# Nuclear Antiferromagnetism in a Registered $^3$He Solid

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Recent heat-capacity measurements of $^3$He adsorbed on graphite by Greywall and Busch are interpreted in terms of a triangular second-layer solid having $\sqrt{7}\times\sqrt{7}$ registry with respect to the first adsorbed layer. The observed entropy change in the millikelvin region is well accounted for by an antiferromagnetic Heisenberg spin Hamiltonian in which only a subset of second-layer spins forming a Kagomé net are strongly coupled.

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Efforts to study nuclear-spin ordering in adsorbed phases of $^3$He have focused in recent years on coverages where layers beyond the first monolayer have formed a solid. The second and possibly higher layers being looser and less tightly bound to the substrate have a much better chance of displaying exchange processes in an accessible temperature range. For the graphite substrate Franco, Rapp, and Godfrin[1] examined a range of coverages down to 3 mK and observed a large magnetization peak at the coverage $\rho\simeq 0.24$ atom/Å$^2$. Subsequent measurements[2] (at this coverage but lower temperature) and theoretical analysis[3] have confirmed earlier expectations[4] that this second-layer spin system is a Heisenberg nearest-neighbor ferromagnet on a triangular lattice. Franco, Rapp, and Godfrin[1] also observed a less prominent anomaly at a significantly lower coverage, $\rho\simeq 0.18$ atom/Å$^2$, where earlier heat-capacity measurements by Van Sciver and Vilches[5] already showed evidence of a second-layer melting peak. The existence of a solid at this low density was questioned in a neutron-diffraction study[6] that failed to detect a second-layer Bragg peak. This controversy has recently been intensified by the millikelvin heat-capacity measurements of Greywall and Busch[7] which show not only consistency with the higher-temperature measurements[5] but reveal a sharp peak at 2.5 mK. This unexpected finding is strongly suggestive of the low-energy scale of particle exchange in an ordered quantum solid. In this Letter I propose a structure for the low-density second-layer solid which has $\sqrt{7}\times\sqrt{7}$ registry with respect to the first $^3$He layer. A particularly appealing property of this structure is that it naturally leads to a magnetic Hamiltonian that has a hope of explaining a particular puzzle posed by the 2.5-mK peak.

At the coverages of interest, the first $^3$He layer forms a highly compressed triangular lattice which is probably only very weakly modulated by the incommensurate graphite substrate. Using the value $\rho_1=0.114$ atom/Å$^2$ for the first-layer density given by the neutron-diffraction measurement of the lattice constant,[8] Greywall and Busch[7] have determined the second-layer density $\rho_2=0.064$ atom/Å$^2$ at the coverage where the entire second layer has formed a solid. The latter density should be compared with the density $\rho_1=0.064$ atom/Å$^2$ in the submonolayer coverage regime where a triangular structure having $\sqrt{3}\times\sqrt{3}$ registry with the graphite is formed.[9] In the first layer, and presumably also in the second, an incommensurate triangular structure stabilized entirely by crowding of the $^3$He hard cores first forms at somewhat higher density. Registry of the second layer with respect to the graphite is out of the question since the modulation of the graphite-$^3$He potential at a distance $z_2\sim 5.2$ Å above the graphite plane[10] has decayed by the factor $\exp(-Gz_2)\sim 10^{-7}$, where $G$ is the magnitude of the shortest in-plane reciprocal-lattice vector of the graphite structure. When the possibilities of registry with respect to the first $^3$He layer are explored, the proximity of $\rho_2/\rho_1\simeq 0.56$ to the fraction $\frac{4}{7}$ immediately suggests the $\sqrt{7}\times\sqrt{7}$ structure shown in Fig. 1. The second layer decomposes into a Kagomé net of *"A"* sites (see Fig. 1) located at saddle points between adjacent dimples in the first layer and *"B"* sites located directly above a first-layer atom. The main benefit of commensuration is conferred by the more favorable $A$ sites which outnumber the $B$ sites three to one. The actual localization of atoms, even those on $A$ sites, is probably helped to a large degree by the repulsion of the neighboring hard cores. The amplitude of zero-point

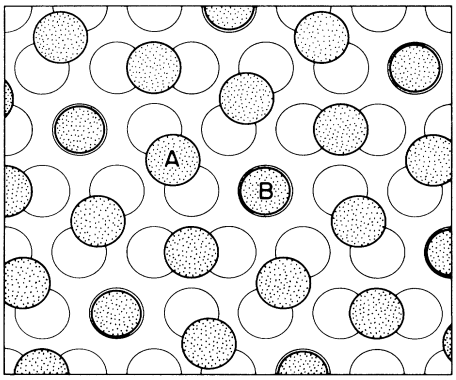


FIG. 1. Proposed $\sqrt{7}\times\sqrt{7}$ structure of the second $^3$He layer. Both the first-layer atoms and second-layer atoms (shaded) form triangular lattices. The second-layer $A$ sites have more favorable potential energy than the $B$ sites and form a Kagomé net.

motion should therefore be very large and the associated Debye-Waller factor may well explain the negative neutron-diffraction results.[11]

Before I propose a specific form of spin Hamiltonian for the $\sqrt{7}\times\sqrt{7}$ structure it is necessary to review the low-temperature properties that this Hamiltonian will hopefully reproduce. While a cusplike "exchange peak" in the heat capacity is in itself surprising, what is even more troublesome is the fact noted by Greywall and Busch[7] that the corresponding entropy change (in units of $k_B$) falls short of the expected ln2 per second-layer spin, being closer to the value $\frac{1}{2}$ ln2. Of the two possibilities that the spins are either (1) partially disordered below the peak or (2) retain some order above the peak, the second appears to be ruled out by the magnetization measurements of Franco, Rapp, and Godfrin.[1] These show quite clearly that the anomaly already mentioned above approaches the magnetization of free spins at high temperatures. In addition, the magnetization is observed to go below the free-spin value at lower temperatures. This antiferromagnetic behavior is in sharp contrast to the ferromagnetic signal at the higher coverage.

In the absence of four-particle and higher-order exchange processes[12] the spin Hamiltonian for the $\sqrt{7}\times\sqrt{7}$ structure will have the Heisenberg form with separate exchange constants $J_{AA}$ and $J_{AB}$ assigned to the two kinds of near-neighbor spins. The magnetization measurements require that at least $J_{AA}$ has the antiferromagnetic sign since otherwise the ground state would have a nonvanishing moment. Since the steric constraints imposed by the $^3$He cores play less of a role in suppressing exchange in low-density structures such as the $\sqrt{7}\times\sqrt{7}$, it can be argued that the antiferromagnetic pair process will dominate the ferromagnetic three-particle process. Accepting this as a justification for the (positive) sign of $J_{AB}$ as well, there remains the problem of deciding among the alternatives (1) $J_{AB}\gg J_{AA}$, (2) $J_{AB}\sim J_{AA}$, and (3) $J_{AB}\ll J_{AA}$. Of these only choice (3) appears to offer an explanation of the "partial ordering peak" seen in the heat capacity.[7] The $B$ spins, being uncoupled, would already account for half of the missing $\frac{1}{2}$ ln2 low-temperature entropy while frustration in the ordering of the $A$ spins on the Kagomé net (see below) may well provide the other half. As for a possible microscopic explanation of the choice (3) one notes the following: The exchange of an $AA$ or $AB$ pair is mostly inhibited by their common near neighbors. In the case of $AA$ exchange one of these is an $A$ atom while the other is a $B$, while for $AB$ exchange both "inhibitors" are $A$ atoms. Since the $B$ atoms occupy manifestly less stable positions with respect to the first layer, one expects them to be less effective inhibitors of exchange than $A$ atoms. Thus an $AA$ pair attempting to exchange frequently find their neighboring $B$ atom "out of the way" with the result that $J_{AA}>J_{AB}$. In the following I will in fact assume (without justification) that $J_{AA}\gg J_{AB}$ and restrict my attention to temperatures greater than $J_{AB}/k_B$. Even with the $B$ spins effectively out of the picture, the remaining system of antiferromagnetically coupled $A$ spins is still sufficiently peculiar to require special attention.

The Hamiltonian for the $A$ spins may be written in the form

$$H=J\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j\,, \tag{1}$$

where $J=J_{AA}$, the $\mathbf{S}_i$ are spin-$\frac{1}{2}$ operators, and the sum is over nearest neighbors of the Kagomé net. It is easy to see that the classical analog of Eq. (1) has a ground state with finite entropy. First, one notes that the lowest-energy state for three classical Heisenberg spins on a triangle of the Kagomé net is the planar configuration where the angle formed by any pair of spins is 120°. This condition is easily satisfied on all the triangles by selecting a particular such set of three spins and assigning them to sites in such a way that neighboring sites are given different spins. The ground-state entropy of the three-state Potts model thus formulated is then easily bounded away from zero. While it is not immediately obvious what this implies for the quantum-mechanical model (1), if nothing else it shows that the usual spin-wave approach (which adds the fluctuations about a *particular* classical state) has problems from the start. A different approach, which exploits special properties of the Kagomé net, is suggested by rewriting Eq. (1) in the form of a sum over the Kagomé net's constituent triangles:

$$H=J\sum_r[\tfrac{3}{2}P_{3/2}(\mathbf{S}_{r_1}+\mathbf{S}_{r_2}+\mathbf{S}_{r_3})-\tfrac{3}{4}]\,. \tag{2}$$

In Eq. (2) the sum extends over all triangles $r$ of near-neighbor sites $r_1,r_2,r_3$ on the Kagomé net; $P_{3/2}$ is a spin-$\frac{3}{2}$ projection operator. In a number of recent studies[13-16] a projection-operator representation similar to Eq. (2) has been used to construct a class of antiferromagnetic Heisenberg Hamiltonians having exotic ground states. The present model would belong to this class if it were possible to construct a "simple" state that was annihilated by each of the projection operators in Eq. (2). Anderson's[17] construction of a ground state involving "valence bonds," where spins are paired to form singlets, is potentially useful in this context. All that is required it that on every triangle of the Kagomé net two spins form a valence bond. Unfortunately, a simple counting argument shows that this condition cannot be realized on every triangle. If $N$, $N_2$, and $N_3$ are respectively the number of sites, valence bonds, and triangles on the Kangomé net, then $2N=3N_3$ and $N_2\leq N/2$. Combining these we have $N_2\leq\frac{3}{4}N_3$ where equality corresponds to a "dimerized state," i.e., one where every spin forms a valence bond with some other (near-neighbor) spin. Thus, exactly one-quarter of all triangles in a dimerized state will lack a valence bond and are naturally viewed as "defects." The expectation value of $H$ in any dimerized state, $J(0\times\frac{1}{4}-\frac{3}{4}\times\frac{3}{4})N_3=-\frac{3}{8}JN$, is a significant improvement over the classical ground-state energy

$-\frac{1}{4}JN$.

It is tempting to attribute the other half of the missing $\frac{1}{2}\ln 2$ entropy in the $^3$He experiment to a low-lying manifold of states where the $A$ spins are dimerized. Although it has not yet been proven for the Kagomé net, it is probably true that the dimerized states are (excepting boundary effects) linearly independent[18] so that the entropy may be calculated by enumerating dimer coverings. For the Kagomé net, the latter reduces to a rather trivial transfer matrix problem involving successive rows of triangles. A triangle may be in any of four states (three with valence bonds, one without). When these are assigned to triangles row by row in the order 1, 1′, 2, 2′, etc., as shown in Fig. 2(a), then the triangles in the unprimed rows always have exactly two choices of state whereas the triangles in the primed rows always have their state uniquely determined. This gives two choices for every two triangles (three spins) or an entropy of $(N/3)\ln 2$. Combining this with the entropy of the (disordered) $B$ spins, we arrive at an entropy per second-layer spin of $(\frac{1}{3}\times\frac{3}{4}+1\times\frac{1}{4})\ln 2=\frac{1}{2}\ln 2$. While neither this result nor the experimental determination of a missing entropy by a linear extrapolation of the low-temperature heat capacity[7] has a clear interpretation, the agreement in the two numbers is encouraging.

Implicit in the above entropy calculations was the assumption that there is a good correspondence between the dimerized states and a set of low-lying energy eigenstates. A dimerized state $\Psi$ fails to be an energy eigenstate because an application of $H$ to $\Psi$ generates fluctuations (next-nearest-neighbor valence-bond configurations) in the vicinity of all its "defect triangles." While this will certainly renormalize the energy of defect triangles, it may also introduce effective interactions among them. The properties of the Kagomé net, however, conspire to make the latter a relatively small effect. To see this one notes that the three triangles surrounding a defect triangle each have a valence bond and isolate, to a first approximation, the fluctuations at different defect triangles. The renormalization of a defect triangle can be estimated by considering $H_r$, the restriction of $H$ to a triangle $r$ and its three neighbors, and a dimerized state $\Psi_0$ having a defect at $r$. The relations

$$H_r\Psi_0=-\tfrac{9}{4}J\Psi_0+\tfrac{3}{4}J\Psi_1\,,\quad(\Psi_1,H_r\Psi_1)=-\tfrac{1}{4}J$$

serve to define a two-level system consisting of $\Psi_0$ and a normalized and orthogonal state $\Psi_1$. The ground state, having energy $-\frac{5}{2}J$, is given by the linear combination $(3\Psi_0-\Psi_1)/\sqrt{10}$. Aside from showing that the amplitude of fluctuations is small, this calculation also provides a new upper bound on the ground-state energy of the whole system, $-\frac{5}{12}JN$. Presumably at the next level of renormalization the energy expectation values will begin to depend on the detailed valence-bond configuration in a dimerized state.

A further consequence of the dimerized states' failure to be energy eigenstates is the possibility of resonance. At all except the very lowest temperatures this is probably a relatively unimportant effect since the requirement that two dimerized states be able to resonate "easily" turns out to impose strong constraints on the valence-bond configuration. Two dimerized states which differ by the fewest number of valence bonds are related by the alternate arrangements of valence bonds around the star shown in Fig. 2(b). Resonance alone lowers the average energy of each of the three defect triangles in this configuration by an amount $\frac{3}{20}J$ or about 60% of the energy reduction achieved by the renormalization discussed in the previous paragraph. Although renormalization (i.e., fluctuations into intermediate states) will further reduce the energy of the resonating state, it is perhaps more meaningful to compare just the energy gain of resonance with the entropy lost by having all the defect triangles organized into such star configurations. Making the approximation that the latter is nearly all of the $(N/3)\ln 2$ entropy of the dimerized states and taking $\frac{3}{20}J\times\frac{1}{4}N_3=\frac{1}{40}JN$ as the resonance energy gain by having everywhere stars, one arrives at an estimate $0.11J/k_B$ for the temperature above which resonance effects are relatively unimportant. Below this temperature one would expect a form of ordering where translational symmetry is broken, say, by a crystallization of the stars into a periodic array.

To supplement partially the qualitative arguments above, the twelve-spin cluster with periodic boundary conditions shown in Fig. 3 was diagonalized numerically.

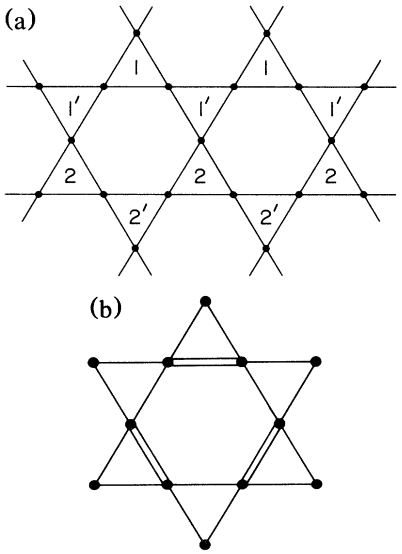


FIG. 2. (a) Decomposition of the Kagomé net's triangles into an ordered sequence of rows 1, 1′, 2, 2′, etc., for the purpose of calculating the entropy of dimer coverings (see text). (b) Three valence bonds (double lines) in a star configuration which when rotated 60° produce another dimerized state.

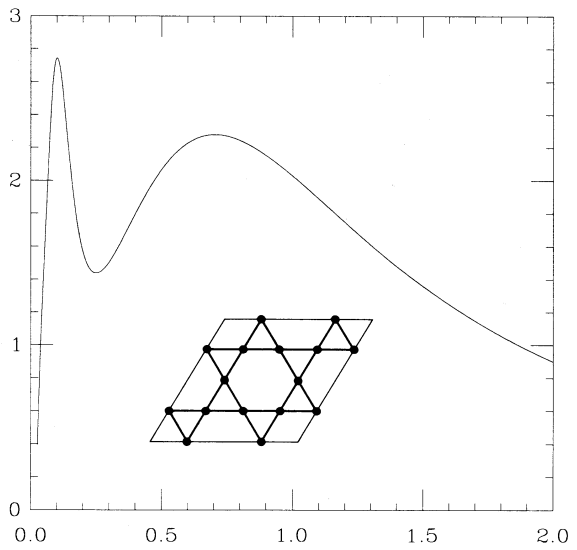


FIG. 3. Heat capacity in units of $k_B$ for the twelve-spin cluster with periodic boundary conditions shown below the curve. The unit of temperature is $J/k_B$.

The heat capacity, computed directly from all 4096 eigenvalues, displays two prominent peaks (Fig. 3). Although the seven lowest-lying states are singlets, there is no clear evidence of a "spin gap"[19] in that a large number of triplet states contribute to the low-temperature peak as well. Whether this reflects a deficiency in the above analysis or simply is an artifact of the small system size, one should treat with caution the interpretation of the high-temperature peak as condensation into a "singlet liquid." Using the experimental peak temperature,[7] 2.5 mK, to set either the scale of the maximum, $k_BT/J=0.70$, or the point where the entropy equals the experimental peak entropy,[7] $k_BT/J=0.57$, one obtains $J/k_B\sim 3.5$–$4.5$ mK. From this estimate, and the assumption that things are not changes significantly by a finite $J_{AB}$, the low-temperature peak is placed at about 0.4 mK. The usefulness of high-temperature expansions in extracting the parameters of the spin Hamiltonian is doubtful because the experimental heat capacity is found to be sensitive, at high millikelvin temperatures, to $^3$He coverage and fails to show the leading $1/T^2$ behavior. The two problems may be related and a peculiarity of registered phases in general. For coverages slightly below or above the ideal value, a registered phase will contain vacancies or interstitials. It is likely that these will locally melt the solid thereby generating sources of liquidlike heat capacity that could dominate any $1/T^2$ contribution.

The low-density second-layer phase of adsorbed $^3$He, tentatively identified as registered by Greywall and Busch,[7] merits further experimental study because of its potential for exhibiting unusual nuclear antiferromagnetism. If the model presented in this Letter is correct, then lower-temperature magnetization measurements should find, below 2.5 mK, a saturation consistent with a state where three-quarters of the second-layer spins form a singlet liquid while the remaining quarter remain free. Provided the coupling between the two kinds of spins is sufficiently weak, the model further predicts that the singlet liquid will freeze into a "valence bond solid."[14] The latter would reveal itself in the heat capacity as a phase transition, most likely first order, near 0.4 mK.

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*Note added.*—Recent numerical simulations[20] find a 1 K melting temperature for the $\sqrt{7}\times\sqrt{7}$ structure in agreement with experiment.[5]

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