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Very-low-temperature specific heat of quinolinium(TCNQ)$_2$, a random-exchange Heisenberg antiferromagnetic chain*

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Measurements of the specific heat of quinolinium(TCNQ)$_2$ (quinolinium di-tetracyanoquinodimethanide) are reported for the temperature range $0.07 < T < 5$ K and magnetic field range $0 < H < 20$ kOe. The results do not fit a model in which the magnetic contribution to the specific heat C_H is that of a regular antiferromagnetic chain, a quarter-filled band, or isolated magnetic impurities. A good fit to the data is obtained using the Bulaevskii model for a random-exchange Heisenberg chain with a density of states having the form $\rho(\epsilon) = Ak^{\alpha-1}|\epsilon|^{-\alpha}$, where ϵ is the quasiparticle energy and A and α are parameters chosen to fit the data. For the sample used, a good fit is obtained using $A = (1.03 \pm 0.11) \times 10^{-3}$ K$^{\alpha-1}$ and $\alpha = 0.82 \pm 0.01$.

I. INTRODUCTION

In this paper we report measurements of the specific heat of the charge-transfer compound quinolinium(TCNQ)$_2$ (quinolinium di-tetracyanoquinodimethanide), over the temperature range 0.07–5 K in magnetic fields up to 20 kOe. The motivation for this work has been to understand and characterize the low-temperature magnetic properties of quinolinium(TCNQ)$_2$.

At temperatures on the order of 300 K, quinolinium(TCNQ)$_2$ has been described as a one-dimensional (1D) organic metal on the basis of its electrical conductivity,[1] crystal structure,[2] and nuclear spin-lattice relaxation rate.[3]

In the low-temperature regime, the electrical conductivity associated with the electrons transferred from the quinolinium to the TCNQ chains becomes very small. This indicates that either the electrons become localized, that they remain delocalized in a band which is filled at low temperature, or that they are partially localized on interrupted metallic chains. The latter possibility can be ruled out as inconsistent with low-temperature nuclear spin-lattice relaxation measurements[4] which display characteristics that are far removed from those expected of nuclear relaxation by conduction electrons, even when account is taken of the exotic embellishments which can occur in one-dimensional systems.[5] As indicated later in this paper, the magnetic properties point rather strongly to electron localization at low temperatures, at least for those electrons involved in magnetic effects. The magnetic properties can originate in the transferred electrons, electrons left on the quinolinium chains because of incomplete charge transfer,[6] or magnetic impurities.

There has been some controversy in the interpretation of the magnetic properties at low temperatures. One point of view has been to treat the transferred electrons as a regular one-dimensional Heisenberg antiferromagnet or a narrow quarter-filled electronic band.[7,8] In this interpretation, the low-temperature magnetic susceptibility χ is divided into a slowly varying part due to the 1D states plus a rising Curie tail attributed to paramagnetic impurities.[7] The low-temperature specific heat is then expected to be the sum of a term linear in temperature (T) from 1D states, a term cubic in T from the lattice, and a magnetic-field-dependent Schottky anomaly from the magnetic impurities.[7]

Another viewpoint has been to treat the low-temperature magnetic properties as intrinsic,[9,10] due to disorder in the orientation of the asymmetric quinolinium molecule,[11] and resulting in the physical properties of a random-exchange Heisenberg antiferromagnetic chain[10] (REHAC). This point of view has been supported most clearly in the static χ and high field magnetization (M) measurements down to 100 mK by Bulaevskii *et al.*,[10] and the resonant χ measurements of Tippie and Clark[12] down to 30 mK. Furthermore, the phenomenological model of Bulaevskii *et al.*[10] used to explain the measurements exhibits a remarkable consistency in interpreting all the thermodynamic properties.

More recently, it has been shown by Theodorou and Cohen[13] that the temperature and field dependence of the thermodynamics of the Bulaevskii model can be arrived at for the low-temperature limit on a microscopic basis via the Hubbard model and electron localization by a random electrostatic potential.

However, there is one property, the magnetic part of the specific heat at constant field (C_H), for which interpretation of the experimental sit-

uation has been less clear than for χ and M. The problem has been that the measurements have not been carried low enough in temperature to clearly indicate one interpretation over the other.[7,8] This question is resolved by the measurements presented in this paper, which go much lower in T and strongly support the REHAC models.

There are two other substances for which the same type of model appears to be appropriate, acridinium(TCNQ)$_2$ and N-methylphenazinium-TCNQ (NMP-TCNQ). In the case of acridinium(TCNQ)$_2$, measurements of χ,[10] M,[10] and C_H,[7,14] all point to an explanation in terms of a REHAC model. Low temperature measurements[10] in NMP-TCNQ of χ and M also show such behavior. Results on C_H are less clearcut, as there is disagreement in experimental values,[7,11,15,16] probably due to sample degradation or different phases of the material.[17] In the very-low-temperature regime there is evidence[16] for an important contribution due to interacting electron spins, but the observed values of C_H deviate significantly from the prediction of the REHAC model described above. Because of the problems commonly encountered with multiple-phase NMP-TCNQ samples, we have chosen to concentrate on quinolinium(TCNQ)$_2$.

II. EXPERIMENTAL DETAILS AND RESULTS

The sample used in these measurements was obtained from K. Holczer, G. Grüner, and A. Janossy of the Central Research Institute of the Hungarian Academy of Sciences. It was prepared according to the method of Melby *et al.*,[18] using carefully purified starting materials. Conductivity measurements similar to those described in the review by Shchegolev[19] were observed. The sample was stored either in air or vacuum. No major effects on electrical conductivity of the sort attributed to acetonitrile solvent[20] were observed. Static magnetic susceptibility measurements made by Holczer[21] also show the same type of behavior as that reported by Shchegolev.[19] The mass used in the specific-heat measurements was 20.0 ± 0.2 mg. The polycrystalline sample was mixed with 10.0 ± 0.2 mg of Apiezon N grease for thermal contact and the resulting mixture mounted to the calorimeter. Details of the calorimeter and its use will be published elsewhere.[22]

The addenda specific heat was measured in a separate run in which 10.0 ± 0.2mg of N grease was added to the calorimeter. The addenda contribution was as follows: 10% at 75 mK, 15% at 250 mK, 34% at 1 K, and 45% at 4 K. Typical temperature errors are 1% above 1 K, 2% down to 100 mK, and 4% below 100 mK. The variation in our spurious heat leak (≃1 nW) is the main cause of errors in specific heat at the lowest temperatures. Typical error bars are 10% for specific-heat measurements. A thermal relaxation method was used. The heating waveform in all measurements was adjusted so that the temperature change of the calorimeter during the thermal relaxation was less than 1% of the temperature. Magnetic field accuracies are 1% or better.

Now we turn to a presentation of the data. The sample specific heat (addenda subtracted) as a function of temperature at zero magnetic field (H) is shown in Fig. 1 by the circles (and dotted line above 500 mK). It is separated into a lattice term (solid line) proportional to T^3 and a term which we attribute to magnetic degrees of freedom (dashed line) represented as $T^{0.18}$. Above 500 mK subtraction of the T^3 term leaves the crosses as the magnetic part. Below 500 mK the T^3 term is negligible, and the entire magnetic contribution is given by the circles. The T^3 term obtained in this work is the same as that observed for quinolinium (TCNQ)$_2$ by Delhaes *et al.*[7] and about 15% smaller than that of Etemad *et al.*[8] The behavior of the magnetic part C_H as a function of H is shown for several values of T in Fig. 2. The solid curve is our fit of the Bulaevskii model,[10] which is discussed in more detail in Section III.

III. INTERPRETATION AND DISCUSSION

First let us consider the separation we have made of C_H into lattice and magnetic parts. Our justification for subtracting a T^3 term and attrib-

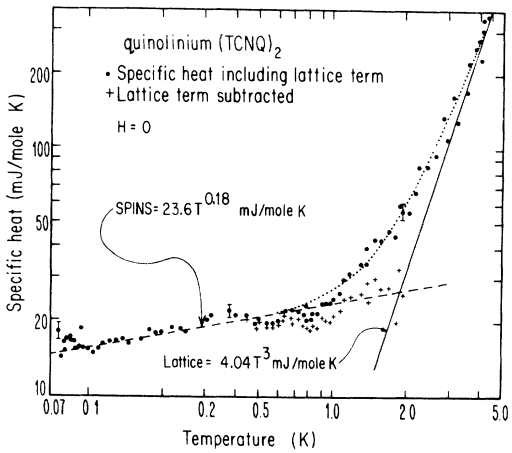

FIG. 1. Total specific heat C as a function of temperature for quinolinium(TCNQ)$_2$ at $H = 0$. The experimental values (circles, dotted line) are separated into a lattice term cubic in temperature (solid line) and a magnetic part (crosses, circles below 0.5 K, dashed line). The power law for the magnetic part $C_H = 23.6T^{0.18}$ mJ/mole K is interpreted as due to random exchange Heisenberg chains.

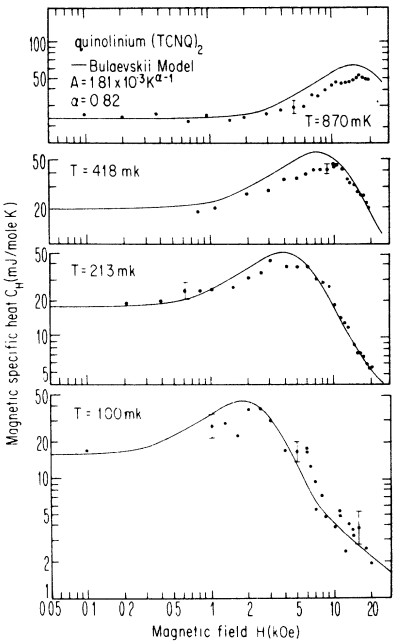

FIG. 2. Magnetic specific heat C_H of quinolinium(TCNQ)$_2$ as a function of magnetic field for several values of the temperature. The solid curves are calculated using the Bulaevskii model.

uting it to the phonon contribution is as follows. Although the electronic properties of the system may be highly anisotropic because of the directed nature of some of the electron wave functions,[23] there is little reason to believe that the structure is anisotropic enough with regard to binding and lattice vibrations to have a phonon specific heat below 2 K which deviates substantially from a T^3 behavior. This is shown, for example, in the compound TTF-TCNQ, (tetrathiafulvalenium-tetracyanoquinodimethanide), where the phonon contribution to the specific heat[24] is not masked at low T by a large magnetic contribution. In this case, there is a small deviation from T^3 behavior around 14 K, presumably due to a peak in the density of acoustic-phonon states caused by a relatively soft phonon. But at lower temperatures (down to 1.7 K) the specific heat rather accurately follows a T^3 behavior. In addition to the arguments just given, we can extract a rather crude upper limit to the phonon contribution at the lowest temperatures from the low-temperature parts of Fig. 2, where it is seen that a magnetic field of 20 kOe reduces C_H by about a factor of 10 at 100 mK and a factor of 4 at 213 mK. Since the phonon contribution should be independent of H, the value of C_H remaining above 20 kOe is an upper limit on the phonon contribution at these temperatures. In fact, from the behavior of C_H in the high-field regime, one can infer that the upper limit to the phonon contribution is substantially less. Hence, our measurements show quite directly that for the lowest temperatures, the phonon contribution is at most a small fraction of C_H. For the purpose of further discussion it will be assumed that the phonon contribution to C_H behaves as T^3.

There are also some arguments which support our attribution of the nonphonon part of C_H to magnetic degrees of freedom. First, from Fig. 2 it is clear by the behavior in a magnetic field that most of C_H at the lower temperatures is magnetic in origin. The second point is that, as discussed below, there is very good agreement between the experimental results and the Bulaevskii model, which treats magnetic degrees of freedom. Finally, one might ask what reasonable nonmagnetic alternatives exist for the nonphonon part of C_H. We have examined several possibilities, such as an unfilled band of electrons ($C_H \propto T$) and tunneling states associated with disorder in the orientation of the quinolinium molecule, but are unable to find any such alternative that is consistent with what is known about quinolinium(TCNQ)$_2$. In our further discussion it will be assumed that the nonphonon part of C_H is of magnetic origin.

Let us begin our discussion of the magnetic part of C_H by briefly pointing out that its major features are neither due to regular Heisenberg antiferromagnetic chains, a quarter filled band, nor to noninteracting magnetic impurities. If its origin were regular chains or a quarter filled band, we should see[7,25] $C_H \propto T$ and independent of H for reasonable values of bandwidth or exchange interaction, which strongly disagrees with the experimental result. Also, if C_H were due to noninteracting paramagnetic impurities, it would be zero for $H=0$ and show a Schottky anomaly[7] as a function of H. Figure 1 shows instead a large contribution for $H=0$. In Fig. 2 there is a peak in C_H reminiscent of a Schottky anomaly. This point is examined in more detail in Fig. 3, which shows C_H at $T=213$ mK as a function of $g\mu_B H/kT$, where g is the electron g value (=2), μ_B the Bohr magneton, and k Boltzmann's constant. The behavior of a Schottky anomaly corresponding to $N=8.35 \times 10^{21}$ spins/mole would give the contribution shown by the dashed line. Although the observed experimental peak in C_H corresponds roughly to that of a Schottky anomaly for electrons, the behavior away from the peak is quite different, with this difference exceeding a factor of 10 in the high and low-field regions.

In contrast to the above, the Bulaevskii model does give a good account of the observed low-temperature thermodynamic properties of quinolinium (TCNQ)$_2$ over a wide range of temperature and

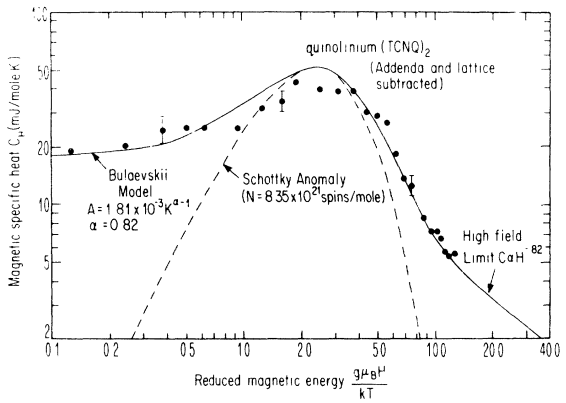

FIG. 3. Magnetic specific heat C_H of quinolinium(TCNQ)$_2$ as a function of $g\mu_B H/kT$ at 213 mK. The solid curve is calculated using the Bulaevskii model. The high-field limit is seen to occur only for $g\mu_B H/kT \gtrsim 18$. Comparison with C_H for the Schottky anomaly of noninteracting impurities (dashed line) shows that C_H is not caused by such impurities.

field. For this reason, all of our further discussion will be in terms of this model.

The Bulaevskii model has two adjustable parameters, A and α, which are used to specify a phenomenological density of states (ρ)

$$\rho(\epsilon) = Ak^{\alpha-1}|\epsilon|^{-\alpha}, \tag{1}$$

where ϵ is the energy of a state. The states are filled using Fermi statistics for the quasiparticles, which are used in a fermion representation of the localized electron spins. It is the spirit of the model to fit A and α to a wide range of thermodynamic properties. The form of $\rho(\epsilon)$ given by Eq. (1) is assumed to hold only for small ϵ. Clearly, it cannot continue for all ϵ, as $\rho(\epsilon)$ would be nonintegrable. On physical grounds there must be an upper limit on the magnetic interactions which corresponds roughly to the maximum, or nearest-neighbor exchange interaction between spins. It is therefore expected that there will be an upper cutoff on ϵ with perhaps some structure in $\rho(\epsilon)$ near the cutoff. However, as long as experiments are restricted to kT or $g\mu_B H$ much less than the range of ϵ for which $\rho(\epsilon)$ changes from Eq. (1), these deviations are not expected to appear in the measurements. These same arguments can also be made for changes associated with finite lifetimes of the quasiparticles.

It should be pointed out here that Theodorou and Cohen[13] have arrived at results very close to the Bulaevskii model. By using a disordered Hubbard model they have calculated a random, antiferromagnetic exchange interaction J between spins with a distribution function $\rho(J)$ having the form[26]

$$\rho(J) \propto J^{-\alpha}, \quad 0 < \alpha < 1. \tag{2}$$

They speculate that the ϵ of the Bulaevskii model can be associated with J, thereby suggesting a microscopic model for the phenomenological $\rho(\epsilon)$ of the Bulaevskii model. Furthermore, this model permits them to calculate $\rho(J)$ for all J and, in the case of NMP-TCNQ, shows a large peak in $\rho(J)$ corresponding to the nearest-neighbor exchange interaction. At higher J, $\rho(J)$ rapidly drops to zero. They can apply a cluster model, which gives the same behavior for χ, C_H, and M in the high- and low-field limits as the Bulaevskii model (discussed below). Their model has not yet been developed enough to provide a fully quantitative description of the intermediate field regime, nor a fully quantitative connection among χ, M, and C_H.

The results of the Bulaevskii model needed for our discussion are[27]

$$C_H(T,H) = ANk(g\mu_B H/k)^{1-\alpha} Y_\alpha(t), \tag{3}$$

$$Y_\alpha(t) = t^{-2}\int_0^\infty x^{-\alpha}\left(\frac{(1+x)^2}{\coth^2[(1+x)/t]} + \frac{(1-x)^2}{\coth^2[(1-x)/t]}\right)dx, \tag{4}$$

$$t = 2kT/g\mu_B H, \tag{5}$$

and

$$M = g\mu_B N\left(\frac{1}{2} - \int_{-\infty}^{\infty}\frac{A|\epsilon|^{-\alpha}d\epsilon}{1+\exp[(\epsilon+g\mu_B H)/kT]}\right), \tag{6}$$

where N is the number of spins and x is the dimensionless variable $\epsilon/g\mu_B H$. In the low-field limit, $g\mu_B H \ll kT$, Eqs. (3)–(6) reduce to[10]

$$C_H(T,0) = 2(1-2^{\alpha-1})\Gamma(3-\alpha)\zeta(2-\alpha)ANkT^{1-\alpha} \tag{7}$$

and

$$\chi(T, H\to 0) = 2(1-2^{1+\alpha})\zeta(-\alpha) \times \Gamma(1-\alpha)(Ag^2\mu_B^2/k)NT^{-\alpha}, \tag{8}$$

where $\Gamma(z)$ and $\zeta(z)$ are the gamma function and Riemann function, respectively. In the high-field limit, $g\mu_B H \gg kT$, Eqs. (3)–(6) give[10]

$$C(T,H) = \tfrac{1}{3}\pi^2 ANkT(g\mu_B H/k)^{-\alpha} \tag{9}$$

and

$$M(0,H) = (1-\alpha)^{-1} g\mu_B NA(g\mu_B H/k)^{1-\alpha}. \tag{10}$$

Our fitting of the data to the parameters of the Bulaevskii model has been done as follows: Measurements[12] of χ were analyzed using Eq. (8) to obtain the exponent α on the same sample used for specific-heat measurements. Our reason for doing so is that the uncertainty in the determination of α from χ is much less than with the spe-

cific-heat experiments. An independent value of A is also obtained from the χ measurement. It is important to make the χ measurement used to obtain α on the same sample as the specific heat, as there is some difference in the value of α obtained from χ as measured on samples of different origin.[12]

The value of α obtained for our sample as described above is $\alpha = 0.82 \pm 0.01$. We then use Eq. (7) applied to Fig. 1 to obtain $A = (1.81 \pm 0.1) \times 10^{-3}$ K$^{\alpha-1}$. The corresponding curve $C_H(T, 0) = (23.6 \pm 1.0)T^{0.18 \pm 0.01}$ mJ/mole K is indicated as the dashed line on Fig. 1, where it is seen to give a good fit to the data over the range 0.07–2 K. The interplay between the choice of α and A is such that a 5% decrease in α would force an increase of 2% in A to fit the data.

In the intermediate-field regime it is necessary to compare the data with numerical calculations using Eqs. (3)–(5). This has been done using the same values of A and α given above. The results at several temperatures are shown as the solid curves on Fig. 2, where it is seen that a fairly good agreement with the experimental results is obtained. These curves are moderately sensitive to the choice of α, in that a 5% decrease in α results in a 12% decrease in the height of the peak in C_H. It is tempting to try the high-field limit of C_H given in Eq. (9) as a means of determining α. Unfortunately, it is necessary to go to rather large values of H before this limiting behavior occurs. This point is illustrated in Fig. 3, where it is seen that the high-field limiting behavior is delayed until H is increased to nearly eight times that value which corresponds to the peak in C_H.

At this point it is appropriate to discuss the extent to which our results truly represent the properties of quinolinium(TCNQ)$_2$ as opposed to being an uncontrolled impurity effect. The question will be considered from the point of view of crystal phases, measurements of electrical conductivity, magnetic susceptibility, electron spin resonance, and specific heat. To the best of our knowledge, there is but a single phase of quinolinium(TCNQ)$_2$, which suggest that all measurements have been made on the same phase of the material. This is in contrast to the case of NMP-TCNQ, where the appearance of multiple phases has plagued the interpretation and comparability of many experimental measurements.[28]

The property showing the greatest variability in quinolinium(TCNQ)$_2$ is the electrical conductivity. Although measurements on different samples give about the same conductivity above 150 K, there are substantial variations on the behavior of σ at low temperatures. Some of these differences have been attributed to small amounts of acetonitrile solvent in the sample.[20] They could also be caused by other impurities or different degrees of disorder in the sample. However, these different values of σ are large only in the low-temperature regime, where σ is very small and strongly dependent on imperfections. Since our sample was prepared using standard techniques, was stored under conditions to eliminate acetonitrile, and had an electrical conductivity showing the classical form,[19,20] we believe it to be nearly intrinsic, with only a very low level of nonintrinsic imperfections.

The variations in χ among different samples of quinolinium(TCNQ)$_2$ is much less than for σ.[12,19,21] This is as expected, for the observed values of χ are such that a large fraction of the transferred spins are involved. Hence measurements of χ should more clearly represent the intrinsic properties of the material than do the values of σ at low temperatures. For example, at room temperature, measurements of[12,19,21] χ show that nearly all of the transferred electrons contribute to χ.[29] Over the temperature range 10–0.1 K,[19] and lower,[12] samples from different origins have all shown the behavior of Eq. (8). There are small sample-dependent differences in the exponent α, for which values in the range 0.73–0.86 have been observed.[12]

It is instructive to augment the consideration of χ with results obtained from low- and high-field electron-spin-resonance (ESR) measurements. First, we note that the low-field ESR linewidth undergoes smooth, modest changes over the entire temperature range from 30 mk to 300 K.[12] At all temperatures it is strongly narrowed by exchange or motion. In addition the g tensor of the 10-GHz ESR is nearly constant over the temperature range 1.5–300 K.[30] These observations indicate that the susceptibility over the whole temperature range is due to the same type of electrons. Since they are almost all of the transferred electrons at room temperatures, it is very likely that the observed χ is mainly intrinsic to quinolinium(TCNQ)$_2$. This is important with regard to our interpretation of C_H, as we attribute it to the same spin degrees of freedom which are responsible for χ.

Finally, we consider the evidence from C_H itself. The agreement in the region of overlap between our measurements and those published for other samples[7,8] tends to support the idea that our results are intrinsic to the material. Also, the agreement between χ and C_H within the framework of the Bulaevskii model (discussed below) taken with our earlier remarks about χ is evidence that our C_H measurements reflect mainly intrinsic

properties of quinolinium$(TCNQ)_2$, with room for a small amount of nonintrinsic behavior attributed to varying disorder and small amounts of impurities, such as may be responsible for the small sample variations observed in the exponent α measurements of χ.[12]

Now we turn to the implications of our experimental results. The first point to be made is that the Bulaevskii model gives a good account of both the susceptibility[12] and specific heat over a wide range of T and H. The same value of α gives a good fit to both measurements. There is, however, a difference of about 50% in the value of A (the χ value[12] for A is $A=(1.03\pm0.11)\times10^{-3}\ \mathrm{K}^{\alpha-1}$). Although measurements of M have not been made on this sample, in the basis of the other work[10] we expect that such measurements would show agreement with χ and C_H within the framework of the Bulaevskii or similar models.[13,31] At this point it is not clear whether the 50% discrepancy in A is an artifact of the Bulaevskii model, the sample, or the measurements. We do not feel that this is an important challenge to the main point of this work, namely, that one is observing the properties of a random exchange Heisenberg antiferromagnetic chain. (Alternatively, it might be called a one-dimensional antiferromagnetic spin glass.) We do not know of any other type of model which comes close to describing the data.

It is worth pointing out that Eq. (1) of the Bulaevskii model appears to hold over a remarkably large range of energy. This can be seen by noting that measurements at large H or T probe that part of the density of states for which $\epsilon \lesssim g\mu_B H$ or $\epsilon \lesssim kT$, whichever is larger. Measurements[10] of M to about 70 kOe and[10,12] χ to ~10 K indicate that Eq. (1) is appropriate for energies up to $\epsilon/k \simeq 10$ K. Our experiments on specific heat bear this out up to $\epsilon/k \simeq 3$ K. At the low end of the scale, measurements of χ agree with Eq. (1) down to 30 mK,[12] and perhaps even as low as 8 mK.[32] Our specific-heat measurements support the same conclusion down to ~70 mK. Taken together, the evidence indicates that Eq. (1) is valid over the range $10^{-2} \lesssim \epsilon/k \lesssim 10$ K, a factor of 10^3 in energy!

An important question is whether the observed low-temperature magnetic properties of quinolinium$(TCNQ)_2$ are one dimensional. If one follows the model of Theodorou and Cohen,[13] or accepts their speculation that ϵ and $\rho(\epsilon)$ of the Bulaevskii model are to be associated with J and $\rho(J)$, a clearcut consequence is that the low-temperature magnetic properties of quinolinium$(TCNQ)_2$ are strongly one dimensional. The reason for this is that the form of $\rho(J)$ in Eq. (2), with a singularity at $J=0$, happens only for the one-dimensional case.[33] Their analysis indicates that in two or three dimensions, $\rho(J)\to 0$ as $J\to 0$, which then leads to a completely different low-temperature behavior.

Finally, we comment on the number of spins responsible for the low-temperature magnetic properties of quinolinium$(TCNQ)_2$. From our values of $A=1.81\times10^{-3}\ \mathrm{K}^{\alpha-1}$ and $\alpha=0.82$, Eq. (1) can be integrated up to $\epsilon/k=10$ K, with the result that the number of quasiparticle states with $|\epsilon|/k<10$ K is 1.83×10^{22}/mole, a molar concentration of 3.0%. Following the speculation of Theodorou and Cohen indicated above, this corresponds to a molar concentration of about 3.0% for spins with an exchange interaction $J/k<10$ K. One might ask what is the situation for the other 97% of the spins. If we follow the model of Theodorou and Cohen, the other spins are involved in exchange interactions for which $J/k>10$ K. In their application of the model to NMP-TCNQ, Theodorou and Cohen[13] found that the asymptotic form for $\rho(J)$ [Eq. (2)] was followed to fairly large values of J, and then had a large peak near the nearest-neighbor value for J. Presumably the behavior is similar for quinolinium$(TCNQ)_2$.

It is instructive to see what this means for χ and C_H. We will restrict the comments to the limit $H\to 0$. They are easily extended to finite H. Roughly speaking,[13,31] only those spin pairs coupled by $J/k<T$ will participate in χ and C_H. Spins with $J/k\gg T$ will have settled into a well-separated nonmagnetic singlet state, as with an antiferromagnetic exchange coupled pair. The spins for which $J>kT$ are effectively removed from the system. At room temperature, most of the spins can participate in χ.[29] As T is decreased, the number of participating spins decreases, until at 10 K, it is only about 3%. As one goes still lower in T, even fewer spins take part. The detailed behavior of C_H and χ then follows from the form of $\rho(J)$.

In summary, we have measured the specific heat of quinolinium$(TCNQ)_2$ over the temperature range of $0.07<T<5$ K and magnetic field range $0<H<20$ kOe. Below 1.5 K it is dominated by magnetic degrees of freedom, which are interpreted as being a random-exchange Heisenberg antiferromagnetic chain. The model of Bulaevskii *et al.*[10] gives a good quantitative fit to the data.

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[26]According to Ref. 13 there is a logarithmic term which multiplied the right-hand side of Eq. (2). However, its effect is expected to be so small that we have neglected it.

[27]Equations (1), (3)–(5), (7), and (9) are taken from Ref. 11; Eqs. (6), (8), and (10) are taken from Ref. 10. The following corrections have been made: $k^{\alpha-1}$ multiplied by Eq. (3), $t^{\alpha-2}$ multiplied to Eq. (4), and the exponent $1-\alpha$ changed to $-\alpha$ in Eq. (9).

[28]There is evidence for an ordered and disordered phase of the "phase 1" NMP-TCNQ, which has segregated stacks. "Phase II" NMP-TCNQ has alternating or nonsegregated stacks [see, for example, C. J. Fritchie, Jr., Acta Crystallogr. 20, 982 (1966); H. Kobayashi, Bull. Chem. Soc. Jpn. 48, 1373 (1975); B. Morosin, Phys. Lett. A 53, 455 (1975); and G. Fujii, I. Shirotani, and H. Nagano (unpublished). In addition [A. Epstein (private communication)] some materials thought to have been NMP-TCNQ has actually had an extra proton attached to the nitrogen opposite the CH_3 group in NMP.

[29]This can be illustrated with a naive model by calculating the molar concentration of *free* spins following a Curie law needed to produce the measured χ. By using the results of Ref. 19, we find that at 300 K, 50% of the transferred spins are required. This number reduces to 14% at 100 K, 5.2% at 30 K, 2.7% at 10 K, 1.8% at 3 K, and 1.4% at 1 K. Because of the antiferromagnetic interactions in the system, the actual number of spins involved is always larger than that indicated by a free-spin calculation.

[30]J. Sanny and W. G. Clark (unpublished). Although the g-tensor measurements do not as yet go into the very-low-temperature regime, they do go well into the range where the low-temperature behavior of χ is observed.

[31]There is a third model which shares many of the features of those described in Refs. 10 and 13. It treats the chains as a system of independent exchange coupled pairs having a probability distribution the same as that in Ref. 13. Details of this model will be published elsewhere.

[32]Preliminary results [W. G. Clark and G. Frossati (unpublished)] for χ of quinolinium(TCNQ)$_2$ down to $T \simeq 8$ mK indicate a continuation of the behavior observed down to 30 mK in Ref. 12.

[33]M. H. Cohen and G. Theodorou (private communication).