

Phase Transition of Alkali Metal Cation-TCNQ Anion Radical Simple Salts

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(Received March 7, 1972)

The phase transition at 1 bar has been observed in alkali metal cation-TCNQ anion radical simple salts by means of measurements of the electrical resistivity of their single crystals. The temperature dependence of the resistivity under high hydrostatic pressures has been studied in order to investigate the effect of the pressure on this phase transition. The nature of this phase transition has been discussed. The pressure-induced new phase has also been found in these TCNQ salts at room temperature; thus, more than three phases (α , β , γ ...) are considered to exist in the solid phase of these TCNQ salts.

It has been shown, from the measurement of the volume change under high pressures by Bridgman, that several molecular organic solids exhibit pressure-induced phase transitions.¹⁾ He has described that it appears that polymorphism is an even more common phenomenon among organic than among inorganic compounds in the temperature range of solid CO₂ temperatures up to 200°C and up to about 50 kbar; this can be expected, because it has appeared that the chance that a substance will exhibit polymorphism is roughly greater the lower the melting point, and, in general, the melting points of organic substances are lower than those of inorganics. The molecular interactions in the crystals of organic substances which he had studied are principally van der Waals interactions.

Ion radical salts, which have attracted interest because of their peculiar electrical and magnetic properties, and which have been studied extensively,^{2,3)} contain complicated molecular interactions, such as the Coulomb forces, the van der Waals forces and the charge-transfer forces. These molecular interactions have different effects on the inter-molecular distances, so that pressure-induced phase transitions, whose mechanism would be different from that in the organic neutral molecular crystals, may be expected to occur in the ion radical salts.

Recently, McConnell and his co-workers⁴⁾ have determined the pressure-induced phase transitions in triphenylmethylarsonium(TCNQ)₂ (TCNQ: 7,7,8,8-tetracyanoquinodimethane) from the pressure dependence of the exciton magnetic resonance. They have explained the observed P-T phase diagram in terms of a simple theory of non-interacting triplet excitons, contrary to Chesnut's theory,⁵⁾ where the phase transition is attributed to attractive exciton-exciton interactions.

In this paper we will report on the effect of pressure on the phase transitions of the crystalline M⁺(TCNQ)⁻ salts (M⁺=alkali metal cation) occurring at 1 bar,

which have been found by Vegter *et al.*,⁶⁾ and the new pressure-induced phase transitions found in these crystals from the pressure dependence of the electrical resistivity at room temperature.

Experimental

Preparation of Single Crystals. Crystals of Na(TCNQ), K(TCNQ), and Rb(TCNQ) were prepared at room temperature by a diffusion process in a solution of commercially-available metal-iodide and TCNQ purified by recrystallization from acetonitrile distilled from phosphorus pentoxide and by sublimation *in vacuo*.⁷⁾ An apparatus different from that described by Pott and Kommandeur⁸⁾ was used for crystal growing; a test tube of a suitable length within metal-iodide crystals was left standing in a 200 ml Erlenmeyer flask within TCNQ crystals; in both of them acetonitrile was poured, and then the flask was covered and allowed to stand two or three weeks at room temperature. Crystals of Cs(TCNQ) were prepared by the metathesis of CsCl with Li(TCNQ) in water using above-mentioned apparatus. The crystals had various sizes; for example, 0.7×0.3×0.1 mm³—0.4×0.3×0.2 mm³ for Na(TCNQ) and 15.0×1.0×1.0 mm³—2.0×0.3×0.3 mm³ for K(TCNQ). Crystals of Li(TCNQ) have not been available large enough for single-crystal measurements in this way. The polycrystalline powder samples of Li(TCNQ) and K(TCNQ) were prepared by mixing boiling acetonitrile solutions of TCNQ and metal iodide.⁷⁾

Electrical Measurements. The electrical resistivity was measured by means of the direct-current method, with two-electrode probes, because of the high resistance of small crystals. Electrical contacts to the crystals were made with silver paste. A high-pressure cylinder with an inside diameter of 30 mm and a piston distance of 80 mm was used. The maximum attainable pressure is 15000 kg/cm² in this cylinder. Silicone oil of low viscosity was used as the pressure-transmitting medium. The pressure was measured with a manganin gauge. The high-pressure apparatus and the high-pressure plug, with a sample mounting and a heater, are shown in Fig. 1.

Only one end of the crystal, in the form of a needle, was fixed vertically on the bakelite base with silver paste in order to prevent the crystal from breaking from the difference

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5) D. B. Chesnut, *ibid.*, **40**, 405 (1964).

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8) G. T. Pott and J. Kommandeur, *Mol. Phys.*, **13**, 373 (1967).

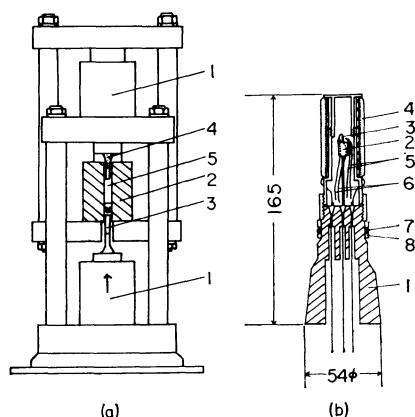


Fig. 1. Schematic diagram of high-pressure apparatus.

- a) high pressure cylinder settled on Kennedy type 1000 ton press (1) 1000 ton press (2) high pressure cylinder (3) piston (4) high pressure plug (5) silicone oil
 b) high pressure plug with a sample mounting and a heater.
 (1) hardened steel high pressure plug (2) bakelite base
 (3) crystal (4) nichrome wire heater around alumina cylinder
 (5) copper-constantan thermocouple (6) electrical lead
 (7) O-ring (8) brass ring

in the compressibilities of the crystal and the base when pressure was raised.

The nichrome wire heater around the alumina cylinder, the outside of which was fixed by cement, was used for heating the samples. The temperature was measured by means of a copper-constantan thermocouple placed near the crystal.

Optical Measurements. The measurement of the electronic absorption spectra was carried out using a Cary recording spectrophotometer, Model 14M. The temperature dependence of the absorption spectra was measured on samples rubbed on glass plates using a high-temperature optical cell in about 10^{-2} Torr, the temperature being measured by means of a copper-constantan thermocouple.

Results and Discussion

A. Effect of Pressure on the Phase Transition. The $M^+(\text{TCNQ})^-$ crystals available here for electrical measurements are almost like the twinning crystals. In the case of $\text{Rb}(\text{TCNQ})$, two kinds of crystals, whose external appearances are different, were prepared in the same batch by the method described above. One is a reddish-purple needle similar to $\text{K}(\text{TCNQ})$, and the other is a dark purple needle similar to $\text{Cs}(\text{TCNQ})$ or the prism. The yield of reddish-purple crystals constitutes a small percentage of the total yield of $\text{Rb}(\text{TCNQ})$ crystals. The physicochemical properties are remarkably different between the two crystals.⁹⁾ For example, the electrical resistivity, ρ , at room temperature is about $10^5 \Omega \cdot \text{cm}$ and $10^2 \Omega \cdot \text{cm}$, and the activation energy, E_a , obtained from the expression $\rho = \rho_0 \exp(E_a/kT)$ is between 0.41 and 0.53 eV and between 0.16 and 0.19 eV for the reddish-purple $\text{Rb}(\text{TCNQ})$ and the dark purple one respectively. The electronic absorption spectra are also different, as has been shown in Fig. 2.

9) Recently, by means of X-ray analysis, the difference of the crystal structure between reddish-purple $\text{Rb}(\text{TCNQ})$ and dark purple one was made clear. I. Shirovani, H. Kobayashi, N. Sakai, and Y. Saito, This Bulletin, to be published.

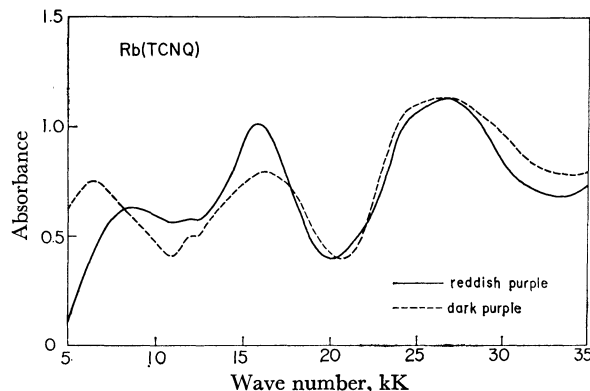


Fig. 2. Electronic absorption spectra of reddish and dark purple $\text{Rb}(\text{TCNQ})$.

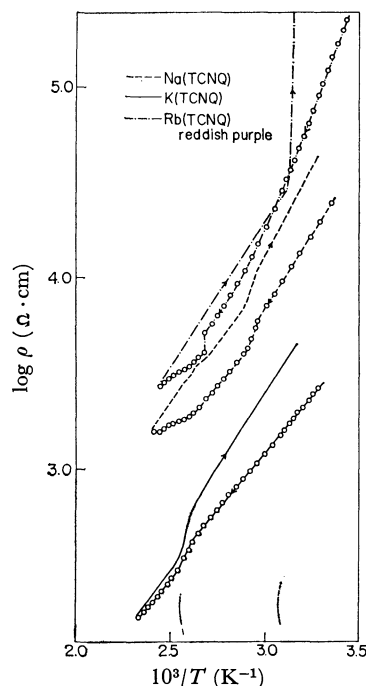


Fig. 3. Electrical resistivity as a function of reciprocal temperature of $\text{Na}(\text{TCNQ})$, $\text{K}(\text{TCNQ})$, and reddish-purple $\text{Rb}(\text{TCNQ})$ in 10^{-2} Torr.

Figure 3 shows the electrical resistivity of $M^+(\text{TCNQ})^-$ crystals as a function of the reciprocal temperature. This measurement was carried out in about 10^{-2} Torr. The presence of the anomalies in resistivity was observed at about 338, 391, and 374°K for Na-, K-, and reddish-purple $\text{Rb}(\text{TCNQ})$ respectively. The resistivity, ρ , and the activation energy, E_a , of these $M^+(\text{TCNQ})^-$ crystals varied from crystal to crystal.

The activation energy of $\text{Na}(\text{TCNQ})$ is from 0.23 to 0.32 eV below the transition temperature and from 0.16 to 0.22 eV above. The resistivity decreases by a factor of about 0.8 at the transition point. In thermal cycles for the same crystal, the resistivity during cooling is higher than that during the initial heating and the room-temperature resistivity in the second thermal cycle is higher than the initial value by a factor of about 1.2. However, the agreement of the transition temperature among several specimens, among heating

and cooling processes, and among repeated measurements of the same crystal is excellent. The heat of transition of Na(TCNQ) is very small, but it was distinctly observed by the preliminary measurements by means of a differential scanning calorimeter, this is in contrast with the case reported by Vegter *et al.*⁶⁾

The activation energy of K(TCNQ) is from 0.23 to 0.45 eV below the transition point and from 0.15 to 0.31 eV above. In this salt, the resistivity changes slowly over a 5 to 8°K interval before a linear $\log \rho$ versus $1/T$ relationship in the region of the low activation energy is obtained. The amount of the change in the resistivity at the reverse transition on cooling is larger than that at the transition on heating. The agreement of the transition temperature among the several specimens is within $\pm 6^\circ\text{K}$.

In the case of reddish-purple Rb(TCNQ), the activation energy is from 0.41 to 0.53 eV below the transition point and from 0.28 to 0.37 eV above. The abrupt decrease in the resistivity by a factor of about 0.6 was observed at the transition, but most of the crystals break down at the transition point, and so it is difficult to obtain accurate measurements of the transport behavior in the high-temperature phase. A large hysteresis in the transition temperature was observed. The transition point is $374 \pm 1^\circ\text{K}$ upon heating and $323 \pm 4^\circ\text{K}$ upon cooling.

A similar abrupt change in resistivity was observed at about 231 and 254°K for the dark purple Rb(TCNQ) crystals and Cs(TCNQ) crystals respectively. The amount of the change in resistivity at the transition point is very small, and no change in the activation energy was observed above and below the transition point for these salts.

TABLE 1. TRANSITION TEMPERATURE AND HEAT OF TRANSITION FOR $M^+(\text{TCNQ})^-$ SALTS

	Transition temperature ($^\circ\text{K}$)		Heat of transition ^{a)} ΔH (cal/mol)
	Present work	After Vegter <i>et al.</i> ^{a)}	
Na(TCNQ)	338	348	unobservable
K(TCNQ)	391	395	60
Rb(TCNQ)			
reddish-purple	374	381	1010
dark purple	231	—	—
Cs(TCNQ)	254	210	unobservable

a) Ref. 6)

The transition temperatures observed in the present electrical measurements for various salts are summarized in Table 1, along with the data reported in Ref. 6. The disagreement of the transition temperatures may be due to differences in the methods of measurement or to the differences in the purity of the samples. The scattering values of the activation energy among several specimens seem to be mainly due to the influence of impurities on the electrical conduction.¹⁰⁾

10) N. Sakai, I. Shirotani, and S. Minomura, *ibid.*, **45**, 3314 (1972).

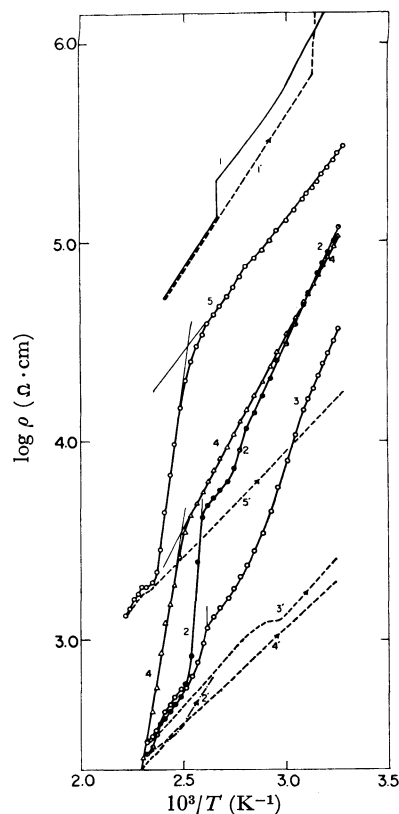


Fig. 4. Electrical resistivity as a function of reciprocal temperature under several constant high pressures of reddish-purple Rb(TCNQ).
curve 1: 0 kbar, 2: 2.2 kbar, 3: 4.2 kbar, 4: 8.3 kbar, 5: 10.4 kbar.

The effect of the hydrostatic pressure on the transition temperature was studied in order to obtain information about the nature of the phase transition in $M^+(\text{TCNQ})^-$. Figure 4 shows the resistivity as a function of the reciprocal temperature under several constant high pressures for the reddish-purple Rb(TCNQ) crystal. The transition temperature of 374°K at 1 bar rises with an increase in the pressure. The transition seems to be sluggish under high pressures. The curves of $\log \rho$ versus $1/T$ under high pressures seem to be complicated because of the appearance of the new pressure-induced phase transition to be described in the next section, B. Although the breakdown of crystals at the transition point occurring at one atmosphere did not occur under high pressures, different crystals were used for each run because of the possibility of the high-temperature phase being quenched at room temperature under high pressures. The activation energy in the low-temperature phase decreased with an increase in the pressure ($dE_a/dP \sim -0.01$ eV/kbar). The pressure dependence of the activation energy in the high-temperature phase was not well known because of the limited temperature region.

Figure 5 shows a phase diagram of the reddish-purple Rb(TCNQ). The slope obtained from the curve is calculated to be:

$$dP/dT = +0.36 \text{ kbar/deg.} \quad (1)$$

The discontinuity in volume at the transition may be calculated from the Clausius-Clapeyron relation for

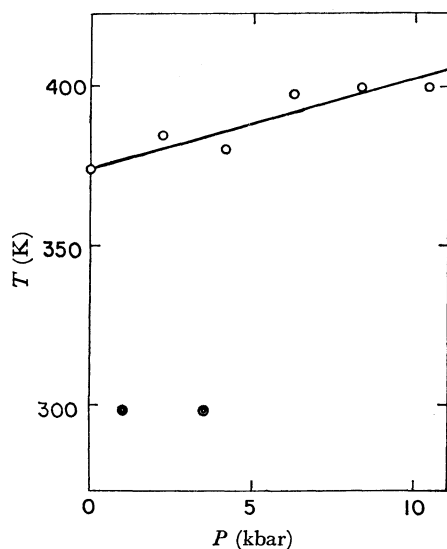


Fig. 5. Phase diagram of reddish-purple Rb(TCNQ). Pressure-induced phase transition points (see the text) are also written in at room temperature.

the first-order transition:

$$dP/dT = \Delta S/\Delta V, \quad (2)$$

where ΔS is the total change in entropy between the two phases. ΔS is evaluated from the latent heat of transition. The ΔS for the reddish-purple Rb(TCNQ) is about 2.65 cal/mol·deg, judging from the data in Table 1; consequently, ΔV is 0.31 cm³/mol.

The temperature dependence of the resistivity under several constant high pressures was measured also for Na- and K(TCNQ). In these salts, the small amount of change in the resistivity at the transition point became obscurer with an increase in the pressure, and so it was difficult to obtain the pressure coefficients for the transition temperature over a wide region of pressures. The preliminary value of dP/dT for Na(TCNQ) is +0.014 kbar/deg up to about 4 kbar. Data concerning the phase transition for various ion radical salts are summarized in Table 2.

TABLE 2. DATA CONCERNING THE PHASE TRANSITION FOR VARIOUS ION RADICAL SALTS

	dP/dT (kbar/deg)	ΔS (cal/mol·deg)	ΔV (cm ³ /mol)
Rb(TCNQ)	+0.36	2.65 ^{a)}	+0.31
W.B.P.	+0.1 ^{b)}	2.19 ^{c)}	+0.91 ^{b)}
$[(C_6H_5)_3PCH_3]^+-(TCNQ)_2^-$	negative	1.72 ^{d)}	~-2
$[(C_6H_5)_3AsCH_3]^+-(TCNQ)_2^-$	negative	—	~-3.51 ^{e)}

a) Ref. 6, b) Ref. 11, c) Ref. 12, d) Ref. 13, e) Ref. 4.

The ΔV at the transition of $[(C_6H_5)_3AsCH_3]^+-(TCNQ)_2^-$ has been obtained by the following treatment, proposed by McConnell and his co-workers.⁴⁾

The condition for phase equilibrium—that the Gibbs free energies, including the spin-exchange free energy for a strongly-alternating linear array without any exciton-exciton interaction of the two phases, be equal at the transition point—leads to the following

equation for the P - T phase separation curve:

$$P = -(\Delta E^0/\Delta V^0) + (kT/\Delta V^0) \ln [(1-\rho_I)/(1-\rho_{II})] \quad (3)$$

where the quantity ρ is the triplet excitation density as defined by the equation of the molar paramagnetic susceptibility as:

$$\chi_p = \rho N_0 g^2 \beta^2 / 3kT, \quad (4)$$

and is related to the energy separation between the thermally-accessible triplet state and the ground state by the following equation:

$$\rho = 3[3 + \exp(J/kT)]^{-1}. \quad (5)$$

When Eq. (3) is led, it has been assumed that the two crystal forms have very similar crystal structures, and that the phonon heat capacities of the two phases are equal and are essentially independent of the pressure, and, further, that the thermal coefficients of the volume expansion of both phases are small, nearly equal, and independent of the pressure.

The value of ΔV^0 of $[(C_6H_5)_3AsCH_3]^+-(TCNQ)_2^-$ has been determined to be -11.7 Å³/spin pair from the measurement of P , T , ρ_I , and ρ_{II} at the transition point. The ΔV value of the negative sign indicates a decrease in the crystal volume at the transition to the high-temperature phase, which is the high-pressure phase for $[(C_6H_5)_3AsCH_3]^+-(TCNQ)_2^-$.

The total change in entropy between the two phases is composed of electronic terms, lattice terms, and spin-ordering terms:

$$\Delta S = \Delta S_{\text{electronic}} + \Delta S_{\text{lattice}} + \Delta S_{\text{spin}}. \quad (6)$$

The electronic entropy change may be neglected in these ion radical salts because of the small number of carriers. Although, in the case of $[(C_6H_5)_3AsCH_3]^+-(TCNQ)_2^-$, the $\Delta S_{\text{lattice}}$ has been neglected in the treatment by McConnell and his co-workers, the $\Delta S_{\text{lattice}}$ seems to be the main factor in the entropy change in the reddish-purple Rb(TCNQ). The contribution of ΔS_{spin} to ΔS will be several percent in the reddish-purple Rb(TCNQ), as in the cases of Würster's Blue Perchlorate (W.B.P.) and $[(C_6H_5)_3PCH_3]^+-(TCNQ)_2^-$. This was estimated from the data of K(TCNQ).⁶⁾ For the case of the reddish-purple Rb(TCNQ), the following equation¹¹⁾ for the phase-separation line may be used instead of Eq. (3):

$$P = -(\Delta E/\Delta V) + T\Delta S_{\text{lattice}}/\Delta V + (kT/\Delta V) \ln [(1-\rho_I)/(1-\rho_{II})]. \quad (7)$$

The ΔV values of the positive sign in the reddish-purple Rb(TCNQ) and W.B.P. indicate an increase in the crystal volume at the transition to the high-temperature phase. Recently, the structure determination of the reddish-purple Rb(TCNQ) has been carried out by means of an X-ray diffraction study at a low temperature (-160°C) by Hoekstra, Spoelder, and Vos.¹⁴⁾ The crystal of the reddish-purple Rb-

11) R. C. Hughes, A. W. Merkl, and H. M. McConnell, *J. Chem. Phys.*, **44**, 1720 (1966).

12) H. Chihara, M. Nakamura, and S. Seki, *This Bulletin*, **38**, 1776 (1965).

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(TCNQ) belongs to the monoclinic symmetry of the $P2_1/c$ space group, with lattice constants of $a=7.187$, $b=12.347$, $c=13.081$ Å, and $\beta=98.88^\circ$ at -160°C , and with those of $a=7.30$, $b=12.40$, $c=13.13$ Å, and $\beta=98.8^\circ$ (which are preliminary values) at room temperature, including four molecules in a unit cell.

The room-temperature W.B.P. is orthorhombic, the space group is $Pn2n$ or $Pnmn$, with a unit cell of dimensions $a=5.98$, $b=10.21$, and $c=10.23$ Å, which includes two molecules in a unit cell; at $\sim 77^\circ\text{K}$ through the phase transition at 186°K , it changes to a monoclinic symmetry with lattice constants of $a=11.70$, $b=20.22$, $c=10.17$ Å, and $\gamma=92.7^\circ$.¹⁵⁾

According to these crystal data, the rates of the volume change to the molar volume at the transition point are about 0.5% and about 0.17% in W.B.P. and the reddish-purple Rb(TCNQ) respectively. The volume change in Rb(TCNQ) must considerably smaller than that in W.B.P.

Figure 6 shows the temperature dependence of the electronic absorption spectra of the reddish-purple Rb(TCNQ).

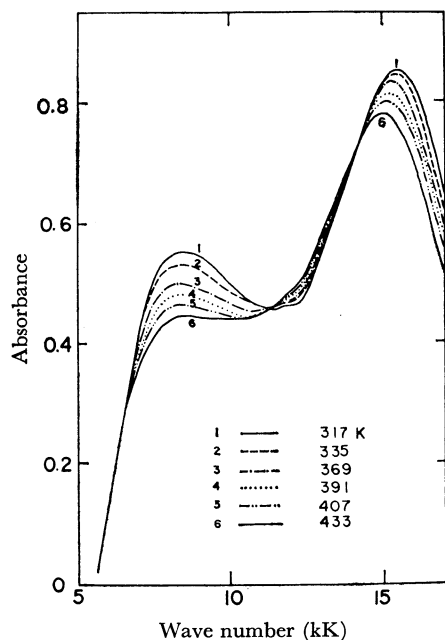


Fig. 6. Temperature dependence of the electronic absorption spectra of reddish-purple Rb(TCNQ).

Figure 7 shows the absorbance of two absorption peaks and the energy of the peak in the higher-energy region as a function of the temperature for the reddish-purple Rb(TCNQ), K(TCNQ), and Na(TCNQ). The absorption spectra of these crystalline TCNQ salts are similar to those of the dimer of the TCNQ anion radical in an aqueous solution.¹⁶⁻¹⁹⁾

It has been reported that the TCNQ units in the reddish-purple Rb(TCNQ) are stacked in a plane-to-

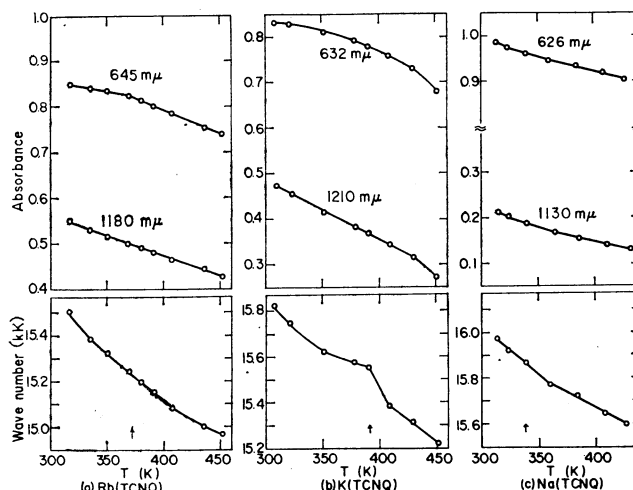


Fig. 7. Absorbance of two absorption peaks and the energy of the peak in the higher energy region as a function of temperature.
(a) reddish-purple Rb(TCNQ) (b) K(TCNQ) (c) Na(TCNQ)

plane manner and that the interplanar spacings of 3.159 and 3.484 Å alternate within a row, and the Rb^+ ions also form rows along the a axis, with alternating distances of 3.483 and 3.726 Å between the ions at -160°C .¹⁴⁾ It is certain that there is a bimolecular association of TCNQ anion radicals in the column in the reddish-purple Rb(TCNQ) crystal. The preliminary structure determination of K(TCNQ) by Anderson and Fritchie²⁰⁾ has shown that the TCNQ anions are stacked plane-to-plane in the column, but it is not certain whether or not there is a bimolecular association of TCNQ anions in the column.

If the phase transition observed in $\text{M}^+(\text{TCNQ})^-$ is similar to that at about 190°K in W.B.P., the mechanism of which has been explained by the dimerization scheme, that is, the presence of dimerized Würster's Blue species at low temperatures,^{12,15,21,22)} it may be expected to occur at the transition point where the absorbance of the charge-transfer absorption band in the near-infrared region changes abruptly, and the peak positions may be expected to shift considerably so that the spectra correspond to those of the TCNQ anion monomer. However, as has been shown in Figs. 6 and 7, the absorbance and the peak energy decrease almost monotonously with an increase in the temperature, and no abrupt change or shift at the transition point was observed except for the small peak shift in K(TCNQ). The spectra seem to be similar to those of the dimer of the TCNQ anion radical above the transition temperature. A little shift of the isosbestic points was observed above and below the transition point.

Although any inequality of interaction between neighboring TCNQ anions in the column would become smaller in the high-temperature phase, the

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16) R. H. Boyd and W. D. Phillips, *ibid.*, **43**, 2927 (1965).

17) Y. Iida, *This Bulletin*, **42**, 71 (1969).

18) N. Sakai, I. Shirota, and S. Minomura, *ibid.*, **43**, 57 (1970).

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22) T. Sakata and S. Nagakura, *Mol. Phys.*, **19**, 321 (1970).

bimolecular association of TCNQ anion radicals seems to be preserved in the high temperature phase in the reddish-purple Rb(TCNQ). The phase transition may be principally the result of the change in the manner of packing between the Rb⁺ ions and the TCNQ⁻ column, because the crystals fractured at the transition point in spite of the slight change in the arrangement of TCNQ anions and the small volume change.

On the other hand, only a slight change in the TCNQ⁻ column would be expected in the case of M⁺(TCNQ)⁻ salts except for the reddish-purple Rb(TCNQ).

B. New Pressure-induced Phase. In M⁺(TCNQ)⁻ salts anomalies in the pressure dependence of resistivity were found at room temperature; they seem to be attributable to the new pressure-induced phase transition. This is analogous with the fact that a number of inorganic substances show anomalies in the electrical resistivity at their pressure-induced phase transition.^{23,24}

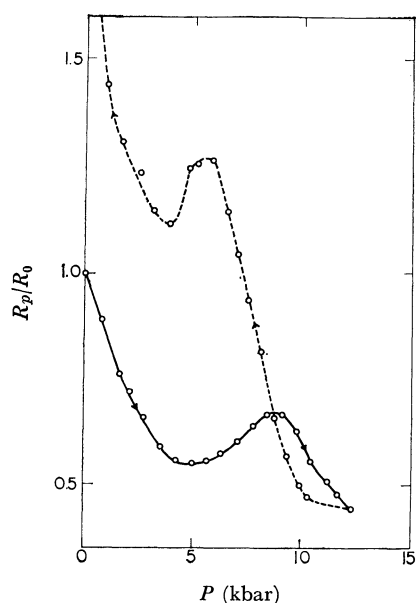


Fig. 8. Relative resistance as a function of pressure at room temperature in the pellet of polycrystalline Li(TCNQ).

Figure 8 shows the relative resistance as a function of the pressure at room temperature in Li(TCNQ). Four high-pressure runs were made on the polycrystalline powder samples pressed into pellets with a pressure of 7 kbar. The main features were identical in all the runs. The resistance decreases up to about 5 kbar, and then it increases, attaining its maximum at about 8.5 kbar and then again decreasing. As the pressure decreases, the minimum and the maximum of resistance shift to about 4 and 5.5 kbar respectively. It is likely that the phase transition occurs around 5 kbar, and that it is complete by about 8 kbar. The phase transition in Li(TCNQ) has not been observed in the temperature range from -150°C to +230°C at

one atmosphere.⁶⁾ Therefore, the transition found here must be a pressure-induced phase transition.

It has been reported that the resistance decreases monotonously under very high pressures in the range from 28 to 170 kbar.²⁵⁾ In that pressure region, the pressure dependence of the resistance in the new high pressure phase seems to be shown.

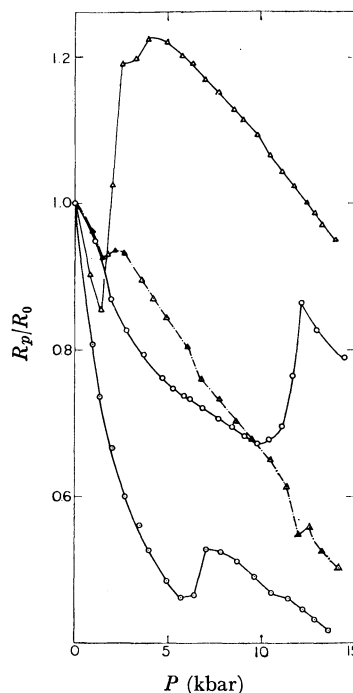


Fig. 9. Relative resistance as a function of pressure at room temperature in several Na(TCNQ) crystals.

—○— and —●—: $\rho_{a//}$, —△— and —▲—: $\rho_{b//}$.

Figure 9 shows the pressure dependence of the relative resistance at room temperature in several Na(TCNQ) crystals. The crystal axis along which the resistance had been measured was assigned on the basis of a preliminary X-ray analysis by Konno *et al.*,²⁶⁾ according to which columns of TCNQ⁻ ions are parallel to the *a* axis. The anomalies in the resistance were found in all the crystals. However, the pressures at which the anomalies were observed were somewhat different from crystal to crystal. Further, the manner of the anomalies varies; for example, some crystals show a discontinuous rise in resistance, while other crystals show only a change in the slope in the curve of the relative resistance *versus* the pressure around the equal pressure. It is likely that the manner of the anomaly differs with different crystal axes. Probably the phase transitions occur about 1.5, 6, and 10–11 kbar.

Figures 10, 11, and 12 show three typical results in eight measurement runs of the pressure dependence of the resistance in K(TCNQ) crystals. The measurements of the resistance were carried out along the needle axis. K(TCNQ) crystals exhibited a strange behavior in the pressure dependence of the resistance.

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25) I. Shirovani, T. Kajiwarra, H. Inokuchi, and S. Akimoto, This Bulletin, **42**, 366 (1969).

26) M. Konno and Y. Saito, private communication.

That is, in spite of all the crystals having a similar outside appearance, some crystals revealed that the resistance increased with an increase in the pressure, while others revealed the reverse. It was also observed in some crystals that the pressure dependency of the resistance in the course of the first increase in pressure was remarkably different from that in the course of the second increase in pressure after the release of the pressure on the same crystal, as has been shown in Fig. 12. The crystals seemed not to be damaged after the second measurement. The anomalies in the resistance were observed around 2, 5, and 9 kbar.

The pressure dependence of the resistance was measured on polycrystalline powder samples of K(TCNQ)

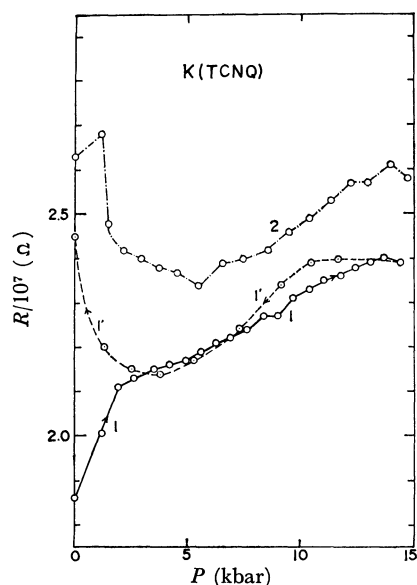


Fig. 10. Resistance as a function of pressure at room temperature in K(TCNQ) crystal A. (1) the first increasing pressure run, (1') release of pressure run, (2) the second increasing pressure run.

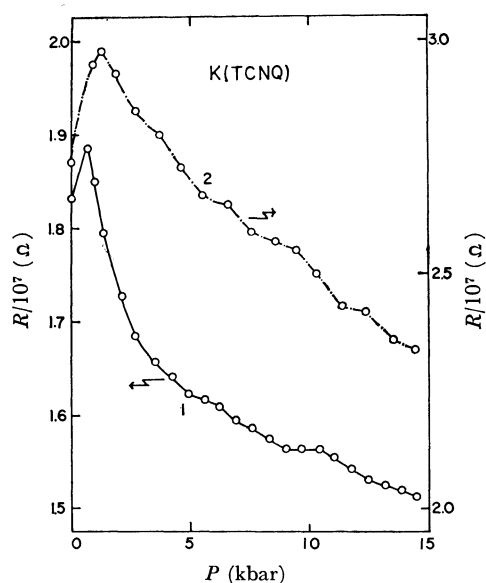


Fig. 11. Resistance as a function of pressure at room temperature in K(TCNQ) crystal B. (1) the first increasing pressure run, (2) the second increasing pressure run.

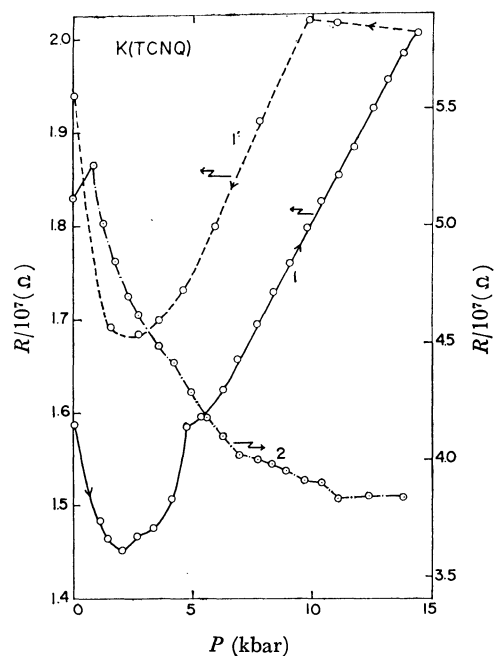


Fig. 12. Resistance as a function of pressure at room temperature in K(TCNQ) crystal C. (1) the first increasing pressure run, (1') release of pressure run, (2) the second increasing pressure run.

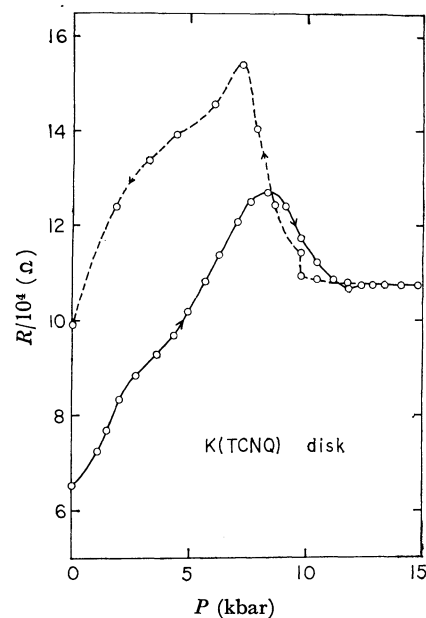


Fig. 13. Resistance as a function of pressure at room temperature in the pellet of polycrystalline K(TCNQ).

pressed into pellets with a pressure of 7 kbar; this was done in order to investigate whether or not the variation in the pressure dependency in crystals was due to the difference in methods of sample preparation; the results are shown in Fig. 13. Four runs were made. The main features were identical in all the runs. The resistance increased up to about 8.2 kbar, and then decreased with an increase in the pressure. The reason for this disagreement in the powder sample and the crystal samples is not clear at present. However, because any imperfection, such as a chemical impurity

or a lattice defect, has an influence on the electrical conduction, it is probable that the slight difference in the imperfection was reflected in the pressure dependence of the resistance. It is possible that each crystal prepared simultaneously by a diffusion process has a different imperfection.

The change in the slope at about 2.2 kbar and the maximum of resistance at about 8.2 kbar in the powder sample seem to correspond to the anomalies around 2 and 5 or 9 kbar respectively observed in the crystal sample. The pressure-induced phase transition must have occurred at those pressures.

Recently, a preliminary experiment was carried out concerning the pressure dependence of the lattice constants of K(TCNQ) by means of X-ray powder diffraction analysis under hydrostatic high pressures.²⁷⁾ No marked changes in the diffraction pattern were observed up to 4.5 kbar. Therefore, the transformation of the crystal structure at those pressure-induced phase transition points, if any, would be very slight.

The effect of a very high pressure on the resistance

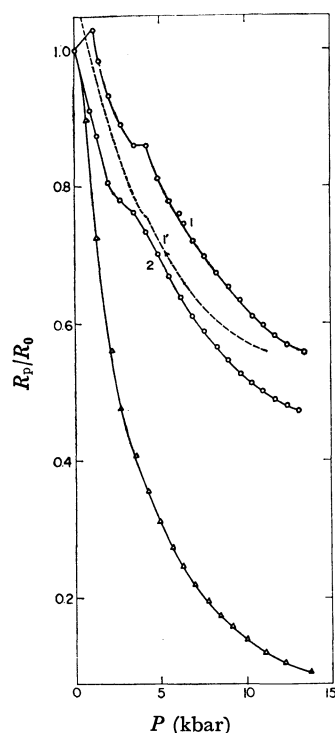


Fig. 14. Relative resistance as a function of pressure at room temperature in Rb(TCNQ).

—○—: reddish-purple crystal (1) the first increasing pressure run, (1') release of pressure run, (2) the second increasing pressure run, —△—: dark purple crystal.

27) M. Yokota, private communication.

of the powder K(TCNQ) has been studied in the pressure region from ~ 20 to ~ 500 kbar, and it has been reported that there is a distinct break in the slope of the resistance-pressure curve at 250–300 kbar.²⁸⁾ However, no explanation for this phenomenon has yet been provided.

Figure 14 shows the pressure dependence of the relative resistance in both the reddish- and dark purple Rb(TCNQ) crystals. The anomalies were found at about 1 and 3.5 kbar, at which the new pressure-induced phase transition occurs, in the reddish-purple Rb(TCNQ). These new pressure-induced phase transition points are written in the phase diagram as has been shown earlier in Fig. 5. More than three phases ($\alpha, \beta, \gamma, \dots$) are considered to exist in the solid phase of Rb(TCNQ); consequently, it is possible that the boundary line shown in Fig. 5 is due to the transition from the new pressure-induced phase to the high-temperature phase in the region of higher pressures. The anomaly at about 1 kbar disappeared in the course of the first release of pressure and the second increase in pressure. In the case of the dark purple Rb(TCNQ), on the other hand, the resistance decreased monotonously with an increase in the pressure, and no anomalies in resistance corresponding to those in the reddish-purple Rb(TCNQ) were observed up to 13.5 kbar. Whether or not the pressure-induced phase transition occurs in the dark purple Rb(TCNQ) is not yet clear.

The effect of pressures up to 7 kbar on the electronic absorption spectra of these $M^+(\text{TCNQ})^-$ salts has been studied.¹⁸⁾ No marked change in the absorption spectra has been observed in the pressure region above and below the transition pressure found here.

For the present, the nature of the new pressure-induced phase transition found in $M^+(\text{TCNQ})^-$ salts is not known. The TCNQ ions are arranged with some periodicity in the column in the TCNQ^- anion radical salts. It would be expected that the phase transition arises from a change in the periodicity in the TCNQ^- column. Even a slight change in the external condition would affect the stabilization of the crystal lattice in the ion radical salts because of the complicated molecular interaction in them. The phenomena of the presence of numerous modifications over a wide region of pressure and temperature would appear to be rather general in the ion-radical salts.

The authors would like to thank Miss Michiko Konno for performing the X-ray diffraction experiment.

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