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Electrical Conductivity in Crystalline Hexamethylbenzene

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The influence on the electrical property of organic crystals of their phase transition has been found for phthalocyanine,[1,2] chlorpromazine,[3] phenanthrene,[4,5] and so on. It has, however, been reported by Kronick and Labes that no change was discernible in the electrical property accompanying the phase transition of hexamethylbenzene crystals at 110°C.[6] Recently, Chojnacki has found an increase in the electrical conductivity of hexamethylbenzene at the transition point, while he has reported no change in the activation energy for conduction at that point.[7]

The crystal structure of hexamethylbenzene below 110°C is a triclinic modification, belonging to the space group of $C_1'—P_{\bar{1}}$. A unit cell whose dimensions are a=8.92Å, b=8.86Å, and c=5.30Å (α=44°27′, β=116°43′, γ=119°34′) at 20°C contains one molecule.[8] Through the phase transition, the molecules within the plane of the molecular rings shift slightly, so that the triclinic symmetry becomes orthorhombic. Here, the unit cell whose dimensions are a=9.06Å, b=15.70Å, and c=7.52Å (at 155°C) belongs to the space group of $D_{2h}^{23}F_{mmm}$ and contains four molecules.[9]

This paper will report on studies of the temperature dependence characteristic of the electrical conductivity

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of crystalline hexamethylbenzene. The results of the increase in the activation energy through the transition will be discussed in connection with both crystallographic forms.

Experimental

Material. Hexamethylbenzene of an extra pure grade obtained from Tokyo Kasei Kogyo Co., Ltd., was purified by recrystallization from a chloroform solution and then by the zone-melting technique.[10]

Electrical Measurements. The powdered specimen was packed in a rigid Teflon cylinder and compressed between the metal (stainless steel) plungers which were used as electrodes. Their effective area was 1 cm^2. The specimen compressed under a pressure of 120 kg/cm^2 was 1—2 mm thick. The electrical measurements were then carried out by means of a vibrating-reed electrometer (Takeda-TR15) in a vacuum of 10^{-3}—10^{-4} mmHg, while applying a voltage of 100V to the cell.[4,5] The sample heating rate was 0.2—0.4°C per minute.

Dilatometric Measurements. A dilatometric investigation was made by using a modified differential dilatometer of the type originated by Chevenard.[11] Our dilatometer was designed to magnify 2000 times the differential expansion between the specimen and an equal length of fused silica used as the standard.

In this study, the heating rate was about 0.9°C/min, except in the vicinity of the anomalous point, where the temperature was raised as slowly as possible.

Samples were prepared by casting molten rods of zone-refined hexamethylbenzene 11.7 mm in length.

Results and Discussion

In the electrical investigation over the temperature range of 85—130°C, a distinct anomaly was found in the temperature dependence of the electrical resistivity of crystalline hexamethylbenzene. A typical example of the temperature dependence of the electrical resistivity in the heating process by the DC method is shown in Fig. 1. The relation between the logarithm of the resistivity and the reciprocal absolute temperature shows an anomaly at 110±3°C, while the relations both below and above that point are linear. The reproducibility of this amonalous phenomenon was good within the range of experimental error.

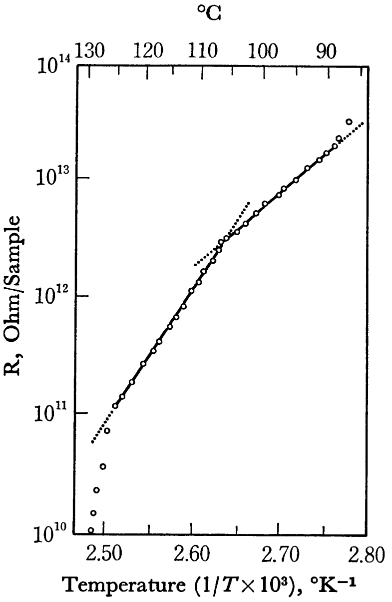

Fig. 1. The temperature dependence of the electrical resistivity of crystalline hexamethylbenzene for heating.

Assuming the resistivity, R, to obey the usual semiconductor relation:

$$R = R_0 \exp\left(\Delta\varepsilon/2kT\right) \tag{1}$$

the values of the activation energy for conduction, $\Delta\varepsilon$, obtained from the above relation, were found to be, respectively, 2.5 eV and 4.5 eV below and above the anomalous point.

In the electrical study by Kronick and Labes, using a hexamethylbenzene specimen cast between glass plates, no anomaly was reported. The activation energy was 1.78 eV. According to the report by Chojnacki, the increase in the electrical conductivity of a pellet specimen made from powdered hexamethylbenzene crystal under a pressure of 1000 atm. doubled, the activation energy for conduction did not change, and the activation energy was 2.0 eV.

There seems to have been no anomaly in the results reported by Kronick and Labes caused by their measurement technique. On the other hand, Chojnacki discussed his experimental results, in which no change was found in the activation energy at the phase transition, on the basis of these being no dependence of the $\Delta\varepsilon$ on the crystallographic direction. However, his discussion may be confused because one cannot regard the effect on the electrical conductivity influenced by the crystal-phase transition as being equal with the anisotropy of conductivity.

The intrinsic band-gap energy can be fundamentally induced from the crystal ionization potential, I_c, and the crystal electron affinity, A_c, corresponding to the energy gap between the top of the valence band and the bottom of the conduction band, $\Delta\varepsilon_0$.[5] If the values of I_g and A_g are available, the intrinsic band-gap energy, $\Delta\varepsilon_0$, may be calculated from the following equation:

$$\Delta\varepsilon_0 = I_c - A_c \tag{2}$$

Thus, Eq. (3) is derived from Eq. (2):

$$\Delta\varepsilon_0 = I_g - A_g - P_+ - P_- \tag{3}$$

where I_g and A_g are the gaseous ionization potential and the electron affinity respectively, and where P_+ and P_- are the stabilization energies attributed to polarization by positive and negative centers in the crystal respectively.

If the activation energy for conduction, $\Delta\varepsilon$, is equal to the band-gap energy, $\Delta\varepsilon_0$, the activation energy will vary more or less with the change in the crystallographic form, since the stabilization energy of polarization, P, depends on the crystal structure. However, $\Delta\varepsilon$ probably does not depend on the crystallographic direction, because P would have little anisotropy.

In the dilatometric study, a distinct discontinuity

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11) P. Chevenard, *Rev. Met.*, **14**, 610 (1917).

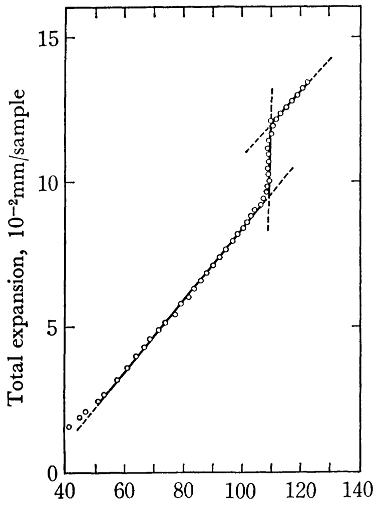

Fig. 2. The linear expansion-temperature relation of hexamethylbenzene crystal for heating.

was found in the linear expansion-temperature relation of the hexamethylbenzene crystal at 110.3°C. Figure 2 gives, as a typical example, a graphical representation of the total linear expansion of Sample No. 2 (listed in Table 1) plotted against the temperature, where the curve consists of three distinct lines. These phenomena were quite reversible with the temperature. These features of the expansion-temperature relation show that the thermal expansion coefficient of the specimen is almost constant below or above 110.3°C, but that it undergoes an abrupt change of linear expansion at the transition point. Each expansion coefficient can be evaluated from the slope of each line. The results are summarized in Table 1, where β_I is the mean coefficient of the linear thermal expansion between the temperatures of 40°C and Ttr. (the transition point) and where β_{II} is the coefficient between Ttr. and 130°C.

Table 1. The mean coefficient of linear thermal expansion of hexamethylbenzene crystal measured with a dilatometer

Trial	Ttr., °C	β_I ($\times 10^{-4}$)	β_{II} ($\times 10^{-4}$)
Sample No. 1	111.2	1.01	0.794
Sample No. 2	110.0	1.06	0.814
Sample No. 3	109.8	1.08	0.811
Average	110.3	1.05	0.806

The molar volumes calculated from the data of the crystal structure,[8,9] using the results obtained from our experiments of the thermal expansion, are 156.11 cm^3/mol in the triclinic system at 110°C and 159.43 cm^3/mol in the orthorhombic system at 110°C. Thus, the increase in the molar volume by the phase transition at 110°C is 2.13% of the molar volume at 110°C in the triclinic system.

Through the transition from a triclinic system to an orthorhombic system at 110°C, the increase in the molar volume would induce a decrease in the stabilization energy of polarization, *P*. Therefore, it seems reasonable, from Eq. (3), that an increase in the activation energy at the transition point was found in these experiments.