PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

Experimental and Theoretical Hall Mobilities of Holes and Electrons in Naphthalene[†][*]

D. H. Spielberg[‡]
Queens College of the City University of New York, Flushing, New York 11367

and

A. I. Korn
New York City Community College of the City University of New York, Brooklyn, New York

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 October 1970)

The Hall effect for electrons and holes has been measured in high-purity single crystals of naphthalene. 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 crystal. The average ratios μ_H/μ_D for electrons are B_aI_b, +1.1; $B_aI_{c'}$, +0.9; B_bI_a, +2.8; $B_bI_{c'}$, +2.2; $B_{c'}I_a$, −3.0; and $B_{c'}I_b$, −2.9. The ratios for holes are B_aI_b, −3.9; $B_aI_{c'}$, −2.7; B_bI_a, +0.57; $B_bI_{c'}$, +0.37; $B_{c'}I_a$, −3.6; and $B_{c'}I_b$, −3.7, where the B's and I's are the magnetic field and the current directions, respectively. The theoretical ratios of Hall to drift mobilities have been calculated by band theory using the transfer integrals evaluated from three different types of wave functions by other investigators. It was found that the wave functions used by Katz, Rice, Choi, and Jortner yielded values which agreed best.

I. INTRODUCTION

Crystals of some of the aromatic hydrocarbons behave electrically like narrow-band semiconductors even though their specific conductivity is very low. Partial success has been achieved in predicting the carrier drift mobilities of anthracene and naphthalene by band calculations based on the tight-binding approximation.[1-6] Unfortunately, the drift mobilities, typically of the order of 1 cm^2/V sec, have a range of values that cannot be used as firm evidence that the band rather than the hopping model is the better one.[7]

The introduction of magnetic fields into the charge transport calculations showed that charge carriers in these materials are capable of exhibiting an anomalous Hall effect.[8,9] Although anomalous behavior is still not sufficient evidence for firm conclusions, good comparison of Hall data with a specific calculation would suggest that there is merit to the model on which the calculation is based. In the work reported here, the Hall mobilities for both electrons and holes in naphthalene were measured and are compared with the theoretical values which would be predicted from various choices of wave functions.

II. MATERIAL AND PROCEDURE

Scintillation-grade naphthalene (K & K Chemical Co.) was further purified by chromatography, vacuum sublimation, and zone refining. Analysis by gas chromatography indicated that the impurity content was less than 1 ppm.

Single crystals were grown by the Bridgman method and oriented sections were cut with a string saw. An optical finish was obtained by polishing them on a tissue wetted with ethanol. Typical sample dimensions were 2 × 2 × 6 mm with orthogonal axes in the a, b, and c' directions, the long dimension being that of the electric field.

TABLE I. The Hall mobilities in naphthalene computed from the measured Hall voltages for photoinjected electrons and holes at room temperature. $B_{\parallel}$ and $I_{\parallel}$ indicate the axis to which the magnetic field B and the current I are parallel. The Hall mobility is given in cm^2/V sec.

	Electrons		
$I_{\parallel}/B_{\parallel}$	a	b	c'
a		+1.7	−1.8
b	+0.55		−1.5
c'	+0.54	+1.3	
		Holes	
a		+0.46	−2.9
b	−4.7		−4.4
c'	−1.4	+0.19	

TABLE II. The drift mobilities (in cm^2/V sec) in naphthalene at room temperature for electrons and holes drifting along the *a*, *b*, and *c′* directions.

Electrons	
μ_a	0.6
μ_b	0.5
$\mu_{c'}$	0.6
Holes	
μ_a	0.8
μ_b	1.2
$\mu_{c'}$	0.5

The method used for measuring the Hall mobility was that of measuring the Hall voltage. The crystal was mounted with a copper plate for a dark electrode and a transparent quartz plate with a tin oxide coating for the illuminated electrode. A guard ring was painted on the crystal outside of the illuminated area to inhibit surface currents. Charge carriers were photoinjected with a 1000-W mercury-xenon lamp with all wavelengths greater than 4000 Å filtered by a Corning 7-59 filter and a 0.27-molar solution of copper sulfate to ensure that the carriers were generated on the surface rather than in the interior of the crystal. The crystal was placed in a helium-filled chamber which contained some naphthalene flakes to retard sublimation.

The measuring system used was that developed by Korn *et al.*[10] for anthracene. The only important difference was that a 20-kG Varian conventional electromagnet was used instead of a superconducting magnet. The method of measuring and the correcting of the data for space-charge and geometric effects were the same as those described earlier and had the same measuring error, which is believed to be within 30%. Several measurements were made for each direction and crystals from two different boules were measured to check consistency. The data reported here are the averages, with the mean deviation being within the estimated experimental error.

TABLE IV. Ratios of the Hall mobility to the drift mobility in naphthalene for photoinjected electrons and holes at room temperature. $B_{\parallel}$ and $I_{\parallel}$ indicate the direction to which the magnetic field *B* and the current *I* are parallel.

	Electrons		
$I_{\parallel}/B_{\parallel}$	*a*	*b*	*c′*
a		+2.8	−3.0
b	+1.1		−2.9
c′	+0.9	+2.2	
	Holes		
a		+0.57	−3.6
b	−3.9		−3.7
c′	−2.7	+0.37	

III. RESULTS

The Hall mobilities were computed from the measured Hall voltages by considering space-charge effects and sample geometry in the same manner as that reported for anthracene.[10] These mobilities averaged over several measurements are shown in Table I, where the minus sign indicates that the Hall effect is anomalous. The mean deviation from the average was about 30%.

The drift mobilities, measured in the same crystals by the pulsed photoconductivity method, are given in Table II. The dielectric constants, measured to obtain the space-charge correction, are given in Table III. The ratios of the Hall mobilities of Table I to the drift mobilities of Table II are given in Table IV. In Table IV it is seen that the Onsager relations are obeyed within the estimated error of the measurements.

IV. DISCUSSION

Band-theory calculations in the tight-binding approximation have been performed[1–8] for anthracene and naphthalene by several investigators and the intermolecular resonance integrals between molecule 1 and molecule *n*, shown schematically in Fig. 1, were evaluated. It had been found that the only interactions which were significant were $n = 2, 3, 4, 5, 6, 9$, and 10. The variation of the energy bands as a function of the electron wave vector $\vec{k}$ is given as[3]

$$E(k) = \pm 2E_2 \cos\vec{k}\cdot\vec{c} + 2E_3 \cos\vec{k}\cdot\vec{b} + 4E_4 \cos\vec{k}\cdot\vec{b}\cos\vec{k}\cdot\vec{c} + 2E_5\cos\vec{k}\cdot\vec{a} + 2E_6\cos\vec{k}\cdot(\vec{a}+\vec{c})$$
$$\pm 4E_9 \cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b} \pm 4E_{10}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b}\cos\vec{k}\cdot(\tfrac{1}{2}\vec{a}+\vec{c}) , \tag{1}$$

where only the significant terms have been retained. Since there are two molecules per unit cell in the crystal lattice of naphthalene, there are two bands each (+ and −) for both holes and electrons which arise from the symmetric and antisymmetric combinations of molecular wave function in a unit cell.

TABLE III. Dielectric constants at 1 kHz and room temperature for naphthalene along *a*, *b*, and *c′* directions.

ϵ_a	3.0
ϵ_b	1.9
$\epsilon_{c'}$	4.2

TABLE V. Ratio of the Hall to the drift mobilities for naphthalene as calculated from the wave functions of the indicated investigators.

	Holes			Electrons		
Magnetic field parallel to	*a*	*b*	*c′*	*a*	*b*	*c′*
Ref. 2	−15.8	1.1	−15.8	−9.9	1.5	−10.7
Ref. 3	− 1.3	0.08	− 1.3	0.70	1.3	− 1.9
Refs. 4 and 5	−0.21	0.75	− 0.2	0.82	0.87	− 0.095

Le Blanc[1] and Thaxton *et al.*[2] used a single Slater wave function to calculate the E_n's. Katz *et al.*[3] used a linear combination of Slater wave functions to obtain a more accurate representation of the molecular wave function at large distances. Silbey *et al.*[4,5] extended the calculations of Katz *et al.* by including the effects of molecular vibrations.

LeBlanc[8] and Friedman[9] have calculated the Hall to drift mobility ratio μ_H/μ_D for anthracene in the *ab* plane from the Jones and Zener[11] solution of the Boltzmann transport equation

$$\frac{\mu_H}{\mu_D}=\frac{kT\langle V_j^2 M_{ii}^{-1}-V_j V_i M_{ji}^{-1}\rangle}{\langle V_i^2\rangle\langle V_j^2\rangle}\;, \tag{2}$$

where M_{ij}^{-1} is the symmetric inverse effective-mass tensor defined as

$$M_{ij}^{-1}=\frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j}\quad .$$

In the present work, the value of μ_H/μ_D for naphthalene was obtained from Eq. (2) for each of the three types of wave functions for which the transfer integrals had been evaluated. The indicated integrations for averages were calculated numerically by a computer by use of a three-dimensional Gaussian quadrature[12] over the first Brillouin zone. (A three-dimensional Simpson's rule was also used for some of the calculations and gave results that agreed with those obtained by the Gaussian method.) Five Legendre points were used in an interval for the Gaussian method of integration. The number of intervals along a particular direction was taken proportionally to the size of the Brillouin zone in that direction. The results are shown in Table V where, because of Onsager relations, only the magnetic field direction needs to be specified.

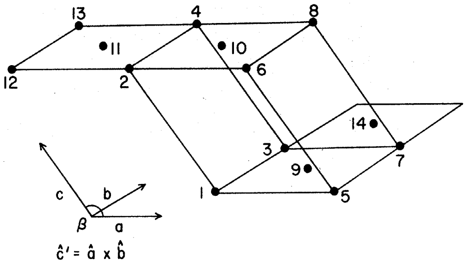

FIG. 1. Unit cell of napthalene. Solid points indicate molecular centers in the cell and at sites adjacent to the cell. Numbering system is that used by Katz *et al.* (Ref. 3).

When the theoretical ratios of μ_H/μ_D of Table V are compared to the experimental results of Table IV it is seen that although all three choices of wave functions yield the correct signs for holes, only those of Katz *et al.* and Silbey *et al.* yield the correct signs for electrons. When the magnitudes of these two sets of results are compared with experiment, it is seen that the wave function of Silbey *et al.* yields ratios at least an order of magnitude too small in the $\vec{c}\,'$ direction for electrons and in the $\vec{a}$ and $\vec{c}\,'$ directions for holes. The wave function of Katz *et al.* yields results in good agreement with the electron experiments and with the $\vec{a}$ and $\vec{c}\,'$ directions for holes but, when the limit of error is used, the theoretical value is a factor of 3–4 smaller than the experimental value in the $\vec{b}$ direction for holes. Because of the good agreement with most of the experimental data, it is concluded that the wave function of Katz *et al.* is the better choice and that the band model is applicable.

Solid-state measurements, such as those reported here, appear to be useful as a test for the selection (or rejection) of molecular wave functions. Inappropriate wave functions may be rejected by their failure to predict the experimentally determined physical property.

---

†Submitted by D. H. Spielberg in partial fulfillment of the requirements for the Ph.D. degree at the City University of New York.

*Work supported in part by the U. S. Atomic Energy Commission and the U. S. Army Research Office, Durham, N. C.

‡Present address: Materials Science Laboratory, Universal Oil Products Research Center, Des Plains, Ill. 60016.

[1] O. H. LeBlanc, 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] S. H. Glarum, J. Phys. Chem. Solids, 24, 1577 (1963).
[8] O. H. LeBlanc, Jr., J. Chem. Phys. 39, 2395 (1963).
[9] L. Friedman, Phys. Rev. 133, A1668 (1964).
[10] A. I. Korn, R. A. Arndt, and A. C. Damask, Phys. Rev. 186, 938 (1969).
[11] H. Jones and C. Zener, Proc. Roy. Soc. (London) 145A, 268 (1934).
[12] J. B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins Press, Baltimore, Md., 1958).

PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

Atomic Vibrations in the (00.1) Graphite Surface: Observation with Low-Energy Electron Diffraction and Lattice-Dynamic Calculations

G. Albinet, J. P. Biberian, and M. Bienfait
Laboratoire de Croissance Cristalline – Centre Universitaire de Marseille-Luminy
13 *Marseille* 9e, *France*

(Received 25 September 1970)

Low-energy electron diffraction has been used to measure the variation of the surface Debye temperature $\Theta_\perp$ in the [00.1] direction of graphite as a function of the energy of incident electrons. A change (hexagonal-trigonal) in the symmetry of the diffraction diagram, depending on the penetration of electrons, was observed. This change in symmetry has been made use of in selecting, from the many other values of $\Theta_\perp$ we had measured, the one associated with the first layer of the (00.1) surface of graphite, namely (690 ± 70) °K. Furthermore, the dynamics of the Born lattice has been applied to compute the Debye temperature of the first layer of the surface associated with the normal ($\Theta_\perp$) and parallel ($\Theta_\parallel$) directions of the (00.1) face. The computed value of $\Theta_\perp$ is in fairly good agreement with the one determined experimentally. The computed value of $\Theta_\parallel$ is close to that previously obtained by other authors using different methods of calculation.

I. INTRODUCTION

The measurement technique of mean-square displacement for surface atoms by low-energy electron diffraction (LEED) is now a well-established technique[1]; nearly all the cubic metals have been studied in this way. The interpretation of the results, however, remains problematical owing to the lack of a precise definition of the surface. Experimentally, $\langle u^2 \rangle$ is determined by using a beam of progressively decreasing energies of the incident electrons, thereby, obtaining smaller and smaller penetration of the surface layers. Hitherto, it has been assumed that the pattern obtained with the smallest energy of incident electrons is representative of the surface structure. This bold hypothesis is a consequence of the absence of any precise LEED theory.

A pseudokinetical theory linking the diffracted intensity to $\langle u^2 \rangle$ was proposed by Jones, McKinney, and Webb,[2] but recently Baudoing *et al.*,[3] taking Ni as an example, showed that the above theory is not elaborate enough to explain the experimental observations. It can be said that, at present, it is not possible to ascertain which pattern – among those obtained with very low-energy electrons – corresponds to the vibrations in the first layer of the surface.[4]

In this paper, we shall first report the measurement of the mean-square displacement $\langle u^2 \rangle_\perp$ perpendicular to the (00.1) surface of graphite as a function of the electron energy. Then a means of obtaining the precise value of $\langle u^2 \rangle_\perp$ associated with the first atomic layer of the surface is suggested. Finally, a calculation based on Born lattice dynamics[5] is provided to check the experimental results.

II. EXPERIMENTAL

If the incident electrons strike the surface normally and observation is made on the reflected electrons in the same direction (or in one very close to that), the intensity I of the specular spot is given by the expression[6]

$$I = K \exp(-16\pi^2/\lambda^2)\langle u^2 \rangle_\perp , \quad (1)$$

where λ is the wavelength associated with the electrons. Here the term K stands for the contribution due to the diffraction and the exponential corresponds to the diffusion due to the thermal vibrations.

The mean-square displacement $\langle u^2 \rangle$ depends on the temperature T. Usually[1] another parameter, the Debye temperature Θ, is introduced to describe $\langle u^2 \rangle$; this parameter is independent of T in the harmonic approximation except at low temperatures. $\langle u^2 \rangle$ and Θ are linked by the relation