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Spin-Peierls transition in N-methyl-N-ethyl-morpholinium-ditetracyanoquinodimethanide [MEM-(TCNQ)$_2$]

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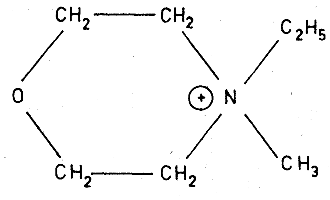
In this paper we reinterpret the magnetic-susceptibility data and present and discuss specific-heat data on MEM-(TCNQ)$_2$ in terms of a spin-Peierls transition theory. We find that the data can be described reasonably well by a mean-field spin-Peierls transition theory which suggests that at low temperatures the TCNQ chain should be tetramerized. The magnetic susceptibility above the transition temperature is shown to behave like a one-dimensional Heisenberg antiferromagnet. The consequences of this behavior on the relative magnitude of the on-site Coulomb interaction are discussed.

I. INTRODUCTION

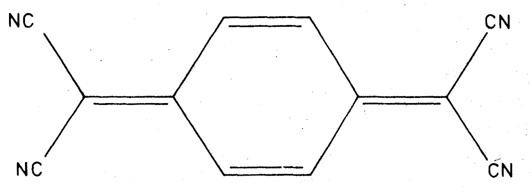
In recent years considerable interest has arisen in phase transitions in linear-chain compounds such as the tetracyanoquinodimethane(TCNQ) salts. As Peierls[1] first showed a half-filled one-dimensional band will show a phase transition to a dimerized phase, while Beni and Pincus[2] found that a similar transition will occur in an infinite one-dimensional chain of spins. Many such phase transitions have been found in TCNQ compounds,[3] but it has usually been difficult to establish their exact nature. A transition characterized by the one-electron wave vector $2k_F$ has long been known to exist in tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ), and recently a dynamic instability of wave vector $4k_F$ has also been found.[4] Various attempts have been made at explaining the origin of the latter.[5,6]

It is the purpose of this paper to reinterpret previously reported magnetic-susceptibility measurements[7,8] of methyl-ethyl-morpholinium-(TCNQ)$_2$ (see Fig. 1) and to present and discuss specific-heat data, in the light of recent crystallographic-structure determinations.[9,10] Bosch and Van Bodegem[9] have previously reported the detailed structure at 113 K. For this discussion it is of great importance to note that the TCNQ chains at this temperature are strongly dimerized, as shown in Figs. 2 and 3. There is a phase transition at about 335 K above which the conductivity is metallic[11] and the TCNQ chains are almost regular, as shown in Figs. 4 and 5. According to the magnetic susceptibility[7,8] as well as the specific heat reported here, there is another phase transition at about 20 K. The crystal structure below 20 K has not yet been determined, but recent x-ray measurements[12] have shown that the unit cell doubles along the chain direction indicating a tetramerized structure.

If we were to label these two phase transitions in



N – Methyl – N – ethylmorpholinium$^+$ (MEM$^+$)



7,7,8,8 – Tetracyanoquinodimethane (TCNQ)

FIG. 1. MEM and TCNQ molecules.

terms of the one-electron wave vector at the Fermi level in the high-temperature phase then the transition at 335 K would correspond to a $4k_F$ distortion and that at 20 K to a $2k_F$ distortion. In this paper we will concentrate on the details of the low-temperature transition.

II. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility of MEM-(TCNQ)$_2$ as measured with a vibrating-sample magnetometer (Foner balance) and corrected for the diamagnetic contribution is shown in Fig. 6. There are two aspects of these data, the temperature dependence between 20 and 300 K and the sharp dip below 20 K which we will now discuss.

In a previous publication[7] we argued that both the magnitude and the temperature dependence of the susceptibility between 20 and 300 K pointed to a large repulsive on-site Coulomb interaction (U). We therefore used a theory for a highly correlated metal to successfully describe the temperature dependence of the susceptibility. The fit is shown as a semidotted line in Fig. 6. That theory however, was based on a regular chain which as we now know is certainly not applicable to MEM-(TCNQ)$_2$. In fact knowing that we should use a large U limit and considering the strong dimerization of the TCNQ chain, the Bonner and Fisher calculation[13] might be more suitable. This calculation for a one-dimensional antiferromagnetic chain with uniform exchange is based on the assumption of complete localization which in our case would correspond to a spin of $\frac{1}{2}$ on every TCNQ dimer. Such a situation would prevail for an interdimer transfer integral (t_2) much smaller than the effective Coulomb repulsion energy of two electrons on one dimer (U'). U' will of course be much smaller than the repulsion energy of two electrons on one TCNQ molecule (U) and will depend on the intradimer transfer integral (t_1).

Of importance at this moment is that, for $t_1 >> t_2$, large U also implies large U' (i.e., $U' >> t_2$) and we will be dealing with a spin-$\frac{1}{2}$ Heisenberg chain.[14] The fully drawn line in Fig. 6 shows the result of a fit of the Bonner and Fisher calculation, using a g value of 2.003 as determined by electron-spin resonance and an exchange interaction J of 53 K. (J is defined by

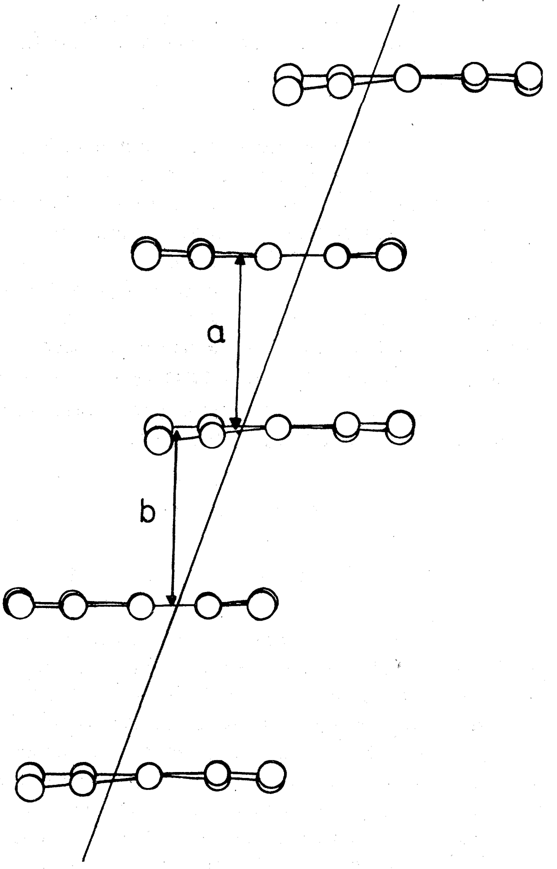


FIG. 2. TCNQ molecules in MEM-(TCNQ)$_2$ as seen along their longest axis at 113 K. The drawn line indicates the chain direction.

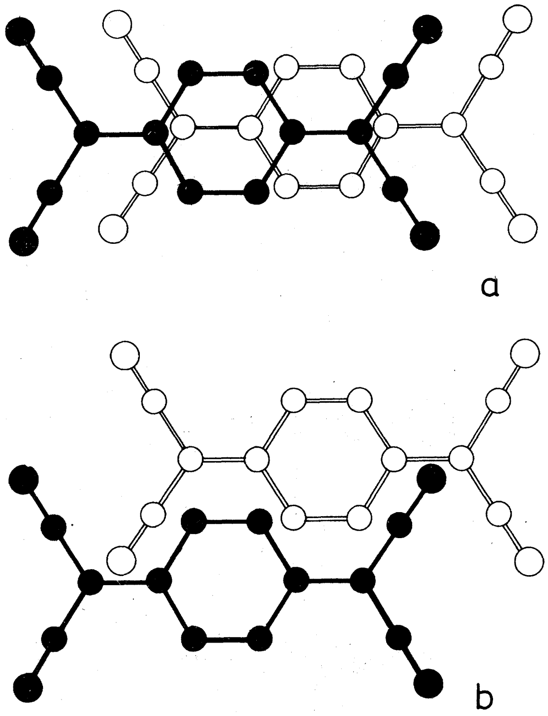


FIG. 3. (a) Intradimer overlap (ring-external bond type) and (b) interdimer overlap, as seen perpendicular to the TCNQ plane at 113 K.

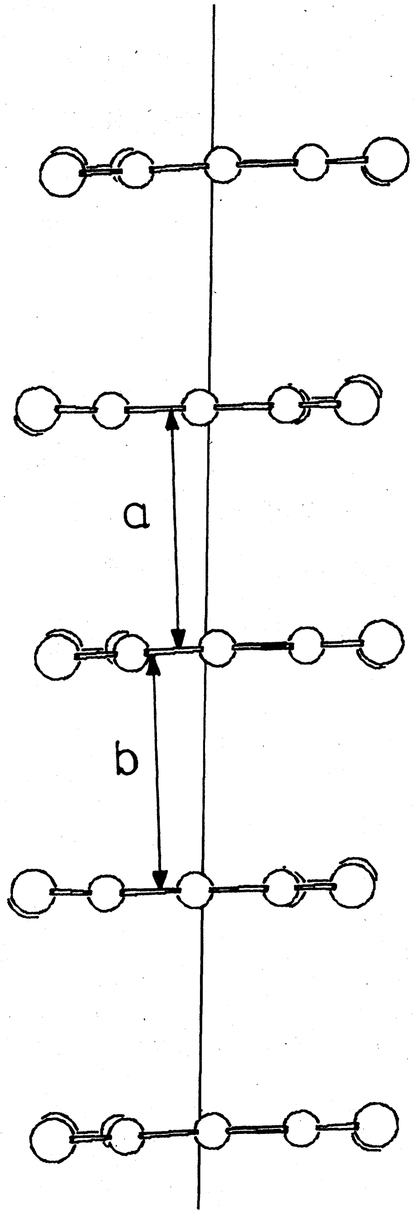


FIG. 4. TCNQ molecules as seen along their longest axis at 346 K. The drawn line indicates the chain direction.

the Hamiltonian $H=2J\sum_i\vec{S}_i\cdot\vec{S}_{i+1}$.) Below 20 K the susceptibility dips sharply below the Bonner and Fisher curve extrapolating to zero at 0 K. This drop in the magnetic susceptibility is accompanied by a phase transition as seen in x-ray diffraction[12] and the specific heat. Kuindersma suggested[7] that at this temperature antiferromagnetic coupling causes a breakdown of the correlated metal state resulting in a small lattice distortion corresponding to a tetramerization. Starting with a dimerized chain above the phase transition with electrons localized on dimers, a tetramerization of this kind should be called a spin-Peierls transition. Jacobs *et al.*[15] have recently reported spin-Peierls transitions in (TTF)[$CuS_4C_4(CF_3)_4$] and related compounds and we will in a discussion of the MEM-$(TCNQ)_2$ data follow the same approach. Pytte treated a Hamiltonian describing spins ($S=\frac{1}{2}$) with one-dimensional Heisenberg-type interaction, coupled to a three-dimensional lattice[16]:

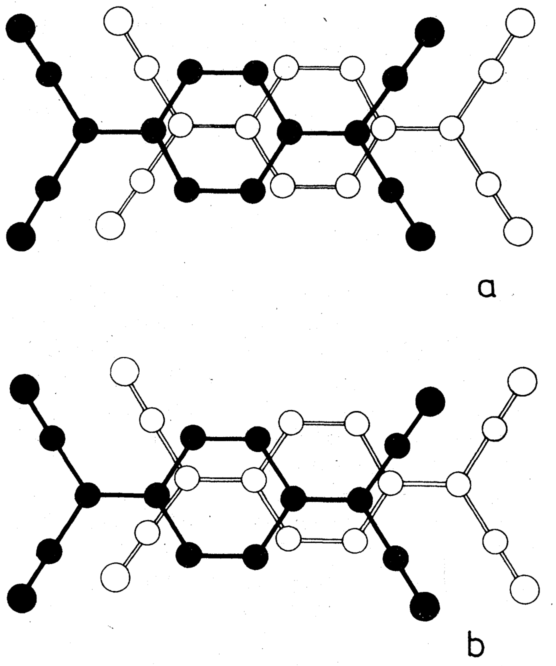


FIG. 5. (a) Intradimer overlap and (b) interdimer overlap, as seen perpendicular to the TCNQ plane at 346 K.

$$H=\sum_l 2J(l,l+1)(\vec{S}_l\cdot\vec{S}_{l+1}-\tfrac{1}{4}) ,$$

$$J(l,l+1)=J+[\vec{u}(l)-\vec{u}(l+1)]\cdot\vec{\nabla}J(l,l+1) ,$$

where l labels the sites and $\vec{u}(l)$ is the displacement of the site l. He transformed this Hamiltonian to a system of pseudofermions, and he obtained a Fröhlich-like Hamiltonian. Rice and Strässler[17] and others[18] have shown that this Hamiltonian, which is of the same form as for a conventional Peierls transition, leads to a second-order phase transition with $q=2k_F$ at finite temperature (T_c). Below T_c a gap $2\Delta(T)$ appears in the excitation spectrum, which separates the singlet ground state from spin-wave excitations. This $\Delta(T)$ follows a BCS-type temperature dependence. The dimerization of the spin sites leads

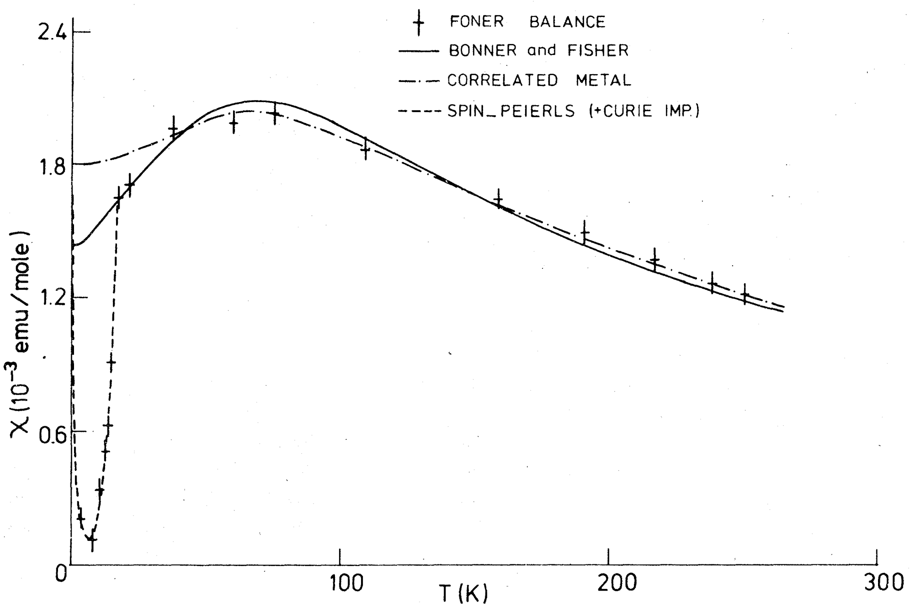


FIG 6. Spin susceptibility: experimental points as obtained on a Foner balance and theoretical fits with the correlated metal model ($U \sim 0.4$ eV, $4t \sim 0.1$ eV) and the Bonner and Fisher model ($J = 53$ K, $g = 2.003$). Also indicated is the theoretical curve below the spin-Peierls transition.

to an alternating exchange, which we can write

$$J_{1,2} = J[1 \pm \delta(T)] \ ,$$

$$\delta(T) = \frac{\Delta(T)}{2pJ} \text{ with } p \cong 1 + \frac{2}{\pi} \ .$$

Now the susceptibility $\chi(T)$ goes to zero at zero temperature instead of remaining finite as in a uniform Heisenberg chain. We can calculate $\chi(T)$ knowing J and $\delta(T)$ with the results of Bulaevskii's work.[19] He finds in a Hartree-Fock approximation

$$\chi(T) = \frac{Ng^2\mu_B^2}{k} \frac{\alpha(T)}{T} \times \exp\{-2[1+\delta(T)]J\beta(T)/T\}$$

in the interval $0.033 < T/2J < 0.25$. $\alpha(T)$ and $\beta(T)$ are tabulated constants for given values of $\gamma(T) = J_2/J_1$.

The Bonner and Fisher theory when fitted to χ above 20 K yielded $J = 53$ K so this formula is valid in the range $3.5 < T < 26.5$ K which is quite sufficient for our purpose. The best fit to the data was found for

$$T_c = 17.7 \text{ K}, \quad \delta(0) = 0.16 \ .$$

This is shown in Fig. 7, where the dotted line represents the sum of the Bulaevskii result and a small Curie impurity

$$\chi_{\text{Curie}}(T) = 0.75 \times 10^{-3}/T \text{ emu/mole} \ .$$

The calculated susceptibility was scaled to the Bonner and Fisher result at $T = T_c$ by a factor of 0.84. A number of the same magnitude was used by Jacobs *et al.*[15] in their susceptibility fit.[20] This yields a magnetic gap at $T = 0$ K of $2\Delta(0) = 56$ K. We find $\Delta(0)/T_c = 1.58$ while the BCS theory predicts a value of 1.76.

It should be mentioned that the Knight shift, which measures the electron-spin density at the position of the TCNQ protons, follows the same behavior. This is illustrated in Fig. 8.

It is surprising that a mean-field model works so well for a one-dimensional electron system coupled to a lattice. A purely one-dimensional system will not show a phase transition at finite temperature, because of fluctuations, which are neglected in a mean-field model.

III. SPECIFIC HEAT

The heat-capacity measurements were performed on samples consisting of ~0.035 moles of small crystals. The specimen was sealed inside a copper capsule together with a small quantity of ^{3}He gas. The capsule was suspended in an evacuated can placed in a ^{4}He cryostat. Between the capsule and the outer can a temperature-controlled heat screen was fitted, which enabled us to perform very accurate measurements up to about 50 K. Temperature readings were obtained from a calibrated germanium thermometer,

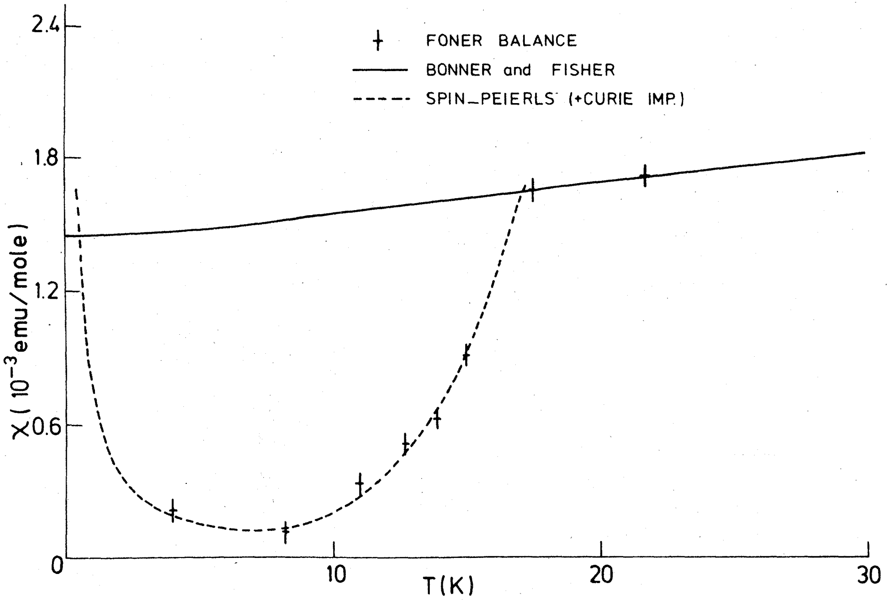


FIG. 7. Spin susceptibility below 30 K: Foner balance results with the Bonner and Fisher fit ($J=53$ K, $g=2.003$), and the sum of the spin-Peierls result [$T_c=17.7$ K, $\Delta(0)=28$ K] and a small Curie contribution (0.2 mole% impurities).

attached to the capsule and measured with an ac resistance bridge operating at 172 Hz. An overall check of the accuracy of the system was performed by measuring the specific heat of 99.999% spectrographic pure copper. The data below 25 K were compared with the copper reference equation reported by Osborne *et al.*,[21] those above 25 K with the selected values given by Furukawa *et al.*[22] The absolute precision of the measurements was estimated to be better than 1% in the whole temperature region.

The specific heat of MEM-$(TCNQ)_2$ was measured for $2.5 < T < 52$ K. The experimental data are plotted in Fig. 9. Inspection of Fig. 9 shows a small anomaly near 18 K. As a first step towards the interpretation of the results we considered the data at low temperatures. A plot of C_p/T vs T^2, given in Fig. 10, reveals that below 6 K the data can be represented by only a T^3 law

$$C_p(T)=0.0141\,T^3\ \text{J/mole K}\ (\Theta_D=74.5\ \text{K}) \ .$$

This clearly demonstrates the absence of an electronic contribution at low temperatures. Secondly, we performed a quantitative analysis of the results at higher temperatures by fitting the data above 21 K to the sum of a lattice contribution C_L and an electronic contribution C_E. The electronic contribution was described by two different models. The first fit was performed using the $S=\frac{1}{2}$ antiferromagnetic linear-chain model given by Bonner and Fisher,[13] with the value $J=53$ K obtained from the susceptibility data presented above. In order to investigate whether a partly delocalized electron model might give a significantly better description of the data, a second fit was performed using the correlated metal model given by Kuindersma.[7]

The lattice contribution was approximated by the expression for a pseudo-one-dimensional system given by Kopinga *et al.*[23] Since the anomaly at 18 K is very small compared to the total heat capacity, it is obvious that any attempt to estimate C_E below 21 K by extrapolating C_L down to $T=0$ will result in rather large inaccuracies. These inaccuracies may be suppressed by fitting C_L simultaneously to the data below 6 K, which can be represented by only a lattice contribution, as was shown above. We wish to note that such a procedure—like all previous attempts[24,25] to estimate C_E by extrapolation of C_L—assumes that the transition has only a minor effect on the lattice heat capacity. The results of the fit using the model of Bonner and Fisher and the fit using the model of Kuindersma are shown in Figs. 11 and 12, respectively. The dots denote the experimental data minus the calculated lattice contribution, the drawn curve reflects the corresponding model for the electronic contribution as if no transition occurs. Especially at higher temperatures, the scatter in the experimental data seems rather high. This is due to the fact that a plot of $C_p - C_L$ attributes the experimental scatter (~0.4%) fully to the electronic contribution, which is, of course, not quite realistic.

After the subtraction of C_L, the experimental entropy gain for $T \leq 21$ K may be compared with the

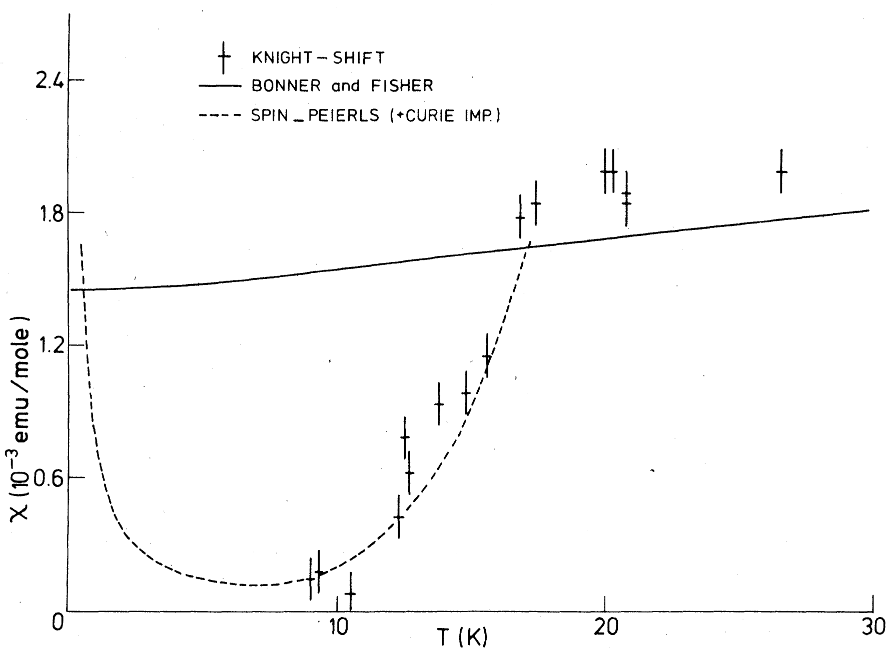


FIG. 8. Knight shift, expressed as a susceptibility in emu/mole, with the same theoretical curves as in Fig. 7.

theoretical prediction in the case that no transition would have occured. The experimental entropy gain was found to be slightly larger than the corresponding theoretical prediction; the difference, however, being within the experimental uncertainty (see Table I).

Next, the phase transition was analyzed within the mean-field model, using a more or less similar procedure as described by Craven *et al.*[24] The λ-shaped anomaly was approximated by a triangular function, in such a way that the entropy associated with this function was equal to the experimental entropy gain at the transition. The triangular function is denoted by the broken line in Figs. 11 and 12. The resulting mean-field transition temperature of ~19 K is in good agreement with the value of 18 K obtained from susceptibility measurements. Within the frame-

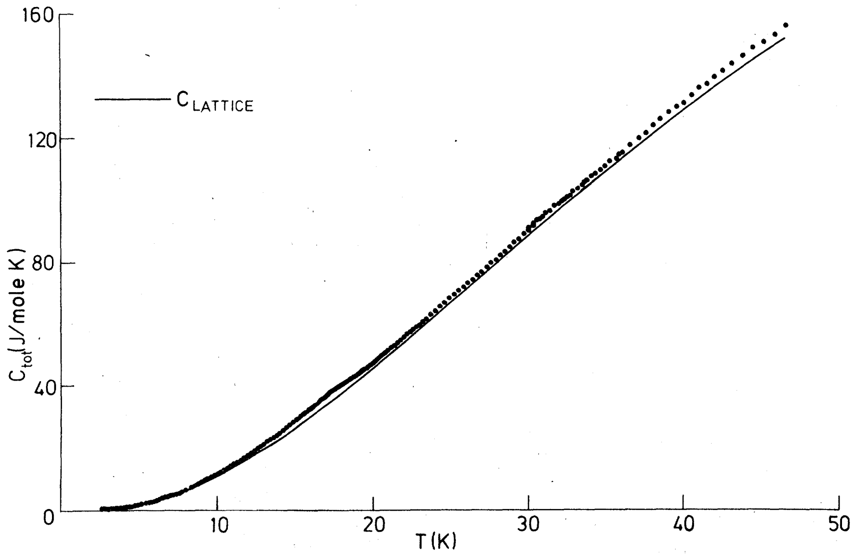


FIG. 9. Experimental total specific heat (below 50 K) indicated by dots. The drawn line is the lattice contribution.

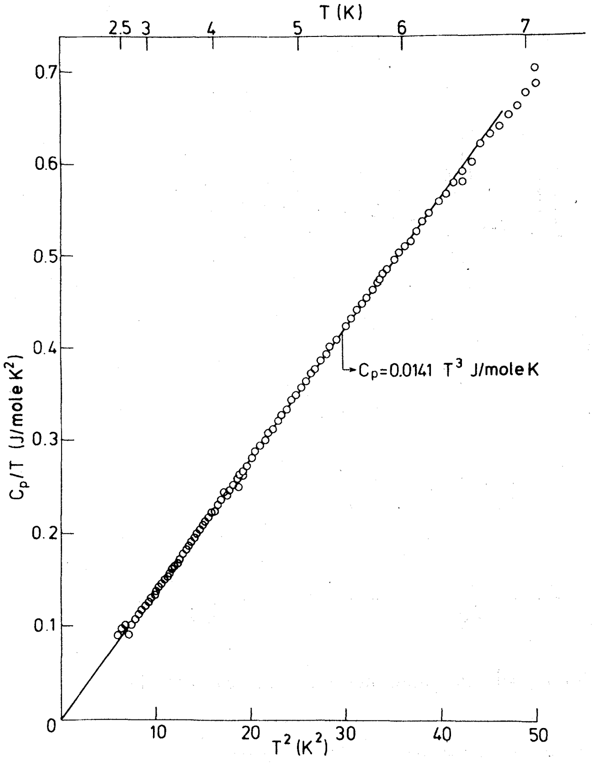


FIG. 10. Plot of C_p(tot)/T vs T^2, below 7 K, indicating the Debye character: $C_p(T) = 0.141 T^3$ J/mole K (Θ_D = 74.5 K).

work of the mean-field approximation, the observed jump in the triangular-shaped function may be compared with the jump of the specific heat as predicted by the BCS model. This jump is given by $\Delta C_E = 1.43 \gamma T_c$, if $C_E(T) = \gamma T$ for temperatures above T_c.[25] Unfortunately, for the $S = \frac{1}{2}$ antiferromagnetic chain with $J = 53$ K, the observed transition temperature 19 K is located above the region in which the linear relation $C/R = 0.35 T/J$ (see Ref. 13) is valid. Because, however, the deviations are not very large, we have approximated the value of γ by the slope of the theoretical curve just above 19 K. The results of the analysis are summarized in Table I. Given the fact that the uncertainty in the determination of C_E below 21 K may be rather large, due to the uncertainty in the interpolated behavior of C_L, the agreement between theory and experiment is satisfactory for both theoretical models.

It appears to be of some value to try to correlate the dependence of C_p on T below T_c with the spin susceptibility in this range. This turned out to be an almost impossible task, but the following attempts were made. In the range $7 < T < 12$ K the specific heat can be fitted by an equation of the type $C_p = a \exp(-bT_c/T)$, where a and b of course depend on the type of theory used to fit the high temperature results. The values are given in Table II. Now the BCS theory also can be cast in this form for this limited temperature range, at least with $\Delta(0)/T_c = 1.76$. The values of a and b, however, are then much smaller than was found experimentally (see Table II). We therefore attempted to fit the susceptibility with a

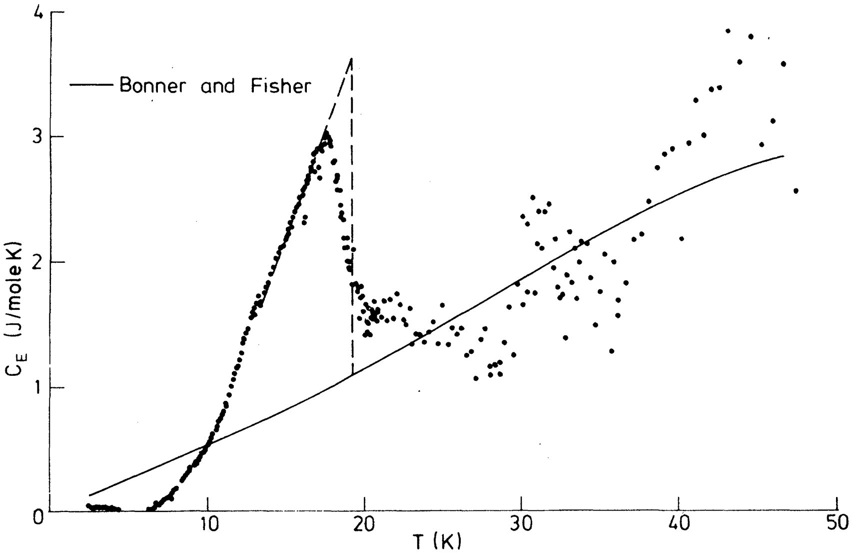


FIG. 11. Electronic contribution to the specific heat, as determined by subtraction of the calculated lattice contribution from the experimental data, to fit the Bonner and Fisher result ($J = 53$ K) represented by the drawn curve. The broken line is the triangular approximation, leaving the entropy gain in the transition unaltered ($T_c = 19.2$ K).

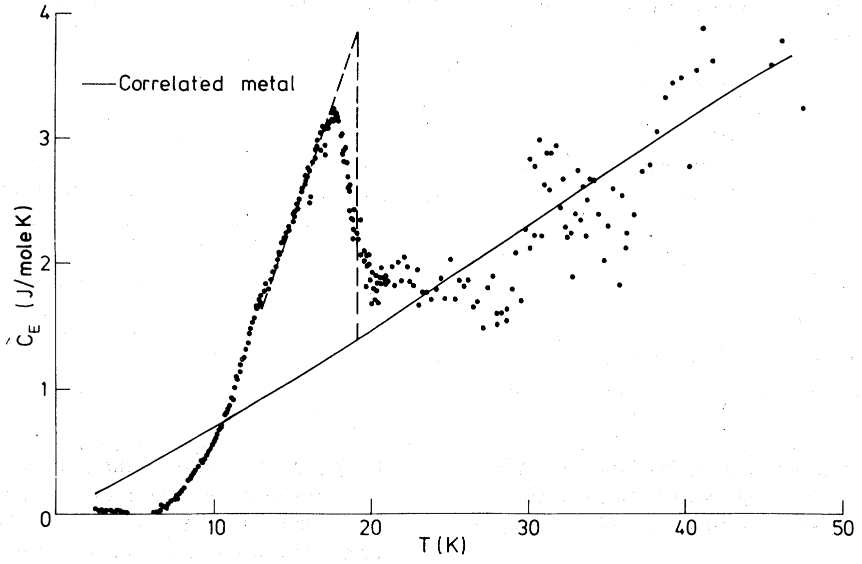


FIG. 12. Electronic contribution to the specific heat, determined as in Fig. 11, but now to fit the correlated metal result ($U \sim 0.4$ eV, $4t \sim 0.1$ eV) represented by the drawn line. The broken line again is the triangular approximation ($T_c = 19.1$ K).

much simpler theory, such as the singlet-triplet model, which amounts to the neglect of the smaller of the two exchange integrals in the tetramerized system. The best fit to the susceptibility then yields a singlet-triplet separation of about 70 K, but now the values of a and b derived for the specific heat data are much too large (see Table II). It appears, as seems logical, that the proper BCS theory gives too much pairing of the spins, while a singlet-triplet model leaves them too free. As a last resort the scaled BCS gap ($\Delta(0)/T_c = 1.58$) as obtained from the susceptibility was used as a singlet-triplet gap to calculate the specific heat. Although the temperature dependence is now quite close to the experimental one, the absolute value of C_p is much too high, as might be expected from the neglect of the smaller exchange integral (see Table II). The conclusion must be that at present we do not have a simple calculation available to connect the behavior of the specific heat of MEM-(TCNQ)$_2$ well below the phase transition to its spin susceptibility.

IV. CONCLUSIONS

The magnetic susceptibility of MEM-(TCNQ)$_2$ between 20 and 300 K can be described by the Bonner and Fisher one-dimensional Heisenberg model with antiferromagnetic exchange of 53 K between neighboring spins. In both the susceptibility and the specific heat a phase transition is observed at about 18 K, below which the behavior can be satisfactorily explained with a spin-Peierls theory. The susceptibility is fitted by using Bulaevskii's equation for an alternating linear antiferromagnet with a BCS-like temperature dependence for the magnetic gap, giving the following result: $\delta(0) = 0.16$ and $T_c = 18$ K. The specific-heat data were analyzed in a similar way and yielded the proper entropy gain just above T_c. The transition is accompanied by a dimerization of the spin sites which means that the TCNQ chains tetramerize. In terms of the one-electron Fermi wave vector in the uniform chain (k_F) this would correspond to a $2k_F$ distortion. The magnetic suscep-

TABLE I. Electronic contribution to the specific heat: entropy gain and triangular approximation.

	entropy gain at $T = 21$ K (J/mole K)		T_c (K)	γ (J/mole K^2)	ΔC_E (J/mole K)	
	theory	experiment			theory	experiment
Bonner & Fisher	1.14	1.4 ± 0.2	19.2	0.067	1.84	2.5 ± 0.4
Correlated metal	1.46	1.5 ± 0.2	19.1	0.073	1.99	2.5 ± 0.4

TABLE II. Electronic contribution to the specific heat: values of the exponential fit parameters *a* and *b*.

	experiment		theory		
	BF (Ref. a)	corr. met. (Ref. b)	BCS	singlet-triplet constant gap (70 K)	singlet-triplet BCS-like gap $[\Delta(0)/T_c = 1.58]$
a	9.7	9.1	1.24	28.1	62.4
b	2.6	2.6	1.44	3.0	2.7

[a] Using Bonner and Fisher theory for C_E above T_c.

[b] Using correlated-metal theory for C_E above T_c.

tibility as well as the semiconducting behavior in the dimerized state strongly suggest that electron correlation effects play an important role: MEM-$(TCNQ)_2$ is a high-U material.

In addition to the low temperature transition there is a transition at 335 K in which the conductivity increases by 3 orders of magnitude and the TCNQ chains become almost uniform. This transition, in terms of k_F, would be a $4k_F$ transition. In the light of the high value of U it is of interest to make some remarks about the nature of these two transitions. It is known that in the high U case a $4k_F$ transition is expected,[6,26] which in a quarter-filled system like MEM-$(TCNQ)_2$ corresponds to the formation of dimers. Each dimer can accommodate one electron in its bonding orbital, thus avoiding double occupancy, and lowering the one-electron energy. Since the Coulomb repulsion is not considerably affected by the $4k_F$ distortion, the transition can occur at high temperature in spite of the large value of U. If we now consider the dimers as electron sites we have a half-filled band which will show a $2k_F$ transition to a tetramerized state. In this transition, however, U does play an important role. For large U, it therefore occurs at low temperature. It would seem then that U separates the two transitions. The $2k_F$ transition clearly is a spin-Peierls transition because the spin degrees of freedom are lost. In the same way the $4k_F$ transition could be called an electronic-Peierls transition, because the electronic degrees of freedom are lost.

ACKNOWLEDGMENT

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