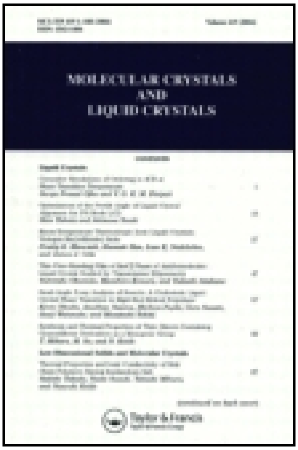

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Crystal Field Effects, Interchain Charge Transfer and the Phase Transition of DMTM$(TCNQ)_2$

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CRYSTAL FIELD EFFECTS, INTERCHAIN CHARGE TRANSFER AND THE PHASE TRANSITION OF DMTM(TCNQ)$_2$

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Abstract Preliminary structural data for the low temperature phase of the pseudo one-dimensional conductor DMTM(TCNQ)$_2$ strongly indicate, that the peculiar converse changes in electrical behaviour of this compound at T_c = 272K should be attributed to crystal field effects. The loss of monoclinic symmetry at T_c, most probably accompanied by an ordering of the DMTM cations, affords an inequivalent crystal potential at successive sheets of TCNQ ions. The potential difference reduces the energy gap for electron transfer in a lateral direction between the successive sheets.

INTRODUCTION

In the past decade, the study of the relations between crystal structure and physical properties of a series of alkyl-substituted (thio)morpholinium(TCNQ)$_2$ complexes, has concentrated on the Peierls transition encountered in several of these compounds [1,2]. The general picture is that, on cooling from a high temperature metallic phase, a $4k_F$ or electronic Peierls transition to a semiconducting phase will occur, whereas at lower temperatures a $2k_F$ or spin Peierls transition may be expected, below which the spin susceptibility gradually drops to zero. Recently, Oostra [3] has described the remarkable electrical properties of DMTM(TCNQ)$_2$ (DMTM = N,N-dimethyl-thiomorpholinium). This compound shows, on cooling through a phase transition at T_c = 272K, a tenfold increase in electrical conductivity, whereas the activation energy drops from 0.25 eV to 0.03 eV. The present note describes a tentative explanation for this puzzling behaviour.

EXPERIMENTAL

1. Behaviour at the transition

The electrical conductivity of DMTM$(TCNQ)_2$ as a function of temperature is shown in Fig. 1. The transition point was determined both from the conductivity measurements and from changes in the X-ray diffraction pattern. In both cases some hysteresis was found, indicative for the first order character of the transition. For the respective methods, T_c was found to be 267K and 268K on cooling, and 277K and 274K on heating. The crystal quality is remarkably little affected by the transition, which is a rare phenomenon for a (first order) phase transition.

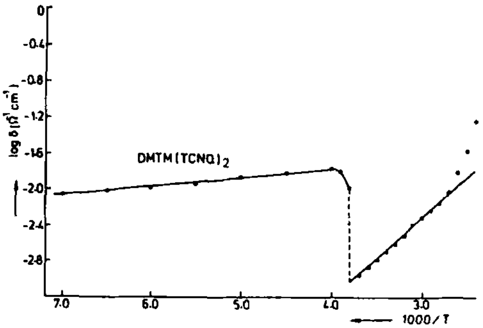

FIGURE 1

Electrical conductivity of DMTM$(TCNQ)_2$

2. Crystal structure above T_c

The structure of DMTM$(TCNQ)_2$ at room temperature was determined from X-ray diffraction data. Crystal data are given in Table 1; fig. 2 shows a projection of a structure along a. Full structural details will be published elsewhere.

The structure is isomorphous with that of DMM$(TCNQ)_2$ at room temperature (DMM = N,N-dimethyl-morpholinium) [4]. The DMTM groups are located at mirror planes, which implies the occurrence of static or dynamic disorder over (at least) two positions related by these planes. The TCNQ stacks are dimeric. As described for DMM$(TCNQ)_2$ [4] the structure is built up from

TABLE 1. Crystal data of high and low temperature phases of DMTM(TCNQ)$_2$ with standard deviation in parentheses.

	above T_c		below T_c
crystal system	monoclinic		triclinic
space group	$P2_1/m$		$P\bar{1}$
temperature (K)	294	273	264
a (Å)	7.846(3)	7.845(1)	7.853(1)
b (Å)	27.051(14)	26.948(8)	27.293(4)
c (Å)	7.914(3)	7.911(2)	7.924(1)
α (°)	90	90	80.44(2)
β (°)	55.56(3)	55.42(2)	55.24(1)
γ (°)	90	90	80.52(1)
V (Å^3)	1385	1377	1371

sheets of parallel TCNQ stacks, between which the DMTM's are located. From Table 1 it is seen, that a 273K, just above the phase transition, only the cell parameters b and β have decreased significantly, whereas a and c have remained the same within the experimental error.

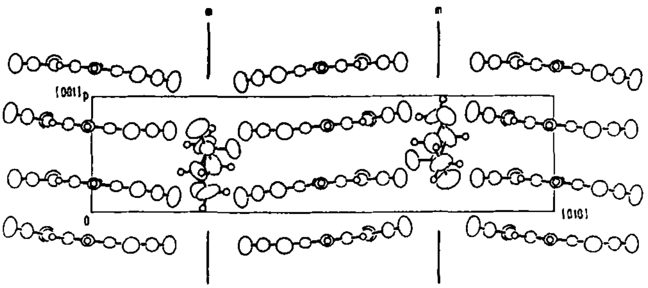

FIGURE 2. Projection of the room temperature crystal structure of DMTM(TCNQ)$_2$ along the unit cell a-axis. Mirror planes are denoted by m.

3. Crystal structure below T_c

At the phase transition the crystals get twined, which has hampered a complete crystal structure determination of the low temperature phase so far. The unit cell parameters below T_c, however, allow some tentative conclusions. Table 1 shows, that the transition hardly affects the unit cell a, c plane, indicating that the geometry of the TCNQ sheets does not undergo essential changes. Also the length of the b-axis remains almost the same. The essential change at the transition is a lowering of the symmetry from monoclinic to triclinic, caused by a rotation of the b-axis relative to the a, c plane by about 10°. The loss of monoclinic symmetry implies that below T_c the mirror planes (and the 2_1 axes) have disappeared. Successive sheets at b=0 and b=½ are no longer crystallographically equivalent, and are shifted somewhat with respect to each other.

DISCUSSION

As mentioned above, the presence of mirror planes above T_c implies disorder of the DMTM groups. It is reasonable to assume, that the loss of mirror symmetry at low temperatures is caused by an ordering of these groups. In this respect it is noted that the isomorphous compound DMM$(TCNQ)_2$ shows ordering of the cations at 260K, albeit with completely different structural changes [5]. In DMTM$(TCNQ)_2$ the inversion centres in the sheets are probably retained since the sheet structure remains practically the same. Irrespective of whether the space group is $P\bar{1}$ or P1, however, sheet A at b=0 and sheet B at b=½ are no longer equivalent, but surrounded in a different way by DMTM groups. The different situations are schematically illustrated in the upper drawings of Fig. 3. The presence of inequivalent stacks in DMTM$(TCNQ)_2$ was also concluded from the magnetic susceptibility [3].

As a consequence of their inequivalent surroundings, the sheets are subject to a different crystal potential. In the high

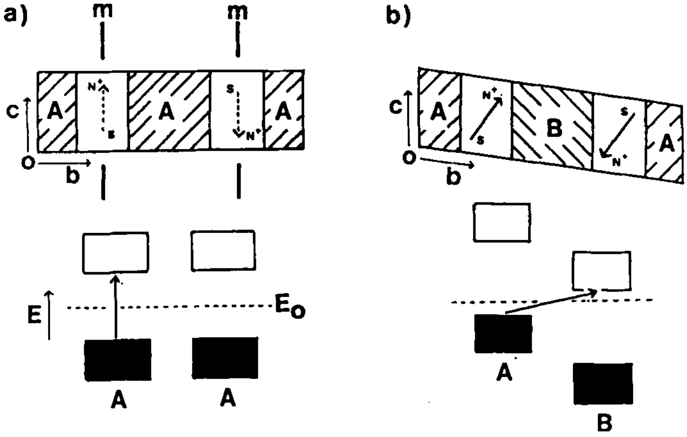

FIGURE 3. Schematic drawing of the structures of DMTM(TCNQ)$_2$ and of the energy levels of the TCNQ stacks. a) above T_c, b) below T_c. The (dotted) arrows in the upper drawings denote the (average) S→N directions of the DMTM groups. A and B refer to the different types of TCNQ sheets. Arrows in the lower drawings represent the smallest energy excitations.

Hubbard U limit, the dimerization of the TCNQ-chains in this $\frac{1}{4}$-filled band system, gives rise to full 'valence' and empty 'conduction' bands, rendering the chains non-conductive. The crystal potential shifts the bands, thereby reducing the gap between the valence band of one sheet and the conduction band of the other. For DMTM(TCNQ)$_2$ this shift, causing the reduction of the activation energy at T_c from 0.25 to 0.03 eV, is schematically illustrated in Fig. 3. It is interesting to note that if the shift is larger than the gap of the separate chains, electrons are spontaneously transferred to the lowered conduction band, thus allowing them to move and give a considerable contribution to the temperature independent conductivity.

The above crystal field arguments nicely account, at least qualitatively for the peculiar conductivity behaviour of DMTM(TCNQ)$_2$. It is suggested, that alternations of the crystal field are also responsible for the anomalous spin susceptibility behaviour observed in other TCNQ-salts [6,7]. Further evidence for the present propositions can probably be obtained from the full low temperature crystal structure of DMTM(TCNQ)$_2$, which is currently in progress. Independent of those results, however, the possibility of special effects connected with alternations in the crystal fields seems to be a challenging and as yet overlooked feature in the study of TCNQ salts. Particularly, because semimetallic behaviour is to be expected if the shifts of the energy bands are large enough. In any case, the recognition of these effects emphasizes the importance of laterally extended interactions in compounds with an alleged one-dimensional character.

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