Low Temperature Heat-Capacity Anomalies in Two-Dimensional Solid ^{3}He

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The heat capacity of second-layer solid ^{3}He adsorbed on graphite has been measured down to extremely low temperatures below 100 μK. We observed a double-peak structure for a low-density registered solid, which strongly suggests that the system is a highly frustrated spin-1/2 two-dimensional (2D) antiferromagnet with a disordered ground state. As the density increases it approaches a 2D nearest-neighbor Heisenberg ferromagnet with a single rounded peak, which can be explained semiquantitatively by considering higher-order exchange processes up to six-spin exchange. [S0031-9007(97)04414-1]

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The physics of frustrated low-dimensional quantum antiferromagnets has attracted much attention for a long time because magnetically disordered ground states are in prospect there. So far, the second layer ^{3}He just solidified from the fluid phase physisorbed on graphite is one of the most promising materials for a highly frustrated and truly two-dimensional (2D) quantum antiferromagnet. Greywall [1] first measured its heat capacity down to 2 mK, a temperature comparable to the exchange interaction (J) among the nuclear spins ($S = \frac{1}{2}$) due to quantum mechanical tunneling of neighboring atoms. From entropy analysis he suggested a possible low temperature heat-capacity anomaly, otherwise a half of the spin entropy is missing. Elser [2] proposed that the second layer is a registered solid with a $\frac{4}{7}$ density ratio with respect to the first layer solid. While the $\frac{4}{7}$ phase itself has a triangular lattice structure, he inferred that three quarters of the atoms are magnetically decoupled from the rest forming a Kagome lattice, i.e., the Kagome model. As a result of geometrical frustration a double-peak structure in the heat capacity, which has not been observed experimentally yet, is predicted from this model.

Roger discussed this problem from a different insight [3]. He argued importance of higher order exchanges up to six-spin ring exchanges, i.e., the multiple spin exchange (MSE) model. Competition between antiferromagnetic (AFM) interactions associated with exchanges of even number spins and ferromagnetic (FM) ones of odd number can be another resource of the frustration. In fact, a second specific-heat peak or a shoulder is also predicted at very low temperatures from this model.

In this Letter we present results of heat-capacity measurements of the second-layer solid ^{3}He adsorbed on graphite down to 90 μK for areal densities near solidification (AFM phase) as well as higher densities with fluid overlayers (FM phase). We observed, for the first time, a clear double-peak structure in the heat capacity of the AFM phase which strongly suggests that this phase would be the first real 2D antiferromagnet with a fully frustrated disordered ground state.

The substrate used in this experiment is exfoliated graphite (Grafoil) with surface area of 450 m^2. The temperature of the silver sample cell was determined by a platinum pulsed-NMR thermometer below 45 mK and by a carbon resistance thermometer above 18 mK. Both thermometers were calibrated above 1 mK against a ^{3}He melting curve thermometer. The heat capacity was measured by the adiabatic heat-pulse method above 0.2 mK in zero magnetic field. Below 0.9 mK we also employed the relaxation method [4]. The data obtained with the two different techniques agree well in an overlapped temperature region. Details of the experimental techniques will be discussed elsewhere.

Heat-capacity (C) data at densities $\rho = 17.8$, 18.2, and 18.4 nm^{-2} are shown in Fig. 1. In this density regime the second layer is the $\frac{4}{7}$ registered solid and the dominant interaction is AFM [5]. Note that the underlying compact first-layer solid ($\rho_1 = 11.4$ nm^{-2}) gives a negligible contribution to the heat capacity in this temperature range, i.e., $C(\mathrm{mJ/K}) \leq (1.4 \times 10^{-9})/T^2$, because of its small exchange frequency ($|J| < 3$ μK) [6]. Contributions from phonons both in the first and second layers are also negligibly small [1]. Near $T = 1.8$ mK we observed a broad maximum presumably due to short-range ordering. For $T > 3$ mK our data agree reasonably well with the previous results of Greywall [1,7].

The most striking feature in our data is a second peak observed at a much lower temperature ($\approx$0.3 mK) than that of the rounded first peak. The 2D nearest-neighbor Heisenberg antiferromagnet on a triangular lattice (HAFT) should give only a single peak at $T \approx 0.55J$ and a rapid decrease as $C \propto T^2$ at $T \ll J$ due to 2D AFM spin waves [8]. Our data clearly indicate that there are anomalously many low-lying excited states, which would be a typical property in frustrated systems. The dashed line in Fig. 1 is a result of an exact diagonalization calculation for a sixteen-spin cluster within the MSE model [3]. It has a reasonable similarity to our data, although the theory predicts a higher second-peak temperature and larger heat capacities near the first peak compared to the measurement.

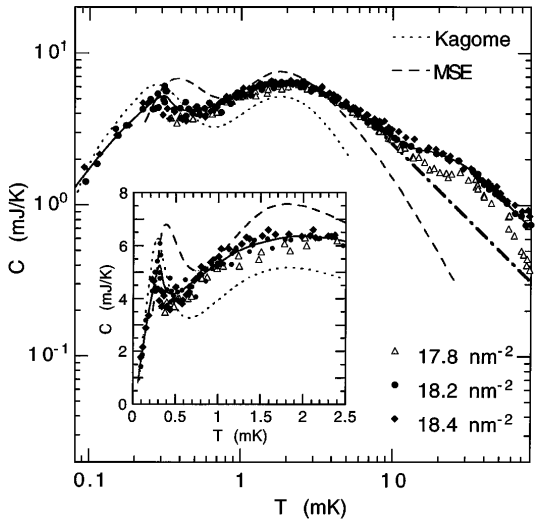

FIG. 1. Heat-capacity data at densities near the second-layer solidification. The solid line is a guide for the eye for the data at 18.2 nm^{-2}. The dotted line is from the Kagome model ($J = 2.59$ mK; Ref. [2]). The dashed line is from the MSE model ($J = -3.23$ mK, $J_4 = J_6 = 0.81$ mK; Ref. [3]). The exchange parameters were determined so that the first-peak temperatures coincide with the experiment. Note that three quarters of N_2 are assumed to contribute to the spin heat capacity in the Kagome model (see text). The dash-dotted line is proposed true high-temperature behavior. The inset shows a linear plot of the low-temperature data.

In this calculation, only two adjustable parameters, an effective two-spin exchange ($J = J_2 - 2J_3$) and a higher order exchange ($J_4 = J_6$), are considered for simplicity, where J_2, J_3, J_4, and J_6 are two-, three-, four-, and six-spin exchanges, respectively. The observed double-peak structure suggests that the system has nearly maximum frustration ($J_4/J = -1/4$) [3].

Recent mean-field calculations and Monte Carlo ones [9] on the classical MSE Hamiltonian showed several distinct ground states depending on the frustration parameter ($\equiv J_4/J$). For $-3/4 \leq J_4/J \leq -1/4$, they predict a state with nontrivial degeneracy due to the competing MSEs. It is plausible that in the quantum limit ($S = \frac{1}{2}$) the degeneracy is removed by quantum tunneling creating quasidegenerate low-lying states which result in a second heat-capacity anomaly.

Another explanation for our data is the Kagome model which predicts a qualitatively similar double-peak structure (dotted line in Fig. 1) [2]. The simplest version of this model with only the nearest-neighbor interaction gives, however, consistently smaller heat capacities than the measurement by about 30% near the first peak. It is implied that the second peak corresponds to condensation to a spin liquid or the spin-Peierls state with an excitation gap ($\approx$0.25 J) [10]. The experimental heat capacity varies as $C \propto T$ below the second peak being inconsistent with an exponentially rapid decrease expected from the spin-gap formation. It should be noted, however, that the numerical calculations for finite spin clusters may not be accurate enough in this temperature region [11].

At high temperatures above 10 mK the heat capacity decreases anomalously slowly compared to a theoretically expected $C \propto 1/T^2$ behavior. Moreover, a small but clear bump is seen near 30 mK at 17.6 (not shown here) and 17.8 nm^{-2}, which becomes broader at 18.2 and 18.4 nm^{-2}. Greywall observed a similar rounded peak near 50 mK at $\rho = 17.8$ nm^{-2} (see Fig. 3 of Ref. [1]). This anomaly does not come from a remnant of the second-layer fluid because it cannot be fitted by adding any fractions of the fluid heat capacity with a broad peak above 60 mK [1] to the spin heat capacity. The origin of this anomaly is not known at this moment. If it is associated with any of the fluid components such as those trapped in substrate heterogeneities, its quasiparticle effective mass should be much larger than that for the uniform 2D fluid ($m_3^* < 6m_3$ [1]). Or it could be intrinsic to the low-density registered solid. For example, zero-point vacancy motions or itineracy of the spins may play important roles [12].

The present heat-capacity data are significantly different from recent measurements by other workers [13] where they claimed that the heat capacity in the AFM phase can be well described by the HAFT model in the whole temperature range ($0.8 < T < 50$ mK) they studied. We should, however, point out that their data are likely in error by several tens % [13] as was suggested recently by the authors themselves [14].

Let us now turn to the data at higher densities (23.0 and 26.0 nm^{-2}) where the exchange interactions are predominantly ferromagnetic [5,6]. Measured total heat capacities (C_{tot}) can be fitted well to the following expression:

$$C_{\text{tot}} = N_2\,\text{PA}[2/3] + \gamma T + \alpha T^3 \qquad (1)$$

at temperatures $T > 5$ mK for 23.0 nm^{-2} (inset of Fig. 2) and $T > 2.5$ mK for 26.0 nm^{-2}. In this equation N_2 is the number of second-layer atoms and PA[2/3] is a [2/3] Padé approximant to the high-temperature series expansions for the specific heat up to the fifth order for the MSE Hamiltonian [15]. The last two terms are from the degenerate fluid overlayers.

Spin heat capacities after subtracting the fluid contributions are plotted in Fig. 2 (main figure). There are several important differences here from the behavior in the AFM phase. First of all, the second peak disappears, leaving only the first peak which is narrower and higher than that in the AFM phase. Below the peak temperature (T_{peak}), the heat capacity decreases as $C \propto T$ over a decade of temperature, being consistent with the 2D FM spin-wave theory. In addition, the data converge rather rapidly to the $C \propto 1/T^2$ behavior at $T \gg T_{\text{peak}}$ without showing any high-temperature anomalies. All of these indicate that, with increasing density, the system approaches a pure 2D nearest-neighbor Heisenberg ferromagnet on the triangular lattice with magnetic long-range order at $T = 0$. These properties can be qualitatively represented by density variations of the MSE frequencies [16].

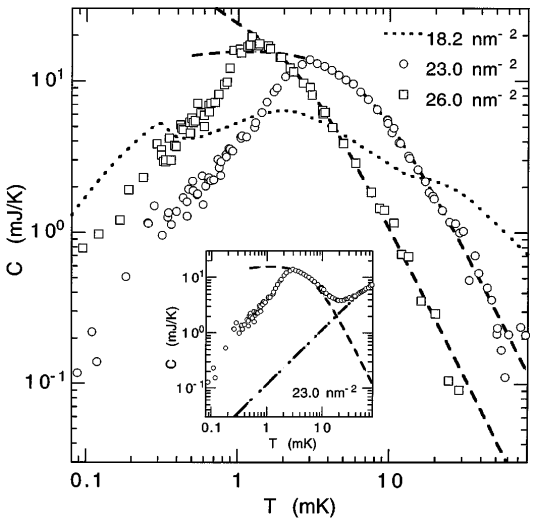

FIG. 2. Nuclear-spin heat capacities at high densities where the interactions are FM. The dashed lines are the fitted N_2 PA[2/3] terms in Eq. (1), where $J = -3.30$ mK, $J_4 = J_6 = 0.20$ mK, $\gamma = 115$ mJ/K^2, and $\alpha = -3730$ mJ/K^4 for 23.0 nm^{-2} and $J = -1.09$ mK, $J_4 = J_6 = 0.026$ mK, $\gamma = 153$ mJ/K^2, and $\alpha = -4920$ mJ/K^4 for 26.0 nm^{-2}. The inset shows the total heat capacity before subtracting the fluid-overlayer contribution (double-dotted line).

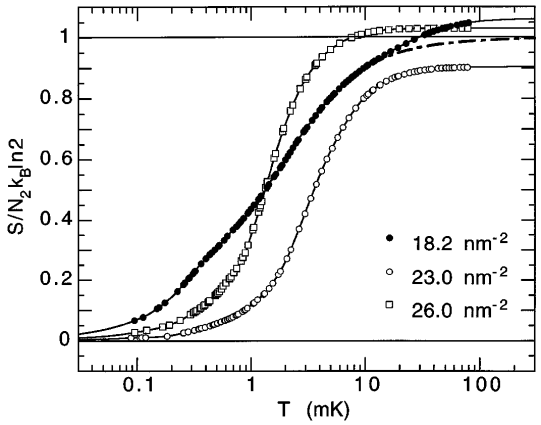

FIG. 3. Nuclear-spin entropies deduced from the heat-capacity data. The dash-dotted line for 18.2 nm^{-2} is an estimation when the $C \propto 1/T$ behavior is held above 7 mK (see text).

One curious observation in the previous heat-capacity measurements [1,14,17] was a small temperature independent contribution (β). We also observed this β term in a wide temperature range ($0.1 < T < 80$ mK) in the second-layer fluid phase ($\rho = 15.0$ nm^{-2}) [18]. We believe that this term is associated with nuclear-spin degrees of freedom in a glassy solid ^{3}He trapped in the substrate heterogeneities as was proposed by Golov and Pobell [19]. The number of second-layer atoms participating in the β term (N_β) can be roughly estimated as

$$N_\beta = \left(\int_{T_L}^{T_H} \frac{\beta}{T}\, dT \right) \Big/ \, k_B \ln 2 , \qquad (2)$$

where the logarithm of exchange interaction in the glassy solid is distributed uniformly over $T_L < |J| < T_H$. Substituting $\beta = 0.5$ mJ/K, $T_H \approx 80$ mK, and $T_L \approx 0.1$ mK to Eq. (2), we have $N_\beta \approx 4 \times 10^{20}$. Another estimation for N_β is $(4-6) \times 10^{20}$ from comparing the present β value with those ($7-11$ μJ/K m^2) reported in almost thoroughly heterogeneous substrates like Vycor glass [19] or sintered silver powders [20]. We assumed here 6.75 nm^{-2} for the mean density of the glassy solid. The excellent agreement between the two different estimations strongly supports the idea of the glassy solid. In this Letter, fixed β (=0.5 mJ/K) and N_β values ($=4.3 \times 10^{20}$) had been subtracted from all the heat-capacity data and N_2 values regardless of density [21].

Entropy changes deduced from the present heat-capacity data are shown in Fig. 3, where we used a ρ_2 vs ρ relation proposed in Ref. [1]. We assumed the asymptotic $C \propto T$ behavior for $T < 90$ μK and $C \propto 1/T^2$ for $T > 80$ mK. It is clear that we have directly measured almost the whole temperature variation of spin heat capacity in this system and that the entropy deficit should be less than 10% if it exists. It is intriguing to note that if we assume C(mJ/K) $= 0.0251/T$ above 7 mK for the data at 18.2 nm^{-2} (dash-dotted line in Fig. 1) we obtain the net entropy change divided by ln 2 as $\Delta S = 1.00$. While using the heat capacity calculated from the MSE model (dashed line) for $T > 3$ mK, we obtain $\Delta S = 0.90$ which is too small. This fact supports the anomalously weak temperature dependence ($C \propto 1/T$) at high temperatures in the AFM phase originally claimed in Ref. [1]. The proximity to $\Delta S = 1$ for the data in the AFM phase rules out the simplest Kagome model which demands $\Delta S = 0.75$ [2]. The somewhat smaller ΔS value at 23.0 nm^{-2} may suggest that the currently used ρ_2 scale [1] is overestimated by about 9% near $\rho = 23$ nm^{-2} where no scattering experiments have yet succeeded to determine the lattice constant unambiguously [5].

In conclusion we have shown, from the observation of double-peak structure in the spin heat capacity, that the low density second-layer solid ^{3}He on graphite is a fascinating frustrated 2D quantum antiferromagnet. The MSE model can explain semiquantitatively the low temperature anomaly as well as the heat capacities at higher densities, but not for the high temperature anomaly in the AFM phase. Obviously, further theoretical works are necessary to account for the present experimental results.

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