Low-temperature magnetism of quinolinium(TCNQ)$_2$, a random-exchange Heisenberg antiferromagnetic chain. I. Static properties

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Measurements of the magnetic susceptibility (χ) using low-field electron spin resonance over the temperature range 30 mK $< T <$ 300 K are reported for a polycrystalline sample of quinolinium-di-tetracyanoquinodimethanide, as well as over a more limited range in T for two other polycrystalline samples and one single-platelet sample. In all cases, below $\sim$20 K, $\chi \propto T^{-\alpha}$, where for each preparation batch α is constant. The temperature dependence of χ is interpreted as evidence that quinolinium-di-tetracyanoquinodimethanide is a random-exchange Heisenberg antiferromagnetic chain with a high concentration of spins. It is speculated that the variation in α between different preparation batches may be due to variations of short-range order introduced by different conditions of crystal growth. The relation of the observed χ to the microscopic exchange coupling is discussed in terms of recent renormalization calculations and the quasiuniversal behavior predicted by them. The absence of a sharp magnetic phase transition is interpreted as the suppression of an ordering transition by disorder.

I. INTRODUCTION

During recent years much interest has been directed to the study of disordered systems and to one-dimensional systems. In this paper we report the low-temperature magnetic susceptibility (χ) of quinolinium(TCNQ)$_2$ (quinolinium-di-tetracyanoquinodimethanide), a member of a class of materials which are both disordered and one dimensional. More precisely, in preliminary reports of this work[1,2] and other published work [3–9] very strong evidence is found that below 20 K this material behaves as a random-exchange Heisenberg antiferromagnetic chain (REHAC).

Several interpretations have been applied to previous measurements of χ in quinolinium (TCNQ)$_2$.[3,4,6,7,10–15] One important reason for this is that most experimental work that has been reported does not go below 1.5 K. Because of this limitation, the low-temperature behavior of χ was not well enough defined to point to a unique interpretation. The early exception was the measurements of χ and magnetization (M) down to 0.1 K reported by Bulaevskii *et al.*[3] using static methods. It was this work which first clearly pointed out the importance of random-exchange models for the interpretation of the low-temperature χ in these materials. In this paper we report further low-temperature measurements of χ in quinolinium(TCNQ)$_2$. They extend and complement those of Bulaevskii *et al.* in that they use electron-spin-resonance (ESR) methods, go to lower temperatures (30 mK), cover several different batches of material, and include work on a single platelet sample.

The overall behavior of χ for quinolinium(TCNQ)$_2$ as seen in earlier experimental work and that of Fig. 1 (discussed in more detail below) shows a nearly flat temperature (T) dependence above 30 K and below 20 K a steady rise of the form

$$\chi = CT^{-\alpha} \tag{1}$$

where C and α are constants and $\alpha \sim 0.8$. The main emphasis of this paper is the low-temperature region below 20 K where the random-exchange characteristics are most evident.

According to the earlier theoretical models, two of the properties characteristic of REHAC behavior

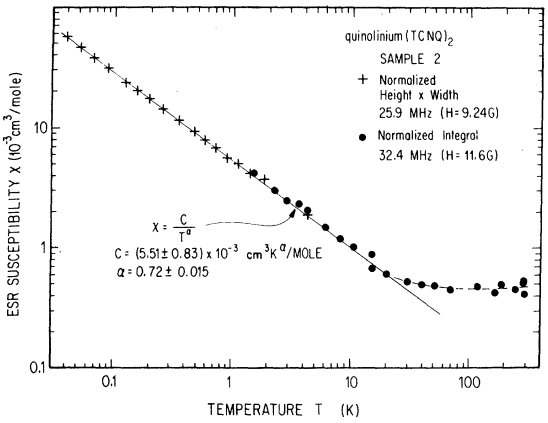

FIG. 1. ESR susceptibility as a function of temperature for sample 2. The crosses are obtained from the product of the height and the width of the absorption line shape and the circles are obtained by integrating the area under the absorption. The power law at low T is evidence of REHAC behavior.

are[2-4,13,14,16] $\chi \propto T^{-\alpha}$, and a low-temperature, high-field magnetization $M \propto H^{1-\alpha}$. Recent renormalization results[17-19] indicate that there may be minor modifications to these exponents. All of the successful theoretical models contain as essential ingredients the notions of one dimensionality and randomness in the exchange couplings. As discussed more completely in Sec. IV, this randomness leads to a divergence in the density of states (and hence in χ) as the energy of the elementary magnetic excitations goes to zero. The renormalization work shows that this can happen even if there is no corresponding divergence in the distribution of exchange coupling [$P(J)$]. It also indicates an extreme insensitivity to the functional form of $P(J)$ and therefore a quasiuniversal behavior for the thermodynamic properties.

There are now many systems for which REHAC behavior has been reported at low temperatures. The first of these[1-8,20-23] were pure segregated stack TCNQ salts with equal spacing on donor and acceptor chains and having asymmetric donors, such as quinolinium(TCNQ)$_2$. Later this behavior was observed in such materials into which additional disorder had been introduced by chemical doping or irradiation.[7,20,24,25] More recently, such behavior has been reported even for TCNQ salts having symmetric donors, but with additional disorder introduced by chemical doping or irradiation.[7,20]

There are several reasons for choosing quinolinium(TCNQ)$_2$ for the study reported here. The preparation of single-phase material is straightforward. There is little or no change in magnetic properties with time or moderate exposure to air. Finally, many related measurements on this material have been made at low T. These include the specific heat,[8,22] high-field magnetization,[3,26] double resonance, and g-shift identification of the magnetic species,[2] as well as dynamic magnetic properties reported in our ESR linewidth and spin-relaxation paper which accompanies this one[9] and reports of nuclear spin relaxation.[27,28]

II. EXPERIMENTAL DETAILS

The samples used in this work were supplied by K. Holczer (Central Research Institute for Physics, Budapest), A. J. Heeger (University of Pennsylvania), and N. Rysava (Institute of Physics, Prague). They are labeled, respectively 1,2,3.

Measurements of χ were made using low-field ESR. This technique could be used because at all temperatures investigated the ESR absorption line is very narrow, having a half width at half maximum linewidth ($\Delta H_{1/2}$) for the absorption amounting to only 0.05 − 0.3 G. Small (~5 mg) polycrystalline samples were packed into thin-walled quartz tubes, and the magnetic resonance coil wound on the outside of the tube. Quartz was used instead of Pyrex to avoid the spurious ESR signal found in Pyrex. Some measurements were made on a single platelet (approximately $0.002 \times 0.008 \times 2$ mm^3) of quinolinium (TCNQ)$_2$. In this case a small coil of 60 turns was wound with an inside diameter of 25 μm from 13-μm-diameter insulated Cu wire. The sample was then carefully inserted into the coil. All of the ESR absorption measurements were made at constant frequency with a swept magnetic field (H). The absorption signal was recorded directly on a signal averager over many sweeps. Checks of the line shape were made for a wide range of conditions. In all cases, a Lorentzian shape was observed. Absolute values of χ were obtained at 4.2 K or below using the Schumacher-Slichter technique,[29] in which the proton NMR intensity is compared with the ESR intensity at the same frequency, temperature, and spectrometer setting, but at different values of H. The absorption was measured using a Q-meter circuit[30] which operates down to very low excitation levels to avoid magnetic resonance saturation or heating at low temperatures. Most experiments below 4.2 K were done with the sample in direct contact with He in the mixing chamber of a dilution refrigerator. Above 4.2 K, a gas-flow system was used. Over the entire range of measurement covered, the low-field limit $g\mu_B H \ll k_B T$ (g is the electron g value, μ_B is the Bohr magneton, and k_B is Boltzmann's constant) was satisfied. Typical measurement uncertainties in relative measurements of χ for the bulk samples ranged from 3% at 30 mK to 15% at 300 K and in the absolute calibration was about 15%. The uncertainty in the relative measurements of χ for the single-platelet sample was 6%, and the uncertainty in T was 2 to 3%.

III. EXPERIMENTAL RESULTS

Our measured values of χ for the three samples are shown in Figs. 1–3. In most cases the area under the absorption line has been integrated to obtain χ. The one exception is Fig. 1, where the crosses are the area obtained from the product of the height and width of the ESR absorption line. Since we have verified that the line shape is Lorentzian, the two methods are equivalent. It should also be noted that the χ scale for the single platelet (Fig. 3) measurement is arbitrary. Because of the small mass of this sample (5×10^{-8} g), it was not possible to obtain a reliable proton comparison signal. Finally we point out that Fig. 3 shows results for "crushed" and uncrushed samples. The crushing in this case consisted of mashing the sample with a small glass rod until the needles took on the appearance of a powder to the unaided eye.

There are several points demonstrated in Figs. 1–3 and based on other measurements which we single

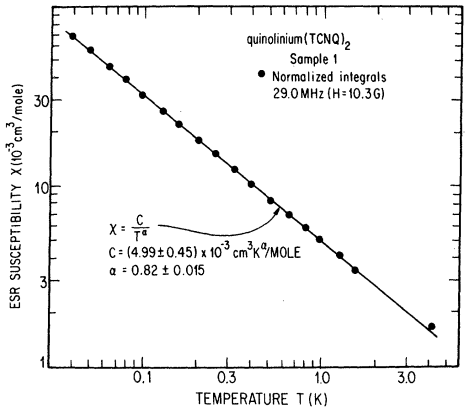

FIG. 2. ESR susceptibility as a function of T for sample 1. All points are obtained by integrating the area under the absorption curve. The power law with $\alpha < 1$ is evidence of REHAC behavior.

out for interpretation They are the following:

(1) Below 20 K, $\chi = CT^{-\alpha}$ [Eq. (1)]. The measurements yield a very accurate determination of α. In fact, if we take into account all uncertainties associated with the measurement (spectrometer, noise, thermometry, etc.), the uncertainty in α is typically less than 1.5% for the powders and 3% for the single platelet. The measured values of C and α for the different samples are summarized in Table I.

(2) Different preparation batches have slightly different values for C and α, as indicated in Table I. The range in α we have observed for $Qn(TCNQ)_2$ is $0.72 < \alpha < 0.85$.

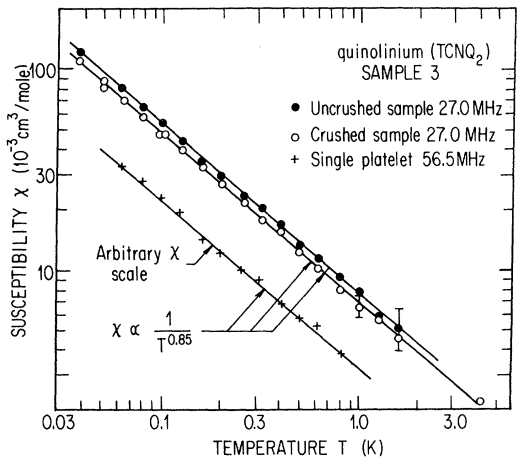

FIG. 3. ESR susceptibility as a function of T for sample 3. The circles are absolute measurements for uncrushed (closed circles) and crushed (open circles) preparations. The crosses are relative measurements on a single platelet of about 5×10^{-8} g. The fact that all these slopes are equal indicates that all parts of the batch have the same exponent α.

TABLE I. Sample properties.

Sample	Exponent α	Amplitude factor C 10^{-3} cm^3 K$^\alpha$/mole
1	0.82 ± 0.015	5.0 ± 0.5
2	0.72 ± 0.015	5.5 ± 0.8
3 (uncrushed)	0.85 ± 0.015	7.6 ± 1.9
3 (crushed)	0.85 ± 0.015	6.6 ± 1.0

(3) The value of α observed for a preparation batch is uniform and stable. This is seen in Fig. 3 where the result is shown for three samples taken from the same batch. In other experiments, we have repeated χ measurements on samples after relatively long exposures to air and delays of more than one year. In each case no change in α was observed.

(4) Crushing the samples to a powder with a glass rod (as opposed to compression into a pellet[31]) has little or no effect on χ. This is seen in Fig. 3, where the difference in χ observed for a crushed and noncrushed sample is within the experimental uncertainty for our absolute measurement of χ.

IV. INTERPRETATION

Now we present our interpretation of the experimental results. The main result of this paper is that for all samples of quinolinium$(TCNQ)_2$ investigated, the low-temperature susceptibility varies as $\chi \propto T^{-\alpha}$ [Eq. 1]. This, along with many other measurements of low-temperature magnetic properties, identifies quinolinium$(TCNQ)_2$ as a REHAC.

There are several theoretical models which support this identification. Bulaevskii *et al.*[3] first pointed out the importance of random exchange to explain the observed physical properties and proposed that the Hamiltonian should be

$$\mathcal{H} = 2\sum_i J_i \vec{S}_i \cdot \vec{S}_{i+1} - g\mu_B H \sum_i S_i^Z, \tag{2}$$

where $\vec{S}$ is the electron spin operator, i indexes the ith magnetic ($S = \frac{1}{2}$) site on a chain, and J_i is the antiferromagnetic exchange coupling $\vec{S}_i$ to $\vec{S}_{i+1}$. The exchange is restricted to nearest neighbors and the constant J_i is taken to be a random variable whose distribution of values is discussed somewhat later. In the work of Bulaevskii *et al.* a spinless fermion model with a phenomenological density of states was used to fit the thermodynamic properties. In particular, $\chi \propto T^{-\alpha}$ [Eq. (1)]] was obtained using the density of states

$$N(\epsilon) = A\,|\epsilon|^{-\alpha}, \tag{3}$$

where ϵ is the energy and the amplitude factor A and exponent α are constants. Nearly identical results are obtained with the exchange-coupled-pair (ECP)[2,16] model using a (plausible) probability of coupling strengths of the form

$$P(J) = BJ^{-\alpha}, \tag{4}$$

where B and α are constants. This form for $P(J)$ has been proposed by Theodorou and Cohen both on the basis of the Hubbard model with diagonal disorder,[13,14] and on rather general conditions[32] whose applicability appears reasonable for quinolinium $(TCNQ)_2$. They also applied a cluster model to the REHAC and obtained the behavior $\chi \propto T^{-\alpha}$. More recently, renormalization methods have been applied to this problem[17,18][but only for small (H)]. They also show that a behavior nearly indistinguishable from $\chi \propto T^{-\alpha}$ should occur. Finally, by doing numerical calculations on finite linear chains Soos and Bondeson[19] have shown that this type of behavior also occurs even if only two values of nearest-neighbor exchange are distributed at random on the chain. In fact, they are able to fit $\chi(T)$ in our Fig. 1 over the entire range of T using one localized spin per formula unit and a nearest-neighbor exchange which is 230 K for 90% of the couplings and 70 K for the other 10%. They are also able to fit the intermediate field properties, such as the magnetization and specific heat.

Since all of the models discussed above indicate $\chi = CT^{-\alpha}$, it is natural to try to go from our observed values of C and α to the microscopic distribution for J_i in Eq. (2). Unfortunately, at the present level at which the problem is understood, this is impossible. The most important reason lies in the results of the renormalization work,[17–19] where it is seen that the value of α which characterizes the thermodynamic behavior is nearly the same for a very wide choice of coupling distributions $P(J)$. As discussed more fully below, this result shows that a quasiuniversal behavior is expected of all REHAC's as long as J is substantially random and covers a sufficient range of values.

The next experimental results on which we comment are our observations that different preparation batches have different values of α (Table I) covering the range $0.72 \pm 0.015 < \alpha < 0.85 \pm 0.015$, but that different parts of a given batch have the same value of α and that it is very stable in time. These facts suggest that pure quinolinium$(TCNQ)_2$ has different degrees of disorder according to the conditions under which crystal growth takes place. In view of the insensitivity of α to the details of $P(J)$ as shown by the renormalization calculations,[17–19] and changes in the amount and nature of the disorder by neutron irradiation,[33], the observed range of variation in α is surprisingly large. We have no explanation of why it is so large, but offer one speculation[2] which should be checked with further calculations and experiments. All of the theories presented so far assume that there is no correlation in J_i. Our speculation is that the distribution of J's may not be purely random, but may be correlated over short distances and that the value of α observed in χ is sensitive to the details of this correlation, such as its coherence length. An example of how this correlation in J could occur in quinolinium$(TCNQ)_2$ is suggested by recent diffuse x-ray-scattering work.[34] These results are consistent with the existence of short-range order in the orientation of the donor electric dipoles. If this is also the disorder responsible for the randomness of J, as has been previously suggested,[3,6,13,14] it could mean that there is in fact some correlation in J. Work on complex TCNQ salts with asymmetric donors has shown that there is a delicate balance between entropy and energy considerations in determining the degree to which the donor electric dipole moments are ordered.[6] Under these circumstances it is reasonable that the coherence length for ordering in the orientation of the donor molecules should be a sensitive function of the conditions under which the material is crystallized, and may be responsible for the variation in α observed in different batches of quinolinium$(TCNQ)_2$.

Further evidence that growth conditions might play an important role in determining α can be seen in comparing our low-T ESR measurements on as-grown quinolinium$(TCNQ)_2$ with ESR[33] (to 40 mK) and static[7] (to ~ 2.5 K) measurements on quinolinium$(TCNQ)_2$ into which disorder has been increased up to an 8% defect concentration by fast neutron irradiation. The microscopic details of disorder associated with neutron damage are, of course, quite different from those associated with the growth of pure materials; one expectation is that the neutron induced disorder is highly random. In the irradiation experiments,[7,33] it was found that although the amplitude factor C increased by a factor of 3 on going from as-grown material to an 8% defect concentration, α increased only from 0.79 to 0.86. By contrast the as-grown samples listed in Table I cover a range in α that is a bit larger, but with a range in A which is much smaller. This and the x-ray data suggest that as far as the exponent α is concerned, short-range order associated with growth conditions plays a more important role than does purely random disorder, such as that created by neutron irradiation. At present, this conclusion is highly speculative. Further experimental and theoretical work is needed to clarify it.

The final experimental result to be discussed is the fact that our crushed sample has the same χ as the uncrushed one (Fig. 3). This means that either our method of crushing does not increase the surface area enough to observe the effects attributed to[31] absorbed O_2 or that in our way of doing the experiment the ESR is not sensitive to it.

Now we turn to several points of interpretation prompted by these and related experiments. The first point is that the exchange is highly isotropic, i.e., of the Heisenberg form expressed in Eq. (2). This can be seen from the fact that a single, narrow, ESR line is observed in polycrystalline samples. On the basis of what is known of uniform antiferromagnets, if there were important anisotropic terms, the ESR line would be much broader.

Another question is what are the spins responsible for χ? Double resonance and g-shift experiments[2] have shown that the observed ESR signal is due to spins located on the TCNQ chains. This means that either charge transfer from the quinolinium donor chains to the TCNQ acceptor chains is complete, or that for some reason the spin density on the donor stacks is not observed by ESR. The point can be examined further by comparing our ESR measurement of Fig. 1 with the static χ measurement of Bulaevskii *et al.*[3] (Both samples have the same value of α.) It is seen that both results are identical within experimental error over an extremely wide range of T. This suggests that all of the spins are picked up in the ESR measurement, and that they therefore are all on the TCNQ chains.

Probably the most fundamental questions related to our experiments are what is the microscopic $P(J)$, and what are the physical insights needed to understand the correspondence between our measure $\chi(T)$ and $P(J)$? A discussion of these points follows.

An essential ingredient of the divergent $\chi(T) = CT^{-\alpha}$ is that there be a substantial number of elementary magnetic excitations with energies distributed near zero. The recent renormalization work[17–19] shows how this can be accomplished through the generation of weak *effective* couplings in a *random* chain even if the actual couplings are not weak. These weak effective couplings should generate the low-energy excitations. The simplest example of this is found in the decimation procedure of Ma *et al.*[17] It can be understood by considering the sequence of random antiferromagnetic couplings shown in Fig. 4, where the height of the bridge between nearest neighbors represents the strength of the corresponding J. Since spins 2 and 3 are coupled weakly to the rest of the chain relative to each other, they can be taken as an exchange coupled pair with a singlet ground and triplet excited states $2J_2$ above the ground state. For the purpose of calculating the low-energy states of the system, S_2 and S_3 will be in the singlet state and appear as a complete break in the magnetic chain. (Their contribution to χ is that of a "large J" pair in Fig. 2 of Ref. 16.) But the weak coupling J_1 mixes in some of the triplet state of S_2 and S_3, which then couples to S_4. According to perturbation theory, this generates a very weak effective coupling J_{eff} between S_1 and S_4 given approximately by

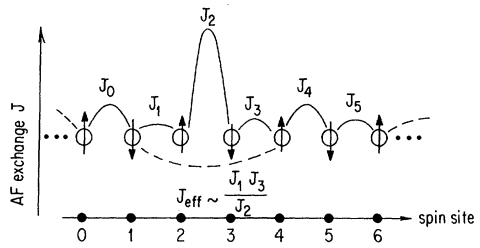

FIG. 4. Generation of weak effective exchanges in one dimension by bridging through a pair with a very large J. The height of the line connecting adjacent spins represents the strength of the exchange between them. The lower dashed line connecting sites 1 and 4 represents J_{eff} between these spins as a result of the large J_2. The actual distance between spin sites is not uniform, and is one cause of the distribution of J's (see Fig. 1 of Ref. 16).

$$J_{\text{eff}} \simeq \frac{J_1 J_3}{J_2}, \tag{5}$$

as indicated schematically by the dashed line between them in Fig. 6. In this way the original chain is replaced by one ECP with a large splitting $2J_2$ plus a truncated chain containing an effective coupling that is much smaller than any of the original couplings. Other work on this point creates a similar picture; in the work of Soos and Bondeson,[19] for example, a small J_{eff} is generated by a uniform chain segment having an even number of spins.

The details of how the weak effective couplings determine $\chi(T)$ are contained in the renormalization calculations. The really interesting point is that a quasiuniversal low-T divergence is obtained for $\chi(T)$ which is almost independent of the detailed form of $P(J)$.

Even though this quasiuniversality tends to obscure the correspondence between $P(J)$ and $\chi(T)$, there are still some comments which can be made relating $\chi(T)$ to $P(J)$. Except for the double-δ-function model of Soos and Bondeson, all of the published renormalization calculations[17–19] show a weak temperature dependence of α. This is in contradiction to our experimental results (Figs. 1–3) and those of others[2,3,21,24,33] which show that, over three decades in T, α is independent of T. It may be that this discrepancy is due to the fact that the $P(J)$'s used in most of the renormalization calculations employ a simple cutoff at large J instead of a peak at nearest- and next-nearest-neighbor separations, as obtained by Theodorou and Cohen using the Hubbard model.[13,14] This point is supported by the finite chain calculation[19] in which an excellent fit is obtained for $\chi(T)$ of quinolinium(TCNQ)$_2$ over the entire temperature range measured using a $P(J)$ with 90% of the couplings having a value $J = 230$ K (the other 10% having $J = 70$ K).

There are at present at least two very different microscopic pictures for $P(J)$ which promise to give a good fit to χ at low T. The first, exemplified by the work of Theordorou and Cohen,[13,14,32] is one of strong localization by a random disorder potential with fluctuations on the order of the Coulomb repulsion over a molecular distance scale. The other corresponds to uniform one-dimensional chain segments interrupted at random by a smaller J, as exemplified in the double-δ-function model of Soos and Bondeson.[19] [Although their model is expressed in terms of each electron being fixed to a site, it is easy to show[35] that it is nearly equivalent to the problem of randomly interrupted strands of correlated electrons which can then provide a mechanism for the observed electrical transport[4,36] in quinolinium(TCNQ)$_2$.] This situation indicates that it is very difficult to interpret $\chi(T)$ in terms of microscopic parameters for $P(J)$, and no such attempt will be made here.[37]

A related question is how many localized spins are responsible for χ? This is difficult to answer because the status of spin localization at different T is not completely clear, and the effect of antiferromagnetic interactions is to reduce χ by an amount that is difficult to know. For these reasons, our discussion of these points is necessarily speculative. As far as the question of localization is concerned, several points can be made. It is clear from the behavior of the electrical conductivity[4,36] and the nuclear relaxation[27,28,38] that a substantial number of electrons are mobile at high temperatures, where $\chi(T)$ is nearly flat. Below about 20 K, both the low electrical conductivity[4] and random exchange responsible for $\chi \propto T^{-\alpha}$ require some degree of localization of the electrons on the TCNQ stacks by disorder. But the details of the localization, which are required for a quantitative interpretation going beyond use of the available phenomenological models, are presently unavailable. All that is required of random exchange is that the localization distance of the magnetic entities over some relevant time scale should be on the order of or less than their spacing. The magnetic intities could be independent spins or groups of spins acting collectively. Clearly, much more theoretical and experimental work is needed to clarify these questions.

What can be obtained from measurements of χ is a *lower limit* on the number of spins in the problem. This is done by invoking the idea that the result of antiferromagnetic interactions is to reduce χ over what it would be for spins with no interactions. [Here, $\chi \equiv \chi(q=0, \omega=0)$, where q and ω are the wave vector and frequency, respectively.] It then follows that the actual number of spins is greater than the number ($N_{\rm eff}$) of free $S=\frac{1}{2}$ spins with a Curie $\chi_C = N_{\rm eff} g^2 \mu_B^2 / 4k_B T$ needed to fit the observed values of χ. A convenient representation of the free-spin lower limit is the active spin concentration f, which is defined as the number of free spins per formula unit and shown for sample 2 (Fig. 1) on Fig. 5. Reference to this figure shows that f is 50% at 300 K, 1% at 0.3 K, and extrapolates down to 0.3% at 7 mK. It is seen that at the highest T, essentially all of the spins are needed to produce χ. Near the crossover around 12 K, $f=3\%$, which indicates that the number of spins actually responsible for χ in the low-T region (where $\chi = CT^{-\alpha}$) is large compared to 3%.

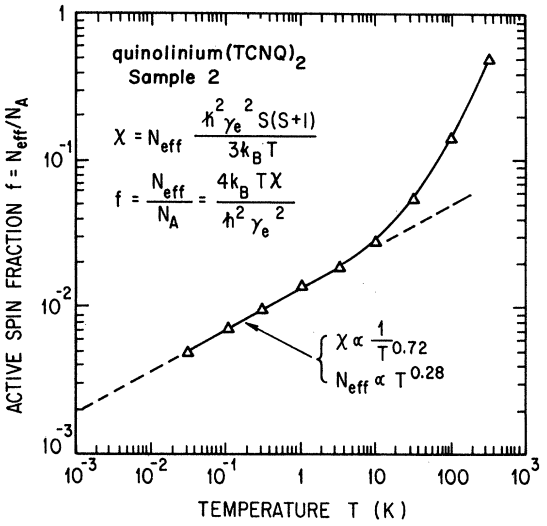

FIG. 5. Active spin fraction as a function of T for sample 2.

It is possible to go one step further and ask what is the behavior of $P(J)$ if one simply fits the ECP model to χ for the entire temperature range shown on Fig. 1. By replacing χ for a single ECP with a simple truncated ECP approximation, as shown on the inset of Fig. 6, $P_{\rm ECP}(J)$ is easily obtained and is

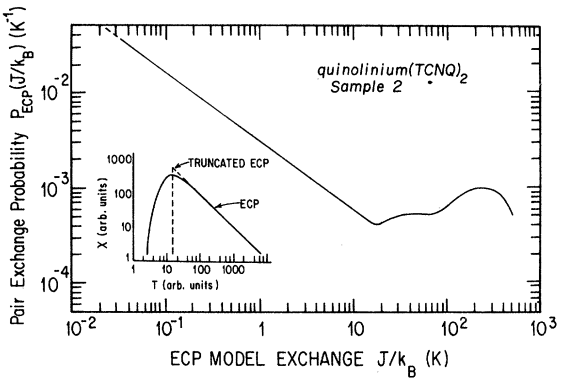

FIG. 6. Exchange probability as a function of T for the truncated ECP model. The part of the curve below 10 K is derived from our results and those above from the more accurate high T results of Ref. 3. At high T, two peaks are seen which are suggestive of the nearest- and next-nearest-neighbor terms in the model of Theodorou and Cohen (Refs. 13 and 14).

shown in Fig. 6. This figure uses the data of Fig. 1 below 10 K and the more accurate high-T data (sent to us by G. Theodorou) of Bulaevskii *et al.*[3] Details of the calculation are presented elsewhere.[39] Because of the renormalization of J described earlier, it is difficult to attach much significance to $P_{ECP}(J)$ at low T. But at high T no such renormalization is expected. There it is seen that $P_{ECP}(J)$ has two broad peaks, one at $J=35$ K with $\sim 10\%$ of the couplings and another at $J=250$ K with $\sim 90\%$ of the couplings.[40] These features correspond rather closely to the nearest-neighbor and next-nearest-neighbor peaks in $P(J)$ found by Theodorou and Cohen[13,14] in their application of the Hubbard model to NMP-TCNQ or alternatively to the double-δ-function model used by Soos and Bondeson.[19]

It is natural to ask to what extent is the observed behavior $\chi = CT^{-\alpha}$ a one-dimensional result? In terms of the earlier theoretical work,[2,13,14,32] this was believed to be a strongly one-dimensional result. The situation is more obscure with regard to the renormalization calculations.[17–19] Some insight on it can be obtained by considering the decimation procedure discussed in relation to Fig. 4. The weak effective couplings are generated by working through the excited state of a strongly coupled pair. In a one-dimensional system there is no other path with a lower energy through which the interaction can operate. On the other hand, in a two- or three-dimensional system a different route with a moderate direct coupling or a bridge through an excited state of lesser energy can commonly occur. Hence, in higher dimensionalities there should be fewer weak effective couplings, and it can reasonably be speculated that the quasiuniversal form for χ [Eq. (1)] will not be observed.

There is one other difference between the one- and higher-dimensional cases. In one dimension, with nearest-neighbor exchange, frustration[41] cannot occur, whereas in higher dimensions it can. It is also possible that this effect may play a role in distinguishing one-dimensional from higher-dimensional behavior in a random antiferromagnet. More theoretical work is needed to resolve these questions.

A final point to be made about quinolinium $(TCNQ)_2$ is that to the lowest temperatures attained in this work, there is no evidence of magnetic long-range order, as is typically found in the three-dimensional ordering of uniform Heisenberg antiferromagnetic chains. This ordering is associated with weak coupling between chains and the buildup of coherence to moderate lengths along the chains.[42] There are several reasons why no magnetic phase transition is seen in quinolinium$(TCNQ)_2$. First, because of the directed nature of the TCNQ π orbitals, the coupling between chains may simply be too weak. In addition, the disorder in J undoubtedly inhibits the buildup of coherence along the chain. An additional factor is that in some sense the system can be thought of as dilute at low temperatures, thereby reducing the spin coupling, and hence the transition temperature. There are two views of the origin of this point. Miljak *et al.*[20] propose that the spins responsible for χ at low temperature are a low concentration of defects which are localized at all temperatures. A somewhat different view is that proposed in this paper in connection with Fig. 4: the spins are concentrated, but progressive condensation of spins with a large exchange into a nonmagnetic singlet state leads to a pseudodilution of the system at T is decreased.

Very recent work[43] has shown that below about 5 mK a significant deviation from the one-dimensional property $\chi = CT^{-\alpha}$ is observed in quinolinium $(TCNQ)_2$. The reported behavior has some features in common with that of a spin-glass, which suggests that around 5 mK there is a crossover to three dimensionality via the dipolar interactions between spins on different chains.[43]

V. CONCLUSIONS

We have reported measurements of χ for quinolinium$(TCNQ)_2$ over the temperature range 30 mK $< T <$ 300 K. Below about 20 K, $\chi \propto T^{-\alpha}$, which we interpret as evidence that this material is a REHAC. It is speculated that the constancy of α within a preparation batch and its variation between batches is due to the effect of different conditions of crystal growth on disorder. We point out that although the relation between $\chi(T)$ and $P(J)$ is obscured by the quasiuniversal behavior indicated by recent renormalization models, some conclusions about the spin concentration and distribution of couplings can still be drawn. Even though the spin concentration is relatively high, no sharp magnetic phase transition of the kind normally seen in uniform one-dimensional antiferromagnets is seen. This is attributed to the suppression of the coherence length on the TCNQ chains by disorder.

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