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Electrical Conduction of TCNQ Ion Radical Salts under High Pressure

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With an increase in the pressure, the electrical resistance of several TCNQ anion radical salts dropped rapidly in the low-pressure region and levelled off at high pressures. The temperature dependence of the resistance of compressed salt was studied over the region from 77°K to 200°K. The values of the activation energy decreased with an increase in the pressure. However, the metallic behaviour was not observed under very high pressures. The conduction mechanism of TCNQ salts was discussed from the point of view of a band scheme.

During the past decade, there has been a great expansion in the amount of high-pressure work, even in the field of molecular crystals.[1,2] Generally speaking, the electrical conductivity of aromatic crystals, typical organic semiconductors, increases with an increase in the pressure. Since the mobility of the charge carriers in the crystal is not very sensitive to applied pressure,[3] the large increase in the conductivity under high pressure is mostly due to the great increment in the concentration of the charge carrier.[4,5] Similar phenomena have also been observed with charge-transfer complexes;[6] the resistance of the less conductive compound has dropped sharply with an increase in the pressure, although that of the high conductive complex had not shown any pronounced effect of the pressure.[7]

Several TCNQ ion radical salts with aromatic cations have a very high conductivity, in one case the highest yet reported for organic semiconductors, and a very small activation energy.[8] The conductivity of these solids arises from the motion of the odd π-electron among the TCNQ sites and they show semiconductive behaviour.[9] As the pressure increases, the resistance of some TCNQ salts falls rapidly in the low-pressure region until it levels off under high pressure.[10] However, the pressure effects on their thermal activation energy are still not known.

In this paper we will report our results on the temperature-dependence measurements of the resistance of several TCNQ salts at high pressure and will discuss their conduction mechanism.

Experimental

The samples used in the experiment were quinolinium-$(TCNQ)_2$ $(Q(TCNQ)_2)$, bipyridinium$(TCNQ)_2$ $(BiP(TCNQ)_2)$, 4-amino-2, 3, 5, 6-tetramethylanilnium-$(TCNQ)_2$ $(DAD(TCNQ)_2)$, cobaltinium$(TCNQ)_2$ $(CoC(TCNQ)_2)$, and lithium(TCNQ) (Li(TCNQ)). These compounds were provided by Kondow, who has reported their preparations in detail previously.[9] The samples were studied in the form of powder pressure-fused into flat platelets. The high-pressure cell for resistance measurements was similar as those used previously.[5]

The temperature dependences of the electrical resistance were measured under a constant pressure in the temperature range of 77°K—200°K. The calibration of the pressure with the cell was made using bismuth and lead phase changes at known pressures.

Results

Figures 1 and 2 show the effect of the pressure on the resistance of three TCNQ salts at room temperature. As has been observed in the case of other organic semiconductors, TCNQ complexes showed a decrease in resistance with an increase in the pressure. The decrement was much slower in the high-pressure region. The resistance of less conductive salts such as Li(TCNQ) showed a marked pressure dependence. However, those of

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[6] Y. Okamoto, S. Snah and Y. Matsunaga, *J. Chem. Phys.*, **43**, 1904 (1965).

[7] M. Schwarz, H. W. Davies and B. T. Dobriansky, *ibid.*, **40**, 3257 (1964).

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[10] R. B. Aust, G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **41**, 2003 (1964).

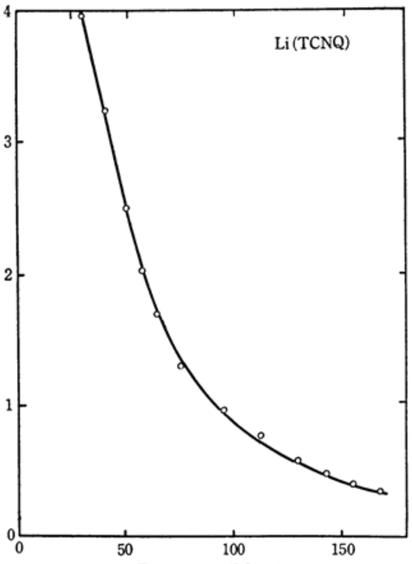

Fig. 1. The pressure dependence of the electrical resistance of Li(TCNQ) salt at room temperature.

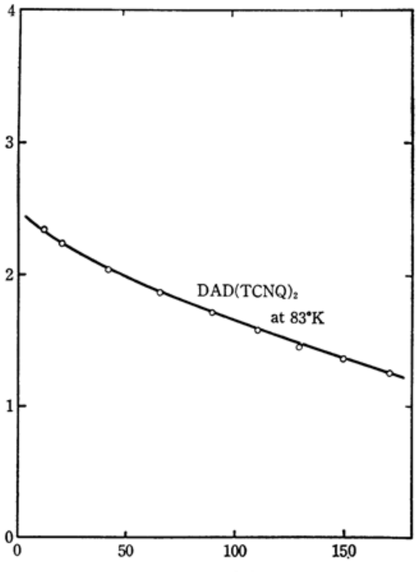

Fig. 3. The pressure dependence of the electrical resistance of DAD(TCNQ)$_2$ salt at 83°K.

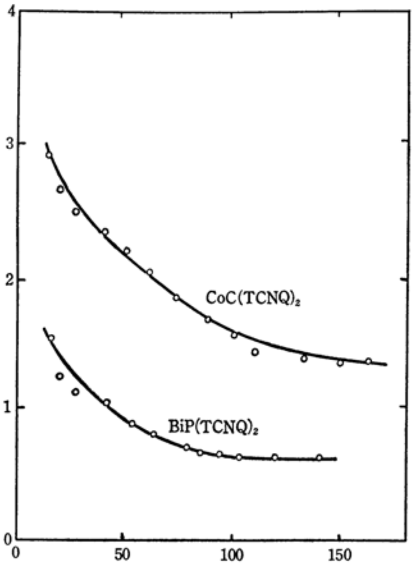

Fig. 2. The pressure resistance curve of TCNQ salts, CoC(TCNQ)$_2$ and BiP(TCNQ)$_2$, at room temperature.

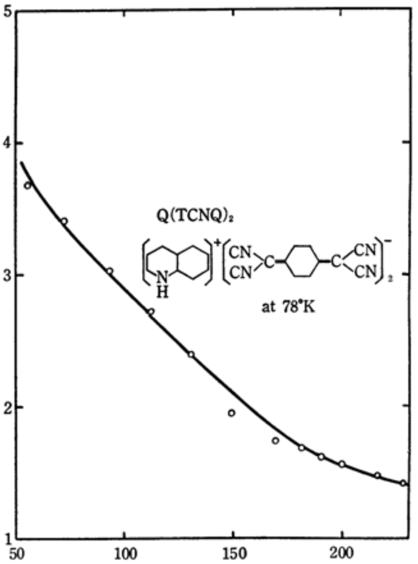

Fig. 4. The pressure resistance curve of Q(TCNQ)$_2$ at 78°K.

TABLE 1. THE ACTIVATION ENERGY OF TCNQ SALTS AT HIGH PRESSURE

Compound	ρ(Ωcm)	Activation energy (eV) at 1 bar	at high pressure	
Li(TCNQ)	5×10^5	0.32[a]	0.07 (169 kbar)	
CoC(TCNQ)$_2$	6.5	0.034[b]	0.05 (150 kbar)	
DAD(TCNQ)$_2$	2	0.08[a]	0.012 (228 kbar)	
BiP(TCNQ)$_2$	0.5	——[b]	0.038 (46 kbar)	0.017 (130 kbar)
Q(TCNQ)$_2$	0.25	0.03[a]	0.035 (30 kbar)	0 025 (208 kbar)

a) Ref. 8 (W. J. Simons *et al.*).

b) L. R. Melby *et al.*, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

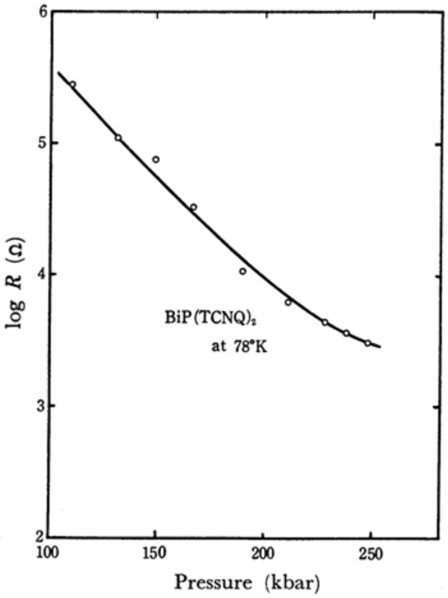

Fig. 5. The relation between pressure and electrical resistance for BiP(TCNQ)$_2$ at 78K°.

the high-conductive salts, such as Q(TCNQ)$_2$ and DAD(TCNQ)$_2$, were insensitive to pressure at room temperature.

Figures 3,4 and 5 show the pressure-resistance curve in the low-temperature region for DAD-(TCNQ)$_2$, Q(TCNQ)$_2$ and BiP(TCNQ)$_2$ respectively. Above 100 kbar, the resistance of Q-(TCNQ)$_2$ at room temperature rose with an increase in the pressure and drifted upward with time.[10] In the low-temperature region, at 78°K, these phenomena were not found; this means that no chemical reaction occurred.

The activation energies decreased with an increase in the pressure, but did not converge to zero up to 200 kbar. Table 1 shows the values of the activation energies under high pressures.

Discussion

A pressure-induced phase transition to the conducting state has been found for inorganic semiconductors, such as silicon and germanium;[11] their crystal structures change from the diamond type to the white-tin type.[12] However, molecular crystals have not become metallic except for I_2, Se, SnI_4 and pentacene*1 under high pressures. Though the behaviour of the pressure-resistance relation of these exceptional crystals is similar to that of organic semiconductors, the energy gaps become zero without crystal transformation at high pressures.[2]

Kepler *et al.* proposed that Q(TCNQ)$_2$ shows a metallic behaviour at atmospheric pressure: temperature-independent conductivity as high as 10^2 ohm^{-1} cm^{-1} and temperature-independent paramagnetic susceptibility.[8] Recently, on the other hand, we have found that Q(TCNQ)$_2$ behaves as a typical semiconductor:[9] it shows a temperature-dependent conductivity of the single crystal, a slightly-temperature-dependent magnetic susceptibility, and also an absorption edge in the far infrared-wavelength region (about 40 cm^{-1}).

In accordance with Mott's criterion for the metal-semiconductor transition,[13] LeBlanc proposed that:

$$2E = C - \varDelta \tag{1}$$

where E is the activation energy, C is the electrostatic energy, and $\varDelta$ is the band width.[14] When the $C > \varDelta$ relation is satisfied, the system is semiconductor, and when $C < \varDelta$, the system is metal. The same author estimated the values for TCNQ salts as:

$$\varDelta \simeq 0.1\,\text{eV} \quad \text{and} \quad C < 0.5\,\text{eV} \tag{2}$$

Since $\varDelta$ seems to be more sensitive to the pressure than C does in the first approximation, these compounds may be expected to become metals under high pressure. On the contrary, as Table 1 shows, their energy gaps did not reach zero, at least not up to 200 kbar.

Generally, an increase in the pressure results in an increase in the band width. An energy band of a molecular crystal such as anthracene widened 5—6 times at 161 kbar as compared with the value at atmospheric pressure.[4] However, the band width of high-conductive TCNQ salts seems to be less affected by the pressure.*2

In several TCNQ salts with aromatic cations, the line shape of the absorption curve at the edges can be expressed by Eq. (3) at room temperature;[9]

$$k \propto (\nu - \nu_G)^n$$
$$(\nu_G = 36.5\,\text{cm}^{-1};\ n = 0.46 \pm 0.05 \text{ for Q(TCNQ)}_2) \tag{3}$$

where k is the absorption coefficient; ν, the wave number of the incident light, and ν_G and n, the constants. The shape of this absorption edge is due to the direct allowed transition from the valence band to the conduction band. Further, the slightly-tempeature-dependent paramagnetic susceptibility of Q(TCNQ)$_2$ can be explained tentatively in terms of the band theory.[9]

On the other hand, the mobility of the carrier is less than 0.1 cm^2/V·sec,[8] though the energy gap

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11) S. Minomura and H. G. Drickamer, *J. Apply. Phys.*, **34**, 3043 (1963).

12) J. C. Jammison, *Science,* **139**, 762 (1963).

*1 The confirmation of the transition from semiconductor to metal is very difficult, because the chemical change is superposed on the transition.

13) N. F. Mott, *Phil. Mag.*, **6**, 287 (1961).

14) O. H. LeBlanc, *J. Chem. Phys.*, **42,** 4307 (1965).

*2 Their compressibility has not been measured. Probably, they are less compressible than ordinary hydrocarbon solids.

of high conductive TCNQ salts is very small; moreover they have partly-filled bands when considered simply, but they do not show a metallic behaviour even at high pressures. Considering these points, the conduction mechanism can not be explained by the usual band theory. Therefore, on the basis of the experimental results we suggest that even if a conduction band exists, the band width is probably very narrow.

Generally, a presssure coefficient for the optical energy gap of inorganic semiconductors agrees with the value determined by measuring the intrinsic resistivity as a function of the pressure. A similar behaviour has been observed in such molecular crystals as quaterrylene ($C_{40}H_{20}$).[15] If the pressure effect of the far-infrared absorption spectra of TCNQ salts could be studied, these electronic states could be discussed in detail.

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15) I. Shirotani, H. Inokuchi and S. Akimoto, This Bulletin, **40**, 2277 (1967).