Electrical Conduction in Thiantrene

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Electrical Conductivity, Organic Compounds

Electrical conductivity of thiantrene monocrystals was observed. The experimental results were interpreted as a "hopping" mechanism between the molecules of crystal.

Charge transport in monocrystals of organic sulphur compounds, has been the object of intensive researches, both theoretical and experimental, with the aim of determining the nature of charge carriers, their concentration and mobilities. In the present paper we study the current *vs* voltage characteristics of thiantrene monocrystals, in which, as is well known, the sulphur atoms use $d\pi$ as well as $p\pi$ orbitals[1] to give conjugation, even though the molecule is not flat[2]. Sulphur-orbital overlap is considerable (closest intermolecular approach of sulphur atoms is 3.77 Å [3]) and it may be thought that electrical conduction is by band or hopping, but we prefer a hopping mechanism. The experimental data are in accord with this hypothesis.

Experimental

Suitable crystals are grown by evaporation from an alcohol solution, in the form of radiating clusters of prisms, elongated in the b-direction. All the electrical measurements, at fields up to 1388 V/cm, are carried out in N_2 atmosphere, allowing the current to reach steady state value. Silver paste has been painted on both sides of the crystals, perpendicular to the *b*-axis, and copper wires are then stuck to the electrodes and connected with the resistivity measurement apparatus. It is not possible tu use a guard electrode due to the thinness of the specimens (of the order of 100 μm). The temperature ranges between 20 and 90 °C. The unit cell is monoclinic and contains 4 molecules as was ascertained by Lynton and Cox[4] and Rowe and Post[3].

Results and Discussion

The current-voltage relation is linear and changes slope with temperature. Log plots of the current density J against the square root of the electrical field ε at different temperatures fit the Poole-Frenkel formulae (Fig. 1), but the variation of σ (electrical conductivity) with the field at the lowest temperature and its constancy at the highest temperatures (Fig. 2), shows that at the lowest temperatures after release from traps, charge carriers drift a distance proportional to the applied field; at the highest temperatures all the traps are thermally ionized and the distance travelled is independent of the applied field[5]. We think that the centres are now the S atoms. From the temperature dependence of σ (Fig. 3), it follows:

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

where $\Delta E = 0.24$ eV.

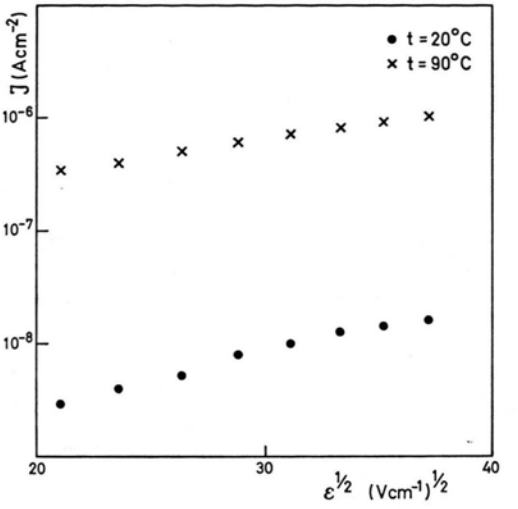

Fig. 1. Plot of the bulk dark current density J against the square root of the applied field (at two temperatures).

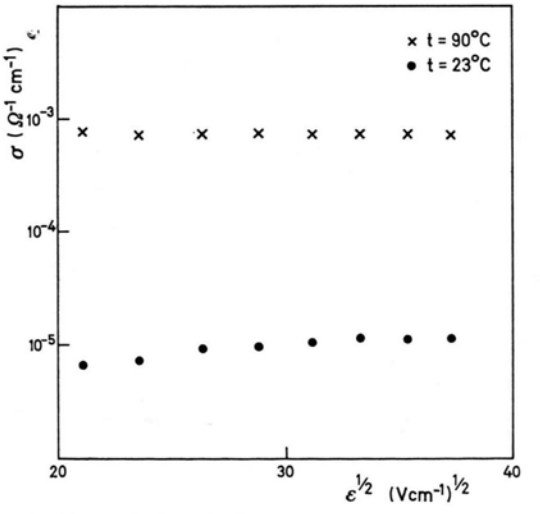

Fig. 2. Plot of electrical conductivity σ against the square root at the applied field.

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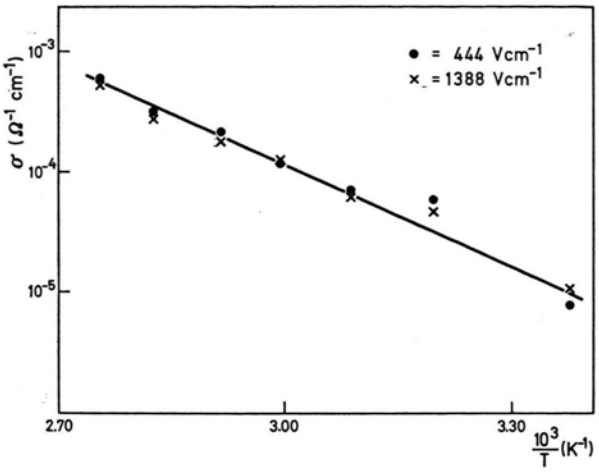

Fig. 3. σ — $1/T$ relation.

The carrier concentration may be evaluated as:

n = number of molecules/cm³ × number of S atoms in the molecule. At $T = 308$ K, the number of charge carriers is 9.10^{17}/cm³. (We have supposed the charge carriers to be electrons, and it is well known that S atoms are electron donors.) From $\sigma = ne\mu$ we obtain for the mobility $\mu \approx 10^{-8}$ cm² V⁻¹ s⁻¹. The low mobility value is in accord with the hopping mechanism. Of course we would have higher values for μ if there were many trapping centres in the crystal. For the sake of comparison, we observe that the semiempirical relation of MANY, HARNICK and GERLICH[6] gives $\mu \approx 10^{-11}$. Log σ *vs* $T^{-1/2}$ [7] for the hopping in one dimension (the direction of applied field) gives a straight line, but we doubt whether it has real physical meaning, due to the limited range of assayed temperature.

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