Two-Dimensional Ferromagnetism of a ^{3}He Film: Influence of Weak Frustration

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^{3}He films adsorbed on the atomically flat surface of graphite provide a model system for the study of two-dimensional magnetism on a triangular lattice. We have made a study of the regime in which the $T = 0$ ground state of the second ^{3}He layer is a fully polarized ferromagnet. NMR, using broadband SQUID detection, at a range of low fields above the spin-flop transition, and over a wide temperature range 0.3–200 mK, has enabled us to disentangle the influence of sample finite size effects and magnetic field on the spin-wave spectrum. We demonstrate that the spin-wave spectrum is governed by a different effective exchange constant than that determining the high temperature magnetism. This is understood in terms of frustrated atomic ring exchange.

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The influence of low dimensionality on magnetism, studied using quasi-two-dimensional insulating materials [1] and ultrathin metallic films [2] continues to be a subject of both fundamental and technological interest. See [3] for a recent compendium of systems. The Mermin-Wagner theorem [4] states that no long-range order occurs at nonzero temperature for a two-dimensional magnet with isotropic short-range interactions. However in layered materials a variety of effects inevitably intervene to give rise to long-range magnetic order at finite temperature, such as weak interlayer exchange coupling, anisotropy of the exchange interaction, and anisotropy arising from the dipolar interaction. Layered cuprates provide excellent examples of the $S = 1/2$ two-dimensional quantum Heisenberg antiferromagnet on a square lattice [5,6]. Corresponding two-dimensional ferromagnetic materials with Heisenberg exchange are lacking, with the notable exception of ^{3}He films adsorbed on graphite, which provide an ideal model magnetic system [7].

Exfoliated graphite provides an atomically flat surface on which the ^{3}He is physisorbed, growing as atomic layers. The active magnetic system is the second solid layer, consisting of ^{3}He atoms with nuclear spin $1/2$ on a triangular lattice. This sits atop a paramagnetic first layer, of density 11.1 nm^{-2}, and may be covered by a liquid film of one or more layers. The second layer is a quantum solid with large zero point motion; the interchange of atoms between sites leads to an isotropic magnetic exchange interaction between nuclear spins. The competing interactions are extremely weak; in particular, the spin-orbit coupling arising from the nuclear dipole-dipole interaction is 3 orders of magnitude smaller than the exchange interaction. Furthermore exchange between the first and second layer is also weak, of order the dipole energy. The second-layer exchange parameters are directly measurable and can be calculated from first principles by path integral Monte Carlo methods.

The pioneering experiments of Franco *et al.* [8] demonstrated that ^{3}He films on graphite could be cooled to low mK temperatures, and revealed the existence of a "ferromagnetic anomaly," a peak in the Curie-Weiss temperature at a coverage (total number density of atoms) of around 24 nm^{-2}. This led to the proposal of a model two-dimensional Heisenberg nuclear ferromagnet with the absence of a finite temperature phase transition [9], consistent with the Mermin-Wagner theorem, and was followed by extensive measurements of the heat capacity as a function of coverage [10]. In a seminal paper [11] Roger pointed out the central importance of magnetic frustration in this system, arising from competing atomic ring exchange with Hamiltonian $H = \sum_n (-1)^n J_n P_n$, where P_n is the operator for the cyclic exchange of n particles. Magnetic frustration arises from competition between odd and even permutations, giving rise to ferromagnetic and antiferromagnetic exchange coupling, respectively, as well as geometric frustration from the triangular lattice. The frustration is tuned by varying the total coverage; in this way the system can be tuned from a quantum spin liquid [12–16] to a ferromagnetic ground state. Above the ferromagnetic anomaly, compression of the second layer by fluid overlayers leads to suppression of exchange.

Strikingly frustration by competing ring exchange leads to different effective exchange constants governing the leading order high temperature dependence of thermodynamic properties [11,17]. For example the high temperature magnetization has Curie-Weiss constant $\theta = -3J_\chi$, while the leading order term in the heat capacity may be written as $C = (9Nk_B/4)(J_c^2/T^2)$. Here J_c and J_χ are different combinations of the J_n. Simultaneous measurements of the heat capacity and magnetization [18] demonstrated that $J_c \neq J_\chi$.

A detailed analysis of available data using multiple spin exchange high temperature series expansions [19] yielded some insight into the coverage dependence of the exchange parameters J_n.

In this Letter we concentrate on the regime for which the magnetic ground state is believed to be a 2D ferromagnet. A central result is the demonstration of the strong influence of weak frustration on the spin-wave dispersion. We are able to self-consistently explain how the magnetization approaches full polarization in different magnetic fields (which determine the spin-wave gap), empirically taking into account finite size effects. This is in contrast to previous work, which made the assumption that spin-wave dispersion is governed by the same effective exchange constant that determines the high temperature magnetization. It is remarkable that in this weakly frustrated ferromagnetic system the high temperature $T > J$ and low temperature $T < J$ magnetization are governed by distinct effective exchange constants. And by measurements of both we can gain direct and quantitative insight into the frustration, which remains significant at the ferromagnetic anomaly.

Our sample of exfoliated graphite had a surface area of 2 m^2. Pulsed NMR was performed on the ^{3}He adsorbate using dc SQUID detection. The receiver coil formed part of a superconducting flux transformer with the SQUID input inductance, and the SQUID was operated in flux-locked-loop mode with a bandwidth of 3 MHz. This broadband setup allowed NMR measurements in different magnetic fields; in these experiments we used 1.54 and 3.09 mT. Our spectrometer, crucially, had a recovery time following the transmitter pulse of <10 μs, permitting capture of the free-induction decay with minimal truncation, and consequent limited distortion of the inferred line shape. This was particularly important for the broad NMR signals observed from strongly polarized samples.

A sequence of NMR lines as a function of temperature is shown in Fig. 1, with the static magnetic field applied perpendicular to the exfoliated graphite sheets. At low temperatures a large frequency shift of the line occurs due to the strong spin polarization of the ^{3}He film and the resulting internal field due to the dipolar interactions. Line broadening arises from the distribution of relative orientation of graphite surface. The frequency shift is given by $\Delta\omega = \Omega(1\text{–}3\cos^2\theta)$, where Ω/γ is the dipolar field arising from the spin polarization of the sample. Here θ is the angle between the surface normal and the static field, along z, and γ is the gyromagnetic ratio. This expression holds in the limit that $\Omega \ll \gamma B_0$, and predicts a spectrum extending (neglecting spin-spin relaxation) over the range $-2\Omega < \Delta\omega < \Omega$ as observed. The clear maximum at -2Ω arises from graphite surfaces oriented perpendicular to the static field.

In this Letter we present measurements in fields such that the spins are oriented along the magnetic field. We note that in sufficiently low magnetic fields the magnetization vector is in general misoriented relative to the magnetic field due to the dipolar field; when $\gamma B_0 \ll \Omega$ the dipolar interaction forces the spins to lie in the plane [20]. For $\theta = 0$ the onset of this tilting occurs when $B_0 < 2\Omega/\gamma$. This can be thought of as an incipient "spin-flop" transition. We avoid this regime by operating in static magnetic fields significantly larger than $2\Omega/\gamma$.

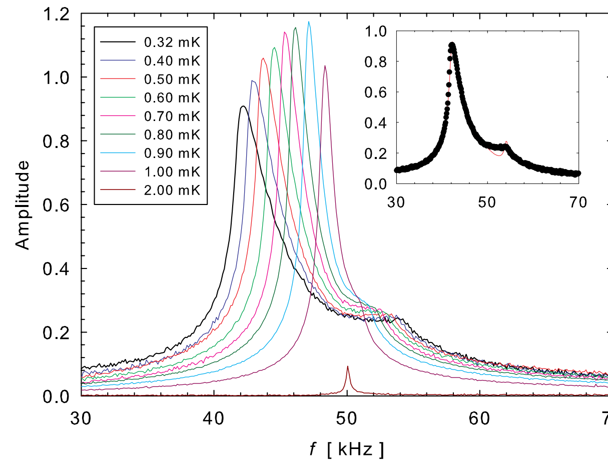

FIG. 1 (color online). NMR line shape for a thin film of ^{3}He physisorbed on the surface of graphite for temperatures in the range 0.32–2 mK. Data shown are in a static magnetic field of 1.54 mT, at coverage 24.66 nm^{-2}. Inset: fit to mosaic spread of platelet orientations for data taken at 0.32 mK (see text).

Ω provides a precise measurement of the magnetization of the ferromagnetic sample, insensitive to a variety of potential instrumental effects or any potential non-FM regions of the layer that may be induced by weak substrate heterogeneity. The dipolar field can be written as the sum of an isotropic part and an anisotropic part $(\mu_0/4\pi)(\Sigma/2d^3)[\mathbf{m} - 3m_z\hat{\mathbf{z}}]$, where $\mathbf{m}$ is the ^{3}He nuclear moment, d the lattice parameter, and $\Sigma = 11.034$ is the triangular lattice sum. In NMR only the anisotropic part contributes to the resonance frequency. This leads to $\Omega = \gamma K \mu_0 M/2$, with $K = 1.061$, where the magnetization $\mathbf{M} = 1.2408\mathbf{m}/d^3$ [21].

Analysis of the full line shape, at both measuring fields, provides a characterization of distribution of platelet orientations. We write the probability distribution as $P(\theta) \propto a + \exp[(-1 + \cos\theta)/\sigma^2]$; this comprises a von Mises distribution, with a mosaic spread of σ and a fraction of randomly oriented platelets a. We find $\sigma = 19 \pm 1°$ and $a = 0.025 \pm 0.005$. The analysis of the temperature-dependent line shape also confirms that the negatively shifted peak can be used as a precise measure of the intrinsic dipole field. Hence the ratio of sample magnetization to the saturation magnetization discussed below is determined from the frequency of the negatively shifted peak relative to its $T = 0$ value.

At low temperatures the magnetization is controlled by the thermal excitation of spin waves [22,23].

$$\frac{M}{M_0} = 1 - \frac{\alpha T^*}{J_s} + \frac{\alpha T}{J_s} \ln\left[\exp\left(\frac{T^*}{T}\right) - 1\right] - \frac{2}{N}\left[\exp\left(\frac{T_B}{T}\right) - 1\right]^{-1}.$$

The effective gap in the spin-wave dispersion arises from a finite size cutoff to the spectrum and the Zeeman energy, $T^* = T_0 + T_B$, where $T_B = (hf/k_B) = 4.8 \times 10^{-5} f$ mK/kHz and $T_0 = 8\pi^2 J_s/N$, where N is the number of spins on a platelet and $\alpha = 1/2\pi\sqrt{3}$. Here the final term is the $k = 0$ spin-wave term introduced in [23], which corresponds to the uniform precession of N spins on an assumed isolated platelet. We have confirmed that, at finite size this analytic form agrees well with numerical evaluation of the lattice sums. These spin waves can be safely treated as noninteracting [24]. Since in the weak static magnetic fields used in this experiment, $T_B \ll T$, while $T \gg T^*$ and $T^* \ll J_s$, we can simplify to

$$\frac{M}{M_0} = 1 - \frac{\alpha T}{J_s} \ln\frac{T}{T_B + 8\pi^2 J_s/N} - \frac{T}{T_B}\frac{2}{N}.$$

Thus the effective exchange interaction J_s and sample size N are the relevant system parameters, with J_s depending on coverage, while T_B is under direct experimental control. Measurements in a low magnetic field are particularly useful, since this increases the importance of the final term, which depends directly on N. Figure 2 shows, at a coverage slightly above the ferromagnetic anomaly $24.66\ \mathrm{nm}^{-2}$, that in fact the field dependence is rather weak. If we fit the low temperature data at 1.54 and 3.09 mT, constraining $J_s = J_\chi$, as done by previous work, then for $J_s = 1.82$ mK we find $N = 680$ and $N = 1290$, respectively. This inconsistency is resolved, by taking J_s as a free parameter. As a consequence the effective sample size N we infer is significantly larger.

A straightforward analysis shows that this form has only a weak dependence on N for $N > 10J_s/T_B$. The data allow us to set a lower bound of $N \sim 5000$. We find that we can consistently fit the 1.54 and 3.09 mT data with $J_s = 0.70 \pm 0.03$ mK, where the quoted error is obtained by comparing fits with $N = 5000$ and $N \to \infty$. This result implies a platelet size of >25 nm; an upper bound on platelet size of 60 nm is set by our x-ray diffraction measurements of the crystallite size.

Fitting the high temperature magnetization at $24.66\ \mathrm{nm}^{-2}$ over the temperature range $5 < T < 200$ mK, to the sum of a Curie law term (first layer), ferromagnetic high temperature series expansion for the second layer [25], and a fluid term (modeling fluid overlayers), at both magnetic fields, we infer $J_\chi = 1.82 \pm 0.07$ mK, in good agreement with previous work [7,9].

The experimental finding that $|J_s| < |J_\chi|$ is a clear signature of the predicted influence of frustration by multiple spin exchange interactions, overlooked in previous experimental work. The exchange coefficient governing spin-wave dispersion is $J_s = J_2 - 2J_3 + 4J_4 - 10J_5 + 2J_6$ [26], while the effective interaction governing the Curie-Weiss constant is $J_\chi = J_2 - 2J_3 + 3J_4 - 5J_5 + 5/8J_6$ [17].

The essence of the result is simply understood in a "minimal model": the J, J_4 model [26]. Here the effective Heisenberg exchange $J = J_2 - 2J_3$ [where $J < 0$ (FM) due to the dominance of three spin ring exchange] is frustrated by four spin exchange J_4. Then $J_\chi = J + 3J_4$ and $J_s = J + 4J_4$, giving rise to significant differences in J_χ and J_s for modest and realistic values of $J_4/J \sim -0.2 \to -0.1$. Clearly, in this model, $J_s - J_\chi$ directly determines the four spin exchange.

We have explored the coverage dependence of this effect above the ferromagnetic anomaly, in order to understand the evolution of frustration with coverage.

From extrapolation of the frequency shift data (Fig. 3), using the spin-wave formula, we have determined the zero temperature dipolar frequency shift. Under the assumption that this shift corresponds to a fully polarized sample on a triangular lattice, with the lattice sum discussed earlier, we infer the density of the second layer. The results, shown in Fig. 4, are in good agreement with both theoretical

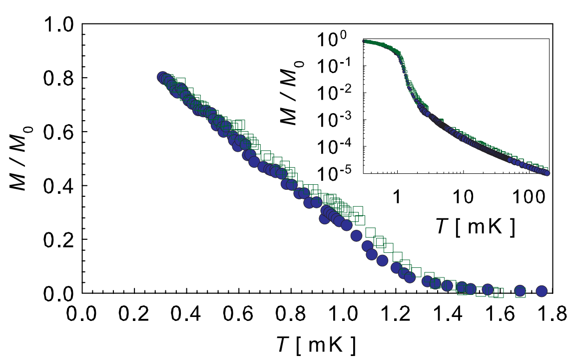

FIG. 2 (color online). Magnetization of ^{3}He film relative to its saturation value, as determined from the NMR line shift Δf, as a function of temperature. Measurements in 1.54 mT (closed blue circles) and 3.09 mT (open green squares) show a very weak dependence on magnetic field. Insert: Relative magnetization over full measured temperature range.

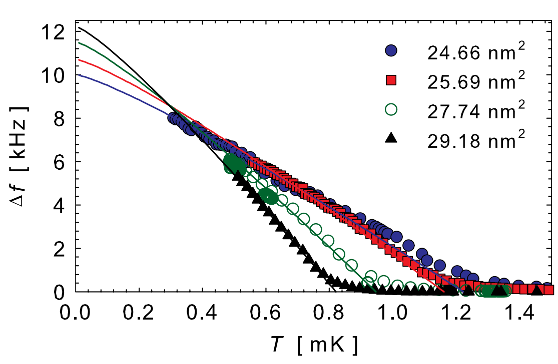

FIG. 3 (color online). Frequency shift at a range of coverages above the ferromagnetic anomaly. Lines show theoretical fit, from spin-wave theory, extrapolated to $T = 0$.

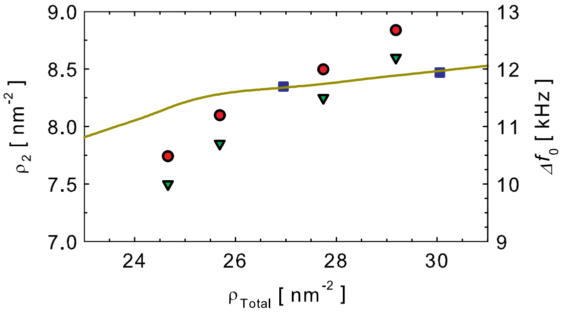

FIG. 4 (color online). Comparison of second layer density (red circles) inferred in present experiment from $T = 0$ dipolar frequency shift (green triangles), with neutron scattering data (blue squares) [28] and theoretical model (solid line) [27].

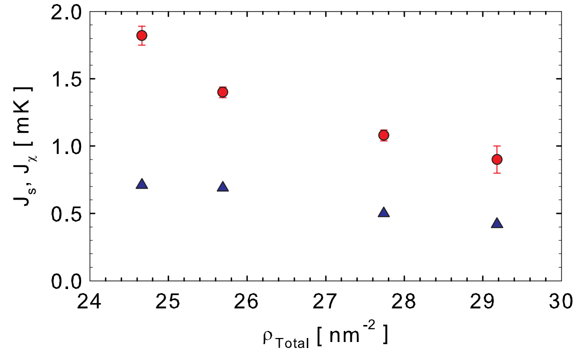

FIG. 5 (color online). Comparison of J_χ (red circles) and J_s (blue triangles) experimentally determined in this work. The difference arises from atomic ring exchanges that frustrate the dominant ferromagnetic Heisenberg exchange interaction.

estimates [27] and a direct neutron scattering determination at two coverages [28]. This confirms that, for these coverages and measured frustration, the magnetic ground state is a fully polarized ferromagnet at $T = 0$, in agreement with theory [12].

The coverage dependence of the exchange coefficients J_χ and J_s is shown in Fig. 5. In order to analyze the coverage dependence of the frustration we adopt the same parametrization as [19] $J_6 = \nu J_4$, $J_5 = \eta J_4$. This previous work found that $\nu \approx 0.5$ and $0.2 \leq \eta \leq 0.4$. The observation that $|J_s| < |J_\chi|$ imposes the constraint that $\eta < 0.3$. We conclude that frustration above the ferromagnetic anomaly is significant, and only weakly coverage dependent in the range studied with $J_4/|J| \sim 0.1$–0.2.

Previous measurements of the magnetization of the second layer at 0.03–0.48 mT have been interpreted as a finite temperature phase transition [29]. We note that these magnetic fields are comparable to or smaller than the spin-flop field. The influence of the dipolar interaction on the spin-wave dispersion at long wavelengths was first considered in [30] and more recently in [31]. The present experiment was performed in magnetic fields $B_0 \gg \Omega/\gamma$, where we expect the influence of the dipolar interaction to be a small perturbation compared to the Zeeman gap, and finite size effects. Our work cannot rule out the occurrence of a finite temperature phase transition in this system at $\gamma B_0 < \Omega$, particularly, given the interesting NMR spectra observed in surface boundary layers [20]. In the limit $\gamma B_0 \ll \Omega$, the dipolar interaction forces the spins into the plane, and thus into the XY symmetry class, leading to a distinct ground state [32].

In conclusion we have unambiguously demonstrated the necessity of including the effects of frustrated multiple spin exchange to understand the spin-wave dispersion of ferromagnetic ^{3}He films. Over a range of coverages immediately on the high density side of the "ferromagnetic anomaly" weak frustration leads to a difference in the effective exchange constants determining the Curie-Weiss temperature and the spin-wave velocity. Measurements in low magnetic fields but with $\Omega \ll \gamma B_0$ have allowed a robust analysis; there is no evidence for a finite temperature phase transition. More detailed calculations of the spin-wave dispersion to explicitly include ring exchange, spin-wave interactions [24], and also the influence of the dipole interaction to all orders of $\Omega/\gamma B_0$ are desirable. At lower coverages we expect a quantum critical point at which, in the minimal model, $J_s = J + 4J_4 = 0$ and the spin-wave velocity vanishes, while necessarily $J_\chi = J + 3J_4 < 0$ and so the high temperature behavior looks ferromagnetic. We hypothesize that this accounts for the concurrence of "antiferromagneticlike" heat capacity and "ferromagneticlike" magnetization [18] signifying a novel ground state at intermediate coverages between the quantum spin liquid and a ferromagnetic ground state [33]. Further experimental and theoretical work is encouraged since ^{3}He films arguably provide the best system for the study of frustrated two-dimensional magnetism currently available.

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