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Phase Transitions of the 1:2 Complex of *N*-Ethyl-*N*-methylmorpholinium and 7,7,8,8-Tetracyanoquinodimethan, MEM(TCNQ)$_2$ above Room Temperature

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The thermal expansion coefficient, the electrical conductivity, and the crystal structure (at 325 K) of MEM(TCNQ)$_2$ were examined. A new phase transition was observed at 315 K, where the thermal expansion coefficient jumps. This second-order transition may be triggered by the molecular motion of MEM cations and can be regarded as a precursor of the first-order transition around 62 °C. The molecular motion of MEM cations reduces the electrostatic lattice energy and leads to a structural change. The structural instability of TCNQ columns around 335 K is not attributable to the electron-electron correlation effect in the one-dimensional system, but to the change in the energy balance between the charge-transfer interaction and the electrostatic energy.

In the crystals of anion radical salts of 7,7,8,8-tetracyanoquinodimethan(TCNQ), TCNQ molecules stack to form one-dimensional columns. The periodicity of TCNQ columns frequently reflects a lattice instability characteristic of one-dimensional electronic systems. The "$2k_F$-structure" is associated with the Peierls instability, which has been observed in such well-known one-dimensional metals as TTF–TCNQ and KCP.[1] The "$4k_F$-instability" has also been observed in TTF–TCNQ. Sawatzky, Huizinga and their co-workers[2] have performed extensive studies of the physical properties of the 1:2 complex of *N*-ethyl-*N*-methylmorpholinium and TCNQ (MEM(TCNQ)$_2$) and found a series of the phase transitions. When $T>335$ K, MEM(TCNQ)$_2$ has nearly uniform columns of TCNQ and shows metallic behavior. The nearly uniform columns are transformed to diadic ones at 335 K, below which point MEM(TCNQ)$_2$ is semiconductive. The diadic columns change to tetradic ones at 19 K, where a non-magnetic spin-Peierls state appears. Although the 335 K transition has been reported to be a (electronic) Peierls transition,[2] the electrical conductivity of the "metallic phase" is relatively small (50 $(\Omega\,\mathrm{cm})^{-1}$). Therefore, it may be worthwhile to try to make clear the lattice instability which causes the 335 K transition.

The thermal expansion, the electrical resistivity, and the crystal structure of MEM(TCNQ)$_2$ at 325 K were studied.

Experimental

Black crystals were grown from a mixture of hot solutions of TCNQ and *N*-ethyl-*N*-methylmorpholinium iodide in acetonitrile. X-Ray oscillation and Weissenberg photographs showed that the well-developed plane of the crystal is (010). The maximum dimensions of the specimen are about 10 mm × 2 mm × 1 mm.

Thermal Expansion. The thermal expansion was measured over the temperature range of 293—363 K along the c and b* directions, which are parallel and perpendicular respectively to the TCNQ stacks. The results are shown in Figs. 1 and 2. The values of $L_\perp(\alpha_\perp)$ are less accurate than those of $L_{//}(\alpha_{//})$ because of the diffculty of the crystal alignment ($L_{//}(L_\perp)$ is the length of the crystal parallel (perpendicular) to TCNQ columns, and $\alpha_{//}(\alpha_\perp)$ is the corresponding thermal expansion coefficient). The typical crystals used had the dimensions of 7 mm and 0.7 mm along the c (//) and b* (⊥) directions respectively.

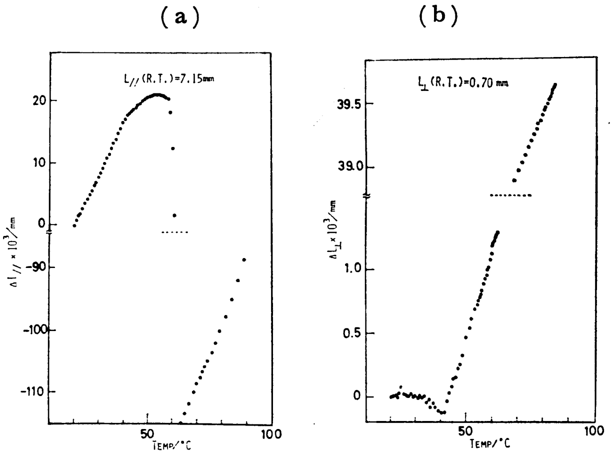

Fig. 1. Thermal expansion parallel to c(a) and b*(b).

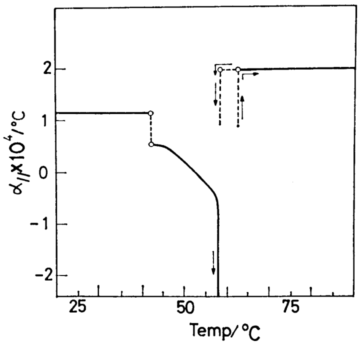

Fig. 2. Thermal expansion coefficient $\alpha_{//}$ (parallel to c).
The arrows indicate the cooling and heating processes. The hysteresis are observed around 60 °C.

The discontinuous change in $L_{//}(L_\perp)$ at 335 K (Tc_1) and $\alpha_{//}(\alpha_\perp)$ at 315 K (Tc_2) show the first-order phase transition at Tc_1 and the second-order phase transition at Tc_2. Above Tc_2, the thermal expansion coefficient ($\alpha_{//}$) decreases with the temperature and becomes negative above 326 K. Thus, the second-order phase transition is a precursor of the discontinuous contraction of the crystal at Tc_1. The transition temperature, Tc_1 agrees well with that obtained from the electrical conduction experiment.[2] The temperature dependences of $\alpha_{//}$ and $\alpha_\perp$ are as follows:

(i) $T>Tc_1$: Around Tc_1, $L_{//}$, $L_\perp$, $\alpha_{//}$, and $\alpha_\perp$ show hysteresis. Since the crystals were cracked at Tc_1, it was difficult to obtain accurate data above Tc_1. The transition

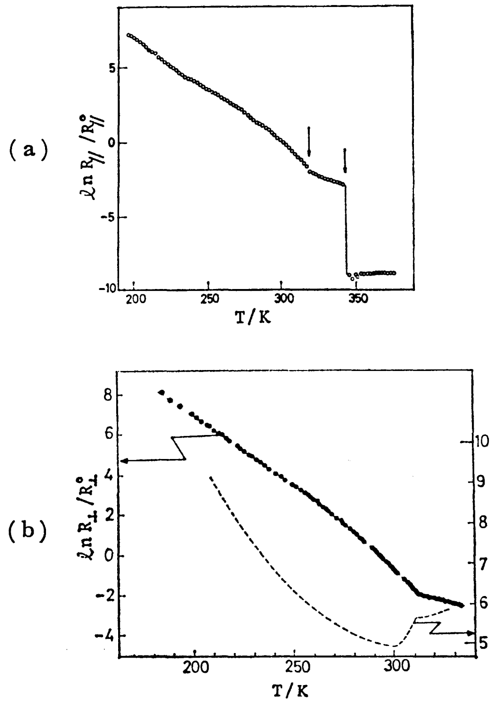

Fig. 3. (a) Electrical resistivities parallel to the TCNQ columns ($R_{//}$). The room-temperature value of $R_{//}$ ($=R^{\circ}_{//}$) is $10^4\,\Omega$ cm. (b) Electrical resistivities perpendicular to the TCNQ columns ($R_{\perp}$) and anisotropy of the resistivities ($R_{//}/R_{\perp}$). The room-temperature value of $R_{\perp}(R^{\circ}_{\perp})$ is $5\times10^4\,\Omega$ cm.

temperature, Tc_1 determined from the heating process is 335 K, but that determined from the cooling process is about 328 K. The crystal shrinks along the TCNQ column (//c) and elongates along the direction perpendicular to it (//b*). The thermal expansion coefficients above Tc_1 are $\alpha_{//}=2\times10^{-4}$/deg and $\alpha_{\perp}=9\times10^{-5}$/deg.

(ii) $Tc_2<T<Tc_1$: With an increase in the temperature, $\alpha_{//}$ decreases and becomes negative, while $\alpha_{\perp}$ is almost constant (9.6×10^{-5}/deg).

iii) 293 K$<T<Tc_2$: $\alpha_{//}$ is 1.15×10^{-4}/deg, and $\alpha_{\perp}$ is much smaller than $\alpha_{//}$ ($<10^{-5}$/deg).

Electrical Resistivity. Huizinga and Sawatzky[2] have reported a "metal-semiconductor transition" at 335 K (Tc_1). The conductivity of the ' metallic state" is 10^3 times larger than that of the semiconducting state. Since the thermal-expansion experiments revealed a second-order phase transition, the d. c. electrical resistivities were measured around the transition temperature by the use of a standard four-probe technique. Gold wires 0.025 mm in diameter were bonded to the crystal by means of silver conducting paint. The results are shown in Fig. 3. The room-temperature resistivities were $R_{//}=10^4$ cmΩ and $R_{\perp}=5\times10^4\,\Omega$ cm, where $R_{//}$ and $R_{\perp}$ indicate the resistivities parallel (//c) and perpendicular (//a*) to the c axis. Since the crystals were cracked at Tc_1, it was difficult to obtain the resistivities accurately above Tc_1. As has previously been reported,[2] the parallel resistivity, $R_{//}$, jumps at Tc_1 by a factor of 10^2—10^3. A slight anomaly was observed at Tc_2, where $\mathrm{d}\ln(R_{//}/R^{\circ}_{//})/\mathrm{d}T^{-1}$ becomes very large (>1500 K). The perpendicular resistivity, $R_{\perp}$, shows a similar temperature dependence.

Crystal Structure at 325 K. Since the new phase transition has been found at Tc_2, the crystal-structure analysis was made to obtain the structure information above Tc_2.

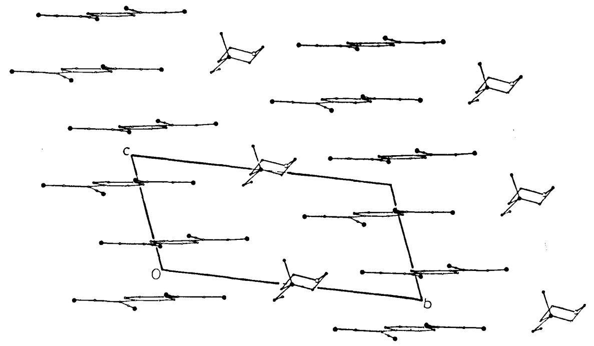

Fig. 4. The crystal structure of MEM(TCNQ)$_2$ at 325 K.

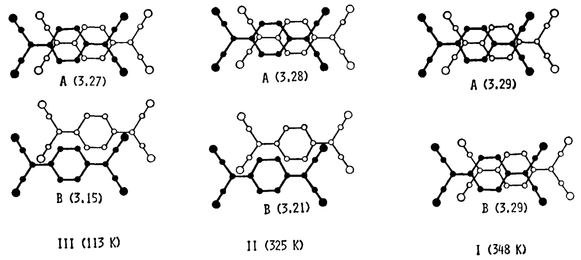

Fig. 5. The mode of intermolecular overlappings of TCNQ of the three phases (at 325 (this work), 113[3]) and 348 K.[6]) The interplanar distances are given in parentheses.

The lattice constants were determined by the use of a Rigaku automated four-circle diffractometer. The crystal data are: $(C_7H_6NO)^+(C_{12}H_4N_4)^-$, *F.W.*=538.6, triclinic, $P\bar{1}$, $a=7.796(5)$, $b=15.308(8)$, $c=6.993(5)$ Å, $\alpha=111.96(6)$, $\beta=74.87(4)$, $\gamma=111.82(6)^{\circ}$, $U=711.3$ Å^3, $F=(000)=281$, $Z=1$, and $\mu(\text{Mo }K\alpha)=0.9\ \text{cm}^{-1}$. The intensity data were collected at 52 °C with monochromated Mo $K\alpha$ radiation up to $2\theta=55^{\circ}$. The number of the significant reflections ($|F_o|>3\sigma(|F_o|)$ is 1710.[3,4])

Starting with the atomic parameters of the low-temperature structure reported by Bosh and Bodegom,[3]) the crystal structure was refined. The hydrogen atoms of TCNQ were included; however, those of MEM could not be located. The final R value was 0.088. The atomic parameters are given in Table 1.*

The crystal structure, shown in Fig. 4, is almost identical to the structure at 113 K[3]) and that at 323 K reported very recently.[5]) The TCNQ columns have a diadic structure. The TCNQ molecules the centers of the coordinates of which lie at $z=0.27$ and those with centers $z=-0.27$ form a dimer. The least-squares plane through two crystallographically independent TCNQ molecules are: $0.0168X+0.1106Y-0.9441Z+1.6284=0.0$ and $0.0350X+0.1002Y-0.9382Z-1.6513=0.0$, where X, Y, and Z are the coordinates(Å) referred to the crystal axes, a, b, and c respectively. These two planes are almost parallel to each other (the dihedral angle between the planes is *ca.* 1.1°). The angles between the normals to TCNQ planes and c are 19.2 and 20.2°, slightly smaller than those observed at 113 K (20.5 and 21.3°).[3]) The mode of overlapping between adjacent TCNQ molecules is shown in Fig. 5, together with those obtained at different temperatures.[3,6]) The interplanar distances between

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* A list of the observed and calculated structure factors and a table of anisotropic thermal parameters are kept as Document No. 8231 at the Chemical Society of Japan.

Table 1. The final atomic coordinates ($\times 10^4$)

Atom	x	y	z	B_{eq}/Å^2 a)
N(1)	3061(18)	4283(8)	3708(22)	6.86
C(2)	3327(18)	3573(11)	3489(23)	5.40
C(3)	3490(17)	2641(9)	3175(21)	4.72
C(4)	5419(21)	2697(11)	3252(27)	6.43
N(5)	6801(18)	2676(10)	3358(25)	7.86
C(6)	2135(16)	1794(9)	2937(18)	3.97
C(7)	2285(18)	818(10)	2629(22)	4.93
C(8)	892(15)	21(8)	2463(17)	3.16
C(9)	−915(17)	−11(9)	2419(20)	4.28
C(10)	−1177(16)	904(10)	2663(21)	4.65
C(11)	205(16)	1759(10)	2863(20)	4.36
N(12)	−5763(16)	−878(10)	2103(26)	7.79
C(13)	−4314(19)	−912(11)	2229(23)	5.39
C(14)	−2452(17)	−903(9)	2153(18)	3.97
C(15)	−2206(17)	−1791(9)	2008(21)	4.38
N(16)	−2036(16)	−2495(8)	1851(21)	6.40
N(17)	−3009(20)	−4298(10)	−3584(25)	8.05
C(18)	−3203(18)	−3552(9)	−3425(21)	4.71
C(19)	−3510(17)	−2643(9)	−3279(19)	4.35
C(20)	−5277(17)	−2692(9)	−3462(22)	4.63
N(21)	−6746(17)	−2782(11)	−3707(25)	7.72
C(22)	−1943(16)	−1744(9)	−2901(19)	4.02
C(23)	−2270(15)	−872(9)	−2730(17)	3.58
C(24)	−821(19)	4(10)	−2476(22)	5.39
C(25)	1064(15)	23(8)	−2401(17)	3.63
C(26)	1280(16)	−917(9)	−2628(20)	4.37
C(27)	−212(17)	−1765(8)	−2847(19)	4.22
N(28)	5771(16)	893(10)	−2329(26)	7.45
C(29)	4365(17)	883(9)	−2193(23)	5.02
C(30)	2497(16)	858(9)	−2227(21)	4.44
C(31)	2343(18)	1808(10)	−1946(21)	4.82
N(32)	2172(18)	2554(8)	−1748(20)	6.17
N(33)	107(34)	5023(15)	119(33)	8.06
C(34)	2358(23)	4970(11)	−460(33)	8.13
C(35)	3425(28)	5830(11)	1039(32)	8.73
C(36)	1710(26)	6810(13)	1478(48)	13.38
C(37)	348(22)	5873(13)	−173(50)	13.74
C(38)	−489(36)	4851(25)	2142(35)	14.78
C(39)	−812(31)	3974(23)	−1595(43)	16.98
C(40)	−2983(38)	3925(18)	−1103(43)	13.57
O	3521(15)	6710(8)	622(22)	8.72

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

the neighbouring TCNQ molecules are 3.21 Å (interdimer) and 3.28 (intradimer). They are 3.15 and 3.27 Å at 113 K.[3] The interdimer distance increases by 0.06 Å with an increase in the temperature from 113 K to 325 K, while the intradimer distance stays nearly constant. That is, the difference in the interplanar distances decreases. The bond lengths and angles are shown in Fig. 6.

The anomalous molecular structure and thermal parameters indicate a large thermal motion of MEM, which is consistent with the NMR observation of the onset of molecular motion around 300 K.[2] Since no significant structural change in TCNQ columns occurs at Tc_2, the second-order phase transition is considered to be triggered by the thermal motion of the MEM cations.

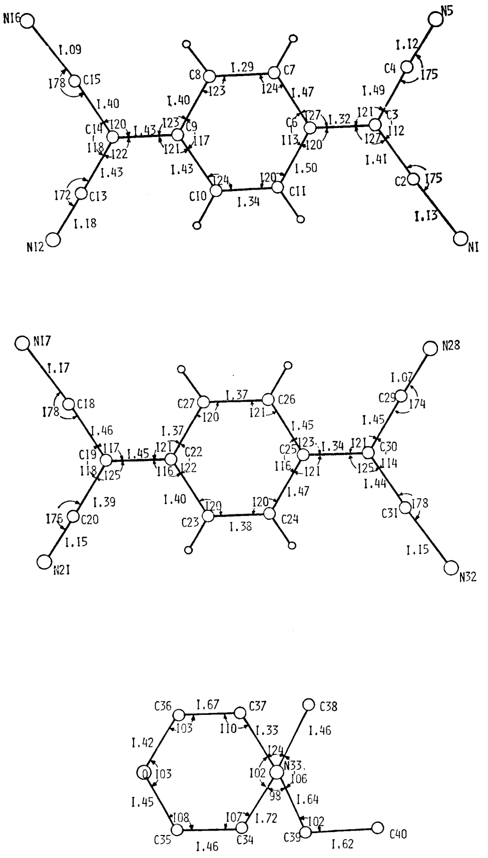

Fig. 6. The bond lengths and the bond angles. The e.s.d.'s of the bond lengths are 0.02 Å(TCNQ) and 0.02—0.04 Å(MEM) and those of the bond angles are 1—2°(TCNQ) and 1—3°(MEM). The bond lengths of C–H is 0.98—1.06 Å.

Discussion

In a quarter-filled system like MEM(TCNQ)$_2$, the diadic and tetradic columns of TCNQ correspond to the $4k_F$- and $2k_F$-structures respectively. The $4k_F$-structure has been frequently discussed in connection with the electron correlation. Sumi[7] has proposed a series of possible structural-phase transitions in a highly correlated linear-chain system: a uniform-$4k_F$ transition and $4k_F$-$2k_F$ transition. Since both types of transitions have been found, MEM(TCNQ)$_2$ has been regarded as a typical high-U material. The origin of the $2k_F$- and $4k_F$-structures has been considered to be correlated with the general principle of the periodical instability of the one-dimensional electronic system.[2]

However, as has been shown in this paper, the "$4k_F$-phase" contains an additional second-order phase transition at Tc_2. The thermal-expansion anomalies suggest that the second-order phase transition at Tc_2 is a precursor of the first-order phase transition at Tc_1. The diadic structure of TCNQ columns is transformed into an almost regular one at Tc_1.[2] Since the phase transition does not alter the intermolecular overlapping between intradimer molecules, TCNQ molecules are considered to move in pairs on passing through Tc_1. The change in the mode of the intradimer overlapping indicates the rotation of the TCNQ dimer about 20°.

The thermal expansion experiments showed that the length of the crystal ($L_{//}$) is shortened by about 4.5% at Tc_1.[8] If the transition does not change the interplanar distances, the crystal must be shortened along the TCNQ columns by the rotation. The magnitude of the contraction is estimated as $\Delta L_{//}/L_{//}=1-\cos 20°$ $(=0.05)$. Since the observed contraction (4.5%) agrees well with the estimated value, the discontinuous contraction of the crystal is considered to be mainly due to the rotation of the TCNQ dimers.

Each TCNQ dimer has an excess electron. The structure is stabilized by the Coulomb interaction between the MEM cations and the excess electrons in dimers. The small interplanar distance between TCNQ molecules indicates that the charge-transfer interaction also plays an important role. At high temperatures ($T>Tc_2$), the Coulomb interaction is reduced by the large thermal motion of MEM cations. Then, the MEM cations cannot restrain the movement of the excess electrons along the column. The interdimer charge-transfer interaction becomes importants. Figure 5 shows that in a diadic structure, the interdimer charge-transfer interaction is negligibly small, but it becomes as large as the intradimer one in a nearly uniform structure. This indicates that the diadic structure is transformed to a uniform one to gain a larger charge-transfer stabilization energy. As has been mentioned before, the crystal contracts along the direction parallel to the TCNQ columns (//c) and expands along the direction perpendicular to it (//b*). The expansion suggests a decrease in the Coulomb interaction between MEM cations and the excess electrons in TCNQ columns (see Fig. 4), while the contraction implies an increase in the charge-transfer interaction along the columns.

Lacoe, Gruner, and Chaikin have reported on the thermoelectric power(TEP) of MEM(TCNQ)$_2$.[9] Above Tc_1, TEP is -65 μV/K, which suggests that the spin entropy of the excess electron makes the dominant contribution, as in other highly correlated quarter-filled band TCNQ salts. This indicates that the excess electrons are uniformly distributed in the TCNQ columns above Tc_1. As the temperature is lowered, the TEP increases faster, suggesting a change in the semiconducting gap.

However, the temperature dependence of $R_{//}$ (see Fig. 3) shows that the semiconducting gap does not alter around Tc_2. The anomaly around Tc_2 may be attributable to the change in $\mu(T)$. The mobility, $\mu(T)$, is considered to change by an order of magnitude. In other words, the mobility depends strongly on the thermal motion of MEM.

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