Current-Voltage Characteristics in Phenanthrene Single Crystals*1

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The nature of semiconduction in organic solids has not been as yet elucidated satisfactorily, though many experiments have been made on aromatic hydrocarbons and related organic compounds. Further experimental studies are needed to establish the mechanism of electrical conduction in these materials. One such study is to find out how much impurity exists in an organic crystal to be measured, whether it is chemical or physical, and, further, what role it plays.

Information about trapping centers in anthracene has been obtained through the conductivity glow-curve method by Bryant, Bree, Fielding and Schneider,1) the measurement of space-charge-limited currents has been carried out for anthracene by Mark and Helfrich,2) and the behavior of bulk currents in metal-free phthalocyanine has recently been interpreted as the currents by Heilmeier and Warfield.3)

In this paper, the current-voltage characteristics of phenanthrene single crystals are studied in detail, and the results are analyzed as space-charge-limited currents phenomena. The information for trapping centers of phenanthrene obtained through the above-mentioned analysis will be discussed in comparison with the related results previously obtained for organic solids.

Experimental

Sample Crystals. — The starting material was Eastman Kodak chemical-purpose-grade phenanthrene, which was purified by recrystallization and sublimation in a manner described previously.4) As it was desired to obtain rather thin crystals in order to observe current-voltage characteristics up to very high electric fields, the crystals used in these experiments were sublimation flakes grown in the vessel shown in Fig. 1. A small quantity of purified phenanthrene was placed in a glass vessel equipped with conduit pipes for the flow of nitrogen gas, and the vessel was sealed with a glass stopper bearing a copper rod with a round copper plate. Purified nitrogen was used as the ambient gas in order to prevent the oxidation of phenanthrene. The whole assembly was then placed in a heating furnace. Phenanthrene began to sublime at about 65°C, and flaky crystals grew on the copper plate, which remained nearly at room temperature.

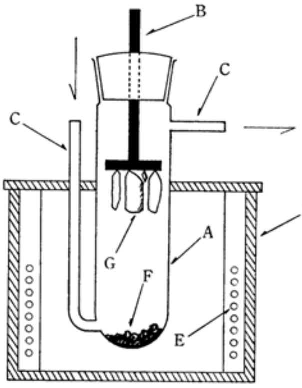

Fig. 1. Apparatus used to grow flaky single crystals of phenanthrene.

A: Glass vessel
B: Copper rod with a round plate
C: Conduit pipe
D: Heating furnace
E: Heating coil
F: Phenanthrene powder
G: Flaky crystals

The crystals were approximately 10 μ thick and had surface areas of 36—100 mm^2. About six hours were required to grow these crystals, which were confirmed to be single crystals by examination with a polarizing microscope. It was found that their developed plane coincided with the ab plane of the crystal without exception.

Specimen Cell and Measuremnts.—An electrical conductivity cell of the sandwich type was prepared on a teflon block in a manner reported previously.4) Silver paste (Ecco Bond), which was found to make ohmic contact with these samples, was applied as electrodes, and a guard-ring electrode was grounded in order to prevent an effect of the surface current.

The measuring apparatus consisted of a vibrating-reed electrometer (Takeda TR-88), and a dry-cell power supply. As the bulk current of guard-ringed samples was found to show no difference between the current in air and that in nitrogen gas within the

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*1 Presented at the Symposium on Molecular Structure, Sendai, October, 1963.

1) F. J. Bryant, A. Bree, P. E. Fielding and W. G. Schneider, *Discussions Faraday Soc.*, 28, 48 (1959).

2) P. Mark and W. Helfrich, *J. Appl. Phys.*, 33, 205 (1962).

3) G. H. Heilmeier and G. Warfield, *J. Chem. Phys.*, 38, 163 (1963).

4) S. Matsumoto and T. Tsukada, This Bulletin, 37, 1545 (1964).

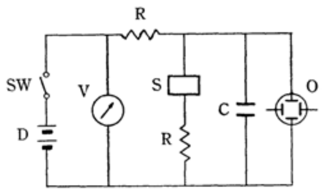

Fig. 2. Circuit used for estimation of the voltage at which a steep increase of current through a sample crystal occurs.

SW: Circuit switch
V: Voltmeter
S: Sample crystal
O: Oscilloscope
D: Dry cell
R: Registor
C: Capacitor

range of experimental error,*2 the measurements were carried out in air.

The circuit shown in Fig. 2 was used to determine more exactly the voltage at which a steep increase of current through a sample crystal occurs; when the circuit is closed by a switch, the effect is merely to charge the capacitor so that a voltage is slowly built up across the capacitor and, at the same time, across a sample crystal. On the other hand, it can be observed that, when the voltage reaches a higher value where the current through a sample crystal rises steeply, the discharge of the capacitor occurs suddenly, and the built-up voltage across the capacitor falls. The above-mentioned phenomena were observed with a oscilloscope.

Results and Discussion

The current-voltage characteristics obtained can typically be divided into three regions, as is shown in Fig. 3: (1) at low voltages, up to 2×10^4 V. per cm., the dependence of the current on the voltage obeyed Ohm's law, (2) at intermediate voltages, the current increased with the square of the voltage, and (3) at higher voltages, over 5×10^4 V. per cm., the current rose steeply with the voltage. This behavior is similar to the currnt-voltage relation characteristic of the space-charge-limited currents in solids.

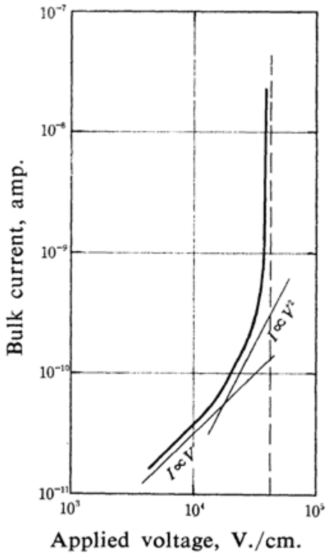

Fig. 3. Typical current-voltage characteristics of phenanthrene single crystal.

The theoretical treatment of space-charge-limited currents has been developed by Rose⁵⁾ and Lampert⁶⁾. Smith and Rose also experimentally demonstrated space-charge-limited currents with crystals of cadmium sulfide.⁷⁾ Ruppel observed that with zinc sulfide,⁸⁾ and so forth.

When a sufficiently large field is applied to an insulator with ohmic contact electrodes, carriers will be injected into the bulk of the material to form a current which is limited by space-charge effects. The following equation can be given for the space-charge-limited current in a solid,

$$I=10^{-12}\,V^2\mu\varepsilon A/4\pi l^3 \tag{1}$$

where μ and ε are the drift mobility and the dielectric constant respectively, V is the applied voltage, l is the electrode spacing, and A is the cross-sectional area. The magnitude of this current in a trap-free material can be quite large, but in practice it is reduced by trapping effects; trapping centers capture the injected carriers, thus reducing the density of free carriers.

As long as the Fermi level, which rises when current injection occurs, is further from the bottom of the conduction band than E_t, the trap depth, and moves in a region of the forbidden gap where the level density is much less than N_t, the trap density, the ratio of free electrons, n, to trapped electrons, n_t, is constant and independent of the applied voltage. In this region, the current is given by:

$$I_t=10^{-12}\,V^2\mu\varepsilon Ar/4\pi l^3 \tag{2}$$

where, if N_c is the effective density of the state in the conduction band, r is approximately given by:

$$r=n/n_t=(N_c/N_t)\exp\left(-E_t/kT\right) \tag{3}$$

Thus, the transition from the ohmic region of current-voltage characteristics to the square-law dependence of the current on the voltage at a higher field is associated with the condition where the space-charge-limited currents become comparable with the intrinsic bulk-current.

[*2] The same result for the effect of an ambient atmosphere on the current through the guard-ringed samples of phenanthrene has been explained in a previous paper.⁴⁾

5) A. Rose, *Phys. Rev.*, **97**, 1538 (1955).
6) M. A. Lampert, ibid., **103**, 1648 (1956).
7) R. W. Smith and A. Rose, ibid., **97**, 1531 (1955).
8) W. Ruppel, *Helv. Phys. Acta*, **31**, 311 (1958).

Accordingly, if V_t is the voltage at which the above-mentioned transition occurs, the concentration of bulk-free carriers, n_o, which means that of free carriers before injection, is given by:

$$n_o = 10^{-12}\, V_t \varepsilon r/4\pi e l^2 \qquad (4)$$

The extremely steep rise of the current at more higher fields corresponds to the condition in which the traps have been essentially filled; the current rises very steeply with the voltage toward the curve characteristic of trap-free behavior. The density of traps which have been filled is calculated from the voltage, V_{tf}, where the current rises steeply:

$$eN_t = CV_{tf}/1A = 10^{-12} V_{tf}/4\pi l^2 \qquad (5)$$

where C is the capacity of a sample, and A is the cross-sectional area.

The current-voltage characteristics obtained from sample 63-5 and sample 63-7 are illustrated in Fig. 4. These results were analyzed as space-charge-limited currents phenomena.

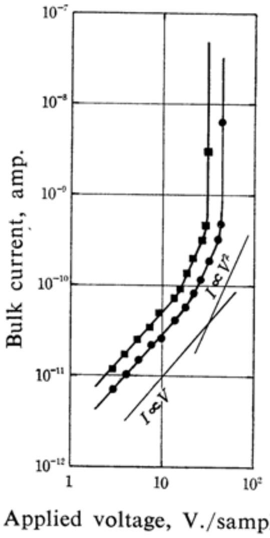

Fig. 4. Current-voltage characteristics of sample 63-5 (■) and sample 63-7 (●).

If the crystal of sample 63-5 is absolutely trap-free, the theoretical space-charge-limited current I at 22 V. is calculated to be 5.89×10^{-3} amp. with Eq. 1, where the values of $\varepsilon=3$ is adopted,[9] and μ is assumed to be 0.1 cm²/V.·sec.[*3] The experimentally-observed current in Fig. 4, that is, I_t for this sample at the same voltage, is 1.15×10^{-10} amp. Therefore, 1.95×10^{-8} is evaluated as the value of r.

In Fig. 4, V_t, at which point the transition from the ohmic region to square-law behavior occurs, is observed to be about 15 V. Thus, a value of $1.2\times10^6\ \mathrm{cm}^{-3}$ is obtained from Eq. 4 as the concentration of bulk-free carriers. The resistivity $5.2\times10^{13}\ \Omega$ cm., calculated from the formula $\rho=(en_o\mu)^{-1}$ by using $n_o=1.2\times10^6$ cm^{-3} obtained above, is in good agreement with the observed resistivity, $5.4\times10^{13}\ \Omega$ cm., for the ohmic region of current-voltage characteristics of sample 63-5. This self-consistence may support the applicability of space-chage-limited currents analysis for the results of sample 63-5. This consistence is found to exist also for sample 63-7.

The trap density, N_t, can be determined from the voltage, V_{tf}. V_{tf} was determined by using the circuit of Fig. 2. When the observed value of V_{tf}, 30 V., for sample 63-5 is inserted in Eq. 5, the value of N_t can be calculated as $1.24\times10^{14}\ \mathrm{cm}^{-3}$.

Here, the trap-depth, E_t, can be evaluated from Eq. 3, if the effective density of the state in the conduction band, N_c, is known. If we adopt $N_c=5.76\times10^{15}\ \mathrm{cm}^{-3}$, which is obtained by inserting $n_o=1.2\times10^6\ \mathrm{cm}^{-3}$ and $\Delta\varepsilon=1.14$ eV.[4)] into relation, $n_o=N_c\exp(-\Delta\varepsilon/2\,kt)$, E_t for sample 63-5 is estimated to be 0.55 eV.

Similar results were also obsained for sample 63-7 through analyzing its current-voltage characteristics. The results are summarized in Table I.

Table I

	$n_o\cdot\mathrm{cm}^{-3}$	$N_t\cdot\mathrm{cm}^{-3}$	$E_t\cdot$eV.
Sample 63-5	1.2×10^6	1.2×10^{14}	0.55
Sample 63-7	1.1×10^6	1.0×10^{14}	0.55
Average	1.2×10^6	1.1×10^{14}	0.55

The trap density, $N_t=1.1\times10^{14}\ \mathrm{cm}^{-3}$, for phenanthrene obtained here is comparable to the corresponding value for anthracene, $7.6\times10^{13}\ \mathrm{cm}^{-3}$, obtained by Mark and Helfrich,[2)] and to that for phthalocyanine, $10^{12}-10^{14}\ \mathrm{cm}^{-3}$, obtained by Heilmeier and Warfield.[3)] It is worthy of notice that the value of the trap density is in the order of $10^{12}-10^{14}\ \mathrm{cm}^{-3}$ for all of these organic molecular crystals, and that the trap density of this order seems to be rather low for an organic solid in which some chemical impurity is generally difficult to remove and in which the imperfection of crystal is likely to occur because of the weak binding strength characteristic of molecular crystals. Both facts, their low trap-densities and their agreement, being of the order of $10^{12}-10^{14}\ \mathrm{cm}^{-3}$, might give a key to the establishment of the nature of the trap in organic molecular crystals, although further experimental studies are needed to solve the problem.

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[9] H. Kronberger and J. Weiss, *J. Chem. Soc.*, Part II, **1944**, 464.

[*3] This value of μ is estimated from the observed mobility of similar aromatic hydrocarbons. Although whether the assumed value is reasonable or not has to be examined by measuring the mobility, the accurate value is not indispensable in the following discussion.

The question of whether electrons or holes are trapped in phenanthrene can not as yet be decided either.

Summary

The obtained current-voltage characteristics of phenanthrene single crystals exhibited three distinct types of behavior: (1) at low voltages, up to 2×10^4 V. per cm., the dependence of the current on the voltage obeyed Ohms' law, (2) at intermediate voltages, the current increased with the square of the voltage, and (3) at higher voltages, over 5×10^4 V. per cm., the current rose steeply with the voltage. These results have been analyzed as space-charge-limited currents phenomena, and a value of $1.2\times10^6\ \mathrm{cm}^{-2}$ has been obtained as the concentration of the bulk-free carriers from the transition voltage between the ohmic region and the square-law behavior. The resistivity calculated by applying this value is in good agreement with the resistivity observed for the ohmic region of current-voltage characteristics.

The trap density of $1.1\times10^{14}\ \mathrm{cm}^{-3}$ has been evaluated from the voltage where the current rose steeply. Although this value seems to be rather low for an organic solid, it is comparable to the trap densities for organic molecular crystals ever obtained.

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