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Suppression of the Peierls Transition in MEM(TCNQ)$_2$ Through Doping With METM

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SUPPRESSION OF THE PEIERLS TRANSITION IN MEM(TCNQ)$_2$ THROUGH DOPING WITH METM

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Abstract Results of d.c-conductivity and X-ray measurements on a series of (METM)x (MEM)1-x (TCNQ)$_2$ salts are presented. It is found that on adding METM the $4k_F$-phase transition temperature drops fast. A tentative interpretation is given in terms of the (thio-) morpholinium group.

INTRODUCTION

One point of interest in the quasi-one-dimensional compounds is the Peierls distorted phase, present in many of these compounds. In this paper we present experimental results, which shed some light on the role played by the counterions in determining the stability of this phase.

D.C.-CONDUCTIVITY

For (METM)x (MEM)1-x (TCNQ)$_2$ salts, for a number of values for x, the d.c.-conductivity has been measured as a function of temperature. In figure 1 graphs of the conductivity versus T^{-1} are given. Clearly visible is the $4\ k_F$ transition, manifested by achange in conductivity of several orders of magnitude at some, x-dependent, temperature. From figure 1 several conclusions can be drawn. On increasing x, the transition temperature, T_c, drops fast. In the

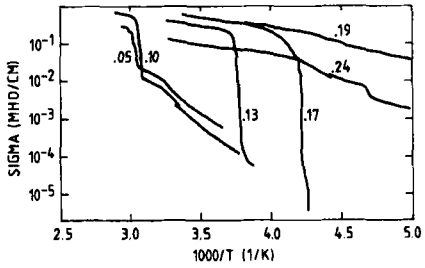
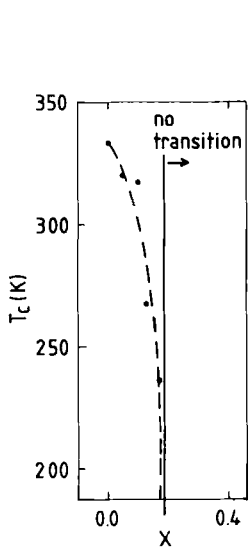


FIGURE 1 The d.c. conductivity as a function of temperature for (METM)x (MEM)1-x $(TCNQ)_2$ for x = .05 .10 .13 .17 .19 and .24

samples with x = .19 and x = .24 as well as in pure $METM(TCNQ)_2$ no transition can be detected. The transition temperature as a function of x is given in figure 2. At larger values of x a precursor effect of the phase transition is observed as a bending downwards of the conductivity versus 1/T curve. At small values of x no precursor effect is observed. On increasing x the precursor effects become more pronounced.

X-RAY MEASUREMENTS

For a number of samples the lattice parameters were determined from eighty to hundred high-order reflections, measured on a Nonius CAD4 diffractometer. From these values the unit-cell volume was calculated. The latter quantity is given, as a function of x, in figure 3. The most remarkable result is that the cell-volume is independent of the composition of the crystals, whereas the difference in occupied space by sulfur atom and an oxygen atom is about 15 $Å^3$.



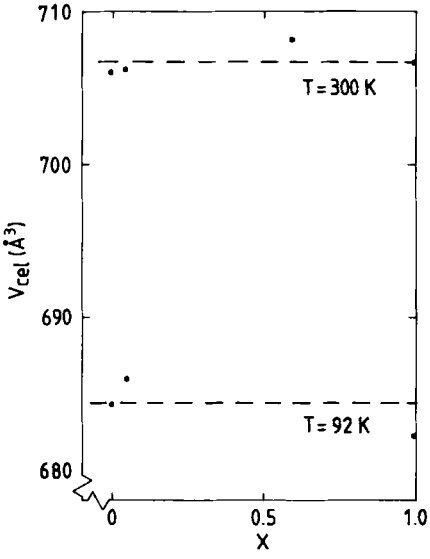


FIGURE 2 The transition temperature of the 4 k_F Peierls transition as a function of x.

FIGURE 3 The unit-cell volume at T = 92 K and at T = 300 K as a function of x.

For a pure MEM(TCNQ)$_2$ it follows from a structural X-ray analysis[1] and from NMR experiments[2] that the morpholinium group is dynamically disordered. A unit-cell containing only one formula unit sufficies to describe the structure (figure 4). The X-ray analysis of METM(TCNQ)$_2$[3] shows that the thiomorpholinium group is ordered. The ordering is such, that the sulfur atoms of successive molecules along b are directed in opposite direction. Thus, a unit-cell with a doubled b-axis is now necessary (figure 4).

The X-ray analysis of the composite crystals show that for small x the morpholinium group is still completely disordered. Somewhere at x = .16 the additional reflections of the METM cell appear,

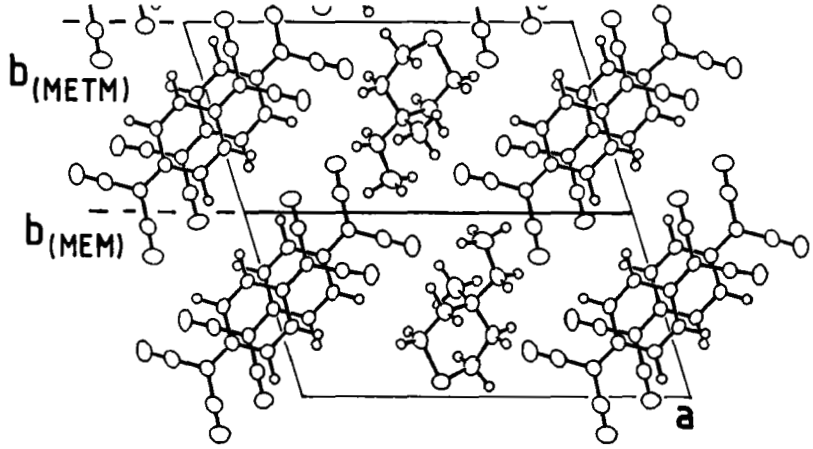


FIGURE 4 Projection of the structure along c, showing the MEM and the METM unit cell. This figure shows the kations in the ordered (METM) state.

indicating an ordering of the (thio-)morpholinium group.

DISCUSSION

The results presented in this paper can be summarized as follows. (METM)x (MEM)1-x $(TCNQ)_2$ crystals have a 4 k_F Peierls transition of which T_c drops fast with increasing x, to disappear at about at x = 0.18. X-ray and NMR measurements show a dynamically disordered morpholinium group for x = 0[1,2]. On increasing x the ordering of the (thio-)morpholinium group starts at x = .16 to reach completeness at x ≈ .20. These results give strong evidence for the following interpretation.

In strict one-dimensional systems there is no dimerized state, only fluctuations are present[4]. Introducing a three-dimensional coupling of the lattice makes a dimerized state possible; below a certain transition temperature the chain is dimerized, above this temperature it is uniform. The magnitude of the transition temperature depends exponentially on the negative of the phonon frequency.

In pure MEM(TCNQ)$_2$ the morpholinium group is dynamically disordered. This means that there is empty space in the crystal between the stacks and, therefore, that the three dimensional coupling is weak. For MEM(TCNQ)$_2$ the transition temperature is high, at about 340 K. As the empty space of MEM(TCNQ)$_2$ is filled by the METM ions the structure becomes more rigid and the three-dimensional coupling is increased. Keeping in mind that most of the 4 k_F and 2 k_F transitions occur through lateral motions of the TCNQ ions[5,6], it can be concluded that the formation of the 4 k_F soft phonon is suppressed and the transition temperature is lowered. Apparently, at $x \approx .20$ the structure has become so rigid that a 4 k_F transition does not take place anymore.

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