Electrical Behavior of Alkali Metal Cation-TCNQ Anion Radical Simple Salts under Very High Pressures.

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The electrical resistance of alkali metal cation–TCNQ anion radical simple salts was measured over the wide pressure range from 0 to 500 kbar at room temperature. The least resistivities for Group A (Li–, Na–, K–, and Rb(I)–TCNQ) are about 0.2—3 Ω cm, while those for Group B (Rb(II)– and Cs–TCNQ) are about 0.06—0.1 Ω cm. The possibility of insulator-metal transition at high pressures is discussed. Above 140—175 kbar the electrical resistance of simple TCNQ salts increases with an increase in the pressure and drifts upward with the time. The solid-phase reaction is observed under very high pressures.

The electrical,[1,2] optical,[3–5] and magnetic properties[6,7] and the crystal structures[8,9] in simple alkali metal cation–TCNQ anion radical salts (M–TCNQ) have been studied. Phase transitions have been observed in the temperature range from −150 °C to +230 °C;[10,11] further, new, pressure-induced phase transitions have been investigated at room temperature.[11] According to the differences in the physical properties and crystal structures, alkali metal–TCNQ salts may be classified into two groups. Li–, Na–, K–, and Rb(I)–TCNQ salts are contained in Group A. These salts have exhibited typical semiconductive behavior. The dimerized structure in the TCNQ^- columns appears to be typical.[8] Rb(II)– and Cs–TCNQ, on the other hand, belong to Group B. The X-ray study of Rb(II)–TCNQ shows a triclinic structure consisting of linear chains of identical TCNQ molecules stacked face-to-face and equally separated from one another.[9] This columnar structure resembles that found in the crystals of such metallic TCNQ salts as *N*-methylphenazinium–TCNQ (NMP–TCNQ).[12,13] However, no insulator-metal transition has been observed in the wide temperature range from 170 to 570 K[2] and up to 14 kbar at room temperature.[11] The interplanar spacing between the TCNQ^- anion in Rb(II) salt, 3.43 Å, is much longer than that, 3.26 Å, in NMP–TCNQ. If this distance, 3.43 Å, can be contracted to about 3.2 Å by compression, it seems that it would be possible to observe a pressure-induced phase transition to the conducting state at high pressures.

In this paper, we will present our findings on the pressure dependence of the electrical resistance of M–TCNQ salts and will discuss the possibility of insulator-metal transition at high pressures. Further, we will present some results on the solid phase reactions that were found under very high pressures.

Experimental

Conductivity measurements were performed using a split-sphere apparatus[14] constructed at Osaka University. A schematic diagram is shown in Fig. 1. A sphere made of hardened steel was split into six wedge-shaped segments, the centers of which were all truncated so that a central hollow space could be made. Into this space we placed eight cubic anvils made of tungsten carbide. A corner of each cubic anvil was cut off to form a triangular face. When these eight cubic anvils were put together, the eight triangular faces formed an octahedral hollow space in the center of the whole sphere. The specimen to be compressed was embedded in the pyrophyllite octahedron, which served as a pressure-transmitting medium.

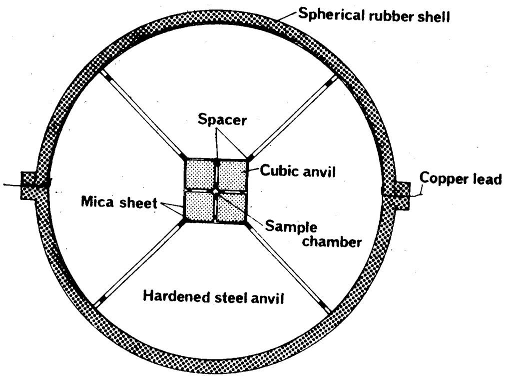


Fig. 1. Cross-section of the split-sphere apparatus showing the arrangement of inner cubes, outer segments, and spacers.

Since these inner and outer anvils were equally separated and put together with soft cardboard spacers sandwiched between them, it was possible to construct a sphere with a diameter slightly larger than before the splitting. When the anvil assemblage covered with a pair of semispherical rubber shells was compressed with a fluid, the sphere shrunk uniformly, reducing its diameter toward that of the original sphere. Quasi-hydrostatic high pressures could, as a result, be generated in the octahedral specimen chamber. The details of the sample arrangement and pressure calibration have been described elsewhere.[15]

The samples used in the experiment were Li–, Na–, K–, Rb(I)–, Rb(II)–, and Cs–TCNQ. The preparation of these compounds has been reported in detail previously.[2,11] The samples were studied in the form of powder pressure-fused into flat platelets.

Results and Discussion

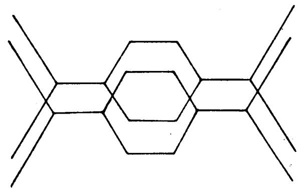
According to the differences in their physical properties and crystal structures, simple TCNQ salts may be classified into two groups. As is shown in Table 1, Li–, Na–, K–, and Rb(I)–TCNQ salts are contained in Group A, while Rb(II)– and Cs–TCNQ belong to Group B. It is known that crystals of Rb(I)–TCNQ

Table 1. Physical properties of simple M–TCNQ salts

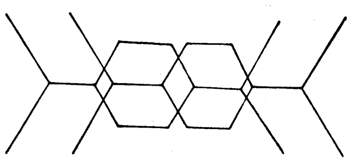
	Resistivity (Ω cm)		Transition temperature (K)		Location of charge transfer band[a,d] (10^3 cm^{-1})
	Single crystal[a] along the needle axis	Microcrystal[b]			
Li–TCNQ		5×10^5	No phase transition observed		8.0
Na–TCNQ	$\sim1\times10^3$	1×10^5	338[a]	348[c]	8.3
K–TCNQ	$\sim5\times10^3$	1×10^4	391	394	8.3
Rb(I)–TCNQ	$\sim3\times10^5$		374	381	8.6
Rb(II)–TCNQ	$\sim1\times10^2$		231	223	6.5
Cs–TCNQ	$\sim6\times10^2$	3×10^3	254	210	6.5

a) Ref. 2, 9 b) Ref. 1 c) Ref. 8 d) Ref. 5

in Group A have a monoclinic symmetry and that the TCNQ$^-$ ions are stacked face-to-face to form columns of diadic units of TCNQ$^-$. Within a column, two different intermolecular spacings, 3.159 and 3.480 Å, appear alternately.[8] On the contrary, the TCNQ radical ions in Rb(II) salt form columns constructed from monadic units of TCNQ$^-$. The spacing between TCNQ$^-$ is 3.43 Å.[9] Figure 2 exhibits the mode of overlapping between the nearest TCNQ$^-$ ions in both Rb salts.



Rb(I)-TCNQ

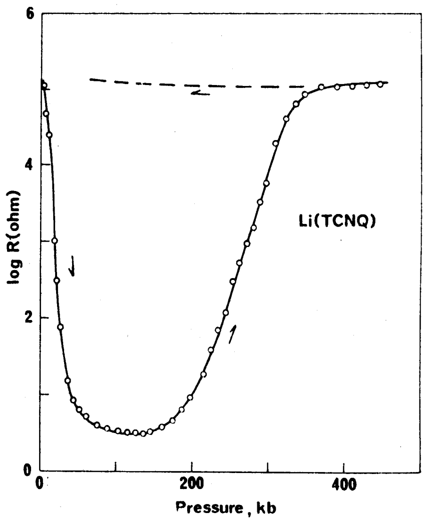


Rb(II)-TCNQ

Fig. 2. The mode of overlapping between nearest TCNQ$^-$ in both Rb–TCNQ salts.

The columnar structures of TCNQ salts seem to be closely related to the electrical conductivity.[12] The TCNQ salts with diadic, triadic, and tetradic are low or intermediately conductive. The mode of overlapping between the nearest TCNQ ions in these salts is similar to that found in the Rb(I) salt. The highly-conductive salts, such as NMP–TCNQ, are constructed of monadic units of TCNQ. The mode of overlapping between the nearest TCNQ ions in these salts resembles that found in the Rb(II) salts.

The effect of the pressure on the electrical resistances of TCNQ salts in Group A is shown in Figs. 3a and 3b. Their electrical resistances decreased rapidly with an increase in the pressure and reached their minimum in the pressure range of 145—175 kbar. The behavior of the curve was reproducible below this pressure region. The least resistivities of the TCNQ salts are given in Table 2. The least resistivity of Li–TCNQ is much smaller than that of the other salts in Group A.



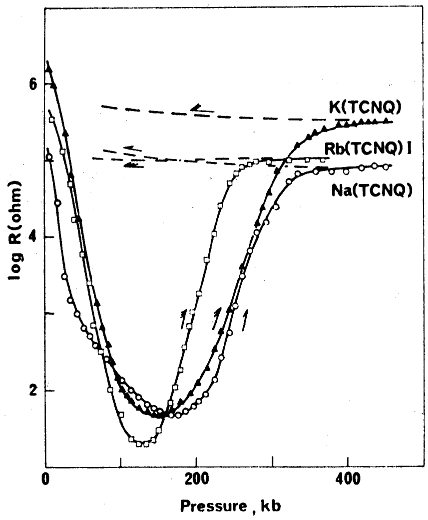


Fig. 3a and 3b. Pressure dependence of the electrical resistance of TCNQ salts in Group A.

In a previous paper,[11] we have reported that the electrical behavior of their single crystals is very complex under pure hydrostatic pressure. Several pressure-induced phase transitions are observed in the pressure range of 0—15 kbar at room temperature. However, the crystal structures do not change drastically.[16]

If the dimerized structure found in the columns of

Table 2. Minimum resistivity and minimum pressure

Compound	$P_{\min}$[a] (± 5 kbar)	$\rho_{\min}$[b] (Ω cm)
Li–TCNQ	135	$\sim 2\times10^{-1}$
Na–TCNQ	174	$\sim 3\times10^{0}$
K–TCNQ	148	$\sim 3\times10^{0}$
Rb(I)–TCNQ	135	$\sim 1\times10^{0}$
Rb(II)–TCNQ	170	$\sim 6\times10^{-2}$
Cs–TCNQ	152	$\sim 1\times10^{-1}$

a) Ref. 24. b) The resistivity was calculated from the resistance data by measuring the dimensions of the retrieved specimen after the compression.

typical alkali metal–TCNQ salts is converted into the monomeric structure by the compression, and if the mode of overlapping between nearest $TCNQ^-$ ions in the column is then changed that of the Rb(II)-salt type, TCNQ salts may behave like metal at high pressures. However, the electrical resistances of Group A decreased monotonously with the pressure up to the pressure of minimum resistance. The least resistivities of all the TCNQ salts but Li–TCNQ were about 1—3 Ω cm at room temperature. No anomalous behavior arising from the phase transition to the metallic state was observed.

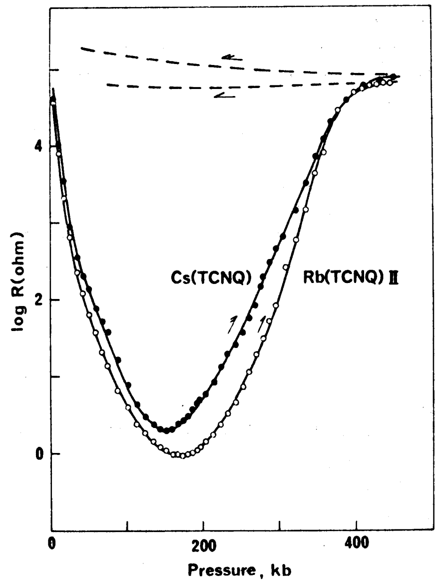


Fig. 4. Pressure dependence of the electrical resistance of TCNQ salts in Group B.

Figure 4 shows the effect of the pressure on the electrical resistances of TCNQ salts in Group B. The resistances decreased by a factor of approximately 10^4 in the first 150 kbar at room temperature. The least resistances are about one-tenth of those of Group A. The least resistivity in Rb(II)–TCNQ was about $6\times10^{-2}\,\Omega$ cm at 170 kbar. As is shown in Table 3, this value is less than the resistivities of a compacted specimen of the metallic TCNQ salts at atmospheric pressure.

The compressibility of Rb(II)–TCNQ has not been measured, but it is probably comparable to that of aromatic crystals.[16] From the relation between the pressure and the volume for molecular solids given by Samara and Drickamer, the average intermolecular distance at 170 kbar was estimated to be about 88% of that at atmospheric pressure.[17] Therefore, we can expect the interplanar spacing in Rb(II) salts around 170 kbar to be much shorter than 3.26 Å in NMP–TCNQ at 1 bar.

The magnetic-susceptibility and conductivity measurements for NMP–TCNQ indicate a metallic state above 200 K, with a continuous transition to an insulator below 200 K.[18] Similar behavior has also been observed in quinolinium–$TCNQ_2$ (Q–$TCNQ_2$),[19,20] acridinium–$TCNQ_2$ (Ac–$TCNQ_2$),[20] and tetrathiofulvalenium–TCNQ (TTF–TCNQ).[21,22] X-Ray studies of these metallic TCNQ salts show monoclinic or triclinic structures consisting of linear chains of identical TCNQ molecules stacked face-to-face and equally separated from one another.[12] This structure resembles that of Rb(II)–TCNQ. The electrical resistivities, the transition points, and the interplanar spacings between TCNQ molecules for metallic TCNQ salts are given in Table 3. These physical properties are also compared with those of Rb(II)–TCNQ near 170 kbar in this table.

On the basis of these data, we suggest that Rb(II)–TCNQ may show metallic behavior near 170 kbar.

The metal-insulator transitions in one-dimensional

Table 3. Comparison of physical properties between Rb(II)–TCNQ around 170 kbar and metallic TCNQ salts

	Rb(II)–TCNQ	NMP–TCNQ	Q–$TCNQ_2$	Ac–$TCNQ_2$	TTF–TCNQ
Resistivity at room temperature microcrystal (Ω cm)	6×10^{-2} [a] (170 kbar)	0.5[b]	0.25[c]	0.3[d]	
Single crystal along the needle axis (Ω cm)	10^2 (1 bar)[e] 8[e] (14 kbar)	7×10^{-3} [b]	10^{-2} [f]	10^{-2} [f]	10^{-3} [g]
Interplanar spacing (Å)	below 3.2[h] (170 kbar)	3.26[i]	3.22[j]	3.25[j]	3.17[k]
Metal-insulator transition temperature (K)		200[l]	240[f]	140[f]	60[g]

a) Present work. b) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965). c) Ref. 1. d) P. Dupuis and J. Neel, *C. R. Acad. Sci. Paris, Ser. C*, **265**, 688 (1967). e) Ref. 2, 9. f) Ref. 20. g) Ref. 21, 22. h) The predicted value from the compressibility of organic solids. i) Ref. 13. j) Ref. 12. k) T. E. Phillips, T. J. Kistenmacher, J. P. Ferrais, and D. O. Cowan, *Chem. Commun.*, **1973**, 471. l) Ref. 18.

crystals such as TCNQ salts have been observed only along the conductive axis in the single crystals. The electrical resistivity along the needle axis in Rb(II) salt has been measured at hydrostatic pressures up to 14 kbar. The resistivity at this pressure is about 8 Ω cm at room temperature.[11] If the resistivity along the conductive axis were to be studied at higher pressures, an insulator-metal transition would probably be observed.

The compaction conductivity of microcrystals of metallic TCNQ salts indicates an exponentially-activated behavior because of inter-particle contact resistance. Their activation energy does not become zero even at very high pressures.[23] Recently, Heeger *et al.*[22] have reported a new experimental technique, a voltage-shorted compaction (VSC) device, for obtaining information on the bulk electrical properties from the compaction of samples. When this technique is used, the electrical behavior of microcrystalline sample does not show the thermally-activated process. For the study of the insulator-metal transition of compacted samples at high pressures, this technique may be very useful.

Solid-Phase Reaction. As is shown in Figs. 3 and 4, above 140—175 kbar the electrical resistances of the TCNQ salts increased rapidly with the increase in the pressure and drifted upward with the time. As is shown by the broken curve, this electrical behavior is irreversible. These phenomena arise from the solid-phase reaction. The minimum pressure[24] at which the reaction was induced is given in Table 2. It should be noted that for Group B this pressure is larger than for Group A except in the case of Na–TCNQ.

The pressure-induced solid-phase reactions for TCNQ and TCNQ salts have already been investigated under very high pressures by Drickamer *et al.*[25] The electronic absorption peaks at 300—900 nm and the infrared spectra on the basis of the C≡N stretching vibration disappear under very high pressures. This seems to indicate a reaction between C≡N bonds in adjacent TCNQ molecules. Considering the similar reaction for simple alkali metal–TCNQ salts, the difference in crystal structures may be very important. The interplanar distance and the magnitude of overlapping between C≡N bonds in TCNQ salts seem to be closely correlated with the pressure-induced solid-phase reaction. As has been mentioned above, Rb(I)–TCNQ has a short interplanar distance, 3.159 Å, and the overlapping between the C≡N bonds in Rb(I) salt is larger than that in Rb(II) salt. Therefore, we can expect that the reactivity of Group A is more sensitive to the pressure than that of Group B. The differences in minimum pressure shown in Table 2 may show the strength of the reactivity at high pressures.

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