PHYSICAL REVIEW B VOLUME 50, NUMBER 17 1 NOVEMBER 1994-I

Onset of ferromagnetic exchange in adsorbed ^{3}He films

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(Received 22 August 1994)

Nuclear magnetic resonance experiments are reported on multilayer ^{3}He films adsorbed on the surface of graphite. Initially the second layer exhibits antiferromagnetic exchange, which has been measured as a function of coverage. Measurements of the nuclear magnetic susceptibility and resonant frequency for coverages around the third layer promotion precisely identify the onset of ferromagnetic exchange in the film. The evolution of the structure of the film is discussed in the light of these results and previous heat-capacity and NMR data.

Multilayer films of ^{3}He adsorbed on the surface of graphite offer the possibility of studying quantum exchange processes in two-dimensional solid helium.[1] The exchange energies are typically of order millikelvin, much larger than the dipolar energy, and show an interesting coverage dependence with the growth of the film. This is in marked contrast with the rapid and monotonic decrease in exchange with increasing density observed in bulk helium. The anomalous behavior is clearly connected to the details of the evolution of the film with coverage.

Helium films adsorbed on graphite grow as distinct atomic layers. For ^{3}He films the completed first layer is a compressed paramagnetic solid and essentially magnetically inert. There exists a rather good picture, from neutron-scattering measurements,[2] of the structure and density of the completed first layer as a function of coverage. However in the coverage range of interest our understanding of the second solid layer is based solely on the interpretation of thermodynamic data. This layer is solid above a total coverage of order 0.18 Å^{-2},[3] at which density the nuclear exchange is antiferromagnetic (AFM).[4] According to the heat capacity measurements of Greywall and Busch,[3] a fluid overlayer forms at 0.184 Å^{-2}. With increasing coverage, magnetization measurements find a crossover to ferromagnetic (FM) exchange, which shows a distinct anomalous peak around 0.23 Å^{-2}.[5] Very similar behavior is observed when the graphite is preplated by a monolayer of ^{4}He,[6] eliminating the first paramagnetic ^{3}He solid layer.

Ideally at any coverage we would know the density and the structure of the second layer solid and the nature of the fluid overlayer. Greywall[7] has proposed a phase diagram in which the second layer evolves through two registered structures to an incommensurate solid. Schiffer *et al.*[8] have interpreted their low temperature NMR measurements to support this phase diagram. Recently Godfrin *et al.*[9] have argued that the third layer fluid condenses into two-dimensional "puddles." These effects are important in understanding the nature of atomic exchange in the film.

Indeed one of the main interests of this system is the potential for new kinds of exchange processes. Intralayer exchange involves the permutation of atoms within the second solid layer; such processes are similar to those occurring in bulk solid helium, which have been described by the multiple spin exchange model with considerable success.[10] On the other hand interlayer exchange is unique to the two-dimensional solid. In this class one can have AFM processes in which an atom from the second layer goes into a virtual fluid state[11] or FM indirect exchange involving two pairwise exchange processes between a solid and a fluid atom.[12] However a particular feature of two-dimensional systems, which may be of importance, is the existence of registered "solids" stabilized at relatively low density by the periodic potential of the surface. It is believed that the second layer first "solidifies" in this way.[13] One would expect these structures to constitute extreme quantum solids, perhaps to the extent that the conventional picture of a quantum solid may break down.[14] These systems may admit new kinds of intralayer and interlayer exchange not fully considered hitherto.

In this paper we report NMR measurements at a fine grid of coverages in the vicinity of the crossover from AFM to FM exchange. The magnetic susceptibility and frequency of the NMR line have been measured down to 0.5 mK. Measurements of the frequency shift of the NMR line are particularly sensitive to ferromagnetic exchange processes in the film or in regions of it.[8] The shifts are caused by the demagnetization field arising from the large polarization at low temperature present in these regions.[15]

Measurements of the ^{3}He susceptibility were made by field swept continuous wave NMR at a frequency of 920 kHz and numerically integrating the NMR line shape. The sample consisted of a stack of sandwiches of two 0.15 mm grafoil sheets diffusion bonded to each side of a silver foil. Previously the grafoil had been baked at 1100 °C to reduce the level of magnetic impurities. Adjacent sandwiches were separated by Mylar sheets to ensure rf penetration into the stack. Overall the stack was 25 mm in diameter and 20 mm long. Thermal contact to the cold plate was made by diffusion bonding the silver sheets to a silver rod, attached to the cold plate by a cone joint, whose design had a typical resistance of less than 20 nΩ. Thermometry was provided by measuring the nuclear magnetic susceptibility of platinum wires, similarly mounted on the cold plate and calibrated by a ^{3}He melting curve thermometer. The thermal link to the nuclear stage consisted of a 9 mm diameter silver rod, also connected to the cold plate by a cone joint. As a check of thermal equilibrium a sample of 1.5 layers was found to exhibit no detectable deviation (i.e., $<1\%$) from Curie's law down to 0.5 mK.

The coverage scale was determined by measurements, through second layer promotion, of the NMR line shape. The

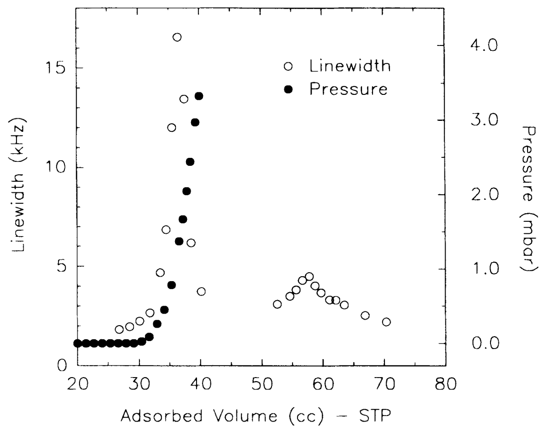

FIG. 1. Isotherms of NMR linewidth (10 mK) and vapor pressure (4.2 K). Second layer promotion occurs at 36.2±0.3 STP cm^3.

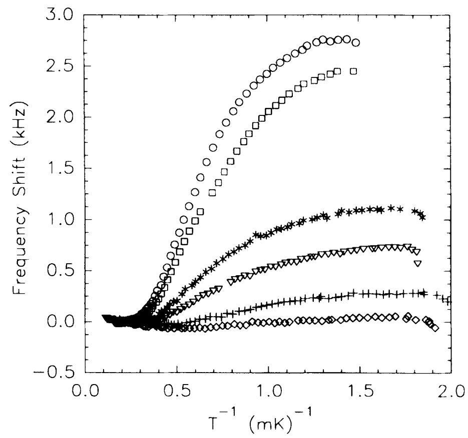

FIG. 3. Frequency shift of the maximum of the NMR line shape as a function of temperature at various coverages. (◇) 0.193 $Å^{-2}$, (+) 0.196 $Å^{-2}$, (▽) 0.198 $Å^{-2}$, (*) 0.200 $Å^{-2}$, (□) 0.211 $Å^{-2}$, (○) 0.222 $Å^{-2}$. Data for coverages 0.185 and 0.188 $Å^{-2}$ show zero shift and are not plotted for clarity.

linewidth exhibits a sharp maximum, as shown in the 10 mK isotherm in Fig. 1, and we identify this with the onset of promotion to the second layer.[16] At this temperature and with a fluid second layer all of the signal comes from the first layer; the initial decrease in linewidth on formation of the second layer arises from motional narrowing due to exchange between first and second layer spins. At higher fluid densities there is a tendency for the line to broaden; this effect will be discussed elsewhere. The coverage at the linewidth maximum agrees with that determined from a 4.2 K helium isotherm, performed on the same sample and using the point-*B* criterion,[17] to better than 1%. In order to facilitate comparison with other work we adopt the so-called commensurate coverage scale[18] and define the coverage at this point as 0.114 $Å^{-2}$.

Measurements of the magnetic susceptibility were made as a function of temperature and coverage in order, at first, to detect the solidification of the second layer. Two signatures of solidification are a clear step in the magnetization isotherms at 3.2 mK, Fig. 2, and a second cusplike feature in the 10 mK linewidth isotherm, Fig. 1.[19] A precise indication of the complete solidification of the second layer is given by attempting to fit the susceptibility data above 2 mK as the sum of two terms; a Curie law term to represent the contribution from the first layer and a high-temperature series expansion[20] to describe the second layer. The quality of this fit is the best guide to the complete solidification of the second layer. At 0.185 $Å^{-2}$ the second layer is certainly solid with $J=-0.72$ mK, the data and fit are shown in the inset to Fig. 2. At the lower coverage of 0.182 $Å^{-2}$ the fit quality is poor and suggests that solidification is not quite complete; forcing a fit through this data would erroneously give an exchange constant of -1.5 mK. The coverage dependence of the exchange parameter is also shown in Fig. 2. The results compare very well with previous data on ^{4}He preplated graphite converted to the commensurate coverage scale, both in the AFM and the FM regime, as is to be expected. Other workers have obtained evidence of significantly stronger AFM exchange;[5] the origin of such discrepancies is not clear. A fuller account of our results in the AFM regime will appear elsewhere.

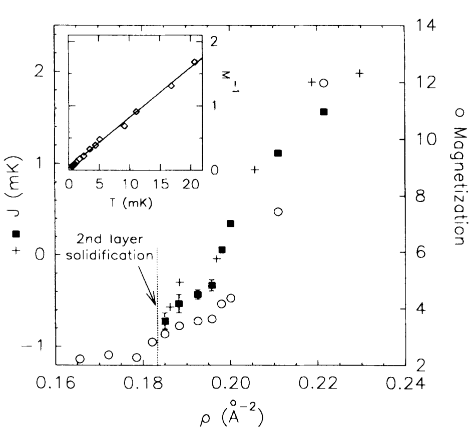

FIG. 2. Isotherms of magnetization at 3.2 mK (○), and exchange parameter J for pure ^{3}He films (■). Also shown are data of Ref. 6 for ^{4}He preplated graphite (+). Inset shows fit to magnetization at 0.185 $Å^{-2}$.

Continuing the measurements to higher coverages we find evidence of a break in the coverage dependence of the magnetization and exchange parameter in the vicinity of 0.195 $Å^{-2}$, Fig. 2. However the most distinct signature of some underlying change in the film at this coverage is the frequency shift of the NMR line. In the present experiments this is determined from the shift in the maximum of the line. Measurements as a function of temperature at various coverages are shown in Fig. 3. It is quite clear from the isotherms of the frequency shift at 0.8 mK, Fig. 4, that it is zero below 0.195 $Å^{-2}$. The rapid increase above this coverage can be understood in terms of the large demagnetization fields in regions of the sample for which the exchange is FM.[8] Thus our measurement clearly identifies the onset of FM in the film to occur at the coverage 0.195 $Å^{-2}$.

A comparison with heat-capacity isotherms is particularly informative, since a break in the coverage dependence of the

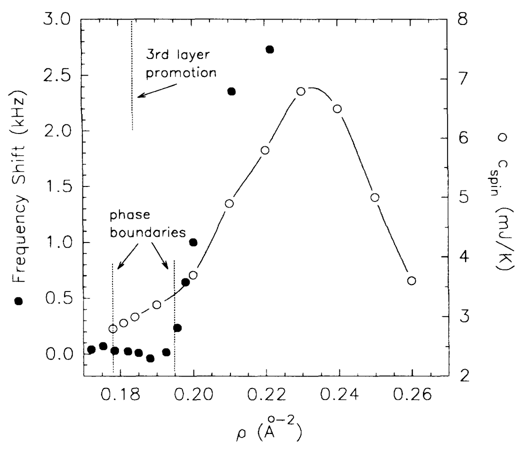

FIG. 4. Isotherm of frequency shift (0.8 mK) and spin heat capacity from Ref. 7 (3.0 mK).

spin heat capacity is also found at this coverage. Since we detect second layer solidification to occur at a coverage in agreement with Ref. 7, we can state that both magnetization and heat-capacity data are in agreement that a change in the state of the film occurs at 0.195 Å^{-2} and further that this is associated with the onset of ferromagnetism. This feature does not coincide with promotion to the third fluid layer. According to Ref. 7 the fluid coverage at this point is 0.007 Å^{-2}. The data for magnetization, frequency shift, and exchange parameter when plotted against the third layer coverage n_3 all show a distinct break at this coverage, as can be seen from the 0.8 mK isotherms of Fig. 5, where we take n_3 from Ref. 7. The behavior of the magnetization vs n_3, reported here is consistent with the results of Schiffer *et al.*[8]

We now turn to a discussion of this work in the light of the results and ideas of other workers. Recent experiments of Schiffer *et al.*[8] report measurements of the $T=0$ magnetization and frequency shift above a total coverage of 0.204 Å^{-2}; in this regime the frequency shift scales only weakly with coverage while the magnetization is strongly coverage dependent. These authors persuasively argue that this points to the presence of ferromagnetic "islands" coexisting with AFM regions of the second layer. They attribute this to coexistence of two structures in the second layer, in accord with the second layer phase diagram of Greywall.[7] However Godfrin *et al.*[9] have reexamined the heat-capacity data of Ref. 7, in particular the contribution from the third fluid layer, and argue convincingly that the behavior as a function of third layer coverages demonstrates two-dimensional condensation of the third layer fluid. These authors then, plausibly, identify the ferromagnetic islands with those regions of the second layer covered by liquid puddles with interactions dominated by the indirect exchange mechanism.

We now consider the implications of the extra information from our detailed study of the film in the crossover region from AFM to FM exchange. According to one point of view,[9] the structure of the second layer and in particular commensuration effects are not of primary importance. It is argued that the proportionality of second layer magnetization and heat capacity to n_3 demonstrates a coexistence between FM islands consisting of regions of the second layer covered by liquid and uncovered AFM regions. In fact near promotion these quantities are not proportional to n_3. The data reported here, consistent with earlier observations, show clearly that a finite fluid density is required before the onset of ferromagnetic exchange, as can be seen from Fig. 5. Conceivably, as proposed in Ref. 9, this might arise from the effects of substrate heterogeneity which localize the fluid at the edge of the graphite platelets when the third layer first forms. The measurements of frequency shift and J are not linear in n_3.

A different view, while acknowledging that there is evidence that third layer puddles have an important role in determining the ferromagnetic exchange, proposes that there is also structural evolution in the second layer which has an important influence on the exchange. In Fig. 4 are shown the phase boundaries of the two registered phases $R2a$ and $R2b$ proposed by Greywall.[7,21] According to this interpretation taken in conjunction with the data reported here, the onset of ferromagnetism coincides with the establishment at the coverage 0.195 Å^{-2} of the $R2b$ phase with a density 0.075 Å^{-2} (in the presence of third layer fluid). There is, however, a lack of consensus on the subsequent evolution of the second layer. Greywall,[7] relying on an indirectly inferred scale for the second layer density ρ_2 as a function of total coverage, claims that the density of the film continues to increase as the solid moves through a region of coexistence between $R2b$ and incommensurate solid. On the other hand in experiments on ^{4}He preplated graphite the second layer coverage was inferred directly.[6] This ρ_2 scale agrees quite well with that of Greywall up to a total coverage of 0.2 Å^{-2}. There is thus agreement that the density of the second layer at the onset of ferromagnetism is 0.075 Å^{-2}. A second layer solid of this density is consistent with a structure in $\frac{2}{3}$ registry with the first layer.[22] However it was found[6] that subsequently ρ_2 remains constant over a coverage range of approximately 0.04 Å^{-2}, through the ferromagnetic anomaly. This behavior and the subsequent evolution of the second layer density in a series of steps, is entirely consistent with the puddling hy-

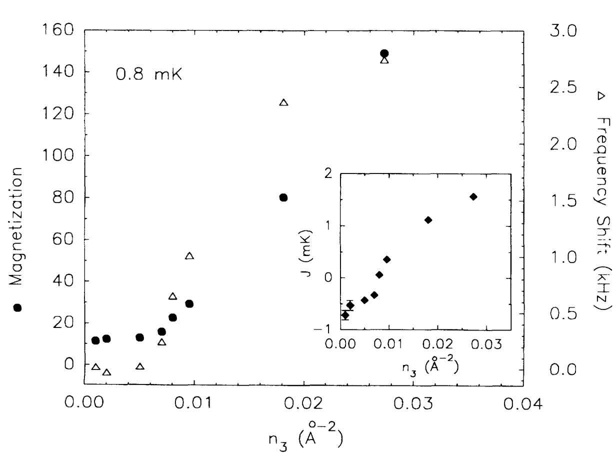

FIG. 5. Isotherms (0.8 mK) of magnetization, frequency shift, and (inset) exchange parameter as a function of third layer fluid coverage.

pothesis. The plateaus of ρ_2 correspond to regions for which the fluid puddles, while risers occur in coverage ranges over which the fluid is uniform with increasing density.

Thus these results, in conjunction with previous work, lead us to propose a scenario in which structural changes in the second layer solid, similar to those proposed by Greywall but differing in detail, do occur over the coverage range of interest. There is accumulating evidence that indirect exchange is important. The possibility that the pronounced anomaly first detected by Franco *et al.*[5] may derive from such exchange involving a second layer solid in $\frac{2}{3}$ commensuration with the first layer, should be considered.

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[22] A possible candidate structure is the honeycomb ($\sqrt{3}\times\sqrt{3}$ $R30°$), in principle observable by neutron scattering. See also Ref. 7.