BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2073—2077 (1967)

Charge-carrier Mobility in Anthracene Single Crystals

Yusei MARUYAMA and Hiroo INOKUCHI

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo

(Received March 22, 1967)

In order to examine the effect of space-charge polarization in the course of drift-mobility measurements in anthracene single crystals, we employed a pulse electric field and measured the change in photoresponses according to the light-delay times. No distinct reduction of photoresponses was found, and the value of mobility was nearly the same as the one obtained by measurement with the conventional dc field. To obtain knowledge of the microscopic mobility in anthracene crystals, we also measured the photo-Hall effect of anthracene using the Redfield, Kobayashi and Brown method. The observed Hall mobility was in the range of 25—200 $cm^2/V \cdot sec$. This large value of Hall mobility will be briefly discussed in terms of the multiple-trapping effect.

The drift mobility for anthracene single crystals has been measured by several workers;[1] the value has been reported to be of the order of the magnitude of 1 $cm^2/V \cdot sec$. In the experimental method employed by them, the pulsed photoconductivity measurement, a large dc electric field was applied to the crystal; then, if the crystal had a considerable dark conductivity, a space-charge field might be built up in the crystal by the dark current during the measurements. This space-charge field would reduce the net electric field-strength driving the photogenerated charge-carriers in the crystal, and then the drift mobility would be apparently evaluated to a smaller value. To avoid this difficulty, a pulse electric field or an ac field should be employed. In this report, the experimental methods and the results using the pulse-field technique will be described.

It is another important problem whether or not the observed mobility is a microscopic one.*1 If many shallow traps are present in the crystal, the drift mobility may be reduced to a smaller value than the true one. In such cases, the Hall mobility is generally believed to be closer to the microscopic mobility than the drift mobility.

Recently, Dresner observed the photo-Hall effect in anthracene and found that the Hall mobility for electrons exceeded 50 $cm^2/V \cdot sec$ and 30 $cm^2/V \cdot sec$ for holes.[2] He employed the Se-Te alloy as an electrode material having good ohmic contact with the specimen, and observed the Hall signal on the illuminated surface by applying a dc electric field.

In the usual dc Hall-effect measurements, it is necessary to establish a steady-state Hall field polarization through a transverse charge displacement due to the Lorentz force and to assure the free transport of carriers through a crystal-electrode contact. These requirements are sometimes difficult to satisfy in insulating photoconductors, or high-impedance substances. Thus there is a possibility that the Hall signal will be so much disturbed that it cannot be distinguished from the noise, or if not, that it will be observed as smaller than the true value.

To eliminate the effect of the polarization, pulse and transient methods should be employed. In this report, we will present the results of our measurements of the photo-Hall effect of anthracene using the method of Kobayashi and Brown,[3] which is a refinement of the Redfield technique.[4]

Experimental

Drift Mobility Measurement by Pulse Electric Field. At first, for the measurement of the drift mobility, we intended to use a bridge circuit,[5] but the balancing operation made it too difficult to obtain a high sensitivity for detecting a small photo-signal. Then, a syncroverter switch*2 was empolyed in order to charge an electric field on the specimen instantaneously and to observe a signal after opening the relay.[6]

Figure 1 shows a block diagram of the experimental arrangement: When a mercury-wetted contact relay switches off the coil circuit of the syncroverter switch (S-switch) by a rotary cam, a field pulser and a synchroscope are triggered by the differentiated signal of the coil circuit. The S-switch is opened 20—30 μsec after this signal. Within this period the pulse electric field is charged on the crystal. After the S-switch is opened, a light pulser is triggered by an appropriately

1) O. H. LeBlanc, *J. Chem. Phys.*, **33**, 626 (1960); R. C. Kepler, *Phys. Rev.*, **119**, 1226 (1960).

*1 The microscopic mobility is the quantity involving the true velocity of electrons in the conduction band.

2) J. Dresner, *Phys. Rev.*, **143**, 558 (1966).

3) K. Kobayashi and F. C. Brown, *Phys. Rev.*, **113**, 507 (1959).

4) A. G. Redfield, *ibid.*, **94**, 526, 537 (1954).

5) F. C. Brown, *J. Phys. Chem. Solids*, **4**, 206 (1958).

*2 Micro-reed-relay.

6) K. Kobayashi, private communication.

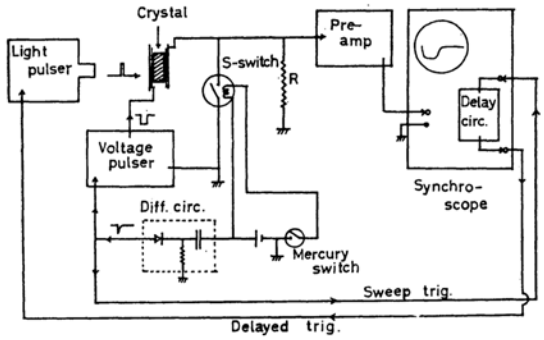

Fig. 1. Block diagram of experimental arrangement for drift mobility measurement.

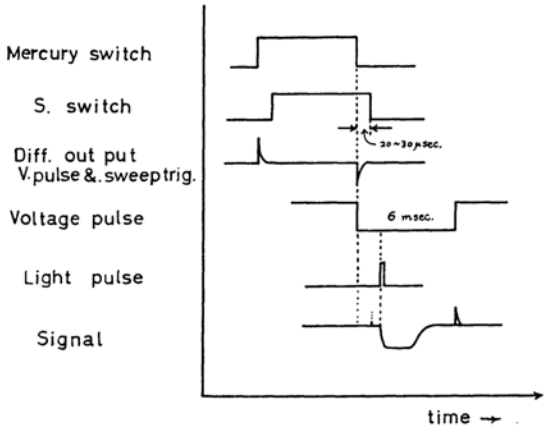

Fig. 2. Mutual timing relation among signals.

delayed signal from the synchroscope and a photo-signal is observed on the oscilloscope screen. One cycle of this operation is carried out every fifteen seconds. Figure 2 shows the mutual timing relation among these signals.

Syncroverter Switch. A micro-reed-relay, model SRA-III (Nippon Electric Company Ltd.), was used. The mechanical delay of the response at the contact point was 20—30 μsec. The chattering noise, however, continued for about one millisecond after the contact point was opened; the delayed time for the light pulse could not be made shorter than this interval, one millisecond. When the input resistance was small enough, about 22 kΩ, the time for charging the field was very short, less than one microsecond; then no relay was needed and a photo-signal was observable with a sufficiently short delay time, 5 μsec.

Electric-field Pulser. Single flat-top large-amplitude pulses were supplied by a pulse generator, followed by a paraphase driver and a push-pull amplifier employing two 6DQ6Bs.*3 The output of the pulse generator was about 100 V, and the duration was variable over the range of 0.05—10 msec. The field pulse was variable from 0 to 1600 V and from 0.05 to 10 msec in duration. Both phases of pulses, plus and minus, were available in about the same amplitude. In this experiment the negative pulse was applied, since its rise time was much shorter, being less than about 5 μsec, than that of the plus pulse.

*3 Toshiba Electric Co.

Samples. Anthracene crystals, zone-refined and grown by the Bridgman technique,*4 were used for this measurement. The crystals, about one to two millimetres thick, were cut from large ingots, and the mobility in the direction perpendicular to the cleavage or the ab plane was observed.

The Hall Mobility Measurement. We tried to measure the Hall effect of anthracene by the Redfield, Kobayashi, and Brown method.[3,4] The electrode geometry of this method is indicated in Fig. 3. In this geometry, the electric field in the y-direction is applied

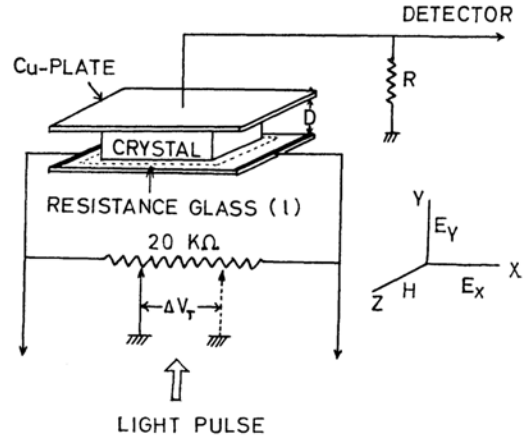

Fig. 3. Single electrode Redfield geometry; the Kobayashi and Brown method.

from outside the crystal at the same time of the application of the x-direction electric field under the z-direction magnetic field in such a way that the current density is directed in the x-direction. In other words, the component of the current density in the y-direction is zero at the time of the injection of carriers by the illumination of a light pulse. Thus the establishment of a Hall field due to carrier displacement in the y-direction inside the crystal is not required, and the observation of the Hall angle is not influenced by the carrier concentration and the time. The electrodes are blocked completely from the crystal by inserting Mylar sheets, and the drift of carriers in the y-direction is observed from the induced charge flow in the external circuit. Thus, there is no difficulty with the contact problem in these measurements. The total amount of drift of charge, however, must be kept small by the illumination of light of a low intensity or of short duration in this electrode arrangement.

Figure 4 shows the block diagram for whole system. When a mercury-wetted contact relay is switched off by a rotary cam, a pulser and a synchroscope are triggered by the differentiated signal of the switch. A square-wave electric field, 10 msec in duration, from the pulser is applied to a coil of the syncroverter switch, and then a voltage pulse of about 100 V, floated from the ground, is applied to the resistance film electrode (Nesa glass electrode). The potential gradient on the resistance film provides the longitudinal component, E_x, of the electric field, so that carriers will be deflected by the transverse magnetic field (z-direction). The transverse electric field (y-direction) is applied by varying

*4 Kindly provided by Professor I. Nakada.

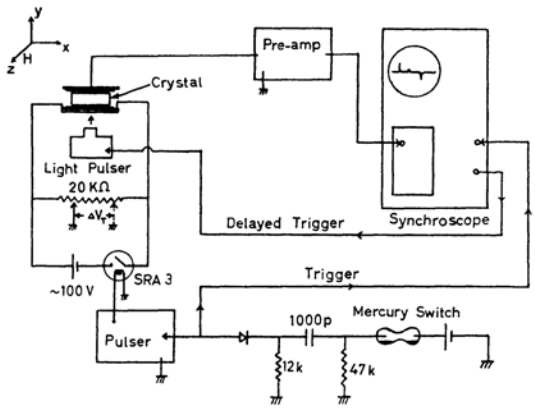

Fig. 4. Block diagram of experimental arrangement for photo-Hall effect measurement.

the position of the ground tap on a potentiometer (a herical-ohm resistor). Brief single pulses of light, about 1 μsec in duration, from an air spark triggered by a hydrogen thyratron are started by the delayed signal from the synchroscope delaying circuit.

When the carriers are released in the crystal by a pulse of light, the charge is induced on the upper equipotential signal electrode by the drift of the carriers within the volume of the crystal. This induced charge is detected by a preamplifier and a wide-band oscilloscope (Tektronix 545 A). The input time constant of the system, consisting of amplifier, leads and crystal, is such that an integrated charge, Q, is registered for a drift of carriers in the volume of the crystal.

The data for $+H$(forward) and $-H$(reverse), and also the reading at $H=0$, were taken. The balance was achieved by varying the position of the ground tap on the potentiometer. The change in resistance, ΔR, is proportional to ΔV, the change in voltage between opposite points on the electrodes. With a $+H$ magnetic field, the potentiometer is carefully adjusted for no response with light pulses on; a similar balance, $Q=0$, is obtained with $-H$. The potential difference, ΔV_T, between $+H$ and $-H$ cases is expressed by the relation:[3]

$$\Delta V_T/D\overline{E_x} = -2\mu_H H/c = 2\theta_H, \qquad (1)$$

where D is the thickness of the specimen; $\overline{E_x}$, the mean field strength in the x-direction; μ_H, the Hall mobility; c, the light velocity, and θ_H, the Hall angle.

The potentiometer used was a ten-turn-type helical-ohm resistor, the dial division of which could be read to $1/10^3$. Let ΔR_T be the potentiometer dial readings corresponding to ΔV_T, and L, the length of the resistance film; the relation:

$$\Delta V_T = LE_x(\Delta R_T/10^3), \qquad (2)$$

is then obtained. From Eqs. (1) and (2), the Hall mobility, μ_H, is given as:

$$\mu_H = \frac{c\cdot\Delta R_T\cdot L}{2H\cdot D\cdot 10^3}.$$

Samples. Thin sublimated crystals and crystals the surfaces of which were dissolved with xylene to thinner flakes, were employed.*5

Results and Discussion

Drift Mobility. When the input resistor was one megohm, the wave-form observed on the oscilloscope was a charge pulse (Q pulse). This form was desirable for the measurements of the relation between the pulse heights and the delay time of the light pulse, and for the finding of the saturation of the photo-induced charge. For the former measurement, however, 22 kΩ input resistor was used to obtain a shorter delay time for the light pulse.

Figure 5 shows the photoresponse of the anthracene crystal as a function of the delay of the light pulse, measured from the initial point of the rise of the field pulse. Since the input resistor was 22 kΩ, the current pulse height was taken for

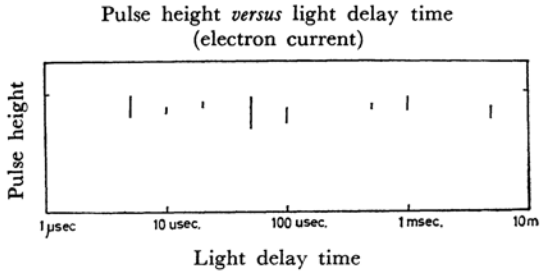

Fig. 5. Typical photoresponses *versus* light-delay times. The length of the lines indicates the fluctuation of the pulse heights observed for several times measurements.

the photoresponse. The field pulse, 6 msec in duration and 1600 V high, was applied to an anthracene crystal 0.90 mm thick and the light delay time was taken in the range of 5 μsec—5 msec. When the crystal was illuminated just after the duration of a field pulse, a photo-signal reversal in polarity was observed and the height of the signal increased with the repeated application of field pulses in the dark. These facts imply the formation of a polarization field by the dark current. No discernible change in response, however, was observed in this range of delay time; therefore, it seems either that the time for setting up a space-charge polarization field will be less than 5 μsec or that the polarization field is not so large as to modify the external field.

The values of the mobilities in the c'-direction were 0.2—0.3 cm^2/V·sec for the electron and 0.05—0.1 cm^2/V·sec for the hole, nearly equal to the values for the case of the dc field.*6

*5 The light which is effective in producing charge carriers is absorbed within a thin surface layer of the crystal. However, carriers generated in the bulk of the crystal are effective in this Hall-effect measurement; therefore, a thin crystal as possible is preferrable for the Hall effect measurement of anthracene.

*6 The field dependence of the mobility was observed. The mobilities slightly decreased with an increase in the field.

The polarization effect by a photocurrent was clearly recognized, and the depression of the pulse height and of the transit time followed, unless the polarization was dissipated. Consequently, a steady, low-intensity white light could be used to release the polarization. Repeated illumination of the light pulses was also used, until no reverse photo-signal at zero field was observed.

Figure 6 shows the saturation behaviour of the charge response with an increase in the applied field. The critical field for saturation was about 2×10^4 V/cm. From this value and the relation of $w=\mu E\tau$, where w is the average range or Schubweg of the carriers, μ, the mobility, E, the electric field strength, and τ, the mean time for trapping, τ is calculated to be 5×10^{-5} sec, equating w at the saturation field with the crystal thickness, 0.9 mm. On the other hand, τ is also calculable from the decay of the photocurrent pulse height. The value is about 5×10^{-4} sec.

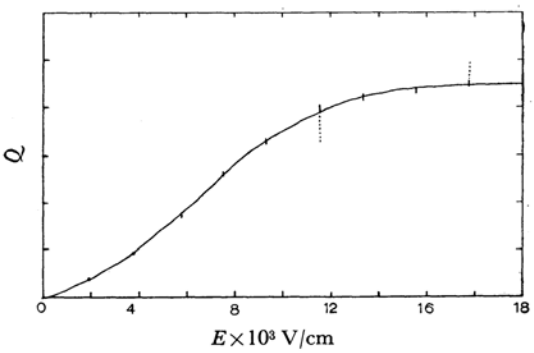

Fig. 6. Saturation behaviour of the charge response *versus* the applied electric field.
E_s $\sim2\times10^4$ V/cm, τ $\sim4.5\times10^{-5}$ sec

Hall Mobility. In Fig. 4, V_x was supplied with a dry battery (about 100 V), and L (the length of the resistance film) was 7.5 mm; then $E_x=V_x/L$ ~133 V/cm. The magnetic field strength used was 2×10^4 gauss. The lower limit of the measurements was $\mu_H\geqq10$ cm²/V·sec in terms of mobility; this limit was determined by means of the minimum potentiometer dial reading.

The Hall mobilities, μ_H, obtained are shown in Table 1.

TABLE 1. THE OBSERVED HALL MOBILITIES OF ANTHRACENE

	Thickness, D	ΔR_T	μ_H
Crystal-I	0.064 mm	0.4—0.7	120—200 cm²/V·sec
Crystal-II	0.383 mm	0.5—1.0	25— 50 cm²/V·sec

The two-carrier effect was involved in the observed mobility, but it was impossible in this experiment to know the value of mobility for either the electron or the hole separately. Because of two-carrier effect, it was also impossible to examine the anomaly in sign of the Hall mobility.[7] The temperature dependence of μ_H will be examined in the future.

The measurement of the magnetoresistance for anthracene was also made for similar crystals. The variation in the pulse height of the photocurrent in the presence of a magnetic field was observed in the transverse case: $\vec{H}\perp\vec{E}$. The electric field, E, was about 10^4 V/cm and the magnetic field, H 2×10^4 gauss. E was applied across the crystal between two plane-parallel electrodes, and the photocurrent was measured by the same method as the drift mobility.

The magnetoresistance mobility, μ_M, is given by the relation:[8]

$$\mu_M=\frac{c}{H}\sqrt{\frac{\sigma(0)-1}{\sigma(H)-1}},$$

where $\sigma(H)$ and $\sigma(0)$ are the conductivity with and without a magnetic field respectively. The electron currents and the hole currents were discerned from each other by the polarization of the illuminated electrode.

The magnetoresistance mobility for hole currents was in the range of $5.8\times10^2-1.0\times10^3$ cm²/V·sec, and for electron currents, in about the 1.5×10^3 cm²/V·sec range. These values, however, were not very reliable, since these measurements were carried out under inhomogeneous illumination, in the presence of noise from the magnetic field and a fluctuation in the intensity of the light pulses.

However, from these results regarding μ_H and μ_M, it may safely be said that the microscopic mobility for carriers in the anthracene crystal is at least of the order of 10^2 cm²/V·sec.

The dc photo-Hall effect in the transient state was also observed. The Hall mobility for holes was measured to be 34—92 cm²/V·sec. The electrode arrangement was a conventional type.

The reason why the Hall mobility of anthracene is anomalously large in comparison with the drift mobility is a new basic problem and rather difficult to answer at present. One possible interpretation is the multiple-trapping effect by shallow traps in the drift-mobility measurements. For a single set of shallow traps, the drift mobility, including the effect of traps, is given by:

$$\mu_D=\mu\left(\frac{1}{1+\tau_g/\tau_t}\right)$$

where μ is the mobility in the absence of traps; τ_g, the mean life of carriers in the traps, and τ_t, the mean trapping time for carriers in the conduction band.

7) L. Friedman, *Phys. Rev.*, **133**, 1668 (1964); O. H. LeBlanc, *J. Chem. Phys.*, **39**, 2395 (1963).
8) H. H. Tippins and F. C. Brown, *Phys. Rev.*, **129**, 2554 (1963).

The authors are indebted to Professor K. Kobayashi and Dr. H. Fujita for their kind direction and valuable discussions. Thanks are also due to Dr. H. Ohigashi for his cooperation in the drift mobility measurements. They are grateful also to the Fuji Film. Co. for its financial support. One of the authors, Y. M., would like to express his thanks to the Sakkokai Foundation for its financial support of his study.