Nuclear-Spin Heat Capacity of Submonolayer Solid ^{3}He Films

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The heat capacity of submonolayer solid ^{3}He films adsorbed on graphite has been measured for temperatures between 2 and 200 mK. Over a very narrow range of coverages an anomalously large nuclear-spin exchange is observed. This peak is analogous to the more dramatic anomaly previously observed for the second-layer system when compressed by a few overlying fluid layers. The implication is that the proposed indirect exchange involving the fluid atoms cannot be the responsible mechanism.

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The second solid layer of ^{3}He adsorbed on graphite exhibits a dramatic and fascinating evolution of nuclear magnetic properties[1,2] as this system transforms, with increasing areal density, from what is believed to be a registered phase into the incommensurate solid phase.[1] Freezing of the second layer into the registered structure occurs prior to third-layer promotion[3] and here the nuclear spins exhibit unusual antiferromagnetic properties.[1-5] At higher densities, however, the second layer shows ferromagnetic character which climaxes, perhaps coincidently, as atoms are promoted into the fourth layer.[1] Because of the weaker binding to the substrate, the third and fourth adsorbed layers do not solidify and constitute degenerate 2D Fermi fluids.[6] The presence of these fluid layers considerably complicates the analysis of the ferromagnetism, since it is not clear if these overlayers serve only to compress the second layer or if they play a more active role such as participating in an indirect exchange of second-layer atoms.[7,8] Moreover, the presence of these overlayers makes estimates of the second-layer density less certain, and this is important because it appears that the ferromagnetic anomaly occurs at a second-layer density ρ_2 slightly below that corresponding to the transition into the pure incommensurate solid phase S. In fact, it has been inferred[1] that the interface between a registered phase and the S phase may be quite directly responsible for the ferromagnetism.

In this Letter we present low-temperature heat-capacity results for the *first* layer of ^{3}He on graphite which clarify several of these issues. The advantage of working with the first layer is that, because of the stronger binding to the substrate, the monolayer system can be compressed well into the S phase without the complication of overlayers. The drawback is that the nuclear-spin heat capacity for the first layer is an order of magnitude smaller than that of the second and therefore considerably more difficult to measure. As a function of coverage, the very-low-temperature spin heat-capacity isotherms for the first layer evolve through a series of anomalies which are remarkably similar to those observed for the second layer. This includes a well-defined peak which definitely occurs before the system has given way to the pure incommensurate solid phase. This peak is analogous to the ferromagnetic anomaly of the second layer, implying that the primary cause of the second-layer ferromagnetism cannot be the suggested indirect exchange of second-layer atoms involving those in the overlayers. The coverage location of the first-layer peak does support the claim that the anomaly occurs in a transitional region and that the boundary separating registered and incommensurate solid phases may be playing a dominant role. In addition, the new first-layer data at somewhat lower coverages show a first-order freezing into the $\frac{1}{3}$ registered phase and evidence for the possible existence of vacancies and interstitials in the vicinity of the registered coverage.

The heat-capacity measurements were made in the temperature interval between 2 and 200 mK for 35 coverages spanning the complete monolayer regime. The apparatus used and also the results for the lower-coverage pure fluid phase have already been discussed in a previous publication.[6]

Smoothed results for selected coverages, given in units of atoms/Å^2, are shown in Fig. 1. Note that the upper row of curves has a heat-capacity scale which is 10 times more sensitive than the lower row and therefore corresponds to much smaller heat capacities. At the lowest coverages the ^{3}He atoms constitute a two-dimensional Fermi fluid whose heat capacity increases smoothly with increasing density. Near $\rho=0.041$ the signal suddenly begins to decrease; this is the onset of first-order freezing into a registered phase. At 0.064 the solidification is complete, with the system existing in the pure $\frac{1}{3}$ registered phase R and exhibiting a small nuclear-spin exchange tail. At higher coverages, as the system evolves towards the fully incommensurate solid phase, the exchange contribution to the heat capacity increases,

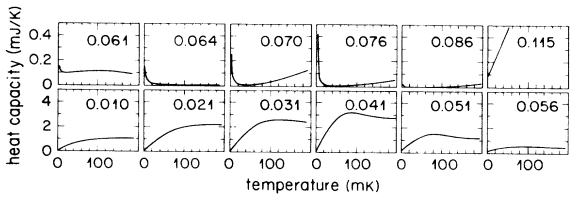

FIG. 1. Smoothed heat-capacity results for several of the samples studies. The numbers give coverages in atoms/Å^2. Note the more sensitive heat-capacity scale for the upper row of curves.

reaches a maximum at $\rho = 0.076$, and then decreases to a very small value before atoms are promoted into the second layer near 0.115.

The heat-capacity results are plotted as a function of areal density in Fig. 2 for several isotherms. The isotherms at 2.5 and 5 mK, for $0.064 < \rho < 0.1100$, are dominated by the nuclear-spin contribution to the heat capacity, while the 50- and 200-mK isotherms are at high enough temperature to be little affected by this term. To help in the interpretation of these results, the phase diagram is included at the top of this figure. The data points shown in this portion of the figure give the location of heat-capacity melting peaks from Refs. 9 and 10. The extrapolations of the phase boundaries to zero temperature are based on the data presented in this paper. All of the component parts of this figure are joined by vertical dashed lines which correspond to special coverages. These are labeled *a* through *g*.

For $\rho < a = 0.043$ atoms/Å^2 the first layer exists as a pure phase Fermi fluid *F*. At *a* the system moves into *F*-*R* two-phase coexistence. This is indicated by the

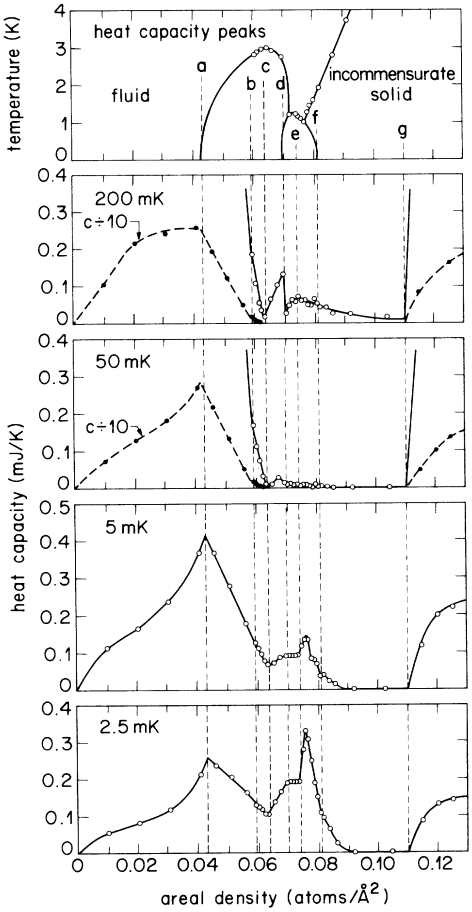

FIG. 2. Heat capacity as a function of coverage for several isotherms. The heat capacity at 2.5 and 5 mK is sensitive to the nuclear-spin contribution. Comparison is made with the phase diagram based on data from Refs. 9 and 10. The extrapolations of the phase boundaries to zero temperature are based on the data presented in this paper.

linear coverage dependence, which is required for a two-phase region and also by comparison with the heat-capacity results for the second layer[1,3] at a comparable second-layer coverage. For the second layer, the transformation of liquid into solid can be quite directly monitored because of the large magnitude of the exchange heat capacity; the solid-phase signal at very low temperature grows as the higher-temperature fluid signature decreases. The upper boundary of the two-phase coexistence is located presumably at *c*. In fact, our coverage scale was adjusted by a few percent so that $\rho = c$ would correspond to 0.0635 atoms/Å^2 which is the coverage corresponding to the $\frac{1}{3}$ registered phase on graphite.

Very recent magnetic-susceptibility data[11] have been interpreted as indicating that a fluid-solid coexistence begins at a coverage near 0.035. This conflicts[12] with our data and also with earlier heat-capacity results by Hering.[13]

Complicating the assignment of registry at *c* in the change in slope at *b* (0.0595 atoms/Å^2) is easily visible in the 50- and 200-mK isotherms. One possible explanation is that the system solidifies into the *R* phase with a 6% concentration of zero-point vacancies. These vacancies would then be eliminated as the coverage is increased from *b* to *c*. The heat capacity measured at $\rho = b$ should then be due mainly to the vacancies since there should be no fluid present and the contribution from the registered solid is negligibly small, except below roughly 20 mK. The nearly temperature-independent heat capacity measured at this coverage implies a specific heat of $0.2k_B$ per vacancy.

It is also possible, however, that there are no vacancies and that the changes in slope of the isotherms at *b* are a consequence of the rather small size of the homogeneous regions on the Grafoil[14] substrate. Assuming the homogeneous regions to have a diameter of 100 Å implies that the fraction of atoms located on the perimeter is roughly 4% and some of these atoms (those on weak sites) may be more difficult to localize. If this is the correct interpretation of the data, then complete registry should be assigned to a coverage corresponding to the extrapolation of the behavior between *a* and *b* out to a coverage *b'* located between *b* and *c*. The fact that the heat capacity decreases to a minimum at $\rho = c > b'$ might indicate that the weak-site atoms completely lose their fluidlike character only when the local perimeter density is greater than the density at the interior of the regions.

The low-temperature nuclear-spin heat-capacity data obtained at the registered coverage (i.e., at $\rho = c$) are shown plotted on log-log scales as solid circles in Fig. 3. Note that the data between 5 and 20 mK are more nearly proportional to $1/T$ than to $1/T^2$ as would have been expected for a Heisenberg system at high temperature. This approximate temperature dependence is very similar to that observed for the second-layer registered phase over the same temperature region. This is puzzling because the magnitude of the first-layer spin heat capacity

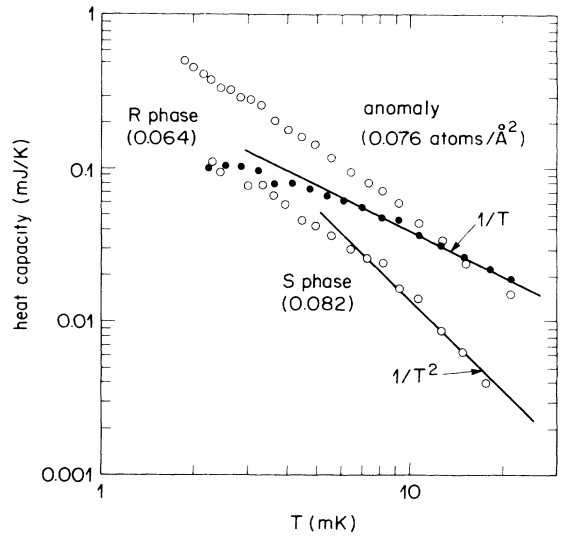

FIG. 3. Nuclear-spin heat capacity. The data obtained for the $\frac{1}{3}$ registered phase show a $1/T$ temperature dependence. This contrasts with the $1/T^2$ dependence observed at higher coverages.

is 20 times smaller than that of the second layer, implying exchange energies roughly a factor of 4 smaller or reduced temperatures (T/J) a factor of 4 larger. We would have therefore expected to be closer to the limiting $1/T^2$ temperature dependence. This suggests that the unusual T dependence may not be a simple consequence of the low areal density and the importance of higher-order exchange terms, but may be peculiar to the registered phases. At higher coverages the spin heat capacity is consistent with a $1/T^2$ temperature dependence, as indicated in Fig. 3.

All of the monolayer data obtained for $\rho > c$ exhibit a solidlike heat-capacity signature with an exchange contribution at low temperature and a high-temperature contribution increasing roughly as T^2. A fluidlike contribution with the heat capacity proportional to T is observed only for $\rho > g$ when atoms are promoted into the second layer.

The linear density dependence observed for most of the isotherms for the density range between c and d suggests a two-phase region; however, the higher-density phase would have to be a solid with a smaller effective Debye temperature and a larger effective exchange energy, compared to the registered phase. It would also be difficult to explain the large discontinuity seen at d in our 200-mK isotherm and also in higher-temperature isotherms obtained by Hering.[13] We propose instead that the R lattice softens between c and d because of the incorporation of interstitials or more probably heavy domain walls. The increasing number of defects eventually causes the lattice to become unstable against phase separation into two different registered structures, the $\frac{1}{3}$ phase and perhaps a $\frac{2}{5}$ phase.[1] Certainly the existence of a second registered phase on graphite is consistent with the shape of the phase diagram. If the lattice with $\rho \gtrsim c$ exists with interstitials, their concentration reaches 9% at d. If we assume a regular stripped arrangement of superheavy domain walls then at d every seventh row of atoms is a domain wall. It is somewhat surprising that there is no observable discontinuity at d in the lowest-temperature isotherms, although there is a discontinuous change in slope.

Heat-capacity isotherms for the second-layer system do not show a density dependence analogous to the c-d region of the first layer. This could be explained by the much weaker corrugation in the potential experienced by the second-layer atoms. Immediately above the registered phase coverage, the lowest-temperature isotherms for the second layer develop a density dependence which is extremely similar to that of the first layer for $\rho > d$. Here the spin isotherms for both layers show a plateau region with the spin heat capacity changing very little (d-e), followed by a peak (between e and f), and then a region (above f) where the dropoff from the peak suddenly slows. The implication is that, except for the region immediately above the $\frac{1}{3}$ registered phase of the first layer, both layers experience a very similar evolution as the systems transform from the registered to the incommensurate solid structures. This is also supported by the very similar silhouettes for the first- and second-layer phase diagrams.[1] We claim therefore that the spin peak that we observe for the first layer between e and f and the large ferromagnetic peak of the second layer, observed at about the same layer density, are a consequence of the same physical mechanics.

From the comparison with the phase diagram at the top of Fig. 2, we claim that $\rho = e$ corresponds to the system existing in a pure registered phase R_{1b} and place the spin heat-capacity peak in the transitional region between the R_{1b} and the S phases. The ferromagnetic peak of the second layer was located precisely at the same relative location in the second-layer phase diagram, although the analysis of these results was considerably more involved due to the presence of fluid overlayers. The higher precision of the second-layer data, associated with the much larger heat capacity, allowed us to determine with little ambiguity that the anomaly did not coincide with the crossing of a phase boundary.

The fact that the heat-capacity peak is observed in the first layer implies immediately that in-plane interactions must be mainly responsible for the magnetic anomalies in both the first and second layers. Of course, indirect interactions involving the overlayer fluid atoms may enhance the second-layer effect.

Since the anomaly occurs within a transitional region, it cannot be associated with either of the pure phase end components. The conclusion is that the interface separating the two solid phases must be playing a very important role and this interface may be rather unusual since one of the two phases is a registered solid which may experience local melting at the boundary. In fact, it

seems probable that as ρ approaches f, the system consists of only the incommensurate solid coexisting with a high-density fluid. If the crossover to this F-S coexistence region takes place at the density of the ferromagnetic peak, this could explain the much simpler ρ and T dependence of the spin heat-capacity results on the high-coverage side of the peak, relative to the behavior on the low-coverage side (see Fig. 23 of Ref. 1). But it still remains unclear if the anomalous magnetism should be associated directly with the fluid or if the fluid only enhances the exchange of the atoms in the solid phase.

The emphasis above has been placed on the striking similarities between the spin heat capacities of the first and second layers. There remains, however, the sizable difference in their magnitudes. In the vicinity of the registered phases one would expect significant differences in exchange rates due to the differences in the potential-energy corrugations experienced by the atoms. But away from these registered regions one might have expected the two layers to behave in a nearly identical manner. The fact that there are large differences in exchange rates for the incommensurate phases is an indication that atomic motion is not strictly two dimensional. The wave function has extent in the direction perpendicular to the substrate which is very important for exchange.[5] And this extent for the second layer is much larger because of the overall weaker binding to the substrate.

That this wave-function extent in the Z direction is playing an important role in the exchange process can be demonstrated quite directly. At a total coverage of 0.26 atoms/Å^2 the adsorbed ^{3}He consists of two solid and at least two fluid layers. The first solid layer is highly compressed and has a negligible exchange rate while the second solid layer exists in the incommensurate phase with a J value of $\sim$0.8 mK. As the coverage is increased, atoms are added to the fluid layers, but the densities of the first and second layers change very little. Yet, the J for the second layer decreases in the limit of several layers to less than 0.4 mK which is comparable to the J of the first layer at the same density. An explanation is that the fluid layers confine the motion of the second-layer atoms to more strictly two-dimensional motion.

In conclusion, the work that has been presented here should provide important direction for future theoretical attempts to explain the anomalous magnetic properties observed previously for the second-layer ^{3}He solid and now also for a true monolayer film. The presence of the feature in the first-layer data implies immediately that in-plane interactions must be mainly responsible. The location of each anomaly, at a respective layer density slightly below that corresponding to the 2D system entering into the pure incommensurate solid phase, suggests that the transitional nature of the layers must be critical.

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[14]Grafoil is an exfoliated graphite manufactured by Union Carbide.