Detection of Ferromagnetic Domains in a Two-Dimensional Nuclear-Spin System

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(Received 22 September 1986)

We observe magnetic ordering of the ^{3}He spins at the surface of exfoliated graphite. In very low applied magnetic fields (≤ 3 G) we find new modes in the NMR resonance spectrum with the amplitude of these lines increasing sharply below 0.8 mK. We interpret our results in terms of a ferromagnetically aligned spin system, and conclude that there must be an anisotropy in the graphite planes.

PACS numbers: 67.70.+n, 67.50.−b, 67.80.Jd, 75.50.Dd

When ^{3}He is in contact with a wall it has been shown to have a tendency towards ferromagnetic behavior at very low temperatures.[1-4] The ^{3}He-substrate system potentially provides a very interesting magnetic system. With a Grafoil substrate (exfoliated graphite) we have a large number of planes which are atomically flat over many lattice sites. The simplest description of ^{3}He on these planes is an isotropic, exchange-coupled (~ 1 mK/atom), Heisenberg-type, two-dimensional magnet. Spin anisotropy is much smaller (~ 0.1 μK/atom). The spin anisotropy occurs through the magnetic dipole interaction and eventually favors spin orientations within the planes. Dipole-induced three-dimensional effects are weak as a result of the large separation of the substrate surfaces. The main problem with this characterization is the nonideal structure of the substrate. The Grafoil substrate has flat domains[5,6] only of order 100 Å, and the spins on different domains may not be exchange coupled.

Experimentally the ferromagnetic tendency has been seen in two ways. One is a Curie-Weiss component in the susceptibility observed whenever ^{3}He is in contact with large surface areas.[1] The second is a shift in the magnetic resonance line which would normally appear at the Larmor frequency.[2] This shift has been seen only for a Grafoil substrate, and is taken to indicate a locally high degree of polarization for the ^{3}He boundary layer. Recent experiments on thin films consisting of a few monolayers of ^{3}He on sintered silver[3] or Grafoil[4] indicate that the magnetic properties are also strongly dependent on the presence of the adjoining liquid layers. One significant aspect of all previous experiments made on this system is that they have employed magnetic fields H_0 for which the energy μH_0 could itself account for a significant polarization of the localized ^{3}He surface spins. These comparatively large magnetic fields have inevitably smeared out any possible evidence of a sharp magnetic transition.

In this paper we present measurements by use of applied magnetic fields which are more than 2 orders of magnitude smaller than in previous experiments, so that the applied fields can be smaller than the dipole field exerted on a ^{3}He nucleus by its neighbors. In this regime, we observe striking changes in the behavior of the NMR signals. We see both a rapid increase in the sample magnetization and the appearance of additional resonant modes displaced from the Larmor frequency. We attribute these features to the onset of a two-dimensional ferromagnetic ordering over large coherence regions.

The system we study here consists of liquid ^{3}He confined in a Grafoil sample of volume 0.05 cm^3 (surface area around 1 m^2). Recent neutron-scattering experiments[6] have shown that both the first and second ^{3}He layers on Grafoil solidify in triangular lattices that are incommensurate. Our sample is cooled by means of a continuous liquid ^{3}He column in contact with the nuclear stage of a copper demagnetization cryostat. Temperatures are monitored by measurement of the susceptibility of a lanthanum-diluted cerium magnesium nitrate (LCMN) sample also in thermal contact with the ^{3}He of the nuclear stage. The LCMN susceptibility is calibrated against the superfluid ^{3}He phase diagram with the ultrasonic attenuation of the liquid as an indication of the transition. The temperature scale we use[7] sets $T_c = 2.491$ mK along the melting curve and $T_c = 0.929$ mK for $P = 0$ bar.

The details of the NMR system which permits low-field measurements on the Grafoil cell have been published elsewhere.[8] In brief, we use a dc SQUID based system with a dc–50-kHz bandwidth and a pulse recovery of around 30 μs. In our cell the signal-to-noise ratio for the ^{3}He sample at 20 mK and 1 kHz ($H_0 \sim 0.3$ G) is about one to one with a 90° pulse. All other measurements described in this paper were taken with use of pulses of just a few degrees so as not to push the ^{3}He spin system out of thermal equilibrium. The geometry of the cell is depicted in the inset in Fig. 1. Our magnetic field is applied perpendicular to the Grafoil sheets by the trapping of a persistent current in a superconducting aluminum cylinder. The tipping field and the SQUID pickup coil axis are oriented at 90° to one another in the plane of the Grafoil. Free-induction–decay signals (FID's) were recorded through a transient recorder interfaced to a computer, while the temperature was swept slowly with the static field H_0 and ^{3}He pressure P held constant ($P = 1.1$ bars for all the data presented here).

In Fig. 1 we show the NMR frequency spectrum measured at various applied fields. The dashed line marks the ^{3}He Larmor frequency ($\gamma H_0/2\pi$) as recorded at 15 mK. The solid points and the crosses record the frequencies for modes which appear in the spectrum only for temperatures below 1 mK. Those frequencies marked in Fig. 1 were recorded at 0.42 mK. At the higher fields a single mode appears at an average of 2.5 kHz below the Larmor frequency. At such fields the boundary-layer spins should be aligned with the static field H_0, pointing perpendicular to the Grafoil sheets. If we assume that the shift arises from the demagnetizing field of a ^{3}He layer, the 2.5-kHz shift translates into a 15% polarization as discussed below.

The most surprising feature in the frequency spectrum appears at the lower applied fields where the spectra include modes displaced well above the Larmor frequency. In Fig. 2 we show the growth of the displaced modes in the NMR signals recorded at several temperatures and applied fields. Figure 2(a) contains the free-induction decays and associated Fourier-transform amplitudes for three temperatures with an applied field $H_0 = 1.3$ G. The dashed vertical line indicates the 4.3-kHz Larmor frequency for this field. The FID's in Fig. 2(a) record the direct signals induced in the SQUID pickup coil by the precessing magnetization. The first FID in Fig. 2(a) is at $T = 1.1$ mK and shows a single frequency ringing that already has a fraction of 0.99 due to the surface signal and a T_2 that represents a linewidth substantially broader than the static field inhomogeneity. As the Grafoil sample cools we see the T_2 decrease rapidly and the NMR response break up into broad modes as exhibited in the signals at 0.51 and 0.40 mK. One mode appears here around 9.0 kHz with another slightly below the Larmor frequency. A careful analysis of this signal also shows that there is a small residue of the original Larmor-frequency line that diminishes with temperature. In all low-frequency runs the new modes appear to grow at some displaced frequency rather than continuously shifting away from the Larmor line.

Figure 2(b) shows two additional Fourier-transform families taken at applied fields of 0.3 and 7.5 G. In the 0.3-G run a displaced mode appears at 4.5 kHz and is much greater in amplitude than the 0.95-kHz Larmor line. With $H_0 = 7.5$ G, however, a dominant peak grows around 21.6 kHz, noticeably below the 24.3-kHz Larmor line. From the spectra in Fig. 2(b) one may note that

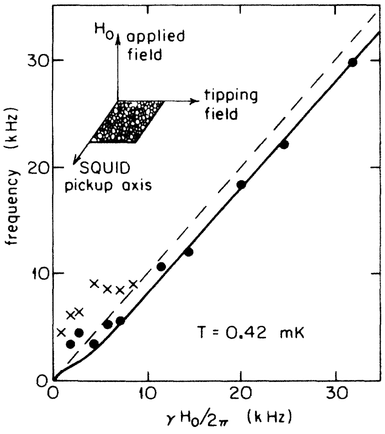

FIG. 1. NMR frequencies vs applied field at a temperature of 0.42 mK. The dashed line is the Larmor frequency as measured at 15 mK. Additional modes that appear below 1 mK, grouped in higher and lower frequencies, are shown by the crosses and filled circles. The solid line is the predicted spectrum for a 2D array with an anisotropy energy due only to the dipole fields of the aligned spins. The inset depicts the cell geometry.

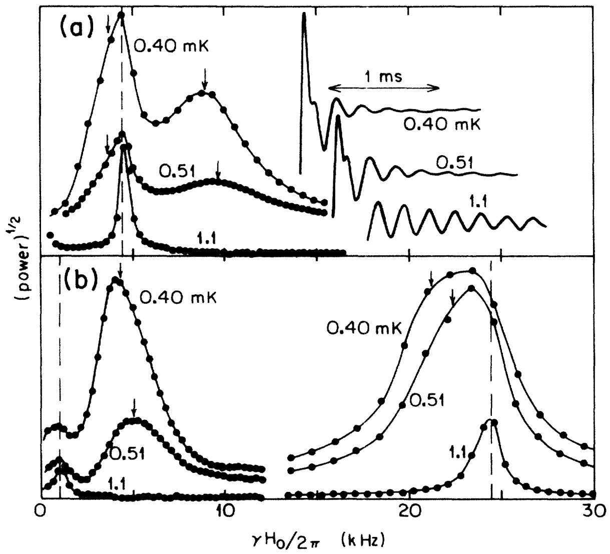

FIG. 2. (a) Fourier-transform power spectra and associated free-induction decays with an applied field of 1.3 G. Arrows point to the center frequencies of the low-temperature modes as fitted by a Gaussian line. Vertical dashed lines indicate the high-temperature (15 mK) Larmor frequency. (b) Two additional Fourier-transform families which show displaced modes growing above (for $H_0 = 0.3$ G) and below ($H_0 = 7.5$ G) the Larmor frequency.

the modes appearing in the lower applied field are noticeably narrower than those for the higher field.

The resonant frequencies producing the signals in Fig. 2 cannot be readily determined from the Fourier transforms because the linewidths are broad and overlap. Instead we fit the FID's directly with use of a Gaussian decay for each line. When $H_0 < 2.5$ G we find it necessary to construct the fit using two displaced modes in addition to a small residual Larmor-frequency signal. The arrows in Fig. 2 mark the frequencies of the displaced modes as derived from this fitting procedure. The solid points and crosses in Fig. 1 were also obtained through this fitting procedure.

Figure 3 displays the temperature dependence of the displaced-mode amplitudes for $H_0 = 0.3$ and 6.0 G. The constant liquid signal is much smaller in amplitude and is not displayed here. The displaced signals grow rather sharply below 0.8 mK and are accompanied by a drop in the amplitude recorded at the Larmor frequency. This implies that the two lines arise from the same regions. The 6.0-G displaced signal is appreciably larger in amplitude than the signal at 0.3 G. This increase in signal is due to the higher field, but may also arise in part from changes in the SQUID's sensitivity to the magnetization caused by reorientation of the domains. The higher-field signal also shows more temperature rounding at the transition than its low-field counterpart.

We interpret the extra peaks in the NMR spectra as arising from the collective modes within the ^{3}He surface layers ordered over large domains by the exchange interaction. The shift of the frequency from the Larmor frequency is a measure of the anisotropy energy for reorientation of the magnetization of these domains.

We first attempt to explain the spectrum in the ideal case where there is no anisotropy energy other than that from the aligned ^{3}He magnetic-dipole sheets. At large applied fields the spins orient along the field, perpendicular to the sheets. The reverse demagnetizing field λM_0 gives a *negative* frequency shift. (For a fully polarized triangular-lattice sheet with $a = 3.2$ Å, λM_0 is 4.78 G giving a 15.5-kHz shift.) In small applied fields, the demagnetizing field forces the spins into the planes. A *positive* frequency shift, as seen experimentally, is obtained if the external field is misaligned from the normal. This is expected for Grafoil where the planes have a spread of ± 15° from the nominal normal.[9] Quantitatively, for a field angle θ_h to the normal, the magnetization is at an angle θ_m given by

$$h_0 \sin(\theta_m - \theta_h) = \tfrac{1}{2}\sin(2\theta_m), \tag{1}$$

where $h_0 = H_0/\lambda M_0$. Following a tipping pulse the magnetization precesses around this equilibrium direction at the frequency $\omega\gamma\lambda M_0$ with the dimensionless frequency

$$\omega^2 = (h_0\cos\theta_h - \cos\theta_m)^2 + h_0\sin\theta_h(h_0\sin\theta_h + \sin\theta_m). \tag{2}$$

Note that for small h_0, ω^2 is proportional to the in-plane field $h_0\sin\theta_h$, i.e., to the externally induced in-plane anisotropy. Equations (1) and (2) generate the spectrum shown by the solid line in Fig. 1 for a Gaussian distribution of the angles θ_h with $\sigma = 15°$ and $\lambda M_0 = 0.77$ G (corresponding to a 2.5-kHz negative frequency shift at high fields). Though the shape qualitatively agrees with that seen in the data, the magnitude of the low-field positive frequency shifts is far too small. It is also not clear from the data whether the frequency of these modes would vanish as the applied field is dropped to zero.

The measured low-field positive shift reflecting an in-plane anisotropy is in fact larger than estimated for *fully* polarized spins and a field misalignment as large as 30°. It is hard to account for this large anisotropy in the ideal system. Anisotropy fields due to edge effects of the 2D Grafoil domains are reduced from λM_0 by d^{-1}, with d the domain size in lattice units, and 3D effects are also small. It is unlikely that the NMR couples to higher spin-wave modes within single disconnected domains, since the overlap of such modes with the H_1 field will be very small.[10] Exchange-enhanced positive shifts are seen in antiferromagnets,[11] but there is little reason to suggest such a radical conclusion at this stage. One possible explanation of the in-plane anisotropy is a distribution of paramagnetic impurities, e.g., oxygen or dangling bonds. This requires more investigation.

The main result of this work is the appearance of new displaced modes in the low-field NMR frequency spectrum. Small fields, of order of a few gauss, have a dramatic effect on this spectrum. Since the magnetic energy per spin in such fields is $10^{-4}k_BT$ this is direct evidence for large exchange-aligned domains. There are several suggestions concerning the source of the exchange interaction.[12-14] The existence of two shifted

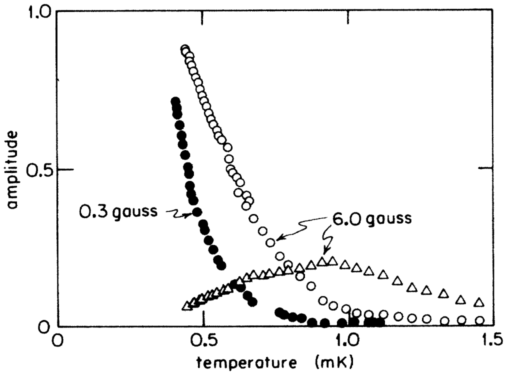

FIG. 3. Line amplitudes vs temperature for $H_0 = 0.3$ and 6.0 G (arbitrary scale): Solid circles, 0.3-G displaced mode; open circles, 6.0-G displaced mode; open triangles, 6.0-G Larmor-frequency line. The 0.3-G displaced-mode amplitude has been multiplied by 5 for display purposes. The 0.3-G Larmor-frequency line is too small to display on this scale.

lines at low fields and the precise explanation of the positive frequency shifts remain to be elucidated. The role of the substrate and the field geometry should be addressed through additional experiments.

We wish to thank C. M. Gould and P. Kumar for helpful discussions. Three of us (L.J.F., S.N.Y., and H.M.B.) are supported by the National Science Foundation through Grant No. DMR85-01090, and one of us (M.C.C.) through the National Science Foundation under Grant No. DMR84-12543. Another of us (A.L.T.) is supported by the Science and Engineering Research Council (U.K.) under Grant No. GR/C 08237.

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[1] A. I. Ahonen, T. Kodama, M. Krusius, M. A. Paalanen, R. C. Richardson, W. Schoepe, and Y. Takano, J. Phys. C **9**, 1665 (1976); A. I. Ahonen, T. A. Alvesalo, T. Haavasoja, and M. C. Veuro, Phys. Rev. Lett. **41**, 494 (1978); H. M. Bozler, T. Bartolac, K. Luey, and A. L. Thomson, Phys. Rev. Lett. **41**, 490 (1978); and H. Godfrin, G. Frosatti, D. Thoulouze, M. Chapellier, and W. G. Clark, J. Phys. (Paris), Colloq. **39**, C-287 (1978).

[2] H. M. Bozler, D. M. Bates, and A. L. Thomson, Phys. Rev. B **27**, 6992 (1983).

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

[4] H. Franco, H. Godfrin, and D. Thoulouze, Phys. Rev. B **31**, 1699 (1985); H. Franco, R. E. Rapp, and H. Godfrin, Phys. Rev. Lett. **57**, 1161 (1986). These authors argue that the first ^{3}He monolayer contributes only a paramagnetic susceptibility and that the ferromagnetic component arises from the second ^{3}He monolayer.

[5] J. K. Kjems, L. Passell, H. Taub, J. G. Dash, and A. D. Novaco, Phys. Rev. B **13**, 1446 (1976).

[6] H. D. Schidlberg, H. J. Lauter, H. Godfrin, and R. Haensel, in Proceedings of the Banff Conference on Quantum Fluids and Solids, Banff, Alberta, October 1986, Canadian Journal of Physics (to be published).

[7] D. S. Greywall, Phys. Rev. B **33**, 7520 (1986). At temperatures below 1 mK the choice of temperature scale results in considerable variation in the reported values of T. However, the temperatures we quote can be easily converted to other reported scales.

[8] L. J. Friedman, A. K. M. Wennberg, S. N. Ytterboe, and H. M. Bozler, Rev. Sci. Instrum. **57**, 410 (1986).

[9] Studies of the orientation of the crystal planes in Grafoil show that we can expect approximately $\frac{2}{3}$ of the sample to follow a normal distribution of 15° from the nominal plane with the balance roughly isotropic. We do not observe a signal that is attributed to the isotropic part. See C. Bouldin and E. A. Stern, Phys. Rev. B **25**, 3462 (1982), and Ref. 5.

[10] Spin-wave stiffness effects on the lowest, quasiuniform mode are a reflection of the boundary anisotropy energies, and are small as estimated in the text.

[11] D. D. Osheroff, M. C. Cross, and D. J. Fisher, Phys. Rev. Lett. **44**, 792 (1980).

[12] H. Jichu and Y. Kuroda, Prog. Theor. Phys. **67**, 715 (1982), and Prog. Theor. Phys. **69**, 1358 (1983).

[13] J. M. Delrieu, M. Roger, and J. H. Hetherington, J. Low Temp. Phys. **40**, 71 (1980); M. Roger, Phys. Rev. B **30**, 6432 (1984).

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