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First Order Phase Transition in Methyldiethylcyclohexylammonium (MDCA) (TCNQ)

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The title compound undergoes a first order phase transition at 370 K. The electrical and magnetic behaviours are consistent with a structural change from a highly dimerized structure at low temperature to a more regular one.

I INTRODUCTION

Phase transitions in quasi-one-dimensional materials are of considerable current interest.[1] In this paper we report experimental determination on a first order phase transition observed in a TCNQ (tetracyanoquinodimethane) salt with methyldiethylcyclohexylammonium (MDCA) cation. The crystal structure has been determined at room temperature.[2] The TCNQ entities stack in the usual chain-like fashion with two interplanar distances, respectively 3.22 and 3.46 Å. There is no close contact between the chains, so as the structure can be considered quasi-one-dimensional.

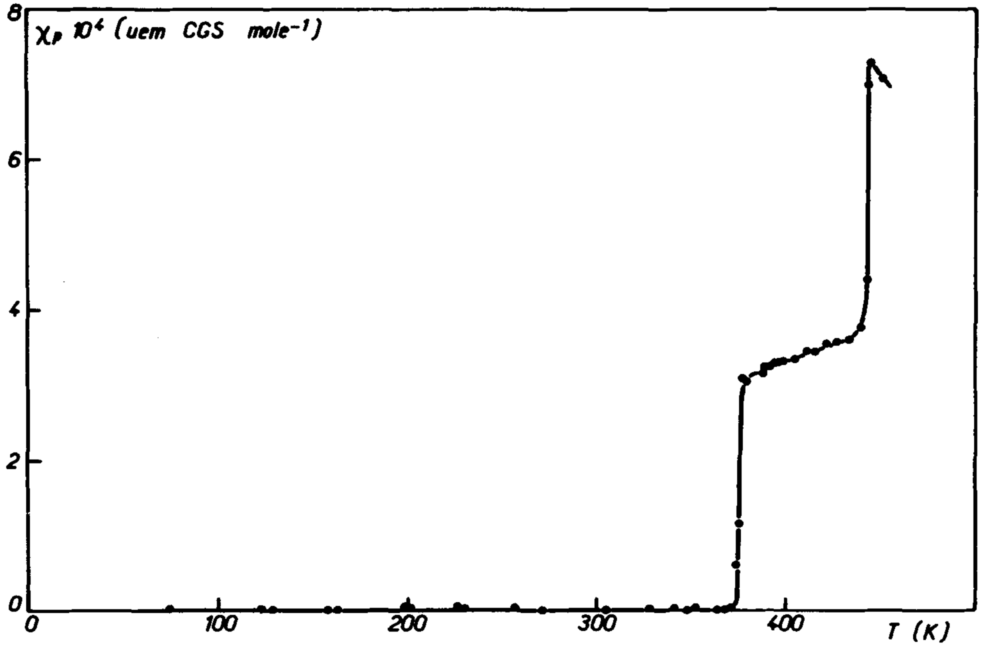

FIGURE 1 Temperature dependence of paramagnetic susceptibility.

II EXPERIMENTAL RESULTS

1 Magnetic susceptibility

The first evidence of the occurrence of phase transition was given by static and dynamic (EPR) magnetic susceptibility measurements. Figure 1 shows the thermal behaviour of paramagnetism measured by the Faraday's method and after subtracting the core diamagnetism calculated from Pascal's constants. Two discontinuities of χ_p appear clearly, corresponding to two successive phase transitions at about 370 K and 430 K, the second one being close to the decomposition temperature. Both transitions are reversible.

2 Calorimetric measurements

D.S.C. measurements gave the following values of the enthalpy of transition:

$$\Delta H_{370\,\mathrm{K}} = 6600 \pm 300 \text{ cal/mole} \quad \text{and} \quad \Delta H_{430\,\mathrm{K}} = 250 \pm 30 \text{ cal/mole}$$

The thermal variation of specific heat C_p measured by adiabatic calorimetry is shown in Figure 2. At about 370 K a jump of specific heat occurs which confirms the nature first order of the transition. Such a C_p-jump was already found for Diethylcyclohexylammonium $(TCNQ)_2$ which undergoes a first order phase transition at 347 K.[6] The second transition could not be observed because of the sublimation of the compound and we will no longer consider it in this paper.

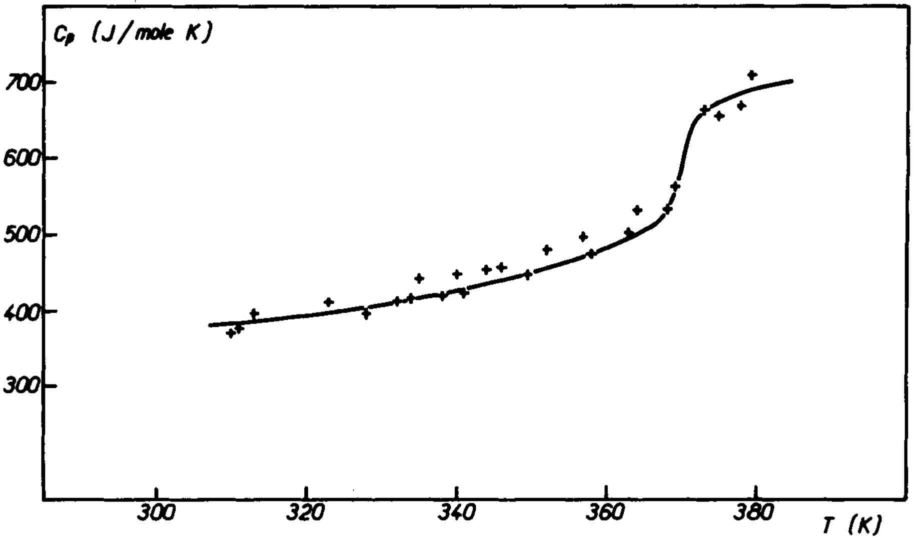

FIGURE 2 Temperature dependence of specific heat.

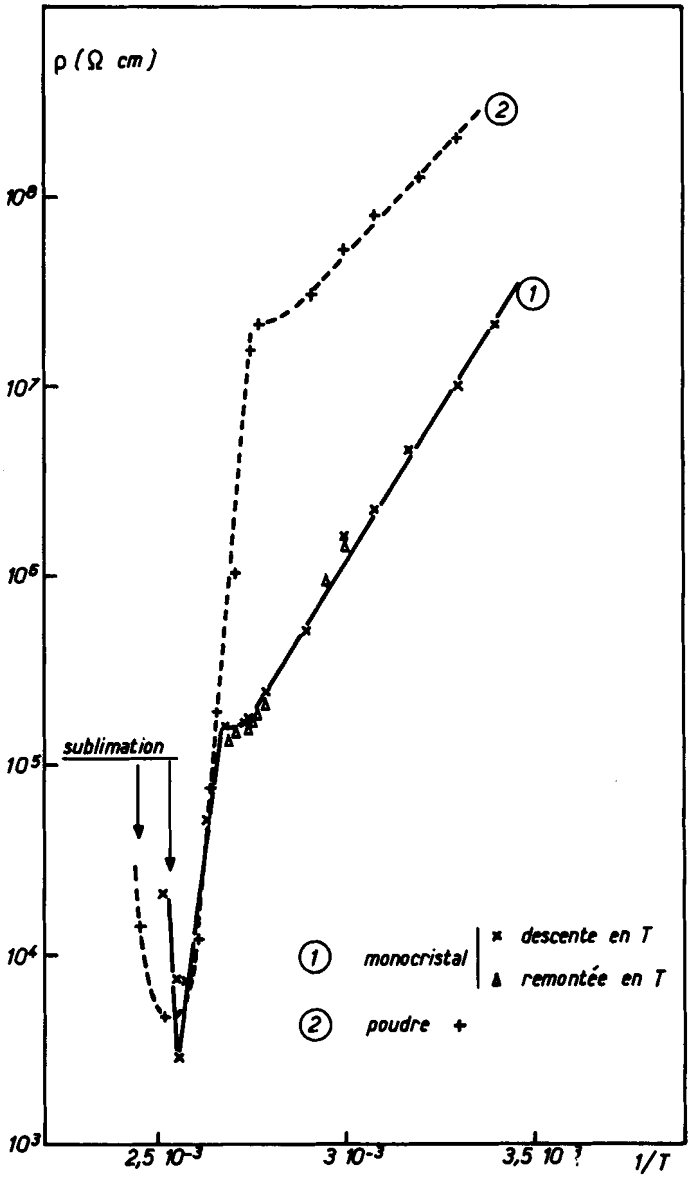

FIGURE 3 Variation of the resistivity with reciprocal temperature.

3 d.c. Electrical conductivity

The variation of the d.c. resistivity with reciprocal temperature is shown in Figure 3 for a single crystal (curve 1) and compressed powder (curve 2). The room temperature phase exhibits a semi-conducting behaviour with an activation energy of about 0.3 eV. At the transition a sudden rise of the conductivity occurs.

4 Low frequency electrical conductivity and dielectric permittivity

Figure 4 represents the measured conductivity σ_{me} versus the frequency f (in logarithmic scale) for temperature ranging from 321 K to 430 K. This frequency dependence of σ is similar to those found in other TCNQ salts.[3]

The permittivities have been measured with the sample being inserted between the plates of a condenser belonging to a resonant circuit. The real part ε' is frequency independent at constant temperature, taking into account

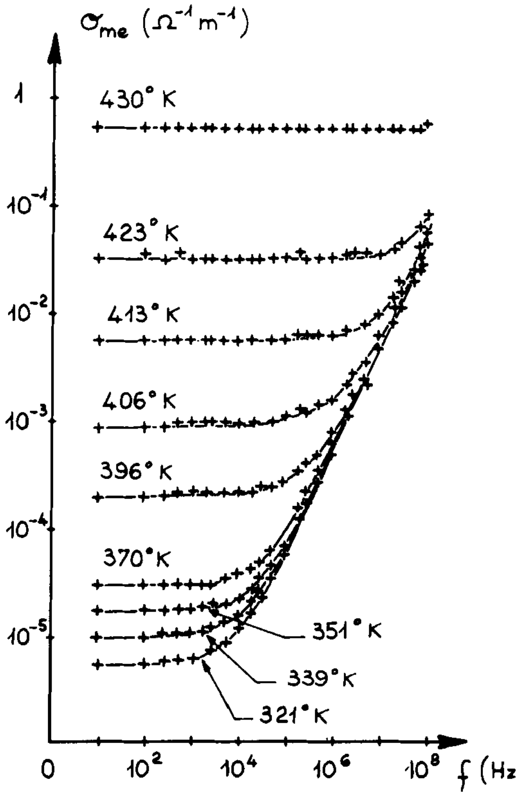

FIGURE 4 Double logarithmic plot of the measured conductivity σ_{me} vs. the frequency.

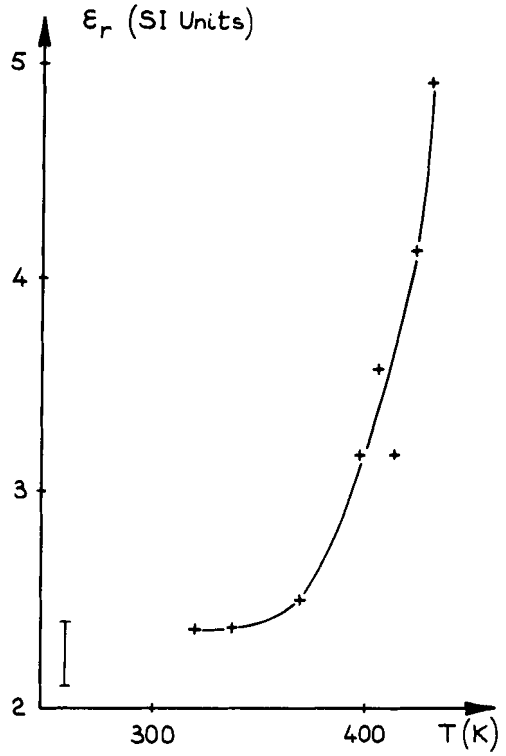

FIGURE 5 Variation of the relative permittivity ε_r with temperature.

the inaccuracy of the measurements. The relative permittivity ε_r shows a sharp increase after the transition (Figure 5). As for the imaginary part of the permittivity, the variation of $\log(\omega\varepsilon'')$ versus $\log f$ is shown on Figure 6 with ω being the angular frequency. We found that $\varepsilon'' \alpha \omega^n$, where n is an empirical exponent depending on temperature.

III ANALYSIS OF THE RESULTS

The magnetic behaviour before and after the transition may be interpreted by assuming a singlet ground state and a paramagnetic excited triplet state. Indeed EPR spectra of the low temperature phase showed the line splitting characteristic of triplet excitons. The splitting caused by the dipole–dipole interaction of the electrons in the triplet state, can be described in the principal axis system by the Hamiltonian:

$$H_{d-d} = DS_z^2 + E(S_x^2 - S_y^2) \qquad (1)$$

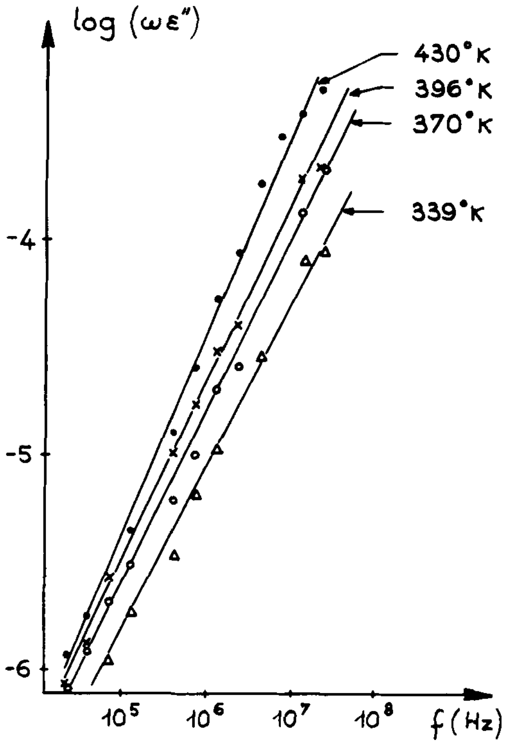

FIGURE 6 Double logarithmic plot of $\omega\varepsilon''$ vs. the frequency.

where D and E are the zero-field splitting (ZFS) parameters and S_x, S_y, S_z are the spin components of the triplet state. D and E and the orientation of the ZFS principal axes (X', Y', Z') can be determined from single crystal measurements of the angular dependence of the doublet splitting d about three mutually perpendicular axes (X, Y, Z). Chesnut[7] has shown that d may be written as:

$$d = C_1 \cos^2 \Phi + C_2 + C_3 \sin \Phi \cos \Phi \tag{2}$$

where: $C_1 = 3D \sin^2 \theta - 3E \cos 2\Psi(1 + \cos^2 \theta)$

$C_2 = -D + 3E \cos 2\Psi$

$C_3 = 6E \sin 2\Psi \cos \theta$

where θ, Ψ and Φ are the Eulerian angles describing the orientation of the principal axes (X', Y', Z') relative to the laboratory coordinate system (X, Y, Z). The results are shown in Figure 7. The curves calculated from expression (2) (solid lines) lead to $|D| = 146$ G and $|E| = 13$ G and to the directions of principal axes shown in Figure 8 relative to the TCNQ stacking.

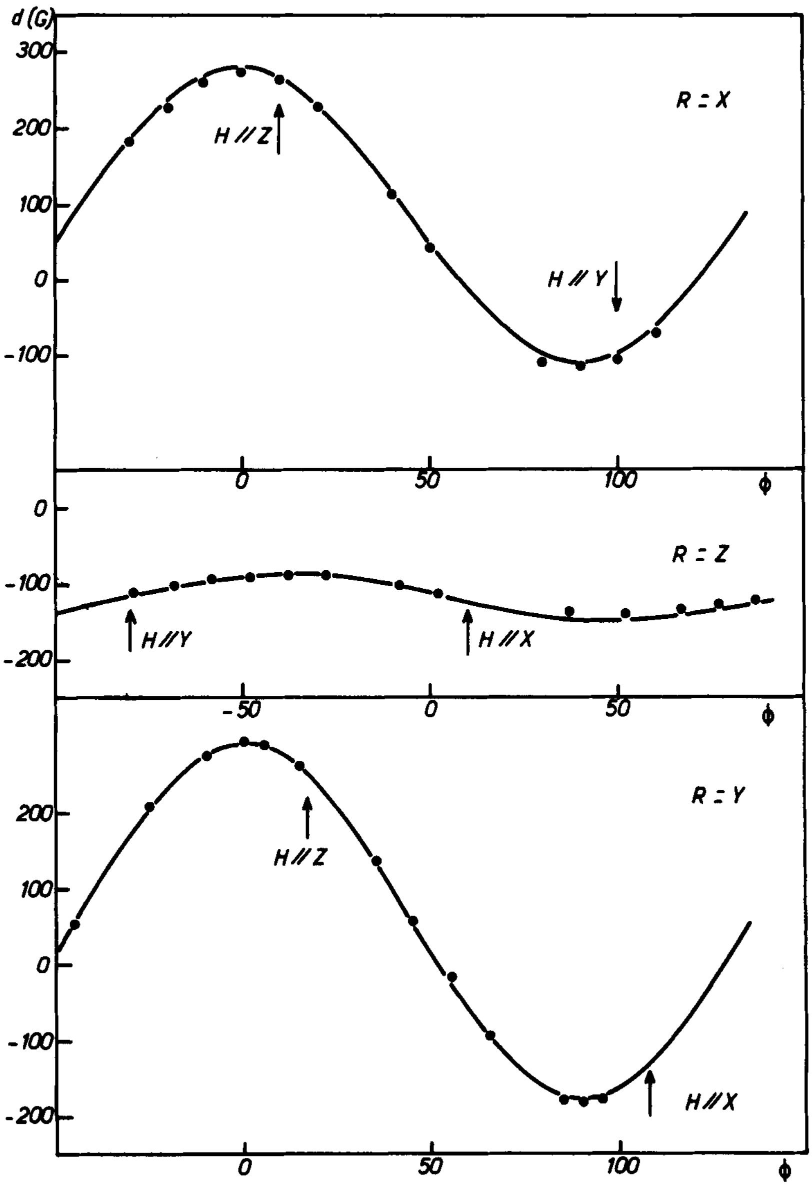

FIGURE 7 Angular variation of the doublet separation d measured at room temperature about each rotation axis R. Points are experimental, solid lines are the fittings with Eq. (2).

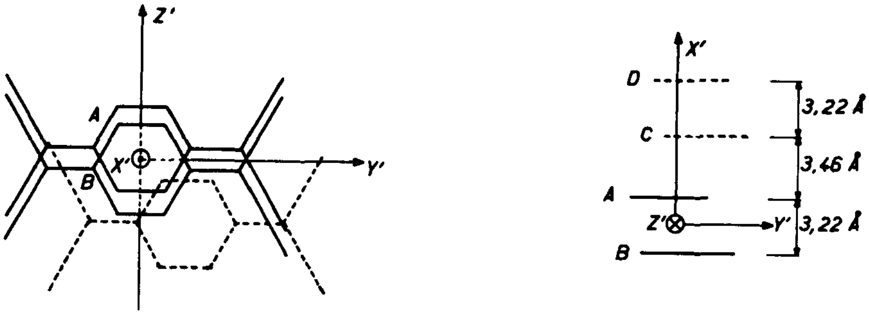

FIGURE 8 Orientation of the fine structure principal axes relative to the TCNQ stacking.

These D and E values are comparable to those found in other TCNQ salts of 1:1 stoichiometry and may be accounted for, given the crystal structure and the spin distribution on TCNQ$^-$ anion radicals.[8]

So, the triplet character of the magnetic excitations being evidenced, the paramagnetic susceptibility must obey the singlet–triplet law:

$$\chi_p = \frac{Ng^2\mu_B^2 S(S+1)}{3\,\mathrm{kT}} \frac{3}{3+\exp(J/\mathrm{kT})}$$

where $S = 1$, J is the energetic distance between the singlet and triplet levels and the other symbols have their usual meaning. From the temperature dependence of χ_p one gets the following values of J: 0.20 eV and 0.07 eV respectively before and after the phase transition.

The magnetic behaviour is coherent with the crystal structure of the low temperature phase which consists of quasi isolated TCNQ$^-$ dimers (diads) comparable to supermolecules with two unpaired electrons. The structure of the high temperature phase is not known but the decrease of the magnetic gap must be due to an increase of the interplanar distance into the diads.

Similarly the poor conductivity below the transition is well understood given the structure: the interdiad distance is high (3.46 Å) and the interdiad molecular overlap is not favorable to a good conductivity. The increase of the conductivity at the transition could be due to a more regular structure or to a better overlap of TCNQ molecules.

The frequency behaviour of conductivity may give further insight in the conduction mechanism. The experimental results of Figure 4 are correctly represented by a theoretical function used in a previous paper:[4]

$$\sigma_{me} = \left[(\sigma_0 + A\omega^s)^2 + \left(A\omega^s \tan\left(\frac{s\Pi}{2}\right) + \varepsilon\omega\right)^2\right]^{1/2}$$

Where A is a proportionality factor coming from empirical equations proposed by Pollak and Geballe,[5] s is an adjustable parameter and ε the real part of the dielectric permittivity. The fitting of the data by this expression (solid lines in Figure 4) leads to *s* values close to 0.8 whatever the temperature. This fact together with the good agreement between theory and experiment suggest that a significant part of the conductivity occurs by hopping conduction between localized states. This conduction mechanism does not seem affected by the phase transition at 370 K.

Acknowledgement

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References

1. See for example: Lecture Note in *Physics*, vol. 65, Springer Verlag, Berlin, 1977.
2. D. Chasseau, J. Gaultier, and C. Hauw (to be published).
3. J. C. Giuntini, D. Jullien, and J. V. Zanchetta, Proceedings of the 4th international symposium on the organic solid state, Bordeaux, 1975; I. F. Shchegolev, *Phys. Stat. Sol.* (a), **12**, 9 (1972).
4. J. C. Giuntini, D. Jullien, J. V. Zanchetta, F. Carmona, and P. Delhaes, J. Non Cryst. Solids (in press).
5. M. Pollak and T. H. Geballe, *Phys. Rev.*, **122**, 1742 (1961); N. Kumar and J. Heinrichs, *J. Phys. C.*, **9**, 2331 (1976); A. K. Jonscher and M. S. Frost, *Thin Solid Films*, **37**, 267 (1976).
6. S. Flandrois, P. Delhaes, J. C. Giuntini, and P. Dupuis, *Phys. Letters A*, **45**, 339 (1973).
7. D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).
8. S. Flandrois and J. Boissonnade, *Chem. Phys. Letters*, **58**, 596 (1978).