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A Fully Ordered Phase of the Mixed Valency Complex of Trimethylamine with 7,7,8,8 Tetracyano-*p*-quinodimethane and Iodine

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In addition to previously described partially disordered crystals of TMA^+ $TCNQ^{2/3-}$ $(I_3^-)^{1/3}$ a fully ordered phase can be prepared by crystallization at room temperature or below. Its relation to the previously reported disordered phase is described. The occurrence of different degrees of disorder implies that measurements of physical properties such as electrical conductivity must be accompanied by X-ray characterization of these solids.

INTRODUCTION

Crystals of composition $(NMe_3H^+)\,TCNQ^{2/3-}\,(I_3^-)_{1/3}$ (≡I) (Me = methyl, TCNQ = tetracyano-*p*-quinodimethanide) have attracted considerable attention, as they have an unusual ternary composition with both the TCNQ and iodine forming segregated linear stacks, and a conductivity σ that is high at room temperature and strongly temperature-dependent.[1–5] In samples measured by Abkowitz *et al.* the conductivity is as large as 20 $(\Omega\ cm)^{-1}$ at 300 K, has a maximum at 230 K, and shows a transition (maximum in d ln σ/dT^{-1}) at 150 K.[2,3,5] Variations in conductivity behavior among different

crystalline samples have been reported, and conductivity-temperature ($\sigma(T)$) curves published by different authors show significant variations.[1,2]

We report here the existence of a new phase of I which has a fully ordered structure, unlike the crystals previously described in the literature which show diffuse layer lines in their diffraction pattern, and have a partially disordered structure.[6]

CRYSTAL GROWTH

Crystals were grown from acetonitrile (purified by distillation over P_2O_5) solutions as described by Abkowitz *et al.* (1977). When a concentrated solution was allowed to stand at room temperature or below fully ordered crystals were obtained, even if the solvent evaporated rapidly. Crystals with diffuse layer lines as described by Cougrand *et al.*[1] and by Filhol *et al.*[6] could only be prepared by evaporation of the solvent at an elevated temperature of about 60°C. Crystals obtained in this way tend to be smaller than those obtained at lower temperatures.

DESCRIPTION OF THE ORDERED CRYSTALS

The diffraction pattern of I consists of two lattices, the main (A) lattice being due to NMe_3H and TCNQ scattering, while the second (B) lattice, which corresponds to the previously observed diffuse lines, results from the scattering of the iodine atoms. The main structural features have been described in detail by Filhol *et al.* who found the structure to consist of separate TCNQ and iodine columns parallel to the *b*-axis of the space group C2/m, with the NMe_3H molecules linked by hydrogen bonding to the TCQN cyano groups.[6]

An oscillation photography parallel to the *b*-axis of the *A* lattice (b_A) shows that the *A* lattice has a mirror plane perpendicular *b*, as previously reported. But this plane is not present in the B lattice diffraction pattern, indicating the absence of mirror symmetry perpendicular to the column direction in the iodine lattice. The repeat period along the iodine columns, which we label c_B, equals 3/2 b_A, so that the $(hk3)_B$ layer coincides with $(h2l)_A$. Analysis of $(hk1)_B$, $(hk2)_B$, $(hk3)_B$ and $(hk4)_B$ Weissenberg photographs shows the *B* lattice to be pseudomonoclinic with its b axis parallel to $(104)_A$ and its *a*-axis in the $(001)_A$ plane but inclined to a_A by 17.6°, as illustrated in Figures 1a and 1b. Cell dimensions of both lattices are given in Table I.

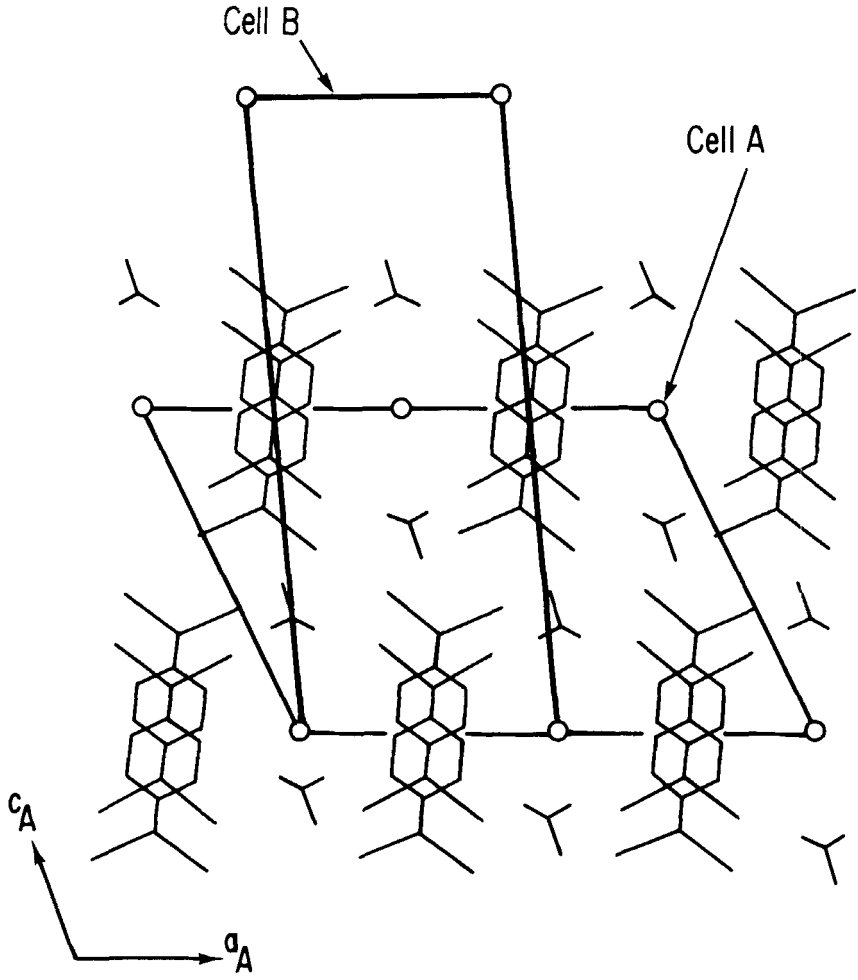

FIGURE 1a Relation between the iodine (B) and TCNQ (A) unit cells in the ordered phase. The projection along b_A is shown; heavy lines indicate the iodine unit cell. The iodine a axis is inclined relative to the plane of the paper, while the TCNQ axis is in the plane. Open circles indicate iodine columns.

The iodine unit cell contains two columns, one at $(00z)_B$, and one in the center of the cell at $(1/2\ 1/2\ z)_B$. Relative to the TCNQ stacks the column at $(10z)_B$ is shifted by one TCNQ spacing with respect to its symmetry equivalent at $(00z)_B$. Some of the TCNQ molecules are at the same height as I—I bonds in both iodine columns which border each TCNQ stack, while others are next to one bond and an intermolecular gap between I_3^- ions (Figure 1b). If we label these arrangements X and Y respectively the sequence

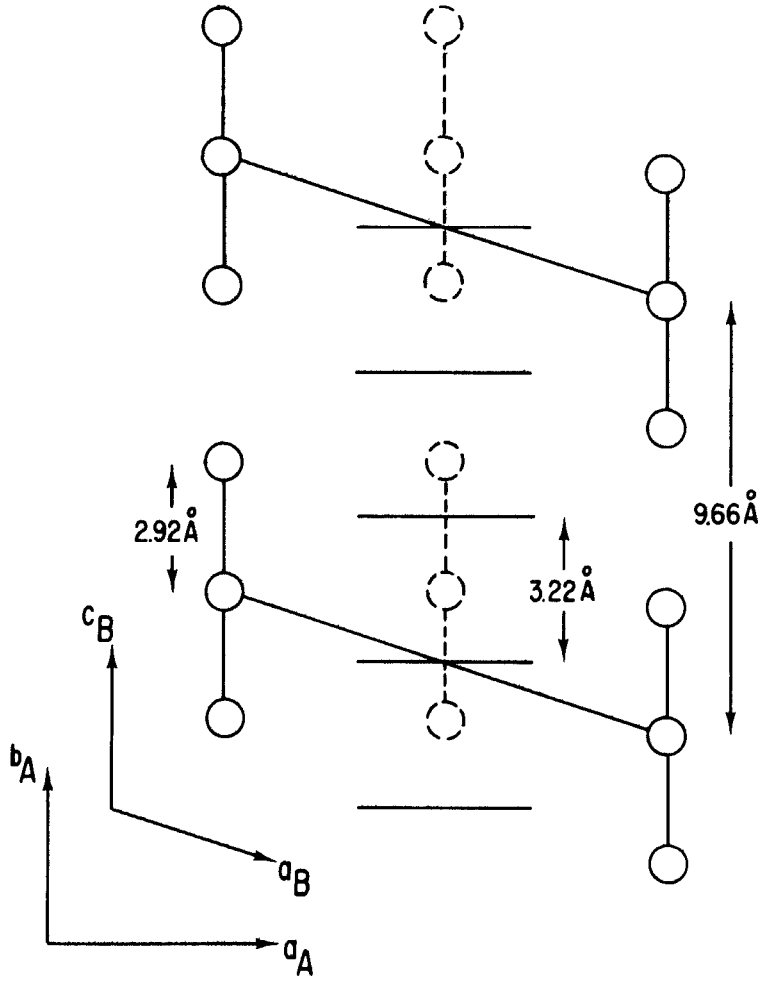

FIGURE 1b Relation between the iodine and TCNQ cells in the $(ab)_A$ plane. Dotted iodine columns are at $(1/2\ 1/1\ z)_B$. The iodine-iodine distance is as given in Ref. 6.

may be described as $XYYXYYXYY\cdots$, representing the three fold increase in periodicity along the columns in the crystal's supercell.

The position of the iodine atoms at $(1/2\ 1/2\ z)_B$ may be derived from the observed intensities. In the indexing of the iodine lattice the $(hk3)_B = (h2l)_A$ layer shows the reflections with $h + k = 2n + 1$ only, indicating a displacement of the columns at $(1/2\ 1/2\ z)_B$ of 1/6, 1/2 or 5/6 with respect to the column at the origin. But in $(hk4)_B$ both the $h + k = 2n + 1$ and $2n$ parity groups are present, with much larger intensities for the former group. This rules out a

TABLE I

Cell dimensions of NMe_3H TCNQ (= *A*) and iodine (= *B*) lattices

	A[a]	*B*[b]
a	20.304(2)Å	10.65
b	6.437(1)	25.18
c	13.887(2)	9.66
α	90°	90°
β	115.2(1)	107.6
γ	90	93.6
V	1642 Å^3	2464 Å^3

[a] As determined from the centering of 24 reflections on an automatic X-ray diffractometer.

[b] Calculated from the geometrical relationship to the A lattice.

displacement of $1/2c_B$ which would have imposed the condition $h + k = 2n$ only. It follows that columns at $(00z)_B$ and $(1/2\ 1/2\ z)_B$ are related by $\Delta z = +1/6$ (which is equivalent to $\Delta z = -1/6$), as illustrated in Figure 1b.

DISCUSSION

Since the TCNQ molecules bear a negative charge of 2/3e the one-dimensional band is only 1/3 filled. It has been argued that the perturbing potential exerted by the iodine chains, which have triple the periodicity, leads to a narrow gap semiconductor.[2–5] Any perturbation of the $XYYXYYXYY\cdots$ sequence periodicity in the iodine columns, such as occurs due to disorder, may therefore alter the electrical properties of the crystals.

In the disordered crystals described by Filhol *et al.* short-range ordering along the a_A axis exists with a coherence length of 150 ± 40Å.[6] This coherence length is likely to vary from specimen to specimen and it does indeed go to infinity for the fully ordered crystals. Thus the perturbing influence of the iodine atoms on the TCNQ stacks may itself be sample dependent and physical properties may consequently vary somewhat from sample to sample. The variation in the diffraction pattern therefore offers a likely explanation for the previously observed variation in the $\sigma(T)$ behavior of different samples. Thus, for example, the variation in the temperature dependence of the dc conductivity may be reflecting a change in the magnitude of the semiconductivity energy gap between ordered and disordered crystals,[7] as well as a change in the temperature dependence of the mobility[8,9] due to additional scattering from the (random) potentials.

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