Crossover Behavior of a Random-Exchange Heisenberg Antiferromagnetic Chain at Ultralow Temperatures

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Measurements of the magnetic susceptibility (χ) of quinolinium (tetracyanoquinodimethane)$_2$ are reported over the temperature range 0.45 mK$< T <$ 40 mK with use of low-field ESR. Down to 7 mK, it is found that $\chi \propto T^{-\alpha}$ with $\alpha = 0.81$ characteristic of a random-exchange Heisenberg antiferromagnetic chain (REHAC). At lower temperatures, the susceptibility peaks, the ESR linewidth greatly increases, and an internal field rapidly builds up. These changes may be due to either hyperfine or dipolar interactions, signalling a crossover from one-dimensional REHAC to a three-dimensional behavior—possibly a dipolar spin-glass.

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There has been a large amount of recent activity in the study of materials which are random-exchange Heisenberg antiferromagnetic chains (REHAC). An important experimental signature of a REHAC is a magnetic susceptibility χ which is observed at low temperatures as [1-3]

$$\chi(T) = AT^{-\alpha}, \qquad (1)$$

where T is the temperature, and the amplitude factor A and exponent α are constants which depend on the material and its preparation.[2]

In this communication, we report the results of experiments designed to investigate the ultralow-temperature behavior of a REHAC. The property measured is the low field ESR absorption of quinolinium (tetracyanoquinodimethane)$_2$ [Qn(TCNQ)$_2$] at several frequencies (ν) between 11.4 and 24 MHz (4.2 G$<H<$8.5 G for free electrons) over a range 0.45 mK$<T<$40 mK. From this, we obtain accurate knowledge of χ and the ESR line shape for temperatures a factor of 60 lower than previously available.

Our major discoveries in this work are an increasing deviation from Eq. (1) as T is lowered below about 7 mK, and an internal field and pronounced ESR line broadening which develop below 8 mK, rising to ~3 G at 0.5 mK. These results are the first experimental demonstration of the low-T crossover away from REHAC behavior.

An ideal REHAC consists of a chain of localized spins in which nearest neighbors are coupled by a Heisenberg Hamiltonian of the form $\sum_i J_i \vec{S}_i \cdot \vec{S}_{i+1}$, where J_i is a random variable >0. Both disorder and one dimensionality (1D) are key elements in the physics of such systems. All models for the thermodynamics of a REHAC predict that the susceptibility should obey Eq. (1). These models include that of Bulaevskii *et al.*,[1] the cluster model of Theodorou and Cohen,[4] and the exchange-coupled-pair (ECP) model of Clark *et al.*[5] Several renormalization calculations have recently appeared[6-8] which demonstrate that the singular character of Eq. (1) is a quasiuniversal behavior with $\alpha \sim 0.8$ for a wide class of distributions of J. The origin of randomness in Qn(TCNQ)$_2$ and the application of Eq. (1) to a REHAC are discussed at length elsewhere.[1-10]

Qn(TCNQ)$_2$ was chosen for this work because it is easy to prepare stable, single-phase samples, and many of its low-temperature magnetic properties are known.[2,9,10] Our sample (provided by G. Grüner) was produced with use of standard techniques and showed the normal electrical and magnetic properties associated with Qn(TCNQ)$_2$.[1,2,11] The Q-meter ESR spectrometer operates at very low excitation levels and provides a highly accurate (~1%) calibration of the signal. Sweeps from negative H through zero to positive H were made with use of a small superconducting magnet. The direct absorption (signal) was fed to a computer for recording and analysis. The rf level was low enough to avoid ESR saturation or heating. The sample (~5 mg) was immersed in pure ^{3}He cooled by a nuclear demagnetization cryostat. A Pt NMR thermometer covered the entire temperature range and a zero-sound transducer marked the ^{3}He superfluid transition at 1.15 mK (^{3}He pressure, 0.8 bar). We estimate an uncertainty of $<3\%$ and a resolution of 0.5% in T. The calibration of H is better than 0.1%, and the inhomogen-

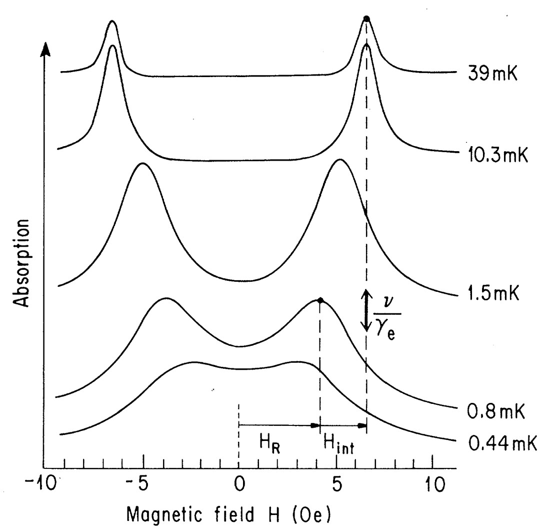

FIG. 1. Electron-spin-resonance absorption signals of $Qn(TCNQ)_2$ resulting from sweeping H through both positive and negative fields at 18.3 MHz and several temperatures. At 39 mK, the peak occurs at the field for a free electron, ν/γ_e, as indicated by the double arrow. The shift of the peak towards zero field as T is decreased indicates the buildup of an internal field, whose relation to the external field for resonance and ν/γ_e at 0.8 mK is shown pictorially at the bottom of the figure.

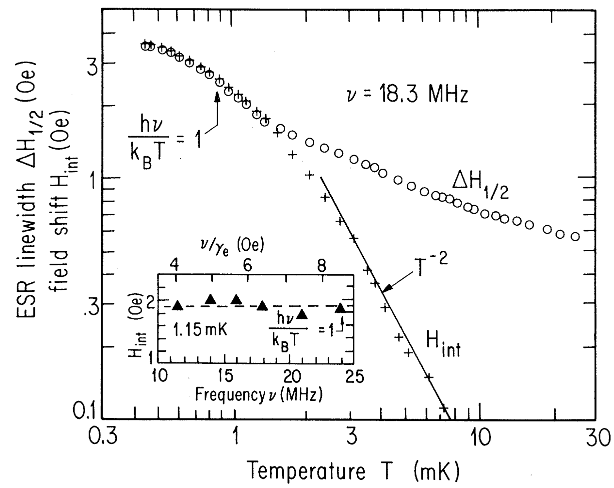

FIG. 2. ESR linewidth and field shift as a function of T for $Qn(TCNQ)_2$. The same scale is used for both quantities. The inset shows that H_{int} is independent of ν, i.e., that it acts as an internal field and not as a temperature-dependent g shift.

eity of H had a negligible effect on our measured half width at half maximum linewidth $\Delta H_{1/2}$.

The ESR absorption at $\nu = 18.3$ MHz and several different temperatures is shown in Fig. 1. At high temperatures a single, narrow, Lorentzian line corresponding to γ_e for free electrons is seen. One unexpected effect is that as T is lowered, the field corresponding to the peak of the resonance line (H_R) shifts to lower values, implying the buildup of an internal field (H_{int}), defined as

$$H_{int} = \nu/\gamma_e - H_R, \tag{2}$$

where γ_e is the electronic gyromagnetic ratio. The buildup of H_{int} is accompanied by an increase in $\Delta H_{1/2}$. Both are shown quantitatively in Fig. 2 for 18.3 MHz. There, it is seen that $\Delta H_{1/2} \propto T^{-2}$ at the high-T end, and that below ~1.5 mK, $\Delta H_{1/2}$ follows H_{int} closely. Nearly identical behavior (not shown) is observed at 11.4 and 24 MHz. The inset of Fig. 2 shows H_{int} as a function of ν at T = 1.5 mK. Since H_{int} is independent of ν, we conclude that the shift is in fact an internal field and not a g shift. Another property we have found is that on the time scale of our experiment (~50 s), H_{int} follows H, as indicated by the symmetry of the ESR signal about $H = 0$ and lack of hysteresis or an anisotropy field of the kind reported by Monod and Berthier[12] for field-cooled *Cu*Mn.

Throughout the entire field and frequency range covered by our experiments a good fit to the absorption is obtained by use of two Lorentzian lines centered at $\pm H_R(T)$, with the height and $\Delta H_{1/2}$ as additional adjustable parameters, even when there is enough overlap to generate a substantial absorption signal at $H = 0$.

Figure 3 shows $\chi(T)$ at 11.4 and 18.3 MHz obtained by calculating the area under the ESR absorption curve with use of the parameters which fit the line shape. The absolute value of χ is obtained by joining our relative measurements up to 40 mK to the absolute ESR measurements of Sanny[13] on the same sample from 300 K down to 40 mK. He has also verified that within an experimental uncertainty of ± 10%, χ(4.2 K) is independent of ν between 10 and 34 MHz.

Several features are evident in Fig. 3. Above about 7 mK, $\chi \propto T^{-\alpha}$ with $\alpha = 0.81$ (this value of α is the same as that observed on this sample by Sanny from 40 mK to 10 K). Below 7 mK, there is a progressively larger deviation below $\chi \propto T^{-\alpha}$, which culminates in a gently rounded peak near 1 mK. This peak shifts from 1.4 mK at 11.4 MHz to 0.75 mK at 18.3 MHz. In addition, there is a small inflection which goes from ~2.3 mK at 11.4 MHz to ~1.4 mK at 18.3 MHz.

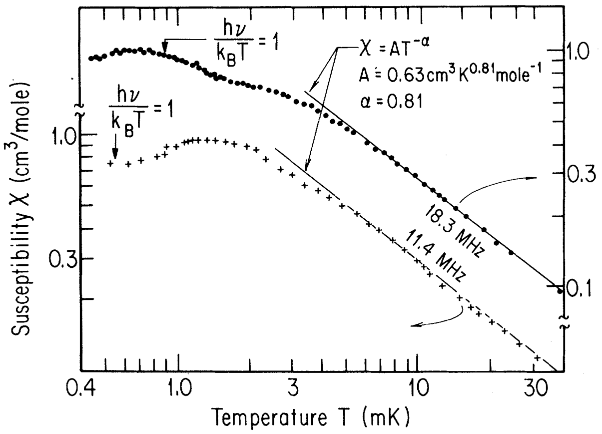

FIG. 3. Absolute susceptibility as a function of temperature at two frequencies. Note the use of left-right broken scales; χ above 7 mK is independent of ν. The deviation of χ from the REHAC behavior $\chi = A\,T^{-\alpha}$ observed below 7 mK indicates a crossover to another behavior, perhaps that of a dipolar spin-glass.

There are several conclusions to be drawn from these experiments. First, it is demonstrated that the REHAC behavior (i.e., g=free-electron value, and $\chi \propto T^{-\alpha}$) continues accurately down to about 7 mK in Qn(TCNQ)$_2$. Below 7 mK, a substantial deviation develops in the form of the peak in χ and the rapid growth of $H_{\rm int}$ and $\Delta H_{1/2}$. The peak in χ is a new effect, and not simply a manifestation of thermal saturation. The deviation from $\chi \propto T^{-\alpha}$ occurs well above $T = h\nu/k_B$, as indicated by the arrows on Fig. 3, whereas thermal saturation does not start in a REHAC until $T \simeq h\nu/k_B$.[14]

We interpret these changes below 7 mK as evidence that the physical properties are becoming dominated by a new set of interactions. Two possibilities are considered here. Since there are a number of relevant points which are not yet determined, our discussion is qualitative and speculative. It is assumed that the spins responsible for χ are on the TCNQ chains, as has been established above 30 mK.[2,13]

One interaction to consider is the electron-nuclear (hyperfine and dipolar) interaction. From studies of TCNQ$^-$ in solution[15] and (TCNQ)$_2^-$ in the solid state,[16] it is known that each of the four protons on a single TCNQ$^-$ ion generates a magnetic field of about 0.8 G for an electron on the same molecule. Thus, an electron hyperfine structure a few gauss wide occurs for a single molecule.[10] Since this splitting is 0.5 mK, a substantial effect on the ESR spectrum at the lowest T in our experiments would be expected. But exchange narrowing of the ESR and electron-spin-state delocalization,[9,10] both of which are known to exist in Qn(TCNQ)$_2$, complicate the situation to an extent that is difficult to evaluate at present. An obvious test for the importance of the electron-nuclear interaction is to modify it by repeating our experiments with use of Qn(TCNQ)$_2$ in which the protons have been replaced by deuterons. We are undertaking such a project.

The other interaction is the dipolar interaction among the electrons. Although the behavior of χ above 30 mK is dominated by 1D exchange, at lower T the electron-electron dipolar interaction in 3D should become important in a REHAC for the following reasons. As can be inferred from renormalization-group[6-8] and other[17] calculations, the antiferromagnetic exchange tends to push spins into a collective singlet ground state. What is left looks like a random, pseudo-dilute-spin system becoming more dilute as the temperature is lowered. Because of the exponential falloff of the exchange interaction, the dipolar interaction, which varies as r^{-3}, will dominate χ if T is low enough. Furthermore, in a dilute-spin system, there are many more possibilities for interchain than intrachain dipolar interactions. Therefore, a crossover to 3D behavior is expected.[17]

We believe there is a serious possibility that the properties exhibited by Qn(TCNQ)$_2$ below ~7 mK indicate that it takes on the character of a 3D dipolar spin-glass. It has several characteristics which are qualitatively similar to those seen in more conventional spin-glasses. These include a maximum in χ at the spin-glass temperature T_g, a rounding of the maximum in the presence of a magnetic field, and the observation of an internal field and enhanced linewidth in ESR measurements as T_g is approached from above.[18]

Two features of Fig. 2 should be pointed out because they serve as an important guide for work on theoretical models applicable to our experiments. They are the approach of $H_{\rm int}$ and $\Delta H_{1/2}$ to about the same value at the lowest T, and the behavior $\Delta H_{1/2} \propto T^{-2}$ above 2.5 mK independent of ν. The former suggests that $H_{\rm int}$ has a substantial degree of randomness in magnitude or direction or both. However, the latter feature rules out a simple model in which a local, random $H_{\rm int}(T)$ is simply added vectorially to H.

An interesting aspect of our measurements is that there is no evidence of a sharp magnetic phase transition in Qn(TCNQ)$_2$ even though at high T it starts out as a dense magnetic system[10]

(1 spin per formula unit). We attribute its absence as due to the reduction of spin density by antiferromagnetic interactions and the supression of long-range coherence by disorder.

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BOSE-EINSTEIN CONDENSATION OF A RELATIVISTIC GAS IN *D* DIMENSIONS. Ralf Beckmann, Frithjof Karsch, and David E. Miller [Phys. Rev. Lett. 43, 1277 (1979)].

The line above Eq. (3) should contain $d\sigma_d(p)$ [in place of $d\sigma_d(0)$].

The first terms on the right-hand sides of both Eqs. (4) and (5) should be preceded by minus signs.

In Eq. (6), for the modified Bessel function $K_\nu(x)$ the integrand should have the term $(t^2-1)^{\nu-1/2}$ [in place of $(t^2-1)^\nu$].

ENHANCED RAMAN SCATTERING BY ADSORBATES INCLUDING THE NONLOCAL RESPONSE OF THE METAL AND THE EXCITATION OF NONRADIATIVE MODES. W. H. Weber and G. W. Ford [Phys. Rev. Lett. 44, 1774 (1980)].

The $d^3\rho$ and $d^3\rho'$ integrations in Eqs. (16) and (17) should be two dimensional, over the directions parallel to the surface, and thus should read $d^2\rho$ and $d^2\rho'$. In Eq. (16) the factor $E_z^*(\vec{\rho}\,')$ should be replaced by $E_z^*(\vec{\rho})E_z(\vec{\rho}\,')$. The integral in Eq. (19) should be two dimensional, and thus d^3p should read d^2p.