Frustration by Multiple Spin Exchange in 2D Solid ^{3}He Films

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Measurements of the magnetization and heat capacity of the second layer of ^{3}He films adsorbed on graphite indicate that the evolution of the exchange from antiferromagnetic to ferromagnetic arises from a tuning of the competing exchange processes. At certain coverages the coexistence of an antiferromagnetic heat capacity with a ferromagnetic magnetization is a clear manifestation, predicted by theory, of frustration. At the ferromagnetic anomaly the system is well described by series expansions for a 2D Heisenberg ferromagnet on a triangular lattice. [S0031-9007(97)02842-1]

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The idea of multiple spin exchange (MSE) has proved to be of central importance in the understanding of the properties of solid ^{3}He [1,2]. In this quantum solid the large zero point motion leads to the interchange of atoms between crystalline sites. Because of the effects of "steric hindrance" arising from the strong short range repulsive potential between atoms in the bcc or hcp lattice, the cyclic permutation of three atoms is favored over the simple interchange of two particles. ^{3}He is a spin-$\frac{1}{2}$ fermion and hence these processes lead to an effective nuclear spin interaction which for two and three particle exchange is of the Heisenberg form. In general the Hamiltonian is $\mathcal{H} = \sum_n (-1)^n J_n \mathcal{P}_n$, where $\mathcal{P}_n$ is the operator for a cyclic permutation of n particles. Exchange of an even number of particles is antiferromagnetic (AFM), while that of an odd number is ferromagnetic (FM), so the competition leads to a system which is intrinsically frustrated. The exchange constants are typically of order mK, much larger than in other nuclear spin systems. An important consequence of the relative simplicity of this system is that the exchange can be calculated from first principles by path integral Monte Carlo techniques [3].

Solid ^{3}He films provide a model two-dimensional magnetic system exhibiting a number of striking properties [4] which are generally less well understood than its bulk counterpart. In this case ^{3}He films are physisorbed on the atomically flat surface of graphite. Here we concentrate on coverages up to three layers. The present understanding is that the first two layers solidify, the third forming a fluid overlayer. The magnetically active layer is the second solid layer since the completed first layer is essentially paramagnetic [5,6] and exchange between the first and second layer is a weak effect. Novel features of the evolution of the magnetism of these films with coverage are an anomalous peak in the (FM) exchange constant [7], while at lower coverages exchange is AFM [8–10].

In this Letter we report new heat capacity and magnetization measurements which show that the crossover from AFM to FM exchange can be understood as a result of a variation with coverage of the delicate balance of cyclic exchanges (frustration due to MSE) on the geometrically frustrated triangular lattice, as suggested by Roger [11]. An important feature of this work is that both measurements are performed on the same cell, removing any possible ambiguities arising from differences in coverage scale. In this paper we assume that promotion to the second layer occurs at 0.109 Å^{-2}, to facilitate comparison with previous results [12]. The present heat capacity results improve on previous work [12] in a number of ways. They extend to significantly lower temperatures, typically 0.7 mK, and benefit from a negligible addendum through the use of a small lanthanum-diluted cerium magnesium nitrate (LCMN) thermometer, which provides a continuous readout of temperature. The thermal relaxation time between the cell and this thermometer was less than 30 seconds. The cell was isolated from the nuclear stage by a zinc superconducting heat switch. The residual heat leak to the sample chamber was typically 400 pW, the consequent drift in sample temperature allowed heat capacity data to be taken above 0.7 mK with typical temperature steps of 5%. Further information is given elsewhere [13].

It is important to realize that measurements of the heat capacity as well as those of the magnetization can be used to determine the character of the exchange. To leading order the magnetic susceptibility is given by $\chi = C/(T - \theta)$ where $\theta = 3J_\chi$ while the heat capacity is $c = (9/4)Nk_B(J_c^2/T^2)$. For a Heisenberg nearest neighbor magnet $J_c = J_\chi = J$. In this case, clearly θ determines the sign of J. However, the heat capacity measured down to $T \sim J$ also shows distinctive behavior depending on the sign of J, due to the higher order terms in the high temperature series expansion (HTSE). Results for the HTSE for a $S = \frac{1}{2}$ Heisenberg nearest neighbor on a triangular lattice [14] are shown in Fig. 3 (inset). In the case of MSE, $J_c = J_\chi$ if only two and three spin exchange are included, with effective exchange constant $J = -(J_2 - 2J_3)$. In general the difference between J_c and J_χ is a measure of effects of frustration due to higher order cyclic exchange processes [15].

It is established that at the FM anomaly, corresponding to a coverage 0.24 Å^{-2}, the magnetization is well described by the HTSE for a triangular lattice [16], with an exchange constant $J_\chi \approx 2$ mK [6,10,16,17]. The present heat capacity data show a broad heat capacity maximum, attributable to short range order in the 2D FM, that is in marked contrast to the sharp "peak" observed in previous work [12] at 2.5 mK [18]. The suggested interpretation of this peak was a finite temperature phase transition, unexpected in an ideal isotropic model 2D Heisenberg ferromagnet. However, we find, for the first time and consistent with the magnetization results, that the heat capacity is also well described by the HTSE extended by the method of Padé approximants. The inferred exchange constant J_c agrees well with J_χ. Thus frustration due to four and higher order cyclic ring exchanges is small. The system is essentially Heisenberg with effective exchange constant $J = -(J_2 - 2J_3)$, which is positive (FM) due to three spin exchange.

In more detail, Fig. 1 shows a fit of the heat capacity to $c = n_2 k_B P A(J/T) + \beta + \gamma T$. The first term is the spin exchange contribution, calculated using the Padé approximants to the HTSE [14]. The second term, also found when the second layer is fluid, is probably attributable to effects of residual heterogeneity of the exfoliated substrate [19]. The final term arises from the heat capacity of the fluid overlayer. Data down to 3 mK are fit by $J_c = 1.83$ mK. It is also possible to fit the experimental data to $T/J \sim 0.5$ using a $\{5, 8\}$ Padé; we then find $J_c = 1.90$ mK [20]. These exchange constants are in excellent agreement with those inferred from magnetization measurements [6,16,17]. The number of second layer spins n_2, inferred from the fit is a factor of order 0.8 smaller than expected from the best estimates of the second layer density [10,12]. This may be attributable to the morphology of the exfoliated substrate, and is possibly due to spins at the edges of the two dimensional ^{3}He crystallites [6] (typical dimension $\sim$100 Å). Measurements of the saturation magnetization at the FM anomaly also find a value smaller than expected by a factor of approximately 0.8 [6,16].

Prior to the formation of a fluid overlayer, the system is AFM. In this case the maximum heat capacity per spin is a factor of 2 smaller than at the FM anomaly and the temperature dependence is well described by the HTSE for an AFM on a triangular lattice (HAFT) [13]. The values of J_χ from magnetization measurements are negative, but a factor of order four smaller than the effective exchange constant inferred from the heat capacity by fitting to the HTSE, which we identify with J_c [21]. This is clear evidence for frustration due to four spin and higher order ring exchanges, which drive the system AFM at these coverages.

On increasing the coverage above third layer promotion (found to occur at 0.187 Å^{-2}) we find a further striking manifestation of the frustration in this system. In the high temperature regime $T > J$, one measured property (the heat capacity) continues to show the characteristics of AFM exchange, while another (the magnetization) is clearly FM. Thus at a coverage of 0.196 Å^{-2} (Fig. 2) we find that the nuclear magnetic susceptibility is FM with $J_\chi = 1.0$ mK, while the temperature dependence of heat capacity remains well described by the HTSE for a HAFT. The fit to the heat capacity gives $J_c = -1.9$ mK. This AFM-like heat capacity in a regime where the magnetization is FM persists up to a coverage 0.21 Å^{-2}. Thus while the sign of J_χ changes at 0.189 Å^{-2}, shortly after promotion, the scaled heat capacity approximately collapses onto on a single curve (the HTSE for an HAFT) for a wide coverage range from 0.178 to 0.21 Å^{-2}; see Fig. 3 [22]. Here $c_s/n_2 k_B$ is plotted against T/J, where c_s is the spin heat

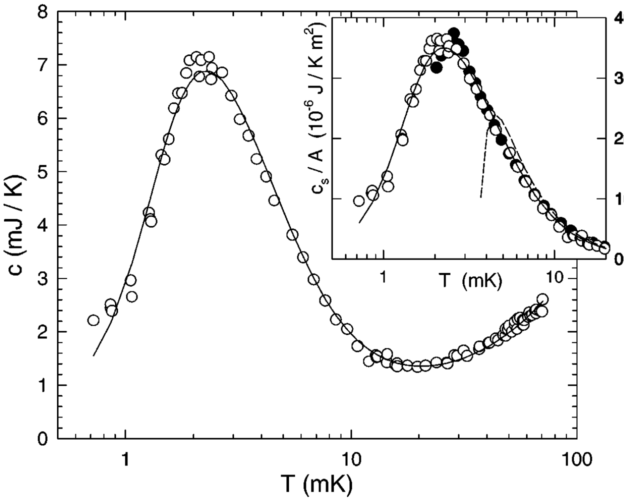

FIG. 1. Total heat capacity at 0.24 Å^{-2}. For details of fit, see text. Inset: Comparison of present spin heat capacity results (○) with data (●) and HTSE fit (dashed line) from [12]. Data scaled by sample surface area (*A*). Solid line is present HTSE ($\{5, 8\}$ Padé; $J_c = 1.9$ mK).

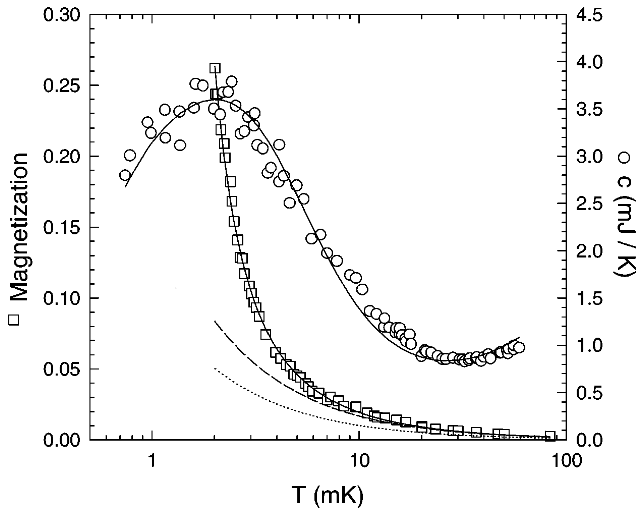

FIG. 2. Magnetization and total heat capacity at 0.196 Å^{-2}. Full lines are fits to data using HTSE. Also shown for comparison; first layer contribution to magnetization and that of two paramagnetic layers (dotted and dashed lines).

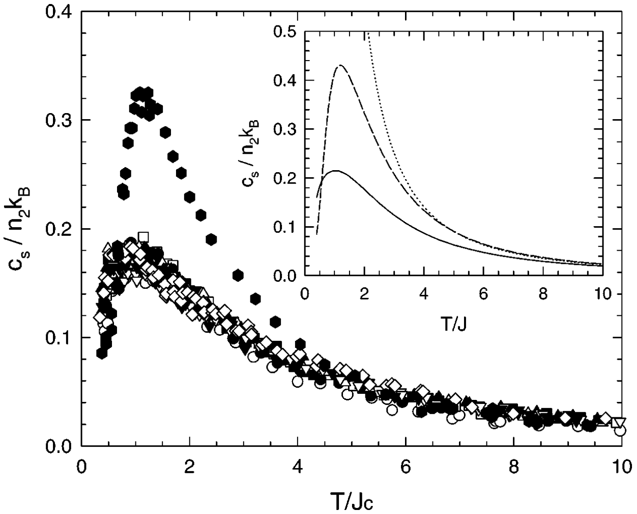

FIG. 3. Comparison of scaled spin heat capacity (AFM) for coverages in range (0.178−0.202 Å^{-2}) with that at FM anomaly (0.24 Å^{-2}). Inset contrasts predictions for AFM (full line) and FM (dashed line) systems (HTSE for nearest neighbor exchange on a triangular lattice). Dotted line shows leading order $1/T^2$ term.

capacity, J is determined from the present fit to the HTSE, and the values of n_2 are taken from Ref. [12].

The very different behavior of the heat capacity and magnetization is clearly seen in the isotherms plotted in Fig. 4. The break in the magnetization isotherm occurs close to third layer promotion and near where J_χ changes sign, while the heat capacity appears quite precisely constant over a much wider coverage range. This result is strong evidence against the various models of two phase coexistence that have been invoked to describe the transition from AFM to FM [6,12,23]. However, they are in agreement with predictions from numerical studies of 4 × 4 spin clusters [24], in which the exchange Hamiltonian is diagonalized for different values of the frustration. These find that the transition from AFM to FM behavior occurs at different values of the frustration for the heat capacity and magnetization [25]. In the ^{3}He film the model is that the frustration, by higher order cyclic exchange processes, of the effective Heisenberg exchange interaction $J = -(J_2 - 2J_3)$, is tuned by the ^{3}He coverage. Further exact diagonalization studies of larger clusters and the evaluation of HTSE in the MSE model are required to determine the evolution of the thermodynamic variables of the system with frustration. In particular, it is necessary to account in more detail for the temperature and coverage dependence of the heat capacity.

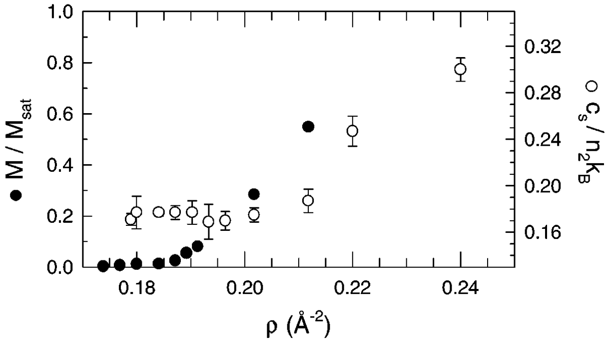

FIG. 4. Isotherm of spin heat capacity at $T/J_c = 1$ and magnetization at 0.8 mK.

Exchange constants inferred from HTSE fits both to the magnetization and heat capacity (Fig. 5) reveal a number of new features. The coverage dependence of J_c shows a clear break at the point (0.187 Å^{-2}) that the third (fluid) layer begins to form. This promotion is identified by the appearance of a linear term in the heat capacity. At the same coverage $|J_c|$ exhibits a minimum. This is clear evidence of the influence of the fluid layer on the balance of exchange processes, as proposed, either by introducing a new indirect (RKKY-like) exchange process or by providing a steric hindrance to "out of plane" motion in intralayer processes [11]. Here we simply regard the fluid overlayer as providing a mechanism for tuning the frustration [25]. The fits to the heat capacity data enable a determination of the coefficient of the linear contribution from the fluid with reasonable accuracy [26]. Except for the lowest fluid coverages ($n_3 < 0.008$ Å^{-2}), where surface heterogeneity may be important, the values of γ indicate a uniform fluid with m^*/m increasing to a value 1.8 at the coverage corresponding to the FM anomaly. For an ideal Fermi gas for this cell $\gamma = 16.3$ mJ/K^2; discounting data for $n_3 < 0.008$ Å^{-2}, the results extrapolate to near this value at $n_3 = 0$. By contrast 2D condensation [23] would give $\gamma \propto n_3$ over a gas-liquid coexistence region.

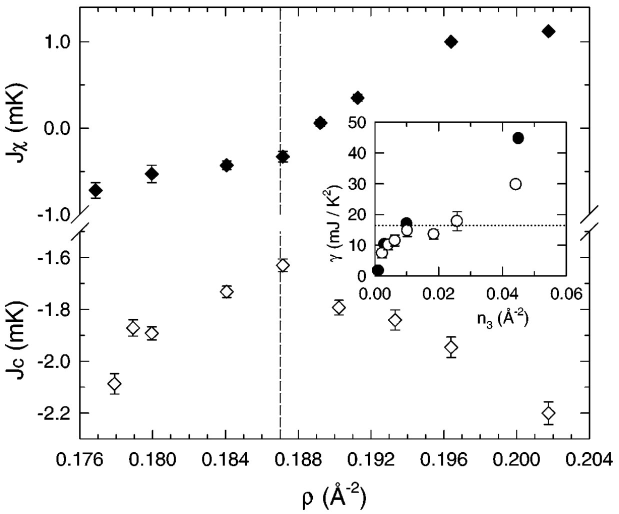

FIG. 5. Coverage dependence of effective exchange constants J_χ and J_c. Vertical dashed line indicates promotion to third layer. Inset: Linear term in heat capacity versus fluid coverage, (○) present data, (●) data from [12]. Dotted line shows Fermi gas result.

In conclusion, the experimental evidence suggests that this system is a unique example of frustrated spin exchange on a triangular lattice. The fluid overlayer is uniform and influences the competing multiple spin exchange interactions by a mechanism that has yet to be established. This provides a means to tune the frustration and hence the magnetic ground state.

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[1] M. Roger, J.H. Hetherington, and J.M. Delrieu, Rev. Mod. Phys. **55**, 1 (1983); M.C. Cross and D.S. Fisher, Rev. Mod. Phys. **57**, 881 (1985); M.C. Cross, Jpn. J. Appl. Phys. **26**, 1855 (1987); D.D. Osheroff, J. Low Temp. Phys. **87**, 297 (1992).

[2] H. Godfrin and D.D. Osheroff, Phys. Rev. B **38**, 4492 (1988).

[3] D. Ceperley and G. Jacucci, Phys. Rev. Lett. **58**, 1648 (1987).

[4] H. Godfrin and R.E. Rapp, Adv. Phys. **44**, 113 (1995).

[5] H. Godfrin, R.E. Rapp, and D.D. Osheroff, Physica (Amsterdam) **163A**, 101 (1990).

[6] P. Schiffer, M.T. O'Keefe, D.D. Osheroff, and H. Fukuyama, Phys. Rev. Lett. **71**, 1403 (1993); J. Low Temp. Phys. **94**, 489 (1994).

[7] H. Franco, R.E. Rapp, and H. Godfrin, Phys. Rev. Lett. **57**, 1161 (1986).

[8] H. Godfrin, R.E. Rapp, and H.J. Lauter, Physica (Amsterdam) **169B**, 177 (1991).

[9] M. Siqueira, J. Nyéki, B.P. Cowan, and J. Saunders, J. Low Temp. Phys. **101**, 713 (1995).

[10] C.P. Lusher, J. Saunders, and B.P. Cowan, Europhys. Lett. **14**, 809 (1991).

[11] M. Roger, Phys. Rev. Lett. **64**, 297 (1990).

[12] D.S. Greywall, Phys. Rev. B **41**, 1842 (1990); Physica (Amsterdam) **197B**, 1 (1994), and references therein.

[13] M. Siqueira, J. Nyéki, B. Cowan, and J. Saunders, Phys. Rev. Lett. **76**, 1884 (1996); Czech. J. Phys. Suppl. S1 **46**, 407 (1996); Suppl. S6 **46**, 3033 (1996); M. Siqueira, Ph.D. thesis, University of London, 1995 (unpublished). The present results are analyzed with an improved background heat capacity for $T > 10$ mK. The heat input in the calorimetry has been checked using a wire wound Pt-W heater. The values of the heat capacity per spin are approximately 20% smaller than those previously reported, arising from an error in the original calibration of the standard volume used to dose in the ^{3}He gas. The surface area of the sample is 182 m^2, based on a ^{3}He density of 0.109 Å^{-2} at second layer promotion.

[14] N. Elstner, R. Singh, and A.P. Young, Phys. Rev. Lett. **71**, 1629 (1993); N. Elstner (unpublished).

[15] For example, following [11], defining $J = J_2 - 2J_3$ and defining a frustration parameter by $J_4 = J_6 = rJ$, then $J_\chi = -J(1 + 3.625r)$ and $J_c^2 = J^2(1 + 5.5r + 10.75r^2)$. In this model J and r are determined from J_χ and J_c.

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

[17] H. Godfrin, K.-D. Morhard, R.E. Rapp, and Yu.M. Bunkov, Physica (Amsterdam) **194B–196B**, 675 (1994).

[18] Recent data also showing the absence of a sharp peak in the heat capacity, near this coverage, are reported in M. Morishita, K. Ishida, K. Yawata, and H. Fukuyama, Czech. J. Phys. Suppl. S1 **46**, 409 (1996).

[19] At this coverage $\beta = 0.52$ mJ/K (a factor of order 2 higher than that reported in Ref. [12], after scaling with surface area).

[20] We should note that convergence at $T \sim J_c$ of the Padé analysis for FM exchange is not as well established as for AFM. For fits to $T < J_c$ we use a $\{5,8\}$ Padé from the 13th order expansion; this is in good agreement with the $\{5,7\}$ Padé.

[21] Since the HTSE fit $c(T)$ well over the whole temperature range, we use it to infer a characteristic exchange energy J. We assume that this J also characterizes the heat capacity to leading order in J/T, or equivalently that $J = J_c$. Support for this procedure is provided by fitting the heat capacity to $c(T) = \beta + A/T^2 + B/T^3$ prior to third layer promotion for $T > 10$ mK. This gives values of J_c and β within 10% of those determined by HTSE, but with larger fitting errors. Note that in the $J_4 = J_6$ model [15], $r \approx -0.3$ at these coverages.

[22] In the $J_4 = J_6$ model, $r \approx -0.19$ at 0.21 Å^{-2}. Note that in this model J_χ changes sign at $r = -0.275$.

[23] H. Godfrin, R.E. Rapp, K.-D. Morhard, J. Bossy, and Ch. Bäuerle, Phys. Rev. B **49**, 12 377 (1994).

[24] B. Bernu, D. Ceperley, and C. Lhuillier, J. Low Temp. Phys. **89**, 589 (1992). Isotherms of the numerically evaluated magnetization and heat capacity for a 4 × 4 cluster show breaks at different frustrations. B. Bernu and M. Roger (private communication).

[25] We assume that indirect exchange can be incorporated into the MSE model as an enhanced J_3.

[26] It should be noted that in this coverage range the values of γ tabulated in [12] at 0.21, 0.22, and 0.23 Å^{-2} are in fact interpolations.