Magnetic Susceptibility of Diluted Pyrochlore and $SrCr_{9-9x}Ga_{3+9x}O_{19}$ Antiferromagnets

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We investigate the magnetic susceptibility of the classical Heisenberg antiferromagnet with nearest-neighbor 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 $SrCr_{9-9x}Ga_{3+9x}O_{19}$ and provide an explanation of the phenomenological model recently proposed by Schiffer and Daruka [Phys. Rev. B **56**, 13 712 (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 of low-temperature disordered phases. In a class of problems, which has received a great deal of attention recently [2], competition between nearest-neighbor 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 $q - 1$ neighbors. 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 (neighboring units share one spin) instead of bonds, as is the case in the more familiar triangular and face-centered cubic lattices.

Since the manifold of ground states does not provide an intrinsic energy scale, any perturbation to the simple nearest-neighbor 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 analog of ice [3–5]. The recent surge in theoretical research on these systems results in large part from experimental developments (see, e.g., Refs. [4,6,7]). Currently, a systematic study of compounds is under way, in which different rare earth and transition metal ions are placed on the pyrochlore lattice, each of which comes with its own peculiar properties (such as anisotropic or longer-range interactions), so that the space of possible Hamiltonians is mapped out increasingly well.

In this Letter, we study the magnetic susceptibility, χ, of a classical pyrochlore Heisenberg antiferromagnet as a function of temperature, both for the pure system and in the presence of disorder. The magnetic susceptibility is a particularly interesting quantity, since, for a large class of geometrically frustrated magnets, its inverse surprisingly stays close to the linear Curie-Weiss law down to temperatures *much lower* than the Curie-Weiss temperature, Θ_{CW}, where mean-field theory predicts a transition [2]. (Eventually, at $T_F \ll \Theta_{\mathrm{CW}}$, such magnets usually, but not always [7], freeze [8], a feature which is absent from the simple classical pyrochlore Heisenberg model [9–12].) However, to our knowledge, no analytical expression, exact or approximate, which is valid at all temperatures, has so far been proposed for pyrochlore or $SrCr_{9-9x}Ga_{3+9x}O_{19}$ (SCGO) antiferromagnets (Fig. 1), although for the kagome lattice there has been some work at $T = 0$ [13], for infinite-component spins [14], and using a high-order high-temperature series expansion [15].

Although the presence of at least a small amount of disorder is inevitable, its effect on pyrochlore magnets has so far been studied only qualitatively [9,12]; again

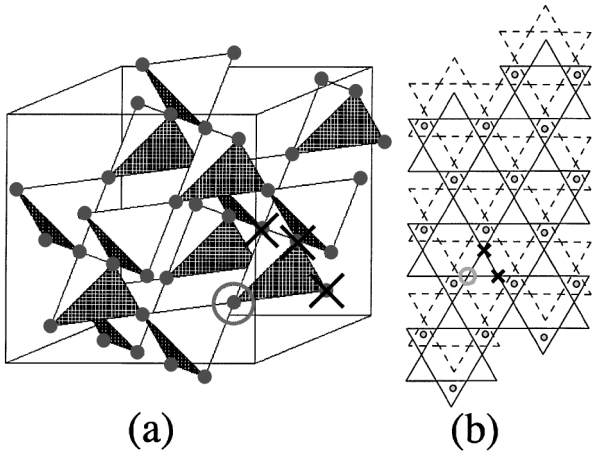

FIG. 1. (a) The pyrochlore lattice, a network of corner-sharing tetrahedra. (b) The trilayer SCGO lattice, consisting of corner-sharing tetrahedra and triangles. The top and bottom kagome layers are denoted by solid and broken lines, respectively, and the intervening triangular lattice by circles. By removing the spins labeled by crosses, only the encircled site of the $q = 1$ unit thus generated is left occupied.

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there has been some work for the kagome lattice at $T = 0$ [16]. Recently, Schiffer and Daruka [17] have made the intriguing observation, described in detail below, that the deviation from linear Curie-Weiss behavior at low temperatures for strongly frustrated magnets appears almost universally as a downturn of χ^{-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 nonmagnetic 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. [17] for SCGO by identifying two mechanisms responsible for the downturn of χ^{-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 [9–12]. A small amount of dilution does not affect this property and induces neither ordering nor glassiness [9]. This ceases to be the case, at the latest, when $1/4$ of all sites are vacant. At this dilution, the possibility of moving local clusters of spins at no cost in energy is lost as the ground-state degeneracy of the magnet ceases to be macroscopic [12]. We make use of this property by treating the weakly diluted lattice as an arrangement of units of $q \leq 4$ spins, which—given the small correlation length characteristic of this regime—are treated as if they were decoupled.

For this approximation, which we refer to as the single-unit approximation, 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 $\mathbf{S}_i$, in the presence of a magnetic field $\mathbf{B}$, to be

$$H_q(\mathbf{B}) = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{i=1}^{q} \mathbf{B} \cdot \mathbf{S}_i \equiv \frac{J}{2} \left(\mathbf{L}_q - \frac{\mathbf{B}}{2J} \right)^2 , \tag{1}$$

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 $\mathbf{B}$. The partition function in zero field, Z_q, is calculated to be

$$\begin{aligned} Z_q &= \int \{d\Omega_i\} \exp(-\beta J \mathbf{L}^2/2) \\ &= (2\pi\beta J)^{-3/2} (2\pi)^q \iiint d^3\mathbf{K} \exp\left(-\frac{K^2}{2\beta J}\right) \\ &\quad \times \left(2 \frac{\sin K}{K}\right)^q , \end{aligned}$$

where the $\{\Omega_i\}$ are the directions of the $\{\mathbf{S}_i\}$, 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,

$$Z_2(T) = T(1 - e^{-2/T}) , \tag{2}$$

$$Z_3(T) = T^{3/2} \{3 \operatorname{erf}(\sqrt{2/T}) - \operatorname{erf}(3\sqrt{2/T})\} , \tag{3}$$

$$\begin{aligned} Z_4(T) = T^{3/2} \{ & 2 \operatorname{erf}(\sqrt{2/T}) - \operatorname{erf}(\sqrt{8/T}) \\ & - \sqrt{T/8\pi}\,(1 - e^{-2/T})^2 \\ & \times (3 + 2e^{-2/T} + e^{-4/T}) \} . \end{aligned} \tag{4}$$

The susceptibility per spin, χ_q (where q is not to be confused with a wave vector), can be obtained from these expressions via the fluctuation-dissipation theorem: $\chi_q = (\langle M^2 \rangle - \langle M \rangle^2)/(3Tq)$. Noting that for one unit $M^2 = \mathbf{L}^2$ is proportional to the energy, we finally obtain (using $\langle M \rangle = 0$), $\chi_q = 2T/(3qJ) \frac{\delta}{\delta T} \ln Z_q(T)$.

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

Let us first consider the clean system, with dilution $x = 0$, where all units have $q = 4$. In Fig. 2, we plot the energy per spin versus temperature in zero field, as obtained from the single-unit approximation and from Monte Carlo simulations. This plot demonstrates the quality of the approximation. The theoretical curves in Fig. 2 are scaled overall to take into account the fact that, in the full system, each spin belongs to two tetrahedra and has six rather than three nearest neighbors. The inset of Fig. 2 shows a plot of the susceptibility. At high temperature, the analytic approximation and the simulation data both follow the Curie-Weiss law and therefore agree. As the temperature is lowered, the analytical result is only approximately valid, since it neglects the emerging longer-range correlations. Still, since these are never 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 $\Theta_{\mathrm{CW}}(x) = (1 - x)\Theta_{\mathrm{CW}}(0)$ [18]. 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 $P_q(x) = \binom{4}{q} (1 - x)^q x^{4-q}$. The effect of a magnetic field on the total spin of a unit is the same for all $q \geq 2$. From Eq. (1), we can read off that $H_q(\mathbf{B})$ is minimized by choosing $\mathbf{L}_q = \mathbf{B}/(2J)$, which is possible for all magnetic fields of strength $B \leq 2Jq$. A difference in the magnetic susceptibility per spin arises only because the total

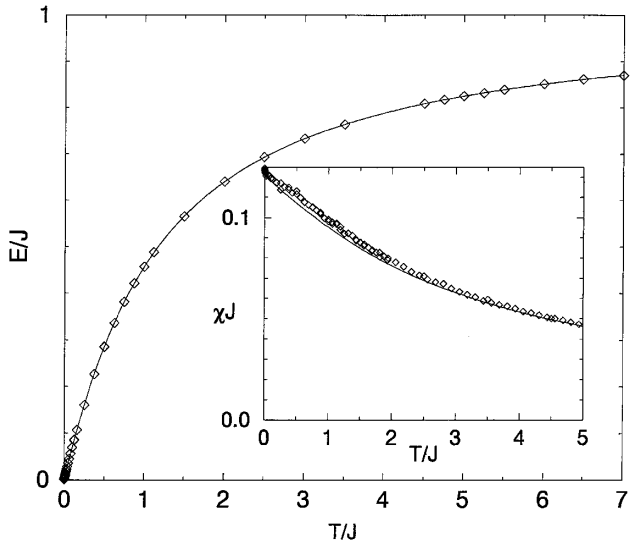

FIG. 2. Zero-field energy and susceptibility (inset) per spin versus temperature from the single-unit approximation (line) and MC simulations on 10 976 spins (diamonds).

magnetization is shared between a total of $q < 4$ spins in a diluted unit. In any case, the susceptibility is finite since $\mathbf{L}_q \propto \mathbf{B}$. This is in striking contrast to the case of $q = 1$, where at $T = 0$ an infinitesimal field suffices to align the spin, and, hence, $\chi_1(0)$ is infinite.

In the full system at low dilution, a unit with $q = 1$ in general corresponds not to an isolated spin but to one which also belongs to a unit with $q \geq 2$ (see Fig. 1). In this regime, there remain sufficiently many undiluted tetrahedra to generate an extensive ground-state dimension and the concomitant finite density of zero-energy modes, i.e., the possibility of reorienting local spin clusters at no cost in energy [12]. As a result, spins separated by a distance larger than the size of such clusters are essentially uncorrelated at all temperatures. Since the spins in the $q = 1$ units are well-separated at low dilution, they behave like *paramagnetic* spins even though they are not isolated.

The behavior at low temperatures is most easily discussed in terms of the thermally averaged square of the total magnetization of the system, $\langle M^2(x,T)\rangle$. By equipartition, a unit with $q \geq 3$ has $\mathbf{L}_q^2 \approx 3T/J$, and one with $q = 2$ has $\mathbf{L}_2^2 \approx 2T/J$, which vanishes as $T \to 0$. By contrast, a unit with $q = 1$ has $\mathbf{L}_1^2 = \mathbf{S}^2 \equiv 1$. Since the magnetization of the system equals the sum of the magnetizations of the units, we obtain $\mathbf{M} = \sum_{\alpha=1}^{N} \mathbf{L}^{(\alpha)}/2$, where the factor $1/2$ accounts for the fact that each spin belongs to two units. Therefore, $\langle M^2(x,T)\rangle = \sum_{\alpha=1}^{N} (\mathbf{L}^{(\alpha)})^2/4 + \sum_{\alpha\neq\alpha'} \langle \mathbf{L}^{(\alpha)} \cdot \mathbf{L}^{(\alpha)'}\rangle/4$. Our computer simulations give $\sum_{\alpha\neq\alpha'} \langle \mathbf{L}^{(\alpha)} \cdot \mathbf{L}^{(\alpha)'}\rangle = 0$ at low temperature, as would be appropriate for completely uncorrelated $\mathbf{L}^{(\alpha)}$. However, from the simulations it appears that this sum vanishes not because the individual terms are zero, but rather because the terms in the sum exactly cancel for $T \to 0$. Hence, $\langle M^2(x,T)\rangle = 6TN(1-x)\chi(x,T) = \sum_q N_q(x)\mathbf{L}_q^2(T)/4$, where $N_q = NP_q(x)$ is the number of units with q spins, and $\mathbf{L}_q^2$ is given by the single-unit expression derived above. The estimate $\langle M^2(0)\rangle = N_1/4 = Nx^3(1-x)$ is asymptotically exact in the limit $x \to 0$. For increasing dilution, terms higher order in x change the situation. For example, the configuration depicted in Fig. 3, which is improbable at small x, contains two $q = 1$ units but has a vanishing magnetization at $T = 0$.

In Fig. 4, 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. The temperature $\tilde{T}$ below which the paramagnetic regions dominate can be defined as the point where the magnetization due to the $q = 1$ units equals that of the other units combined, which gives $\tilde{T} \propto x^3$. This is why the temperature at which the downturn of χ^{-1} becomes visible is small and increases with disorder.

Finally, we address in detail the work by Schiffer and Daruka [17], who proposed and successfully used a two-population model to fit the measured χ to a form $\chi = C_1/(T + \Theta_{w1}) + C_2/(T + \Theta_{w2})$. Here, C_1 and Θ_{w1} are the Curie constant and Curie-Weiss temperature of a "correlated" population which forms momentless clusters as $T \to 0$, while C_2 and Θ_{w2} are the parameters for an "orphan" population, which was surmized to be excluded from the correlated population. Analyzing experimental data on SCGO from Refs. [19], they found that Θ_{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 $\Theta_{w1}(x) = (1-x)\Theta_{w1}(0)$ and $C_2(x) \propto x$.

The model we have presented above for the pyrochlores also applies to SCGO [12], 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 $\langle 111\rangle$ direction (Fig. 1). 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].

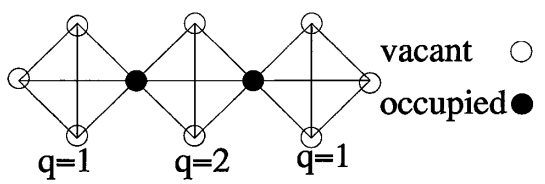

FIG. 3. A configuration containing two $q = 1$ units but with vanishing magnetization at low T.

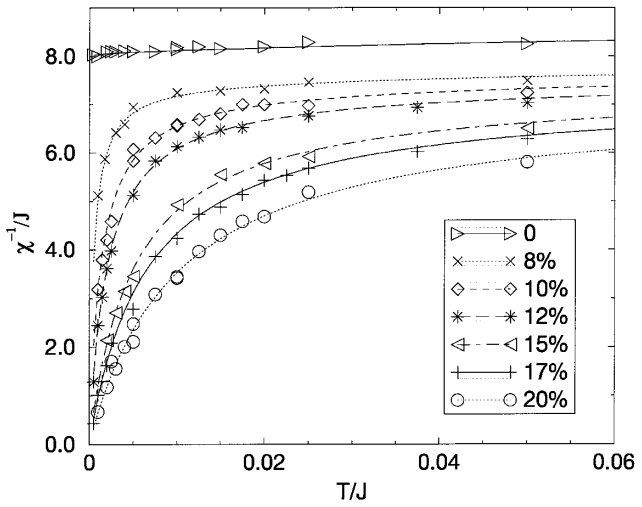

FIG. 4. The inverse susceptibility for different dilutions x. The lines are given by the single-unit approximation without any adjustable parameters. Data points are from MC simulations of a lattice of 5488 tetrahedra.

The two main differences for a theory of SCGO are as follows. First, only two spins (in a triangle not associated with a site of the triangular lattice, as shown in Fig. 1b) 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 $4x^3$ as in the pyrochlore. Second, 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 $H_4(\mathbf{B}) = (J/2)\{[\mathbf{L}' - \mathbf{B}/(2J)]^2 - (1 - J'/J)\mathbf{B} \cdot \mathbf{S}_t\}$, where $\mathbf{S}_t$ is the spin in the triangular layer, and $\mathbf{L}' = (J'/J)\mathbf{S}_t + \sum_{q=1}^{3} \mathbf{S}_i$. In the zero-field ground state, each $q = 4$ unit has a finite magnetization of magnitude $1 - J'/J$. These individual magnetization 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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