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THE USE OF RANDOM EXCHANGE HEISENBERG ANTIFERROMAGNETIC CHAINS FOR VERY LOW TEMPERATURE THERMOMETRY AND COOLING : QUINOLINIUM $(TCNQ)_2$

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Résumé.- Nous présentons et interprétons les résultats des mesures de RPE effectuées jusqu'à 2,5 mK sur $Qn(TCNQ)_2$, qui est un composé unidimensionnel décrit par un modèle de Heisenberg à échange antiferromagnétique aléatoire. Les caractéristiques observées suggèrent que ce composé peut être avantageusement utilisé jusqu'à $T \lesssim 1$ mK comme thermomètre et comme élément réfrigérant dans une désaimantation adiabatique.

Abstract.- Observations of the ESR signal of $Qn(TCNQ)_2$, a random exchange Heisenberg antiferromagnetic chain material, are reported and interpreted down to $T \lesssim 2.5$ mK. The observed characteristics suggest that this material may be a useful thermometer and coolant via adiabatic demagnetization down to $T \lesssim 1$ mK.

1. INTRODUCTION.- The purpose of this paper is to present a preliminary report of the suitability of a new type of magnetic system, the random exchange Heisenberg antiferromagnetic chain for very low temperature thermometry and cooling by adiabatic demagnetization. Although the material on which our analysis is based is quinolinium $(TCNQ)_2$ [$Qn(TCNQ)_2$], there are similar materials which may be as good, or better than $Qn(TCNQ)_2$ in this application. There are two key properties of this material which adapt it to this use : (a) from about 10 K down to very low temperatures it follows a simple susceptibility law $\chi(T) = AT^{-\alpha}$, where A and $\alpha \sim 0.8$ are constants which depend on the material and its conditions of preparation, and (b) it has an extremely narrow electron spin resonance (ESR) line (~ 0.2 - 1 G). This latter property permits the use of relatively simple low-field ESR techniques for temperature measurement, and suggests that the effective local fields are small enough that demagnetization to very low temperatures can be obtained.

2. PHYSICAL MODEL.- The real physical system is believed to be described /1,2/ by a one-dimensional nearest neighbor Heisenberg hamiltonian

$$\mathcal{H} = 2 \sum_i J_i \vec{S}_i \cdot \vec{S}_{i+1} - g\mu_B H \sum_i S_i^z \qquad (1)$$

where $\vec{S}_i$ is the spin (S = 1/2) localized at the i^{th} magnetic site of the chain, g the g-value of the spin, μ_B the Bohr magneton, H an applied external field, and J_i a random nearest neighbor antiferromagnetic exchange interaction with probability distribution

$$P(J) = \text{const.}\ J^{-\alpha}, \qquad (2)$$

for $J \lesssim 10$ K. An exact treatment of the thermodynamic properties of $\mathcal{H}$ does not exist. Therefore we introduce an exchange coupled pair (ECP) model in which the J_i for even i are zero, i.e., the system is approximated by a collection of isolated interacting pairs of spins with the same P(J) as equation 2. Each pair forms the well known singlet ground and triplet excited states with a zero field splitting 2J. The free energy is

$$F(T,H) = -k_BT \int_0^{J_o} P(J)\ \ell n\, \zeta(J)dJ \qquad (3)$$

$$\zeta(J) = 1 + e^{-\beta h} + e^{\beta h} + e^{\beta J} \qquad (4)$$

where $\beta = (k_BT)^{-1}$, T is the temperature, and $h = g\mu_BH$. An upper cutoff on P(J) at $J_o \sim 10$ K is introduced, as at low temperature pairs with J > 10 K will be in the singlet state and not contribute to the magnetic properties of the system. This model works very well for the interpretation of such properties as the susceptibility /1,3/, specific heat /4/ at constant field (C_H), and high field magnetization /1/ ; and it gives essentially the same results as other models /1,2/ proposed for $Qn(TCNQ)_2$.

3. THERMOMETRY.- Consider the low field ($h \ll k_BT$) susceptibility of $Qn(TCNQ)_2$. The ECP model gives

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$$\chi(T) = \frac{2(g\mu_B)^2\ N(1-\alpha)}{J_o^{1-\alpha}(k_BT)^\alpha} \int_0^\infty \frac{dx}{x^\alpha(3+e^x)} = \frac{const.}{T^\alpha} \qquad (5)$$

ESR absorption measurements of χ on several samples show that the power law behavior is closely followed /3/. These measurements are easily made over a frequency range 10-50 MHz, corresponding to a resonance field in the range 3-15 G. Preliminary data show that χ continues to increase down to 2.5 mK, and that it probably continues to follow equation 5. No evidence of any phase transitions or magnetic ordering is seen.

These results show that $\chi(T)$ measured by low field EST is a viable thermometer down to $T \sim 2.5$ mK. We have reasons to believe that in fact in can be used to much lower temperatures, but further experiments at lower T are needed to clarify this point.

4. COOLING.- The ECP model result for the entropy (S) is

$$S(H,T)=Nk_B(1-\alpha)\left(\frac{k_BT}{J_o}\right)^{1-\alpha} \int_0^\infty \frac{dx}{x^\alpha} \times \left[\ell n\zeta(x,y) - \frac{xe^x + y(e^y-e^{-y})}{\zeta(x,y)}\right], \qquad (6)$$

where $\zeta(x,y) = 1 + e^y + e^{-y} + e^x$, $y = h/k_BT$, and N is the number of pairs with $J < J_o$ (N per formula unit is $\sim 3\times 10^{-2}$ for $Qn(TCNQ)_2$ /5/. The behavior of S is shown on figure 1 for the typical value $\alpha = 0.8$. Before discussing this figure we point out the regions in which its main features have been verified by specific heat measurements /5/. For $H = 0$ the region down to 70 mK has been covered, and above 100 mK, the field range up to 20 kOe has been explored. Since this amounts to only a small part of figure 1, the discussion which follows constitutes a prediction of the ECP model. First, note that the low and high field limits behave as $S \propto T^{1-\alpha}$ and $S \propto TH^{-\alpha}$ respectively. It is easily seen that an adiabatic demagnetization from H = 1 kOe to H = 10 Oe starting at 30 mK produces a final temperature of 0.5 mK. In fact, on the basis of figure 1, demagnetization from H > 3 kOe to H < 10 Oe can produce very low temperatures.

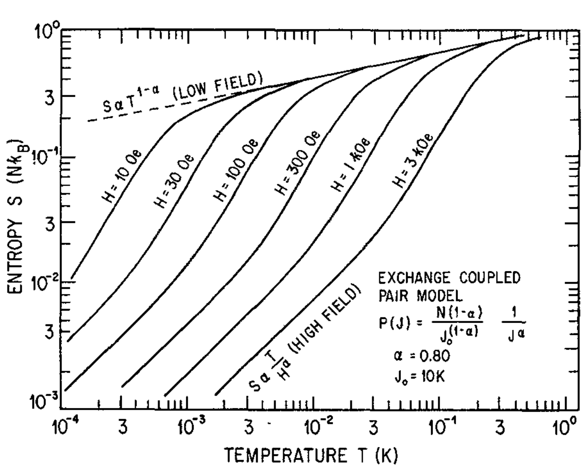

Fig. 1 : Entropy of the ECP model as a function of T and H

The above conclusion is based on an idealized ECP model. In reality the lowest temperature attained by cooling can be limited by local fields. Measurements at higher temperatures suggest this is not a severe limitation for $Qn(TCNQ)_2$. For example, we observe a fullwidth at half maximum ESR linewidth (ΔH) at H = 15 Oe and $.03\ K < T < 10\ K$ given by $\Delta H = (7.7 \pm 0.4)\times 10^{-2}\ \ell n\left[(70 \pm 4)K/T\right]$. Preliminary measurements down to $T \sim 2.5$ mK are consistent with this behavior. Extrapolation of this result to much lower T gives $\Delta H \sim 1$ G. If, as is often the case, this linewidth characterizes the effective local fields which ultimately limit the lower temperature use of a magnetic system, $\Delta H \sim 1$ G corresponds to a minimum useful temperature $T_m \sim g\mu_BH/k_B \sim 0.14$ mK, which is low indeed !

5. CONCLUSION.- We have shown that random exchange Heisenberg antiferromagnetic chain systems such as $Qn(TCNQ)_2$ are useful for thermometry down to 2.5 mK. On the basis of extrapolations of properties measured above 2.5 mK, it is shown that this material has a strong potential as a thermometer and for cooling by adiabatic demagnetization down to much lower temperatures.

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