Effects of site dilution on the magnetic properties of geometrically frustrated antiferromagnets

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Abstract

The effect of site dilution by non magnetic impurities on the susceptibility of geometrically frustrated antiferromagnets (kagome and pyrochlore lattices) is discussed in the framework of the Generalized Constant Coupling model, for both classical and quantum Heisenberg spins. For the classical diluted pyrochlore lattice, excellent agreement is found when compared with Monte Carlo data. Results for the quantum case are also presented and discussed.

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Introduction.- During recent years, geometrically frustrated antiferromagnets (GFAF) have emerged as a new class of materials, that exhibit novel phases at low temperatures. The elementary unit in these systems is based on the triangle, which makes it impossible to satisfy all the antiferromagnetic interactions at the same time, leading to frustration. Examples of GFAF are the pyrochlore and kagome lattices. Experimentally, it is found that the susceptibility in materials belonging to this class exhibits a high temperature phase in which it follows the Curie–Weiss (CW) law. Below the Curie–Weiss temperature, geometrical frustration inhibits the formation of a long range ordered (LRO) state, and the system remains paramagnetic, even though there are strong correlations between units. This phase is universally present in these systems, and it is called the cooperative paramagnetic phase. Finally, at a certain temperature, $T_f$, which depends on the particular material and, usually, is well below the CW temperature, there appear non universal phases: some of the systems remain paramagnetic down to zero temperature, or even some of them form a spin glass state, even though the amount of disorder in the structure is very small.

In the simplest theoretical description of GFAF, the spins on the lattice are regarded as Heisenberg spins with only nearest neighbor (NN) interactions. In this picture, it is predicted that the non trivial degeneracy of the ground state inhibits the formation of a LRO state, and the system remains paramagnetic down to zero temperature. However, due to the presence of frustration, the NN exchange does not fix an energy scale on the problem, and any small perturbation can break the non trivial degeneracy of the ground state and lead to some kind of ordered state. Therefore, it is especially important to incorporate these possible perturbations in any model that tries to explain the low temperature phases of these systems. Examples of perturbations present in real systems are next nearest neighbor (NNN) interactions, small anisotropies, long range dipole–dipole interaction, or dilution by non magnetic impurities, to cite some.

Of course, before trying to understand the non universal behavior observed below $T_f$, it is very important to fully explore models that quantitatively describe the universal cooperative paramagnetic phase. In a series of recent papers, the present authors have shown how very simple models based on small clusters can provide a very accurate description of the universal cooperative paramagnetic regime in these systems, when compared with both Monte Carlo (MC) and experimental data. The purpose of the present work is to study what are the effects of site dilution by non magnetic impurities of the otherwise perfect pyrochlore and kagome lattices on the magnetic properties in this same regime. This problem is relevant for establishing comparisons with experimental data as, obviously, any real material contains a certain amount of dilution. On more phenomenological grounds, this problem was discussed in Refs. 12,13,14.

The model.- The central idea of the models in Refs. 12,13,14 is based on the experimental and numerical observation that the correlations in these systems are always short ranged. Therefore, we can start by studying the properties of a small cluster and, later, add the interactions with neighboring spins outside the cluster in an approximate way. In the simplest approach, these interactions can be modeled as a mean field. A more refined approximation consists on treating these interactions as created by an effective field which is fixed by a self consistency condition, the so called generalized constant coupling (GCC) approach. This self consistency condition is constructed in the following way: we consider the magnetization per spin of a unit with
\(p\) spins (a triangle for the kagome lattice or a tetrahedron for the pyrochlore lattice, for example), in the presence of the internal field created by the neighboring \(p-1\) spins outside the unit, and the magnetization of an isolated spin in the presence of the internal field created by the \(2(p-1)\) neighboring spins, and we equate both quantities, obtaining in this way an equation for the internal field

\[
m_p \left( \frac{[H_0 + (p-1)H']}{T} \right)/p = m^{\text{CW}} \left( \frac{[H_0 + 2(p-1)H']}{T} \right).
\]  

(1)

In this expression, \(H_0\) is the applied magnetic field and \(H'\) is the internal field; \(m_p\) represents the magnetization of a unit with \(p\) spins and \(m^{\text{CW}}\) the corresponding magnetization for a single spin in the presence of the internal field created by its \(2(p-1)\) NN. Expressions for these quantities can be found in references [3] and [4] for the classical and quantum cases, respectively. Of course, this equation can only be solved numerically in the general case but, in the paramagnetic limit, \([H_0 + 2(p-1)H']/T \ll 1\), we can expand it up to first order in the internal field in terms of the susceptibility of an isolated unit and obtain an analytical expression for the susceptibility per spin in the presence of the internal field

\[
\chi^{\text{gg}}_p(T) = \frac{1}{3J} \frac{1 + \varepsilon_p(T)}{1 - \varepsilon_p(T)},
\]  

(2)

where

\[
\varepsilon_p(T) = \frac{2T^2}{\mu} \frac{\partial}{\partial T} \ln Z_p(T) - 1,
\]  

(3)

with \(T\) a dimensionless temperature defined by \(T/\bar{T}\), where \(\bar{J} = J s_0^2\) in the classical limit (\(J\) is the positive antiferromagnetic exchange coupling and \(s_0\) the length of the spin) and \(\bar{J} = J s_0 (s_0 + 1)\) in the quantum case. \(Z_p\) is the partition function of an isolated unit with \(p\) spins. Expressions for this quantity in the classical limit can be found in Ref. [4]. In the quantum limit, this quantity is given by

\[
Z_p(T) = \sum_S g(S) (2S + 1) e^{-\frac{S(S+1)}{3s_0(s_0+1)}T},
\]  

(4)

where \(S\) represents the total spin of the unit and \(g(S)\) the corresponding degeneracy.

Let us now consider the effect of substituting some of the magnetic ions in the lattice by non-magnetic ions. We will assume that the distribution of non-magnetic impurities is completely random, so the number of units with \(q = 1, 2, \ldots\) magnetic ions for a lattice formed by units with \(p\) ions, for a concentration of non-magnetic impurities \(x\), is given by

\[
P_q^p(x) = \begin{pmatrix} p \end{pmatrix} (1-x)^q x^{p-q}.
\]  

(5)

The self-consistency condition that determines the internal field \(H'\) is given, in this case, in terms of the averaged magnetization for different types of units

\[
(1-x) m^{\text{CW}} \left( \frac{[H + 2(p-1)(1-x)H']}{T} \right) = \frac{1}{p} \sum_{q=1}^{p} P_q^p(x) m_q \left( \frac{[H + (p-1)(1-x)H']}{T} \right),
\]  

(6)

where the \((1-x)\) factor in front of the CW magnetization takes into account the reduction of the total number of magnetic ions upon dilution from \(N\) to \(N (1-x)\), whereas the prefactor in the argument of both magnetizations stands for the reduction in the number of NN.

Figure 2: Classical susceptibilities for the diluted (a) kagome and (b) pyrochlore lattices. The inset shows the same quantity at very low temperatures. The curve labeled as “Curie-Weiss” is given by \(1/(1 + T)\) in this temperature scale.

Equation (8) can be solved for \(H'\), in the paramagnetic region, along the same lines mentioned above, by introducing the function

\[
\varepsilon_p(T, x) = \frac{2T^2}{(1-x)p} \frac{\partial}{\partial T} \ln Z_p(T, x) - 1,
\]  

(7)
which reduces to (8) for $x = 0$, where $Z_p(T, x)$ is an averaged partition function defined by

$$Z_p(T, x) = \prod_{q=1}^{p} Z_q(T)^{\nu_q(x)}.$$  \hspace{1cm} (8)

With these definitions, eq. (8) can be solved in the paramagnetic regime to obtain the averaged susceptibility

$$\chi_p(T, x) = \frac{1 - x + \frac{1}{3} J T}{1 - \bar{\tau}_p(T)}.$$  \hspace{1cm} (9)

The corresponding internal energy per spin is given by

$$\nu_p(T, x) = J \bar{\tau}_p(T, x),$$  \hspace{1cm} (10)

and the specific heat

$$\bar{\tau}_p(T, x) = \frac{\partial}{\partial T} \bar{\tau}_p(T, x).$$  \hspace{1cm} (11)

Discussion: The pyrochlore and kagome lattices have been extensively studied by numerical methods in the classical limit. Therefore, there is a wealth of available data obtained from MC simulations that allow us to estimate the accuracy of our model in the classical limit. Actually, this comparison was recently carried out by the present authors for the non diluted lattices considered in this work, and it was found that both the susceptibility and specific heat are essentially exact for the pyrochlore lattice down to 0 K. In the case of the kagome lattice, however, the susceptibility was found to be again essentially exact, but the MC specific heat deviates slightly as we go to 0 K, due to the order by disorder effect which, obviously, is not included in our model. We will not repeat such a comparison here, as it can be found in Ref. [3].

There are also some results from MC calculations for the case with site dilution but, unfortunately, only for the pyrochlore lattice. They have been compared with the predictions of our model in the classical limit in Fig. 1. As can be seen, the susceptibility predicted by our model is essentially exact down to 0 K. It is important to notice that the curves in that figure do not include any adjustable parameter or global scale factor. Of course, it would be extremely interesting to test the predictions of the model for the kagome case too.

In Figs. 2 and 3 we have plotted the classical and quantum susceptibilities predicted by our model for different concentrations of non magnetic impurities. The quantum susceptibilities depicted there are for the kagome spin 5/2 and spin 1, and pyrochlore spin 3/2. The first one would correspond to the iron jarosites compounds and the last one to ZnCr$_2$O$_4$. The second one would correspond to Mo$^{4+}$ ions on a kagome lattice, and has been included to stress the differences between integer and half integer values of $s_0$ in our model. In these figures, we have rescaled the temperature by the CW temperature

$$\chi_{CW}(x) = \frac{2 \epsilon(x-1/2)}{\epsilon(x)} (1 - x),$$  \hspace{1cm} (10)

and the susceptibility by the CW constant $C_{CW}(x) = \frac{\epsilon(1-x)}{\epsilon p}$. The advantage of this rescaling is that all the curves for different concentrations fall on the same curve at high temperatures, which makes it easier to identify the nontrivial effects of dilution at low temperatures (that is, those which do not come from a reduction of $(1-x)$ factor in both the CW temperature and CW constant).

From those figures, we can see that the main effect of dilution in the quantum kagome and pyrochlore systems, and
also in the classical kagome lattice is that the intensity of the maximum in the susceptibility decreases as the concentration of impurities increases and, eventually, this maximum disappears for a certain amount of non magnetic impurities. In the classical pyrochlore lattice, there is no maximum in the susceptibility, but only a shoulder, due to the formation of short range correlations in the tetrahedral unit. Again, this shoulder disappears for a certain amount of non magnetic impurities. Another effect of dilution is related to the upturn of the susceptibility at low temperatures. Both the classical non-diluted kagome and pyrochlore lattices susceptibilities go to a finite value at 0 K. In the quantum case, the pyrochlore susceptibility in the pure system falls to zero at 0 K. The kagome susceptibility falls to zero for integer values of the individual spins or diverges for half integer values of $s_0$, even in the absence of dilution. This divergence is related to considering a cluster with an odd number of half integer spins, which has a ground state with a $\frac{1}{2}$ total spin momentum. This problem of the model and its implications has been discussed in Ref. [4].

When we add a certain amount of dilution, there is a divergence of the susceptibility as we approach $T = 0$ for all the cases considered in this work. This upturn in both the classical kagome and pyrochlore lattices, and also in the quantum pyrochlore and quantum kagome lattices with integer values of $s_0$, is due to the appearance of loose spins in the system. However, in the quantum kagome with half integer values of $s_0$, this upturn is present even in the pure system, as commented above. In the quantum pyrochlore lattice with half integer $s_0$, both the loose spins and triangular units contribute to this upturn of the susceptibility.

Even though we will not present a detailed comparison with experimental measurements here, it is interesting to note that some of the features exhibited by the calculated quantum susceptibilities are qualitatively similar to those experimentally found in pyrochlore systems [5], [6], [7], iron jarosites [8] (where these last two systems are considered as experimental realizations of the kagome lattice), namely, a maximum in the susceptibility for both the pyrochlore and kagome lattices. The disappearance of this maximum with increasing dilution and the upturn of the susceptibility below the maximum for pure samples has been also observed in the iron jarosites compounds. However, a lot of caution has to be exercised when comparing the present model with experimental data for two main reasons: first, the region where the maximum of the susceptibility is observed, it is precisely the region where spin freezing starts to take place and, obviously, this effect is not accounted for in our model. Second, it is not obvious that the distribution of non magnetic impurities in real systems is purely random and this fact could lead to important quantitative differences when trying to use this model to interpret experimental data.

In any case, we think that the present model could provide further insight in the properties of the geometrically frustrated antiferromagnets in the cooperative paramagnetic region.

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