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# Electrical Conduction in TCNQ Anion Radical Salts

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The temperature dependence of the electrical resistivity of single crystals of TCNQ anion radical salts with alkali metal, quinolinium, and triethylammonium cations has been investigated at temperatures between 300 and 540°K. It has been observed in these salts that the activation energy increases in the region of higher temperatures. In the cases of Na- and K(TCNQ) crystals, the reversal of the sign of the thermo-e.m.f. from the *p*-type to the *n*-type has been observed around the temperatures at which the activation energy increases. An interpretation of the experimental results is presented.

The salts based on the anion-radical of 7,7,8,8-tetracyanoquinodimethane (TCNQ) exhibit room-temperature electrical conductivities ranging from $10^2$ to about $10^{-5}\ \Omega^{-1}\cdot\text{cm}^{-1}$.[1-3] The magnitude of the electrical conductivities depends strongly on the nature of the cation. For example, the salts with metal cations generally show low to intermediate conductivities ($10^{-5}$—$10^{-2}\ \Omega^{-1}\cdot\text{cm}^{-1}$), while the salts with cations of planar aromatic heterocyclic molecules show high conductivities ($\sim 10^2\ \Omega^{-1}\cdot\text{cm}^{-1}$). It has been reported that several TCNQ salts with aromatic cations show metallic behavior of temperature-independent conductivities as high as $10^2\ \Omega^{-1}\cdot\text{cm}^{-1}$ and temperature-independent paramagnetic susceptibilities which can

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1) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

2) J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).

3) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).

be interpreted by assuming that the charge carriers are degenerate, as in a metal.[2,4] Recently, it has been found, contrary to the results of Kepler, that the highly conductive salts behave as typical semiconductors; that is, they have an electrical conductivity and a magnetic susceptibility which depend slightly on the temperature, and also absorption edge at about 40 cm$^{-1}$.[5] The electrical conduction mechanism of these TCNQ$^-$ anion radical salts has subsequently been discussed by several authors.[5–12] On the other hand, only a few studies have been made in connection with the electrical conduction in less conductive simple salts with metal cations.[13,14] The mechanism of electrical conduction in the TCNQ$^-$ anion radical salts seems to be yet unclear in spite of many investigations.

It has been suggested in another paper[15] that the electrical conduction near room temperature in alkali metal cation-TCNQ anion radical simple salts may be due to such extrinsic properties as impurities or defects. This suggestion is based on the scattered values of the activation energy and the pressure coefficient of resistivity from crystal to crystal. In this paper, electrical measurements in the high-temperature region will be reported in more detail.

## Experimental

Crystals of alkali metal cation-TCNQ anion radical salts were prepared by the method described in Ref. 15. Crystals of quinolinium(TCNQ)$_2$[Q(TCNQ)$_2$] and triethylammonium(TCNQ)$_2$[TEA(TCNQ)$_2$] which had been synthesized according to the method developed by the du Pont group[1] were provided by Kondow.

The electrical measurement was made along the needle axis in most crystals by the potential-drop method, with two electrode probes in about $10^{-2}$ Torr. Electrical contacts to the crystal were made with du Pont ♯4817 silver paste.

A qualitative analysis of the Seebeck effect was carried out in the following manner. Some temperature difference was created during a short time between two junction to the needle crystal, one end of which was fixed vertically on the alumina base connected to a heater. The thermo-e.m.f. appeared transiently in the absence of an applied voltage between the two junctions, the sign of the cold junction being the sign of the Seebeck coefficient.

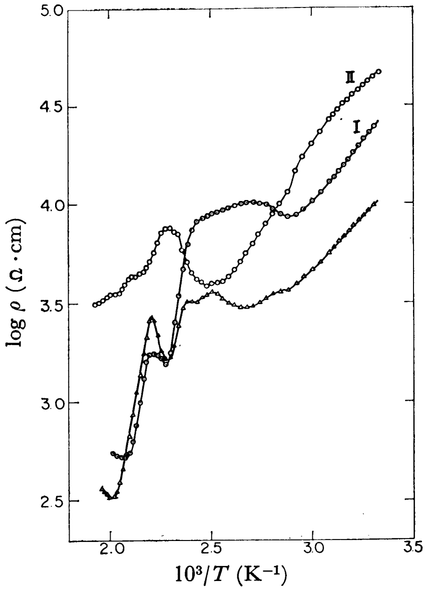

Fig. 1. Electrical resistivity as a function of reciprocal temperature of two Na(TCNQ) crystals. Two thermal cycles for one crystal are shown as Roman numerals I and II.

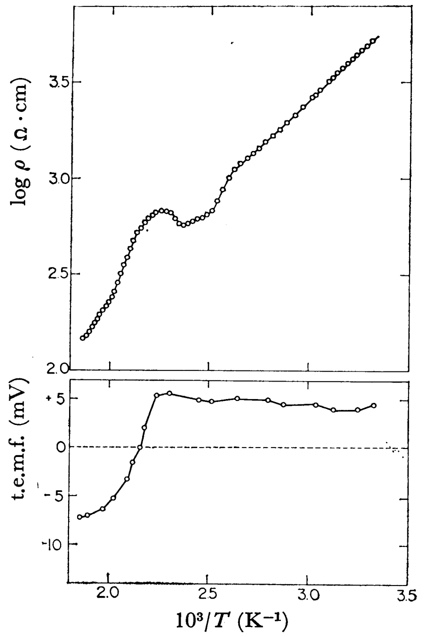

Fig. 2. Electrical resistivity and thermo-e.m.f. as a function of reciprocal temperature of Na(TCNQ).

## Results

Figure 1 shows the electrical resistivity as a function of the reciprocal temperature of two Na (TCNQ) crystals. Two thermal cycles for one crystals are shown by the Roman numerals I and II. Figure 2 shows the electrical resistivity and the thermo-e.m.f. as a function of the reciprocal temperature of the Na (TCNQ) crystal measured at the same time. Only the sign of thermo-e.m.f. can be significant because of the qualitative measurement. The positive thermo-e.m.f. corre-

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4) R. G. Kepler, *J. Chem. Phys.*, **39**, 3528 (1963).

5) T. Kondow, K. Siratori, and H. Inokuchi, *J. Phys. Soc. Japan*, **23**, 98 (1967).

6) K. Siratori and T. Kondow, *ibid.*, **27**, 301 (1969).

7) I. F. Shchegolev, L. I. Buravov, A. V. Zvarykina, and R. B. Lyubovskii, *ZhETF Pis. Red.*, **8**, 353 (1968) [*JETP Lett.*, **8**, 218 (1968)].

8) L. I. Buravov, D. N. Fedutin, and I. F. Shchegolev, *Zh. Eksp. Teor. Fiz.*, **59**, 1125 (1970) [*Sov. Phys. JETP*, **32**, 612 (1971)].

9) E. Menefee and Y. H. Pao, *J. Chem. Phys.*, **36**, 3472 (1962).

10) O. H. LeBlanc, Jr., *ibid.*, **42**, 4307 (1965).

11) I. Shirotani, T. Kajiwara, H. Inokuchi, and S. Akimoto, This Bulletin, **42**, 366 (1969).

12) J. P. Farges, A. Brau, D. Vasilescu, P. Dupuis, and J. Néel, *Phys. Stat. Sol.*, **37**, 745 (1970).

13) R. M. Vlasova, T. I. Grishaeva, L. D. Rozenshtein, A. I. Sherle, and A. A. Berlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 3, 659 (1968).

14) R. M. Vlasova, A. I. Gutman, V. V. Kuzina, and A. I. Sherle, *Fiz. Tverd. Tela*, **12**, 3654 (1970) [*Sov. Phys. Solid State*, **12**, 2979 (1971)].

15) N. Sakai, I. Shirotani, and S. Minomura, This Bulletin **45**, 3321 (1972).

sponds to the positive carrier, *p*-type. The behavior of these curves is very complicated. The minimum and the maximum points in the resistivity and an increase in the activation energy were observed in the high-temperature region, above 400°K. The electrical resistivity, $\rho$, and the activation energy, $E$, obtained from the expression: $\rho=\rho_0\exp(E/kT)$ varied from crystal to crystal. The activation energy of Na (TCNQ) is between 0.23 and 0.32 eV near room temperature and between 0.6 and 1.1 eV in the high-temperature region. The sign of the thermo-e.m.f. is reversed from the *p*-type to the *n*-type above the temperature around which the activation energy increases.

Figures 3 and 4 show similar data for several specimens of K(TCNQ) crystal. The minimum and the maximum points in the resistivity, an increase in the activation energy, and the reversal of the sign of the thermo-e.m.f. from the *p*-type to the *n*-type were observed in the higher-temperature region, passing through the phase-transition point similarly to the case of Na(TCNQ). The activation energy of K-(TCNQ) is between 0.15 and 0.45 eV in the lower-temperature region and between 0.4 and 0.6 eV in the high-temperature region. The temperature at which the sign of the thermo-e.m.f. was reversed fell remarkably upon the second thermal cycling in the measurement of the same specimen.

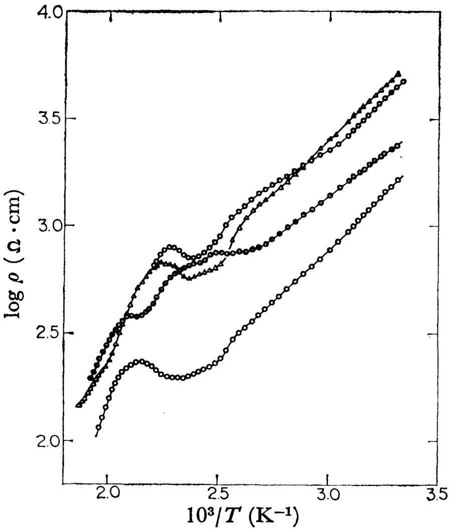

Fig. 3. Electrical resistivity as a function of reciprocal temperature of several K(TCNQ) crystals.

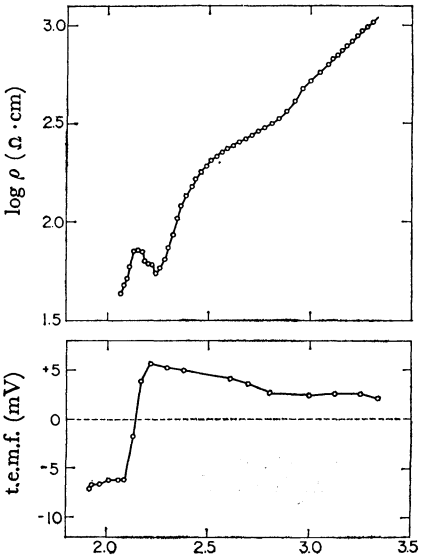

Fig. 4. Electrical resistivity and thermo-e.m.f. as a function of reciprocal temperature of K(TCNQ).

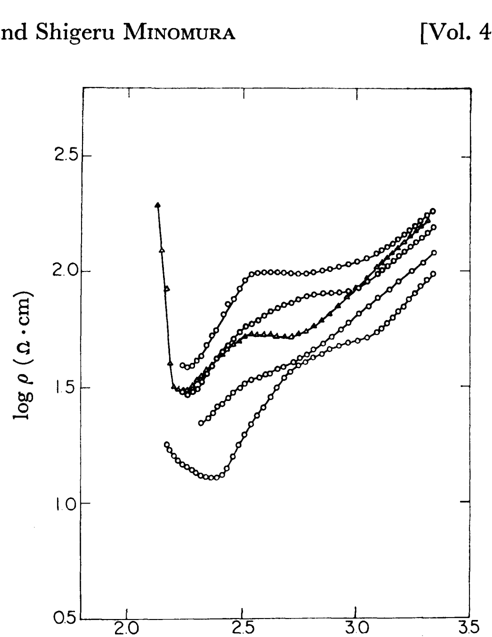

Fig. 5. Electrical resistivity as a function of reciprocal temperature of several dark purple Rb(TCNQ) crystals.

Figure 5 shows the temperature dependence of the resistivity in several specimens of dark purple Rb-(TCNQ) crystals. The activation energy was observed to depend on the temperature, and to increase in the higher-temperature region, similarly to the cases of Na(TCNQ) and K(TCNQ). However, the reversal of the sign of the thermo-e.m.f. was not observed. The sign is positive, *p*-type, over all the temperature range measured. The activation energy of dark purple Rb-(TCNQ) is between 0.16 and 0.22 eV near room temperature and between 0.22 and 0.4 eV in the high-temperature region. The abrupt increase in the resistivity at high temperatures is due to the decomposition of this salt. On the other hand, the dark purple Rb(TCNQ) crystal in the form of a prism obtained from the same batch reveals a temperature dependence of the resistivity different from the above-exhibited results on that in the form of needle, as is shown in Fig. 6. The relation of log $\rho$ *versus* the reciprocal temperature is not linear over the temperature range measured, and it is monotonous, without any discontinuity in activation energy, at high temperatures. The resistivity and the activation energy at room temperature of dark purple Rb(TCNQ) prisms ($\rho_{25}\sim10^4$ $\Omega\cdot$cm and $E\sim0.34$ eV) are larger than those of needles ($\rho_{25}\sim10^2$ $\Omega\cdot$cm and $E\sim0.16$ eV). It has not yet been investigated whether or not the two kinds of dark purple Rb(TCNQ) have an identical crystal structure.

Polymorphism has been shown in Rb(TCNQ) crystals.[16] The reddish-purple Rb(TCNQ) crystal with a crystal structure different from that of the dark purple Rb(TCNQ) crystal shows a larger resistivity

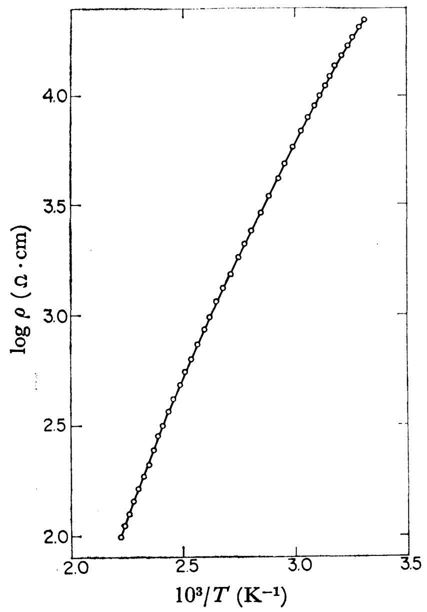

Fig. 6. Temperature depencence of the resistivity for dark purple Rb(TCNQ) with the form of prism.

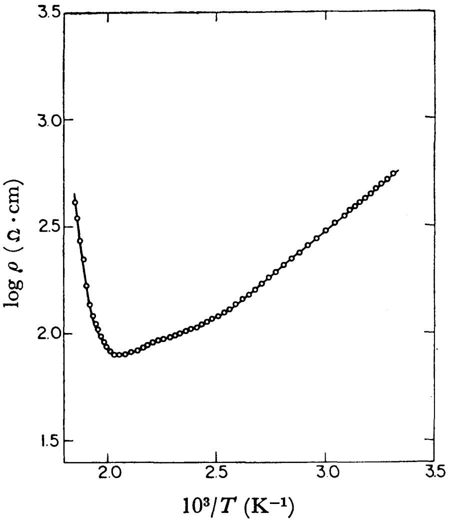

Fig. 7. Temperature dependence of the resistivity for Cs(TCNQ) crystal.

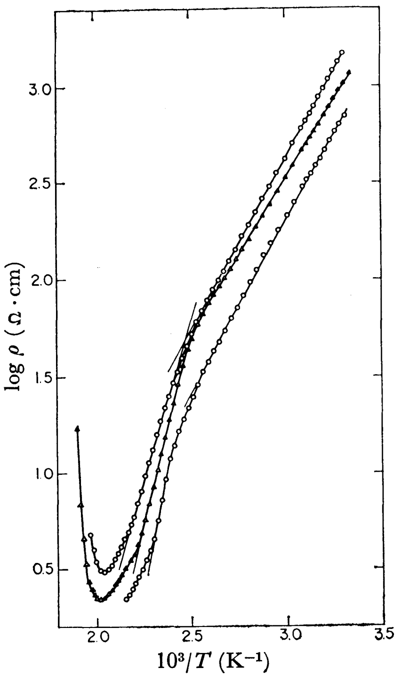

Fig. 8. Electrical resistivity as a function of reciprocal temperature of three $Cs_2(TCNQ)_3$ crystals.

and activation energy than those of the dark purple Rb(TCNQ) crystal ($\rho_{25} \sim 10^5\,\Omega\cdot$cm and $E \sim 0.51$ eV). Since most of the reddish-purple Rb(TCNQ) crystals broke down at the phase transition point of 374°K, accurate measurements could not be made in the higher-temperature region. The thermo-e.m.f. shows a positive sign below the phase-transition temperature.

Figure 7 shows the temperature dependence of the resistivity of the Cs(TCNQ) crystal. The outside appearance of this salt resembles that of the dark purple needles Rb(TCNQ). The resistivity changes almost monotonously with the temperature. The abrupt increase in the resistivity at high temperature is due to the decomposition of the compound. The resistivity at room temperature is about $6\times10^2\,\Omega\cdot$cm. The activation energy is about 0.16 eV in the region from room temperature to about 400°K. The sign of the thermo-e.m.f. is positive over the temperature range measured.

Moreover, the temperature dependence of the resistivity of some salts of the $M^+(TCNQ)_n^-$ type with a value of $n$ higher than one was measured in order to investigate the electrical conduction mechanism in connection with the case of alkali metal cation-TCNQ anion simple salts. Figure 8 shows the resistivity as a function of the reciprocal temperature of three specimens of $Cs_2(TCNQ)_3$ crystals. The discontinuity in the activation energy was observed in the high-temperature region. In one specimen the discontinuity in the activation energy occurred at about 397°K, below and above which the activation energies were 0.32 and 0.78 eV respectively. The sign of the thermo-e.m.f. is negative over the temperature range measured. The abrupt increase in the resistivity at high-tempera-

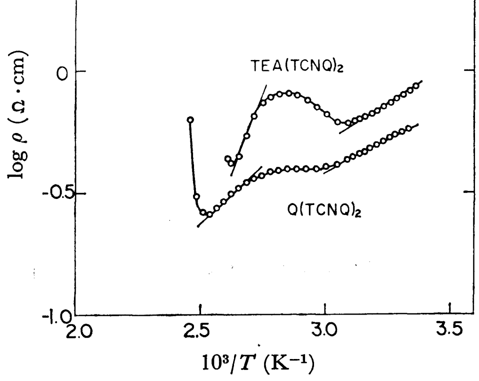

Fig. 9. Electrical resistivity as a function of reciprocal temperature of $Q(TCNQ)_2$ and $TEA(TCNQ)_2$ crystals.

TABLE 1. SEMICONDUCTIVITY DATA OF SEVERAL TCNQ ANION RADICAL SALTS

| | Present work | | | Previous work (Ref. 2) | |
|---|---|---|---|---|---|
| Compound | Resistivity at 25°C (Ω·cm) | Low temp. activation energy (eV) | High temp. activation energy (eV) | Resistivity at 23°C (Ω·cm) | Activation energy (eV) |
| Na(TCNQ) | $\sim1\times10^{3}$ (//) | 0.23—0.32 | 0.6—1.1 | $1\times10^{5}$ (powder) | 0.33 |
| | $\sim3\times10^{4}$ (⊥) | | | | |
| K(TCNQ) | $\sim5\times10^{3}$ (//) | 0.15—0.45 | 0.4—0.6 | $1\times10^{4}$ (powder) | 0.35 |
| | $\sim2\times10^{5}$ (⊥) | | | | |
| Rb(TCNQ) | | | | | |
| reddish purple | $\sim3\times10^{5}$ (//) | 0.44—0.53 | | | |
| | $\sim3\times10^{6}$ (⊥) | | | | |
| dark purple | $\sim1\times10^{2}$ (//) | 0.16—0.22 | 0.22—0.4 | | |
| Cs(TCNQ) | $\sim6\times10^{2}$ (//) | ~0.16 | | $3\times10^{3}$ (powder) | 0.18 |
| $Cs_2(TCNQ)_3$ | $\sim5\times10_{2}$ (//) | 0.32—0.35 | 0.68—0.78 | $1\times10^{3}$ (//) | 0.30 |
| | | | | $2.5\times10^{4}$ | |
| | | | | $2.5\times10^{4}$ | |
| TEA $(TCNQ)_2$ | 1 (//) | 0.13 | 0.56 | $2.5\times10^{-1}$ (//) | 0.14 |
| | | | | $2.5\times10$ | |
| | | | | $1\times10^{3}$ | |
| $Q(TCNQ)_2$ | $1\times10^{-1}$ (⊥) | 0.10 | 0.18 | $1\times10^{-2}$ (//) | 0.03 |

(//): parallel to needle. (⊥): perpendicular to needle.

tures is due to the decomposition of the compound.

Figure 9 shows the resistivity as a function of the reciprocal temperature of the $Q(TCNQ)_2$ and TEA-$(TCNQ)_2$ crystals. It was measured perpendicularly to the needle in the single crystal of $Q(TCNQ)_2$. An anomaly in resistivity was also observed in these complex salts. The activation energy near room temperature is about 0.10 eV, and the activation energy in the narrow temperature region from about 370°K to the decomposition temperature of about 395°K is about 0.18 eV, in the case of the $Q(TCNQ)_2$ crystal. The room-temperature resistivity and the activation energy measured here are larger than those generally reported.[1,2,8,25] It should be noted that the temperature dependence of the conductivity is markedly different from those in the direction of the needle reported in Ref. 8 and 25. The room-temperature resistivity and the activation energy of the TEA$(TCNQ)_2$ crystal along the needle axis are about 1.0 Ω·cm and about 0.13 eV respectively. Also in this crystal, the narrow temperature region where the resistivity decreased with an increase in the temperature with the activation energy of about 0.56 eV was observed before the decomposition occured. No qualitative measurement of the thermo-e.m.f. was carried out. At present, the electrical measurement are not sufficient.

The semiconductivity data of several TCNQ anion radical salts are summarized in Table 1, along with data generally reported.

## Discussion

The experimental results described above, particularly the observation of the changes in the sign of the thermo-e.m.f. as a function of the temperature and in the activation energy on Na(TCNQ) and K(TCNQ) crystals, suggest that two carrier effects play important roles in the electrical-conduction process in the crystals of the alkali metal cation-TCNQ anion radical simple salts treated in this work. Alkali metal cation-TCNQ anion radical simple salts are considered to be extrinsic semiconductors in the low-temperature region. This has been expected from the scattered values of the activation energy near room temperature and those of the pressure coefficient of resistivity from crystal to crystal.[15] It was observed that some crystals of K(TCNQ) revealed a resistance increasing with an increase in the pressure, while some revealed the reverse. It has also been reported that the pressure coefficients of the ionization energies of impurities in silicon and germanium vary considerably with the kind of impurity.[17] The simplest scheme of energy levels in the *p*-type extrinsic semiconductors contains an acceptor level. Oxygen may act as an acceptor impurity in alkali metal cation-TCNQ simple salts.

The ionic conduction, on the other hand, may be expected to contribute to the electrical conductivity in these salts. That is, alkali cations may be supposed to move in crystals of these TCNQ salts through lattice defects, such as Frenkel or Schottky defects, and vacancies created by the impurity of divalent metal cations substituted for monovalent alkali metal cations, which are well-known in ionic crystals.[18] The ionic conductivity is known to decrease with an increase in the pressure.[19]

The observed conductivities in alkali metal cation-TCNQ anion radical simple salts were off Ohm's law from the low-electric field; for example, they were off about 40 volts/cm in the K(TCNQ) crystal, and at

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16) I. Shirotani, H. Kobayashi, N. Sakai, and Y. Saito, to be published.

17) W. Paul and D. M. Warschauer, "Solids under Pressure," McGraw-Hill, New York (1963), p. 220.

18) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," 2nd ed. Oxford Univ. Press., Oxford (1948).

19) S. W. Kurnick, *J. Chem. Phys.*, **20**, 218 (1952).

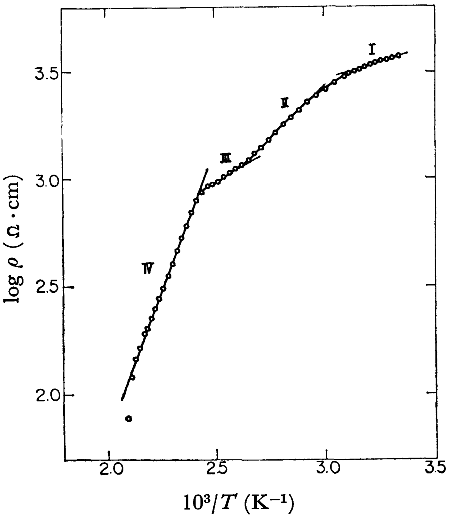

Fig. 10. Temperature dependence of the resistivity for K(TCNQ) crystal containing $Ba^{2+}$ ions of about 0.5 atom%.

higher fields the current increased more than linearly. The negative pressure coefficient of the conductivity, $d\sigma/dP<0$, was observed in some specimens of the K(TCNQ) crystal.[15] These experimental observations seem to show that the contribution of the ionic conduction to the electrical conduction is not negligible. The temperature dependence of the resistvity was measured on the crystal of K(TCNQ) containing $Ba^{2+}$ ions. Since the ionic radius of the $Ba^{2+}$ ion (1.36 Å) is almost equivalent to that of the $K^+$ ion (1.33 Å), it is expected that the vacancies of the $K^+$ ion are added in crystal by the substitution of $Ba^{2+}$ ions for the lattice points of $K^+$ ions. The samples were prepared by the use of a mixture of KI and $BaI_2$ as the cation source. The electrical resistivity as a function of the reciprocal temperature for the K(TCNQ) crystal containing $Ba^{2+}$ ions of about 0.5 atom% is shown in Fig. 10. As is shown in this crystal, the curves of log ρ *versus* $1/T$ for K(TCNQ) crystals containing $Ba^{2+}$ ions seem to consist of four parts, each with a different activation energy. The activation energy near room temperature, which was about 0.08 eV in the case of the sample shown in Fig. 10, was observed to be dependent on the concentration of $Ba^{2+}$ ions; that is, it decreases with an increase in the concentration of $Ba^{2+}$ ions. The ionic conduction may play some part in the electrical conduction in the narrow temperature region near room temperature in the K(TCNQ) crystal. Though the minimum and the maximum points in the resistivity were not observed in crystals of K(TCNQ) containing $Ba^{2+}$ ions, an increase in the activation energy and a change in the sign of the thermo-e.m.f. were observed in the high-temperature region. The high-temperature region, where the activation energy is larger than in the lower temperature region and where the sings of the carriers are negative, seems to be the intrinsic region of the electrical conduction.

It is reasonable that, in the case of $TCNQ^-$ anion radical salts, the electrical conductivity in the intrinsic region arises from the motion of the odd π electrons among the TCNQ sites. LeBlanc[10] has proposed a model in which the odd electrons are localized and occupy highly-ordered positions so as to minimize their mutual Coulomb repulsions in non-conducting states and conducting states arise from the introduction of defects into the ordered ground-state configuration. According to this model, for the smiple salt an odd electron is removed from one $TCNQ^-$, leaving a $TCNQ^0$, and added to a distant $TCNQ^-$ to give a $TCNQ^{2-}$. The "electron" ($TCNQ^{2-}$) and "hole" ($TCNQ^0$), which are independently mobile, can occupy states in a band with the width $\Delta$. The activation energy for conductivity, $E$, is given as:

$$2E = C - \Delta$$

where $C$ is an increase in the electrostatic energy by the formation of $TCNQ^0$ and $TCNQ^{2-}$.

The above mechanism may also be applied to the dark purple Rb(TCNQ) crystal, where the $TCNQ^-$ anions pack in a columnar manner with an equivalent interplanar spacing of 3.28 Å at room temperature.[16] In this salt, the absorption band at 6.5 kK, as is shown in Fig. 11, can be assigned to the charge-transfer band between the $TCNQ^-$ anions, which is located in a lower energy region than that of reddish-purple Rb(TCNQ) at 8.6 kK. In the case of the dark purple Rb(TCNQ), the charge-transfer band can be expected to participate in the intrinsic electrical conduction with, for example, the charge-transfer excited state being the conducting state.

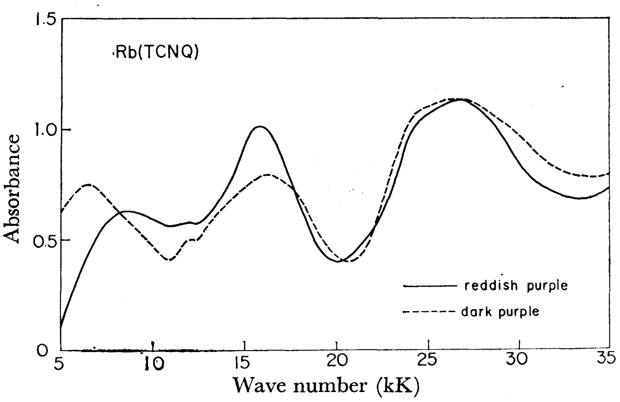

Fig. 11. Electronic absorption spectra of reddish and dark purple Rb(TCNQ).

On the other hand, it has been reported that the TCNQ units in reddish-purple Rb(TCNQ) are stacked in a columnar manner, with alternate interplanar spacings of 3.159 and 3.484 Å at −160°C.[20] It is certain that there is a bimolecular association of TCNQ anion radicals in the column. Although the crystal structures of Na(TCNQ) and K(TCNQ) have not been reported in detail, these salts seem to have a crystal structure similar to that of reddish-purple Rb(TCNQ). It may be considered that the crystalline state of these alkali metal cation-TCNQ anion radical salts is made out of "quasi-molecules" of $(TCNQ)_2^{2-}$, and that the charge-transfer band (Na-(TCNQ): 8.6 kK, K(TCNQ): 8.3 kK) is characteristic

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[20] A. Hoekstra, T. Spoelder, and A. Vos, *Acta Crystallogr.*, *B*, **28**, 14 (1972).

of the intra-quasi-molecular excitation process, in which the electrons are localized in the quasi-molecules. If this is plausible, charge carriers in the intrinsic electrical conduction seem to be produced by the following reaction, in which the electronic state represented is separated by a great distance in the crystal:

$$(\mathrm{TCNQ})_2{}^{2-} + (\mathrm{TCNQ})_2{}^{2-} \rightleftarrows (\mathrm{TCNQ})_2{}^{-} + (\mathrm{TCNQ})_2{}^{3-}.$$

The energy for the charge transfer in the above reaction would be larger than the energy of charge-transfer band around 8 kK.

It has been reported that the TCNQ molecules are arranged with repeating units of three molecules and four molecules in $\mathrm{Cs_2(TCNQ)_3}$ and $\mathrm{TEA(TCNQ)_2}$ respectively, and that an odd $\pi$ electron is localized at the definite TCNQ molecular site.[21,22] It is expected for $\mathrm{Cs_2(TCNQ)_3}$ that the charge transfer will occur between the adjacent pair of $\mathrm{TCNQ^0}$ and $\mathrm{TCNQ^-}$ and between the adjacent $\mathrm{TCNQ^-}$ ions. The absorption bands around 11.7 kK (1.4 eV) and $<$5 kK (0.6 eV) may be assigned to the charge-transfer band between $\mathrm{TCNQ^-}$ ions and to that between $\mathrm{TCNQ^0}$ and $\mathrm{TCNQ^-}$.[23,24] The activation energy for the electrical conduction of about 0.3 eV below 400°K and that of about 0.7 eV above 400°K seem to be related to the charge-transfer band between $\mathrm{TCNQ^-}$ ions and that between $\mathrm{TCNQ^0}$ and $\mathrm{TCNQ^-}$ respectively. This inference would mean that the discontinuity of activation energy in $\mathrm{Cs_2(TCNQ)_3}$ is due to the existence of different conducting states rather than to the existence of an extrinsic electrical conduction arising from impurities or defects. An analogous mechanism may be considered also for other complex TCNQ salts. However, at the present time, the experimental data are not sufficient for us to examine the explanation presented here.

Recently, Farges *et al.* have reported a successful measurement of the Hall effect in single crystals of $\mathrm{TEA(TCNQ)_2}$ at room temperature.[12] From the experimental results of the positive Hall constant and Seebeck coefficient along the *a*-axis, and of the negative Seebeck coefficient along the *c*-axis of highest conductivity, it has been reported that two-carrier effects play a role in the conduction process in $\mathrm{TEA(TCNQ)_2}$. Furthermore, the small activation energy of 0.065 eV calculated from the expression $\rho=\rho_0\exp(E/kT)$ has been reported in the case of samples with evaporated silver contacts. This value of the activation energy is much smaller than the generally-reported values and the value obtained in the present work. Farges *et al.* have also described the introduction of impurities which act as acceptros in their samples.

In the present work, the increase in the activation energy was observed in the higher temperature region for single crystals of $\mathrm{TEA(TCNQ)_2}$ and $\mathrm{Q(TCNQ)_2}$. This also suggests that the high electrical conductivity of these salts is due to the impurity conduction.

Further work is required to make clear the electrical properties in TCNQ anion radical salts. The anisotropy in electrical conductivity and the effect of the pressure on the conductivity in the single crystal of $\mathrm{Q(TCNQ)_2}$ will then be investigated in turn.

The authors would like to thank Dr. Tamotsu Kondow for supplying the samples.

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21) C. J. Fritchie, Jr. and P. Arthur, Jr., *Acta Crystallogr.*, **21**, 139 (1966).

22) H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, *ibid.*, *B*, **26**, 459 (1970).

23) Y. Iida, This Bulletin, **42**, 637 (1969).

24) S. Hiroma, H. Kuroda, and H. Akamatu, *ibid.*, **44**, 9 (1971).

25) V. Walatka, Jr. and J. H. Perlstein, *Molecular Crystals and Liquid Crystals*, **15**, 269 (1971).