Nonanomalous Photo-Hall Mobility in Anthracene at Room Temperature*

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Narrow-band theory and several previous experiments in anthracene are contradicted by the unambiguous measurement of a normal Hall mobility for holes. Room-temperature hole Hall mobilities are 0.8±0.3 (a axis) and 2.5±1.0 (b axis). Band theory is apparently not an appropriate characterization of hole transport in anthracene.

I. INTRODUCTION

ANOMALOUS Hall effects have been predicted in low-mobility materials in both band and hopping models. Recent work in this area has been summarized by Mott[1] and by Klinger.[2] Tight-binding band calculations have been performed for the organic molecular crystal, anthracene, which exhibits drift mobilities of about 1 cm²/V sec at room temperature. LeBlanc[3] and Friedman[4] have predicted a Hall effect anomalous in sign and possibly much larger than the drift mobility. The possible sign anomaly for holes is important, since it has been considered a test of the electronic conduction theory in narrow band molecular crystals. At least five laboratories have reported measurements of such anomalous Hall effects.[5-9] One measurement,[10] in the c' direction, shows only a normal Hall effect for holes. These previous measurements have generally had signal-to-noise problems, and the various results are often contradictory. This paper reports hole Hall mobilities in anthracene which are similar to drift mobilities in sign, magnitude, and anisotropy. Particular attention is devoted to the credibility of this result. The nonanomalous result may be interpreted as evidence against a narrow band model for conduction.

II. METHOD

The difficulty of measurement of low Hall mobilities in photoconducting insulators has been documented by Ahrenkiel and Brown,[11] by Borders and Hodby,[12] and by MacDonald and Robinson.[13] The fundamental problems are poor contacts or crystal polarization.

Microwave methods are prohibited by low transient carrier concentrations in most materials. Hall angles in the range of 10^{-3} to 10^{-4} rad are typical. Additional refinements of the noncontacting Redfield method[14] now allow reliable measurement of photo-Hall mobilities as low as 1 cm²/V sec. The principal improvements involve: (a) replacement of resistive strip electrodes by an electrostatic potential divider; (b) total symmetry of illumination, geometry, and electronics; (c) use of a small digital on-line computer for signal-to-noise enhancement; and (d) both electric and magnetic field polarities are alternated to strip off unipolar and linear drift artifacts. Applied electric fields were in the range, 125–900 V/cm; magnetic fields were 0–30 kOe. Details of the system will be published elsewhere. The information is taken in the form of the electric field rotation necessary to compensate the magnetic-field effect. This Hall angle ϕ, is independent of carrier concentration and is related to the Hall mobility μ_H by the equation $\mu_H = 10^8 \phi/H$, where μ_H is in cm²/V sec, ϕ is in rad, and H in Oe. It should be noted that the method determines the average Lorentz deflection, which is odd in both electric and magnetic fields. Carrier magneto-transport should possess this symmetry, even in a monoclinic crystal such as anthracene, as a consequence of the requirements of the Onsager relations.[15] An additional experimental problem arises, however, in that the principal axes for dielectric properties[16] are not, in general, parallel to crystallographic axes.[17] This means that the internal field $\vec{D}$ is not necessarily in the direction of the external applied field $\vec{E}$. This difficulty is most easily avoided by applying $\vec{E}$ parallel to the crystal b axis, which is also a principal dielectric axis. If this kind of precaution is not observed, the directions of $\vec{H}, \vec{D}$, and observation will not be mutually orthogonal.

III. RESULTS

While the direct measurement of Hall angle serves as an absolute equipment calibration, it was thought

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TABLE I. Mobility comparisons.[a]

Crystal	Temp (°K)	μ_H(Smith)	μ_H(previous)	Carrier	Ref.
NaCl	84		250	electron	14
	200	34.5	25	electron	14
	296	14.3	$13_{-10}{}^{+20}$	electron	14
KBr	84		110	electron	14
	125	88.0	~80	electron	11
	150	43.9	15	electron	14
	296	12.6	12.5±2.0	electron	13
KCl	80		100	electron	b
	90		100±50	electron	14
	125	120.0		electron	
	200	15.5	15	electron	14
	296	9.2	~7[c]	electron	d
Sulfur	296	6–20	~10[e]	holes	e
Diamonds	296	175–1500	1800	electron	14
			1200	holes	14

[a] Mobilities in units of cm²/V sec.
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desirable to employ other, better known, materials as secondary standards. These measurements serve the dual functions of unequivocal determination of electron and hole polarities and verification of the computational procedure. A variety of such measurements are shown in Table I along with the results of previous work. In view of the uncertainty of previous low-mobility measurements, agreement is satisfactory.

In the colored alkali halides, electrons were released in the bulk of the crystal by illumination in the F and L bands. Natural diamonds allow similar bulk carrier generation from defect sites. This is not possible in anthracene and sulfur, where surface generation is a consequence of band-to-band transitions lying at energies higher than the exciton absorption. Even though opposite surfaces are illuminated symmetrically one can imagine errors in absolute value resulting from the nonuniform carrier generation. One can infer from the sulfur results that this kind of error is not larger than a factor of 2.

TABLE II. Room-temperature hole Hall mobility in anthracene.[a]

Orientation	E, a^b B, c'	E, b B, c'	E, a B, b	E, c' B, b	E, b B, a	Other
Reference						
This work	0.8±0.3	2.5±1.0	<1.0	<1.0	0.7±1.0	
5						> ≈30
6						−35±15
7						25–200[c]
8	1.3	2.5	7.8	6.2		
9						5.2[d]
						1.4[c]
10						0.2–2.0[c]

[a] Units of cm²/V sec, positive sign for holes.
[b] The notation E, a B, c' means that the electric field is applied along a and the magnetic field along c'.
[c] "Perpendicular to a-b plane."
[d] "Parallel to a-b plane."

Harshaw anthracene crystals were oriented by their cleavage in the ab plane and by birefringence.[16] Drift mobility experiments showed the dominant photo-excited carriers to be holes. Measured Hall mobilitie are shown in Table II along with results of previous work. The sign is that of holes. This contradicts the theoretical prediction of LeBlanc[3] and the experimental results of Delacote and Schott.[6] Comparison with the drift mobility results of Kepler,[18] $\mu_D(b) \approx 2.0$, $\mu_D(a) \approx 1.0$, and $\mu_D(c') \approx 0.8$, shows that the corresponding values are comparable.

Three factors make the new anthracene results credible: (a) The experimental method is a simple extension of a proven technique; (b) the apparatus yields anticipated results in other materials; and (c) the results are similar to the drift mobility values of Kepler.[18] The conclusion is that the Hall effect is not anomalous.

IV. DISCUSSION

Katz et al.[19] calculate a hole mean free path of 3.5 Å and a bandwidth W of about 0.1 eV in anthracene. When this number is used, LeBlanc's calculation[3] yields a ratio of Hall to drift mobility $\mu_H/\mu_D \approx -1$ for holes in the ab plane, while the present experiment shows this ratio to be about $+1$. The discrepancy is clearly greater than experimental error. Three alternatives may be considered: (a) The bandwidth may be as great as ~ 0.5 eV, the lower limit consistent with the observed essentially equality of drift and Hall mobilities; (b) the LeBlanc-type calculation of Hall mobility may be in error; or (c) band theory may simply be inapplicable.

All available theory[20] and experiments[21] would indicate a bandwidth $\lesssim 0.2$ eV. Thus it appears that the first alternative is incorrect.

Thermodynamic arguments by Kittel[22] and by Kaus[23] indicate that negative effective-mass states are accelerated in the wrong direction by electric, magnetic, and gravitational fields. It is not clear that the LeBlanc-type calculation properly incorporates this constraint. In an isotropic crystal, for example, one might expect no sign anomalies in that the carriers with negative effective mass would undergo two successive reversals of sign of acceleration in electric and magnetic fields.

The third alternative, i.e., something other than band theory, points in the direction of hopping theory[20] or small polaron theory.[24] Temperature-dependent measurements would aid in the choice between alternatives.

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Melting of Sodium Chloride at Pressures to 65 kbar*

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The melting curve for sodium chloride has been determined to 65-kbar. The present curve is in close agreement with those of Clark and Pistorius. The melting relation proposed by Kennedy has been examined in the light of the new melting data. The plot of melting temperature versus compression is slightly concave towards the $\Delta V/V_0$ axis at higher compression. This phenomenon may be due to a pressure dependence of the Grüneisen constant, but may also be due in part to possible uncertainties in the compression.

INTRODUCTION

THE melting temperature of sodium chloride has been determined by Clark[1] to 18 kbar and by Pistorius[2] to 40 kbar in a piston-cylinder apparatus. Kormer et al.[3] have reported data on melting and compression of NaCl at pressures of 540 and 700 kbar from shock-wave experiments.

A number of workers have reported on the compressibility of sodium chloride using a variety of methods. Bridgman[4] determined the compressibility of sodium chloride by static measurements up to 100 kbar. Dynamic measurements of the compressibility of NaCl have been made by Christian,[5] Al'tschuler et al.,[6] and Kormer.[3] Decker[7] has derived an equation of state for sodium chloride using a Born-Mie lattice model, and Keeler[8] has evaluated and reduced the shock-wave Hugoniot to the 25° isotherm.

The use of sodium chloride for high-pressure calibration has been proposed by some authors. Drickamer et al.[9] have expressed the compression of some metals and compounds on an NaCl pressure scale. McWhan[10] studied the lattice parameters of quartz as a function of pressure using NaCl as an internal pressure standard. No phase change takes place in NaCl until circa 250 kbar. Probably a continuous single-valued PVT relation and melting curve for NaCl extends to very high pressures. Recent works by Bassett and Takahashi[11] and by Jamieson[12] and others shows that the low-pressure, 20-kbar transition in sodium chloride suggested by some authors does not exist.

In this investigation, the melting curve of sodium chloride has been extended up to 65 kbar using single-stage piston-cylinder apparatus. The melting relation proposed by Kraut and Kennedy[13] has been examined in the light of the new melting data.

Experimental Method

The experiments were carried out in a piston-cylinder apparatus previously described by Cohen et al.[14] Haygarth and Kennedy[15] have shown that the crushing strength of a cemented tungsten carbide piston increases as the unsupported piston length decreases. In order to achieve the amount of piston travel necessary to generate the required pressure and at the same time to control the length of the unexposed piston, the piston

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