Frustration Due to Competing Cyclic Ring Exchanges in Two-Dimensional Solid ^{3}He

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A new insight is provided into ring-exchange processes occurring in two-dimensional solid ^{3}He layers adsorbed on Grafoil. Three-particle exchange dominates at high and moderate areal density leading to the ferromagnetic properties previously observed. At the low densities corresponding to the observation of commensurate phases, higher-order antiferromagnetic four- and six-spin exchanges are relatively more important and lead to a frustrated antiferromagnetic system. A variety of anomalies recently observed are explained in a unified way.

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Recent experimental studies on nuclear-spin ordering in two-dimensional (2D) ^{3}He layers adsorbed on Grafoil have focused on coverages where the first layer is a high-density solid while the second layer just solidifies. For coverages corresponding to the region near third-layer promotion, the observation at 2.5 mK of a peak in the nuclear-spin contribution to the specific heat[1] has revealed the existence of a low-density solid phase, probably commensurate with the first layer (the possibility of a Kagome net has been suggested[2]). Below 2.5 mK an anomalously large entropy has been estimated.[1] Susceptibility measurements in the same coverage range have shown some antiferromagnetic tendencies.[3] At higher coverages corresponding to a more than half-filled liquid third layer, the second layer undergoes a transition to an incommensurate solid with a 20% higher density.[1,3,4] An abrupt rise of the susceptibility, characteristic of two-dimensional ferromagnetism, is observed at low temperatures[3,4] and the peak observed in the specific heat[1] is two times higher than that corresponding to the commensurate phase. Some information has also been obtained for submonolayer coverages. Specific-heat measurements performed for densities just above the transition to an incommensurate solid monolayer[1] indicate exchange frequencies of order 0.3 mK while the susceptibility obeys an almost Curie law down to $T \approx 1$ mK.[5]

The purpose of the present work is to offer a coherent interpretation of all these observations, in a unified way, through a general spin-exchange model. Because of the hard-core correlations between spin-$\frac{1}{2}$ exchanging fermions, ring-exchange processes such as three- and four-particle cyclic permutations are essential in solid ^{3}He magnetism.[6-10] The Hamiltonian is $H = -\sum_P (-1)^p J_P P^\sigma$, where the P^σ's denote permutation operators, with parity p, acting on spin variables. The sum contains not only pair transpositions (Heisenberg terms) but also ring exchanges involving the most compact n-spin cycles ($n=3,4,\ldots$). A general result[6] is that even and odd permutations, respectively, favor ferromagnetism and antiferromagnetism and all J_P's have the same positive sign. Delrieu, Roger, and Hetherington[7] predicted that three-particle exchange should dominate at high densities in compact triangular lattices, leading to ferromagnetism. The prediction was confirmed experimentally a few years later for the hcp solid.[11] It also accounts semiquantitatively for the ferromagnetism observed in the incommensurate second layer on Grafoil.[12] However, further theoretical investigations[9,10] have proven that higher-order ring exchanges do not decrease as fast as early conjectured. At the much lower densities corresponding to the two-dimensional commensurate structures, higher-order antiferromagnetic ring exchanges should take more importance, reversing possibly the overall behavior from a ferromagnet to an intricate frustrated antiferromagnet.

The variations of various ring-exchange frequencies with interatomic distance have been roughly estimated in the high-density limit through a multidimensional WKB approximation.[9] For a 2D triangular lattice the most important exchange processes come out in the order $J_T > K \approx S \approx J_{NN}$, where J_T, K, S, and J_{NN} represent, respectively, the most compact cyclic exchanges of three, four, six, and two particles. We have

$$J_P \approx C_P s_P \exp(-A_P/g)\,. \tag{1}$$

The dimensionless action A_P is, respectively, $A_3 \approx 8.65$, $A_4 \approx 9.67$, $A_6 \approx 9.72$, and $A_2 \approx 11.26$ for three-, four-, six-, and two-spin exchange. The symmetry factor s_P represents the number of equivalent exchange channels in the $2N$-dimensional configuration space: $s_P = 4$ for pair exchange between first neighbors and $s_P = 1$ for all other ring exchanges considered. C_P is a prefactor of the order 2 K. The variation with density enters through the parameter $g = \hbar(8m\sigma^{*2}\epsilon)^{-1/2}(a/\sigma^*)^5$, which varies strongly with the first-neighbor distance a; m represents the mass of a ^{3}He atom, and $\epsilon = 10.22$ K and $\sigma^* = 0.265$ nm are the parameters of an effective pair potential $4\epsilon(\sigma^*/a)^{12}$ which were determined to account for the variations of the macroscopic elastic quantities pressure and compressibility (see Ref. 9, Sec. IV). Although the applicability of this approximation at densities near melting for ^{3}He is questionable, it already predicted within 30% the correct ratios between the dominant exchange frequencies in bcc ^{3}He, now obtained through Monte Carlo calculations.[10] The application of Eq. (1) to the lowest density at which an incommensurate solid monolayer is observed with $a=0.385$ nm leads to

$$K \approx S \approx J_{\rm NN} \approx J_T/2.5 \approx 0.3\ {\rm mK}\,. \qquad (2)$$

This order of magnitude of four-spin exchange relative to three-spin exchange at low density seems to be confirmed by recent Monte Carlo calculations.[13]

The contribution of ferromagnetic three-spin exchange to the Curie-Weiss temperature Θ is $6J_T$ and that of antiferromagnetic exchanges is $-(3J_{\rm NN}+9K+15S/8)$. With the orders of magnitude given by Eq. (2), both contributions almost cancel and the resulting Curie-Weiss constant is 1 order of magnitude smaller than each term. Note that such a cancellation already occurs in bcc ^{3}He.[7-10] However, there is not such a strong compensation in the leading term of the high-temperature specific heat which is quadratic with respect to various exchange frequencies and roughly has their order of magnitude. This might explain the apparent discrepancies between various measurements on a monolayer.[1]

The previous estimates are for a strictly 2D solid; they do not take into account the finite substrate potential. This might be a reasonable approximation for the first layer which experiences a very strong potential (of order 250 K). For the second layer which is more weakly bounded to the surface, the hierarchy and order of magnitude of various exchange processes might be different. Exchange frequencies are certainly enhanced by the possibility that some atoms have to move in the direction perpendicular to the substrate, in order to reduce the effective exchange barrier (this argument is corroborated by recent Monte Carlo results[13]). Such an escape in the third direction would rather favor the exchanges which have the shortest "WKB path length"[9] and might enhance three-spin exchange with respect to four- and six-spin exchanges in the second layer. This could explain why, for the same density, the susceptibility of an incommensurate monolayer shows a quasi Curie behavior, while a second layer on top of a dense first layer has a ferromagnetic behavior. [Note that Ruderman-Kittel-Kasuya-Yosida interactions involving the third liquid layer[14] and (or) interlayer three-particle exchange might also enhance the ferromagnetic tendency of the second layer.] The same arguments might be used to interpret the decrease of the exchange frequencies by a factor of 4 when the coverage is increased from 2.5 to 5 layers.[1,3,4] Part of this effect comes from the compression of the second layer[12] but the reduction of the motion in the direction perpendicular to the substrate, due to the presence of further layers, should also be taken into account.

The density of the commensurate phase for the second layer is 20% lower with an interatomic distance $a=0.425$ nm. By extrapolating Eq. (1) to this low density, one expects $J_T \approx J_{\rm NN} \approx 2K \approx 2S$, leading to an antiferromagnetic Curie-Weiss constant. The influence of the substrate potential should still be more important for a commensurate structure and it could modify this hierarchy. However, it seems unlikely that the potential created by the first layer suppresses completely all ring-exchange processes to only allow some pair exchanges as conjectured in a recent theoretical model proposed by Elser.[2]

The previous discussion will be illustrated by the following model Hamiltonian:

$$H_{\rm ex} = J\sum^{(1)} P_2 + K\sum (P_4+P_4^{-1}) + S\sum (P_6+P_6^{-1})\,, \qquad (3)$$

where the P_n's denote cyclic permutation operators of n particles; the first sum runs over distinct first-neighbor pairs, the others over the most compact four- and six-spin cycles. Using the property that three-spin exchange operators can be expressed in terms of pair transpositions,[6,8] three-particle exchange (J_T) and pair exchange between first neighbors ($J_{\rm NN}$) have been included in an effective-pair-exchange frequency: $J=J_{\rm NN}-2J_T$.

It is first interesting to investigate some molecular-field (MF) properties of this Hamiltonian in a magnetic field B. For $B_{c2}=(9/\gamma\hbar)(J+4K+2S)<0$, the ferromagnetic state is stable at zero field. If this quantity is positive, there is at zero temperature a transition from the ferromagnetic phase to a canted antiferromagnetic phase [analogous to the "pf" phase occurring in bcc ^{3}He (Ref. 8)] below some critical field B_{c2}. This phase has three sublattices. The component of the staggered magnetization perpendicular to the field rotates by 120° from one sublattice to the other. The parallel component m is given by

$$16(\gamma\hbar/2)B = 72J + (216m^2+72)K + (81m^4+54m^2+9)S\,.$$

The Curie-Weiss temperature is $\Theta=-3(J+3K+5S/8)$. There is some parameter range in which Θ is positive but the ground state is not ferromagnetic ($B_{c2}>0$).

Further information has been obtained by exact diagonalization of the Hamiltonian (3) on a 4×4 spin cluster with periodic boundary conditions. The heat capacity and entropy are shown in Fig. 1 for various parameter ratios. The corresponding susceptibility curves are plotted in Fig. 2. I chose $K=S$, according to the previous discussion, and the ratio $r=K/J=S/J$ is varied from 0 to -0.25 with $J<0$. The temperature is normalized to the square root of the coefficient of the $1/T^2$ term in the high-temperature specific heat:

$$e_2 = 9(J^2+33K^2/4+5JK+SJ/2 + 3SK/2+193S^2/192)\,.$$

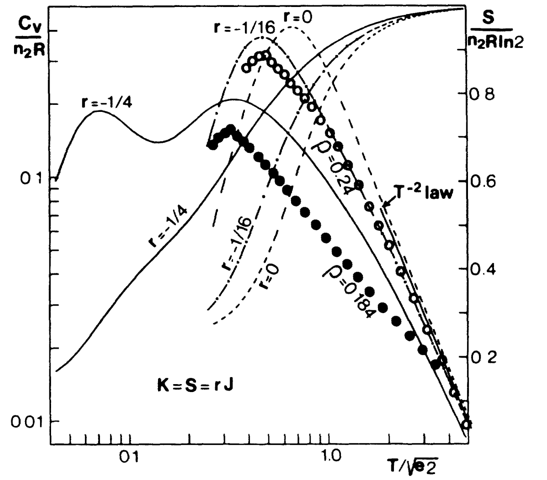

FIG. 1. The specific heat and entropy for a 4×4 spin cluster with various ratios of four- and six-spin exchange relative to effective-pair exchange (solid curves, $r=K/J=S/J=-1/4$; dash-dotted curves, $r=-\frac{1}{16}$; dashed curves, $r=0$) are compared to the experimental data (Ref. 1) at coverages $\rho=0.184$ atoms/Å^2 (commensurate structure, ●) and $\rho=0.24$ atoms/Å^2 (incommensurate second layer, ○).

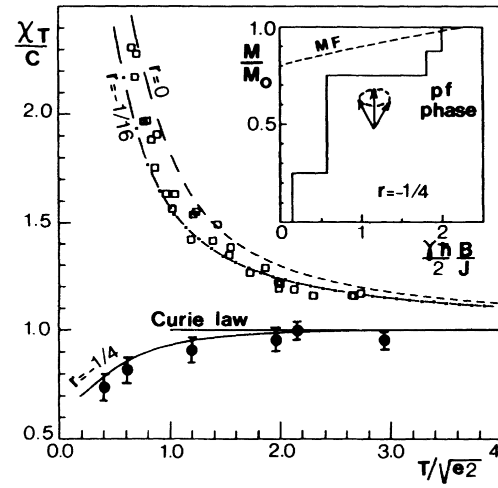

FIG. 2. Product of the susceptibility times the temperature for a sixteen-spin cluster with $r=0$ (dashed curve), $r=-\frac{1}{16}$ (dash-dotted curve), and $r=-\frac{1}{4}$ (solid curve). A Curie contribution of the first layer is added to the susceptibility of the second layer and the result is normalized to the total number of atoms contained in the two first layers. The experimental data for the commensurate phase (●) at second-layer completion (2.01 layers) are taken from Franco's thesis (Ref. 3) and scaled to $\sqrt{e_2}=7.85$ mK corresponding to $K=S=-J/4=1.2$ mK. The experimental data for the incommensurate phase at $\rho\approx0.24$ atoms/Å^2 (□) are taken from Godfrin, Ruel, and Osheroff (Ref. 4) (Fig. 1) and scaled to $\sqrt{e_2}=7.52$ mK corresponding to $16K=16S=-J=3$ mK. Inset: Magnetization in terms of the magnetic field B at $T=0$. The exact result for sixteen spins with $r=-0.25$ (solid staircase) is compared to the molecular-field expectation for the pf phase.

The solid curves correspond to the maximum frustration with $r=-0.25$ (i.e., Θ is small and slightly positive but the ground state is antiferromagnetic with $B_{c2}>0$). The dashed curves correspond to a pure ferromagnetic Heisenberg Hamiltonian with $r=0$. The dash-dotted curves represent an intermediate situation with $r=-\frac{1}{16}$. From $r=0$ to -0.25, the behavior of the specific heat at high temperature evolves from a slightly positive to a large negative deviation with respect to the T^{-2} law and the low-temperature maximum decreases by a factor of 2. The susceptibility evolves from a ferromagnetic behavior to an almost Curie behavior down to $T\approx\sqrt{e_2}$ with a small antiferromagnetic deviation at lower temperatures.

The specific heat is compared to the experimental results obtained by Greywall[1] at $\rho=0.184$ atoms/Å^2 for the commensurate second layer (filled circles) and at $\rho=0.24$ atoms/Å^2 where the incommensurate phase occurs (open circles). The data are scaled to 1 mole taking into account the total area 203 m^2 and the respective second-layer densities $\rho_2=0.0694$ and 0.0813 atoms/Å^2. On the horizontal axis, the curves are scaled to the high-temperature data.

At $\rho=0.24$ atoms/Å^2, the experimental specific heat shows a negative deviation with respect to the T^{-2} law at high temperatures. For this reason, it compares much better with a model including some four- and six-spin exchanges, although for similar coverages the susceptibility curve has been fitted with a pure Heisenberg model.[4] A good agreement for the specific heat is obtained with $r\approx-\frac{1}{16}$. From the temperature scale we deduce $J=-2.1$ mK and $K=S=0.13$ mK. The susceptibility corresponding to $r=-\frac{1}{16}$ can be fitted to the experimental data[3,4] (see Fig. 2) but with larger exchange frequencies ($J\approx-3$ mK). This discrepancy might be simply due to small differences in the coverages at which various experiments are carried out since J varies very rapidly in that range.[3]

When the relative magnitude of four- and six-spin exchange increases, the entropy at constant reduced temperature increases and the specific heat evolves from a unique maximum to a double-peak structure with about half height. The experimental data at $\rho=0.184$ atoms/Å^2 are compared to the model with maximum frustration ($r=-0.25$). A reasonable agreement is obtained with a temperature scaling corresponding to $J=-4.8$ mK and $K=S=1.2$ mK. The first peak in the theoretical curve corresponds approximately to the experimental peak observed at 2.5 mK with a large entropy of order $0.7k_B\ln2$. We do not know whether the double-peak shape is intrinsic or is an artifact of the finite-size calculation. In the thermodynamic limit, the specific heat could only exhibit a very flat maximum and the sharp kink experimentally observed at 2.5 mK might correspond to some Kosterlitz-Thouless transition due to dipolar anisotropic interactions. There is no finite-temperature transition for a pure exchange Hamiltonian which is invariant under rotation. However, dipolar interactions, although small (of order $\delta \approx 0.1\ \mu$K) would lead to a long-range order at $T_c \approx 3J/\ln(J/\delta)$ (i.e., in the millikelvin range).[15] Nevertheless, the finite-size calculation proves that, as experimentally observed, below the peak at 2.5 mK, there is a large remaining entropy of order $0.7k_B \ln 2$ and the specific heat should present a second anomaly (either a maximum or a shoulder). This excess entropy is due to an anomalously large density of quasidegenerate low-lying energy states resulting from the frustration. In Fig. 2 the theoretical susceptibility, for the same parameters $K=S=-J/4=1.2$ mK, is compared to the experimental results of Franco[3] at the same coverage corresponding to second-layer completion. The agreement is good with an almost Curie behavior down to $T \approx \sqrt{e_2}$ and a small antiferromagnetic deviation at lower temperatures. When ring exchanges are further increased ($r < -0.25$), the antiferromagnetic character is enhanced and the double peak in the specific heat disappears to merge again in a factor-of-2 higher single maximum.

The inset in Fig. 2 shows the magnetization in terms of the field at $T=0$ with $r=-0.25$ for a sixteen-spin cluster (solid staircase). It is compared to the MF expectations (dashed curve) for the pf phase. As already observed in bcc ^{3}He,[8] we expect at relatively low field some kind of metamagnetic phase with a large magnetization of order $0.7M_0$ to $0.8M_0$, M_0 representing the saturation magnetization. The transition to the ferromagnetic phase should occur at a field $B_{c2} \approx (2/\gamma\hbar)2J \approx 10$ T. Note that in Elser's model[2] a finite magnetization should also appear at low field and zero temperature since one-fourth of the spins are completely decoupled. However, it should only be $\approx 0.25M_0$. Magnetization measurements in the range of 1 to 10 T could definitively test both models. If the orders of magnitude of various exchange frequencies expected for one incommensurate monolayer just above melting are correct [Eq. (2)], the same behavior of the magnetization should be observed at submonolayer coverages for temperatures and magnetic fields 1 order of magnitude smaller. Further estimates of various exchange frequencies through Monte Carlo calculations, taking fully into account the complexity of the system, are encouraged.

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