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Molecular-motion-induced order-disorder transition in MEM(TCNQ)$_2$

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In this paper we present and discuss proton NMR results on N-methyl-N-ethyl-morpholinium tetracyanoquinodimethanide [MEM(TCNQ)$_2$]. Between 280 and 320 K the MEM molecules show an order-disorder transition due to flipping of the MEM ions over 180°, causing an anomalous increase in the conductivity. At the 335-K phase transition to the metallic state, a rotation of the MEM ions, probably about the N$-$O axis, sets in. The entropy change due to this rotation plus that due to the added electronic degrees of freedom is in reasonable agreement with specific-heat data.

I. INTRODUCTION

The quasi-one-dimensional compound N-methyl-N-ethyl-morpholinium-ditetracyanoquinodimethanide [MEM(TCNQ)$_2$] has been extensively studied because of its interesting physical properties.[1] Two phase transitions are observed, one at 19 and another at 335 K, which can be characterized as a $2k_F$ and a $4k_F$ transition, respectively. The 19-K second-order phase transition has been studied extensively with neutron diffraction,[2] diffuse x-ray scattering,[2] magnetic susceptibility,[1,3] and specific-heat measurements.[3] All the data are consistent with a spin Peierls transition below which the TCNQ chains are tetramerized resulting in a singlet electronic ground state.[3] In the intermediate temperature range ($19 < T < 335$ K) the TCNQ chains are strongly dimerized,[4] giving rise to one-dimensional Heisenberg antiferromagnetic behavior for the susceptibility[1,3] and semiconducting electrical properties.[5] Both these properties indicate a large on-site Coulomb repulsion (U) relative to interdimer bandwidth as discussed in Ref. 6. At the 335-K first-order phase transition the dc and microwave conductivity jump by three orders of magnitude to a value of 30 $(\Omega\,\mathrm{cm})^{-1}$ and become temperature independent.[5] The susceptibility shows a small decrease[1]($\sim 7\%$), while the thermopower goes from zero to -65 μV/K.[7] The transition is accompanied by a large anomaly in the specific heat ($H = 4.8 \pm 0.3$ kJ/mole). X-ray diffraction at 343 K shows that the TCNQ chains are almost uniform above this phase transition.[8] With the crystal structure as a basis a model has been proposed for the electronic structure which, at least qualitatively, explains the physical properties.[6] The $4k_F$ transition is interpreted as an electronic Peierls transition, which occurs because U is large, both in the uniform and in the dimerized phase. Some features, however, like the anomalous increase in the conductivity in between 280 and 320 K and the large enthalpy change at the $4k_F$ transition, cannot be explained by considering only the electronic system on the TCNQ chains. The role of the MEM ions has to be taken into account then.

In this paper we first summarize the structural data in Sec. II, focusing attention on the MEM ions. In Sec. III we report proton-NMR (cw) measurements on MEM(TCNQ)$_2$ and the partly deuterated MEM(TCNQ-d_4)$_2$, which give information on the charges on the TCNQ's and on the molecular motion. In Sec. IV we discuss, using the results of the previous section, how the MEM ions affect the conductivity and contribute to the specific-heat anomaly at the $4k_F$ transition.

II. STRUCTURE

The crystal structure has been determined by x-ray analysis at 113,[4] 294, 323 (just below the $4k_F$ transition), and 343 K (Ref. 8) (just above the transition). The TCNQ molecules always occupy well-defined positions, forming dimerized chains below 335 and almost uniform chains above 335 K. The positions of the MEM ions, however, can only be found unambiguously at 113 K, while above room temperature an increasing disorder is observed. The x-ray data can be successfully interpreted by as-

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suming the presence of two preferred orientations for the MEM ions with occupancies x and $1-x$. x decreases from 1.0 at 113 K to 0.84 at 294 K, 0.63 at 323 K, and 0.50 at 343 K.[8] In Fig. 1 a projection is shown of part of the triclinic unit cell (space group P_1) at 113 K along a vector perpendicular to the longest axis of a TCNQ molecule and lying in the plane of the molecule (i.e., the vector M in the inertial system as used in Ref. 8; the vector M does not correspond to a sum of unit-cell vectors). The TCNQ chains are easily identified. We have labeled the two TCNQ's belonging to a particular dimer as A and B. Note that the morpholinium N atom is almost at a pseudoinversion center in between the chains. The MEM orientation with occupancy x is the one shown in the figure. The orientation with occupancy $1-x$ can in good approximation be obtained by flipping the MEM ion about an axis parallel to the projection axis and passing almost through the nitrogen atom. As seen in the figure the MEM ion nicely fits in the "cage," identified by the broken line. Because of its symmetrical shape the MEM ion will also fit in the flipped position. Above the phase transition it appears to be impossible to locate the atoms of the MEM ion and only a strongly smeared out charge distribution is observed. This means that the disorder has increased even more above the phase transition: x has not only become 0.5, but an additional type of disorder must also be present. Because the TCNQ chains have become almost uniform the "cage" available for the MEM ion has changed shape. Both this change of shape and the observed MEM electrondensity point toward the possibility of a rotation about the N$-$O axis. From the x-ray data alone, however, it is impossible to draw definitive conclusions about the geometry of the extra "disorder" introduced at the transition. Another unclarified issue is whether the disorder, both above and below the transition is static or dynamic. With respect to these two points the combination with NMR line-shape analysis proves to be a powerful tool to clarify what is going on. In the next section we discuss the NMR results on the basis of the known crystal structure.

III. NMR

Proton NMR spectra on MEM(TCNQ)$_2$ were recorded in Groningen at 60 MHz between 190 and 380 K. 250-MHz spectra in between 170 and 410 K were recorded in Grenoble on both MEM(TCNQ)$_2$ and the partly deuterated MEM(TCNQ-d_4)$_2$.[9] Some typical spectra are shown in Fig. 2. Two important features of these spectra are evident: the shift of the TCNQ line to higher field with respect to the MEM line and the narrowing of the wider MEM line with increased temperature. We will first consider the position of the lines and then turn to a discussion of the second moment.

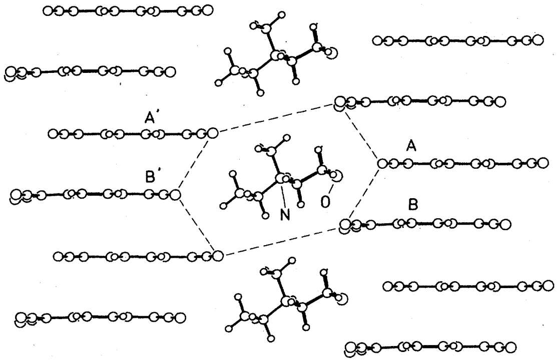

FIG. 1. Projection of part of the unit cell of the dimerized structure along a vector lying in the plane of the TCNQ molecules and perpendicular to their longest axis. A and B (and A' and B') denote pairs of TCNQ's forming a dimer. The broken line is a projection of the "cage" available for the MEM ion. The oxygen atom of the MEM ion is closest to molecule B.

The shift between the MEM and TCNQ position contains two contributions, the major one being the Knight shift of the TCNQ line (Δ) due to the spin density on the molecule, the smaller one being a difference in chemical shift. We observe in the deuterated compound that the small shift of the MEM line relative to the position of neutral TCNQ (Ref. 10) is slightly temperature dependent. At room temperature these positions coincide, and the shift (δ) between the spectrum of the fully protonated and the partly deuterated compounds measured at 250 MHz then is given by $\delta=\frac{1}{3}\Delta$. The factor $\frac{1}{3}$ arises from the relative numbers of MEM and TCNQ protons in the formula unit (16 and 8, respectively). We may calculate Δ using the known spin susceptibility[1] by the formula

$$\Delta=\frac{\gamma_e}{\gamma_N}\chi_r H a_Q ,$$

where

$$\chi_r=\chi/2Ng^2\beta^2 .$$

Taking the scalar hyperfine coupling a_Q from Ref. 10 we get $\delta=0.73$ G, which compares well with the experimental value of 0.68 ± 0.15 G.

The second moments of the NMR spectra recorded for the fully protonated MEM(TCNQ)$_2$

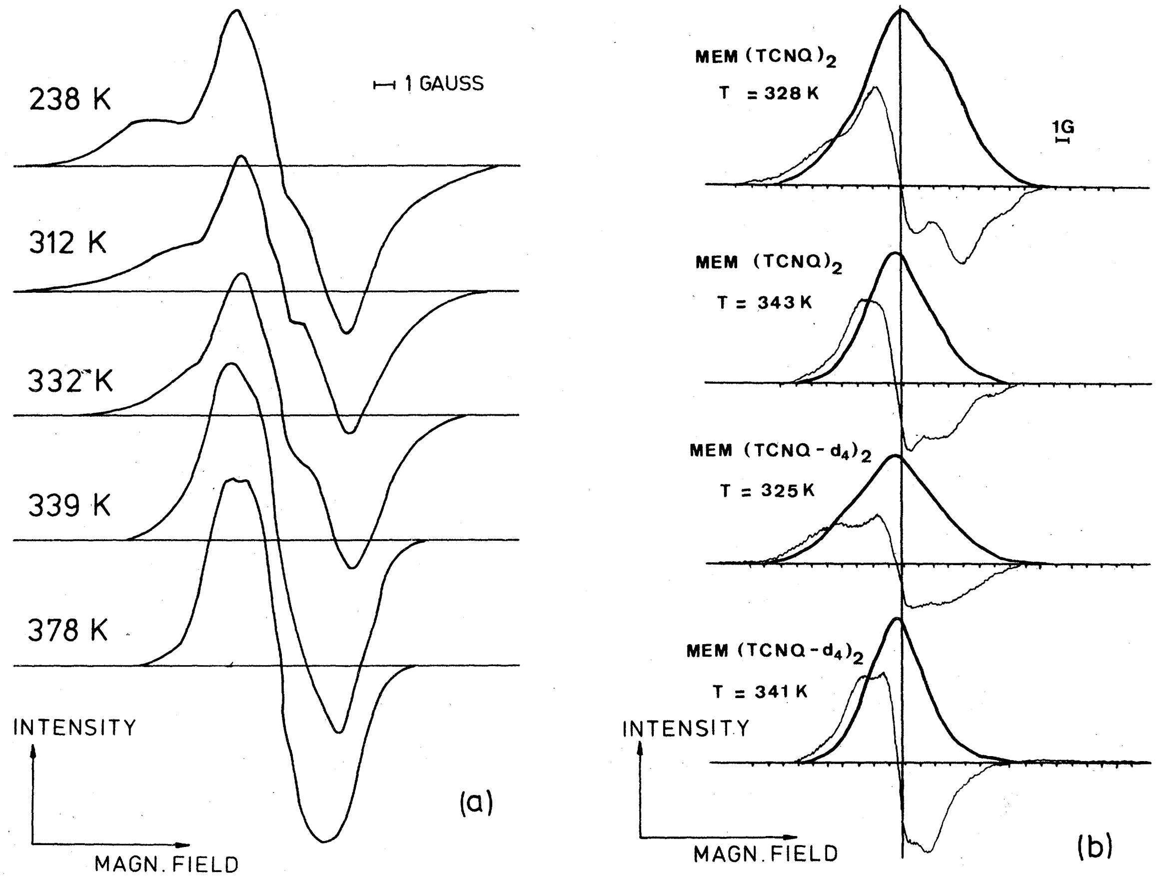

FIG. 2. (a) NMR spectra of MEM(TCNQ)$_2$ at 60 MHz. (b) NMR spectra of MEM(TCNQ)$_2$ and MEM(TCNQ-d_4)$_2$ at 250 MHz.

at 60 MHz [$M_2(60)$] and at 250 MHz [$M_2(250)$], and for MEM(TCNQ-d_4)$_2$ at 250 MHz [$M_2^*(250)$] are shown in Fig. 3 as a function of temperature. We will analyze two aspects of these data, namely, the contribution of the hyperfine interaction to the second moment, as derived from the differences between the curves in Fig 3, which yields information on the spin distribution on the TCNQ dimer, and the temperature dependence of $M_2^*(250)$, which reflects the MEM molecular motions.

The largest contributions to M_2 arise from the dipolar interactions between MEM protons (M_{2d}^{M}) and between TCNQ protons (M_{2d}^{Q}). Further contributions are the hyperfine interactions (M_{2h}) and the dipolar crossed contribution between MEM and TCNQ protons (M_{2d}^{MQ}). For the protonated compound we get

$$M_2=\tfrac{2}{3}M_{2d}^{M}+\tfrac{1}{3}M_{2d}^{Q}+M_{2d}^{MQ}+M_{2h}\ ,$$

where we calculate M_{2d}^{MQ} to be much smaller than 0.5 G^2. For the deuterated compound we get

$$M_2^*=M_{2d}^{M}+M_{2h}^*\ ,$$

where M_{2h}^* is the hyperfine interaction between the electron spin and the MEM protons, which is negligible (<0.1 G^2). We may obtain the hyperfine contribution $M_{2h}(250)$ in two different ways. Firstly, because the hyperfine interaction gives the only field-dependent contribution, we have

$$M_{2h}(250)=M_2(250)-M_2(60)\ ,$$

where we neglect $M_{2h}(60)$, which is 17 times smaller than $M_{2h}(250)$. Secondly we may compare $M_2(250)$ and $M_2^*(250)$ to give

$$M_{2h}(250)=M_2(250)-\tfrac{2}{3}M_2^*(250)-\tfrac{1}{3}M_{2d}^{0}\ ,$$

neglecting M_{2d}^{MQ} and M_{2h}^*. We take $M_{2d}^{Q}=3.1$ G^2, the value found for (ϕ_3^* AsCD$_3$) (TCNQ)$_2$.[10] Both experimental determinations are plotted in Fig. 4, and are seen to agree quite well. At the phase transition we observe a small jump of about 1 G^2.

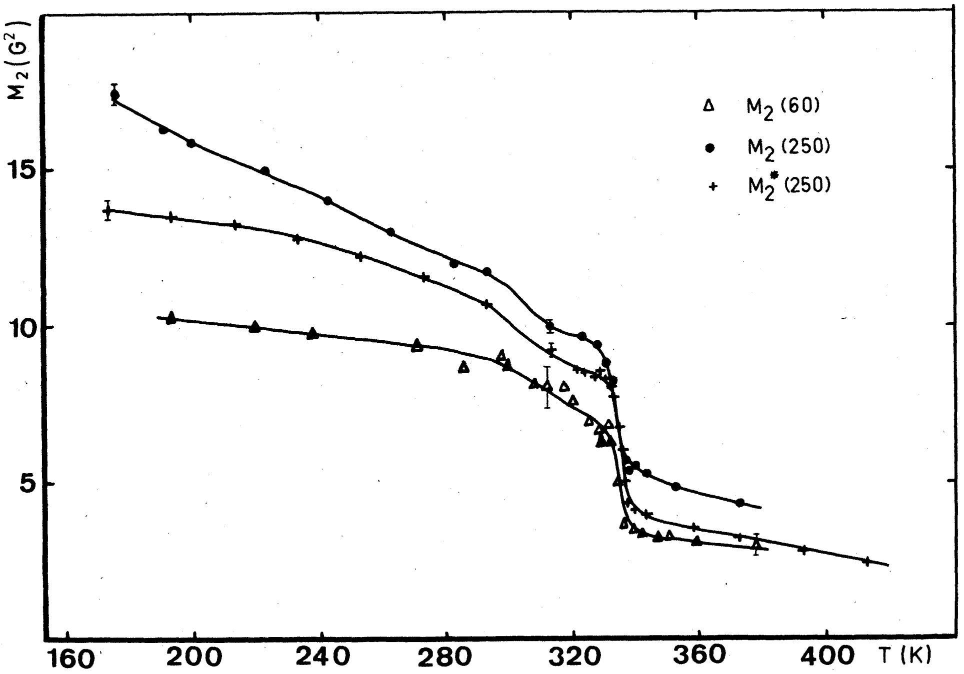

FIG. 3. Proton NMR second moment: MEM(TCNQ)$_2$ at 60 MHz [$M_2(60)$], MEM(TCNQ)$_2$ at 250 MHz [$M_2(250)$] and MEM(TCNQ-d_4)$_2$ at 250 MHz [$M_2^*(250)$]. The solid lines are drawn through the data points.

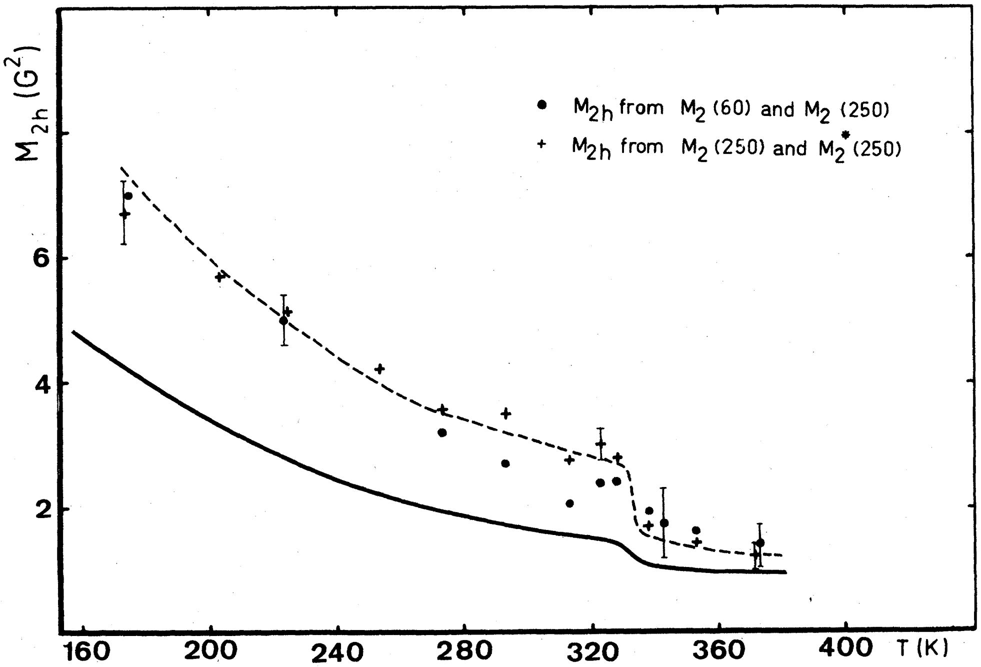

FIG. 4. Hyperfine contribution to the second moment (M_{2h}) at 250 MHz, as determined from comparison of $M_2(60)$ and $M_2(250)$ and from comparison of $M_2(250)$ and $M_2^*(250)$. The solid line is the theoretical curve for $a_Q/\hbar\gamma_e = -1.2$ G, $d_Q/\hbar\gamma_e = 0.6$ G, and $\alpha = 0.24$. The dashed curve is obtained with $a_Q/\hbar\gamma_e = -1.4$ G and $\alpha = 0.56$.

In order to theoretically calculate M_{2h} we have to consider the charge distribution on a TCNQ dimer, because contrary the first moment, the second moment due to hyperfine interaction will contain a contribution of a possible charge asymmetry. This is caused by the proportionality of the hyperfine interaction to the spin density, and hence to the charge density of the electron carrying the spin. In the 113-K crystal structure, as displayed in Fig. 1 the oxygen atom of the MEM ion, which carries a small negative charge because of its electronegativity, is closer to the CN groups of the TCNQ molecule labeled B than it is to those of the one labeled A. It is clear that this will affect the charge distribution over the two TCNQ molecules of a dimer. The bond lengths in the molecules A and B point towards a charge pile up on A. A quantitative estimate of the charges was obtained by Rice *et al.*[11] from an analysis of ir reflectance data: $0.62e$ on A and $0.38e$ on B, which gives a larger hyperfine interaction on A than on B. We may introduce an asymmetry parameter α

$$\alpha=(\rho_A-\rho_B)/e\ ,$$

which gives for M_{2h} (Ref. 10)

$$M_{2h}=\frac{1}{3}\left[\frac{\gamma_e}{\gamma_N}\chi_r H\right]^2[(\tfrac{2}{3}+\alpha^2)a_Q^2+(1+\alpha^2)(d_Q^2+2d_M^2)]\ .$$

a_Q, a_M, d_Q, and d_M are the scalar and dipolar couplings for the TCNQ protons and MEM protons, respectively, and we take $a_M=0$. To compare this expression with experiment a small correction should be included for the difference in chemical shift between MEM and neutral TCNQ. The solid line in Fig. 4 is the result for $a_Q\ /\ \hbar\gamma_e\ =\ -1.2$ G,[10] $d_Q\ /\ \hbar\gamma_e\ =0.6$ G,[10] $d_M/\ \hbar\gamma_e=0.3$ G, $\alpha=0.24$ and using χ from Ref. 1. The discrepancy between this curve and the experimental points may have several causes. Firstly, approximations have been made in the formulas giving M_{2h}, like the neglect of the crossed dipolar contribution to M_2. Secondly the input parameters a_Q, d_Q, and d_M for the calculation of M_{2h} may be too small for MEM $(TCNQ)_2$, and finally the charge distribution may be different from that derived by Rice *et al.*[11] If we assume a symmetrical charge distribution above the phase transition, i.e., $\alpha=0$, and then determine a_Q, leaving the smaller d_Q and d_M unaltered, we find a good fit for $a_Q/\hbar\gamma_e=-1.4$ G. Using this value below the phase transition requires $\alpha=0.56$ to fit the data (broken line in Fig. 4).

Up to now we have neglected any molecular motion. We shall see later on that the MEM molecular motion gives a fluctuating charge distribution on a dimer, and then may cause motional narrowing of the asymmetric hyperfine contribution, which would depress the curves in Fig. 4.

Although the accuracy of the experimental determination of M_{2h} is not very good, our results seem to indicate a larger charge asymmetry than found by Rice *et al.*,[11] and a larger scalar hyperfine coupling than found by Devreux *et al.* in some other TCNQ salts.[10] In order to obtain more accurate results it is necessary to measure the second moment of the partly deuterated compound (MEM-d_{16})$(TCNQ)_2$ as a function of temperature.

To investigate the MEM molecular motions we will now analyze the temperature dependence of the second moment of MEM(TCNQ-d_4)$_2$. The curve in Fig. 3 can be divided into four regions of interest. Below 280 K there is a slight decrease of M_2^*, in between 280 and 320 K it decreases rapidly and from 320 K up to the phase transition it levels off again. On going through the phase transition M_2^* drops sharply and then remains nearly constant. The results of a quantitative analysis in terms of molecular motions are given in Table I. The calculation of M_2^* is given in the Appendix.

The low-temperature value of 14 G^2 agrees well with the calculated value for MEM ions with rotating methyl and ethyl groups. In the x-ray structure determination at 113 K preferred positions are found for the methyl and ethyl groups, including the protons. This means that the motion observed as a reduction of M_2^* from the rigid-lattice value below 280 K is a hindered rotation, as is quite often encountered for alkyl groups in organic crystals. At higher temperatures it is difficult, if not impossible to determine the type of motion from the M_2^* value alone, but the crystal structure gives valuable clues here. In between 280 and 320 K a large decrease of M_2^* is observed. This is associated with the increasing disorder of the MEM ions. Apparently the disorder is of a dynamic type and consists of flipping over of the MEM ions between the two preferred positions as described in Sec. II at an increasing rate. The M_2^* value calculated for such flipping (together with methyl and ethyl rotation) is 8 ± 1 G^2, in good agreement with the experimental value between 320 and 335 K. The activation energy deduced from the M_2^* plot for this process is about 0.7 ± 0.2 eV. Another possibility to explain the reduction of M_2 is a chair-boat or chair-chair conformation change of the MEM ring,

TABLE I. Molecular motion and proton NMR second moment in MEM(TCNQ-d_4)$_2$.

	Calculated M_2^*			Experimental $M_2^*(\mathrm{G}^2)$	
Type of motion	Intra molecular	Inter molecular	Total	Second moment	Temp. range (K)
Rotating methyl groups	15.6	1.5	17	. . .	. . .
Rotating methyl + ethyl groups	11.6	1.5	13	12–14	200–280
Flipping over 180° + rotating side groups	7.1	1.0	8	8.5	320–335
Rotation about N–O axis + flipping + rotating side groups	2–4	0.6	$3\frac{1}{2}$	2.5–4.0	335–410

but this is ruled out by the x-ray data. At the phase transition M_2^* drops to about 4 G^2 indicating that a new motion sets in. This is confirmed by measurements of the dipolar spin relaxation time T_{1D}, which shows a drastic increase (from about 0.3 to 1.0 msec). For a rotation of the molecule as a whole the calculated M_2^* value is 3.5 ± 1 G^2, in agreement with the experimental value above the transition. The axis about which this rotation occurs is very likely the N-O axis, since, as pointed out in the previous section, the cage available for the MEM ion can nicely accomodate the ellipsoidal shape of a molecule rotating in such a way.

IV. CONDUCTIVITY AND SPECIFIC HEAT

It is interesting to look at the consequences of the MEM molecular motion for the electrical conductivity in the semiconducting regime. In Fig. 5 we show the resistivity as a function of inverse temperature. Also indicated is the NMR second moment for MEM(TCNQ-d_4)$_2$ at 250 MHz, demonstrating the correspondence between the two quantities. In general one might have expected a decrease in conductivity with the disorder induced by the MEM ion. This, however, does not occur. In fact the conductivity shows an anomalous increase in the temperature range where the flipping over of the MEM ions becomes important. Below 280 K the conductivity is temperature activated with an activation energy of 0.32 ± 0.02 eV, between 280 and 320 K it rises more rapidly and from 320 K up to the $4k_F$ transition an activation energy of 0.33 ± 0.02 eV is found.[5] From this we conclude that the anomalous change in the conductivity is mainly a result of a changing mobility.

We will show that the increase of the mobility is consistent with the crystal structure and with the electronic structure as described in Refs. 6 and 10. As was pointed out in the previous section a charge difference exists between the molecules A and B. Neglecting at first the interdimer transfer integral (t_2) and taking the on-site Coulomb repulsion (U) to be much larger than the intradimer transfer integral (t_1) the electronic structure for two dimers is as given in Fig. 6. Only the ground state and first excited state are shown, and for simplicity we do not consider spin. Because of the inequivalence of the two TCNQ molecules the wave function for the ground state of an electron on a dimer can be written as

$$\psi_g = \phi_A \cos\theta + \phi_B \sin\theta ,$$

with charges of $e\cos^2\theta$ and $e\sin^2\theta$ on molecules A and B, respectively. In the symmetrical situation $\theta = 45°$ and the charges on A and B are both equal to $0.5e$. In the excited state shown in Fig. 6 an electron has been transferred from one dimer to another. The doubly occupied dimer has one electron on each TCNQ molecule and the wave function is given by

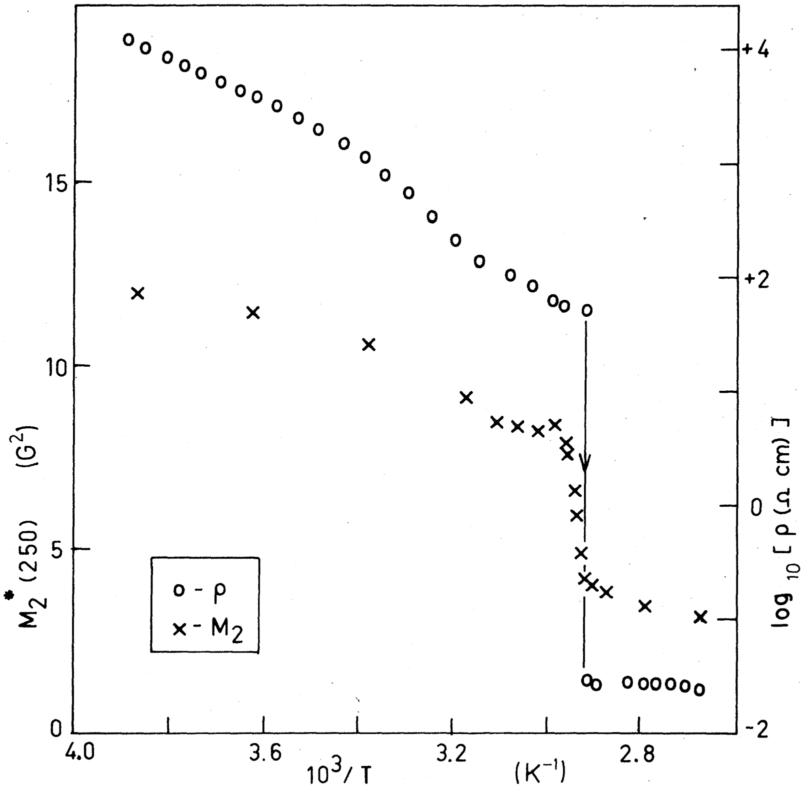

FIG. 5. Second moment of MEM(TCNQ-d_4)$_2$ at 250 MHz and dc resistivity in the chain direction vs inverse temperature.

$$\psi_{ex}=\phi_A\phi_B\ .$$

In fact the electron distribution will also be slightly asymmetric for this excited state, but since U is much larger than t_1 and the potential difference between A and B,[6,11] this asymmetry will be much smaller than in the ground state. To obtain conduction we must now see how the state with two electrons on one dimer (the electron state) and the state with zero electrons (the hole state) propagate through the TCNQ chains. The charge transport will be the result of the one-electron transfer t_2 (where $t_2 << t_1$). For the hole state the effective bandwidth due to t_2 is given by [see Fig. 7(a)]

$$\begin{aligned}W_h&=4\langle\phi_A(i)\cos\theta+\phi_B(i)\sin\theta\,|\,t_2[C_B^\dagger(i)C_A(i+1)+C_A^\dagger(i+1)C_B(i)]\,|\\&\qquad\times\phi_A(i+1)\cos\theta+\phi_B(i+1)\sin\theta\rangle\\&=4t_2\sin\theta\cos\theta\ ,\end{aligned}$$

where i labels the dimer and $C_A^\dagger(C_A)$ and $C_B^\dagger(C_B)$ create (annihilate) an electron in ϕ_A and ϕ_B respectively. For the electron state we obtain [see Fig. 7(b)]

$$\begin{aligned}W_e&=4\langle\phi_A(i)\phi_B(i)[\phi_A(i+1)\cos\theta+\phi_B(i+1)\sin\theta]\,|\,t_2[C_B^\dagger(i)C_A(i+1)+C_A^\dagger(i+1)C_B(i)]\,|\\&\qquad\times[\phi_A(i)\cos\theta+\phi_B(i)\sin\theta]\phi_A(i+1)\phi_B(i+1)\rangle\\&=4t_2\sin\theta\cos\theta\ .\end{aligned}$$

The electron bandwidth involves the other electrons as well since their wave functions charge also. We see that hole and electron bands are the same and that the bandwidth decreases when θ deviates from 45°. The two extremes are $\theta=45°$, the symmetrical situation where $W=2t_2$, and $\theta=0°$ where the charge is concentrated on molecule A and $W=0$.

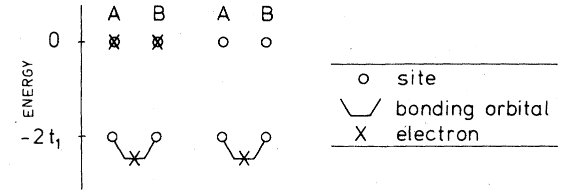

FIG. 6. Ground state and first excited state of two isolated dimers for large U. In the excited state an electron has been transferred to the neighboring dimer, which costs the binding energy of the two electrons.

In order to investigate the effect of disorder we have to look at the flipped-over position of the MEM ion and its distance to the TCNQ molecules. As outlined in Sec. II the flipping occurs about an axis through the MEM nitrogen atom, which leaves this atom in its symmetrical position relative to the molecules A and B of a dimer (see Fig. 1). The oxygen atom in the flipped configuration is in almost the same position relative to A' as it was relative to B before. If the MEM flipping rate is smaller than the intradimer transfer integral t_1, which is certainly the case, the electron density on a dimer will adjust to the MEM orientation, and the conduction bandwidth will be affected. Different possibilities arise for the interdimer transfer, and to obtain the effective transfer we have to take an average. If for instance the role of the A and B molecules is interchanged by the disorder we obtain for the transfer on one side of the dimer $t_2 \cos^2\theta$ and on the other side $t_2 \sin^2\theta$. Because the ordered situation gives only interdimer transfers of the type $t_2 \sin\theta \cos\theta$ the introduction of disorder will always give an increase of the average bandwidth, which in its turn yields a larger mobility. Using the values of Rice *et al.* for the charge asymmetry we expect a band broadening of only about 3% in going from the ordered to the disordered phase. The mobility on the other hand increases by a factor of 3.5. This strong increase in the mobility cannot be explained by the small expected increase in the bandwidth for a simple metal. However, from the ir work of Rice *et al.*[10] it is concluded that the electron molecular vibration interaction is quite large leading to a polaron binding energy of 0.085 eV. This is very likely larger than $2t_2$ so that the conductivity is probably better described in terms of a polaron picture. Although it is difficult to estimate the effect of a small bandwidth increase on the polaron mobility we do expect a strong dependence. From this argument it follows that the mobility should increase above 280 K where the MEM flipping sets in and should become constant again above 320 K where the disorder does not increase anymore.

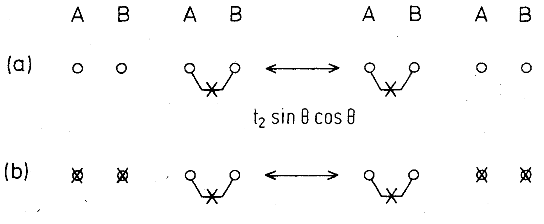

FIG. 7. (a) Hole transfer: the effective interdimer transfer becomes $t_2 \sin\theta \cos\theta$. (b) Electron transfer: the wave functions of all three electrons change, which again gives $t_2 \sin\theta \cos\theta$.

The conductivity gap will also be affected by the mechanism described above. In the simple two-dimer model with a total potential-energy difference Δ between the molecules A and B the gap is given by

$$[(2t)^2+\Delta^2]^{1/2} .$$

The disorder will on the average reduce Δ, causing the gap to become smaller by less than a few percent (using numbers from Ref. 10). Experimentally, however, the error in the conductivity-gap values (twice the activation energy) is too large for a quantitative analysis of this effect. Besides that, the gap is not predicted correctly in a simple model neglecting the polaron effect and, e.g., intermolecule Coulomb repulsion.

At the $4k_F$ transition the material shows an increase in conductivity by three orders of magnitude. This jump was discussed in Refs. 5 and 6. Here we will consider the effect of the MEM motion on the specific-heat anomaly observed. In Secs. II and III it was shown that there is an increase in disorder by the MEM flipping process (x changes from 0.63 at 323 K to 0.5 at 343 K), but the major change for the MEM molecules consists in the appearance of a rotation about the N-O axis. When kT is much larger than the rotation constant ($\hbar^2/2I$, where I is the moment inertia), which is certainly true here, the entropy change associated with this rotation is simply $\frac{1}{2}R$, where R is the gas constant (8.31 J/mole K). Another contribution to the entropy comes from the electronic degrees of freedom associated with the metallic state. An estimate for this contribution can be obtained from the change in thermoelectric power (TEP) which measures the entropy per charge carrier. The measured jump in the TEP is 65 μV/K,[7] which gives an entropy change per mole of $0.75R$. The sum of these contributions is

$$\Delta S=(0.50+0.75)R$$
$$=10.4\ \mathrm{J/mole\,K}\ .$$

From the specific-heat anomaly it was found that $\Delta S=\Delta H/T_C=14\pm1$ J/mole K, which is larger than predicted from MEM rotation and TEP. This is not surprising, because other mechanisms, like increase in MEM flipping disorder and the change of the TCNQ chains from dimerized to uniform, also contribute. It is evident, however, that the major changes are the added electronic degrees of freedom and the MEM rotation.

V. CONCLUSIONS

Using x-ray structural and NMR data we have shown that the MEM molecules undergo fast rotations leading to an order-disorder transition in the temperature range between 280 and 320 K. The rotation involved is most probably one about an axis perpendicular to the N—O axis. This order-disorder transition is accompanied by an increase in the mobility as observed from conductivity measurements which is argued to be qualitatively consistent with an expected increase in the interdimer transfer. At the high-temperature phase transition a drop in the NMR second moment is observed accompanied by a large increase in the conductivity and a first-order crystallographic phase transition. From x-ray diffraction and NMR results we suggest that a rotation about the N—O axis of the MEM molecules sets in at the phase transition. The entropy change due to this extra rotational degree of freedom plus that due to the extra electronic degrees of freedom is shown to be in reasonable agreement with specific-heat data.

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APPENDIX: EFFECT OF MOLECULAR MOTION ON SECOND MOMENT

The second moment for a rigid array of protons is given by[12–14]

$$M_2=\tfrac{3}{2}S(S+1)g^2\beta^2N^{-1}\sum_{j>k}M_{jk}^2\ ,$$

where S, g, β have their usual meaning and N is the number of protons involved. M_{jk} is given by $(3\cos^2\theta_{jk}-1)/r_{jk}^3$, where θ_{jk} is the angle between the H_jH_k vector, connecting the protons j and k, and the magnetic field. For a polycrystalline sample M_{jk}^2 has to be averaged over all orientations giving

$$M_2=\tfrac{6}{5}S(S+1)g^2\beta^2N^{-1}\sum_{j>k}r^{-6}$$
$$=7.159\times10^{-46}N^{-1}\sum_{j>k}r^{-6}\ \mathrm{G}^2\ .$$

In the presence of motion, however, M_{jk} has to be averaged over the motion before M_{jk}^2 can be averaged over all crystal orientations. In that case the second moment is found to be reduced. For a simple rotation the reduction factor is

$$M_2/M_2(0)=\tfrac{1}{4}(1-3\cos^2\gamma)^2\ ,$$

where γ is the angle between the H_jH_k vector and the rotation axis. For a rotating CH_3 group for example ($\gamma=90°$) the reduction factor is 0.25. For a molecule that flips over, intramolecular interactions are reduced by a factor

$$M_2/M_2(0)=\tfrac{1}{4}(1+3\cos^2\alpha)\ ,$$

where α is the angle between the H_jH_k vectors for the two molecular orientations. Using the formulas described above the second moment of MEM $(\mathrm{TCNQ}\text{-}d_4)_2$ can be evaluated. CH_3 protons were replaced by three protons at their average position. The value of M_2 for a flipping and rotating molecule depends on the details of the motion, and is estimated to be 2–4 G^2. The calculated values are shown in Table I. Using the known crystal structure intermolecular contributions were calculated for nearest-neighbor and next-nearest-neighbor molecules. For the other molecules the intermolecular contribution was estimated by taking a constant density of protons. The numbers are given in the table, where the total second moment is listed as well. The error in these values amounts to about 1 G^2.

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