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Charge Mobility of Organic Semiconductors under High Pressure. Anthracene

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The charge mobilities of anthracene single crystals were measured under high pressures up to 7.4 kbar. An experimental apparatus like Kepler's was used. A sample holder was attached in a Drickamer-type high-pressure photocell, with kerosene employed as the pressure-transmitting fluid. The electron mobilities along the a and b crystal axes increased as the pressure applied increased; the values of the charge drift mobility at 7 kbar were 1.7 times as large as those at atmospheric pressure. The electron mobility along the c′ axis was nearly constant. The hole mobility, however, could not be measured, because the tail of the pulse signal, observed on the oscilloscope, was deformed.

It has been revealed that the mechanism of the electrical conduction of many organic crystals, such as condensed aromatic hydrocarbons, is to be interpreted essentially as intrinsic semiconductors. The band gaps of the organic semiconductors have been found from the temperature dependence of the electrical conductivity or the threshold values of the spectral response of the external photoelectric effect.[1)]

The investigation of the charge mobility in the organic crystals has, however, been started only rather recently. The measurement of the drift mobility of anthracene using the method of photocarrier generation was reported by Kepler in 1960.[2)] Since then, many authors have made theoretical interpretations of the experimental data on mobility.[3)] It seems to be established that the carrier conduction is roughly to be interpreted as a band type. However, because of the complexity of the band calculation for the organic crystals, there remains some ambiguity.

The drift mobility of anthracene was found to be 0.3—3 cm^2/V. sec by the method of the photocarrier generation. To explain the small mobility of the aromatic hydrocarbon, it is necessary to assume either that the width of the energy band is very narrow or that the mean free path of the charge carrier is very short. With these assumptions, it is still difficult to explain numerically the mobility along the c′ axis, perpendicular to the ab plane, and more especially, its temperature dependence.

Kepler has established drift mobility for anthracene under high pressures (up to 3.0 kbar) and has explained it by a simple band calculation.[4)] The authors will present in this report the results of their experimental work on mobility measurements under high pressures (up to about 7.4 kbar); we wish to compare the experimental data with the results of the theoretical calculations.

Experimental

Figure 1 shows the experimental apparatus used for the mobility measurements under high pressures. The apparatus of the mobility measurements was like that used by Kepler.[1)]

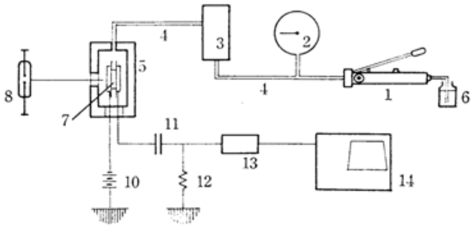

Fig. 1. Experimental apparatus for the mobility measurement under a high pressure.
1. handpump 2. pressure meter 3. pressure intensifier 4. steel pipe 5. high pressure optical cell (see Fig. 2) 6. oil reservoir 7. anthracene crystal 8. xenon flash lamp 9. quartz lens 10. battery 11. condenser 12. variable resistor 13. pre-amplifier 14. synchroscop

The crystals (7 in Fig. 1), approximately 1.5 mm thick (d), were mounted between a conducting glass electrode and a copper plate electrode with a voltage

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[1)] Y. Harada and H. Inokuchi, This Bulletin, **39**, 1443 (1966).

[2)] R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).

[3)] O. H. LeBlanc, *J. Chem. Phys.*, **35**, 1275 (1961); J. L. Katz, S. A. Rice, Sang-il Choi and J. Jortner, *J. Chem. Phys.*, **39**, 1683 (1963); R. Silbey, J. Jortner, S. A. Rice, and M. T. Vala, Jr., *ibid.*, **42**, 733 (1963); Y. Harada, Y. Maruyama, I. Shirotani and H. Inokuchi, This Bulletin, **37**, 1378 (1964).

[4)] R. G. Kepler, "Organic Semiconductors," ed. by J. J. Brophy and J. W. Buttery, The MacMillan Co., New York (1962), p. 1.

supply (10) connected to one of the electrodes and a resistor (12) connecetd to the other. A xenon flash lamp (8) with a pulse width of approximately 1-2 μ sec, was used.[*1] The resistance of the resistor (12) was 10—40 kΩ.[*2] The electric potential applied was 960-1360 V; that is, it was about $6\text{-}9\times10^3$ V/cm (V) on the specimen. When we observed the carrier transport time (t), the time from the light flash to the abrupt change in slope near the end of the pulse on the oscilloscope (14), the charge mobility (μ) may be calculated to be: $\mu=d^2/Vt$.

The mobility was independent of the applied potential in the above electric-field region. Further, the pulse signal observed on the oscilloscope was remarkably affected by the value of the resistor, but the carrier-transport time did not change.

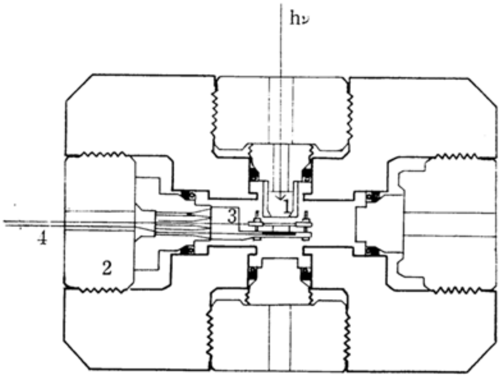

Fig. 2. High pressure optical cell.
1. window (sapphire or quartz) 2. plug 3. sample holder (see Fig. 3) 4. lead (see also Fig. 3)

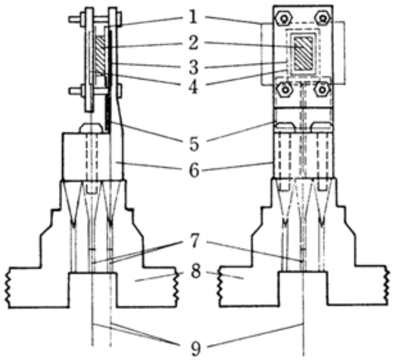

Fig. 3. Sample holder
1. myler thin film 2. anthracene crystal 3. cupper electrode 4. glass electrode 5. Bakelite 6. sample holder 7. ceramic pipe 8. plug 9. lead
Ceramic pipes (7) and leading-wires (9) passed through the oriffices and the orifices were sealed with Araldite D(CY-230).

The anthracene crystal mounted in the high pressure photocell, shown in Fig. 2, was compressed with the pressure-transmitting fluid, kerosene. The mobility was measured under hydrostatic pressures up to about 7.4 kbar. In Fig. 2, the window was made of sapphire or quartz 10 mm in diameter and 10 mm thick.

Figure 3 shows the sample holder, which is made mainly of Teflon. The leading-wires for the photocurrent measurement were passed through the narrow orifices (7 in Fig. 3), and then the orifices were sealed with a high-pressure binding agent.[*3]

The very pure anthracene crystals used in this study were grown by the Bridgman method. The specimens, cut from the anthracene crystal along the ab, the ac′, or the bc′ plane, were polished on fine emery-paper, and then on benzene soaked deer leather.

Results and Discussion

Figure 4 shows the pressure dependence of the drift mobility of anthracene. The pressure dependence of each lattice constant is not yet known because the high-pressure X-ray diffraction technique has not been fully developed. Therefore, the bulk volume change was used as a criterion.

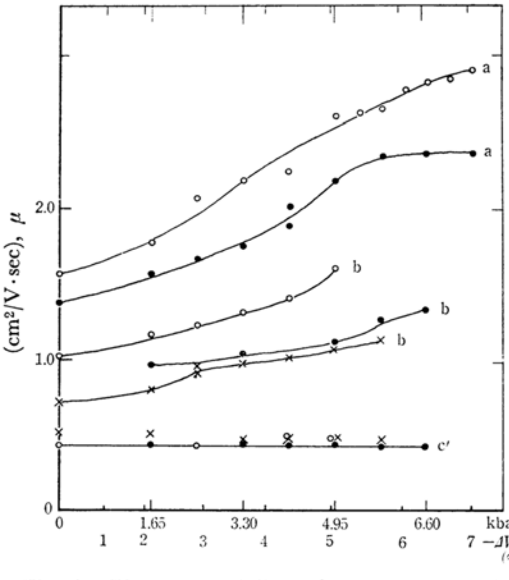

Fig. 4. Electron mobility of anthracene under high pressure.
Curves a are the relation for the anthracene single crystals, prepared from commercial, ○, and synthesized, ●, along a-axis. Curves b are the relation for the commercial anthracene along b-axis, ○ for the fine crystal, and ●, × for the crystal having small cracks along ab plane. Curve c′ is the relation for the anthracene single crystals, prepared from commercial ○, ●, and synthesized, ×, along c′ axis.

[*1] A noise pulse, approximately 7 μ sec long, was associated with the pulse. Therefore, in this instrument, no carrier-transport time shorter than 7 μ sec could be observed.

[*2] The amplification constant of the preamplifier was 10-20.

[*3] Araldite D(CY-230). Ciba Limited. Basle, Switzerland.

The values of the volume change, $(-\Delta V/V)$, were those measured by Bridgman.5)

The same figure also illustrates the drift mobility as a function of the volume change. Throughout the experiment, the accuracy of the observed values was kept about ±5%. The temperature rise attendant upon the compression was negligible. Since the hole mobility of the anthracene crystals was difficult to measure, as will be described later, the results of the electron mobility measurements will be reported in this paper. As is illustrated in Fig. 4, the electron mobility along the c′ axis was approximately constant up to the pressure of 6.6 kbar, and the observed values of the specimens prepared from different crystals were in good agreement.

The electron mobility along the a axis, on the other hand, increased linearly with the pressure up to 3.0 kbar, and further varied superlinearly in the pressure region between 3.0 and 5.0 kbar. Above 5.0 kbar, however, the ratio of increase decreased. Though the reproducibility of the measurements of the mobility and the pressure dependence was not very good, all of the observed values showed the general tendency described above.

In the case of the b axis of the anthracene crystal, it was difficult to observe the mobility because of cleavage along the ab plane. When a specimen was carefully prepared, however, we succeeded in observing the drift mobility up to 5.5 kbar. The general tendency of the mobility as a function of the applied pressure was similar to that measured along the a axis.

The pressure dependence of the charge mobility of the anthracene crystal has been discussed theoretically by several workers, LeBlanc, Katz *et al.*, and Harada *et al.* They carried out a tight-binding band calculation for the pressure dependence of the mobility as a function of the lattice constants.3) The variations in the lattice constants, $\sqrt[3]{-\Delta V/V}$, as a function of the applied pressure were taken from Bridgman's data. When the band theory was applied to the calculation of the drift mobility of the anthracene crystal, we had to take account of the overlap integral of intramolecular vibrations $\langle \chi'/\chi_0 \rangle$, as reported by Silvey *et al.*3) However, the change in the overlap integral was estimated to be very slight under high pressure, the corresponding force constant being very large. Figure 5 shows the results obtained by Harada.*4 The agreement between the experimental values and the theoretical values was not satisfactory.

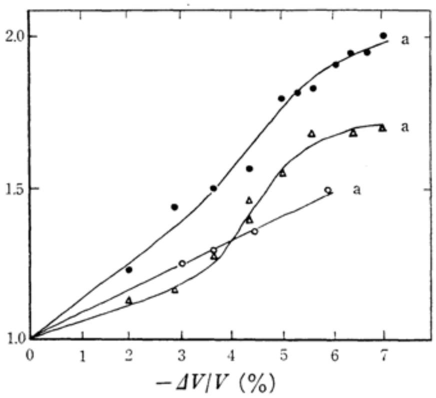

Fig. 5. Comparison between the observed and calculated values of the electron mobility along a-axis. Calculation was carried out by the method of Harada.3) ○ from calculation, ●, △ from observation.

This behaviour suggests that the pressure dependence of the drift mobility cannot be expressed by a simple shortening of the lattice constants. Therefore, we must introduce other effects of compression on the mobility, for instance, the rotation of the co-planar molecular plane in the crystal.6)

The mobility along the c′ axis was nearly constant up to 6.6 kbar, as has been mentioned above. It may be interesting to calculate the variations of the electron mobility along the c′ axis under high pressure using the method proposed by Silvey, for he claims that only his method gives a reasonable value for the electron mobility along the c′ axis.3)

The scattering mechanism of the charge carriers in anthracene was discussed by Friedman.7) He gave the following expressions for the mobility (μ_i) and the mean free path (τ) on the basis of some assumptions:

$$\left.\begin{aligned}\mu_i &\propto \frac{\Theta^2 E^3_s}{E'^2_{s_i}}\cdot\frac{1}{T^2}\\ \tau &\propto \frac{\Theta^2 E_s}{E'^2_{s_i}}\cdot\frac{1}{T}\end{aligned}\right\} \qquad (1)$$

where $E_s = \int \phi_0 V_n \phi_n d\tau$, $E'_{s_i} = \partial E_s/\partial a_i$, Θ is the Debye temperature of the crystal, and a_i is the coordinate along the ith crystal axis. The calculations by Harada showed that E'_{s_i} was nearly constant up to 10 kbar; then the mobility depended on the pressure only through the velocity component, which roughly corresponded to E_s^2/T in Friedman's expression, Eq. (1). From the above consideration, the superlinear increase in the electron mobility along the ab plane up to 5.5

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5) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **76**, 20 (1944).

*4 It is interesting that the values of the mobility variation estimated by Katz were smaller than those by Harada. Harada's agreement between the experimental and theoretical results was better than Katz's. The latter applied a more precise approximation using a linear combination of four Slater-type functions as the carbon-atom-wave function, while the former used only one Slater-type function.3)

6) H. Ohigashi, I. Shirotani, H. Inokuchi and S. Minomura, *J. Chem. Phys.*, **43**, 314 (1965).

7) L. Friedman, *Phys. Rev.*, **140**, 1649 (1965).

kbar may be explained. This consideration, however, is not satisfactory enough to explain the variation in the mobility between 5.0 kbar and 7.4 kbar.

As has already been mentioned, no accurate values of the hole mobility were observed, because the tail of the pulse signal, observed on the oscilloscope, was deformed, perhaps because of the formation of a large number of shallow traps in the crystals. When atmospheric pressure was restored, the pulse signal recovered its original shape; that is, the single crystal specimen used in this work was not disturbed by compression. It was not very clear whether this irregularity was due to a disorder of the lattice created in the crystal or to the interaction of the holes with the pressure-transmitting fluid on the anthracene crystal surface.*5

When the pressure increased from that of an atmosphere to 3 kbar, the photocurrent markedly increased. This behaviour is interesting as compared with the decrease in the fluorescence intensity of anthracene with an increase in the pressure.

A further study aimed at a complete understanding of the drift mobility as a function of the pressure will require a more refined theoretical treatment, including a carrier-scattering mechanism, and also a more precise experimental procedure under high pressure, one examining not only the change in the lattice constants, but also the rotation of the molecules in the crystal.

The authors are greatly indebeted to Dr. Ichiro Nakada and Mr. Satoshi Iwashima for working out the anthracene preparation and purification procedures; they would like also to express their gratitude to Mr. Ichimin Shirotani for his assistance.

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*5 When silicon oil was applied as the medium instead of kerosene, the irregularity of the pulse signal of hole mobility was found to be decreased. However, the operation of the compression pump with the oil was not satisfactory. In the case of electron mobility, this irregularity was not found.