Zero-Field Magnetic Order in the Boundary Layers of ^{3}He on Grafoil

L. J. Friedman, A. L. Thomson,[a] C. M. Gould, and H. M. Bozler
Department of Physics, University of Southern California, Los Angeles, California 90089-0484

P. B. Weichman and M. C. Cross
Department of Physics, California Institute of Technology, Pasadena, California 91125
(Received 28 November 1988)

The low-field NMR spectra of ^{3}He boundary layers on exfoliated graphite show collective modes for $T < 1$ mK. We measure the amplitude and frequency for these modes with the static H_0 field applied parallel to the graphite planes and varying continuously between 0 and 15 G. One of the modes extrapolates to a nonzero frequency and amplitude as the field is dropped to zero. We interpret these nonzero intercepts as an indication of zero-field magnetic order in the ^{3}He boundary layers.

PACS numbers: 67.70.+n, 67.50.Fi

The boundary layer of ^{3}He on graphite has shown properties of a two-dimensional ferromagnet. Experiments performed with ^{3}He bulk liquid[1,2] filling the pores of Grafoil and with a few monolayers[3,4] adsorbed on the surface have both resulted in low-temperature polarizations of the boundary layer which far exceed Curie values. Physical interchanges between the absorbed atoms are a strong possibility for the exchange interaction responsible for the ferromagnetic tendency.[5] This exchange interaction changes with the ^{3}He coverage, so that the inferred exchange energy has a maximum of 6.3 mK at 2.5 monolayers and decreases to less than 1 mK with bulk ^{3}He liquid filling the Grafoil pores. The film experiments[4] have shown that the magnetization of one layer (presumably the second) is well approximated by a two-dimensional Heisenberg model in the relatively large fields used there ($\sim$100 G). In this paper we use SQUID NMR in much lower fields in the simplest geometry (field parallel to the surface) to investigate deviations from the ideal Heisenberg model and the zero-field ordering.

The strict two-dimensional isotropic Heisenberg model has a phase transition only at $T=0$: No finite magnetization can exist for $T>0$ and zero applied field.[6] In the present experimental system, however, there exist long-range dipolar interactions between the ^{3}He nuclei. The dipole energy plays two distinct roles. First, it is anisotropic with the spins preferring to point in the plane of the substrate. The dipole energy therefore breaks the Heisenberg symmetry, reducing it to at most planar (i.e., XY). This effect was seen as a spin-flop transition in a prior experiment with H_0 perpendicular to the Grafoil planes.[2]

The second and more interesting effect of the dipole energy is to allow long-range order at sufficiently low temperatures. Yafet, Kwo, and Gyorgy[7] have shown that the first (low-temperature) spin-wave correction to an assumed ferromagnetically ordered state is finite in two dimensions when the long-range part of the dipole energy is taken into account. The dipole term alters the character of the long-wavelength spin-wave stiffness from $E \propto k^2$ to $E \propto k$. This eliminates the usual infrared divergence and allows a violation of the Mermin-Wagner result.[6]

In this work we report measurements that strongly suggest the presence of zero-field magnetic order in ^{3}He surface layers. When the applied field is below a few gauss, our NMR spectra display two lines in addition to the absorption at the Larmor frequency of the ^{3}He nucleus. We monitor the amplitude and frequency of these additional lines as the applied field is varied between 0 and 15 G. Extrapolation to zero applied field shows a nonzero intercept for one of the lines, indicating collective behavior in very low magnetic fields.

The 1-mK measured onset temperature is of the order of the exchange energy J. Since the dipolar coupling constant δ is of the order of 0.1 μK, and since the transition temperature must vanish with δ, this seems paradoxical at first sight. However, a quick estimate reveals otherwise: At low temperatures and zero field the pure Heisenberg correlation length ξ diverges exponentially in J/k_BT.[8] Dipolar forces become important when the energy $\delta\xi^2$ associated with a cluster of aligned spins of linear size ξ is roughly k_BT. Hence an estimate for T_c is given by the solution to $k_BT_c \sim \delta\xi^2$, which yields

$$k_BT_c \approx \frac{2c_1J}{\ln(c_2J/\delta)}, \tag{1}$$

to leading logarithmic order in J/δ (here c_1 and c_2 are constants of order unity). The transition temperature therefore vanishes very slowly with δ, and is determined primarily by J, consistent with our experiments.

Our Grafoil substrate has about 1 m^2 of surface area and an open volume of 0.05 cm^3 which is filled with liquid ^{3}He during the experiment. The Grafoil had been previously heated in H_2 at 1600 °C and was loaded into the experimental tower in an N_2 atmosphere. A dc SQUID is used as a preamplifier for the NMR detection. The experimental arrangement differs from prior work[2,9] in that the static H_0 field is applied parallel[10] (as opposed to perpendicular) to the Grafoil planes and we may alter this H_0 field even at the lowest temperatures

by using a 400-turn superconducting solenoid powered from a room-temperature current source. Noise from the leads is shorted out with a superconducting shunt.

In Fig. 1 we show a Fourier-transform spectrum that is typical of our low-temperature NMR signals. The three peaks that are evident in the data (squares) are highly reproducible. The lowest peak occurs at the Larmor frequency and may be seen in our data at all but the lowest temperature (0.38 mK) and fields. Above the Larmor-frequency line we see two additional broad peaks. These peaks are always shifted above the Larmor frequency and appear in our signals when the temperature is less than about 1 mK.

Our data are first captured as a free-induction signal in digital form and later fitted with a trial function. Since we consistently see three peaks in our low-temperature Fourier transforms, we use three lines in our fitting function. In Fig. 1 we show the total fit (solid line) to the spectrum in addition to the three separate component lines. For comparison, we also show a high-temperature liquid signal at the Larmor frequency.

The frequencies and amplitudes of the three components of the NMR response show different temperature dependences. The Larmor line itself remains fixed in frequency f_0 as the temperature is decreased. The center line shifts out from the Larmor frequency as the temperature is lowered. We therefore refer to the center line as the "shifted mode" and denote its frequency by f_s. Our fits show that the frequency difference $f_s - f_0$ is proportional to the shifted mode's amplitude. The peak at the far right in Fig. 1 first appears with a frequency that is already displaced above the Larmor frequency (about 1.1 kHz for the run shown in Fig. 1) and we refer to it as the "displaced mode" with frequency f_d. As the temperature is lowered f_d also gradually increases and we finally see it shifted by 2.5 kHz above f_0 in Fig. 1. when $T = 0.38$ mK.

In Fig. 2 we display the low-temperature ($T = 0.38$ mK) field dependence for the difference frequencies between f_s, f_d and $f_0 = \gamma H_0/2\pi$. All points indicate positive frequency shifts relative to f_0. In our prior work[2] with H_0 perpendicular to the Grafoil planes and $H_0 > 3$ G there was a mode observed with a 2.5-kHz negative shift relative to the Larmor frequency. From Fig. 2. we see that the shifted-mode frequency difference $f_s - f_0$ is linear in the applied field. The displaced-mode frequency difference $f_d - f_0$, in contrast, approaches a nonzero value as the applied field is decreased to zero. At higher fields we see a small decrease in $f_d - f_0$.

Our signals from the dc SQUID amplifier are proportional to the sample magnetization, independent of the applied field. Thus, in contrast to a resonant NMR scheme, we can directly compare the relative amplitudes at varying applied fields. In Fig. 3(a) we show the recorded amplitudes versus H_0 for liquid ^{3}He measured in our cell at 15 mK. As expected, the amplitude is linear in the applied field. We also show in Fig. 3(a) the amplitude versus H_0 for the total solid signal at $T = 0.38$ mK. In contrast to the case of the liquid signal, we see that the amplitude does not extrapolate to zero for zero applied field. At the highest fields we see a slight bending over of the curve that may be due to saturation effects. Additional field sweeps reveal zero-field offsets

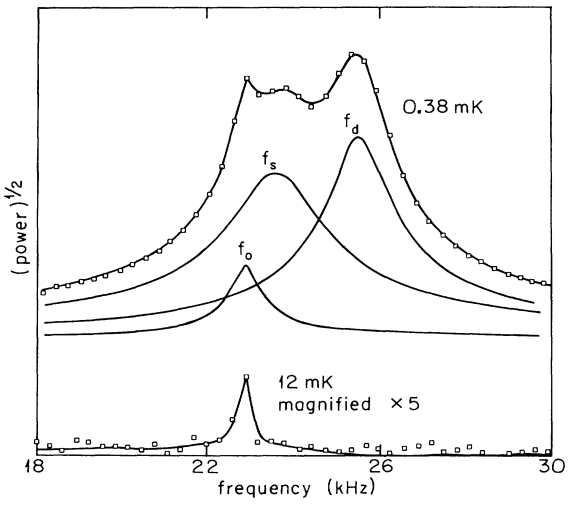

FIG. 1. The Fourier-transform power spectra of the data (open squares) and our fits (solid lines). We show a $H_0 = 7$ G line broken into its three components along with a magnified liquid line that was recorded at 12 mK.

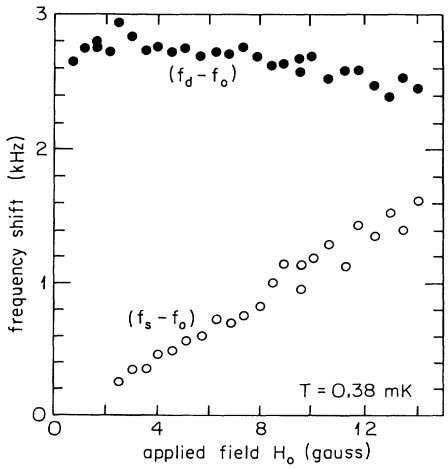

FIG. 2. Field dependence for the frequency shifts of the two modes relative to the Larmor frequency. The open circles record the shifted-mode frequency difference $f_s - f_0$ which is linear in the applied field. The closed circles record the displaced-mode frequency difference $f_d - f_0$ that shows an almost constant displacement of 2.7 kHz above the Larmor frequency.

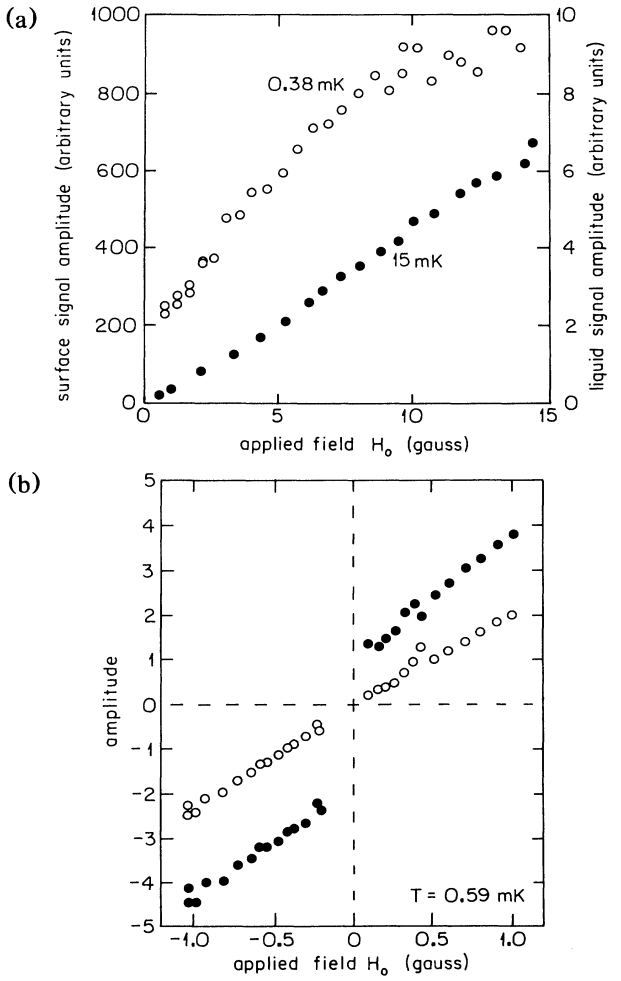

FIG. 3. (a) Total amplitude of the NMR signal at 0.38 and 15 mK (same arbitrary units for each). The high-temperature liquid-signal amplitude extrapolates to zero amplitude for zero field while the surface signal displays an offset. (b) With T =0.59 mK we show the amplitude-vs-field dependence for the two modes contributing to the surface signal. The shifted mode (open circles) extrapolates to zero amplitude for zero field while the displaced mode (closed circles) shows an offset as the field passes through zero.

that grow as the temperature is further reduced. However, no offset may be resolved in a field sweep taken at 0.85 mK.

Our fits to the data reveal that the finite amplitude offset present at zero applied field arises from the contribution of the displaced mode to the total amplitude. This is illustrated in Fig. 3(b). The displaced-mode amplitude extrapolates to a nonzero value at zero field while the shifted-mode amplitude passes directly through zero for zero applied field. The field for the Fig. 3(b) data was swept from negative to positive values. The slight asymmetry in the zero-field displaced-mode offsets may be due to some hysteresis in the system.

The frequency shifts can be used to estimate polarization. For a two-dimensional array of spins (with H_0 parallel to the plane) we expect an NMR line at[2]

$$\omega^2=\gamma^2(H_0^2+\lambda M H_0)\,, \tag{2}$$

with λM giving the dipole demagnetizing field. For full polarization of a triangular lattice of spacing 3.78 Å (second layer of ^{3}He on graphite) the computed λ implies a shift of 4.77 kHz. Our kHz shifts imply polarizations on the order of 30% or greater. We may also estimate the polarization by comparing the amplitude of the low-temperature signal ($T<1$ mK) with the liquid amplitude from high temperature ($T\sim 15$ mK), or by directly expressing the SQUID output voltage in terms of input flux. We have verified that the second method correctly predicts the size of the liquid signal at high temperatures. In contrast to the frequency-shift data, both of these methods imply surface ^{3}He polarizations around 0.4%.

The measurements at a few monolayers[4] in higher fields were consistent with nearly full polarization of the entire surface area. In our low fields, however, surface quality may play an important role for both the observed frequency shifts and polarization. Free-electron spins (dangling surface bonds) occurring at roughly the same density as ^{3}He structural domains[11] ($\sim$100-Å spacing) would also produce an internal field sufficient to account for the 3-kHz shift of the displaced mode. The large field near such an electron spin, of order 1 kG, is much less than the effective field between ^{3}He spins due to the exchange coupling. A single domain should then precess as a single rigid moment, with the electron field averaged over the whole domain determining the shift. Thermal effects and random placement of electron spins should lead to a broadened spectrum of zero-field frequency shifts. Such effects may be responsible for the small recorded amplitudes.

The frequency shift and amplitude behavior of the shifted mode is also qualitatively consistent with Eq. (2). Putting an $M=\chi H_0$ dependence [from Fig. 3(b)] into Eq. (2) we obtain $f_s=\gamma H_0(1+\lambda\chi)^{1/2}$ which is consistent with the shifted-mode frequencies of Fig. 2 with $(1+\lambda\chi)^{1/2}=1.035$. The shifted and displaced modes may arise from two separate regions on the surface. One region would be characterized by an enhanced linear susceptibility, $M\propto H_0$, and the other by an actual ordering that leads to the offsets seen for the displaced mode.

The main theoretical task is a quantitative theory of the 2D ordering. The work of Ref. 7 demonstrates that an ordered state exists at sufficiently low temperatures. If one varies the power-law rate r^{-p} with which the dipole potential decays at large distances, a Kosterlitz-Thouless phase can intervene between the ordered and paramagnetic phases for $4>p>3\frac{3}{4}$.[12] However, in the physical case ($p=3$) one finds that the entire Kosterlitz-Thouless phase is unstable to the addition of a small dipole interaction, and therefore the transition occurs

directly from the paramagnetic to the ferromagnetic phase. For $p > 4$ the force is effectively short ranged, and the Kosterlitz-Thouless phase survives right to $T=0$, consistent with the Mermin-Wagner theorem.[6]

Although dipolar ferromagnets have been treated in higher dimensions within the ϵ expansion about four dimensions, they have not been considered in the geometries necessary to describe the present experiments. The present hope is that some kind of expansion in the decay rate of the dipole force (perhaps about $p=3\frac{3}{4}$), analogous to similar expansions near four dimensions, will yield information about the critical exponents.[13]

In summary, our observations on the field dependence for the frequency and amplitude of the displaced mode point to a collective behavior in fields less than 1 G, consistent with correlated domains of at least 10^4 Å^2. A more uniform substrate such as *ZYX* may be needed to achieve a cleaner realization of the dipole-driven ferromagnetic ordering transition. These experiments have approached the limit of useful low temperatures and magnetic fields for ^{3}He ordering on Grafoil because the size of a magnetic coherence area is approaching the size of the structural coherence allowed by the substrate.

This work has been supported by the National Science Foundation through Grants No. DMR88-00291 (L.J.F. and H.M.B.), No. DMR85-19970 (C.M.G.), No. DMR87-15474 (P.B.W. and M.C.C.), the Weingart Foundation through The California Institute of Technology (P.B.W.), and the Science and Engineering Research Council (U.K.) (A.L.T.).

---

[a]Permanent address: Department of Physics, University of Sussex, Falmer, Brighton BN1 9QH, England.

[1]H. M. Bozler, T. Bartolac, K. Luey, and A. L. Thomson, Phys. Rev. Lett. **41**, 490 (1978); H. Godfrin, G. Frossati, D. Thoulouze, M. Chapellier, and W. G. Clark, J. Phys. (Paris), Colloq. **39**, C-287 (1978); H. M. Bozler, D. M. Bates, and A. L. Thomson, Phys. Rev. B **27**, 6992 (1983).

[2]L. J. Friedman, S. N. Ytterboe, H. M. Bozler, A. L. Thomson, and M. C. Cross, Phys. Rev. Lett. **57**, 2943 (1987); Can. J. Phys. **65**, 1351 (1987); H. M. Bozler, Jpn. J. Appl. Phys. Suppl. **26-3**, 1849 (1987). See references therein for work on substrates other than Grafoil.

[3]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); H. Godfrin, Can. J. Phys. **65**, 1430 (1987).

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

[5]J. M. Delrieu, M. Roger, and J. H. Hetherington, J. Low Temp. Phys. **40**, 71 (1980); M. Roger, Phys. Rev. B **30**, 6432 (1984); M. Roger and J. M. Delrieu, Jpn. J. Appl. Phys. Suppl. **26-3**, 267 (1987); H. Jichu and Y. Kuroda, Prog. Theor. Phys. **67**, 715 (1982); Prog. Theor. Phys. **69**, 1358 (1983).

[6]N. D. Mermin and H.Wagner, Phys. Rev. Lett. **17**, 1133 (1966).

[7]Y. Yafet, J. Kwo, and E. M. Gyorgy, Phys. Rev. B **33**, 6519 (1986).

[8]P. Kopietz, P. Scharf, M. S. Skaf, and S. Chakravarty, State University of New York at Stony Brook report, 1988 (to be published).

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

[10]The effect that the spread in Grafoil plane angles might have on observed NMR signals is discussed in Ref. 2.

[11]H. J. Lauter, H. P. Schildberg, H. Godfrin, H. Wiechert, and R. Haensel, Can. J. Phys. **65**, 1435 (1987); J. K. Kjems, L. Passell, H. Taub, J. G. Dash, and A. D. Novaco, Phys. Rev. B **13**, 1446 (1976); C. Bouldin and E. A. Stern, Phys. Rev. B **25**, 3462 (1982).

[12]P. B. Weichman (to be published).

[13]The possibility of this approach was suggested by D. S. Fisher (private communication).