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ANOMALOUS ELECTRICAL BEHAVIOURS IN $[(C_6H_5)_3PCH_3](TCNQ)_2$ AND $[(C_6H_5)_3AsCH_3](TCNQ)_2$ AT HIGH PRESSURES

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The resistance in $[(C_6H_5)_3PCH_3](TCNQ)_2$ and $[(C_6H_5)_3AsCH_3](TCNQ)_2$ increased with increasing pressure and reached the maximum value at approximately 20 Kbar. The anomalous electrical behaviours at high pressures were discussed.

Generally, the electrical resistance of organic solids decreases sharply until the pressure reaches 100 Kbar region. It has been already reported that the resistance of all TCNQ salts, one of the typical organic semiconductors, decreases at high pressures.[1,2] However, the resistance in the phosphonium and arsonium TCNQ salts increased with increasing pressure and reached the maximum value at approximately 20 Kbar.

In this paper, we report the anomalous electrical behaviours in the TCNQ salts at high pressures.

The electrical resistance of the single crystals, which were prepared by a diffusion process, has been measured up to 7 Kbar under hydrostatic pressure. The pressure was determined by the change of the electrical resistance by a manganin gauge.

Figure 1 shows the effect of the pressure on the electrical resistance of the TCNQ salts. The resistance and the activation energy increased with increasing pressure. A abrupt discontinuity of the resistance, however, was found at several Kbar. This is due to the pressure induced phase transition, which has been

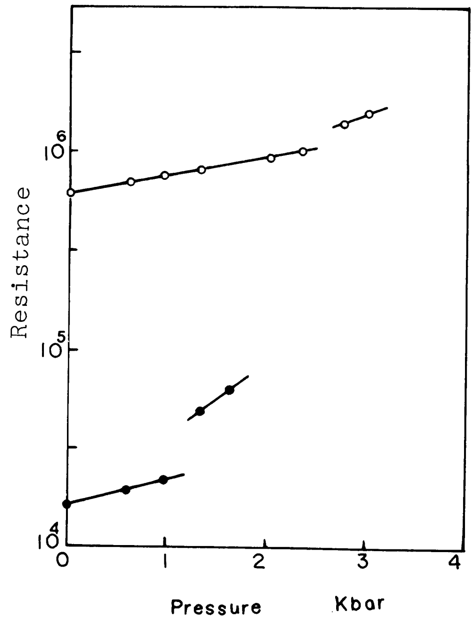

Fig.1 The electrical resistance at high pressure

● $[(C_6H_5)_3PCH_3](TCNQ)_2$

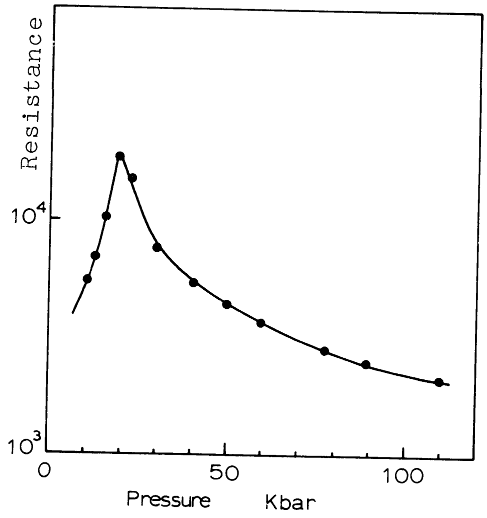

Fig.2 The electrical resistance at high pressure

o $[(C_6H_5)_3AsCH_3](TCNQ)_2$

already studied by McConnell et al.[3] The single crystal specimens broke up spontaneously at the transition pressure.

Generally, since the mobility of the charge carriers in organic crystals is not very sensitive to applied pressure, the change of the resistance with pressure arises from that of the activation energy for carrier formation.[2,4-6] For the energy E_o required to separate the charge in ion radical salts Lyons proposed[7] as

$$E_o = I_D - I_A - P_+ - P_- - Q \qquad (1)$$

where I_D is the ionization potential; P_+ and P_- the polarization energies due to a positive and to a negative charge, respectively; and Q stands for the remaining Coulombic interaction energy between the positive and negative ions formed. The decrease in volume of the crystal at high pressure will produce in the polarization energy P_+ and P_- in the Coulombic interaction energy Q. Therefore, it is expected that E_o decreases at high pressure. Since the activation energy of all TCNQ salts that has been already reported decreases at high pressures, Eq.(1) may be reasonable. However, the electrical behaviour in the phosphonium and arsonium TCNQ salts may not be explained by Eq.(1).

LeBlanc[8] proposed that the activation energy for conductivity, E,

$$2E = C - \Delta \qquad (2)$$

where C is the electrostatic energy and Δ is the band width. The C factor is estimated from the Coulomb repulsion between two electrons at $TCNQ^{--}$ site. The Coulomb repulsion is reduced by the presence of the highly polarizable aromatic cations. The reduction is expected to be roughly by a factor of $(1 - \alpha/r^3)$ where α is the polarizability of aromatic cations, r is some effective distance between a TCNQ molecule and the nearest cation. The similar study has been made by Epstein et al.[9] Though the volume decreases with pressure, the effective distance, r, does not always decrease. The electrical behaviour at high pressure may arise from the increase of the term C with pressure.

In a previous paper, the absorption spectra in the several TCNQ salts has been studied at high pressure.[10] The spectral blue shift in the visible region was observed with change in the pressure on the absorption spectra of simple alkali metal-TCNQ salts. In the case of complex TCNQ salts, the spectral peak shift was not observed.

The pressure dependence of magnetic resonance in the phosphonium and arsonium has been observed in the ranges 1–9 Kbar, and 220–362°K.[3] The pressure induced phase transition has been studied. Observed P–T diagram for $[(C_6H_5)_3AsCH_3](TCNQ)_2$ is explained in term of theory of non interacting triplet excitons. As has been stated earlier, the electrical resistance increased with increasing pressure. The phase transition may closely correlate to the anomalous electrical behaviour.

Figure 2 shows the electrical resistance of polycrystalline $[(C_6H_5)_3PCH_3]$-$(TCNQ)_2$ at high pressure. The high pressure cell for resistance measurement was similar to those used by Balchan and Drickamer.[4] The resistance reached the maximum at 20 Kbar and above this pressure decreased monotonously with increasing pressure. This anomalous behaviour may arise from the ocurrence of new phase at high pressure.

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