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Charge Carrier Production and Mobility in Anthracene Crystals

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The drift mobilities of electrons and holes in anthracene crystals have been measured using a pulsed photoconductivity technique. The mobilities found at room temperature vary from about 0.3 cm^2/volt sec to about 3 cm^2/volt sec, depending on the crystal orientation, and the mobilities increase as the temperature is lowered. The wavelength dependence of the number of charge carriers produced by a pulse of light, as well as other experimental data, indicates that the charge carriers are not produced in the interior of anthracene crystals, but that they are released from a surface layer of the crystal either directly by photons or by excitons which migrate to the surface.

INTRODUCTION

In recent years there has been a marked increase in interest in the semiconducting and photoconducting properties of organic solids.[1] A large part of this work has been directed toward an understanding of the properties of anthracene. Anthracene is essentially an insulator, with a resistivity in the neighborhood of 10^{14} ohm cm, and its resistivity decreases exponentially with increasing temperature with an activation energy of about 0.8 ev.[2] Light with wavelengths shorter than about 4000 A causes photoconductivity in anthracene, but the origin of the charge carriers is not known. The absorption spectra of anthracene crystals can be explained in terms of excited states of the molecules,[3] and therefore the photons are not producing free charge carriers directly. Direct measurements of the mobility of the charge carriers in anthracene have not been reported, but in general it has been concluded that holes are more mobile than electrons[4] and that the mobility is between 10^{-3} and 1 cm^2/volt sec.[5]

The work reported in this paper shows that with very high purity anthracene it is possible to measure the drift mobility of both holes and electrons with a pulsed photoconductivity technique and that their mobilities are on the order of 1 cm^2/volt sec. The experimental results obtained using this technique also indicate that the charge carriers are not produced in the interior of the crystals but are produced at the surface either directly by photons or by excitons which migrate to the surface.

EXPERIMENTAL

The experimental technique used in the present work is similar to one that has been used in the study of ionic mobility in gases[6] and quite recently by LeBlanc[7] in a study of electron drift mobility in liquid *n*-hexane. Crystals one to two millimeters thick were placed between two conducting glass electrodes and held in a sandwich-type arrangement by a phosphor bronze spring. A short pulse of light was applied to one surface of the crystal through the conducting glass electrode. The light, which is effective in producing charge carriers, is all absorbed within 10^{-4} or 10^{-5} cm of the surface of the crystal[3] so that a group of charge carriers is produced near the illuminated electrode. Then under the action of the applied field, charge carriers of the same electrical polarity as that of the illuminated electrode drift through the crystal, and as they do, they displace electrons in the external circuit. With this arrangement no electrical contact between the electrodes and the crystal is necessary, and the crystal surface can be left essentially undisturbed. During the measurements the conducting glass electrodes were physically in contact with part of the crystal surface, but it was found that this contact played no role in the phenomena observed. Placing one-mil "Mylar" sheets between the crystal and the contacts had no effect on the experimental results. A vacuum of about 10^{-5} mm of mercury was maintained in the sample holder during measurements.

Very high purity anthracene crystals were obtained by first chromatographing high purity commercial anthracene in the dark on alumina. This material was sublimed in vacuum and then zone refined. After zone refining the anthracene was transferred into crystal growing tubes under an atmosphere of nitrogen. The crystals were grown by the Bridgeman technique. Estimates of the purity of the crystals based on emission spectroscopy, mass spectrometer measurements, and extrapolations from segregation coefficient measurements using radioactively tagged impurities indicate that they contained less than 2-ppm impurities.

Crystals one to two millimeters thick were cut from large ingots and oriented so that the charge carriers would move in various crystal directions. In early work the cut crystals were polished on benzene-soaked tissue paper according to the method of Compton, Schneider, and Waddington,[4] however, it was found that abrasion had a marked effect on the pulsed photocurrent. There-

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[1] An excellent review of this work has recently been given by G. C. B. Garrett, in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959).

[2] H. Mette and H. Pick, Z. Physik **134**, 566 (1953).

[3] D. P. Craig and P. C. Hobbins, J. Chem. Soc. **1955**, 2309.

[4] See, for example, D. M. J. Compton, W. D. Schneider, and T. C. Waddington, J. Chem. Phys. **27**, 160 (1957).

[5] L. E. Lyons and G. C. Morris, J. Chem. Soc. **1957**, 3648.

[6] See, for example, M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).

[7] O. H. LeBlanc, J. Chem Phys. **30**, 1443 (1959).

fore, in later work the crystals were rinsed in benzene and then acetone after polishing. Crystals prepared with this treatment gave results almost identical with those obtained from freshly cleaved crystals. There was some indication that the charge carrier distribution was smeared out slightly by this treatment.

Light pulses approximately 2 microseconds long were obtained from a xenon flash tube. Power for the flash was obtained from a 1 μf condenser charged to 10 kv. The light was filtered with appropriate Corning glass color filters or was passed through a Bausch and Lomb grating monochromater when monochromatic light was needed.

Electronically, the experimental arrangement consisted of a battery voltage supply connected to one electrode, and a Tektronix type P170CF cathode follower probe connected to the other. The input impedance of this probe is 12 megohms shunted by 5 $\mu\mu$f. It was found that sufficient sensitivity for most of the work could be obtained with 1 megohm in parallel with the cathode follower probe input, and at high electric fields a 0.1-megohm resistor provided a sufficiently large signal. The *RC* time constant of the circuit with the 1-megohm resistor in parallel with the cathode follower probe input was about 20 microseconds. The output of the probe was amplified by a Tektronix type 121 preamplifier and observed with a Tektronix type 533 oscilloscope.

With this experimental arrangement the flash of light produces a group of charge carriers near the illuminated electrode, and their motion through the crystal can be observed on the oscilloscope. The pulses that are observed are up to several hundred microseconds long and show an abrupt change near the end. Figure 1 shows an example of the pulses obtained. The length of the pulses is inversely proportional to the applied field and proportional to the thickness of the crystal with constant applied field. The electric fields that have been used varied from about 100 v/cm to about 6000 v/cm.

The mobility of the charge carriers was calculated from the relation $\mu = d^2/Vt$, where μ is the mobility, d the crystal thickness, V the voltage applied, and t the time between the light pulse and the abrupt change in slope near the end of the current pulse. The length of the tail of the pulses is considerably longer than would be expected from random diffusion. Therefore, it was decided to use the time to the abrupt change in slope rather than the time to half maximum or some other value for the mobility calculations.

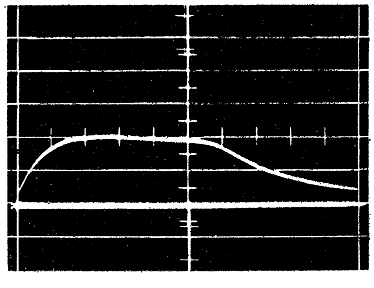

FIG. 1. An example of the pulses obtained. Each division on the horizontal axis represents 50 μsec.

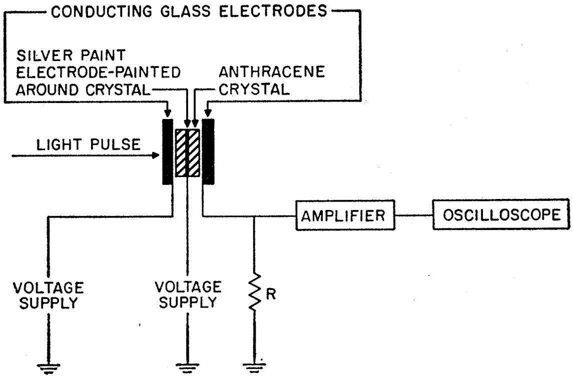

FIG. 2. Block diagram of experimental arrangement with three electrodes.

Space charge effects were investigated by varying the light intensity and consequently the number of charge carriers in a pulse. With some crystals at high light intensities and low applied electric field, some indications of space charge effects were observed, but they were easily eliminated by lowering the light intensity or increasing the applied field.

The possibility that surface current was being observed was eliminated by placing a thin band of silver paint around the center of a cylindrical crystal 4 mm long. The experimental arrangement is shown in Fig. 2. The voltage applied to this third electrode was varied with respect to the voltage applied to the two conducting glass electrodes. This experiment not only verified that surface currents were not important for this experimental arrangement but also showed the direction of motion of the charge carriers. The electric field within the crystal was very badly distorted, but when the voltage applied to the third electrode was equal to that applied to the illuminated electrode, the charge carriers moved very slowly during the first part of the pulse and then rapidly during the last part. The reverse was true when the voltage applied to the third electrode was equal to that applied to the unilluminated electrode. Examples of these pulses are shown in Fig. 3.

This experiment, therefore, verified the fact that the drift mobility of both holes and electrons could be measured with this experimental technique simply by changing the polarity of the voltage applied to the illuminated electrode.

RESULTS

Pulsed photoconductivity measurements have been made on a large number of small crystals cut from approximately ten large crystals. It was found that even with the fairly extensive purification procedure briefly described above the purity of the crystals is marginal

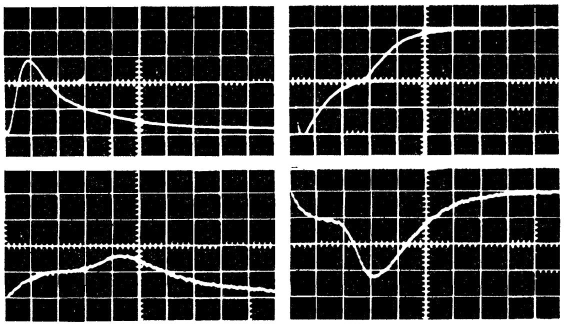

FIG. 3. Examples of the pulses obtained with the three electrode experiment. Left side, positive carriers moving, current increasing upward from bottom line. Right side, negative carriers moving, current increasing downward from top line. Top, high electric field near illuminated electrode, and bottom, low electric field near illuminated electrode. Each major division on horizontal axes represents 100 μsec.

for the experimental technique being used. In the crystals that appear to be less pure, the lifetime of the carriers is reduced so that the magnitude of the pulses decreased with time. The lifetime of the negative carriers appears to be affected most frequently. It is thought that the differences in lifetime are caused by impurities rather than crystal imperfections because all the small crystals cut from one large crystal show the same characteristics, and no correlations between crystal perfection (based on visual observation between crossed polaroids) and charge carrier lifetime have been observed.

In crystals cut from the purest large crystal, the mobilities in the direction perpendicular to the cleavage or *ab* plane were approximately 0.4 and 0.3 cm^2/volt sec for the holes and electrons, respectively. In a direction parallel to the cleavage plane, the mobilities were 2.0 and 1.3 cm^2/volt sec with the electrons being the most mobile in this direction. Because of Mette and Pick's[2] results it was initially assumed that the mobility would be isotropic in the *ab* plane; therefore, the direction of motion in the *ab* plane was not determined. Recent results, however, indicate that the mobility is anisotropic in this plane, but the anisotropy has not been measured because of a lack of a sufficient number of pure crystals.

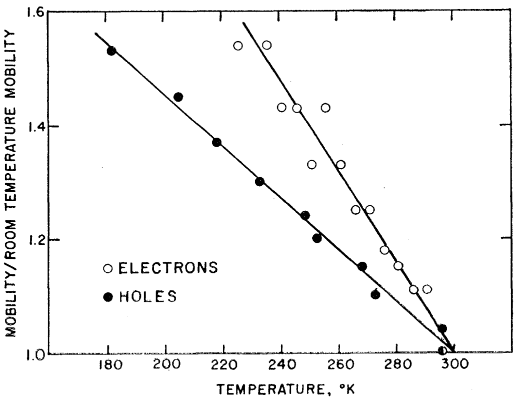

FIG. 4. Temperature dependence of charge carrier mobilities.

The temperature dependence of the electron and hole drift mobilities perpendicular to the *ab* plane is shown in Fig. 4. The measurements were made on two different crystals. In the crystal in which the electron mobility measurements were made, it was not possible to measure the temperature dependence of the hole drift mobility because the pulses became distorted as the temperature was lowered. A similar change in the negative pulse shape occurred below −50°C. In the crystal in which the hole mobility measurements were made, the electron mobility could not be measured, even at room temperature. The temperature dependence of the hole mobility in one direction parallel to the ab plane was measured in a third crystal. The dependence was approximately the same as that observed perpendicular to the *ab* plane.

The number of charge carriers produced by a flash of light was measured as a function of temperature by integrating the area under the pulses. In general, it was found that the number decreased as the temperature was lowered, but different crystals gave different results, indicating that the temperature dependences observed were not intrinsic properties of the anthracene crystal.

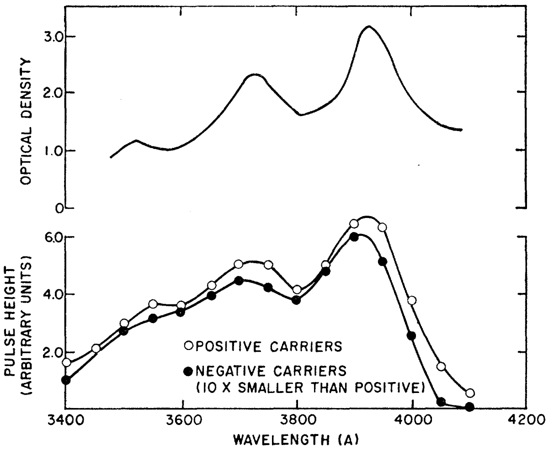

FIG. 5. Wavelength dependence of the number of charge carriers produced by a flash of light. The upper curve shows approximately the absorption spectrum of anthracene.

The wavelength dependence of the number of holes and electrons produced by a pulse of light is shown in Fig. 5. The upper curve in Fig. 5 shows approximately the variation of absorption coefficient at room temperature as determined by Craig and Hobbins.[3] No attempt was made to keep the light intensity constant as the wavelength was varied. It was assumed that any change in the light intensity was gradual and would not reproduce the shape of the anthracene absorption. The conducting glass electrodes became opaque rapidly at wavelengths below 3400 A. The monochromator used had a dispersion of 60 A/mm, and the entrance and exit slits were set at 2 mm.

A similar effect of the strength of absorption on the number of charge carriers produced by a pulse of light was observed by varying the polarization of the light with respect to the crystal axes. Anthracene is dichroic when illuminated normal to the *ab* plane, the larger extinction coefficient being observed when the electric vector is parallel to the *b* axis.

The variation of the number of charge carriers produced as a function of the light intensity is shown in Fig. 6. Bausch and Lomb neutral density filters were used to vary the light intensity. Corning glass color filter No. 3850 was used in addition to the neutral density filters to eliminate the short wavelength region where there might have been variations in the neutral filters.

DISCUSSION

The most significant result of this work is the measurement of the mobility of the charge carriers. Results of dc experiments, as mentioned before, indicate that holes are considerably more mobile than electrons; however, this work shows that their drift mobilities are nearly equal and that in at least one direction parallel to the *ab* plane, electrons are, in fact, more mobile than holes. The reason for the discrepancy between the two types of measurements is apparently involved in the mechanism of the production of free charge carriers. The ratio between the number of holes and electrons produced by a pulse of light depends markedly on the condition of the illuminated surface. When the surface has been abraded or exposed to ultraviolet light in the presence of oxygen, the number of holes observed is 10 to 100 times larger than the number of electrons. Therefore, the large rectification effects observed in dc experiments can be explained by a difference in quantum efficiency for production of free holes and electrons. With the present technique the ratio between the number of holes and electrons produced by a pulse of light has been observed to vary from 100 to 1 to approximately 1 to 10. Perferential trapping of electrons by impurities might also account for the discrepancy if the trapped electrons set up a space charge.

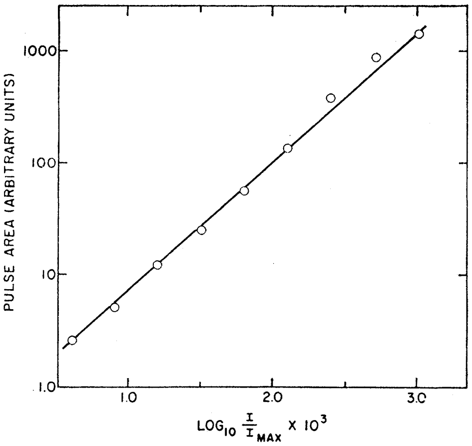

FIG. 6. Light intensity dependence of the number of charge carriers produced by a flash of light.

The temperature dependence of the mobility of the charge carriers appears to eliminate the possibility of an activated or hopping process for the mobility of the charge carriers as suggested by Kommandeur, Korinek, and Schneider.[8] If the charge carrier motion were an activated process, the mobility would decrease exponentially with temperature.

The wavelength dependence of the number of charge carriers produced by a pulse of light supports the proposal by Carswell and Lyons[9] that the charge carriers are produced at the crystal surface. Even though all the light is absorbed within a very short distance in the crystal, it is found that when the light is absorbed most strongly, the largest number of charge carriers is produced. These results indicate that either a photon or exciton concentration effect or a surface effect is involved in the charge carrier production mechanism. However, if two photons or two excitons were required to produce a charge carrier, the number of charge carriers produced by a pulse of light would increase as the square of the light intensity if recombination effects did not interfere. The light intensity dependence, shown in Fig. 6, appears to be slightly superlinear but is far from an intensity-squared dependence.

The wavelength and polarized light dependence observed in this work have previously been observed in anthracene when two electrodes were placed on the same surface of the crystal and the surface was illuminated uniformly between the electrodes.[9] However, when the electrodes were placed on opposite sides of the crystal and the crystal was illuminated through one of the electrodes which was semitransparent, different results were obtained.[4] These results led many to the conclusion that there are two kinds of photoconductivity in athracene, bulk and surface. The present work indicates that the discrepancies were caused by space charge and electrode effects.

The observations reported here, therefore, indicate that charge carriers, both electrons and holes, are released from a surface layer of the anthracene crystal, either directly by photons or by excitons which migrate to the surface, that they move in the bulk of the crystal with mobilities of the order of 1 cm^2/volt sec and that their mobilities increase as the temperature decreases.

ACKNOWLEDGMENTS

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[8] J. Kommandeur, G. J. Korinek, and W. G. Schneider, Can. J. Chem. **35**, 998 (1957).

[9] D. J. Carswell and L. E. Lyons, J. Chem. Soc. **1955**, 1734.