k_0T)\langle \tau v^2 \rangle \cong (e\tau/k_0T)(W^2a^2/\pi^2\hbar^2),$$

where W is the bandwidth, and a the lattice constant, energy definition of the band states requires that

$$(\hbar/\tau) < W.$$

[9] O. H. Le Blanc, J. Chem. Phys. **35**, 1275 (1961).

[10] G. D. Thaxton, R. C. Jarnagin, and M. Silver, J. Phys. Chem. **66**, 2461 (1962).

[11] J. L. Katz, S. A. Rice, S. I. Choi, and J. Jortner, J. Chem. Phys. (to be published). The author would like to thank Dr. Katz for a preprint of this work.

[12] These involve just wave-function overlap and are not the same as the intermolecular transfer (or resonance) integrals relevant to transport.

[13] J. N. Murrell, Mol. Phys. **4**, 205 (1961).

[14] Calculations based on a constant mean free path are usually carried out in addition to those based on a constant τ. In view of the fact that the calculated anisotropies of the drift mobilities are quite similar for both cases, and that, as noted below, both approximations are highly oversimplified, only a constant τ is assumed for the present calculations.

[15] H. Frohlich and G. L. Sewell, Proc. Phys. Soc. (London) **74**, 643 (1959).

Thus, a lower limit on the mobility is given by

$$\mu > \frac{ea^2}{\hbar} \frac{W}{k_0T}.$$

With $a = 3 \times 10^{-8}$ cm, one finds that[16]

$$\mu \gtrsim 0.1 \frac{W}{k_0T} \frac{\text{cm}^2}{\text{V-sec}}.$$

Hence, mobilities of the order of unity are on the borderline of a band description. Mobilities of the order of $0.1-1.0$ are in fact observed experimentally,[6] and therefore, their description by means of band motion is not in clear violation of the uncertainty relation.

Assuming the applicability of a band description and a Boltzmann equation approach, there is a second way in which the present treatment differs from the conventional semiconductor treatment. Namely, as a result of the inequality[1] $W \lesssim k_0 T_r$, the band states are almost equally populated, and, thus, the usual effective mass approximation at the appropriate band edge is inapplicable. As a consequence of this feature, the kinetic coefficients show important quantitative differences from those appropriate to the usual wide-band case $(W \gg k_0 T_r)$. These will be noted explicitly in the subsequent treatment.

The specific purpose of the present paper is to calculate the order of magnitude, sign, and anisotropy of the electrical conductivity, Hall coefficient, magnetoconductivity, thermoelectric power, and thermal conductivity of a large class of organic semiconductors which crystallize in the base-centered monoclinic structure. Assuming[1] that $W \lesssim k_0 T_r$, explicit expressions are obtained for the above coefficients in terms of the relevant band parameters (viz., intermolecular transfer integrals) and the assumed relaxation time[14] τ. In most cases, corrections to these are given in an expansion in essentially powers of $(W/k_0 T_r)$. This extends the earlier treatments[9-11] which, with but one exception,[17] have considered only the anisotropy of the drift mobility, for which only numerical estimates, based on particular values of the band parameters, have been provided. It is the success of the latter calculations in predicting the approximate magnitude and anisotropy of the drift mobility which motivated the extension of the same

[16] It is instructive to compare this condition with that applicable to the conventional wide-band case. Here, with $\mu = e\tau/m^*$, the requirement that $(\hbar/\tau) < k_0T$ leads to the condition that $\mu > (m/m^*) \times 20$ cm²/V-sec at room temperature. [cf. Eq. (3) of Ref. 15; also C. Herring, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 60.] While it is possible that $m^* > m$ so as to allow mobilities of the order of unity, $\mu \neq e\tau/m^*$ for the narrow-band case, as discussed in the text.

[17] The author has recently seen an (unpublished) Hall mobility calculation by Dr. O. H. Le Blanc which is in agreement with the results of the present paper. Dr. Le Blanc has, in addition, gone beyond the first-order corrections in (W/k_0T), and has numerically calculated the Hall mobility for $1/2 \lesssim (W/k_0T_r) < \infty$. See also Ref. 26.

techniques to the calculation of additional transport coefficients.

No claim is made that our results exhibit the correct temperature dependence. This would require a proper treatment of the scattering. However, within the limitations of the present treatment, the narrow-band feature does give rise to characteristic temperature dependences of the transport coefficients which differ from those of the wide-band case. These are noted in the subsequent sections. Finally, particular attention is called to an anomaly in the magnitude and sign of the Hall effect.[17] Namely, as found by the present author in previous studies on narrow-band semiconduction due to small polaron motion,[18] the Hall constant is augmented by $k_0 T$ divided by an "effective" bandwidth parameter. In addition, as a result of the signs of the relevant intermolecular transfer integrals, a sign reversal of the Hall constant occurs for both electrons and holes. This is described in detail later in the paper.

In view of the relatively small amount of work to date on organic semiconductor transport, it is felt that the approach of the present paper is justified in providing at least semiquantitatively correct results. It is hoped that these will provide a basis for additional investigations in this area.

II. ENERGY-BAND STRUCTURE

As discussed in the Introduction, the present work follows the approach of earlier investigations[9–11] in that the anisotropy of the transport coefficients follows solely from that of the energy-band structure. Some discussion of this aspect of the problem is therefore called for. It will be seen that previous band-structure calculations,[9,10] while essentially correct, must be clarified in detail before they can be applied to the transport calculations of the present paper.

It is well known that, due to the small overlaps characteristic of the organic crystals, the motion of the excess charge carrier can be formulated in terms of the tight-binding approximation. This was first done by Le Blanc[9] for the base-centered monoclinic unit cell shown in Fig. 1. Subsequent calculations of this type
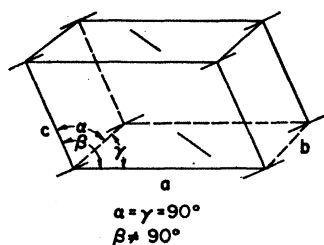

FIG. 1. Base-centered monoclinic crystal structure.

$$\alpha = \gamma = 90°$$
$$\beta \neq 90°$$

were made by Thaxton[10] and Katz.[11] The first two authors claim that, due to the identity of the molecules in the unit cell, the translational symmetry of the crystal can be characterized by a Bravais lattice with basis vectors $(a \pm b)/2$ and c. Such a basis, they claim, gives rise to a single energy band. As pointed out by Katz et al.,[11] however, this is not correct. For, in spite of the identity of the two molecules in the unit cell, the periodic potential is not invariant to a translation by $(a \pm b)/2$. This is due to the difference in orientation between the corner and base-centered molecules. This situation can be approached from two alternate, though essentially equivalent, points of view: The first, given by Katz,[11] constructs the two crystal wave functions as plane-wave superpositions of states which are essentially the symmetric and antisymmetric combinations of the molecular wave functions appropriate to the two molecules per unit cell. The corresponding eigenvalues then give the two energy bands. However, the final diagonalization of the electronic Hamiltonian is independent of the linear combinations of states which form the basis functions. Thus, alternately, the total wave function can be expanded in two Bloch sums. Using the standard procedures and approximations of tight binding, and making use of the identity of the two molecules, the diagonalization of the matrix of the coefficients of the two Bloch sums gives the two energy bands. The final result of either approach is

$$E_{\pm}(\mathbf{k}) = 2E_b \cos(\mathbf{k} \cdot \mathbf{b})$$
$$\pm 2E_\alpha \left[\cos\left(\mathbf{k} \cdot \left[\frac{\mathbf{a}+\mathbf{b}}{2} \right] \right) + \cos\left(\mathbf{k} \cdot \left[\frac{\mathbf{a}-\mathbf{b}}{2} \right] \right) \right]$$
$$\pm 2E_\gamma \left[\cos\left(\mathbf{k} \cdot \left[\frac{\mathbf{a}+\mathbf{b}}{2} + \mathbf{c} \right] \right) \right.$$
$$\left. + \cos\left(\mathbf{k} \cdot \left[\frac{\mathbf{a}-\mathbf{b}}{2} + \mathbf{c} \right] \right) \right]. \quad (2.1)$$

Here, following Le Blanc's notation, E_b, E_α, and E_γ are the intermolecular transfer integral between the molecule at the origin of the unit cell and those at relative vector positions $\mathbf{b}$, $(\mathbf{a}+\mathbf{b})/2$, and $[\mathbf{c}+(\mathbf{a}+\mathbf{b})/2]$, respectively (see Fig. 1). Katz et al. calculate the overlaps between the former molecule and all others in the unit cell. From the order of magnitudes of their results for anthracene,[19] we discard all but those retained in (2.1); this corresponds to Le Blanc's approximations. Now, some convenient simplifications of the band structure are possible for certain directions of $\mathbf{k}$ space. First, consider (2.1) in the $a^{-1}b^{-1}$ plane of reciprocal space

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[18] L. Friedman and T. Holstein, Ann. Phys. (N. Y.) 21, 494 (1963) and L. Friedman, Phys. Rev. 131, 2445 (1963). As noted in these references, the magnitude anomaly is characteristic of trigonal-like crystal structures, and obtains in a hopping as well as a band model. The base-centered monoclinic structure falls into this category.

[19] As pointed out in Ref. 5, anthracene serves as a prototype for the present calculations. For other crystals in which other resonance integrals may be appreciable, a revised band structure can be used to calculate the transport coefficients by the same methods as those used in the present paper.
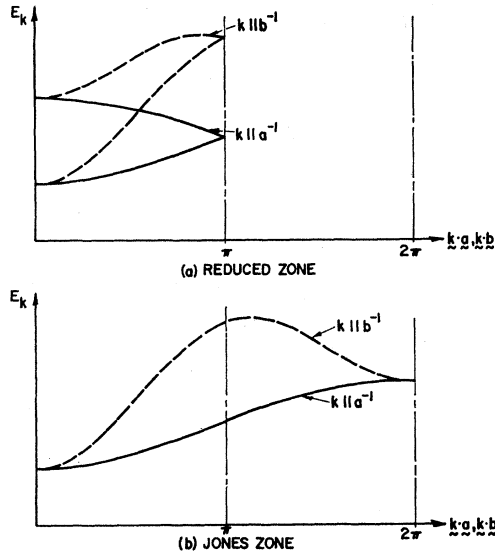
FIG. 2. Energy versus wave vector in reduced and Jones zone schemes for electrons in anthracene.

(i.e., $\mathbf{k}\cdot\mathbf{c}=0$). This can be written

$$E_{\pm}(k_a,k_b,0)=2E_b\cos(\mathbf{k}\cdot\mathbf{b})$$
$$\pm 4(E_\alpha+E_\gamma)\cos\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right). \quad (2.2)$$

In the reduced zone scheme given by $-\pi<\mathbf{k}\cdot\mathbf{a}$, $\mathbf{k}\cdot\mathbf{b}\leqslant\pi$, there are two bands corresponding to the $\pm$ signs of (2.2). The particular cases $E_{\pm}(k_a,0,0)$ and $E_{\pm}(0,k_b,0)$ are plotted in this way in Fig. 2(a). From these, it can be seen that, in both cases, the two bands are degenerate at $(\pm\pi a^{-1}, \pm\pi b^{-1})$, and that they intersect at these points with equal and opposite slopes. As a result, the upper lying bands[20] can be translated by $2\pi a^{-1}$ or $2\pi b^{-1}$ such that, in an extended "Jones zone" of twice the size (i.e., $-2\pi<\mathbf{k}\cdot\mathbf{a}$, $\mathbf{k}\cdot\mathbf{b}\leqslant 2\pi$), $E(k_a,k_b,0)$ is a single-valued function of (k_a,k_b). This is shown in Fig. 2(b). That this operation does in fact transform the $E_{\pm}(k_a,k_b,0)$ into each other can be readily verified from (2.2). Thus, (2.2) can be written

$$E(k_a,k_b,0)=2E_b\cos(\mathbf{k}\cdot\mathbf{b})+4E_\alpha\cos\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right),$$
$$-2\pi\leqslant\mathbf{k}\cdot\mathbf{a}, \mathbf{k}\cdot\mathbf{b}<2\pi, \quad (2.3)$$

in which E_γ has been dropped as a consequence of the fact that $|E_\gamma|<|E_\alpha|$, $|E_b|$. (This approximation is not valid for those cases in which E_γ makes the principal contribution to the current, corresponding to transport along the c' axis.) Also, it should be pointed out that

[20] The question of which band should be translated outside of the reduced zone is arbitrary, and does not affect the final results. This is true as long as one is not concerned with interactions or transitions among the bands in which wave vector conservation plays a role.

the above simplification of the band structure is not possible along the c^{-1} direction, as can be seen from the fact that

$$E_{\pm}(0,0,k_c)=2(E_b\pm E_\alpha)\pm 4E_\gamma\cos(\mathbf{k}\cdot\mathbf{c}).$$

Thus, at $\mathbf{k}\cdot\mathbf{c}=\pi$, there is a real gap of $4|E_\alpha|$. For this case, then, the two bands must be considered explicitly.

A final property of the band structure which will be of interest later in the paper, is the location of the absolute maximum or minimum of E_k. These are easily found from (2.3) by the simultaneous solution of $(\partial E_k/\partial k_a)=0$, $(\partial E_k/\partial k_b)=0$. In the case of electrons, for which $E_\alpha<0$, $E_b>0$, the band minimum is found to occur at $\mathbf{k}\cdot\mathbf{a}=0$, $\cos[(\mathbf{k}\cdot\mathbf{b})/2]=-E_\alpha/2E_b$, at which point the energy is found to be

$$(E_k)_{\min}=-(E_\alpha^2+2E_b^2)/(E_b). \quad (2.4)$$

In the case of the band corresponding to the highest filled binding molecular electron orbital, one has $E_\alpha\gtrsim 0$, $E_b\lesssim 0$. In an identical fashion, the band maximum is given by

$$(E_k)_{\max}=+(E_\alpha^2+2E_b^2)/(-E_b).$$

As will be discussed in connection with the Hall effect, this can be interpreted as the minimum of the hole band, thus:

$$(E_k)_{\min}^{\text{holes}}=-(E_\alpha^2+2E_b^2)/(-E_b). \quad (2.5)$$

The above band extrema are shown in Figs. 2 and 3.

Finally, it will be necessary to know the extrema for the full band structure (2.1). Since $|E_\gamma|<|E_\alpha|$, $|E_b|$, the above critical points corresponding to $(\partial E_k/\partial k_a)=(\partial E_k/\partial k_b)=0$ are assumed to be approximately unaffected. The additional condition $(\partial E_k/\partial k_c)=0$, in
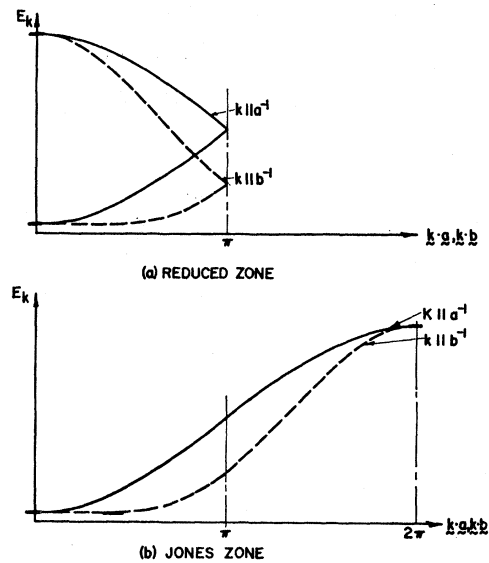

FIG. 3. Energy versus wave vector in reduced and Jones zone schemes for holes in anthracene.

conjunction with the above, then gives the minimum along the c axis at $\mathbf{k}\cdot\mathbf{c}=0$. Thus, to this approximation, (2.4) and (2.5) apply here as well.

III. SOLUTION OF THE BOLTZMANN EQUATION

As discussed in the Introduction, the present approach is based on the solution of the Boltzmann transport equation for an anisotropic energy band, assuming the existence of a constant relaxation time. For the case of applied electric and magnetic fields, the solution is given by the well-known method of Jones and Zener,[21] and has been described by the present author for the narrow-band limit in the case of small polaron band motion.[18]

In the general case of applied dc electric and magnetic fields and a nonvanishing temperature gradient, the steady-state Boltzmann equation reads:

$$0 = -\mathbf{v}_k \cdot \mathrm{grad}_r f_k + \frac{e}{\hbar}\left(\mathbf{F} + \frac{1}{c}[\mathbf{v}_k \times \mathbf{H}]\right)$$
$$\cdot \mathrm{grad}_k f_k - \frac{f_k - f_k^{(B)}}{\tau}, \quad (3.1)$$

where $f_k^{(B)}$ is the Boltzmann distribution function, $\mathbf{F}$ and $\mathbf{H}$ are the external electric and magnetic fields, $\mathbf{v}_k = \hbar^{-1}\,\mathrm{grad}_k E_k$ is the velocity of an electron in Bloch state $\mathbf{k}$, where E_k is given by (2.1) or (2.3), and τ is the relaxation time. The solutions of (3.1) for various choices of applied fields are straight-forward and well known. We therefore simply summarize the final results for the transport coefficients. Their explicit solutions for the energy-band structure (2.1) in the narrow-band limit, will be given in the next section.

Electrical Conductivity

For the case of an applied electric field, the diagonal elements of the conductivity tensor are given by

$$\sigma_{ii}^{(0)} = \frac{e^2\tau}{\hbar^2} \frac{1}{k_0T} \frac{2}{(2\pi)^3} \int d^3k \left(\frac{\partial E_k}{\partial k_i}\right)^2 f_k^{(B)}, \quad (3.2)$$

where the superscript (0) denotes that σ is of zeroth order in H, and the indicated integration is over the Brillouin zone.

Hall Effect

In this case, only $\mathrm{grad}_r f_k = 0$ in (3.1). Making the substitution

$$f_k = f_k^{(B)} - \phi_k(\partial f_k^{(B)}/\partial E_k), \quad (3.3)$$

the Jones-Zener method[21] develops ϕ_k in powers of the magnetic-field strength. To first order in H, we get

$$\phi_k^{(1)} = (e^2\tau^2/\hbar^3c)\mathbf{H}\cdot[\mathrm{grad}_k E_k \times \mathrm{grad}_k(\mathbf{F}\cdot\mathrm{grad}_k E_k)]. \quad (3.4)$$

[21] See, for example, A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1958), 2nd ed., p. 224.

We will be interested in the case where H is along the c' axis; Eq. (3.4) then takes the form

$$\phi_k^{(1)} = \frac{e^2\tau^2H}{\hbar^3c}\left(\frac{\partial E_k}{\partial k_a}\frac{\partial}{\partial k_b} - \frac{\partial E_k}{\partial k_b}\frac{\partial}{\partial k_a}\right)$$
$$\times\left(F_a\frac{\partial E_k}{\partial k_a} + F_b\frac{\partial E_k}{\partial k_b}\right). \quad (3.5)$$

The magnetic-field-dependent part of the current is then given by

$$\mathbf{j}^{(1)} = -\frac{e^3\tau^2H}{\hbar^3c}\frac{1}{k_0T}\frac{2}{(2\pi)^3}\int d^3k\,\mathbf{v}_k\phi_k^{(1)}f_k^{(B)}. \quad (3.6)$$

This expression will be applied in the next section to calculate the Hall effect.

Magnetoconductivity

In order to find the change in conductivity upon application of the magnetic field, one must determine ϕ_k to order H^2. Iterating the Boltzmann equation (3.1) a second time,[21] one gets that

$$\phi_k^{(2)} = -\frac{e\tau}{\hbar^2c}H\left[(E_k)_a\frac{\partial}{\partial k_b} - (E_k)_b\frac{\partial}{\partial k_a}\right]\phi_k^{(1)}, \quad (3.7)$$

where H is again taken along c', $\phi_k^{(1)}$ is given by (3.5), and the partial derivatives are abbreviated by, e.g., $(E_k)_a \equiv (\partial E_k/\partial k_a)$, etc. Substituting (3.5) into (3.7) and carrying out the indicated differentiations, one gets

$$\phi_k^{(2)} = -(e^3\tau^3H^2/\hbar^5c^2)\{F_a[(E_k)_a(E_k)_{bba}$$
$$+(E_k)_a(E_k)_{ba}^2 - 2(E_k)_a(E_k)_b(E_k)_{baa}$$
$$-(E_k)_a(E_k)_{bb}(E_k)_{aa} + (E_k)_b^2(E_k)_{aaa}]$$
$$+F_b[(E_k)_a^2(E_k)_{bbb} + (E_k)_b^2(E_k)_{aba}$$
$$-2(E_k)_a(E_k)_b(E_k)_{bab}$$
$$-(E_k)_b(E_k)_{aa}(E_k)_{bb} + (E_k)_b(E_k)_{ab}^2]\}, \quad (3.8)$$

which is the basis for the magnetoconductivity calculation given in the next section.

Thermoelectric Power

Taking the applied electric field and thermal gradient along the ith crystallographic direction, (3.1) may be readily solved for f_k. From this, one gets the standard expressions for the electronic and thermal currents, given, respectively, by

$$j_i = \left(\frac{eF_i}{k_0T} + \frac{\partial}{\partial x_i}\ln A\right)K_1^i + \frac{e}{k_0T}\left(\frac{\partial}{\partial x_i}\ln T\right)K_2^i, \quad (3.9)$$

and

$$w_i = -\left(\frac{eF_i}{k_0T} + \frac{\partial}{\partial x_i}\ln A\right)K_2^i - \frac{1}{k_0T}\left(\frac{\partial}{\partial x_i}\ln T\right)K_3^i. \quad (3.10)$$

Here, A is the normalization constant for the Boltzmann distribution function, and

$$K_s{}^i = \frac{2}{(2\pi)^3} \int d^3k \tau (v_k)_i{}^2 E_k{}^{s-1} f_k{}^{(B)} \qquad (3.11)$$

are the standard transport integrals for a nondegenerate carrier distribution. In the above integrals, E_k is understood to mean the carrier kinetic energy, and is therefore measured from the relevant band minimum (or downward from the band maximum, in the case of hole conduction).

To obtain the absolute thermoelectric power, one solves Eq. (3.9) under the constraint that $j_i = 0$, giving

$$S^i \equiv \left(\frac{F_i}{\partial T/\partial x_i}\right)_{j_i=0} = -\frac{1}{eT}\frac{K_2{}^i}{K_1{}^i} - \frac{k_0 T}{e}\frac{\partial \ln A}{\partial T},$$

where it be recalled that e is positive (i.e., the charges on the electron is $-e$). Taking $A = e^{\zeta/k_0 T}$, where ζ is the Fermi level,[22] the previous equation becomes

$$S^i = -(eT)^{-1}[(K_2{}^i/K_1{}^i) - \zeta], \qquad (3.12)$$

which is the result we shall apply.

Thermal Conductivity

Solving (3.9) and (3.10) under the constraint that $j_i = 0$, one readily finds that the thermal conductivity is given by the standard expression

$$\kappa^i = \frac{w_i}{(-\partial T/\partial x_i)} = \frac{1}{k_0 T^2} K_1{}^i \left[\left(\frac{K_3{}^i}{K_1{}^i}\right) - \left(\frac{K_2{}^i}{K_1{}^i}\right)^2 \right]. \qquad (3.13)$$

As in the case of the thermoelectric power, the K_s will be found to differ from their wide-band counterparts, leading to important differences in the thermal conductivity. These will be considered in the next section.

IV. EXPLICIT TRANSPORT CALCULATIONS

In the present sections, the energy-band structures given by (2.3) and (2.1) will be substituted into Eqs. (3.2), (3.6), (3.8), (3.12), and (3.13) in order to find the transport coefficients along the various crystallographic directions of interest. As pointed out in the Introduction, we make what is essentially a high-temperature approximation such that the final results are expressed as a power series[23] in the intermolecular integrals divided by

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$k_0 T$. Only the first such correction terms will be calculated.

Electrical Conductivity

Conductivity in the ab Plane

Some simplification of this case is possible due to the circumstance[9–11] that $|E_\gamma| \ll |E_\alpha|$, $|E_b|$, and, thus, the band structure (2.3) can be used to a first approximation.

The constant A of the equilibrium Boltzmann distribution is readily found from normalization requirements, and is given by

$$A = (nab/8)[1 + O(W/k_0 T)^2 + \cdots]. \qquad (4.1)$$

From (3.2), one has

$$\sigma_{aa}{}^{(0)} = \frac{e^2 \tau}{\hbar^2}\frac{1}{k_0 T} 4E_\alpha{}^2 a^2 \frac{nab}{8}\frac{2}{(2\pi)^2}\int_{-2\pi/a}^{2\pi/a} dk_a \int_{-2\pi/b}^{2\pi/b} dk_b$$

$$\times \sin^2\left(\frac{k_a a}{2}\right)\cos^2\left(\frac{k_b b}{2}\right)$$

$$\times \left\{1 - \frac{4E_\alpha}{k_0 T}\cos\left(\frac{k_a a}{2}\right)\cos\left(\frac{k_b b}{2}\right)\right.$$

$$\left. - \frac{2E_b}{k_0 T}\cos(k_b b) + \cdots\right\}. \qquad (4.2)$$

The required integrals are simple averages of trigonometric functions. The result is

$$\sigma_{aa}{}^{(0)} = ne^2 \tau \frac{E_\alpha{}^2 a^2}{(k_0 T)\hbar^2}\left\{1 - \frac{E_b}{k_0 T} + \cdots\right\}. \qquad (4.3)$$

The factor $k_0 T/v_a{}^2$, where $v_a = (E_\alpha a/\hbar)$ is a characteristic velocity, properly has the dimensions of mass.[24] The inverse temperature dependence of Eq. (4.3) and subsequent transport coefficients is simply a reflection of the fact that, in the limit of infinite temperature, the band states are equally populated, and, hence, the currents must vanish.

In an identical fashion, one also gets

$$\sigma_{bb}{}^{(0)} = ne^2 \tau \frac{(E_\alpha{}^2 + 2E_b{}^2)b^2}{(k_0 T)\hbar^2}$$

$$\times \left\{1 - \frac{E_b}{k_0 T}\left(\frac{3E_\alpha{}^2}{E_\alpha{}^2 + 2E_b{}^2}\right) + \cdots\right\}. \qquad (4.4)$$

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[22] The Fermi level ζ is to be measured from the relevant band minimum, and is large and negative, just as in the conventional semiconductor situation. The actual location of ζ, of course, depends on whether the material is intrinsic or extrinsic, the nature of the trap distribution in the forbidden gap, etc.

[23] This assumption permits us to obtain results in analytic form. As to its validity, Refs. 9 and 10 obtain $W = 0.56 k_0 T_r$. Reference 11, however, uses an alternate set of molecular orbitals which are more accurate at the large distances which make the dominant contribution to the overlaps. From these, they obtain results approximately 5 times as large, and this inequality is thereby violated. Assuming this to be the case, it is first to be noted that

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the actual condition required in expanding the Boltzmann factors is $E_k < k_0 T_r$, for each k in the zone. Hence, while $E_k = W$ at the band maximum, the above condition is more nearly satisfied for the other points in the zone whose contributions are summed. In addition, unless $W \gg k_0 T_r$, the results would be expected to be changed only by numerical factors without changing their characteristic features.

[24] It is to be re-emphasized that this is clearly not the effective mass which would be obtained by expanding E_k to order k^2 about the band edge.

The anisotropy of the conductivity in the ab plane is given by

$$\sigma_{xx}{}^{(0)} = \sigma_{aa}{}^{(0)} + (\sigma_{bb}{}^{(0)} - \sigma_{aa}{}^{(0)}) \sin^2\phi(x,a), \quad (4.5)$$

where $\phi(x,a)$ is the angle that an arbitrary x direction makes with the a axis, and $\sigma_{aa}{}^{(0)}$ and $\sigma_{bb}{}^{(0)}$ are given by (4.3) and (4.4), respectively.

Conductivity Along the c Axis

It is simplest first to calculate the conductivity along the c axis, and later infer [cf. Sec. V] the c' axis conductivity of experimental interest.

For this case, the entire contribution comes from overlap in the direction normal to the ab plane. Thus, the E_γ-proportional term in (2.1) cannot be neglected. The full-band structure (2.1) is rewritten in the form

$$E(\mathbf{k}) = 2E_b \cos(\mathbf{k}\cdot\mathbf{b}) \pm 4E_\alpha \cos\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right)$$

$$\pm 4E_\gamma \cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right)\left[\cos\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos(\mathbf{k}\cdot\mathbf{c})\right.$$

$$\left. - \sin\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\sin(\mathbf{k}\cdot\mathbf{c})\right]. \quad (4.6)$$

Now, with the electric field along the c axis, $\mathbf{F} = \hat{c}F_c$,

$$\phi_k{}^{(0)} = -\frac{e\tau}{\hbar}F_c\hat{c}\cdot\left[\hat{a}^{-1}\frac{\partial E_k}{\partial k_a} + \hat{b}^{-1}\frac{\partial E_k}{\partial k_b} + \hat{c}^{-1}\frac{\partial E_k}{\partial k_c}\right]$$

$$= -\frac{e\tau}{\hbar}F_c\frac{\partial E_k}{\partial k_c}.$$

From Eq. (4.6), one gets

$$\frac{\partial E(\mathbf{k})}{\partial k_c} = \mp 4E_\gamma c \cos\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right)\left[\sin\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\cos(\mathbf{k}\cdot\mathbf{c})\right.$$

$$\left. + \cos\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right)\sin(\mathbf{k}\cdot\mathbf{c})\right], \quad (4.7)$$

from which it follows that $(v_k)_c{}^2$ contributions to the integrand of (3.2) are identical for both bands, except for the sign of the Boltzmann factors. Substituting (4.7) into (3.2), one gets

$$\sigma_{cc}{}^{(0)} = ne^2\tau\frac{8E_\gamma{}^2c^2}{(k_0T)\hbar^2}\left\{1 - \frac{E_b}{k_0T} + \cdots\right\}. \quad (4.8)$$

Hall Effect

Magnetic Field Along the c' Axis

For this case, we again use the approximate band structure given by (2.3). For definiteness, we first take the drift current in the b direction, and calculate that

part of j_a which is linearly proportional to H. Under these conditions, (3.6) can be written

$$j_a = \sigma_{ab}{}^{(1)}F_b, \quad (4.9)$$

where

$$\sigma_{ab}{}^{(1)} = -\frac{e^3\tau^2}{c}\frac{1}{k_0T}\frac{2}{(2\pi)^2}H$$

$$\times \iint dk_a dk_b (v_a{}^2 M_{bb}{}^{-1} - v_a v_b M_{ab}{}^{-1})f_k{}^{(B)} \quad (4.10)$$

is an off-diagonal element of the conductivity tensor, and

$$M_{ij}{}^{-1} = \hbar^{-2}(\partial^2 E_k/\partial k_i \partial k_j) \quad (4.11)$$

is the inverse effective mass tensor as a function of k.

Carrying out the integrals, we get

$$\sigma_{ab}{}^{(1)} = \frac{ne^3\tau^2}{(k_0T)\hbar^4 c}\frac{3}{2}E_\alpha{}^2 E_b a^2 b^2\left[1 + O\left(\frac{E_i{}^2}{k_0T}\right)^2 + \cdots\right], \quad (4.12)$$

there being no first-order corrections.

At this point, one can infer the sign of the Hall effect.[17] In zero magnetic field, the current is given by $j_b{}^{(0)} = \sigma_{bb}{}^{(0)}F_b$. Considering first the case of electrons, explicit calculations[9-11] show that, as a result of the particular phases of the Hückel coefficients which characterize the electron distribution over the anthracene molecule,[10] and the difference in sign of the π_z orbitals which overlap in the b direction, E_b is positive. From (4.12) and (4.9), it follows that $j_a{}^{(1)}$ is positive. Hence, the *current* is rotated in the clockwise sense by the magnetic field, and the Hall angle is negative. However, from a classical Lorentz force argument, one can easily convince oneself that the electron *current* should normally be rotated in the counterclockwise sense, i.e., that the Hall angle should be positive. The sign of the Hall effect is therefore reversed for this case. In the conventional wide-band situation, positive contributions to the effective mass are strongly weighted by the Boltzmann factor centered about the band minimum. In the present narrow-band situation, however, with the band states almost equally populated, it turns out that the negative mass contributions $(M_{bb}{}^{-1})$ are more heavily weighted by the transverse velocity $(v_a{}^2)$, leading to the sign reversal. Physically, as result of the inversion of the E_b-proportional part of the band structure, carriers in those k states which are accelerated oppositely the direction of electric force undergo a larger Lorentz deflection than those accelerated in the normal direction, to an extent sufficient to establish the sign reversal.

From the following considerations, it also follows that the Hall effect is reversed in the case of hole conduction: Explicit calculations of the intermolecular overlaps integrals appropriate to an electron in the highest bonding orbital of the neutral anthracene molecule

show that E_b is negative. These band states are entirely occupied according to a Fermi distribution, except for a vacancy in the state of highest energy which, as discussed in Sec. II, occurs at $\mathbf{k \cdot a} = 0$, $\cos[(\mathbf{k \cdot b})/2] = E_\alpha/2E_b$. In order to make use of the methods of the present paper, the above band structure must be reinterpreted in terms of a nondegenerate distribution of holes.[25] To this end, two changes are required: (1) the sign of the charge must be reversed (i.e., $e \rightarrow -e$ in the previous formula), and (2) the sign of the band structure (2.2) must be changed (in effect, E_α, $E_b \rightarrow -E_\alpha$, $-E_b$). This latter change simply means that the hole energy is measured downward from the electron-band maximum. As a check, one can see that, in the wide-band limit, the band maxima for electrons would be properly characterized by a positive effective mass for holes. Having arrived at the proper sign of E_α and E_b in this fashion, the effective-mass concept is of no use in dealing with the narrow-band situation, and is discarded.

To complete the argument, it can be seen that, with the changes $e \rightarrow -e$, E_b (negative) $\rightarrow E_b$ (positive), Eq. (4.12) and hence $j_b^{(1)}$ are negative, for the given orientation of fields. Thus, the Hall angle is positive. For carriers of positive charge and mass, however, conventional Lorentz force arguments lead to a negative Hall angle. Hence, the Hall effect for holes is also reversed in sign.

As can be seen from the above arguments, the question of the sign of the Hall effect depends crucially on the sign of E_b. This, in turn, depends on the relative phases of the Hückel coefficients which make the dominant contribution to the overlap. As can be seen from the calculations,[9,10] this feature varies from crystal to crystal. Thus, each material must be individually examined in this respect before any conclusions can be drawn.

To summarize, the current-field equations

$$j_a = \sigma_{aa}^{(0)} F_a + \sigma_{ab}^{(1)} F_b,$$

$$j_b = \sigma_{ba}^{(1)} F_a + \sigma_{bb}^{(0)} F_b,$$

under the constraint

$$j_a = 0,$$

can be solved in order to obtain the Hall constant. To $O(H')$, one gets

$$R_{ab} = H^{-1}(\sigma_{ab}^{(1)}/\sigma_{aa}^{(0)}\sigma_{bb}^{(0)}). \qquad (4.13)$$

Substituting Eqs. (4.3), (4.4), and (4.12) into Eq. (4.13), one obtains

$$R_{ab} = \frac{1}{nec}\frac{3}{2}\frac{k_0T}{(E_\alpha^2+2E_b^2)/E_b}$$

$$\times\left[1+\frac{2E_b}{k_0T}\frac{2E_\alpha^2+E_b^2}{E_\alpha^2+2E_b^2}+\cdots\right], \qquad (4.14)$$

[25] This result has been checked by doing the integrals for a Fermi distribution of electrons assuming that $(\zeta-E_k)/k_0T \gg 1$.

which, as discussed, is positive for $E_b > 0$, $e \rightarrow e$ (electrons) and negative for $E_b > 0$, $e \rightarrow -e$ (holes).

To check this result, we have taken the drift current along the a axis and have calculated the contribution to the current along b which is linearly proportional to H, i.e.,

$$j_b^{(1)} = \sigma_{ba}^{(1)} F_a,$$

where

$$\sigma_{ba}^{(1)} = -\frac{e^3\tau^2}{c}\frac{1}{k_0T}H\frac{2}{(2\pi)^2}$$

$$\times\int\int dk_a dk_b(v_a v_b M_{ba}^{-1}-v_b^2 M_{aa}^{-1})f_k^{(B)}. \qquad (4.15)$$

[Compare with (4.10)].

The explicit calculation of (4.15) gives

$$\sigma_{ba}^{(1)}(H) = -\sigma_{ab}^{(1)}(H), \qquad (4.16)$$

where $\sigma_{ab}^{(1)}$ is given by (4.12). This verifies the Onsager relations for this case,[26] and provides a check on our result.

In conclusion, we mention that the resonance integrals have implicitly been taken as unaffected by the applied magnetic field. This can be justified by the fact that, although the (nondegenerate) π_z orbital will acquire a first-order correction in H, it can be shown that for potentials which have inversional symmetry, the corresponding first-order corrections to the resonance integrals exactly cancel. Second-order corrections are irrelevant to the Hall effect.

Transverse Magnetoconductivity (Representative Calculation)

The question of principal interest here is how the magnetoconductivity in the narrow-band case compares with that of the conventional situation. Since the ordinary, zeroth order, mobilities are themselves small, we investigate this question for a case in which the electron drift mobility is itself a maximum: namely, we calculate the fractional change in conductivity in the a direction due to application of the magnetic field along c'.

Since, operationally, the current along the b axis must vanish (i.e., $j_b = 0$), the Hall field F_b can be eliminated from the current-field equations

$$j_a = \sigma_{aa}F_a + \sigma_{ab}F_b,$$

$$j_b = \sigma_{ba}F_a + \sigma_{bb}F_b, \qquad (4.17)$$

giving

$$j_a = \left(\sigma_{aa}^{(0)}+\sigma_{aa}^{(2)}-\frac{\sigma_{ab}^{(1)}\sigma_{ba}^{(1)}}{\sigma_{bb}^{(0)}}\right)F_a, \qquad (4.18)$$

where the magnetic-field dependences of the σ's are

[26] The expression used by Le Blanc (cf. Ref. 17) involves essentially the symmetrized quantity $[\sigma_{ab}^{(1)}(H)+\sigma_{ba}^{(1)}(-H)]/2$. The present work, however, explicitly verifies the Onsager relation for the narrow-band case.

noted. The fractional change in σ_{aa}, to order H^2, is then

$$\frac{\Delta\sigma_{aa}}{\sigma_{aa}{}^{(0)}}=\left(\sigma_{aa}{}^{(2)}-\frac{\sigma_{ab}{}^{(1)}\sigma_{ba}{}^{(1)}}{\sigma_{bb}{}^{(0)}}\right)\Big/\sigma_{aa}{}^{(0)}, \quad (4.19)$$

where $\sigma_{ab}{}^{(1)}$ and $\sigma_{ba}{}^{(1)}$ are given by (4.12) and (4.16), and it remains to calculate $\sigma_{aa}{}^{(2)}$. To this end, one has that

$$j_a{}^{(2)}=-e\frac{1}{k_0T}\frac{2}{(2\pi)^2}\int\int dk_a dk_b\frac{(E_k)_a}{\hbar}\phi_k{}^{(2)}f_k{}^{(B)}, \quad (4.20)$$

where $\phi_k{}^{(2)}$ is given by (3.8). The integrations are somewhat laborious, but straightforward. Neglecting variations in the Boltzmann factor, the result is

$$\sigma_{aa}{}^{(2)}=-\frac{ne^4\tau^3}{\hbar^6c^2}\frac{1}{k_0T}\frac{E_\alpha{}^2a^2b^2}{2}(E_\alpha{}^2+E_b{}^2). \quad (4.21)$$

Substituting (4.21), (4.15), (4.16), and (4.3) into (4.19), one gets

$$\frac{\Delta\sigma_{aa}}{\sigma_{aa}{}^{(0)}}=-\frac{e^2\tau^2H^2}{\hbar^4c}a^2b^2\left[(E_\alpha{}^2+E_b{}^2)-\frac{9}{4}\frac{E_\alpha{}^2E_b{}^2}{E_\alpha{}^2+2E_b{}^2}\right]. \quad (4.22)$$

Equation (4.22) is dimensionally of the form

$$(\Delta\sigma/\sigma)\approx-(\omega_c\tau)^2, \quad (4.23)$$

where

$$\omega_c\approx eH/\langle M\rangle c$$

is an "effective" cyclotron frequency,

$$\langle M\rangle\approx\hbar^2/\langle W\rangle a^2$$

has dimensions of mass,[24] and $\langle W\rangle$ is of the order of the bandwidth.

Now, for the normal semiconductor situation, according to Wilson,[27] the result is generally of the form

$$BH^2\approx\frac{\sigma_0{}^2}{(2nec)^2}H^2\approx\left(\frac{eH}{m^*c}\tau\right)^2, \quad (4.24)$$

where m^* is the conventional effective mass. Comparing (4.23) with (4.24), and taking $\langle W\rangle\approx k_0T_r$, one sees that the magnetoconductivity of the narrow-band case is smaller than the standard result by a factor of

$$(m^*/\langle M\rangle)^2\sim10^{-4}.$$

The experimental problem is therefore one of measuring a very small fractional change in a conductivity which is small to begin with, and is therefore probably undetectable.

Thermoelectric Power

In comparison with the Hall effect, the measurement of the anisotropy of the thermoelectric power appears to

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[27] See Refs. 21, p. 216. An additional contribution to the magnetoconductivity, namely the magnetic-field corrections to the resonance integrals (via the molecular wave functions) has been omitted in the present (representative) treatment.

be an even more direct way of obtaining information about the sign of the carriers, the intermolecular resonance integrals, and the Fermi level. The calculation of the thermoelectric power for the narrow-band case follows from (3.12), where the K_ss are given by (3.11).

Before turning to the actual calculations, however, particular attention must be paid to a feature which has been overlooked up to this point: namely, the question of the choice of the zero of energy. In the earlier transport integrals, the band velocities and masses were unaffected by this arbitrariness, while that of the Boltzmann factor was taken up in the normalization. However, the K_s's contain the kinetic energies explicitly, and it is clear that these are to be measured from the electron- and hole-band minima. These, in turn, were calculated at the end of Sec. II, and are given by (2.4) and (2.5), respectively.

We are now in a position to calculate the thermoelectric powers due to applied thermal gradients along the various crystallographic directions. We give only the final results.

Thermal Gradient Along the b Axis

Substituting (2.3), (2.4), (2.5), and (3.11) into (3.12), we get

$$S^{(b)}=-\frac{1}{eT}\left[\frac{3E_\alpha{}^2E_b}{E_\alpha{}^2+2E_b{}^2}\left(1-\frac{5}{3}\frac{E_b}{k_0T}\frac{E_\alpha{}^2+2E_b{}^2}{E_b{}^2}\right.\right.$$
$$\left.\left.+\frac{E_b}{k_0T}\frac{3E_\alpha{}^2}{E_\alpha{}^2+2E_b{}^2}+\cdots\right)+\frac{E_\alpha{}^2+2E_b{}^2}{E_b}-\zeta\right], \quad (4.25)$$

where ζ is also to be measured from the band minimum. Since $E_b>0$ for both electrons and holes, the only dependence of (4.25) on the type of carrier is via the sign of e (i.e., $e\rightarrow-e$ for holes).

Thermal Gradient Along the a Axis

The result here is somewhat simpler than the previous one, namely,

$$S^{(a)}=-\frac{1}{eT}\left[E_b\left(1-\frac{E_b}{k_0T}\frac{3E_\alpha{}^2+E_b{}^2}{E_b{}^2}+\cdots\right)\right.$$
$$\left.+\frac{E_\alpha{}^2+2E_b{}^2}{E_b}-\zeta\right]. \quad (4.26)$$

Thermal Gradient Along the c' Axis

This calculation leads to the somewhat surprising result that $S^{(c')}$ is independent of E_γ, neglecting possible higher order corrections in (E_γ/k_0T). It is found that

$$S^{(c')}=-\frac{1}{eT}\left(2E_b+\frac{E_\alpha{}^2+2E_b{}^2}{E_b}-\zeta\right). \quad (4.27)$$

In comparing (4.25), (4.26), and (4.27) with the standard thermoelectric power of a semiconductor,[28]

$$S = -e^{-1}(2k_0 - \zeta/T),$$

one sees that the last term is the same for both cases. The first terms, however, give the "diffusion" contribution due to the kinetic energy of band motion, and are different. The difference is clearly that k_0T of the wide-band result gets replaced by an appropriate bandwidth parameter. This contribution is therefore reduced from the standard value by an "effective" bandwidth divided by k_0T.

As in the standard semiconductor case, ζ is large and negative, and makes the dominant contribution to the thermoelectric power. In order to infer the bandwidths, however, it would be necessary to subtract $TS^{(i)}$ along two crystal directions (this should eliminate both ζ and the band minimum energy) in the limit of high temperatures. Due to the fact that this remainder will be small compared to the measured values, this procedure may be difficult in practice.

Thermal Conductivity

In order to calculate the electronic contribution to the thermal conductivity from (3.13), we need K_1, K_2, and K_3, where K_S is given by (3.11). It conveniently turns out that the energy-band minima exactly cancel in the two terms of (3.13), and, therefore, need not be of concern.

Thermal Gradient Along the a Axis

From (3.11), it is found that

$$K_1^{(a)} = n\tau E_\alpha^2 a^2/\hbar^2, \quad K_2^{(a)} = E_b K_1^{(a)},$$
$$K_3^{(a)} = (3E_\alpha^2 + 2E_b^2)K_1^{(a)}. \quad (4.28)$$

Substituting (4.28) into (3.13), it is found that

$$\kappa^{(a)} = \frac{1}{k_0 T^2} \frac{n\tau E_\alpha^2 a^2}{\hbar^2}(3E_\alpha^2 + E_b^2), \quad (4.29)$$

which, for dimensional purposes, is recast in the form

$$\kappa^{(a)} = n(\langle v_a \rangle \tau)(k_0^3 T/\langle M_a \rangle)^{1/2}$$
$$\times [(3E_\alpha^2 + E_b^2)/(k_0 T)^2], \quad (4.30)$$

where

$$\langle v_a \rangle = (E_\alpha a/\hbar)$$

is the characteristic band velocity, and

$$\langle M_a \rangle \equiv k_0 T/\langle v_a \rangle^2$$

has the dimensions of mass.

This may be compared with the result for a con-

ventional nondegenerate semiconductor,[29]

$$\kappa = (4/3)nl(2k_0^3 T/\pi m)^{1/2}, \quad (4.31)$$

where l is an assumed constant mean free path.

The narrow-band result (4.30) is smaller than (4.31) due to three factors: (1) $\langle v_a \rangle \tau < l$ of a normal semiconductor, (2) $\langle M_a \rangle > m$, and (3) $(3E_\alpha^2 + E_b^2) \gtrsim (k_0 T)^2$. Also, it is noted that in the narrow-band limit, $\kappa^{(a)} \sim T^{-2}$.

Thermal Gradient Along the b Axis

This calculation is identical to the previous one. One has

$$K_1^{(b)} = n\tau(E_\alpha^2 + 2E_b^2)b^2/\hbar^2,$$
$$K_2^{(b)} = (3E_\alpha^2 E_b/E_\alpha^2 + 2E_b^2)K_1^{(b)},$$
$$K_3^{(b)} = 5E_\alpha^2 K_1^{(b)},$$

from which one gets

$$\kappa^{(b)} = \frac{1}{k_0 T^2} \frac{n\tau(E_\alpha^2 + 2E_b^2)b^2}{\hbar^2}$$
$$\times \left\{ E_\alpha^2 \left[5 - \left(\frac{3E_\alpha E_b}{E_\alpha^2 + 2E_b^2} \right)^2 \right] \right\}. \quad (4.32)$$

The previous comments, of course, apply to this case as well.

V. COMPARISON WITH EXPERIMENT

To date, experimental information on the transport properties of organic crystals is confined almost entirely to determinations of the drift mobilities of electrons and holes in anthracene by means of pulsed photoconductivity techniques.[6] Numerical estimates of these mobilities, by methods quite similar to those used in the present paper, have agreed well with experiment.[9-11] In this section, we wish to show that the explicit expressions obtained for the conductivity tensor also exhibit approximately the correct anisotropy. This, it is felt, establishes some confidence in the thermal and galvanomagnetic coefficients which are calculated by identical methods. Their verification, however, must be left to future experiments.

Conductivity Anisotropy in the ab Plane

Neglecting the correction terms, (4.3) and (4.4) give

$$\frac{\sigma_{aa}^{(0)}}{\sigma_{bb}^{(0)}} = \frac{E_\alpha^2}{E_\alpha^2 + 2E_b^2} \frac{a^2}{b^2}. \quad (5.1)$$

Holes

Taking[9] $E_\alpha = 23.7 \times 10^{-16}$ ergs, $E_b = 25.4 \times 10^{-16}$ ergs, $a = 8.56$ Å, $b = 6.04$ Å, (5.1) gives

$$\sigma_{aa}^{(0)}/\sigma_{bb}^{(0)} \cong 0.6 \text{ (holes)}. \quad (5.2)$$

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[28] See Ref. 21, p. 119.

[29] See Ref. 21, p. 232. The lack of consistency in comparing our constant τ result with one assuming a constant l, is not considered serious for these initial investigations.

Katz's[11] larger values of E_a and E_b give approximately the same ratio (E_a/E_b) as given by the above values, and, hence, would not change (5.2) significantly.

Measurements by Kepler[6] give

$$\sigma_{aa}^{(0)}/\sigma_{bb}^{(0)} \approx 0.5, \tag{5.3}$$

in good agreement with the above prediction.

Electrons

Taking $E_a = -31.6 \times 10^{-16}$ ergs, $E_b = +19.3 \times 10^{-16}$ ergs, (5.1) gives

$$\sigma_{aa}^{(0)}/\sigma_{bb}^{(0)} = 1.2. \tag{5.4}$$

The experimental results,[6] however, give

$$\sigma_{aa}^{(0)}/\sigma_{bb}^{(0)} = 1.7, \tag{5.5}$$

the agreement here not being as satisfactory as in the case of holes. The above two estimates do, however, correctly predict that electrons are more mobile along the a axis and holes more mobile along the b axis.

Anisotropy Along the c' Axis

From (4.8), (4.3), and (4.4), and some simple geometrical considerations, one can readily verify that

$$\frac{\sigma_{c'c'}^{(0)}}{\sigma_{bb}^{(0)}} = \left[\left(\frac{\sigma_{cc}^{(0)}}{\sigma_{bb}^{(0)}}\right)^2 \csc^2\beta - \left(\frac{\sigma_{aa}^{(0)}}{\sigma_{bb}^{(0)}}\right)^2 \cot^2\beta\right]^{1/2} \tag{5.6}$$

For the case of holes, taking $E_a = 23.7 \times 10^{-16}$ ergs, $E_b = 25.4 \times 10^{-16}$ ergs, $E_\gamma = -5.25 \times 10^{-16}$ ergs; $b = 6.04$ Å, $c = 11.16$ Å, $\beta = 124.7°$, (5.6) gives

$$\sigma_{c'c'}^{(0)}/\sigma_{bb}^{(0)} \approx 0.6. \tag{5.7}$$

Kepler's measurements,[6] on the other hand, give

$$\sigma_{c'c'}^{(0)}/\sigma_{bb}^{(0)} \approx 0.4, \tag{5.8}$$

in fair agreement with the above prediction.

APPENDIX A: ESTIMATES EXCLUDING THE POSSIBILITY OF SELF-TRAPPING

As has been pointed out in the introduction, the narrow bandwidths characteristic of organic crystals strongly suggests the possibility of self-trapping due to a local distortion of the molecules. It is the purpose of this section to provide a numerical estimate of this effect in anthracene which indicates that this mechanism is, in fact, negligible.[30]

The basic idea of the self-trapping mechanism is that an excess electron (or hole) localized on a neutral molecule will, in general, cause the nuclear configuration to displace to a new equilibrium configuration appropriate to the molecule ion. The possibility of self-trapping then arises when the binding energy E_b as-

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[30] Estimates of self-trapping by W. Siebrand, Organic Crystal Symposium, Ottawa, 1962 (unpublished), are for smaller diatomic molecules, and are inconclusive with respect to anthracene.
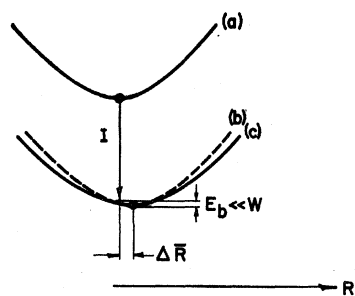

FIG. 4. Configurational coordinate diagram illustrating small binding energy. (a) Potential-energy curve for neutral molecule. (b) Potential-energy curve for molecule ion with the same force constant. (c) Potential-energy curve for molecule ion with the slightly altered force constant. I = electron affinity, E_b = "binding" energy, W = bandwidth.

sociated with this change in configuration is larger than the bandwidth.

To estimate the change in internuclear coordinates, we refer to the work of Balk, De Bruijn, and Hoijtink[31] on the mononegative (and dinegative) anthracene ion. In connection with their calculations of the electronic energy-level scheme of the latter, these authors provide estimates of the (C=C and C–C) bond lengths (actually, bond orders) of the neutral and ion molecules. They find that the variation in bond lengths of the ion is never more than 0.01 Å. The corresponding variations in bond orders, however, exceed the mean change in bond order in going from the neutral to the mononegative ion. Thus, the average increase in bond lengths, $\Delta\bar{R}$, is <0.01 Å. To estimate a maximum binding energy, however, we take $\Delta\bar{R} = 0.01$ Å.

For the force constant appropriate to this deformation, we choose that corresponding to the symmetrical breathing mode of the benzene ring,[32] since the benzene rings of the anthracene molecule would be expected to expand symmetrically upon addition of the excess electron. This force constant is $K \approx 7.5 \times 10^5$ dyn/cm. Thus,

$$E_b < \tfrac{1}{2} K \Delta\bar{R}^2 = \tfrac{1}{2}(7.5 \times 10^5) \times (10^{-2} \times 10^{-8})^2$$

$$\times (1.6 \times 10^{-12})^{-1} \text{ eV} \approx 0.002 \text{ eV},$$

which is at least an order of magnitude smaller than any of the calculated bandwidths. That K is a factor of 10 larger than the above estimate is not reasonable. Also, the change in force constant in going from the neutral to the ion molecule, as estimated from the empirical relation[33]

$$K(\Delta\bar{R})^4 = \text{constant},$$

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[31] P. Balk, S. de Bruijn, and G. J. Hoijtink, Rec. Trav. Chim. **76**, 860 (1957).

[32] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 267.

[33] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1950), Vol. I, p. 456.

is only a matter of a few percent and is negligible. The above phenomenon is illustrated in Fig. 4. The monopositive ion would be expected to exhibit a symmetrical behavior.

The induced polarization of neighboring neutral molecules by the molecule ion has not been studied quantitatively. However, our intuitive feeling is that the delocalization of the extra π electron should substantially reduce the polarization of its environment,

and that the reaction of this polarization back on the electron should be small.

Although other molecules should be examined in this connection if sufficient information is available, it is physically reasonable to assume that the above conclusions apply to organic molecules of comparable or larger size. This may not be true for smaller diatomic molecules (such as iodine), or for those possessing a permanent dipole moment, e.g., $[(TCNQ)^{-}M^{+}]$.

Optical and Electrical Properties and Energy Band Structure of ZnSb*

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(Received 11 October 1963)

Single crystals of p-type ZnSb have been grown by pulling from the melt. The carrier concentration is of the order of 10^{16} cm^{-3}. The Hall mobility is of the order of a few hundred cm^2/sec-V at room temperature, and is highest for current along the c axis and lowest for current along the b axis. Indirect and direct transitions have been observed in the absorption edge. The indirect transitions begin at the photon energy: 0.50 eV at 300°K, 0.59 eV at 77°K, and 0.61 eV at 4.2°K, independent of polarization. The direct transitions appear to begin at the lowest photon energy for $E\|c$ and at the highest photon energy for $E\|a$. The carrier absorption at long wavelengths is highest for $E\|c$. The results indicate that the valence band has three closely spaced bands near the maximum which corresponds to either the point Γ or the points R of the Brillouin zone, while the minimum of the conduction band is at the other position. The effective mass tensor of holes is estimated.

INTRODUCTION

TWO II-V semiconducting compounds, CdSb and ZnSb, have similar crystal structures of orthorhombic symmetry. Being noncubic, these crystals may have interesting anisotropic properties which help to elucidate the structure of the electronic energy bands. Early studies made on polycrystalline material of ZnSb emphasized the thermal and thermoelectric properties which were of interest for technical application of the material. Recently, some investigations of optical and electrical properties have been made on single crystals of CdSb, Zn$_x$ Cd$_{1-x}$ Sb as well as ZnSb. Most studies were made on p-type material; a few measurements were made on n-type CsSb. Anisotropy in conductivity and Hall coefficient has been reported for CdSb by Adronik and Kot[1] and for ZnSb by Kot and Kretsu[2]; the axes of the crystal were not identified.

Štourač, Tauc, and Závětová[3] found that $\sigma_c > \sigma_b$ in the CdSb, Zn$_{0.23}$ Cd$_{0.77}$ Sb and Zn$_{0.25}$ Cd$_{0.75}$ Sb crystals studied; the authors also studied the infrared absorption edge in these crystals and found a difference in the absorption for different polarizations. The absorption was interpreted as due to indirect transitions. The absorption edge in CdSb was measured also by Trei et al.[4] with polarized radiation and was also attributed to indirect transitions. The latter authors studied also magnetoresistance of n- and p-type CdSb. They postulated for CdSb a model with one type of holes and one type of electrons and found that constant energy ellipsoid for electrons as well as for holes have axes along the crystal axes. For ZnSb, absorption edge measurements have been reported by Turner, Fischler, and Reese[5] for unpolarized radiation only. The measurements were made on p-type samples with rather high carrier concentrations, $\sim 4 \times 10^{18}$ cm^{-3}. From the measurements, the energy gap at room temperature was estimated to be approximately 0.53 eV. Finally,

[1] I. K. Andronik and M. V. Kot, Fiz. Tverd. Tela 1, 1128 (1960) [English transl.: Soviet Phys.—Solid State 2, 1022 (1960)]; see also I. K. Andronik, M. V. Kot, and M. V. Emelyanenko, Fiz. Tverd. Tela 3, 2548 (1961) [English transl.: Soviet Phys.—Solid State 3, 1853 (1962)].

[2] M. K. Kot and I. V. Kretsu, Fiz. Tverd. Tela 2, 1250 (1960) [English transl.: Soviet Phys.—Solid State 2, 1134 (1960)].

[3] L. Štourač, J. Tauc, and M. Závětová, *Proceedings of the International Conference on Semiconductor Physics, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 1091.

[4] V. Trei, M. Matyáš, B. Velický, and M. Závětová, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 766.

[5] W. J. Turner, A. S. Fischler, and W. E. Reese, Phys. Rev. 121, 759 (1961).