Heat Capacity of ^{3}He Adsorbed on Graphite at Millikelvin Temperatures and Near Third-Layer Promotion

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The heat capacity of ^{3}He adsorbed on a graphite substrate has been measured for temperatures between 2 and 200 mK and for coverages corresponding to the region near third-layer promotion. The second layer is observed to undergo a first-order transition between the fluid phase and presumably a registered solid. As a function of coverage, the transition is complete before atoms are promoted into the next layer. At 2.5 mK, the nuclear-spin contribution to the heat capacity of the higher coverage state exhibits a peak which appears to be inconsistent with the usual exchange model. One possible explanation attributes the peak to magnetic polarons which form around zero-point vacancies.

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Recent low-temperature magnetization measurements[1] performed on multilayers of ^{3}He adsorbed on graphite exhibit several intriguing and unexplained features. These are readily summarized by the magnetization-versus-coverage curve at 3 mK which shows two anomalies. The first appears in the vicinity of third-layer promotion as a rather abrupt but small increase in the magnetization. The second occurs as a large ferromagnetic peak at a higher coverage when clearly a significant number of atoms are in the third ^{3}He layer. This Letter concerns the first of these anomalies.

The small magnetization peak has been associated[1] with the promotion of atoms into the third layer. However, earlier measurements[2] which extend down to about 50 mK show a dramatic change in the heat capacity at about the same ^{3}He coverage, and this has been interpreted as signifying solidification of the second layer. Subsequent neutron scattering experiments[3] did not detect the presence of solid in the second layer at a somewhat higher coverage, but this may have been due to experimental problems.

The high-precision heat-capacity data presented here provide new information about this system near third-layer promotion. The measurements have been obtained at several closely spaced coverages and for temperatures extending down to 2 mK. A first-order transition occurs in the second layer clearly prior to third-layer promotion. The new phase, which is believed to be a registered solid, exhibits a large nuclear-spin peak at 2.5 mK which is not described by a nearest-neighbor Heisenberg Hamiltonian.

The heat-capacity measurements were made using the standard heat-pulse technique applied to a high-purity silver calorimeter. The interior of the cell was almost completely filled with alternating disks of 0.005-in.-thick Grafoil[4] and 0.002-in.-thick silver foil. These disks were heat and pressure bonded into a single cylindrical mass which was bolted to the base of the cell. Thermal connection between each of the silver foils was made via a thin layer of silver electroplated onto the cylinder. Cooling of the calorimeter to below 2 mK was achieved using a superconducting tin heat switch which joined the cell to a $PrNi_5$ nuclear demagnetization refrigerator. Temperatures were measured using a cerium-magnesium-nitrate (CMN) thermometer of special design.[5] The very fast response time of this device (2 sec at 10 mK, 30 sec at 3 mK) made it possible to extend the measurements down to 2 mK. Below this temperature, the ther-

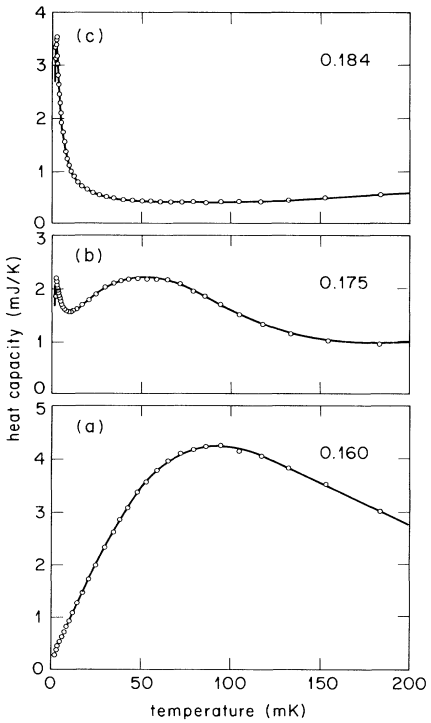

FIG. 1. Heat-capacity data at three coverages near third-layer promotion which show that the second ^{3}He layer undergoes a first-order transition. The numbers give the coverages in atoms per square angstrom.

mometer lost sensitivity due to ordering in the CMN, and the thermal response time grew rapidly.

The total surface area (203 m^2) of the substrate was determined using the substep in the N_2 vapor pressure isotherm at 74 K, corresponding to the transition between the fluid and the $\sqrt{3}\times\sqrt{3}$ solid.[6] Using this surface area it is found that ^{3}He atoms are promoted into the second layer at a coverage of 0.109 atoms/Å^2, which agrees well with the values 0.108 and 0.1065 atoms/Å^2 from neutron scattering experiments.[7,8]

Data at three coverages are shown in Fig. 1. This is the total sample heat capacity; however, the contribution from the first solid layer is less than 10 μJ/K over the entire temperature range and so is negligibly small. For coverages between 0.109 and 0.169 atoms/Å^2, the second layer exists as an interacting Fermi fluid, and exhibits heat-capacity curves which are qualitatively similar, Fig. 1(a): For temperatures less than about 50 mK the heat capacity is nearly linear in temperature. At higher temperatures there is a rounded maximum which grows in amplitude, becomes more clearly defined, and also shifts towards lower temperatures as the coverage is increased. Above 0.169 atoms/Å^2 the second ^{3}He layer undergoes a phase transition as indicated by the sharp deviation away from the lower coverage trend. The rounded peak associated with the fluid now rapidly disappears while a new sharp peak at 2.5 mK grows in amplitude. Figure 1(b) shows a clear coexistence of two phases which identifies this transition as first order.

Figure 2 shows heat-capacity isotherms at 2.5 and at 200 mK for coverages in the vicinity of the transition. From the matched, sharp breaks in both curves, the boundaries of the two-phase region are located at 0.169 and at 0.178 atoms/Å^2. At a slightly higher coverage of 0.182 three is an additional sharp break but only in the 200-mK isotherm, corresponding to the heat capacity again developing a fluidlike contribution. This is attributed to the promotion of atoms into the third layer.

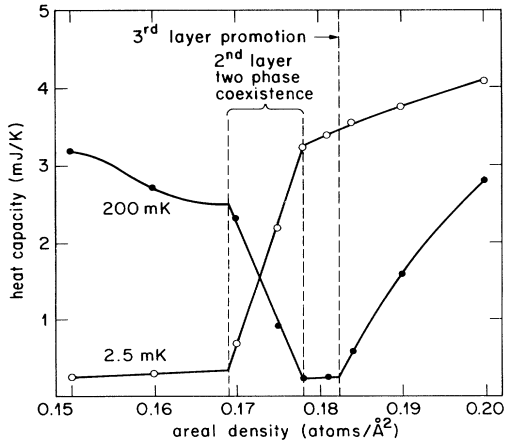

FIG. 2. Heat capacity vs coverage along two isotherms.

The phase transition in the second layer is therefore complete before a significant number of atoms are promoted into the next level.

Van Sciver and Vilches[2] have also reported a phase transition in the same coverage regime based on heat-capacity measurements at higher temperatures. They concluded that the higher-density phase was a solid which exhibited a melting transition near 1K.

In more recent work, Franco, Rapp, and Godfrin[1] noted that neutron scattering experiments[3] performed at 0.203 atoms/Å^2 did not detect the presence of solid in the second layer, and speculated, as a possible interpretation of their magnetization results, that the second layer is completely solid only above 0.24 atoms/Å^2. The newest neutron scattering experiments[8] at 0.297 atoms/Å^2 indicate that at this coverage the second layer is indeed solid. Unfortunately, information about the second layer could not be obtained at lower coverages because the second-layer reflection, presumably due to an incommensurate solid at this density, shifts into one of the graphite substrate peaks.

Our belief is that the transition occurring near third-layer promotion is between the fluid phase and a registered solid. This assessment is based primarily on the very low second-layer density at which the transition occurs. Neutron scattering experiments[8] have shown that when compressed by additional layers the first-layer density is about 5% larger than at second-layer promotion. Our compressed first-layer density should then be 0.114 atoms/Å^2 and the second-layer density should be given by $\rho_2=\rho-0.114$. The two-phase region therefore exists for $0.055\lesssim\rho_2\lesssim0.064$, and third-layer promotion occurs at $\rho_2=0.068$ atoms/Å^2. At a monolayer coverage of 0.064 the first layer is in $\sqrt{3}\times\sqrt{3}$ registry with the graphite substrate and exists as an incommensurate solid only above 0.078.[9,10] A registered second-layer phase is also suggested by the Van Sciver–Vilches results because these authors found that the "melting" peak was detectable only over a very narrow range of coverages, as is the case for the registered phase in submonolayer films.

Registry in the vicinity of 0.064 atoms/Å^2 suggests registry again with respect to the graphite substrate. The corrugation in the graphite potential, however, decreases exponentially with distance above the substrate surface[11] and should be negligibly small at the level of the second-layer atoms. It would seem therefore more likely that registry, if indeed it does occur, occurs with respect to the first ^{3}He layer.

The density of the second registered layer relative to the underlying first layer is $0.064/0.114=0.56$. The relative coverage for perfect registry, however, might be slightly larger than 0.56 because there may be a range of coverages which should be associated with the registered phase. The phase probably exists with vacancies for $\rho\lesssim\rho_{\rm reg}$ and with interstitials for $\rho\gtrsim\rho_{\rm reg}$. But even if an uncertainty of several percent is assigned to this relative

density, no simple lattice structure is obviously identified.

Perhaps associated with a more complicated structure is the fact that although more than 95% of the second layer undergoes the transition over a small coverage range, Fig. 2, the remainder transforms at a much slower rate. Figure 3 is a log-log plot of the nuclear-spin contribution to the heat capacity; i.e., the total sample heat capacity minus a small nonspin contribution determined by a simple extrapolation of the "high-" temperature behavior. The circles are for a coverage of 0.178 where the transition might be expected to be just completed. The dashed curve shows the results for a somewhat higher coverage, 0.184. The rounded peak near 50 mK which is emphasized by the log scales is the remnant of the second-layer fluid, Fig. 1. The amplitude of this peak indicates that ~4% of the second layer remains as a fluid. At 0.181 the fluid contribution has decreased to 2% and at 0.184, as Fig. 3 shows, has almost disappeared. The effect might also be attributable to the inhomogeneity of the surface and to the weakness of the corrugation in the potential implied by the 1-K transition temperature. Concerning possible defects, we note that if an atom is removed from the registered solid, the region surrounding that site may melt forming a small "bubble" of liquid.

The much sharper peak at 2.5 mK, Fig. 3, is due to the nuclear spins in the second layer. The contribution from the spins in the first compressed layer is negligibly small as can be inferred directly from Fig. 1(a) which shows a very small heat capacity near 2 mK, with no exchange tail. Of course the assumption is that there is no increase in the coupling between layers after the second-layer structure transition takes place.

The following are some of our observations about the spin peak: (1) The peak is sharp as a function of temperature and suggestive of a finite-temperature phase transition; (2) for $T < T_{\text{peak}}$ the heat capacity is proportional to T, although the data exist only over a very limited temperature range; (3) for $T \gtrsim T_{\text{peak}}$ the temperature dependence of the heat capacity is weaker than $1/T$; and (4) T_{peak} is very insensitive to areal density. These observations appear to rule out Heisenberg exchange on a triangular lattice. We also note that the heat-capacity peak is probably associated with antiferromagnetic behavior. This is inferred from the data of Franco, Rapp, and Godfrin[1] which show that the low-temperature magnetization at this coverage lies below the paramagnetic value.

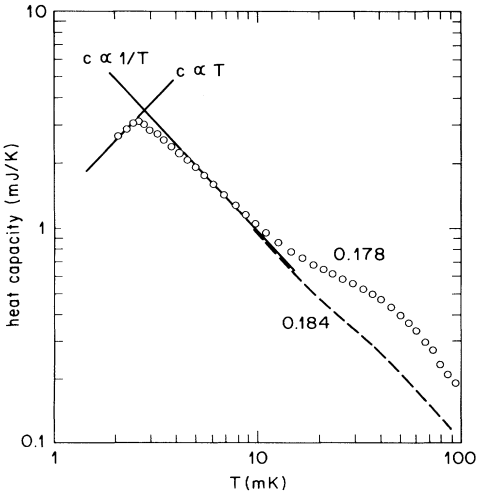

FIG. 3. Nuclear-spin contribution to the heat capacity of the second-layer registered phase. The numbers give the coverages in atoms per square angstrom.

The integration of C/T, assuming $C \propto T$ below T_{peak}, yields an entropy per second-layer atom of about $\frac{1}{4} k_B \times \ln 2$ at T_{peak} and of very nearly $\frac{1}{2} k_B \ln 2$ above 10 mK. The entropy is thus a factor of 2 smaller than expected. This suggests two possibilities: Either the spin system retains significant order at 10 mK or our assumption of a linear heat capacity below T_{peak} is incorrect. The first of these can be ruled out by the magnetization measurements[1] which indicate that at the corresponding coverage and at 10 mK the free spin value is reached for all of the spins. The conclusion therefore must be that the heat capacity has a second peak below 2 mK, corresponding to the ordering of the remaining half of the nuclear-spin degrees of freedom. This double-peaked heat capacity may be an intrinsic property of the perfect registered structure.

Another possible explanation is that spin polarons form around a finite concentration of zero-point vacancies.[12] This immediately divides the spins into two categories: those very near a vacancy and those which are more distant. The distant spins would be governed by a small exchange energy and so would order at a very low temperature. The spins forming the polaron itself should behave very differently. A calculation by Heritier and Lederer[13] shows that such two-dimensional polarons can have either ferromagnetic or antiferromagnetic character depending on the lattice structure. The calculation also shows that the heat capacity should be proportional to $T^{-1/2}$. And indeed, as T_{peak} is approached from higher temperatures, the experimental data do tend towards this particular temperature dependence. What remains difficult to explain is the lack of any significant density dependence in the experimental results. Certainly the number of vacancies should vary rapidly with coverage. It is also difficult to understand why the computed entropy is so close to half the expected value. Nonetheless it would be desirable to have a more complete theory based on the polaron model which would not only predict the temperature dependence of the heat capacity at somewhat higher temperatures but would also predict the behavior of the spin system at very low temperatures.

In conclusion, complementary specific-heat and mag-

netization data now exist for the system consisting of two layers of ^{3}He adsorbed on a graphite substrate. The very-low-temperature data are more complicated than one might have imagined but the system is well defined and should be amenable to relatively simple theoretical modeling. The theoretical understanding of this two-layer structure is an obvious prerequisite for tackling the problem of higher coverage films which exhibit other intriguing magnetic anomalies.

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