PHYSICAL REVIEW B VOLUME 30, NUMBER 5 1 SEPTEMBER 1984

Anisotropy of thermopower in N-methyl-N-ethylmorpholinium bistetracyanoquinodimethane, $MEM(TCNQ)_2$, in the region of the high-temperature phase transitions

M. Almeida and L. Alcácer
Departamento de Quimica, Instituto Superior Técnico, Lisbon, Portugal
and Departamento de Quimica, Laboratório Nacional de Engenharia e Tecnologia Industrial, 2685 Sacavém, Portugal

S. Oostra
Laboratory for Physical Chemistry, University of Groningen, 9747-AG Groningen, The Netherlands

(Received 27 December 1983)

Measurements of the thermoelectric power along the three crystallographic axes of N-methyl-N-ethylmorpholinium bistetracyanoquinodimethane, $MEM(TCNQ)_2$, in the temperature range 280—360 K are reported. The first-order metal-insulator phase transition at 338 K is observed as a discontinuous change between the temperature-independent values $S_a=-50\ \mu V\,K^{-1}$, $S_b=-35\ \mu V\,K^{-1}$, and $S_c=-65\ \mu V\,K^{-1}$ in the metallic phase ($T>338$ K) and the values $S_a=-7\ \mu V\,K^{-1}$, $S_b=-48\ \mu V\,K^{-1}$, and $S_c=+35\ \mu V\,K^{-1}$. In the semiconducting phase, S_b is almost temperature independent, but both S_a and S_c increase upon cooling. At 314 K, a strong anomaly is made evident as a drastic change in the slope of S_a and S_c versus temperature. The electrical conductivity accurately measured along the three crystallographic axes, also shows an anomalous decrease for $T<314$ K. The thermopower and conductivity anomalies at 314 K are consistent with a second-order phase transition which originated in a change of cation motion, and is associated mainly with a decrease in the mobility of the charge carriers, the role of a possible increase in the gap being secondary. For $T<314$ K there is a predominant decrease of the electron mobility mainly along the $\vec{c}$ axis but also along the $\vec{a}$ axis, while, along the $\vec{b}$ axis, both the electron and hole mobilities decrease, remaining equal to each other.

I. INTRODUCTION

N-methyl-N-ethylmorpholinium bistetracyanoquinodimethane, $MEM(TCNQ)_2$, is a quasi-one-dimensional organic conductor which has recently been extensively studied. Two phase transitions have been previously established in this compound at 17.4 and 338 K. The 17.4-K second-order phase transition, as evidenced by magnetic susceptibility[1,2] and by specific-heat studies,[3] has been interpreted as a spin-Peierls transition associated with a tetramerization (dimerization of dimers) of the TCNQ molecules,[4] leading to a singlet ground state in the low-temperature phase ($2k_F$ transition).

The 338-K first-order phase transition is seen as a jump of 3 orders of magnitude in the conductivity along the chain axis ($\vec{c}$), from a value of $\sim 30\ \Omega^{-1}\,cm^{-1}$, independent of temperature in the high-temperature phase, to an activated behavior at lower temperatures.[5] Thermopower, as previously measured on powder,[6] also showed a significant change from 0 to $-65\ \mu V\,K^{-1}$ when warming up, and the magnetic susceptibility has a small discontinuous decrease of $\sim 7\%$. X-ray crystallographic studies show that above 338 K the TCNQ molecules are in an almost uniform chain,[7] while below the phase transition they are strongly dimerized.[8,9] This phase transition has been interpreted as an electronic Peierls transition ($4k_F$), demonstrating that the on-site electronic Coulomb repulsions (U) are large compared to the bandwidth. Consistent with this description between 17.4 and 338 K, the magnetic susceptibility behaves as it does in a one-dimensional Heisenberg antiferromagnet, and the conductivity behaves as it does in a semiconductor.

Other interesting features of this compound include an anomalous increase of the conductivity with increasing temperature at ~ 310 K, which has been suggested to arise from a mobility increase. Crystallographic studies at 323 and 294 K,[8] and proton NMR linewidth analysis[10] indicate that, between these temperatures, there is a significant increase of the thermal motion of the MEM cation, possibly flipping between two preferred orientations. More recently, the study of the thermal-expansion coefficient established a second-order phase transition at 315 K.[11] However, the role of the cation motion on the observed transport properties of the system is not clear yet, and there is less information concerning the anisotropy of the electrical properties of this system.

The thermoelectric power is a transport property, previously only measured in this compound in a powder compaction. The detailed study of that property in single crystals, including the anisotropy, can be used together with the electrical conductivity to probe the mobility of carriers and in that way it is expected to elucidate the anomalous behavior of the conductivity around ~ 310 K and contribute to a better description of the physical properties of this compound. The Seebeck effect, as a zero-current property, is less sensitive to crystal imperfections which are thought to explain some irreproducibility of the conductivity found among samples of most one-dimensional conductors.

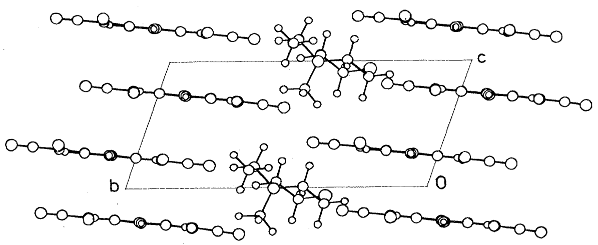

FIG. 1. Projection of the structure of MEM(TCNQ)$_2$ at $-160\,^{\circ}\mathrm{C}$ along {100} onto the plane perpendicular to {100} (Ref. 9).

In this paper we describe a detailed study of the anisotropy of the thermoelectric power and electrical conductivity in MEM(TCNQ)$_2$ above room temperature to gain insight into the nature of the high-temperature phase transitions and into the general physical properties of this compound.

II. CRYSTAL STRUCTURE

A projection of the crystal structure at $-160\,^{\circ}\mathrm{C}$ is shown in Fig. 1. The TCNQ molecules are stacked along $\vec{c}$ (the vertical direction). These chains are part of sheets of TCNQ molecules in the $(\vec{a},\vec{c})$ plane. In the $\vec{b}$ direction the TCNQ sheets are separated by a layer of MEM$^+$ ions, making the TCNQ-TCNQ overlap very small in that direction. In the $\vec{a}$ direction the chains are neighbors, allowing some overlap in that direction. Thus, for the conductivity we expect $\sigma_c \gg \sigma_a \gg \sigma_b$.

III. EXPERIMENTAL

MEM(TCNQ)$_2$ samples used in the present study were single crystals grown from a mixture of hot solutions of TCNQ and MEM iodide in acetonitrile. Most crystals were shaped as shown in Fig. 2, with maximum length of ~ 5 mm. Usually dimensions l_x along the x axis are such that $l_c \gg l_a \gg l_b$, although crystals are obtained with $l_a \sim l_c$ or with $l_b \sim l_a$ as well.

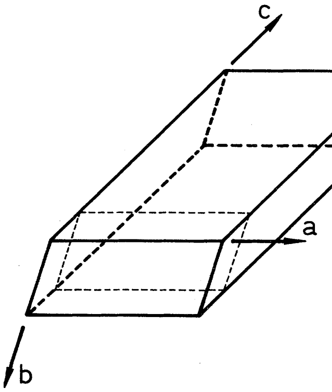

FIG. 2. Single crystal of MEM(TCNQ)$_2$ and crystallographic axis as defined in Ref. 7, used for thermopower measurements. Usually, dimensions l_x along axis x are such that $l_c > l_a > l_b$. Samples in which $l_a > l_b > l_c$ or $l_b > l_a > l_c$ were obtained cleaving slices from thicker crystals along {001} (thin dashed line) and scraping to final geometry.

The thermopower was measured holding the sample between two gold wires in contact with two quartz heat sinks and using a slow alternating-current technique, in an apparatus similar to that described by Chaikin *et al.*,[12] appropriate for long-shaped samples.

Measurements were made along the three crystallographic axes, $\vec{a}$, $\vec{b}$, and $\vec{c}$, described above and as defined in Ref. 7 (see Fig. 2). Although they are not exactly orthogonal (the system is triclinic), the measurements obtained along these natural directions are taken as a good approximation of the principal components of the thermopower tensor. The thermopower along the $\vec{c}$ axis, S_c (parallel to the TCNQ chains), was obtained in the usual needle-shaped crystals where the longest dimensions were ~ 5 mm along $\vec{c}$. The measurements of thermopower along the $\vec{a}$ and $\vec{b}$ axes, S_a and S_b, were not so favorable because samples shaped with longer dimensions parallel to those axes are not naturally observed in crystals. Samples 2—3 mm along $\vec{a}$ and cross sections measuring $\sim 0.5 \times 0.5$ mm^2 were obtained by cleavage and scraping of larger crystals. The most unfavorable conditions were presented in S_b measurements for which the largest crystals were used to cut samples with dimensions up to ~ 2 mm along $\vec{b}$.

The samples were glued, with platinum paint, on ~ 5-mm-long gold wires with diameter 60 and 25 μm to ensure good contact with the opposite ends of the crystal (Fig. 3). These wires were in contact with two heat sinks alternatively heated, the temperature difference between them reaching a maximum of 0.5 K. Under these circumstances the measurements represent an average over 0.5 K around each temperature point. Assuming a thermal conductance of the sample which is several orders of magnitude lower than that of the suspending gold wires, the temperature difference between the extremities of the sample was the temperature difference between the two quartz blocks measured with a copper-constantan thermocouple. The temperature of the sample was also measured with a copper-constantan thermocouple. Under the prevailing experimental conditions, the sensitivity was of the order of $\pm 0.3\ \mu\mathrm{V\,K}^{-1}$. The thermoelectric power was recorded for the three different directions upon heating, in a total number of 10 samples cut from seven different crystals. Typical results obtained for the three

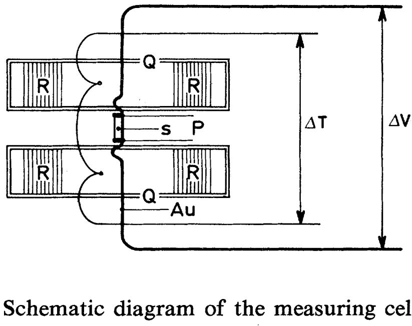

FIG. 3. Schematic diagram of the measuring cell. Q—heat sink of quartz single crystals; R—heating resistances; S—sample; Au—gold wires; P—conducting paint.

components in different crystals are shown in Fig. 4. The extension of the measurements to lower temperatures, particularly in the cases of S_a and S_b, was limited by the increasing resistance of the sample upon cooling below room temperature.

In spite of the not so favorable geometry of the samples used for measurements of S_a and S_b, the experimental values below the first-order transition at 338 K were found reproducible within $\pm 5\ \mu\mathrm{V\,K}^{-1}$ in samples and gold wires of different dimensions. These small variations indicate that the temperature drop across the sample is indeed the temperature difference between the thermal heat sinks. That fact is supported by the small thermal conductivity expected in MEM(TCNQ)$_2$, of the order of $\sim 5\ \mathrm{mW\,K^{-1}\,cm^{-1}}$ as found in triethylammonium bistetracyanoquinodimethane, TEA(TCNQ)$_2$,[13] when compared with the much larger thermal conductivity of gold.

Above the first-order transition, at 338 K, larger variations, which cannot be attributed to differences from sample to sample, were observed. They are interpreted as arising from the possible loss of good thermal contact between the sample and the suspending gold wires, as a consequence of the drastic change of the lattice parameters during the first-order phase transition. The loss of thermal contact after the transition was minimized by placing the sample under a slight pressure exerted by gold wires arranged as springs on the opposite-end faces of the sample. Even so, in the metallic phase ($T > 338$ K), we take, as the significant values of the thermopower, those with larger absolute magnitude.

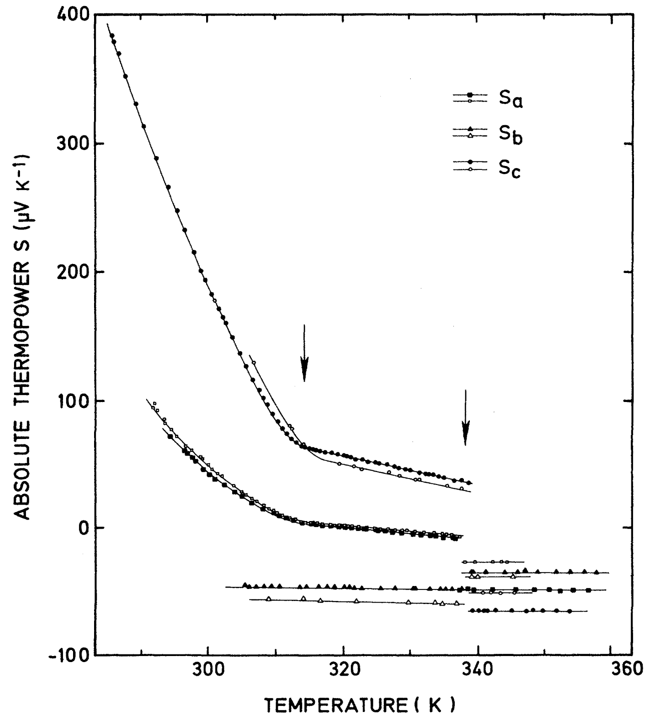

FIG. 4. Absolute thermopower as measured by warming, along the three crystallographic axes of MEM(TCNQ)$_2$ and in different samples: ● and ○ for S_c, △ and ▲ for S_b, and □ and ■ for S_a. The arrows at 314 and 338 K point out the phase transitions as seen in thermopower.

IV. RESULTS

The electrical conductivity as measured in the three principal directions is shown in Fig. 5. In all three directions the conductivity behaves similarly, with metallic behavior above 338 K and semiconducting behavior below. At 314 K a change in slope occurs as is exemplified in Fig. 6 where the activation energies $d\ln\sigma/d(1/T)$ are plotted for the $\vec{b}$ and $\vec{c}$ direction. The activation energy along $\vec{a}$ is intermediate between those along $\vec{c}$ and $\vec{b}$. Between 338 and 316 K the slopes are more or less constant with values of 0.31, 0.27, 0.22 eV in the $\vec{c}$, $\vec{a}$, and $\vec{b}$ directions, respectively. After a rapid rise to ~ 0.8 eV between 316 and 310 K the slopes steadily decline to values of 0.32, 0.37, and 0.42 eV at 250 K (c, a, and b). At this temperature only $d\ln\sigma_c/d(1/T)$ is close to having reached a steady value.

The anisotropy is remarkably low at room temperature: $\sigma_c/\sigma_a \approx 5$ and $\sigma_c/\sigma_b \approx 40$. TEA(TCNQ)$_2$, for example, has $\sigma_c/\sigma_b = 160$ and $\sigma_c/\sigma_a = 2800$,[14] and for tetrahiafulvalen-tetracyanoquinodimethane, TTF-(TCNQ), $\sigma_b/\sigma_a = 500$.[15]

In thermopower measurements the first-order phase transition is observed as a significant discontinuous change in S_c and S_a at 338 K. In the metallic phase, the values of S_a, S_b, and S_c are all negative and close to -50 $\mu\mathrm{V\,K}^{-1}$. In contrast with the metallic phase, for $T < 338$ K, in the semiconducting phases, a very strong anisotropy of the thermopower is observed. S_b remains negative and approximately temperature independent, with a value of $-48\ \mu\mathrm{V\,K}^{-1}$. Near the phase transition, $S_a = -7$ $\mu\mathrm{V\,K}^{-1}$ and $S_c = +35\ \mu\mathrm{V\,K}^{-1}$, both becoming positive and increasing as the temperature decreases.

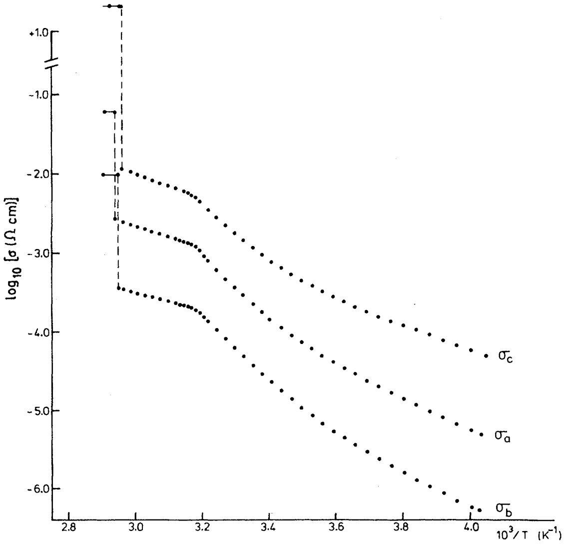

FIG. 5. Electrical conductivity of MEM(TCNQ)$_2$ in the three principal directions.

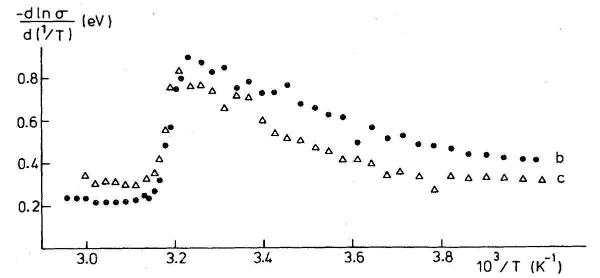

FIG. 6. Plot of $\partial \ln\sigma_c/\partial(1/T)$ (▲) and $\partial \ln\sigma_b/\partial(1/T)$ (●) vs inverse T. Values for $\partial\ln\sigma_a/\partial(1/T)$ are not represented, but are intermediate between those along $\vec{c}$ and $\vec{b}$.

At 314 K there is a noticeable change of slope of S_a and S_c. This can be more clearly observed in Fig. 7 where the S_a and S_c results, as well as the derivatives

$$\frac{\partial S_a}{\partial(1/T)} \text{ and } \frac{\partial S_c}{\partial(1/T)} ,$$

are plotted as a function of the reciprocal temperature. Between 314 and 338 K, the observed slopes are constant,

$$\frac{\partial S_a}{\partial(1/T)}=0.56 \text{ V}, \quad \frac{\partial S_c}{\partial(1/T)}=0.12 \text{ V} ,$$

but at 314 K there is a drastic increase in these parameters, reaching values about 10 times greater below ~300 K. For $T<338$ K there is a slight temperature dependence in the S_b component of the order of 0.1 $\mu V K^{-1}$ over more than 30 K, but within experimental error no net change at 314 K is observed.

V. COMPARISON WITH PREVIOUS DATA

In Fig. 8 we compare the most representative results obtained for S_a, S_b, and S_c, and their mean $S=\frac{1}{3}(S_a+S_b+S_c)$ with the only previous results obtained on a polycrystalline sample, those by Lacoe *et al.*[6] Our results are in reasonable agreement with the previously reported values on powder.

Owing to the difficulty in obtaining large single crystals there is a small amount of information in the literature concerning the anisotropy of the thermopower in TCNQ compounds. To our knowledge it has been only measured in two directions for TTF-TCNQ (Ref. 16) and in three directions for TEA$(TCNQ)_2$ (Ref. 17), N-methyl-2,4,6-methylpyridine$(TCNQ)_2$ [MTMP$(TCNQ)_2$] (Ref. 18), and methyltriphenylarsonium bistetracyanoquinodimethane [MTPAs$(TCNQ)_2$] (Ref. 19). In the first three compounds a significant sign anisotropy was also found, while in the last one only minor differences were detected in the behavior of the three components.

In MTMP$(TCNQ)_2$, which has conductivities close to those of MEM$(TCNQ)_2$ in the semiconducting phases, the direction of lower conductivity also corresponds to the only direction where the thermopower was found to be temperature independent.

VI. DISCUSSION

In the metallic phase ($T>338$ K), according to x-ray structural information,[7] the TCNQ molecules are almost

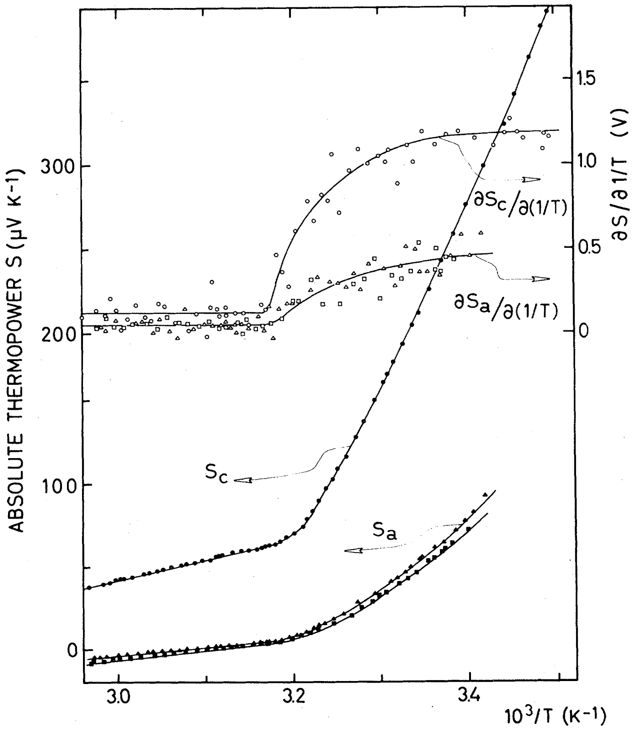

FIG. 7. Plot of S_c (●), S_a, (▲,■), $\partial S_c/\partial(1/T)$ (○), and $\partial S_a/\partial(1/T)$ (△,□) as a function of the inverse of the absolute temperature.

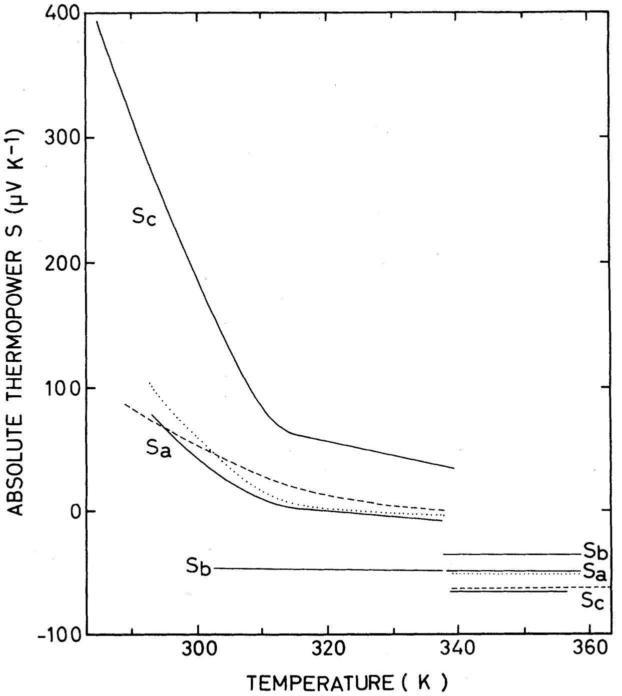

FIG. 8. Comparison of the present results of S_a, S_b, and S_c (solid lines) with those reported by Lacoe *et al.*[6] (dashed lines) on a polycrystalline sample. The dotted lines are the mean of the present results, $\frac{1}{3}(S_a+S_b+S_c)$.

uniformly spaced, with a 3.28-Å interplanar separation and a good type of overlap. Assuming full charge transfer ($\frac{1}{2}$ electron per TCNQ molecule) as suggested by chemical considerations and neglecting the small nonequivalency of the two TCNQ molecules in the unit cell, we have, in first approximation, a quarter-filled band of bandwidth $4t$, t being the intersite transfer integral. Depending on the importance of the on-site electronic Coulomb repulsion (U) relative to the bandwidth, the Fermi level will be placed either at a symmetric place in the middle of the band ($U > 4t$) or below that value ($U < 4t$).

In both cases, metallic behavior is predicted above the transition, in agreement with the observed nearly-temperature-independent conductivity, of the order of 30 $\Omega^{-1}\,\text{cm}^{-1}$ along $\vec{c}$. The observed values of the Seebeck coefficient along the three crystallographic directions are, within experimental accuracy, temperature independent and close to each other. This agrees with a high U value, placing the Fermi level in the middle of the band. In the strong-coupling limit of the Hubbard model ($U \gg 4t$) and assuming band symmetry around the Fermi level, the only contribution to S, as shown by Kwak *et al.*[20] and by Conwell,[21] comes from the spin degrees of freedom. Assuming full charge transfer ($\rho = \frac{1}{2}$) this contribution is given by

$$S = -\frac{k_B}{|e|}\ln\left[2\frac{1-\rho}{\rho}\right] = -\frac{k_B}{|e|}\ln 2 = -59.8\ \mu\text{V}\,\text{K}^{-1}\ , \tag{1}$$

in agreement with the experimental values. The larger deviation of the S_b values can be explained by the previously mentioned loss of good thermal contact after the transition, which became more important due to the unfavorable geometrical conditions.

According to x-ray structural information, below the first-order phase transition at 338 K there is a strong dimerization of the TCNQ chain and the conductivity is activated, as expected for the large-U limit. S_c and S_a in this region are also strongly dependent on temperature, as expected in a semiconductor.

In case of a large U, for a quarter-filled-band dimerized system, the thermopower is given by two independent contributions. One band contribution is found in usual semiconductors, which reflects the asymmetry around the Fermi level, the other is a temperature-independent spin contribution which is a consequence of the large U,[18]

$$S = \frac{k_B}{|e|}\left[\frac{b-1}{b+1}\right]\left[\frac{\Delta}{k_B T} + A\right] - \frac{k_B}{|e|}\ln 2\ , \tag{2}$$

where 2Δ is the gap and $b = \mu_+/\mu_-$ is the mobility ratio of holes and electrons. A is a constant representing an average of kinetic terms and usually of reduced significancy.

In the range 314—338 K both S_a and S_c follow a linear relation as a function of $1/T$. In this temperature range the conductivity also shows a constant activation energy, although somewhat dependent on direction. This suggests a temperature-independent gap and mobility. Therefore, taking the activation energy of σ_c as the value of half of the gap, $\Delta = 0.31$ eV, and from

$$\frac{\partial S_c}{\partial(1/T)} = 0.12\ \text{V} \quad\text{and}\quad \frac{\partial S_a}{\partial(1/T)} = 0.05\ \text{V}\ ,$$

we can estimate the mobility ratios of carriers as

$$(\mu_+/\mu_-)_a \approx 1.4 \quad\text{and}\quad (\mu_+/\mu_-)_c \approx 2.2\ .$$

At 314 K, S_c and S_a start to deviate from the behavior of a semiconductor with temperature-independent gap and mobility ratio, and for $T < 314$ K the conductivity along all directions shows an anomalous decrease upon cooling, the activation energies being strongly temperature dependent (Fig. 6). As the activation energies of the conductivity at lower temperature approach a value close to that found at $T > 314$ K along $\vec{c}$, the anomalous increase of S_a and S_c as well as the faster decrease of the electrical conductivity are regarded primarily as the consequence of a decrease of the carrier mobilities, μ_- decreasing faster than μ_+, thereby increasing b.

For $T < 290$ K, $\partial S_c/\partial(1/T)$ has saturated at a value of 1.2 V, while the activation energy of the conductivity along $\vec{c}$, $E_a(\sigma_c)$ slowly decreases with a value close to 0.5 eV, smaller than $\partial S_c/\partial(1/T)$, indicating that near this temperature region, b is still temperature dependent. A simultaneous change in Δ, although not excluded as we will discuss later, should play a minor role in the observed anomalous behavior of S and σ. A similar indication would probably come from $\partial S_a/\partial(1/T)$ if the value 0.5 V is preserved at slightly lower temperatures, where slowly decreasing $E_a(\sigma_a)$ becomes smaller than 0.5 eV.

The absence of any noticeable change in $\partial S_b/\partial(1/T)$ around 314 K is regarded as a consequence of the very small bandwidth along the $\vec{b}$ axis, the direction of alternation of TCNQ and MEM molecules, and of lowest conductivity. In fact, the almost constant value found for $S_b = -50\ \mu\text{V}\,\text{K}^{-1}$ is not far from the spin-entropy contribution of $-59.8\ \mu\text{V}\,\text{K}^{-1}$ expected to be dominant if there is symmetry around the Fermi level ($\mu_+ = \mu_-$). The differences in S_a, S_b, and S_c reflect the anisotropy of the band structure and the mobility in this compound, the band contribution being more important along $\vec{a}$ and $\vec{c}$, in agreement with the measured larger conductivity along these directions.

The sudden decrease of the electron mobility for $T < 314$ K is a direct consequence of the motion of the MEM molecules which are possibly undergoing a phase transition. The x-ray structural studies of Bodegom[8] at 294 and 323 K showed a significant increase of the cation disorder between two preferred orientations. The dynamical character of the increasing disorder of the MEM molecules, flipping between these two positions in the region of 294—323 K was confirmed by the motional narrowing of proton NMR linewidth.[10] As seen in Fig. 9 this narrowing is faster near 314 K, but starts earlier at ~285 K. According to these results, at low temperatures, the TCNQ molecule A, as a consequence of a preferred orientation of the MEM cation, will carry more charge than TCNQ molecule B, and the electronic wave functions will tend to be more localized in molecule A, that is, the electrons are polaron bound to the cation. The increasing motion of the MEM cation at higher temperatures will make molecules A and B more equivalent and the charge

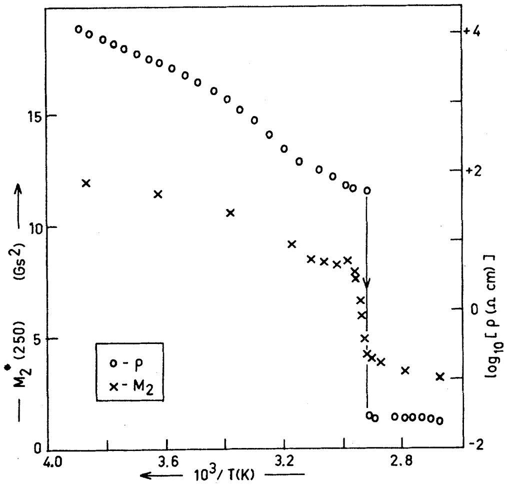

FIG. 9. Second moment of the NMR absorption line of MEM(TCNQ-d_4)$_2$ and ρ_c resistivity in the chain direction (Ref. 10).

distribution more uniform in the dimer, enabling the smearing of the polaron binding of the electron and the increase of the electron mobility. As the results of thermopower and conductivity suggest, for $T > 314$ K the MEM motion should be sufficiently fast to keep the electron-hole mobility ratio at a maximum value. This explanation and the relationship between the mobility, as seen from thermoelectric power, and the conductivity and cation motion, as seen in motional narrowing of proton NMR, is more clearly illustrated in Fig. 9, where the second moment of the proton NMR line of MEM(TCNQ)$_2$ is represented as a function of temperature. At 280 K it starts to slowly decrease as the temperature increases, then decreases fast before 314 K, and then reaches a constant value up to the first-order phase transition.

Finally, we should mention the previously mentioned possibility that the conductivity gap will also depend on cation motion and will be temperature dependent. In fact, as pointed out by Rice *et al.*,[22] the gap which is, in first approximation, $2(t_1 - t_2)$, t_1 and t_2 being the inter- and intradimer transfer integrals, will also have a contribution due to the nonequivalency of TCNQ molecules A and B. This contribution will also be negated by the increasing rate of motion of the MEM molecules, causing the gap to change with temperature. Rice *et al.*[22] could estimate this effect in a maximum value of 0.05 eV, which is too small to explain the observed changes in $\partial S/\partial(1/T)$ or $E_a(\sigma)$.

VII. CONCLUSIONS

The present measurements of the thermopower and conductivity anisotropy clearly show an anomalous behavior at 314 K, consistent with the occurrence of a second-order phase transition, due to the dynamics of the cation and primarily associated with a drastic change of the carrier mobilities. For $T < 314$ K the freezing of the flipping motion of the asymmetric MEM molecules in a preferred orientation significantly decreases the electron mobility more than the hole mobility, along both the $\vec{a}$ and $\vec{c}$ axes, while along $\vec{b}$, both the electron and hole mobilities decrease, but remain equal to one another. During this phase transition, the possible effect of an increase in the gap, although not excluded, plays a minor effect on the transport properties.

The first-order metal-insulator transition at 338 K is seen as a significant discontinuous change in thermopower and conductivity supporting the description of MEM(TCNQ)$_2$ as a correlated system with non-negligible bandwidth along the $\vec{c}$ and $\vec{a}$ axes (strong interchain coupling along the $\vec{a}$ axis).

ACKNOWLEDGMENTS

We gratefully acknowledge the stimulating discussions with Professor J. Kommandeur and Professor C. Haas. This work was partially supported by Junta Nacional de Investigacão Científica e Technológica under Contract No. 413.82.47.

---

[1] S. Huizinga, J. Kommandeur, G. A. Sawatzky, B. T. Thole, K. Kopinga, W. J. M. de Jonge, and J. Roos, Phys. Rev. B **19**, 4723 (1979).

[2] P. I. Kuindersma, G. A. Sawatzky, and J. Kommandeur, J. Phys. C **8**, 3005 (1975).

[3] P. I. Kuindersma, G. A. Sawatzky, J. Kommandeur, and G. S. Schinkel, J. Phys. C **8**, 3016 (1975).

[4] R. J. J. Visser, S. Oostra, C. Veltier, and J. Voiron, Phys. Rev. B **28**, 2074, (1983).

[5] M. Morrow, W. N. Hardy, J. F. Carolan, A. J. Berlinsky, L. Weiler, V. K. Gujral, A. Janossy, K. Holczer, G. Mihaly, G. Grüner, S. Huizinga, A. Verwey, and G. A. Sawatzky, Can. J. Phys. **58**, 334 (1980).

[6] R. C. Lacoe, G. Grüner, and P. M. Chaikin, Solid State Commun. **36**, 599 (1980).

[7] B. van Bodegom and A. Bosch, Acta Crystallogr. Sect. B **37**, 863 (1981).

[8] B. van Bodegom, Acta Crystallogr. Sect. B **37**, 857 (1981).

[9] A. Bosch and B. van Bodegom, Acta Crystallogr. Sect. B **33**, 3013 (1977).

[10] S. Oostra, B. van Bodegom, S. Huizinga, G. A. Sawatzky, G. Gruner, and J. P. Travers, Phys. Rev. B **24**, 5004 (1981).

[11] H. Kobayashi, Bull. Chem. Soc. Jpn. **55**, 2693 (1982).

[12] P. M. Chaikin and J. F. Kwak, Rev. Sci. Instrum. **46**, 218 (1975).

[13] H. Grassi, A. Brau, and J. P. Farges, Phys. Status Solidi B **112**, 633 (1982).

[14] A. Brau and J. P. Farges, Phys. Status Solidi B **61**, 257 (1974).

[15] M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B **10**, 1298 (1974).

[16] J. F. Kwak, P. M. Chaikin, A. A. Russel, A. F. Garito, and A. J. Heeger, Solid State Commun. **16**, 729 (1975).

[17] J. P. Farges and A. Brau, Phys. Status Solidi B **64**, 269 (1974).

[18] M. Przybylski, Physica (Utrecht) **114B**, 307 (1982).

[19] E. Muller, H. Ritschel, and H. Hansel, Phys. Status Solidi **33**, K55 (1969).

[20] J. F. Kwak and G. Beni, Phys. Rev. B **13**, 652 (1976).

[21] E. M. Conwell, Phys. Rev. B **18**, 1818 (1978).

[22] M. J. Rice, V. M. Yartsev, and C. S. Jacobsen, Phys. Rev. B **21**, 3437 (1980).