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Disordered Magnetic Chain Behavior of Quinolinium $(TCNQ)_2$ and Related Materials at Low Temperatures

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I. Introduction. Quinolinium $(TCNQ)_2$ [$Qn(TCNQ)_2$] is a member of a group of complex, uniform segregated stack TCNQ charge transfer compounds with assymetric donors which show high electrical conductivity above 200 K. In recent years, experimental and theoretical work[1-8] has shown that their magnetic properties at low temperatures are those of a random exchange Heisenberg antiferromagnetic chain (REHAC) with a probability of nearest neighbor exchange [P(J)] given for small values of J by

$$P(J) = AJ^{-\alpha}, \tag{1}$$

where J is the strength of the exchange interaction, and A and α are constants. Deviations from this form are expected at large J.[8] For the purposes of this paper we shall simply handle the large value and normalization problem by introducing a cutoff J_M beyond which P(J) = 0. Experimentally observed values of α have fallen in the range $0.58 < \alpha < 0.87$. In addition to the intrinsic interest in exploring this new kind of magnetic system, the study of these properties is useful to gain an understanding of the ground and low lying excited states responsible for the electrical transport.

The main focus of this paper will be the questions where are the spins, and what do they do in terms of their static and dynamic properties? Also, a simple model will be presented which gives a rather good description of the observed thermodynamic properties. Since the most intensively investigated material in question is $Qn(TCNQ)_2$, we will concentrate almost all of our discussion on it.

II. Where are the spins? Any detailed understanding of the properties of $Qn(TCNQ)_2$ must take into account the location of the spins responsible for the magnetic properties of $Qn(TCNQ)_2$. In this section we report two experiments which show that the spins seen by electron spin resonance (ESR) are located on the TCNQ stacks (these Proceedings, II-118).

The first of these is a series of careful measurements at 9 GHz of the g-tensor of $Qn(TCNQ)_2$ at selected temperatures between 1.5 K and 300 K. Since a single, narrow ESR line is observed in the solid state, it is possible to make very accurate measurements. The values of the principal axes of the g-tensor (g_1, g_2, g_3) we observe are shown in Table 1, along with the mean value $\bar{g}$. The uncertainty in the measurements is ± .00005. These values are

Table 1. Principal Axes of the Electronic g-Tensor for $Qn(TCNQ)_2$.

Temperature (K)	g_1	g_2	g_3	$\bar{g}$
300	2.00253	2.00351	2.00243	2.00282
77	2.00253	2.00351	2.00242	2.00282
4.2	2.00259	2.00361	2.00236	2.00285
1.4	2.00260	2.00362	2.00234	2.00285

in agreement with those attributed by Walsh[9] to electron spins on TCNQ stacks in NMP-TCNQ, and $\bar{g}$ is very close to that observed for $(TCNQ)^-$ in solution.[10] Our result is therefore a strong indication that the spins seen in $Qn(TCNQ)_2$ reside on the (TCNQ) chains. But since the characteristics of an unpaired electron left behind on a Qn chain due to incomplete charge transfer[11] are not independently known, we must admit the possibility that the observed electrons are on the Qn stacks and accidentally have the same g-values expected of TCNQ stacks.

To settle this question we have performed a type of double resonance experiment which shows directly that the electrons are on the TCNQ chains. The effect we exploit is the hyperfine field of protons as seen by the electrons. First it must be realized that the very narrow (~ 0.2 G) ESR line shows that the average value of the hyperfine interaction is seen by the electrons. Although the details have not been worked out for the one-dimensional case with random exchange, by analogy to what is known for the uniform one-dimensional[12] and three-dimensional[13] cases we expect that this is an exchange narrowing phenomenon. It is in decided contrast to the case of a noninteracting spin localized on a molecule, where the full hyperfine splittings are seen. Hence, for $Qn(TCNQ)_2$, the field seen by the electron spin (H_e) is

$$H_e = H_o + B < I_z^p >, \tag{2}$$

where H_o is the externally applied magnetic field needed to center the ESR line, B reflects the hyperfine interaction with the protons, and $<I_z^p>$ is the net proton polarization in the vicinity of the electron spin. In the course of an ESR measurement of H_o, NMR techniques are used to set $<I_z^p>$ equal to zero. This causes a change (δH_o) in H_o given by

$$\delta H_o = B < I_z^p >. \tag{3}$$

To show that the spins are on the TCNQ stacks this experiment is done on two $Qn(TCNQ)_2$ samples. In the first, all hydrogen sites are occupied by protons. A hyperfine shift δH_o was observed at 1.5 K, 4.2 K, 77 K, and 300 K. This showed that the expected shift was there, but it could come from protons on either the Qn or TCNQ molecules. Then the experiment was repeated on a sample in which the protons on the TCNQ molecules had been replaced by deuterons. In this case the shift was not observed,[14] showing that the protons which had been removed, i.e. those the the TCNQ molecules, are responsible for the hyperfine interaction with the electron spin. This then locates the electron spin on the TCNQ molecules. More complete details of these experiments will be published elsewhere.

It is interesting to note that the above result shows the spins seen by ESR are located on the TCNQ chains for the entire temperature range 1.5 K to 300 K. Over the same range the transport and susceptibility (discussed below) properties change drastically, as indicated in Table 2. In particular, note that over this temperature range the electrical conductivity goes from $\ll 10^{-5}\ (\Omega cm)^{-1}$ to $50(\Omega cm)^{-1}$, and the molar concentration of free spins needed to give the observed susceptibility from 1.6% to 35%.