Magnetic susceptibility of diluted pyrochlore and SCGO antiferromagnets

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We investigate the magnetic susceptibility of the classical Heisenberg antiferromagnet with nearest-neighbour interactions on the geometrically frustrated pyrochlore lattice, for a pure system and in the presence of dilution with nonmagnetic ions. Using the fact that the correlation length in this system for small dilution is always short, we obtain an approximate but accurate expression for the magnetic susceptibility at all temperatures. We extend this theory to the compound $\text{SrCr}_{9-9q}\text{Ga}_{3+9q}\text{O}_{19}$ (SCGO) and provide an explanation of the phenomenological model recently proposed by Schiffer and Daruka (Phys. Rev. B 56, 13712 (1997)).

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The study of magnetic systems with competing interactions has uncovered a wide variety of different physical phenomena [1], such as glass transitions and the existence low-temperature disordered phases. In a class of problems, which has received a great deal of attention recently [2], competition between nearest-neighbour antiferromagnetic exchange interactions arises due to the fact that, in a group of $q \geq 3$ interacting spins, it is not possible for each spin to be antialigned with all its $q-1$ neighbours. Geometric frustration of this kind can give rise to macroscopic ground-state degeneracies, and as early as 1956, a type of lattice was identified [3] for which the ground-state degeneracy is particularly large. In this kind of lattice, the frustrated units (triangles for the kagome and tetrahedra for the pyrochlore lattice, Fig. 1) are arranged to share sites (neighbouring units share one spin) instead of bonds, as is the case in the more familiar triangular and face-centred cubic lattices.

Since the manifold of ground states does not provide an intrinsic energy scale, any perturbation to the simple nearest-neighbour exchange Hamiltonian has to be considered strong and can potentially select different low-temperature physics from the vast range of possibilities provided by the macroscopic degeneracy. One spectacular example is the recently experimentally discovered magnetic analogue of ice [3–5], such magnets usually, but not always [6], freeze [7], a feature which is absent from disordered magnets (Fig. 1), although for the kagome lattice, there has been some work at $T=0$ [8], for infinite-component spin or approximate, which is valid at all temperatures, has so far been proposed for pyrochlore or SCGO antiferromagnets (Fig. 1), although for the kagome lattice, there has been some work for the kagome lattice at $T=0$ [9], for infinite-component spins [10], and using a high-order high-temperature series expansion [11].

Although the presence of at least a small amount of disorder is inevitable, its effect on pyrochlore magnets has so far only been studied qualitatively [12]; again there has been some work for the kagome lattice at $T = 0$ [13]. Recently, Schiffer and Daruka [14] have made the intriguing observation, described in detail below, that the deviation from linear Curie-Weiss behaviour at low tem-
peratures for strongly frustrated magnets appears almost universally as a downturn of $\chi^{-1}$, and that this tendency becomes stronger as the dilution is increased. This effect still awaits a theoretical explanation.

We present here a theory which provides an expression for the energy and susceptibility of a classical Heisenberg pyrochlore antiferromagnet which is exact at zero temperature and asymptotically correct for large temperatures, being a good approximation in between. Our treatment of the effect of dilution with non-magnetic ions applies in the limit of low disorder and is shown by Monte Carlo (MC) simulations to give reliable results for dilutions as large as 20%. We explain the empirical findings of Ref. [7] for SCGO by identifying two relevant mechanisms responsible for the downturn of $\chi^{-1}$, one due to dilution, the other present even in a pure system.

We start with the fundamental observation that the spin-spin correlations of a pure classical Heisenberg antiferromagnet on the pyrochlore lattice are always short-ranged [1][2]. A small amount of dilution does not affect this property and induces neither ordering nor glassiness [9]. The partition function, to be useful, we have to know the properties of the individual units. These can be obtained exactly using a Hubbard-Stratonovich transformation [12]. We define the Hamiltonian for a group of $q$ spins $S_i$ in the presence of a magnetic field $B$, to be

$$H_q(B) = J \sum_{\langle i,j \rangle} S_i \cdot S_j - \sum_{j=1}^{q} B \cdot S_i = \frac{J}{2} \left( \mathbf{L}_q - \frac{B}{2J} \right)^2 , \quad (1)$$

where we have dropped a constant in the last equality. The sum on $\langle i,j \rangle$ runs over all pairs. $J > 0$ is the antiferromagnetic bond strength, and $\mathbf{L}_q$ is the total spin of the unit. The $g$-factor and the Bohr magneton have been absorbed into the definition of $B$. The partition function in zero field, $Z_q$, is calculated to be

$$Z_q = \int \{d\Omega_i\} \exp(-\beta J\mathbf{L}^2/2)$$

$$= (2\pi \beta J)^{-3/2}(2\pi)^{q} \iint d^3K \exp(-K^2/2\beta J)(2\sin K)^q ,$$

where the $\{\Omega_i\}$ are the directions of the $\{S_i\}$ and $\beta = 1/T$ is the inverse temperature. The final integrals may be evaluated in terms of the error function Erf, and we obtain, up to an overall constant:

$$Z_2(T) = T \left( 1 - e^{-\frac{T}{J}} \right) , \quad (2)$$

$$Z_3(T) = T^2 Erf \left( \frac{\sqrt{2/T}}{T} \right) - Erf \left( \frac{3\sqrt{2/T}}{T} \right) , \quad (3)$$

$$Z_4(T) = T^4 \left\{ 2 Erf \left( \frac{\sqrt{2/T}}{T} \right) - Erf \left( \frac{\sqrt{6/T}}{T} \right) \right\}$$

$$\quad - \sqrt{T/8\pi} \left( 1 - e^{-\frac{T}{J}} \right)^2 \left( 3 + 2e^{-\frac{T}{J}} + e^{-\frac{3T}{J}} \right) . \quad (4)$$

The susceptibility per spin, $\chi_q$, can be obtained from these expressions via the fluctuation-dissipation theorem:

$$\chi_q = \langle (M^2) - \langle M \rangle^2 \rangle / (3Tq) .$$

Noting that for one unit, $M^2 = \mathbf{L}^2$ is proportional to the energy, we finally obtain (using $\langle M \rangle = 0$), $\chi_q = 2T/(3qJ) \partial T \ln Z_q(T)$.

For the full system, the Hamiltonian is given by the sum over the Hamiltonians of all $N$ units, $H = \sum_{\alpha=1}^{N} H_q^{(\alpha)}(B/2)$; here, $q_{\alpha}$ is the number of spins in unit $\alpha$, and the magnetic field is divided by two to avoid double counting.

Let us first consider the clean system, $x = 0$, where all units have $q = 4$. In the inset to Fig. 2, we plot the energy per spin versus temperature from MC simulations on 10976 spins (diamonds). Inset: Zero-field energy per spin versus temperature, both in units of $J$.

![FIG. 2. Susceptibility per spin, $\chi$, versus temperature from the single-unit approximation (line) and MC simulations on 10976 spins (diamonds). Inset: Zero-field energy per spin versus temperature, both in units of $J$.](image-url)
strong, the disagreement never exceeds 5%. Remarkably, at the lowest temperatures, the two meet again, and at $T = 0$, our theory gives the exact result $\chi(0) = 1/(8J)$.

Next, we turn to the diluted system. At high $T$, the effect of dilution is to decrease the average number of bonds of each spin, thus giving a reduced Curie-Weiss temperature $\Theta_{\text{CW}}(x) = (1-x)\Theta_{\text{CW}}(0)$ [3]. The main effect of disorder is seen by considering the susceptibility at $T = 0$. On diluting the pyrochlore lattice, the probability of a tetrahedron containing $q$ spins is given by $P_q(x) = \binom{4}{q} (1-x)^q (x^4)^{4-q}$. The effect of a magnetic field on the total spin of a unit is the same for all units. As $T$ decreases, the disagreement never exceeds 5%. Remarkably, $\Theta_{\text{CW}}(x)$ is improbable at small $x$, contains two $q = 1$ units but has a vanishing magnetisation at $T = 0$.

In Fig. 3, we plot the inverse susceptibility $\chi(T)^{-1}$ for different dilutions in the range $0 \leq x \leq 0.2$ at low temperature. Note that for $x$ as large as 0.2, the agreement of our theory with the MC simulations is excellent.

It is worth emphasizing that at any nonzero dilution, the low temperature susceptibility is dominated by the $q = 1$ units. This is analogous to a Griffiths-McCoy effect as it arises from the rare, local event of three neighbouring sites being vacant. The temperature $T$ below which the paramagnetic regions dominate can be defined as the point where the magnetisation due to the $q = 1$ units equals that of the other units combined, which gives $T \propto x^3$. This is why the temperature at which the downturn of $\chi^{-1}$ becomes visible is small and increases with disorder.

Finally, we address in detail the work by Schiffer and Daruka [12], who proposed and successfully used a two-population model to fit the measured $\chi$ to a form $\chi = \frac{C_1}{T + \Theta_w} + \frac{C_2}{T + \Theta_{w2}}$. Here $C_1$ and $\Theta_w$ are the Curie constant and Curie-Weiss temperature of a ‘correlated’ population which forms momentless clusters as $T \to 0$, while $C_2$ and $\Theta_{w2}$ are the parameters for an ‘orphan’ population, which was surmised to be excluded from the correlated population. Analysing experimental data on SCGO from Refs. [14], they found that $\Theta_{w2}$ can be set to zero, so that the orphan population in this case appears truly paramagnetic. For this compound, they present a series of different dilutions, independently determined to be in the range $0.11 \leq x \leq 0.61$, and find that $\Theta_w(x) = (1-x)\Theta_w(0)$ and $C_2(x) \propto x$.

The model we have presented above for the pyrochlores also applies to SCGO [3], which consists of two kagome layers connected by an intervening triangular layer, and can be thought of as a slab of pyrochlore cut in a $(111)$-direction (Fig. 3). Every other kagome triangle is associated with a site in the triangular layer, and these together form $q = 4$ units which generate the short correlation length required for our theory [12].

The two main differences for a theory of SCGO are as follows. Firstly, only two spins (in a triangle not associated with a site of the triangular lattice, as shown in Fig. 3) have to be removed to generate a $q = 1$ unit. Hence these units occur with a probability $3x^2/2$ at low dilution rather than $4x^2$ as in the pyrochlore. Secondly, an additional mechanism is present even for an
undiluted system, which generates a paramagnetic response in SCGO. If the interlayer coupling, which acts between spins of the triangular and the kagome layers, has strength $J'$ different from $J$, the kagome intralayer coupling, the Hamiltonian for a $q = 4$ unit reads $H_4(B) = (J/2) \left\{ (L' - B/(2J))^2 - (1 - J'/J)B \cdot S_t \right\}$, where $S_t$ is the spin in the triangular layer, and $L' = (J'/J)S_t + \sum_{q=1}^{3} S_q$. In the zero-field ground state, each $q = 4$ unit has a finite magnetisation of magnitude $1 - J'/J$. These individual magnetisation vectors are aligned at $T = 0$ even by an infinitesimal field, yielding an infinite susceptibility. Arguments within the single-unit approximation along the lines of those given above predict a susceptibility that diverges as $1/T$ at low temperatures. The value of $J'/J$ is not known accurately, and there is no reason for it to be exactly 1. For a system known to be clean, the divergence of the susceptibility could be used to estimate this quantity.

As a result, at zero and at low dilutions, the model of Ref. [17] is reasonable even though the orphan population is not excluded from the correlated one but present even for the pure system and enhanced by the creation of $q = 1$ units at small dilution. (Genuinely isolated spins of course appear at high dilution.) The empirical fit $C_2(x) \propto x$ is clearly at variance with our theory, since it yields $C_2(x) = (1 - J'/J)^2/21 + x^2/14$ for small $x$. However, there is no contradiction, since the experimental data consists of only five points, and there are no data points sufficiently close to $x = 0$ to distinguish between the two functional forms of $C_2$.

A quantitative comparison of our theory with experiment may be possible in the pyrochlores, since some compounds can be grown with very small amounts of disorder [20]. Introducing controlled amounts of dilution with nonmagnetic ions can then produce a series of samples allowing measurement of susceptibility as a function of disorder and temperature.

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