

Structural Phase Transition in $(\text{NMe}_4)_2\text{TCNQ}_3$

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Abstract

The structural properties of a neutral/radical 1 : 2 mixed compound, $(\text{NMe}_4)_2\text{TCNQ}_3$, have been studied by the X-ray diffraction method in a temperature range between 25 and 150 °C. The experimental data show that a second order phase transition takes place at around 60 °C and that the high-temperature phase has a monoclinic $C2/m$ structure. The molecular planes of dimerized TCNQ^- radicals, being slipped against each other in the low temperature phase, are expected from the $C2/m$ symmetry to be totally eclipsed in the high-temperature phase. A good fit of the power law $(1 - T/T_c)^\alpha$ to the temperature variation of the intensity of the Bragg reflection arising from the slipped TCNQ^- radicals is obtained with $T_c = 330.7 \pm 0.8$ K and $\alpha = 0.66 \pm 0.05$ for $T \leq T_c$. Influences of this novel phase transition on the electronic properties are discussed.

Tetracyanoquinodimethane (TCNQ), $C_8H_4(CN)_4$, forms charge-transfer compounds in combination with various cationic species. As exemplified by TTF-TCNQ and Na, K, Rb-TCNQ,¹⁾ those compounds exhibit striking structural, electric and/or magnetic properties depending on the degree of the charge transfer from cations to TCNQ and on the dimensionality of the resultant electronic states. The compound $(NMe_4)_2TCNQ_3$, which is examined in this Letter, is one of the neutral-radical mixed compounds that have been synthesized recently by Sugimoto and his coworkers,²⁻⁴⁾ where NMe_4 denotes tetramethylammonium $N(CH_3)_4$. Similar to Cs_2TCNQ_3 ,⁵⁾ the compounds contain neutral and radical TCNQ molecules in a molar ratio of 1 : 2. At ambient conditions $(NMe_4)_2TCNQ_3$ has a monoclinic crystal structure belonging to the space group of $P2_1/n$, in which $TCNQ/TCNQ^{\cdot-}$ and NMe_4^+ form respective columns along the b -axis.²⁾ Crystallographically, the $TCNQ/TCNQ^{\cdot-}$ columns appear to have a period of charge-separated $TCNQ/TCNQ^{\cdot-}/TCNQ^{\cdot-}$ triads. Their molecular planes are oriented perpendicular to the columns. The two radical $TCNQ^{\cdot-}$ molecules conform a ‘slipped’ dimer in which they are displaced against each other in the direction of the short molecular axis. Of interest is the fact that this salt shows a subtle ferromagnetic behavior at room temperature. The saturation magnetization and coercive force are 0.79 emu/mol and ~300 Oe, respectively, although the mechanisms are yet to be studied.

One may expect from the columnar structure of TCNQ and $TCNQ^{\cdot-}$ molecules that electronic properties are anisotropic. Recently Kuroda *et al.* have measured the temperature dependence of the linearly-polarized optical absorption spectrum in $(NMe_4)_2TCNQ_3$.⁶⁾ The observed spectrum is strongly anisotropic, as expected. In addition, a temperature-dependent satellite band is found at a photon energy around 1.3 eV. As temperature is elevated, the intensity of the band decreases continuously and disappears at a certain temperature T_c . Although two different values of T_c , that is, 60 and 126 °C, depending on specimens, are obtained, the observed temperature dependence of the satellite band is reminiscent of the occurrence of some sort of second order phase transition at T_c . As the origin of this satellite band, two alternative interpretations have been proposed: One interpretation is the magnon sideband of a spin-forbidden transition and the other one is the charge-transfer electronic transition associated with the slipped

TCNQ^{•-} dimers.

In this Letter we report on the results of X-ray diffraction measurements of single crystals of (NMe₄)₂TCNQ₃ exhibiting $T_c \approx 60$ °C in a temperature range from room temperature up to 150 °C. Our data clearly show that a second order structural phase transition takes place at a temperature just around 60 °C. This phase transition is suggested to be driven by the displacement of TCNQ^{•-} radicals in such a way that the slipping is reduced with elevating temperature to disappear upon the phase transition. To look into the nature of this novel phase transition in more detail the temperature dependencies of lattice constants and intensity of the Bragg reflections are examined.

Single crystals were recrystallized from a saturated acetonitrile solution by means of a solvent-mixing method using ether.²⁾ Since crystals which exhibit $T_c = 126$ °C can hardly be obtained for unknown reasons, the present experiment was conducted using crystals of $T_c \approx 60$ °C. The specimens were typically 1.0x1.0 mm² wide and less than 0.01 mm thick. The wide surfaces are parallel to the *ab* plane of the *P2₁/n* structure.

X-ray diffraction measurements were performed with a Huber double-axis high-resolution diffractometer. The Cu-K α radiation was generated by a rotating-anode X-ray generator (Rigaku RU-300) at a supplied power of 40 kVx240 mA, and was monochromatized using a pyrolytic graphite crystal. A four-circle diffractometer (Rigaku AFC-5R) with Mo-K α radiation was also employed to determine the extinction rule for the Bragg reflections throughout the three-dimensional reciprocal space. A conventional electric heater was used for high-temperature measurements. The specimen temperature was monitored with a copper-Constantan thermo-couple and controlled within ± 0.2 °C.

Figure 1 shows the temperature dependence of lattice constants. All the lattice constants of a monoclinic unit cell change continuously with temperature, but they show singular behaviors at around 60°C. The singularity is remarkable for the *c* axis and the monoclinic angle β made by the *a* and *c* axes. This result suggests strongly that a structural phase transition of second order takes place at around 60°C. The transition temperature agrees well with the optically determined value of

T_c . A number of monoclinic crystals are known to undergo a phase transition into an orthorhombic structure. In those crystals the monoclinic angle, which is greater than 90° , tends to approach gradually to 90° as temperature is elevated towards the transition point. In the present substance, however, the monoclinic angle increases with temperature and shows an additional increase even though temperature is elevated beyond 60°C . Moreover no orthorhombic unit cells can be found unless an unpractically large area is chosen in the ac plane. This fact excludes orthorhombic space groups for the structure of the high-temperature phase. According to the Landau theory, the space group of the low-temperature phase involved in a second order phase transition is a subgroup of the space group of the high-temperature phase. We decide, therefore, that the $(\text{NMe}_4)_2\text{TCNQ}_3$ crystal maintains a monoclinic symmetry above the transition temperature.

The change in the crystal structure upon a phase transition causes a change in the extinction rule for Bragg reflections. Figure 2 shows the profiles of the Bragg reflection along the reciprocal vectors $\mathbf{K} = (0\ 1\ l)$ and $(0\ 2\ l)$ over a wide range of l at 25 and 65°C . These are typical examples observed at temperatures significantly lower and higher than the transition temperature, respectively. The $(0kl)$ reflections marked with asterisks in Fig. 2, which satisfy the relationship $k + l = 2n + 1$, are observed distinctly at 25°C but disappear at 65°C , where n designates an arbitrary integer. From a careful observation of the Bragg reflections (hkl) using a four-circle diffractometer, a more general extinction rule, $h + k + l = 2n + 1$, turns out to hold for the high-temperature structure. Taking account of the fact that the high-temperature structure maintains the monoclinic symmetry, the observed extinction rule leads us to uniquely assign the space group of the high-temperature phase to $C2/m$. According to the *International Tables for Crystallography*,⁷⁾ the primitive unit cell vectors of the high-temperature phase are given by $\mathbf{A} = \mathbf{a} + \mathbf{c}$, $\mathbf{B} = \mathbf{b}$ and $\mathbf{C} = -\mathbf{a}$, where \mathbf{a} , \mathbf{b} and \mathbf{c} represent the primitive unit cell vectors of the low-temperature monoclinic phase.

Figure 3(a) schematically depicts the arrangement of TCNQ molecules of the high-temperature phase in a unit cell. For comparison, the arrangement of the molecules of the low-temperature phase²⁾ is shown in Fig.3(b). The symmetry operations relevant to the respective

structures are also shown in Figs. 3(a) and 3(b). We note from Figs.3(a) and 3(b) that in addition to the symmetry operations relevant to the low-temperature phase, there appear three more operations of twofold rotation, mirror reflection and inversion in the high-temperature phase. Structures of the two phases are very similar to each other except the configuration of TCNQ \cdot radicals. While in the low-temperature phase the TCNQ \cdot radicals forming a dimer are slipped against each other by 0.87 Å,²⁾ in the high-temperature phase the $C2/m$ symmetry constrains the TCNQ \cdot radicals to be totally eclipsed if projected on the ac plane along the b axis. In many substances including the present one and Cs₂TCNQ₃, TCNQ molecules have a slipped conformation at ambient conditions.⁸⁾ Only in a few substances the eclipsed conformation is known to be rather stable.⁹⁾ In Na-, K- and Rb-TCNQ, on the other hand, a spin-Peierls transition takes place at temperatures considerably higher than room temperature.¹⁰⁾ It is worth noting that throughout the spin-Peierls transition, the TCNQ molecules maintain a slipped conformation.¹¹⁾ To our knowledge, there have been very few observations of the phase transition between slipped and eclipsed conformations of dimerized planar molecules to date.

Taking a look at Fig. 3, one may envisage that slipping of the molecular planes enlarges the thickness of the TCNQ/TCNQ \cdot columns so as to elongate the c axis. In fact, we see in Fig. 1 that in the low-temperature phase this effect results in canceling the thermal contraction, and thus the c axis remains rather constant even though temperature is lowered. Moreover, the slipping causes to relax the canting of TCNQ/TCNQ \cdot columnar arrays from normal to the c axis, so that β decreases more rapidly with lowering temperature in the low-temperature phase than in the high-temperature phase. We note also from Fig. 1 that the temperature coefficient of the b axis in the low-temperature phase is about twice as large as that in the high-temperature phase. There is no doubt that the slip-to-eclipse transformation works to expand the intermolecular spacing. The aforementioned anomalous temperature dependence of the optical absorption spectrum demonstrates that a marked change in the electronic properties, particularly of conjugated π orbitals, is induced by these symmetry-lifting structural changes. As for spins of the dimerized TCNQ \cdot radicals, majority of them might be in the singlet ground state, having a triplet state at 0.01 - 0.1 eV

above the ground state,¹²⁾ at room temperature. Otherwise, in the light of the subtle ferromagnetism observed by Ueda et al.,²⁾ the spins might be ordered in a ferrimagnetic manner. In either case, the reduction of slip distance and the concurrent expansion of intermolecular spacing would also affect the spin interactions.

The Bragg reflections satisfying the relationship $h + k + l = 2n + 1$ in the low-temperature phase are conceived to be produced primarily by slipped dimers. Their intensity should, therefore, reflect the magnitude of slipping. Figures 4 and 5 show the temperature dependence of the diffraction profile and integrated intensity, respectively, of the (018) Bragg reflection. We see in Fig. 4 that the intensity decreases continuously with increasing temperature. The reflection disappears completely at around 60 °C, in coincidence with the singular behavior of lattice constants. The change in the integrated intensity is reversible upon temperature cycling, as seen in Fig. 5, assuring that the phase transition observed here is of second order. To describe these experimental data we choose the power law

$$I(T) = A\left(1 - \frac{T}{T_c}\right)^\alpha, \quad (1)$$

where T is the sample temperature, A is an adjustable coefficient and α is a numerical constant. The least-squares fitting of eq.(1) to the experimental data yields $T_c = 330.7 \pm 0.8$ K and $\alpha = 0.66 \pm 0.05$. The calculated curve is shown in Fig. 5 along with the experimental data. The variation of the integrated intensity is reproduced well by the calculated curve. The value of α is compared with $\alpha = 0.63^{(6)}$ that is obtained from fitting of the same power law as eq.(1) to the temperature dependence of an optical absorption band observed for the polarization of $E // a$ axis.

In summary, X-ray diffraction measurements have been performed in $(\text{NMe}_4)_2\text{TCNQ}_3$ to explore the structural phase transition in a temperature range from 25 to 150 °C. The temperature dependence of lattice constants shows that a second order phase transition takes place at around 60 °C. On the basis of the observed extinction rule for the Bragg reflections the structure of the high-temperature phase is assigned to be monoclinic, belonging to the space group of $C2/m$. One of the most remarkable aspects of this phase transition is that $\text{TCNQ}^{\cdot-}$ radicals forming a slipped

dimer in the low-temperature phase are suggested to displace so as to be totally eclipsed above the transition temperature. The variation of the integrated intensity of the (018) Bragg reflection is expressed by a power law $(1-T/T_c)^\alpha$ well with $T_c = 330.7 \pm 0.8$ K and $\alpha = 0.66 \pm 0.05$, consistent with the previous experiment on the temperature dependence of a charge-transfer optical absorption band.

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Figure captions

Fig. 1. Temperature dependence of lattice constants.

Fig. 2. X-ray diffraction profiles along the reciprocal lattice vectors $\mathbf{K} = (011)$ and $(0\ 2\ 1)$ at 25 and 65 °C.

Fig. 3. Spatial arrangement of TCNQ molecules and symmetry operations in the low-temperature phase (a) and the high-temperature phase (b), where unit cell vectors of $P2_1/n$ are employed for both phases. Fractions put beside molecules indicate the approximate height along the \mathbf{b} axis. For symbols of symmetry operations, refer to *International Tables for X-ray Crystallography*.⁷⁾

Fig. 4. X-ray diffraction profiles of the (018) Bragg reflection at various temperatures.

Fig. 5. Temperature dependence of the integrated intensity of the (018) Bragg reflection. The solid line is the least-squares fit of eq. (1) to the experimental data obtained upon heating (solid circles) and cooling (open circles) a specimen.

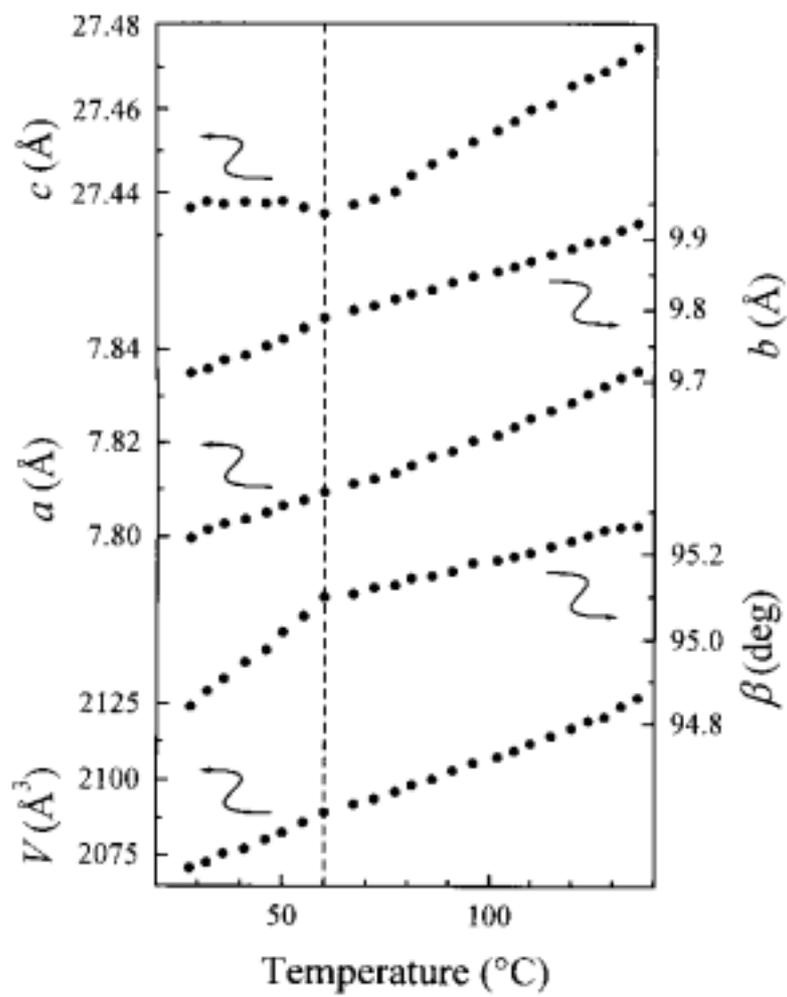


Fig.1

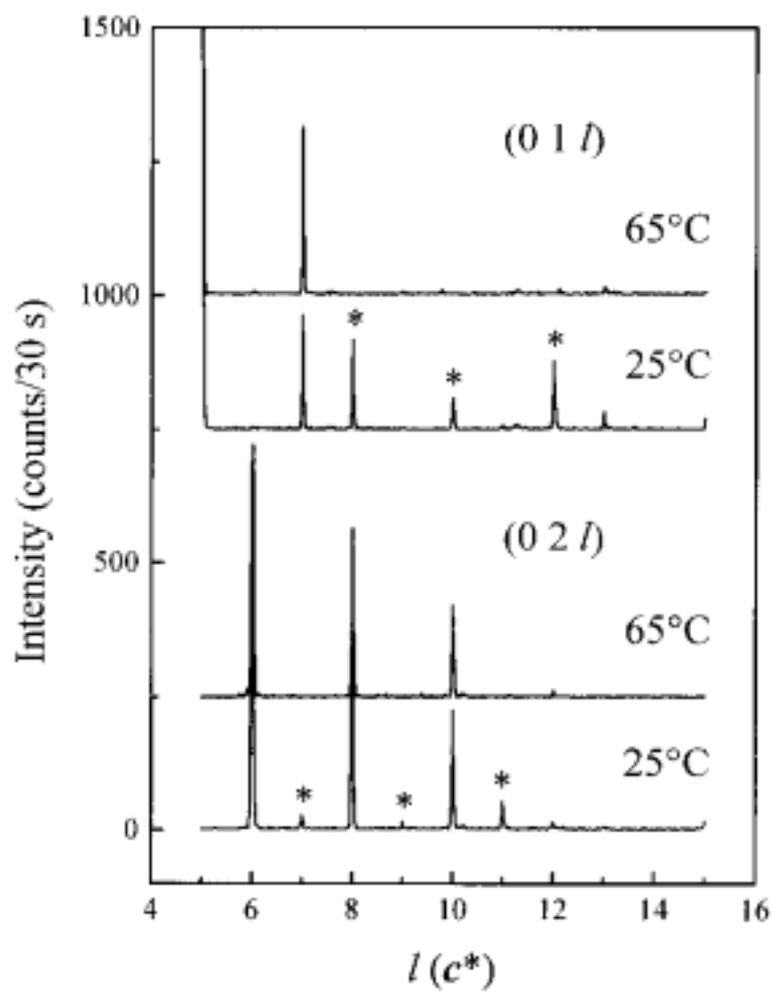
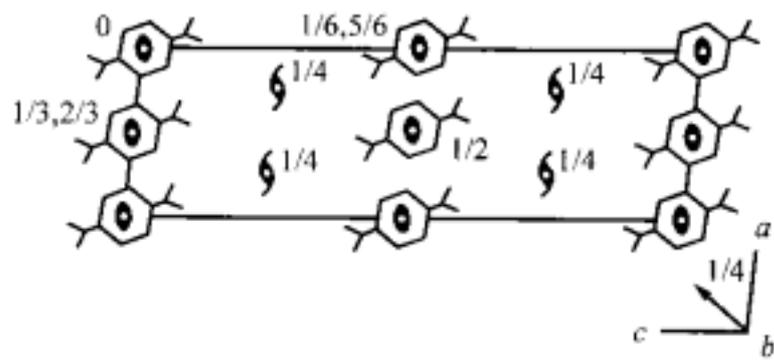


Fig.2

(a) $C2/m$



(b) $P2_1/n$

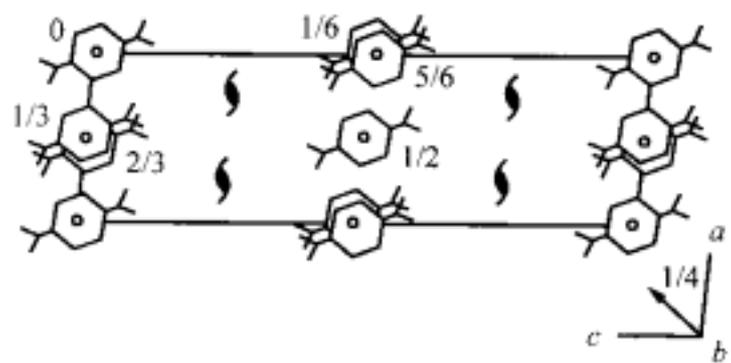


Fig. 3

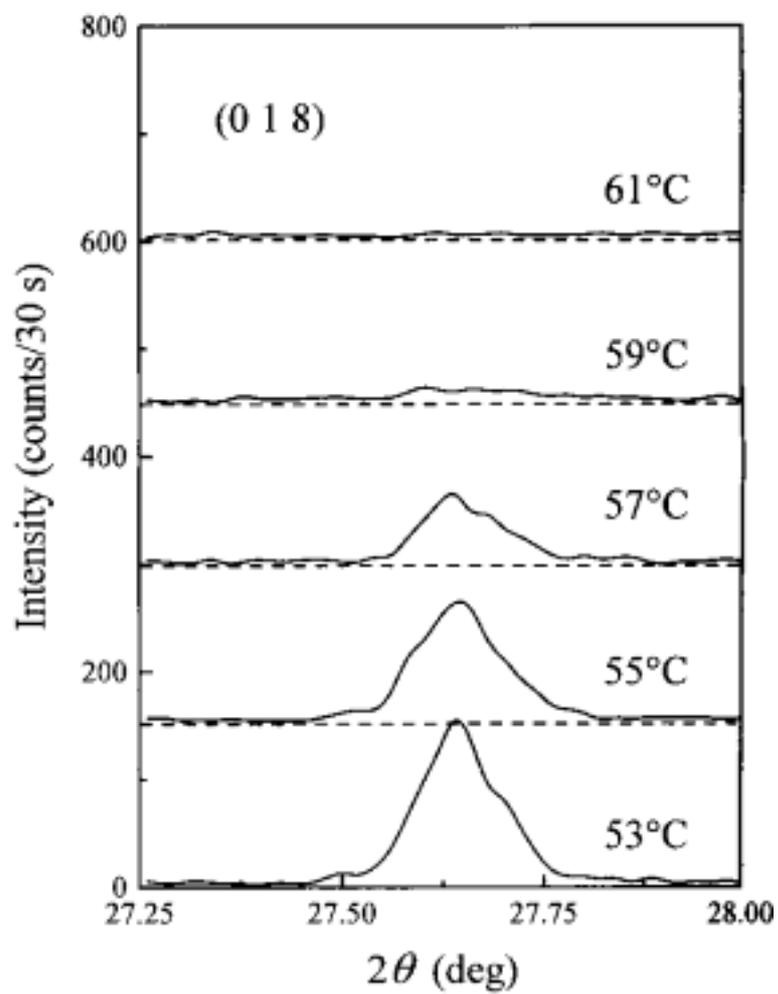


Fig. 4

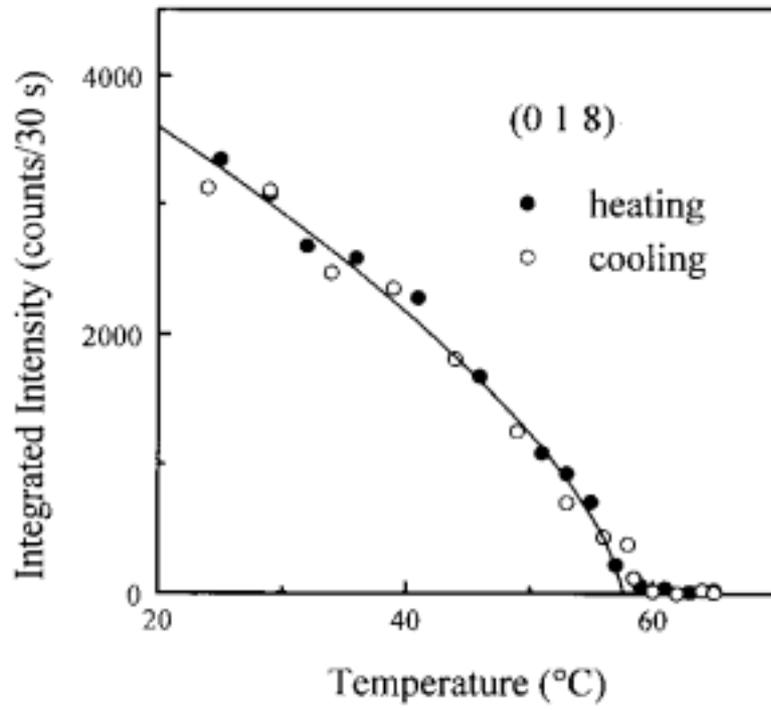


Fig. 5