Hall Mobility of Holes in Anthracene*†

A. I. KORN‡
Queens College of The City University of New York, Flushing, New York 11367

AND

R. A. ARNDT
Brookhaven National Laboratory, Upton, New York 11973

AND

A. C. DAMASK
Queens College of The City University of New York, Flushing, New York 11367
and
Brookhaven National Laboratory, Upton, New York 11973

(Received 27 May 1969)

The Hall effect for holes has been measured in high-purity single crystals of anthracene. The magnetic field was directed along each of the a, b, and c' crystallographic directions, and the electric field was in each of the two directions orthogonal to the magnetic field. The Hall mobilities μ_H were computed from the measurements and the drift mobilities μ_D were measured in the same crystals. The ratios μ_H/μ_D are B_aI_b, -4.3; $B_aI_{c'}$, -4.8; B_bI_a, $+7.6$; $B_bI_{c'}$, $+8.8$; $B_{c'}I_a$, -1.5; and $B_{c'}I_b$, -1.5. These results are consistent with a band model for charge-carrier transport.

INTRODUCTION

THE molecules of anthracene in a crystal lattice are weakly bound to each other and separated by distances of a few angstroms. As a result, overlap between molecular wave functions is expected to be small and the mechanism of charge transport is not immediately obvious. Several calculations have been made using a tight-binding approximation in the usual band theory.[1–6] In order for the band theory to be physically meaningful it must satisfy a restriction placed on the drift mobility by the uncertainty principle.[7] This restriction is such that $\mu_D > 0.1\ W/kT$, where μ_D is the drift mobility, W the bandwidth, and k and T have their usual meaning. As a further restriction, the mean free path of a carrier should be greater than a lattice spacing, otherwise Bloch functions are not suitable wave functions. (The mean free paths in these band calculations have been found to be between 1 and 5 lattice spacings.) The band calculations predict an anisotropy of the drift mobility and its temperature dependence. However, calculations using a hopping model also predict a mobility anisotropy and a temperature dependence.[6] Neither type of calculation fully takes into account all factors such as molecular vibrations, hydrogen atoms, lattice expansion, etc.

Kepler measured the mobility of charge carriers photo-injected into anthracene. Results showed that the drift mobilities of both holes and electrons are of the order of 1 cm²/V sec.[8] Mobilities of this magnitude do not violate the restriction imposed by the uncertainty principle. Although the temperature dependence of the drift mobility was consistent with the band model, this magnitude does not permit a distinction between the band and hopping models.

Photoconductivity measurements were insufficient to check all of the features predicted by the various band calculations and thereby confirm the model. One result of the band calculation is a small width of the conduction band (or valence band for hole conduction), of the order of kT. Because of these narrow bands, this model predicts that the sign of the Hall mobility will be anomalous in certain crystallographic directions.[9,10] Several investigators have attempted to measure the Hall effect, with a variety of results. The high resistivity of anthracene makes this measurement extremely difficult. Dresner measured the Hall effect of surface carriers in the ab plane and reported Hall mobilities of 50 cm²/V sec for electrons and 30 cm²/V sec for holes,[11] although the directions in which the measurements were made was not specified. The sign of the Hall voltage was not anomalous. Delacote and Schott[12] measured a Hall mobility by the split dark electrode

* Work supported by the U. S. Atomic Energy Commission and the U. S. Army Research Office (Durham).

† Submitted by A. I. K. in partial fulfillment of the requirements for the Ph.D. degree at the City University of New York.

‡ Permanent address: New York City Community College of the City University of New York, Brooklyn, N. Y.

[1] O. H. Le Blanc, Jr., J. Chem. Phys. **35**, 1275 (1961).
[2] G. D. Thaxton, R. C. Jarnagin, and M. Silver, J. Phys. Chem. **66**, 2461 (1962).
[3] J. I. 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. Vala, Jr., J. Chem. Phys. **42**, 733 (1965).
[5] R. Silbey, J. Jortner, S. A. Rice, and M. Vala, Jr., J. Chem. Phys. **43**, 2925 (1965).
[6] R. M. Glaeser and R. S. Berry, J. Chem. Phys. **44**, 3797 (1966).
[7] H. Fröhlich and G. L. Sewell, Proc. Phys. Soc. (London) **74**, 643 (1959).
[8] R. G. Kepler, Phys. Rev. **119**, 1226 (1960).
[9] L. Friedman, Phys. Rev. **133**, A1668 (1964).
[10] O. H. Le Blanc, Jr., J. Chem. Phys. **39**, 2395 (1963).
[11] J. Dresner, Phys. Rev. **143**, 558 (1966).
[12] J. Delacote and M. Schott, Solid State Commun. **4**, 177 (1966).

method of Dobrovol'skii and Gritsenko.[13] They presumably used a cleavage plate, and therefore the current was largely in the c' direction. They reported a Hall mobility to drift mobility ratio of -25 ± 10 for holes, although the direction of the magnetic field was not specified. Pethig and Morgan[14] measured the Hall mobility by a similar technique but with dark conductivity and reported 5.5 cm^2/V sec in the *ab* plane and 1.5 cm^2/V sec perpendicular to the *ab* plane. The electric field direction was not specified nor was the carrier sign determined. Smith[15] used a modification of the Redfield[16] method and has measured Hall mobilities of 0.8 ± 0.3 and 2.5 ± 1.0 cm^2/V sec with primary current along the *a* and *b* directions, respectively, and with the magnetic field perpendicular to the *ab* plane. Because of the incompleteness of data, the present experiment was designed to measure the Hall and drift mobilities of holes in each of the six possible combinations of magnetic and electric field directions in order to make available unambiguous results to assist further theoretical development.

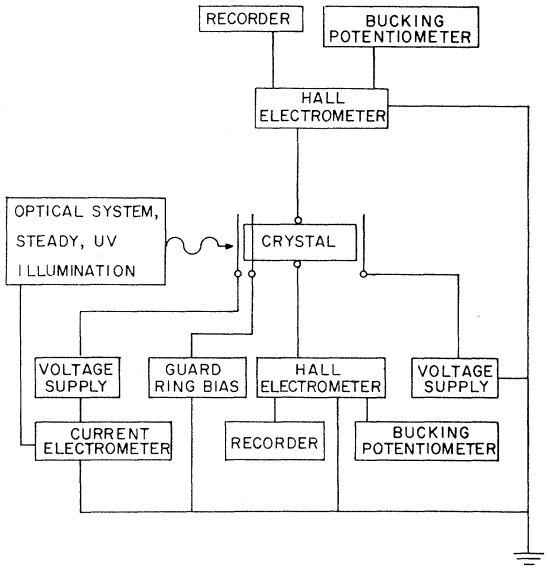

FIG. 1. Block diagram for the measurement of Hall voltage and photoconductivity of anthracene.

SAMPLES AND PROCEDURE

Synthetic anthracene (Eastman H480) was the starting material and it was further purified by chromatography, vacuum sublimation, and zone refining.[17] No impurities were eluted in a gas chromatograph and it was concluded that the total impurity content was less than 1 ppm. The final purity and structural defect concentration of the material was checked by the triplet lifetime, which was found to be between 20 and 25 msec, which is equivalent to the best material which has been reported.[18]

Single crystals were grown by the Bridgman method and oriented sections were cut from boules with a string saw. It is relatively easy to orient the sections since the *ab* plane is the cleavage plane and the *a* and *b* axes can be distinguished by double refraction.[19] An optical finish was obtained by polishing on a xylene-soaked tissue. Typical sample dimensions were $2\times3\times6$ mm with orthogonal axes along the *a*, *b*, and *c'* crystallographic axes.

The method of measuring the Hall mobility was that of measuring the Hall voltage. Because there are very few charge carriers in a crystal held in the dark, light was used to inject carriers. The measurements were restricted to holes since their photocurrents are found to be larger than electron photocurrents. The impedances of the samples were quite high, $\sim10^{12}\,\Omega$, and even with a high primary field (~200 V/cm), vibrating reed electrometers had to be used for voltage and current measurements. The arrangement of the electrometers and voltage supplies is shown in the block diagram of Fig. 1. The bucking potentiometers of Fig. 1 were used to compensate for misalignment voltages of the Hall probes, and the input properties of the electrometers are not affected by the bucking voltages. The line in Fig. 1 connecting the current electrometer to the light source represents a feedback system which adjusted the intensity of illumination by means of a diaphram to keep a constant primary current in the sample. A guard ring was painted around the crystal near the illuminated electrode to ensure that the measured primary current was bulk current. However, this guard ring was masked from the light source so that it would not contribute photocurrent to the sample. In this way, surface currents were kept below the bulk current (typically, 10^{-11} A) by a factor of 10^4. The illuminated electrode was SnO_2-coated quartz and the dark electrode was of copper cemented to the crystal with Eccobond 57C conducting paint.

The light source was a point source 100-W mercury lamp which was focused on the sample by a system of quartz lenses and front-surface mirrors. A filter was inserted in the light path that absorbed all wavelengths longer than 4000 Å in ensure that carriers were generated on the surface rather than in the bulk of the crystal.

The sample was placed in a chamber maintained at 25°C, which contained helium gas that served as a heat exchanger and also retarded sublimation of the sample. This chamber was in an evacuated Dewar and was placed in the center of a superconducting solenoid.

[13] V. N. Dobrovol'skii and Yu. I. Gritsenko, Fiz. Tverd. Tela **4**, 2760 (1962) [English transl.: Soviet Phys.—Solid State **4**, 2025 (1963)].
[14] R. Pethig and K. Morgan, Nature **214**, 266 (1967).
[15] G. C. Smith, Bull. Am. Phys. Soc. **14**, 370 (1969).
[16] A. G. Redfield, Phys. Rev. **94**, 526, 537 (1954).
[17] J. N. Sherwood, in *Methods and Techniques of Fractional Solidification*, edited by M. Zeif (M. Dekker, New York, 1969).
[18] D. F. Williams and W. G. Schneider, J. Chem. Phys. **45**, 4756 (1966).
[19] I. Nakada, J. Phys. Soc. Japan **17**, 113 (1962).

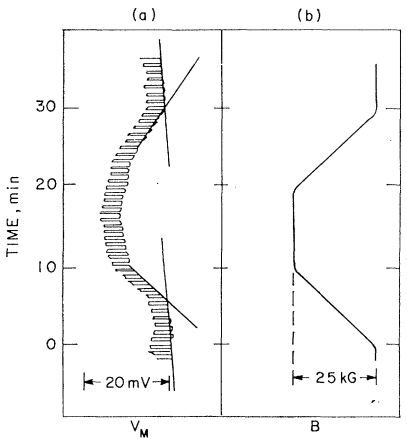

FIG. 2. (a) Hall probe potential as function of time. Straight lines show two areas selected for measurement. (b) Magnetic field as function of time used to generate the Hall voltage of (a). The two traces are out of phase by about 4 min, the time constant of the measuring circuit.

Magnetic fields of up to 50 kG, could be generated at a rate of 2.5 kG/min. In practice, the magnetic field was swept through a typical cycle of 10 min increasing field, 10 min steady field, and 10 min return to zero field.

A Hall probe recording and a plot of magnetic field as functions of time, are shown in Fig. 2. The oscillations, which have a period of approximately $1\frac{1}{2}$ min in the recording of the Hall probe potential, are due to a temperature controller turning on and off. The RC time constant of the circuit causes the time lag in Fig. 2 between the application of the magnetic field and the onset of the increase in the Hall probe voltage V_M. This Hall voltage is determined from the change in average slope of V_M when the magnetic field was changed. This can be done at the several regions of change such as those indicated in Fig. 2. Thus, a check is available for internal consistency of any measurement cycle. Errors in the values can arise from errors in choosing the average slopes and are believed not to exceed 30%. The slope can be affected by instabilities in the photocurrent and thermal effects around the Hall probes. Only those traces showing reasonable stability were accepted for analysis and about five runs were made for each of the directions; the reported values are the averages of these runs. Two or more crystals were used to check consistency of results in each of the magnetic field directions.

TABLE I. The Hall mobilities in anthracene computed from the measured Hall voltages for photo-injected holes at room temperature. $B_{\parallel}$ and $I_{\parallel}$ indicate the axes to which B and I are parallel. The Hall mobility is given in cm²/V sec.

$I_{\parallel}$ \ $B_{\parallel}$	a	b	c'
a		+7.6	−1.5
b	−8.6		−3.1
c'	−3.8	+7.0	

TABLE II. The drift mobilities (in cm²/V sec) in anthrancene at room temperature for holes drifting along the a, b, and c' directions.

μ_a	1.0
μ_b	2.0
$\mu_{c'}$	0.8

The computation of the Hall mobility from the measured photo-Hall voltage was made as follows. A coordinate system was chosen such that the photocurrent and the primary electric field E_x were along the x direction, the Hall voltage was measured along the y direction, and the magnetic field B_z along the z direction. The crystal dimensions along the x, y, and z directions are l, w, and t, respectively. V_M is the voltage measured between the Hall probes. As a result of the finite dimensions of the sample and space-charge effects,

$$V_M \neq V_H, \tag{1}$$

where V_M is given by

$$V_H = \mu_H w E_x B_z, \tag{2}$$

and μ_H is the Hall mobility. It is assumed that

$$V_M = GSV_H, \tag{3}$$

where G is a geometrical factor due to the finite sample dimensions, and S is a factor due to space-charge effects. Both of these factors are discussed in more detail below. The Hall mobility is then computed from

$$\mu_H = V_M/GSwE_xB_z. \tag{4}$$

The observed photocurrent density varied as the square of the applied voltage, and the electric field distribution is then given by a modified Child's law.[20] One of the Hall probe potentials was adjusted to 0 V with respect to ground before application of the magnetic field. (The misalignment voltage was small compared to the applied voltage.) This was done by adjusting the positive bias V_L applied to the illuminated electrode and the negative bias V_D applied to the dark electrode. Then, from Child's law, the electric field

TABLE III. Ratios of the Hall mobility to the drift mobility in anthracene for photo-injected holes at room temperature. $B_{\parallel}$ and $I_{\parallel}$ indicate the direction to which I and B are parallel.

$I_{\parallel}$ \ $B_{\parallel}$	a	b	c'
a		+7.6	−1.5
b	−4.3		−1.5
c'	−4.8	+8.8	

[20] See, e.g., the review by W. Helfrich, in *Organic Solids in Physics and Chemistry of the Organic Solid State*, edited by D. Fox, M. M. Labes, and A. Weissberger (Wiley-Interscience, Inc., New York, 1967), Vol. II.

distribution is given by

$$E_x=(\tfrac{3}{2})V_L^{1/3}(V_L+V_D)^{2/3}l^{-1}, \quad (5)$$

for a Hall probe potential at 0 V with respect to ground. The applicability of Eq. (5) to the present measurements was verified by placing probes along the length of a crystal and measuring the potential distribution.

The geometrical factor G (defined as V_M/V_H in Ref. 21 because they assumed no space-charge effects) has been derived by Isenberg, Russell, and Green[21] as

$$G=(8/\pi^2 w)\sum_{n=0}^{\infty}(-1)^n \tanh[\tfrac{1}{2}(2n+1)\pi w] \times\cos[(2n+1)\pi x/l](2n+1)^{-2}, \quad (6)$$

where x is measured from the geometrical center. In the present case, G varied between 0.8 and 1.0 for the crystals used.

The space-charge factor S, which is the ratio of the measured Hall voltage to the Hall voltage given by Eq. (2), was calculated by Banbury, Henisch, and Many to be[22]

$$S=1-(2L/w)\tanh(w/2L), \quad (7)$$

where L is given by

$$L=(\epsilon_y\epsilon_0 kT/e^2 n_0)^{1/2}, \quad (8)$$

and ϵ_y is the dielectric constant in the y direction of the sample, ϵ_0 is the vacuum permittivity, and n_0 is the equilibrium value of the charge carrier density, i.e., without an applied magnetic field. L is similar in form to the Debye-Hückel length discussed by Shockley.[23] L of Eq. (8) may also be written as

$$L=(\epsilon_y\epsilon_0 kTwE_x\mu_x/eI_x)^{1/2}, \quad (9)$$

where μ_x is the drift mobility of charge carriers drifting along the x direction and I_x is the photocurrent. S varied between 0.1 and 0.3 for the present measurements.

RESULTS AND DISCUSSION

The Hall mobilities computed from the measured Hall voltages for holes are shown in Table I. The drift mobilities for holes were measured in the same crystals by the pulsed photoconductivity method. The measured values of the drift mobilities are shown in Table II. They agree with the values obtained by Kepler.[24] The ratios of the Hall to the drift mobilities are shown in Table III.

The results show the Hall mobility of holes to have an anomalous sign in four of the six direction combinations in anthracene. This means that the holes were deflected in the direction that electrons would normally be deflected by a Lorentz force. The explanation based on a band model is that since the sign of the Hall mobility is dependent upon the relative population of the conducting states, the hole bands are so narrow that the negative effective-mass states have been populated at room temperature. Since these are weighted more than the positive effective-mass states, a reversed sign for the mobility is obtained.[9,10]

It should be noted in Table III that when the current is in the c' direction, the μ_H/μ_D ratio is negative for the magnetic field in the a direction and positive in the b direction. Since anthracene cleaves readily only in the ab plane, it is presumed that the measurements discussed in the Introduction, in which directions were not specified, were made on cleavage plates and, therefore, the current was probably in the c' direction. In view of this and the findings reported here, disparity in sign of the ratio is understandable in cases in which the orientation of the magnetic field was not reported. It should be further noted that if a thin cleavage plate were used then a significant fraction of the current could be due to electrons generated in the bulk of the material. It is not yet determined if anomalous behavior of electrons follows that of holes. If it does not, then it is possible to observe a larger Hall voltage than would be observed with a single-type carrier.

Toombs[25] has calculated the ratio of the Hall mobility to drift mobility for the crystallographic directions as a function of temperature using various band structures. The data presented here agree qualitatively with this calculation but not quantitatively. A unique bandwidth cannot be determined from the experimental data since the exact shape of the band would be required. At present these band shapes are known only within the framework of specific models which are not complete. There exists some experimental data which indicates that the highest-valence bandwidth along the c' direction is somewhat narrower than 0.1 eV.[26] Le Blanc[10] has calculated the mobility ratio for the case of the magnetic field parallel to the c' direction to be expected for various bandwidths. Using his results, the presnet data yield a hole bandwidth in this direction of $\sim$0.08 eV, in agreement with the above measurement of Williams and Dresner.[26]

In conclusion it may be said that the measured anomalous Hall effect cannot be explained by the hopping model and favors the band-model interpretation.

[21] I. Isenberg, B. R. Russell, and R. F. Green, Rev. Sci. Instr. **19**, 685 (1948).
[22] P. C. Banbury, K. H. Henisch, and A. Many, Proc. Phys. Soc. (London) **A66**, 753 (1953).
[23] W. Shockley, Bell System Tech. J. **28**, 435 (1949).
[24] R. G. Kepler, in *Organic Semiconductors*, edited by J. J. Brophy and J. W. Buttrey (The Macmillan Co., New York, 1962).
[25] T. Toombs, Ph.D. thesis, Princeton University, 1968 (unpublished).
[26] R. Williams and J. Dresner, J. Chem. Phys. **46**, 2133 (1967).