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Unusual Behaviors in Electrical Conductivity of Phenanthrene Crystal[1]

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Two kinds of unusual behavior in the temperature dependence of electrical conductivity has been observed. One is the anomaly that the resistance begins to increase remarkably with the rise in the temperature around 64°C; the other is a bending-phenomenon in the linear temperature-dependence of the resistance about 54°C. The observed activation energies for conduction are 3.0—3.3 eV below and 4.5—4.8 eV above the anomaly, the energies of which are almost compatible with the intrinsic band-gap energies for conduction, 3.5 and 4.6 eV, estimated, respectively, from the optical absorption and from the values of the ionization potential and the electron affinity. As for below the bending-phenomenon, the observed activation energy is 1.4—1.6 eV, which is quite small compared with the intrinsic band-gap energies estimated. The anomaly beginning around 64°C is interpreted as due to the crystal-phase transition of a higher-order at 60—70°C; the remarkable increase in resistance may be connected with the changes in the intermolecular interaction in the crystal due to the rearrangement of molecules caused by the phase transition. The bending-phenomenon at about 54°C seems to be attributable to an impurity-effect by oxygen.

In the investigation of the electrical properties of organic molecular crystals, we frequently come across unusual behavior in the temperature dependence of electrical conductivity. The unusual behavior can be mostly associated with either an impurity or a crystal-phase transition. The extensive study of such behavior is very important for the elucidation of the nature of electrical conduction in organic molecular crystals and has, therefore, been carried out by several workers.

The effect of an impurity on electrical conductivity has been studied, for example, for anthracene, pyrene and chrysene containing additives by Northrop and Simpson[2] and for imidazole under successive zone-refining by Brown and Aftergut;[3] there have also been works on the effect of ambient oxygen for naphthalene by Pick and Wissman,[4] for mesonaphthodianthrene and mesonaphthodianthrone by Kuroda and Flood[5], for β-carotene by Rosenberg,[6] and, most recently, for quaterrylene by Maruyama and Inokuchi.[7] The influence on electrical conductivity by the crystal-phase transition has been examined for phthalocyanine by Wihksne as well as by Eley and Parfitt,[8,9] although Harrison and Ludewig attributed the anomaly in conductivity at the transition point to the stronger tendency of the α phase to absorb oxygen,[10] for chlorpromazine by Gutman and Netschey,[11] and so on.

In the course of an extensive study on the electrical properties of polycrystalline phenanthrene, we found two different kinds of unusual behavior in the temperature dependence of the electrical conductivity: one is the anomaly that the resistance begins to increase remarkably with the rise in the temperature around 64°C, and the other is a bending-phenomenon in the linear temperature-dependence of the resistance about 54°C. A brief account of our findings on the former behavior has been presented in a previous communication;[1] further, our thermal analysis, dilatometric investigation, and X-ray study of phenanthrene crystal, carried out in order to elucidate the behavior, have been reported.[12,13] A similar phenomenon has also been reported independently by Andrews, Armington and Rubin,[14] and recently the behavior has been dealt with by Arndt and Damask.[15]

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[13] S. Matsumoto and T. Fukuda, *ibid.*, **40**, 743 (1967).

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This paper will give a detailed presentation of the two different kinds of unusual behavior described above; the behavior will be discussed from the standpoint of the effect of an impurity and the influence of the crystal-phase transition.

Experimental Procedures

The material used in this experiment was finely-ground phenanthrene, purified by a combination of recrystallization and zone-melting. The purification has been described in a previous paper.12)

The powdered specimen was subjected to electrical measurements, under a compression of 120 kg/cm^2, between the metal ends used as electrodes in a teflon cylinder. The cylinder was set in a metal vessel which was evacuated to 10^{-3}—10^{-4} mmHg during the measurements, as is shown in Fig. 1.

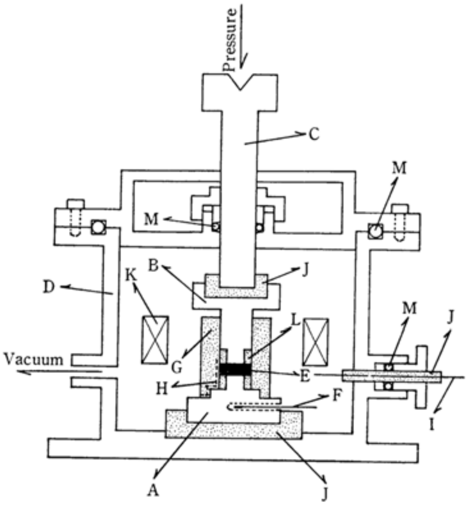

Fig. 1. The apparatus used in measurement of the current through powdered phenanthrene.

A: Lower metal end
B: Upper metal end
C: Piston
D: Metal vessel
E: Specimen
F: Thermocouple
G: Teflon cylinder
H: Exhaust-pass
I: Lead wire
J: Teflon insulator
K: Electrical heater
L: Teflon collar
M: O-ring

The metal ends (A) and (B) were made of stainless steel, and each of them was insulated from either a pison (C) or the vessel (D). The effective area of each metal end as an electrode was precisely 1 cm^2; they were kept separated by 1—2 mm by adjusting the quantity of the specimen (E) under compression. The specimen was compressed by the piston, which was equipped with a mechanical lever-system. The applied voltage between the metal ends was 10—100 V, supplied by a D. C. constant voltage-supply; the current through the specimen was measured with a Takeda electronic micro-micro ammeter TR-5, and its value, togehter with the temperature of the specimen, was recorded continuously by a Toa electronic polyrecorder EPR-3T. The temperature changed from 30°C to 80°C; it was measured by means of a chromel-alumel thermocouple (F) inserted into the lower metal end. The conductivity measurements were made both during heating and during cooling; both the heating and the cooling rate were 0.2—0.4°C per minute.

The teflon cylinder (G) was equipped with a small exhaust path (H) in its inner wall in order to ease the evacuation of air or moisture involved in the specimen. The lead wires (I) attached to the electrodes were led outside the vessel through the seal of a teflon insulator (J).

Results

For electrical conductivity measurements, a number of different samples were adopted and a series of trials of the measurement were carried out on each sample; one series consisted of five trials, each trial being carried out *in vacuo* and under compression. In the first trial, the specimen was first heated gradually from room temperature to 80°C; the second and third trials followed just after the first and second trials, while the fourth and fifth trials were carried out after the specimen had been exposed to air under atmospheric pressure at room temperature for 3 days after the third and for 10 days after the fourth.

In every trial described above except in the first trial and in the trial before which the specimen

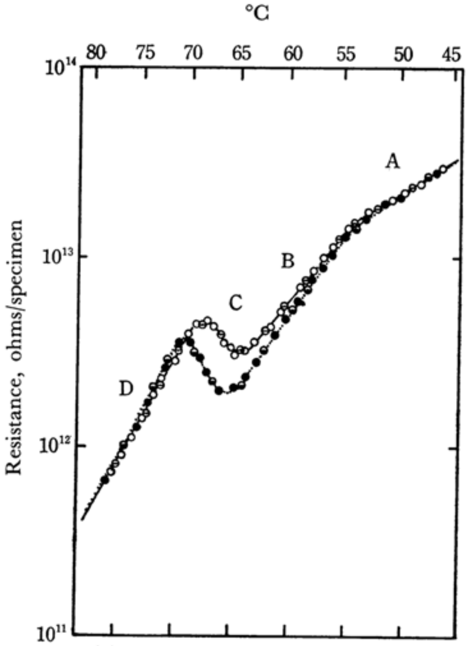

Fig. 2. The typical temperature-dependence of the electrical resistance of phenanthrene crystal:

○ for heating } in the 2nd trial and
● for cooling }
⊖ for heating } in the 3rd trial.
◒ for cooling }

had been exposed to air for a long time, we have found the two kinds of unusual behavior in the temperature dependence of electrical resistance shown in Fig. 2. As for heating process in the region up to about 62°C, the relation between the logarithm of resistance and the reciprocal absolute temperature shows a bending-phenomenon at about 54°C, although the relation in the regions below and above the bending point, (A) and (B), are linear. As the temperature increases further, there appears an anomaly beginning at around 64°C; that is, there occur unexpectedly a slowing-down of the rate of resistance-decrease with the temperature, and then a remarkable increase in the resistance, (C), and finally, above 71°C, another linear portion, (D), appears.

The cooling curve was, as a whole, nearly the same as the heating curve, although the temperature range of the anomaly corresponding to that beginning at around 64°C during heating was shifted towards temperatures higher by a few degrees (1—2°C) during cooling and the anomalous change in the resistance with the temperature during cooling was a little more remarkable than that during heating.

There are several points of major interest in these relation curves in Fig. 2. One is the anomaly at 64—71°C, where the resistance increases remarkably with the rise in the temperature, contrary to our expectation based on an exponential function such as is usually found with various organic semiconductors:

$$R = R_0 \exp(\Delta\varepsilon/2\boldsymbol{k}T)$$

where $\Delta\varepsilon$ is the activation energy for conduction. Other points of interest are the slopes of both linear portions below and above the anomaly, that is, (B) and (D), and, further, the bending-phenomenon in the linear region below the anomaly, the region which consists of two linear portions, (A) and (B), which intersect at about 54°C, the slope of (A) being smaller than that of (B).

The slopes of the portions (A), (B) and (D) can give the activation energy for the conduction of each process. A number of measurements with different samples give the activation energies of 1.4—1.6 eV for (A), 3.0—3.3 eV for (B) and 4.5—4.8 eV for (D).

Let us now compare the results presented above with those in Fig. 3, obtained from the first, fourth and fifth measurement trials. In Fig. 3, the typical heating-curve in Fig. 2 is superposed with a dashed line for convenience.

After the third trial had been carried out, air was introduced into the measurement vessel. In the fourth trial, before which the specimen had been exposed to air for three days, Curve 2 of the temperature dependence of the electrical resistance was obtained; the same anomaly appears at 64—71°C as in Fig. 2, but its extent is less remarkable. Moreover, the bending-phenomenon of Fig. 3, found in the linear region below the anomaly, is shifted by four degrees towards the higher-temperature side, and the resistance in the region below the bending-point is smaller than that in Fig. 2. However, the activation energies for conduction obtained from both linear portions below and above the anomaly, and from the linear portion below the bending point, namely, from the three portions which correspond respectively to the portions (B), (D) and (A) in Fig. 2, are 2.8—3.1, 4.3—4.5 and 1.4—1.5 eV, values which are consistent with the values for the corresponding portions in Fig. 2.

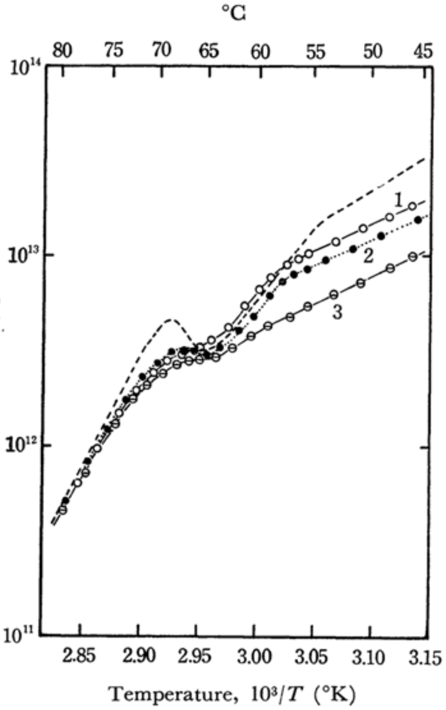

Fig. 3. The temperature dependence of the electrical resistance of phenanthrene crystal: Curve 1 (-○-) for the 1st trial, Curve 2 (··●··) for the 4th trial, Curve 3 (-⊖-) for the 5th trial and the dashed line (----) for the typical heating curve in Fig. 2.

Curve 3 was obtained in the fifth trial, before which the specimen had been exposed to air for 10 days; the anomaly found at 64—71°C is extremely depressed, and at the same time the linear portion corresponding to (B) in Fig. 2 almost disappears. This disappearance may be caused by the fact that the point of the bending-phenomenon in the linear region below the anomaly was shifted very close to the temperature region of the anomaly. The resistance at low temperatures in Curve 3 is smaller than that in Curve 2. In spite of these differences, the activation energies for conduction below and above the anomaly are 1.3—1.4 and 4.3—4.4 eV, which may correspond to the values for the portions (A) and (D) in Fig. 2 respectively.[*1]

The temperature dependence of the electrical resistance in the first trial is shown by Curve 1. The weak anomaly found at 64—71°C in Curve 1 is very similar to that in Curve 3, and there appears no distinct bending-phenomenon below the anomaly as in the case of Curve 3. However, the resistance at low temperatures below the anomaly is not so small as that in Curve 2 or Curve 3. The activation energies for conduction, obtained from the linear portions below and above the anomaly in Curve 1, are 1.1—1.3 eV and 4.2—4.4 eV, which are also consistent with the values for (A) and (D) in Fig. 2 respectively.

Discussion

In the preceding section, we have described two kinds of unusual behavior in the temperature dependence of the electrical conductivity of phenanthrene, which are shown typically in Fig. 2. One is a bending-phenomenon in the linear temperature dependence at about 54°C, and the other is the anomaly that the resistance increases remarkably with the rise in the temperature at 64—71°C. The former behavior, at about 54°C, seems to be due to the effect of air, possibly of oxygen in air, since in every measurement after the specimen has been exposed to air the bending point is shifted towards the higher temperature side and, at the same time, the resistance in the region below the bending point decreases. The longer the time of exposure to air, the more remarkable both the shift of the bending point and the decrease in resistance. Therefore, the conduction below the bending at about 54°C, that is, in the portion (A) in Fig. 2, may be assumed to correspond to the extrinsic semiconduction, and the activation energy for conduction, 1.4—1.6 eV, which was calculated from the slope of the portion (A), may be regarded as the acceptor or donor level caused by oxygen from the valence or conduction band.

In the latter behavior, hardly no shift of the anomalous temperature range, 64—71°C, is observed in any measurement after the exposure of the specimen to air; moreover, the longer the time of exposure to air, the less remarkable the extent of the anomaly becomes, contrary to the former behavior. Therefore, the anomaly at 64—71°C may be not at least directly due to the effect of air.

In previous papers,[1,12,13] the present author has reported that the presence of a higher-order phase transition around 60—70°C in phenanthrene crystal had been confirmed through thermal analysis, dilatometry and X-ray diffraction. This crystal-phase transition is possibly responsible for the above-mentioned anomaly at 64—71°C; not a little change in the intermolecular interaction in the crystal due to the rearrangement of molecules on passing through the transition temperature region may be expected; this change in the intermolecular interaction must be connected with the anomaly in electrical conductivity observed at 64—71°C. Therefore, when the conduction below and above the anomaly, that is, in the portions (B) and (D) in Fig. 2, is assumed to correspond to the intrinsic semiconduction, the activation energies of 3.0—3.3 eV in the portion (B) and of 4.5—4.8 eV in the portion (D), which were calculated from their slopes, may be regarded as the activation energies for the conductions of the low-temperature and high-temperature modifications of phenanthrene crystal respectively. However, at the present time no reasonable explanation is available of why the activation energy of the high-temperature modification is higher by about 1.5 eV than that of the low-temperature modification. The interpretation of this fact must await further study and information.

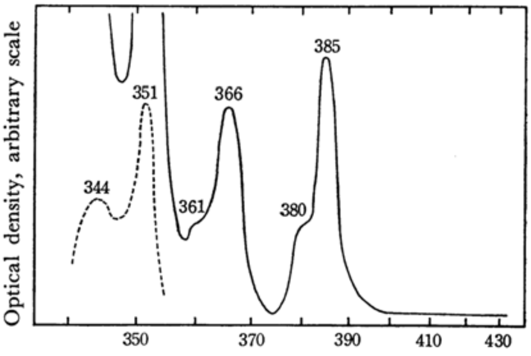

Fig. 4. The absorption spectrum of phenanthrene crystal.

The optical absorption spectrum of phenanthrene crystal is shown in Fig. 4. The crystal adopted was a flake-like single crystal grown by the sublimation method,[16] and the spectrum was obtained through the technigue of reducing the reference light beam of the spectrophotometer (Hitach EPS-2), because the absorption by the crystal is strong. The two kinds of absorption curves in Fig. 4 show those obtained for the same crystal by varying the degree of reducing the reference light beam.

The peak at 351 mμ seems to correspond to the absorption threshold of phenanthrene. Accordingly, the 351 mμ peak may be assigned to the lowest

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[*1] The measurement *in vacuo* just after the fifth trial, gave a temperature dependence of the electrical resistance which was nearly the same as the typical one shown in Fig. 2.

16) S. Matsumoto, This Bulletin, **38**, 997 (1965).

singlet excitation for the phenanthrene molecule in the solid state; if we presume that the band model can be applied to the electronic state of the phenanthrene crystal, the value of 3.5 eV, which corresponds to the wavelength of 351 mμ, may be considered to be the intrinsic band-gap energy for the conduction of the phenanthrene crystal spectroscopically.

The intrinsic band-gap energy mentioned above can also be fundamentally induced from the crystal ionization potential, I_c, and the crystal electron affinity, A_c, since the difference between I_c and A_c corresponds to the energy gap between the top of the valence band and the bottom of the conduction band. Therefore, if the values of both I_c and A_c are available, the intrinsic band gap energy, $\Delta\varepsilon$, may be calculated by means of the following equation:

$$\Delta\varepsilon = I_c - A_c \qquad (1)$$

Here the value of A_c is not experimentally obtained, but it can be evaluated from the following relation:

$$A_c = A_g + P \qquad (2)$$

where A_g is the gaseous electron affinity and P is the stabilization energy attributed to polarization by the remaining positive center in the crystal, which corresponds to the difference between the gaseous ionization potential, I_g, and the crystal one, I_c.(17) The reliable values of I_g, I_c and A_g for phenanthrene are 8.03,(18) 6.45(19) and 0.31 eV(20) respectively; by adopting these values, the value of 4.56 eV is evaluated as the intrinsic band gap energy by means of Eqs. (1) and (2).

The activation energies of 3.0—3.3 eV and 4.5—4.8 eV, which were calculated from the slopes of the linear portions below and above the anomaly at 64—71°C in Fig. 2, are almost campatible with the intrinsic band gap energies for conduction, 3.5 eV and 4.6 eV,*2 which were estimated, respectively, from the threshold of optical absorption and from Eq. (1) with the ionization potential and the electron affinity. This is a reason to assume that the conductions both below and above the anomaly at 64—71°C are intrinsic.

The small activation energy of 1.2 eV for the phenanthrene single crystal,(21) reported previously by the present author, is comparable with the activation energy for conduction below the bending at about 54°C in Fig. 2, 1.4—1.6 eV, so the small activation energy is thought to have been caused by excitation from the impurity level, possibly of oxygen. Further, no appearance of the anomaly in our previous work(21) that the resistance increases remarkably at 64—71°C, might have been caused by the presence of an impurity, possibly of oxygen, as has been pointed out by Andrews, Armington and Rubin.(14)

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*2 It should be kept in mind that this value varies not a little according to the estimation of the stabilization energy attributed to the polarization, *P*.

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