Heat Capacity Study of the Quantum Antiferromagnetism of a ^{3}He Monolayer

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We have measured the heat capacity of the second layer solid in a ^{3}He film adsorbed on the surface of graphite to temperatures below 1 mK, in the regime where the nuclear exchange interaction is antiferromagnetic. The temperature dependence of the data is described by high temperature series expansions for a 2D Heisenberg antiferromagnet on a triangular lattice. There is no evidence for a phase transition down to $J/3$. Comparison with J inferred from the magnetization provides a measure of the frustration due to competing antiferromagnetic and ferromagnetic cyclic exchanges.

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Frustrated quantum spin systems are of fundamental interest, arising from their critical behavior at low temperatures and the question of the existence of long range magnetic order (LRMO) at $T = 0$. In two dimensions the $S = \frac{1}{2}$ nearest neighbor Heisenberg antiferromagnets on a triangular and kagomé lattice are systems with geometric frustration that have been extensively studied theoretically [1]. The finite temperature properties of these systems have been recently investigated by high temperature series expansions (HTSE) [2]. The latter calculations suggest the existence of weak LRMO at $T = 0$ for a Heisenberg antiferromagnet on a triangular lattice (HAFT), where only nearest neighbor interactions are included. There are a number of magnetic materials under investigation to illustrate the influence of geometrical frustration [3]. So far there are only potential candidates for a model HAFT with $S = \frac{1}{2}$, the best known being the quasi-2D compound $NaTiO_2$ [4]. In this Letter we describe an investigation of the antiferromagnetism of a ^{3}He (nuclear spin-$\frac{1}{2}$) monolayer physisorbed on graphite and show that it provides a genuinely two dimensional quantum antiferromagnet on a triangular lattice.

Both 2D and bulk solid ^{3}He are distinct among nuclear magnets in having a large exchange constant (J), typically of order mK, arising from the large zero point motion of the ^{3}He atom in the quantum crystal. These J are much larger than the dipolar interaction of order μK. The exchange Hamiltonian is more complex than simple nearest neighbor Heisenberg exchange. Path integral Monte Carlo calculations [5,6] show that cyclic permutations of atoms occur, as was originally suggested in the multiple spin exchange (MSE) model [7,8]. This introduces another important source of frustration since the cyclic permutation of an even number of particles is antiferromagnetic (AFM), while that of an odd number is ferromagnetic (FM). The heat capacity and susceptibility of a 2D solid ^{3}He layer are sensitive to this competition in different ways [6,8]. In the present experiments these quantities have been measured, for the first time, on the same cell, providing direct evidence of multiple spin exchange and new quantitative information on the degree of frustration.

The heat capacity measurements at low millikelvin temperatures of Greywall [9] established that the second layer of ^{3}He adsorbed on the surface of graphite solidifies prior to the formation of a fluid overlayer. Measurements of magnetization of these films demonstrated that exchange in this layer is AFM and that exchange with the first solid layer is a negligible effect, being of order the dipolar interaction [10]. This system therefore presents itself as an ideal two dimensional antiferromagnet where the only interaction of importance is intralayer exchange.

In this paper we shall present heat capacity results which demonstrate that as far as exchange is concerned the second layer should be thought of as a triangular lattice in which all spins are equivalent, i.e., commensuration between the first and second layers does not have a significant influence on the exchange. The results are well described by recent HTSE for the 2D HAFT [2]; this is the first clear example of an AFM on a triangular lattice to show excellent agreement with these calculations.

Our sample chamber allows heat capacity and NMR measurements to be performed on the same sample. Grafoil disks are bonded to silver foils and connected by diffusion welded bonds to a silver thermal link, which is mounted on a cold plate by a mechanical cone joint. Attached by a similar joint to this plate are a platinum wire NMR thermometer, and an LCMN thermometer. The LCMN thermometer was constructed in a similar way to the CMN thermometer described by Greywall and Busch [11]. It uses 28 mg of salt with a lanthanum dilution of 95%, resulting in a negligible addendum heat capacity, at most a few percent of the ^{3}He heat capacity in the work reported here. It is calibrated against the nuclear magnetic susceptibility of platinum and, at higher temperatures, a melting curve thermometer. The LCMN susceptibility (measured using standard SQUID techniques) follows a Curie-Weiss law down to 0.5 mK. The cold plate is connected to the nuclear stage via a zinc superconducting heat switch, and heat capacity is measured

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by the standard adiabatic method. Vapor pressure and NMR linewidth isotherms were used to characterize the substrate by identifying promotion to the second layer. To facilitate comparison with the previous heat capacity measurements of Greywall [9] we define promotion to occur at 0.109 $Å^{-2}$. Heat capacity isotherms at 2 and 40 mK identify the onset of second layer solidification at 0.169 $Å^{-2}$ and complete solidification at 0.178 $Å^{-2}$, in precise agreement with Ref. [9].

The heat capacity at coverages for which the second layer is solid is shown in Fig. 1. We find that promotion to a fluid overlayer occurs at 0.186 $Å^{-2}$. It can be seen that there is a broad maximum, attributable to exchange and characteristic of short range order in a low dimensional magnet. The maximum shifts to a lower temperature with increasing coverage, corresponding to a decrease in the exchange constant. Importantly, there is clearly no evidence of a sharp feature that would indicate a phase transition at these temperatures, as reported in Ref. [9]. We further note that the measured heat capacity is independent of field within the resolution of the measurements up to 30 mT, the typical field used in magnetization measurements. Considerable insight into this system is obtained if these results are analyzed in terms of the HTSE extended by the method of Padé approximants (PA), as recently published by Elstner, Singh, and Young [2]. Such expansions are believed to give reliable results down to $T/J \sim 0.4$ [12]. They are also characterized by a broad maximum in the heat capacity of order $0.21Nk_B$ in magnitude located at $T/J \sim 1.1$. They show that the leading order term in the HTSE, $c = \frac{9}{4}Nk_B(J/T)^2$, only provides an adequate description (i.e., within 5%) for $T > 10J$. The full Padé approximant, in this paper represented by PA$[J/T]$, is

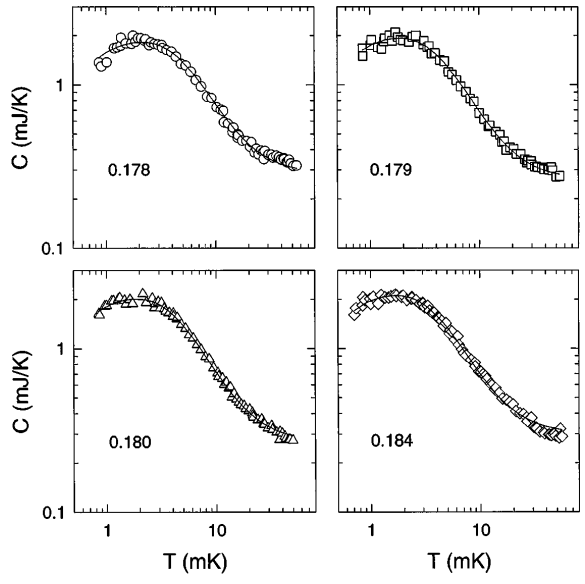

FIG. 1. Heat capacity as a function of temperature at coverages (in $Å^{-2}$) where the film is solid. The full lines are fits to the data using the PA to the HTSE for a spin-$\frac{1}{2}$ HAFT plus a constant (β).

therefore an extremely useful tool in analyzing the present data since measurements at high temperatures on these films are complicated by an additional contribution, believed to arise as a consequence of residual heterogeneities in the substrate. In our measurements this contribution is well described by a constant term; this precludes the clear identification of a $1/T^2$ term in the heat capacity at high T/J [13]. We note that such a constant a term in the heat capacity is also observed when the second layer is fluid. We find the fluid heat capacity to be well described, down to 3 mK, by the form $c = \beta + \gamma T$, in agreement with previous results [14].

The full fit to the data, $c = Nk_B\text{PA}[J/T] + \beta$ gives excellent agreement, as can be seen in Fig. 1. The values of N, the number of AFM spins, inferred from the fit are in good agreement with the total number of second layer spins N_2, known independently from the coverage. This is powerful evidence that the spins are arranged on a triangular lattice and that essentially all spins contribute to the exchange. There is, however, a small systematic deviation, with N smaller than N_2 by on average 3%. If we interpret β/k_B as defining an effective number of "classical" particles responsible for the constant term, we obtain $(3 \pm 1)\%$ of the total number of second layer spins. This would then account precisely for the total number of spins in the layer [15].

To explain the earlier heat capacity data of Greywall [9], Elser [16] had proposed a model in which the second layer solidifies as a triangular lattice in $\sqrt{7} \times \sqrt{7}$ commensuration with the first layer. This was regarded as a kagomé net, formed by $\frac{3}{4}$ of the spins located on equivalent sites, with relatively large nearest neighbor exchange, the remaining $\frac{1}{4}$ of the spins being essentially free, having a much smaller exchange constant with those on the kagomé net. Attempts to fit the present data by the PA for a kagomé net cannot describe the observed temperature dependence or the magnitude of the observed heat capacity [17]. In addition, recent nuclear magnetic susceptibility results of Siqueira *et al.* [10] down to 0.5 mK are inconsistent with the presence of free spins. The susceptibility data are well described by an AFM contribution from the second layer, fit by the HTSE for a triangular lattice, plus a background Curie term due to the paramagnetic first layer. This is consistent with the present heat capacity data and clear evidence that all the second layer spins participate in the exchange. We refer the reader to [10] for further details.

The effective exchange constants inferred from the present heat capacity results as well as those from the susceptibility measurements are shown as a function of second layer density in Fig. 2. The marked difference is understandable within the framework of the MSE model. Including n particle cyclic spin exchange of exchange constant J_n, with $n = 2, 3, 4, 5, 6$, it is found [6] that the effective exchange constants are

$$J_\chi = (J_2 - 2J_3 + 3J_4 - 5J_5 + \tfrac{5}{8}J_6)$$

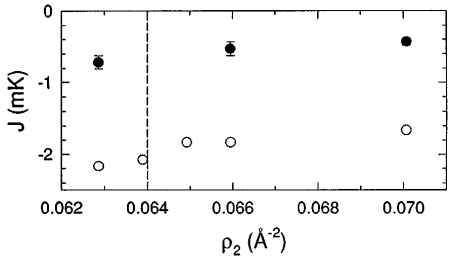

FIG. 2. Comparison between the effective exchange constants, assuming a Heisenberg nearest neighbor AFM exchange, inferred from susceptibility (●) and heat capacity (○) measurements. The dashed line corresponds to solidification of the second layer.

and

$$J_c^2 = \left(J_2 - 2J_3 + \frac{5}{2}J_4 - \frac{7}{2}J_5 + \frac{1}{4}J_6\right)^2 + 2\left(J_4 - 2J_5 + \frac{1}{16}J_6\right)^2 + \frac{23}{8}J_5^2 - J_5J_6 + \frac{359}{384}J_6^2 .$$

Here the Curie-Weiss temperature $\theta = 3J_\chi$, such that to leading order the susceptibility $\chi = C/(T - \theta)$, and to leading order the heat capacity $c = \frac{9}{4}Nk_B(J_c/T)^2$. Thus $J_\chi = J_c$ if only two and three spin exchange are taken into account and the system is equivalent to the Heisenberg nearest neighbor with effective exchange constant $J' = J_2 - 2J_3$. A difference in the two effective exchange constants is a clear signature of the importance of higher order ring exchanges. With some assumptions it is possible to arrive at a quantitative measure of the frustration from the present data. Following Roger [8] we assume $J_4 = J_6$ and ignore 5 spin exchange to define a frustration parameter r, such that $J_4 = rJ'$. If we identify the exchange parameter inferred from our fits to the heat capacity with J_c, then comparison with J_χ yields values of r close to -0.3. This is close to maximum frustration, for which $\theta = 0$, which in Roger's simplified model occurs when $r = -0.275$. At this point $J_c \sim 0.5J'$. The frustration parameter varies very little over the 10% range of second layer densities explored here.

To understand why it is the case that the HTSE for the HAFT accounts so well for $c(T)$, it would be necessary to compare these results with numerical results for spin clusters that are sufficiently large to give reliable results for the detailed temperature dependence of the heat capacity to $T \leq J$. We would expect on the basis of the present experiments that for an almost completely frustrated but still AFM film, the form of $c(T)$ will follow closely that of HAFT, but with an effective exchange constant given by MSE theory. There is some evidence of this in the work of Roger [8] who finds in the case of maximum frustration a heat capacity maximum at $T \sim J_c$ and a heat capacity per spin at the maximum close to that given by the PA.

We note that the experimental results in the two-phase coexistence regime, associated with solidification of the second layer, can be subjected to a similar analysis. As shown in Fig. 3, when the coverage is increased through this region a low temperature exchange maximum develops as the solid fraction increases. There is an associated shift in the maximum to lower temperature, indicating a decrease in the effective exchange constant, that was apparently not observed in previous work [9]. This is confirmed by a detailed fit to the heat capacity using $c = N_s k_B \mathrm{PA}[J/T] + \beta + \gamma T$, where the additional term, linear in T, is to account for a fluid component. The range of the fit is adjusted to retain the validity of this expression. The values of N_s/N_2 determined from these fits increase approximately linearly with coverage, as might be expected in a coexistence region, and are shown in Fig. 4. However, the associated decrease in J shows that this system differs markedly from classical coexistence in the sense that the properties of the localized phase change with the relative proportions of the two phases. The parameter β is, within scatter, constant throughout.

Previous heat capacity measurements on this system [9], when the film is completely solid, appeared to show an entropy deficit; it was this observation that provoked the theoretical model of Ref. [16]. If we extrapolate the present measured heat capacity values linearly to zero from the lowest temperature and integrate the total observed heat capacity, assuming that it is all associated with the spin degrees of freedom, we find an entropy that converges to within 2% of $k_B \ln 2$ per particle at 0.184 Å^{-2} (8% at 0.178 Å^{-2}). On the other hand, if we discount the constant

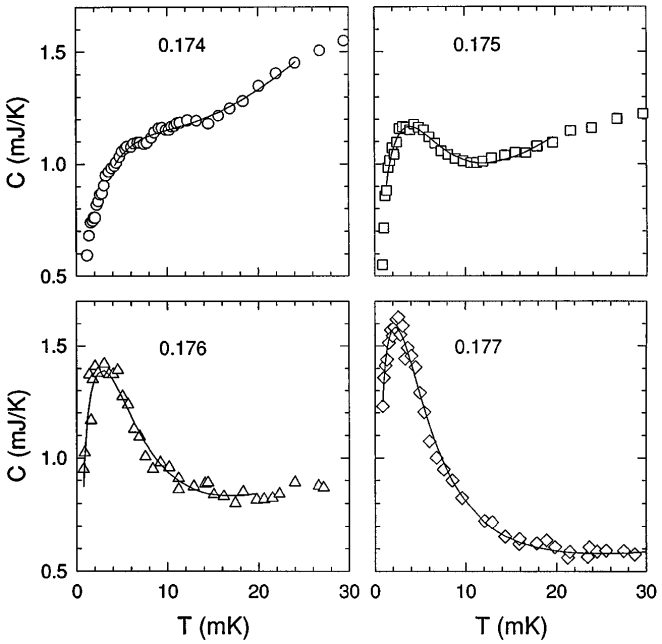

FIG. 3. Heat capacity as a function of temperature for coverages (in Å^{-2}) in the two-phase coexistence region between solid and fluid in the second layer. Lines are fits to the data as described in the text.

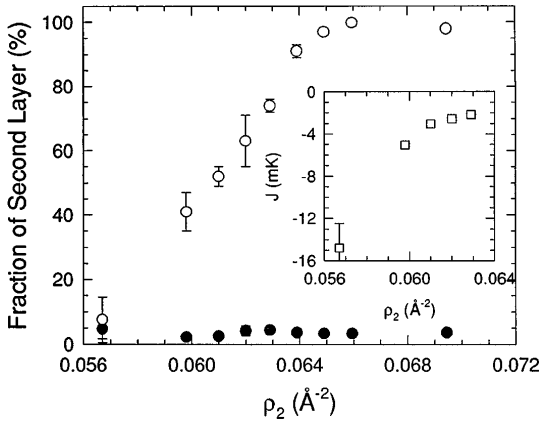

FIG. 4. Solid fraction of the second layer film (○) as a function of second layer density in $Å^{-2}$ ($\rho_2 = \rho - 0.114$). Also shown is the number of "classical" spins associated with the parameter β. The inset shows the evolution of J of the solid phase as the coverage increases in the coexistence region.

term, we find an entropy per particle of between $0.75k_B \ln 2$ and $0.8k_B \ln 2$ [18]. We therefore cannot conclusively rule out further structure in $c(T)$ at $T < 0.5J$.

It is not possible from the present data to establish whether this system has LRMO at $T = 0$. The series expansion results [2] suggest that this should be possible by extending susceptibility measurements to $T/J \sim 0.4$. The fact that the effective exchange constant, J_χ, is of order -0.5 mK and the presence of a large background signal from the paramagnetic first layer increases the technical difficulty of such a measurement. Progress may be possible with preplated substrates.

In conclusion, this work establishes the second layer of ^{3}He adsorbed on graphite, prior to the formation of a fluid overlayer, to be a 2D antiferromagnet on a triangular lattice. It provides a beautiful model for frustrated two dimensional antiferromagnetism. In contrast to previous heat capacity measurements [9], there is no evidence of either a phase transition at finite temperatures or any anomalous temperature dependence of the heat capacity. Comparison of heat capacity and magnetization data from the same cell provide clear evidence of multiple spin exchange and a quantitative measure of the degree of frustration. In principle such 2D ^{3}He solids provide a system with tunable frustration; the nature of the ground state order and the influence of frustration on it are significant questions for the future.

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[13] In Ref. [9] the results were analyzed at a coverage of 0.184 $Å^{-2}$ to find an apparent T^{-1} dependence for the "spin" heat capacity. We believe this arises from an incorrect subtraction of the "nonspin" heat capacity.
[14] D. S. Greywall and P. A. Busch, Phys. Rev. Lett. **65**, 64 (1990).
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[18] We note that integration of the theoretical heat capacity from the PA (Ref. [2]) using the same extrapolation procedure also generates a value of the entropy of $0.8k_B \ln 2$.