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Redetermination of the Crystal Structure and the Electrical Resistivity of Rb-TCNQ-II

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The crystal structure of Rb–TCNQ-II was redetermined. The interplanar distance between the neighbouring TCNQ's is 3.25 Å, which is almost equal to those of highly conducting TCNQ salts. The electrical resistivity and the structure of the TCNQ columns suggest that the complete charge transfer in Rb–TCNQ-II makes this crystal low-conducting. The activation energy of the electrical conduction indicates that the dimerization gap appears below the monomer-dimer transition temperature. The temperature dependence of the electrical resistivities of Rb_2TCNQ_3 is also described.

Among the quasi-one-dimensional molecular crystals known at present, alkali metal salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) are of particular interest because of the simplicity of their crystal and electronic structures.1) The crystal of Rb–TCNQ shows polymorphism. The crystal structure of Rb–TCNQ-II was reported eight years ago.2) However, the recent studies of the crystal structures and the physical properties of alkali–TCNQ suggest that the reported interplanar distance of the TCNQ's of 3.43 Å in Rb–TCNQ-II is too long. Since the intensity data used in the previous work was not considered to be accurate enough,3) the structure was redetermined on the basis of the newly collected intensity data.

Experimental

The crystals were prepared by a diffusion process of RbI and TCNQ in acetonitrile. All the crystals examined were twinned. The lattice constants were determined by means of a Rigaku automated four-circle diffractometer. The crystal data are:4) $Rb^+(C_{12}H_4N_4)^-$, F.W.=289.6, triclinic, $a=9.907(2)$, $b=7.180(2)$, $c=3.886(1)$ Å, $\alpha=88.55(2)$. $\beta=86.86(2)$, $\gamma=94.41(2)°$, $U=273.6(1)$ Å^3, $d_c=1.757$ g cm^{-3}, $Z=1$, space group $P\bar{1}$, $F(000)=141$, μ(Mo $K\alpha$)=45.5 cm^{-1}. The intensity data were collected with monochromated Mo $K\alpha$ radiation up to $2\theta=60°$. The crystal used had approximate dimensions of $0.3\times0.23\times0.07$ mm^3. Of the 1718 accessible reflections, 1240 significant reflections were obtained ($|F_o|>3\sigma(|F_o|)$).

Starting with the positional parameters previously obtained,2) the structure was refined by the block-diagonal least-squares method. Since the twin ratio was not known, the scale factors of $|F(hkl)|$ were determined as: $S(l)\sum_{kh}|F_o(hkl)|=\sum_{kh}|F_c(hkl)|$, where $S(l)$ is the scale factor of the l-th layer ($l=0, 1, 2, 3, 4, 5$) and where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes respectively. The full-matrix least-squares refinement gave the following scale factors: $S(0)=0.846/\sqrt{2}$, $S(l)=0.998$—1.002 ($l=1, 2, 3, 4, 5$). The final R value was 0.059. The weighting scheme was: $w=1/[a+b|F_o|+c|F_c|^2]$ for $|F_o|\geqq5.6$ (absolute scale), $a=11.20$, $b=1.00$, $c=0.033$; $w=0.1$ otherwise. The atomic coordinates are listed in Table 1.†

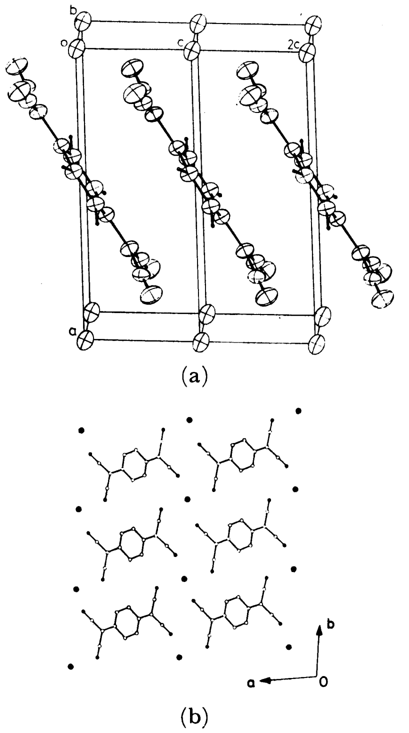
TABLE 1. THE FINAL ATOMIC COORDINATES
The values for fractional coordinates are multipied by 10^4.

Atom	x	y	z	B_{eq}/Å^2 a)
Rb	0000	0000	0000	2.08
N(1)	9073(8)	6878(8)	5413(16)	3.43
N(2)	7633(7)	885(8)	5622(17)	3.80
C(1)	6137(6)	4621(7)	1871(14)	2.13
C(2)	5967(6)	6484(7)	838(15)	2.26
C(3)	5106(6)	3153(7)	977(15)	2.26
C(4)	7248(6)	4226(7)	3808(15)	2.34
C(5)	8265(6)	5693(8)	4675(15)	2.34
C(6)	7442(6)	2390(8)	4817(17)	2.48

a) Equivalent isotropic temperature factor as defined by H. C. Hamilton (*Acta Crystallogr.*, **12**, 609(1959)).

Results and Discussion

Figure 1 shows the crystal structure. The TCNQ's stack along the c axis to form monadic columns. There



(a)

(b)

Fig. 1. (a) The crystal structure of Rb–TCNQ-II. (b) The molecular arrangement.

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† List of the observed and calculated structure factors and tables of anisotropic thermal parameters for non-hydrogen atoms and atomic parameters for hydrogen atoms are kept at the Chemical Society of Japan as Document No. 8152.

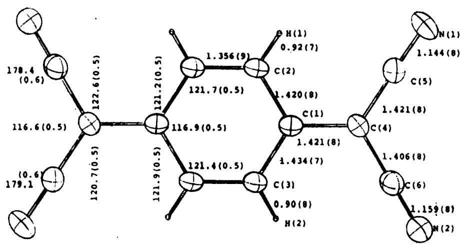

Fig. 2. The bond lengths and the bond angles of TCNQ with the standard deviations in parentheses.

are eight short contacts between Rb and the surrounding nitrogen atoms (≦3.27 Å). The shortest Rb···N distance is 3.052 Å. The bond lengths and the bond angles are shown in Fig. 2. The bond lengths agree well with those of the TCNQ anion[5] but significantly differ from those of neutral TCNQ:[6] the length of the C(1)–C(4) bond is 0.047 Å longer than the corresponding bond length of the neutral TCNQ molecule. The least-squares plane through TCNQ is: $-0.4973(X-0.5a)+0.1828(Y-0.5b)+0.8340Z=0.0$, where X, Y, and Z(Å) are the coordinates referred to the crystal axes a, b, and c respectively. The interplanar distance between adjacent TCNQ's of 3.248 Å is the shortest in alkali–TCNQ salts and almost equal to those of highly conducting salts: Na–TCNQ, 3.39 (80 °C);[7] K–TCNQ, 3.48 (120 °C);[8] NH_4–TCNQ, 3.31;[9] *N*-methylphenazinium–TCNQ (NMP–TCNQ), 3.25;[10] hexamethylenetetrathiafulvalene (2-(5,6-dihydro-4*H*-cyclopenta-1,3-dithiole-2-ylidene)-5,6-dihydro-4*H*-cyclopenta-1,3-dithiole)–TCNQ (HMTTF–TCNQ), 3.25;[11] quinolinium–TCNQ, 3.22;[12] acridinium–TCNQ, 3.26 Å.[13] As described in Ref. 2, the mode of overlap of TCNQ is of the "ring-external bond type" (see Fig. 3), which is found in every highly conductive TCNQ salts.[14]

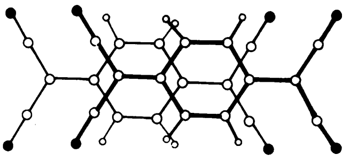

Fig. 3. The ring-external bond type overlapping in Rb–TCNQ-II.

Electrical Resistivities. The d.c. electrical resistivities of Rb–TCNQ-II were measured along the c-axis by the four-probe method (see Fig. 4). The room-temperature resistivity of 50 Ωcm is much smaller than those of the other alkali–TCNQ's,[14] which is consistent with the small intermolecular distance of Rb–TCNQ-II.

Although the structure of the TCNQ columns of Rb–TCNQ-II closely resembles those of NMP–TCNQ and HMTTF–TCNQ, the conductivities of NMP–TCNQ and HMTTF–TCNQ are four orderes of magnitude larger than that of Rb–TCNQ-II. This clearly shows the importance of the intramolecular Coulomb repulsion. Since the ρ of Rb–TCNQ-II is considered to be 1, Rb–TCNQ-II has a Coulomb gap at the Fermi wave number, k_F, where the ρ values of of NMP–TCNQ and HMTTF–TCNQ are 2/3[15] and 0.72[16] respectively. The importance of the Coulomb gap has been elucidated in a recent paper by Torrance *et al.*;[17] they thoroughly examined the physical properties of two isostructural HMTTF compounds, one metallic and the other insulating.

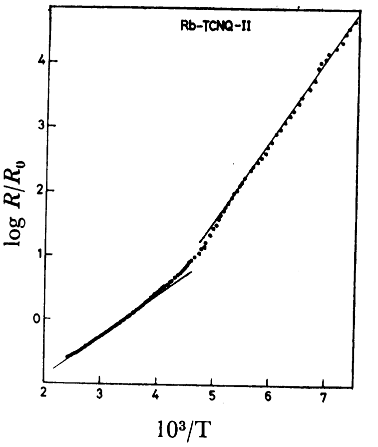

Fig. 4. The temperature dependence of the d.c. electrical resistivity of Rb–TCNQ-II.
The room-temperature resistivity R_0 is 50 Ω cm.

A change in the slope of the log R/R_0 *vs.* $1/T$ curve suggests a phase transition, which has been established by magnetic measurements ($T_C=220$ K).[18] X-Ray oscillation photographs taken around the needle axis showed the doubling of the lattice along the c axis below T_C. Therefore, the transition is a monomer-dimer (M-D) transition. It is well-known that the TCNQ columns in TTF–TCNQ and HMTTF–TCNQ exhibit $2k_F$ instability.[19,20] Although no long-range 3-D ordering is observed down to 20 K, a similar lattice modulation has been observed in NMP–TCNQ.[15] The $2k_F$-distortion in the crystals of organic metals arises from Peierls instability. On the other hand, the dimerization in alkali–TCNQ has been considered to be associated with the instability of the spin-Peierls type.[21] The transition temperatures (T_C) of some simple salts of TCNQ are plotted against the interplanar distances (d) in Fig. 5. Since the dimer structure of alkali–TCNQ

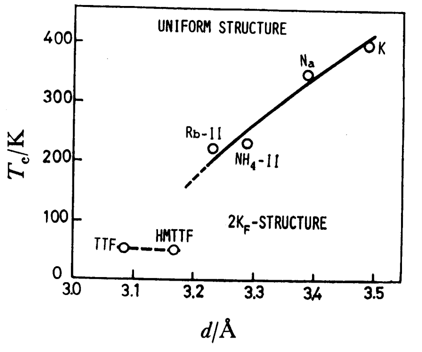

Fig. 5. The relationship between the interplanar distance of TCNQ's (d) and the phase transition temperature (T_c).
The thermal expansion of d was estimated by reference to the temperature dependence of the crystal structure of TTF–TCNQ (A. J. Schultz, C. D. Stuky, R. H. Blessing, and P. Coppens, *J. Am. Chem. Soc.*, **98**, 3197 (1976).

can be regarded as the $2k_F$-structure, the transitions presented in Fig. 5 are "uniform-$2k_F$ transitions." The M-D transition temperatures are almost linearly related to d. The nature of column instability appears to change around d=3.20 Å. Despite the close resemblance of the room-temperature structures of the TCNQ columns, the transition temperatures of Rb–TCNQ-II and HMTTF–TCNQ are quite different from each other.

The activation energies of the conductivities are 0.26 eV below T_C and 0.12 eV above T_C. The increase in the activation energy below T_C indicates the appearance of the dimerization gap. If the energy gap, E_g, is twice as large as the activation energy ($E_g=2E_a$), E_g is 0.24 eV. Since the Coulomb gap U ($\approx$1 eV[22]) is considered to be much larger than 0.24 eV, the conduction cannot be intrinsic.

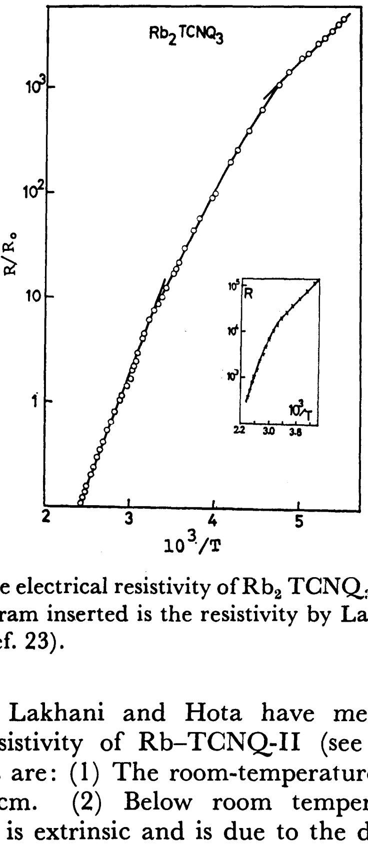

Fig. 6. The electrical resistivity of Rb_2 $TCNQ_3$.
The diagram inserted is the resistivity by Lakhani and Hota (Ref. 23).

Recently, Lakhani and Hota have measured the electrical resistivity of Rb–TCNQ-II (see Fig. 6).[23] Their results are: (1) The room-temperature resistivity is 2×10^4 Ω cm. (2) Below room temperature, the conductivity is extrinsic and is due to the donor levels located 0.18 eV below the conduction band.[24] (3) Above 360 K, the intrinsic hole conduction becomes dominant where the activation energy is 0.44 eV. (4) The conductivity increases with the concentration of the impurity.

Since the room-temperature resistivity and the activation energies are quite different from those obtained by this work, and since their crystals have the form of a truncated pyramid while those used in this work were needle-shaped, the crystals used by Lakhani and Hota appear to be different from Rb–TCNQ-II. Figure 6 shows the resistivities of Rb_2TCNQ_3 measured along the most developed axis of the prismatic crystal (//**a**), which is perpendicular to the TCNQ columns. The room-temperature resistivity is 10^5 Ω cm. E_a is 0.17 eV below 215 K and 0.43 eV above 310 K. Because these values agree well with those of Lakhani and Hota, their crystals are considered to be Rb_2TCNQ_3.

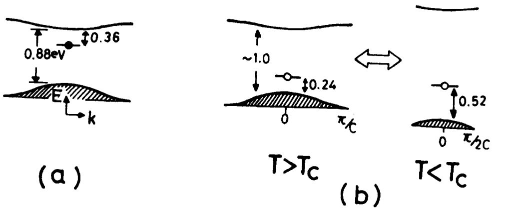

Fig. 7. Schematic representation of the energy-level diagram of Rb–TCNQ.
The intrinsic levels are presented as one-dimensional bands so as to indicate the doubling of the lattice constant at T_c. The band width and the dimerization gaps are assumed to be much smaller than 1 eV.
(a) The energy-level diagram of Rb_2TCNQ_3 based on the two carrier model by Lakhani and Hota (Ref. 23).
(b) The energy-level diagram of Rb–TCNQ-II.

Based on the electrical resistivities and thermoelectric powers, Lakhani and Hota have proposed the two-carrier conduction model of Rb–TCNQ which is presented diagramatically in Fig. 7: donor levels are located 0.36 eV below the conduction band, and the band gap is 0.88 eV. Unlike as in the cases of Cs_2TCNQ_3[27] and Rb_2TCNQ_3, the thermoelectric powers of simple salts of alkali-TCNQ are positive ($T<450$ K), which indicates the hole conduction.[28] The activation energy of 0.12 eV ($T>T_C$) suggests that the impurity acceptor levels are located 0.24 eV above the filled band. Below T_C, the dimerization gap appears, which leads a slightly modified model of the energy diagram (see Fig. 7b). The magnitudes of the Coulomb gap and the band-width have been considered to be of the orders of 1 eV and 0.1 eV respectively. However, their precise evaluation will be required for the better understanding of the electrical properties of alkali-TCNQ.

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4) There are errors in the lattice constants reported in Ref. 2: c and α should be corrected to: $c=3.903\pm0.02$ Å, and $\alpha=92.07\pm0.10$ °. The relationships between the old lattice vectors ($\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$) and the new ones ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) are: $\mathbf{a}=\mathbf{a}'$, $\mathbf{b}=\mathbf{b}'$, and $\mathbf{c}=-\mathbf{c}'$.

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