Nuclear Magnetic Susceptibility of Submonolayer ³He Films Adsorbed on Graphite at Millikelvin Temperatures

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The nuclear magnetic susceptibility of submonolayer ³He films adsorbed on a graphite substrate has been measured for temperatures between 6 and 800 mK. Three distinct surface-density regimes are identified for fractional monolayer coverages below perfect registry. These appear to be a fluid phase with some atoms localized by substrate heterogeneity, a solid-fluid coexistence region, and a registered solid phase with defects. T_2 values inferred from NMR linewidth measurements are also reported.

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Recent experiments^{1,2} on ³He adsorbed on the surface of graphite at millikelvin temperatures have concentrated on the properties of multilayers. Magnetization and heat-capacity measurements indicate a crossover from antiferromagneticlike to ferromagnetic behavior with increasing surface density. In this Letter we report measurements on the magnetic susceptibility of submonolayer films. In this case both the substrate potential and interatomic interactions are important in determining the properties of the film; it is expected that all atomic motion is confined to a single plane, whereas both interlayer and intralayer exchange motion must be taken into account for multilayer films.

In earlier work it has been established, for both ³He and ⁴He, that the submonolayer system exhibits a variety of phases.³ The exposed basal planes of graphite have a rather uniform binding potential of order 200 K with a periodic variation of order 40 K. The binding energy has a maximum at the center of graphite hexagons spaced by 0.246 nm. A single helium atom can tunnel rapidly from site to site resulting in the formation of a band⁴ of width of order 10 K. At low surface densities and temperatures near 4 K, a two-dimensional fluid phase was identified from heat-capacity measurements which gave values approaching k_B per atom.⁵ The helium-helium interaction is repulsive for atoms on nearest-neighbor sites but attractive for those on nextnearest-neighbor sites. The interplay of these interactions and the substrate potential leads to a registered $\sqrt{3} \times \sqrt{3}$ commensurate structure corresponding to the occupation of every third hexagonal site. At higher surface densities an incommensurate solid is formed and eventually, at 10.8 nm $^{-2}$ for ³He films, promotion to the second layer occurs. For submonolayer films the surface can be specified as a function of this monolayer density. In these units perfect registry occurs at $x \approx 0.6$. The nature of the film at coverages below registry has not been definitely established. It was the intention of these experiments to investigate whether the "fluid" phase of ³He can be described as a two-dimensional Landau Fermi liquid and over what range of surface densities the periodic substrate potential has significant influence.

Our measurements indicate three distinct coverage re-

gimes below registry: (i) $x \leq 0.3$, for which the film consists of fluid plus a small number of atoms (equivalent to a fractional monolayer coverage ~ 0.02) localized by substrate heterogeneity; (ii) $0.3 \leq x \leq 0.45$, for which the susceptibility is strongly enhanced above expected degenerate fluid values in a manner consistent with solid-fluid coexistence, demonstrating the instability of the uniform fluid-phase ground state; and (iii) $0.45 \leq x \leq 0.6$, for which the susceptibility shows a decrease from the free spin value from 1 K to 50 mK but follows Curie's law at low temperatures and which we interpret as a phase consisting of the registered solid and defects.

The graphite substrate used in this work is Grafoil,⁶ a commercial form of exfoliated graphite. The surface of Grafoil consists of atomically flat basal-plane platelets of typical dimension 20 nm. Grafoil sheets, 125μ m thick, were bonded to thin copper foils for thermal contact and oriented in the plane of the static and radio-frequency magnetic fields. The nuclear-magnetic-susceptibility measurements were made by integrating the area under the absorption line obtained using continuous-wave NMR at 1.08 MHz. The temperature was determined by a ³He melting-curve thermometer. A cusplike minimum in T_2 served as a precise indicator of second-layer promotion⁷ (x = 1) with an expected accuracy of 1%.

The raw data showed no direct evidence at any coverage of a constant low-temperature susceptibility as expected for a two-dimensional Fermi liquid, although substantial reductions in the susceptibility below the Curie value were observed. In Fig. 1 the experimental values of the susceptibility χ are shown as a function of temperature for a number of coverages, where the results have been normalized by the Curie constant for x=1 (χT $=C_0$ at x=1). C_0 was determined from the measured Curie-law susceptibility in the incommensurate solid at coverages 0.742, 0.785, 0.827, and 0.870. It is found that a good fit to the experimental results at all coverages less than 0.521 is given by

$$\chi T = x_s C_0 + x_f C_0 (T/T_F) [1 - \exp(-T_F/T)], \quad (1)$$

where $C = C_0 x$, and x_s/x_f and T_F are taken as adjustable temperature-independent parameters. Fitting the data by this expression is a useful device for generating iso-



FIG. 1. Normalized susceptibility as a function of temperature at coverages of 0.144 (**n**), 0.195 (\diamond), 0.244 (+), 0.291 (\odot), 0.337 (\diamond), 0.385 (\Box), 0.430 (\blacktriangle), and 0.475 (\bigtriangledown). Curves through data illustrate the fit by Eq. (1). Inset (lower left): Fit to normalized χT for these coverages. Inset (upper right): Coverage dependence of χT at 10, 50, 100, 300, and 1000 mK (reading upwards) with linear interpolations between measured coverages as guides to the eye.

therms of χT . If interpreted literally, it gives the total nuclear susceptibility of a film of coverage $x = x_s + x_f$ with a fraction of solid x_s/x and a fraction of liquid x_f/x . The liquid term is the form of the susceptibility of an ideal 2D Fermi gas⁸ with Fermi temperature T_F . The coverage dependence of χT at low temperatures shows a distinct break at $x \approx 0.3$; for $x \gtrsim 0.3$, χT increases rapidly with surface density. The onset coverage for this behavior can be identified to be approximately constant up to a temperature of 300 mK; at higher temperatures the magnetic susceptibility does not provide a high-resolution signature of the transition. This behavior is shown by the insets of Fig. 1, which illustrate the fitted temperature dependence of χT for various coverages and isotherms of the coverage dependence of χT determined from these fits.

In terms of our fit parameters, this effect corresponds to a break in the coverage dependence of x_s , the monolayer fraction of localized atoms. The coverage dependence of this quantity and the parameter T_F are shown in Fig. 2, where the errors are those estimated by our nonlinear least-squares-fitting routine. The parameter C_0 , as determined from the fit parameter $C=C_0x$, is constant as a function of coverage, as expected, indicating that all the spins contribute to the observed signal.

For $x \le 0.291$ it is found that the parameter x_s is approximately constant at 0.02. This corresponds to a Curie-law contribution from those spins localized by substrate heterogeneity; the monolayer fraction of localized



FIG. 2. Coverage dependence of susceptibility fit parameters, see Eq. (1) and text.

atoms is in agreement with estimates from vapor-pressure studies⁹ and the analysis of low-coverage NMR relaxation-time data.¹⁰ This interpretation is supported by our observation of preferential absorption of ⁴He atoms at these "deep sites." With a ³He monolayer fraction of $x_3 = 0.14$ and $x_4 = 0.025$, the monolayer fraction of localized spins was reduced from $x_s = 0.020$ to 0.004 while the fit parameter T_F remained constant within 10 mK. The effective Fermi temperature of the fluid contribution is consistent with density-dependent interactions in the 2D fluid equivalent to those measured in the second layer of ³He on Grafoil.¹¹ The dependence of T_F on surface density measured in the second layer is given by the curve in Fig. 2.

Between the break point in the coverage dependence of χT and registry (0.3 $\lesssim x < 0.6$) the parameter x_s increases approximately linearly with coverage. The data suggest two distinct regimes and we discuss these separately. Up to $x \sim 0.45$ the increase in x_s is accompanied by a constant value of T_F . This result is consistent with solid-fluid coexistence where it is likely that the solid component is the $\sqrt{3} \times \sqrt{3}$ registered solid. Indeed it has been suggested for submonolayer ⁴He films¹² that such a coexistence is the low-temperature equilibrium state for surface densities below registry. The results reported here provide direct evidence of two-phase coexistence in ³He films. The observation that the coverage at which this coexistence region is entered is temperature independent below 300 mK implies, according to the usual "lever rule" and given that the solid phase is registered, that on cooling the sample below this temperature the relative proportions of the two phases remain constant. This is consistent with the assumption, made in fitting the data. that the parameter x_s is temperature independent. Contrary to the behavior proposed for ⁴He films, the density of both components remains finite at T=0. This coexistence region had not been inferred from earlier heatcapacity data. Unlike the case of ⁴He films the constant-density specific-heat results⁵ for ³He show no evidence of entering such a coexistence region. They exhibit a plateaulike region between 100 and 400 mK. This might suggest continuous solidification on cooling but this interpretation is ruled out by our observations. Such

a plateau is also a characteristic feature of bulk ³He, ¹³ and, in terms of almost localized Fermi-liquid theory, ¹⁴ is understood as arising from the fluid spin degrees of freedom.

The nature of this two-dimensional mixed solid and fluid phase is also of interest. On each Grafoil platelet the film consists of a coexistence of fluid and the $\sqrt{3} \times \sqrt{3}$ solid. If the solid is in the form of clusters, the high quantum mobility will result in fluctuations in the configuration due to exchange within and between clusters as well as interchange between fluid and solid.¹⁵ Measurements of the susceptibility to lower temperatures will establish whether simple two-phase coexistence is adequate to describe the thermodynamics of this system. Theories of the ground state of liquid ³He which have been successful in calculating the ground-state energy and structure factor¹⁶ may be useful in understanding the instability of the homogeneous fluid at coverages above 0.3. These theories find the bulk fluid ground state to be a "nearly solid liquid" with local crystalline structure. It might be expected that the graphite periodic potential would enhance such a tendency to local order in the 2D system.

The experimental results for coverages in the vicinity of registry are shown in Fig. 3. For coverages of 0.475, 0.521, and 0.565, the low-temperature dependence of the susceptibility is well described by Curie's law. At the two lower coverages the low-temperature susceptibility is significantly smaller than the free spin value, as can be seen from the clear decrease in γT between 1 K and 50 mK. If the limiting form of the low-temperature susceptibility is fitted by a power law of the form $\chi \sim T^{-\alpha}$, it is found that the exponent α increases with coverage above x = 0.3 reaching $\alpha = 1$ or Curie's law at x = 0.475. This leads us to propose the density range between $x \sim 0.45$ and registry as a third distinct regime. The existence of this further phase is supported by the jump in the parameter T_F , obtained by fitting Eq. (1) to these data, which occurs between the coverages of 0.430 and 0.475. We suggest that for coverages between approximately



FIG. 3. Inverse effective Curie constant (normalized by the value at x = 1) as a function of inverse temperature, for coverages of 0.475 (\bigtriangledown), 0.521 (**a**), 0.565 (\diamond), 0.611 (**b**), 0.655 (\diamond), 0.698 (\blacklozenge), 0.742 (**c**), and 0.827 (\bigtriangledown).

0.45 and perfect registry, the film consists of the registered solid and defects. These defects could be domain walls since there are three possible sublattices for the registered solid or, alternatively, vacancies. This result is consistent with lattice-gas calculation¹⁷ which find that the $\sqrt{3} \times \sqrt{3}$ solid is stable with respect to a homogeneous disordered phase down to a coverage of 0.43 of 0.50, depending on the method of solution. Furthermore, there is some evidence for the persistence of the registered solid below perfect registry in neutron-scattering data.¹⁸

Those spins in the vicinity of defects would be expected to have a high quantum mobility and hence exhibit the effects of degeneracy. Those spins within the registered solid contribute the free spin susceptibility since they are undergoing only slow spin exchange with their neighbors. An appropriate description of this system may be as a quantum glass with some distribution of effective exchange energies P(J). It is known from other physical systems¹⁹ that, for example, $P(J) \sim J^{-\alpha}$ leads to $\chi \sim T^{-\alpha}$. In our case the exchange energies range from order 100 mK, characteristics of vacancy tunneling, to < 1 mK, characteristic of the registered solid. The configuration for coverages between 0.45 and registry may thus correspond to a bimodal distribution P(J), accounting for the decrease in χT with decreasing temperature at the highest temperatures and its constancy thereafter, as well as the decrease in the magnitude of the effect as registry is approached. In the quantum glass model, the spin entropy of the film may be inferred from the susceptibility results. Following Rice,²⁰ at any temperature there is an effective proportion of "free" spins $n_f(T)$; this function will be determined by the distribution of effective exchange interaction. Then $\chi T \propto n_f(T)$ and the spin entropy per atom is $n_f(T)k_B \ln 2$. The heat capacities inferred in this way reproduce features of the direct measurements⁵ at these densities, particularly the weak temperature dependence between 50 and 500 mK and the small absolute value of order $0.1k_B$ per atom.

This density regime is of considerable general interest since, if the identification proposed here is correct, it offers the possibility of creating ground-state defects simply by appropriate adjustment of the surface density. It has been predicted²¹ that in a triangular lattice, vacancies induce antiferromagnetic spin polarons; it is possible that our observations may be explained within this framework.

For the two coverages above registry (0.61 and 0.655) the low-temperature susceptibility follows Curie's law, but exhibits a small but significant enhancement above the free spin value observed at higher temperatures. This effect is most marked at x = 0.61 and decreases rapidly with increasing surface density. It may originate from rapid three-particle and hence ferromagnetic exchange cycles involving two registered atoms on an interstitial. For coverages in the range 0.74 < x < 0.87, in the incommensurate solid phase, there are no significant deviations from Curie's law at these temperatures.



FIG. 4. Isotherms of the inverse spin-spin relaxation time as a function of coverage.

Further information on the dynamics of the film is provided by measurements of the NMR relaxation times. In this work, approximate T_2 values have been obtained from measurements of the NMR linewidth $1/T_2^*$. The isotherms of $1/T_2$ obtained in this way are shown in Fig. 4. There are distinct signatures at $x \approx 0.6$ corresponding to registry and at $x \approx 0.3$ corresponding to the critical coverage for entering the coexistence region. Above 0.3 K it was observed that $T_2 \propto \sqrt{T}$, characteristic of thermal motion.⁷ It is apparent from Fig. 4 that the observed linewidths continue to increase over the temperature interval 100-10 mK; at the lowest temperatures the values of $1/T_2$ in the "fluid" region are comparable to those observed in the incommensurate solid.

In conclusion, we have made the first systematic measurements of the magnetic susceptibility of submonolayer films of ³He on Grafoil at millikelvin temperatures. These establish the existence of three distinct surfacedensity regimes below registry including a solid-fluid coexistence region for coverages 0.3 < x < 0.45. These results provide strong evidence that the periodic substrate potential is important for coverages well below registry.

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