The Anomalous Temperature Dependence of the Electrical Conductivity of Phenanthrene

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A relatively large anisotropy in the electrical conductivity of the phenanthrene single crystal,[1] and the current-voltage characteristics of the single crystal,[2] characteristics which might be attributable to space-charge-limited currents phenomena, have previously been reported. In the course of an extensive study of the electrical properties of polycrystalline phenanthrene, the present authors have found an anomaly at around 64—71°C in the temperature dependence of the electrical conductivity. In this paper, the observed anomaly and a probable cause for it will be presented.

The powdered phenanthrene, purified by a combination of recrystallization and zone melting, was packed in a polytetrafluoroethylene cylinder with a small exhaust-path and compressed between the metal ends used as electrodes. The pressure of compression was 120 kg./cm^2, and the electrical measurements were carried out under a pressure of $10^{-3}-10^{-4}$ mmHg.

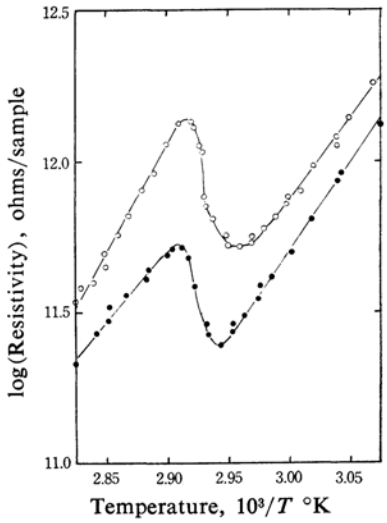

Fig. 1. One example of the temperature dependence (○ for heating, ● for cooling) of the electrical resistivity of phenanthrene, showing an anomaly at around 64—71°C.

A typical example of the temperature dependence of the electrical resistivity measured by the d.c. method is shown in Fig. 1, where an anomaly is observed at around 64—71°C. The linear relationship between the logarithm of resistivity and the reciprocal absolute temperature was broken in this temperature range, after which the resistivity increased abruptly with the rising temperature until it became approximately 6—7 times greater than that below 64°C. However, the linear relationship remained both below and above the anomaly, and there is no significant change in the slopes of each relationship. The anomalous phenomena were quite reversible. The reproducibility of the phenomena for different specimens is good within the range of experimental error.

Hence, the above-mentioned anomaly must be associated with a certain intrinsic property of phenanthrene itself. The large increase in resistivity at the anomalous point may be attributable to the influence of the differences in the molecular arrangement below and above the point; that is, it is probable that phenanthrene has a phase transition at around 64—71°C. However, this transition may not be great in itself, because the anomalous phenomena were quite reversible and no significant change of the activation energy for conduction can be admitted.

A preliminary investigation by differential thermal analysis showed an apparent endothermic peak at about 67°C on a thermogram. This may present evidence on a phase transition of phenanthrene suggested by the above-mentioned anomaly. This study is now in progress.

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1) S. Matsumoto and T. Tsukada, This Bulletin, 37, 1545 (1964).
2) S. Matsumoto, ibid., 38, 997 (1965).