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Cyclotron Resonance in a Molecular Crystal—Anthracene

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Cyclotron resonance of holes orbiting in the ***a-b*** plane of an anthracene crystal has been observed. This represents the first time that this phenomenon has been observed in a molecular crystal. From these experiments, the hole effective mass is determined to be $11m_e$ where m_e is the free-electron mass. The hole scattering time at 2°K was measured in two different crystals and found to be $\sim 7\times10^{-11}$ sec in one crystal and 4×10^{-10} sec in the other.

Cyclotron-resonance experiments have been extremely important for the elucidation of band structure and mobile-charge scattering mechanisms in covalent,[1] ionic,[2] and metallic crystals.[3] In this paper I report the first successful application of this technique to charge carriers in a molecular crystal, specifically to holes in highly purified anthracene crystals. The extension of this technique to molecular crystals is of particular importance because of the absence, at the present time, of any other experimental method capable of unambiguously unraveling detailed band-structure information and carrier-scattering quantities.

The experimental technique used to detect cyclotron resonance is similar in principal to methods used previously.[1] The anthracene crystal is placed in a microwave cavity at a position of maximum electric field. The magnetic field is perpendicular to the microwave electric field and is slowly scanned from 0 to 25 kOe. If ω_c is the fixed microwave frequency, m^* the effective mass of the holes being investigated, and H the variable magnetic field strength, microwave power will be absorbed in the cavity whenever the well-known resonance condition

$$\omega_c = eH/m^*c \tag{1}$$

is satisfied. Scattering by phonons and impurities will tend to broaden the resonance signal. In fact a distinct resonance maximum cannot be observed unless $\omega_c\tau \gtrsim 1$, where τ is the carrier-scattering time. To maximize τ, one works at as low a temperature as possible, in this experiment 2°K, and with highly purified anthracene crystals.

Several modifications of the conventional cyclotron-resonance apparatus were made to meet the peculiar requirements of anthracene. Since the effective mass for both holes and electrons was unknown, I used tunable re-entrant coaxial microwave cavities[4] covering the range from 1 to 4 GHz. In this way I could in principle measure effective masses as high as $70m_e$, where m_e is the free-electron mass.

The holes in anthracene were created by photoinjection[5] from a layer of Ag paste painted onto one side of the crystal. The exciting light from a high-pressure Hg lamp entered the microwave cavity through a small hole in the bottom of the cavity. The light passed through the crystal and struck the Ag layer, injecting holes into the anthracene. The exciting light was chopped at 510 Hz and any change in microwave absorption in phase with this chopped light was detected. By placing various glass filters in front of the light source, I was able to demonstrate that light of any wavelength between 4000 and 8000 Å could produce a cyclotron-resonance signal. For shorter wavelengths the light was entirely absorbed at the front surface. Wavelengths beyond 8000 Å were inaccessible because of the weakness of the Hg lamp in this region. The photoinjection threshold for the Ag-anthracene system is 9250 Å.[5] The spectral dependence of the cyclotron-resonance signal is the only evidence that the observed resonance is in fact due to holes. Electrons cannot be photoinjected from Ag into anthracene.

Figure 1 shows experimental cyclotron-resonance curves for two different anthracene crystals at two different microwave frequencies. In both cases the magnetic field was perpendicular to the a-b crystal plane.[6] In the upper curve the line is very broad indicating that the scattering time is quite short, less than 7×10^{-11} sec. In the lower curve the scattering time is much longer and the peak is consequently much sharper. Here τ is about 4×10^{-10} sec. The difference in τ for the two crystals is probably due to differences in defect concentration. The crystal giving the broad resonance signal appeared to be under considerable strain in the cavity and shattered on warming to room temperature. The other crystal was cycled between 2°K and room temperature three times with no visible sign of deterioration.

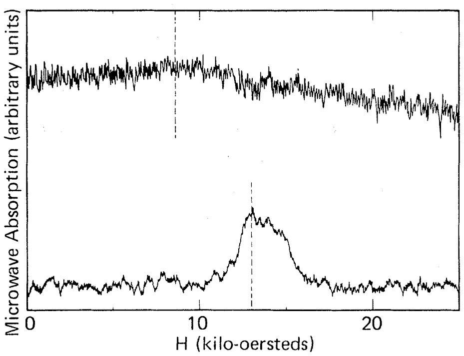

FIG. 1. Experimental cyclotron-resonance curves for holes in antracene at 2°K. The magnetic field was perpendicular to the a-b plane. For the upper curve the microwave frequency was 2.30 GHz and for the lower curve it was 3.50 GHz. The vertical dotted line in both cases represents the point at which a cyclotron-resonance maximum should occur if $m^* = 11m_e$.

Using Eq. (1) we can calculate the position of the cyclotron-resonance maximum if we know the effective mass. Figure 1 indicates this position for both microwave frequencies by the dotted vertical line, assuming an effective mass of $11m_e$. Although the upper curve is quite broad, one quite clearly can see the shift of resonance position with microwave frequency. To facilitate comparison between theory and experiment, Fig. 2 illustrates theoretical resonance curves[1a] expected for an effective mass of $11m_e$ and for the scattering times mentioned previously. In addition to the shift with frequency, also note the good general agreement between theoretical and experimental line shapes. The only free parameters used to construct the curves in Fig. 2 are m^* and τ.

Perhaps it would be well at this point to inject a word of caution. The apparatus used is quite sensitive to small changes in the electronic char-

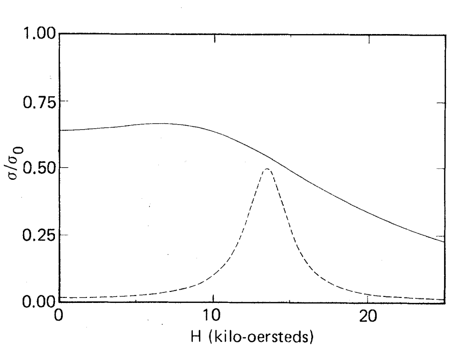

FIG. 2. Theoretical cyclotron-resonance curves. The solid line is for $m^* = 11m_e$, $\tau = 7\times10^{-11}$ sec, and $\omega_c = 2.30$ GHz. The dashed line is for $m^* = 11m_e$, $\tau = 4\times10^{-10}$ sec, and $\omega_c = 3.50$ GHz. The vertical scale is the ratio of the microwave to dc conductivity.

acteristics of the cavity. Spurious signals remain a worrisome possibility. Several experiments were conducted to eliminate this possibility. The signals displayed in Fig. 1 disappear if the light is prevented from entering the cavity. If a piece of fused quartz of the same size as the anthracene crystal and like the anthracene crystal coated on one side with Ag is placed in the cavity, no signal is observed. These two negative results indicate that the signals observed are due to the effect of light and magnetic field on the microwave conductivity of anthracene. That this effect has its origins in hole cyclotron resonance is indicated by the agreement between theoretical and experimental line shapes (Figs. 1 and 2), the linear shift of the resonance position with microwave frequency, and the preliminary observation that turning the magnetic field into the a-b plane shifts the resonance position to higher magnetic fields. Effective-mass anisotropy is observed in Ge and Si[1] and is expected in anthracene.

As an example of the way in which these cyclotron-resonance measurements can be used to understand the band properties of charge carriers in molecular crystals, let us compare the experimental hole effective mass with the effective mass determined from the band-structure calculations of Silbey *et al.*[7] Table I shows the calculated "unidirectional" effective masses for electrons and holes near the bottom of the band. One of the big problems in band-structure calculations on molecular crystals is to evaluate accurately the amount by which the intramolecular vibrations reduce the bandwidth. It is known that these vibrations reduce the triplet-exciton bandwidths in anthracene,[8] naphthalene,[9] and benzene[10] by factors of 3 to 4. If one assumes a similar reduction for holes and electrons, one must multiply the effective masses in Table I by 3 or 4.

To compare the effective masses in Table I with the experimentally determined effective mass, we use the expression derived by Shockley,[11]

$$m^* = [m_a m_b m_{c'} / m_a \alpha^2 + m_b \beta^2 + m_{c'} \gamma^2]^{1/2}, \qquad (2)$$

where α, β, and γ are the direction cosines of the angle between the orthogonal a, b, and c' crystal axes and the magnetic field. For the experiments reported here H was parallel to c'. From Table I and Eq. (2) we get an m^* value of $9.5m_e$ for this case, which must then be multiplied by a factor of 3 or 4. This is clearly not in agreement with the experimental effective mass of $11m_e$. The band-structure calculations seem to underestimate the bandwidth along the a crystal axis. This can also be seen by comparing the theoretical and experimental hole drift-mobility ratios.[7] It thus seems from the experiments reported here and from drift-mobility measurements reported by others that the calculated hole band is too flat in the a direction. More detailed measurements of the hole effective-mass anisotropy should prove valuable in calibrating and assessing the usefulness of band-structure calculations.

TABLE I. Calculated effective masses for electrons and holes in anthracene in units of electron mass.

	m_a	m_b	$m_{c'}$
Electrons	7.70	5.39	4.08
Holes	29.88	3.01	2.65

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