Heat Capacity of Adsorbed ^{3}He at Low Millikelvin Temperatures

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The heat capacity of ^{3}He adsorbed on a silver-powder substrate has been measured for temperatures between 0.4 and 7 mK and for coverages up to 5 atomic layers. The data show several features in common with those obtained for the ^{3}He-on-graphite system, including an anomaly in the exchange contribution to the heat capacity near 2.5 layers. In the graphite-substance experiments the ferromagnetic anomaly is associated with the freezing of the second ^{3}He layer. The second layer on the silver substrate, however, is found not to solidify.

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Subsequent to the first observations by Brewer and Rolt,[1] many experiments involving liquid ^{3}He in contact with various substrates have demonstrated the existence of ferromagnetic tendencies at very low temperatures. That is, in addition to the Pauli magnetic susceptibility describing the bulk liquid, there is a surface term which above a few millikelvins can be described by a ferromagnetic Curie-Weiss relation.

In an attempt to pinpoint more accurately the source of the ferromagnetic behavior, some of the more recent magnetization measurements have been carried out as a function of adsorbed ^{3}He film thickness on both silver[2] and Grafoil[3] substrates. These are in contrast to experiments[4] done on "bulk" liquid ^{3}He samples in contact with a large surface. Using Grafoil[5] as a substrate, Franco, Rapp, and Godfrin[3] studied several ^{3}He coverages between 2 and 3 atomic layers. Near 2.5 layers, these very low-temperature NMR data exhibited a large peak, with the magnetization-versus-coverage curve rising well above the corresponding free-spin values. This peak was attributed to the solid ^{3}He atoms in the second layer. In their model the magnetization grows with increasing coverage as a consequence of the freezing of the second liquid layer (under the additional pressure of atoms in the third layer) into a solid with an anomalously large exchange energy. The decrease in the magnetization at coverages above 2.5 layers is attributed to the compression of the second solid layer and the expected rapid drop in the exchange energy with increasing density.

In this Letter we report the first very low-temperature heat-capacity measurements on adsorbed ^{3}He which provide additional information about the magnetic properties of ^{3}He films. The measurements were performed for temperatures between 0.4 and 7 mK and for coverages up to 5 atomic layers on a sintered silver-powder substrate. A silver substrate was used in order to obtain short thermal relaxation times which are required for the heat-capacity measurements. Although this substrate is not as well characterized as Grafoil, the data do show several features on an atomic coverage scale which leads us to claim that the ^{3}He is being adsorbed approximately layer by layer and that the surface is sufficiently homogeneous to permit direct comparison with the measurements done on multilayers of ^{3}He on Grafoil. We find, in particular, that peaks in the exchange contribution to the heat capacity occur for coverages near 2.5 layers and also near 4 layers even though our measurements indicate that the second ^{3}He layer on silver does not solidify. It remains possible, though, that the anomalies should still be attributed to the second layer. Indeed, magnetism in a liquid layer is consistent with predictions based on the paramagnon model applied to ^{3}He near a surface.[6,7]

The heat-capacity measurements were made with the standard heat-pulse technique (but with nanowatt power levels) applied to a high-purity silver calorimeter. The interior of this vessel was almost completely filled with 147 g of compacted silver powder in the form of eight disks (0.56 cm thick by 3.4 cm diameter) with solid silver hubs. These were attached to the base of the cell with a single silver bolt. From argon Brunauer-Emmett-Teller measurements at 77 K the total surface area was determined to be 151 m^2. Cooling of the cell was achieved by the closing of a superconducting tin heat switch which joined the calorimeter to a $PrNi_5$ nuclear demagnetization refrigerator. The temperature was measured with a lanthanum-doped cerium magnesium nitrate thermometer calibrated with use of the temperature scale of Greywall.[8] This thermometer was located inside a second chamber attached to the base of the calorimeter. The thermometer chamber held roughly 0.5 cm^3 of liquid ^{3}He to provide thermal contact between the paramagnetic salt and the metal base of the thermometer. The addendum heat capacity of the calorimeter was measured prior to the admission of any sample to the cell. Except for the lowest two coverages, the sample heat capacity was greater than the addendum contribution for $T \lesssim 7$ mK. In converting areal densities, ρ, into number of adsorbed layers, we have used the results from recent neutron-scattering measurements[9] on graphite. Although the correct numbers for silver will be

somewhat different, we do not expect these differences to be significant, especially when we bear in mind the uncertainty in our surface-area determination.

Figure 1 shows the heat-capacity data for many of the coverages studied. A common feature of all of the curves is a rise in the heat capacity at the lower temperatures due to contributions from the nuclear spins. Another common feature for data obtained at coverages greater than monolayer completion (at 0.107 atoms/Å^2) is the large, nearly constant term attributable to the ^{3}He atoms in the second layer.

On the basis of the ^{3}He-on-graphite phase diagram, the data at 0.080 atom/Å^2 [Fig. 1(a)] should correspond to a solid monolayer with a Debye temperature of about 20 K.[10] At millikelvin temperatures the lattice contribution to the heat capacity should therefore be negligibly small. The finite "lattice" term which we obtain is presumably due to an improper subtraction of the addendum contribution which is relatively large for this coverage. It is also possible that substrate heterogeneity is playing a role. From a fit of the data, with the leading term of the high-temperature series expression for the 2D (triangular lattice) spin $-\frac{1}{2}$ Heisenberg ferromagnet, namely $c_{ex}/nR = \frac{9}{4}(J/k_BT)^2$, we find the exchange energy to be 50 μK. This value is more than an order of magnitude smaller than the energy recently inferred from spin-lattice relaxation measurements at 1.2 K by Cowan *et al.*[11] for the same ^{3}He coverage, but on graphite. Our exchange energy is, however, in line with the upper limit placed on J by Godfrin[12] on the basis of NMR magnetization measurements at millikelvin temperature, again for ^{3}He on graphite.

For an ideal substrate we would expect that the first atoms promoted into the second layer would constitute a 2D Fermi gas with a very low degeneracy temperature ($T_F^{2D} \propto N$). For $T \gtrsim T_F^{2D}$, $c = Nk_B$; consequently, the heat capacity of a very low-density second layer should be constant in temperature and proportional to the second-layer coverage. At finite ρ_2, however, the situation is considerably more complicated because of adatom-adatom interactions. Specific heat measurements on monolayer ^{3}He films,[13] as well as on bulk ^{3}He,[14] show that both the 2D and 3D Fermi *liquids* reach a plateau value of only a fraction ($\simeq 0.2$) of the classical limit for temperatures near $0.1T_F$. In this plateau region the film specific heat per atom varies inversely with areal density leading to a total measured heat capacity [$c = NC(\rho)$] roughly independent of coverage. In 3D we find the equivalent result that $C(V)/V^{2/3}$ is roughly constant. The weak coverage dependence of the 5-mK heat capacity above 1.5 layers, Fig. 2(c), along with the result that $c_2/N_2k_B \approx 0.2$ leads us to conclude that our heat-capacity data at these coverages correspond to a Fermi liquid in the plateau region. Because the lowest-temperature data, Fig. 1, do not show evi-

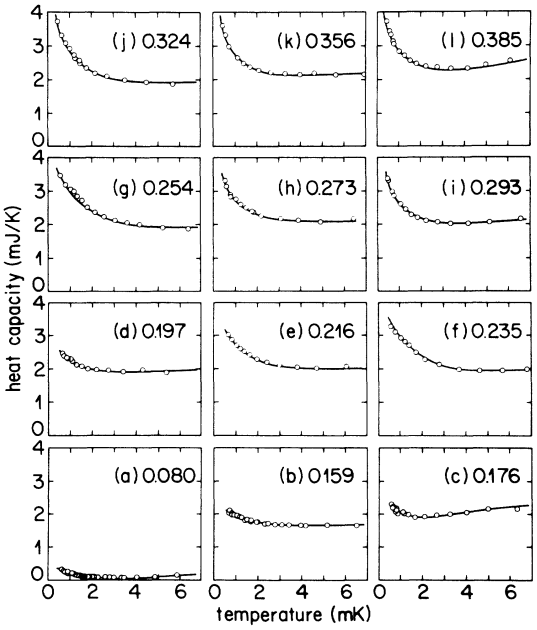

FIG. 1. Heat-capacity results for many of the samples studied. The numbers give the coverages in atoms per square angstrom. The solid curves are guides to the eye.

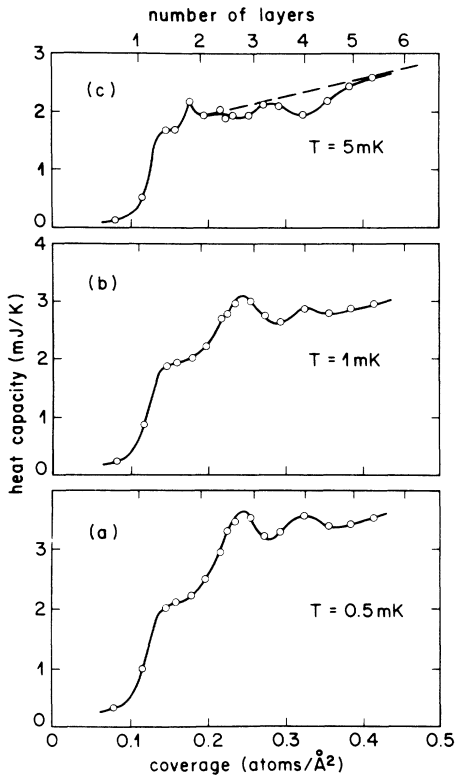

FIG. 2. Heat capacity vs coverage along three isotherms. The dashed straight line shows the expected heat capacity at 5 mK if the second-layer contribution is unchanged by the addition of ^{3}He atoms behaving like those in the bulk liquid at vapor pressure.

dence for the onset of the fully degenerate region, we estimate that T_F for the second-layer liquid must be less than 10 mK which agrees well with the estimate obtained by Franco, Rapp, and Godfrin[3] from magnetization measurements. The very small T_F implies $m_3^*/m_3 \gtrsim 300$!

The heat-capacity data obtained at coverages of 0.176 [Fig. 1(c)] and 0.178 atom/Å^2 show an anomalous temperature dependence. In contrast to the measurements at neighboring coverages which exhibit a nearly temperature-independent heat capacity above 2 mK, these data show a roughly linear increase which is responsible for the peak in the 5-mK heat-capacity versus coverage curve [Fig. 2(c)]. On the basis of the ^{3}He-on-Grafoil neutron-scattering experiments, this anomalous coverage should be less than that corresponding to second-layer completion.

We speculate that the anomalies observed in ^{3}He-on-Grafoil experiments[3,15] at a slightly higher coverage, namely 0.186 atom/Å^2, have a common origin. The heat-capacity measurements of Van Sciver and Vilches[15] performed above 40 mK show a large peak near 1 K which develops sharply as a function of coverage. The anomalous behavior at this density was interpreted as an indication of second-layer solidification. More recent neutron-scattering measurements[16] performed at a significantly higher density, 0.203 atom/Å^2, however, showed no evidence for the presence of second-layer solid. NMR measurements by Franco, Rapp, and Godfrin[3] do show an increase in the second-layer magnetization at 0.186 atom/Å^2, but at 3 mK the magnetization remains considerably smaller than the Curie value. Franco, Rapp, and Godfrin attributed the anomalous magnetization to the promotion of atoms into the third layer. The promotion of a sufficiently small number of atoms would not seriously alter the low-temperature heat capacity of the second layer, but would add a contribution from the atoms in the third layer, which is consistent with our results. The linear excess heat capacity would imply 10 mK $\ll T_{F,3} < 1$ K. However, our anomaly disappears when the coverage is increased slightly. Moreover, this proposal would not explain the high-temperature heat-capacity peak.[15]

Another possible explanation for the anomalies seen in the various experiments is the existence of a partially registered second layer near second-layer completion. Certainly, registry would be consistent with the very narrow range of coverages over which we observe anomalous behavior. In turn, this would explain the absence of second-layer long-range order at 0.203/Å^2 as determined by the scattering experiments.

For coverages greater than two layers (i.e., for $\rho > 0.2$ atoms/Å^2) the data show dramatic variations in the exchange contribution to the heat capacity; the 0.5- and 1.0-mK isotherms in Figs. 2(a) and 2(b) show peaks at densities of 0.25 and 0.32 atom/Å^2. The first of these peaks occurs at the same coverage for which Franco, Rap, and Godfrin reported a large peak in the magnetization of ^{3}He adsorbed on graphite. Unfortunately their results extend only up to coverages of about 0.28 atom/Å^2 and so it is not known if there is a second peak for the ^{3}He-graphite system at higher densities.

At 5 mK, Fig. 2(c), the heat capacity is only very slightly affected by exchange and in the vicinity of 0.25 atom/Å^2 is nearly constant. If solidification of the second layer were occurring at these densities, the heat capacity would have dropped to near zero. Therefore, contrary to the behavior of ^{3}He on graphite, we find that the second ^{3}He layer on our silver substrate remains liquid even when compressed by additional layers. Consequently, our peaks in the exchange heat capacity cannot be associated with solidification.

At higher coverages there are oscillations in the 5-mK heat-capacity data, Fig. 2(c), which are 180° out of phase with the peaks in the exchange contribution [Figs. 2(a) and 2(b)]. As a reference the dashed straight line in Fig. 2(c) shows the heat capacity under the assumption that the second-layer contribution remains constant and that additional layers have a heat capacity corresponding to bulk liquid ^{3}He at vapor pressure. The oscillations in the 5-mK curve, therefore, represent periodic *decreases* in the heat capacity, which, because of their large amplitude, we associate with the second layer. Decreases in the plateau region of the Fermi-liquid heat capacity, as discussed above, can be interpreted to imply enhanced particle interactions. It is less clear which layer should be associated with the accompanying enhanced exchange. One might be tempted to attribute the large exchange to the first layer simply because this is the only solid layer on our substrate. But it is also possible that the second (liquid) layer is responsible for both of the exchange anomalies. Certainly this would be in line with predictions[6,7] based on the paramagnon theory of ^{3}He applied to bulk liquid in contact with a substrate. These calculations indicate that the van der Waals attraction can lead to a surface ferromagnetic instability of the paramagnetic bulk liquid, provided the magnetic susceptibility of the bulk Fermi liquid is sufficiently large. The theory also indicates that an increase in the quasiparticle effective mass should accompany the magnetic instability. These predictions clearly show a direct correspondence with our experimental findings for adsorbed ^{3}He layers.

At coverages of several layers it should be possible to make direct connection with previous magnetization experiments done in confined geometries. Independent of the substrate, most of these yield a ferromagnetic Curie-Weiss temperature of about 0.5 mK. With the assumption of a 2D Heisenberg system, this value implies an effective exchange energy $J/k_B = \theta_W/3 \approx 0.17$ mK. This temperature agrees well with the value 0.14 mK which we extract from our 5-layer results using the leading

term of the high-temperature series expression and assuming that only the second layer contributes to the exchange heat capacity. We conclude that only one layer is contributing to the anomalous magnetism which is in agreement with the recent findings for the graphite substrate.[3,17] It is puzzling that magnetization measurements performed with a silver substrate[2] indicate about 5 magnetic ^{3}He layers which agrees with estimates from early measurements on Mylar and carbon substrates.[18,19]

Assuming that only the second layer contributes, we determine $J/k_B=0.17$ mK at the coverage of the first peak, namely $\rho=0.25$ atom/Å^2. This value is an order of magnitude smaller than the value recently extracted from the magnetization measurements on graphite.[17] A very important difference, however, is that on the graphite substrate the second layer is solid at this coverage. In fact, it is believed that the solidification of the second layer is occurring at coverages corresponding to the rapid rise in magnetization. Our results would suggest, though, that the tremendously large exchange energy for the graphite substrate is not simply the consequence of solidification but is related to the anomalies in the second-layer liquid which we have observed. It is also possible that the second-layer solidification on graphite is triggered by the enhanced quasiparticle interactions.

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[1]D. F. Brewer and J. S. Rolt, Phys. Rev. Lett. **29**, 1485 (1972).

[2]Y. Okuda, A. J. Ikushima, and H. Kojima, Phys. Rev. Lett. **54**, 130 (1985).

[3]H. Franco, R. E. Rapp, and H. Godfrin, Phys. Rev. Lett. **57**, 1161 (1986).

[4]L. J. Friedman, S. N. Ytterboe, H. M. Bozler, A. L. Thomson, and M. C. Cross, Phys. Rev. Lett. **57**, 2943 (1986).

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

[6]M. T. Beal-Monod and A. Theumann, in *Ordering in Two Dimensions,* edited by S. K. Sinha (North-Holland, New York, 1980).

[7]D. Spanjaard, D. L. Mills, and M. T. Beal-Monod, J. Low Temp. Phys. **34**, 307 (1979).

[8]D. S. Greywall, Phys. Rev. B **33**, 7520 (1986).

[9]H. J. Lauter, H. P. Schildberg, H. Godfrin, H. Wiechert, and R. Haensel, Can. J. Phys. **65**, 1435 (1987).

[10]S. V. Hering and O. E. Vilches, in *Monolayer and Submonolayer Helium Films,* edited by J. G. Daunt and E. Lerner (Plenum, New York, 1973), p. 1.

[11]B. Cowan, L. Abou El-Nasr, M. Fardis, and A. Hussain, Phys. Rev. Lett. **58**, 2308 (1987).

[12]H. Godfrin, private communication.

[13]D. C. Hickernell, E. O. McLean, and O. E. Vilches, Phys. Rev. Lett. **28**, 789 (1972).

[14]D. S. Greywall, Phys. Rev. B **27**, 2747 (1983).

[15]S. W. Van Sciver and O. E. Vilches, Phys. Rev. B **18**, 285 (1978).

[16]C. Tiby, H. Wiechert, H. J. Lauter, and H. Godfrin, Physica (Amsterdam) **107B&C**, 209 (1981).

[17]H. Godfrin, R. R. Ruel, and D. D. Osheroff, Phys. Rev. Lett. **60**, 305 (1988).

[18]A. I. Ahonen, T. A. Alvesalo, T. Haavasoja, and M. C. Veuro, Phys. Rev. Lett. **41**, 494 (1978).

[19]D. F. Brewer, A. S. Sachrajda, D. S. Betts, and W. S. Truscott, Physica (Utrecht) **108B**, 1051 (1981).