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Two-population model for anomalous low-temperature magnetism in geometrically frustrated magnets

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Strongly geometrically frustrated magnets are unlike other magnetic materials in that the magnetic susceptibility of such materials appears to follow the Curie-Weiss law down to temperatures well below the Weiss temperature. We present an explanation for this anomalous behavior through a phenomenological model of two separate spin populations. The predictions of this model quantitatively describe the experimental data for a wide variety of lattice topologies and levels of disorder. The apparent dual nature of the ground state in some of these materials and the insensitivity of the ground state to disorder also can be understood within this model. [S0163-1829(97)07146-4]

There has been a great deal of both theoretical and experimental interest in the properties of magnetic materials in which nearest-neighbor antiferromagnetic exchanges are frustrated by the geometry of the lattice.[1–3] Such frustration can lead to a high degeneracy of ground states, and the absence of long-range magnetic order down to zero temperature in an ideal system.[4] A class of strongly geometrically frustrated magnetic materials has recently been identified[2] in which the frustrated nearest-neighbor antiferromagnetic interactions are highly isotropic and dominate other spin-spin interactions—leading to a large number of nearly degenerate spin states. In such materials, long-range magnetic order (typically spin-glass-like) occurs only at a temperature (T_c) well below the energy scale of the antiferromagnetic exchange interactions (as indicated by the Weiss temperature, Θ_w). The unusual magnetic properties of these frustrated materials allow them to serve as model systems for the more general phenomenon of frustration observed in systems such as Josephson-junction arrays and neural networks.[5]

As noted in a recent review by Ramirez,[2] the magnetic susceptibility ($\chi = M/H$) in strongly geometrically frustrated magnets is highly unusual, appearing to obey the Curie-Weiss law ($\chi^{-1}(T) \propto [T+\Theta_w]$) even at temperatures well below $|\Theta_w|$. This linearity of $\chi^{-1}(T)$ is rather unexpected since the Curie-Weiss law is derived from a mean-field calculation in the high-temperature limit ($T \gg |\Theta_w|$). Indeed, *such behavior is seen in no other magnetic systems*. In the present work, we explore the temperature dependence of $\chi^{-1}(T)$ in this intermediate temperature regime ($T_c < T < |\Theta_w|$). We show that the deviation from linear behavior in $\chi^{-1}(T)$ as $T \rightarrow T_c$ is almost universally negative, and we present a phenomenological model which explains the intermediate-temperature magnetic behavior of these materials. The expected susceptibility under this model describes the experimental measurements of $\chi^{-1}(T)$ throughout the entire range $T_c < T \lesssim |\Theta_w|$ extraordinarily well. Furthermore, the model has strong implications for the unexplained low-temperature properties of some of these materials.

Despite considerable interest in geometrically frustrated magnets, the exact nature of the magnetic ground state of such materials is not understood, especially in the context of the high levels of disorder present in many of the compounds. Theoretically, there have been numerous predictions of unusual low-temperature behavior[1,6–8] in geometrically frustrated magnets due to the highly degenerate nature of the ground states. Experimentally there is also substantial evidence for anomalous low-temperature behavior. In $Gd_3Ga_5O_{12}$ (gadolinium gallium garnet or GGG) a spin-glass-like transition has been observed in the virtual absence of disorder,[9] and long-range antiferromagnetic order can be induced by application of a strong magnetic field.[10] In the *kagomé* compound $SrCr_{9p}Ga_{12\text{-}9p}O_{19}$ (SCGO), several[11–13] experiments suggest the existence of a spin-liquid-like state at temperatures well below an apparent spin-glass transition in the bulk magnetization. Similar behavior has been observed in the fluorine-based pyrochlore $CsNiCrF_6$.[14] To date there has been no explanation for this dual nature of the ground state, i.e., how spin-liquid-like behavior can coexist with an apparent freezing of the spins. Also puzzling is that the low-temperature behavior is rather robust against the introduction of strong disorder. In the case of SCGO, the substitution for as many as 60% of the magnetic ions with nonmagnetic ions does not appear to significantly alter the low-temperature thermal and bulk magnetic properties.[11]

While most attention paid to geometrically frustrated magnets has centered on the low-temperature properties, there is a surfeit of data at intermediate temperatures. Previously published intermediate temperature $\chi^{-1}(T)$ data from various geometrically frustrated materials are replotted in Figs. 1 and 2. The spins in each of these materials are situated on topologically distinct frustrated lattices: $S=3/2$ *kagomé* [SCGO (Refs. 11,15)], $S=1/2$ two-dimensional triangular [$NaTiO_2$ (Ref. 2)], $S=5/2$ pyrochlore [$CsMnFeF_6$ (Ref. 16)], $S=5/2$ face-centered cubic [$Cd_{1-x}Mn_xSe$ (Ref. 17)], and $S=7/2$ garnet [GGG (Ref. 9)]. In each case, $\chi^{-1}(T)$ is linear down to temperatures well below $|\Theta_w|$, as it is in other strongly geometrically frustrated magnets such as $Zn_{1-x}Co_xS$ (Ref. 18) and films of ^3He on HD plated grafoil.[19] The common negative sign of the deviation from linearity at the lowest temperatures corresponds to a relative increase in magnetization above an extrapolation of the Curie-Weiss law—opposite of what one might expect from

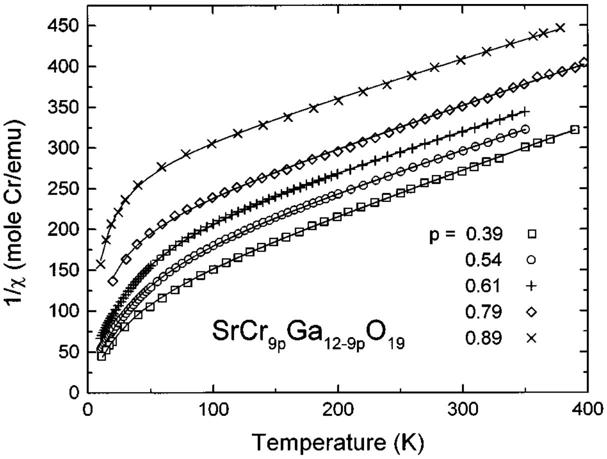

FIG. 1. The inverse magnetic susceptibility of $SrCr_{9p}Ga_{12-9p}O_{19}$ for various values of p (Refs. 11,15). The solid lines are fits as described in the text.

incipient antiferromagnetic correlations. Note that the behavior is qualitatively the same, regardless of the level of disorder which varies from ~1% in GGG to ~60% in SCGO and $Cd_{1-x}Mn_xSe$.

No previous efforts have been made to explain the origin of the common intermediate temperature behavior of $\chi^{-1}(T)$ or treated geometrically frustrated magnets in the presence of strong site disorder. The downturn in $\chi^{-1}(T)$ in SCGO has been attributed by one author to the presence of defects without elaboration,[7] while another work suggests the downturn in $Cd_{1-x}Mn_xSe$ might be the natural consequence of higher-order terms in the series expansion of $\chi^{-1}(T)$.[20] Some theoretical work has addressed the effect of a small percentage of nonmagnetic defects,[6] but not more than ~20% defects or other than in the low-temperature limit. On the other hand, concepts developed to understand the low-temperature limiting behavior can be applied toward understanding the intermediate temperature magnetism. In some theoretically predicted ground states[6,8] for ideal frustrated systems, the spins combine to form antiferromagnetically correlated momentless clusters. Experimental data taken on SCGO in particular have also been interpreted to imply the existence of such clusters in which the spins fluctuate, while maintaining approximately zero net moment as $T \rightarrow 0$,[12,13] and data on magnetic semiconductors such as $Cd_{1-x}Mn_xSe$ have been interpreted to imply the development of ordered antiferromagnetic clusters which also have approximately zero spin.[21] Since these clusters are presumably developing as the temperature is being reduced toward T_c, their development must impact the magnetic behavior at intermediate temperatures. No predictions have been made, however, of how the development of such clusters impacts the magnetic susceptibility, particularly in the presence of disorder.

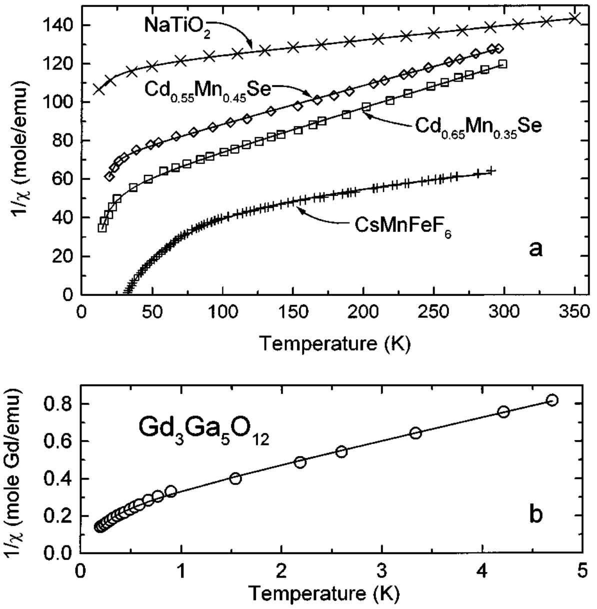

FIG. 2. The inverse magnetic susceptibility of $NaTiO_2$ (Ref. 2) (the magnetic units for this material are arbitrary), $CsMnFeF_6$ (Ref. 16), $Cd_{1-x}Mn_xSe$ (Ref. 17), and GGG (Ref. 9). The solid lines are fits as described in the text.

We propose a model to explain the intermediate temperature behavior of frustrated magnets based on the development of antiferromagnetically correlated spin clusters. In this model we assume that, as the temperature of a frustrated magnet is lowered, most of the spins become strongly correlated with their nearest neighbors and form local antiferromagnetic clusters as discussed above.[22] Since some disorder is inherent in these materials, a small fraction of the spins will be excluded from these correlated clusters. We hypothesize that these excluded ''orphan'' spins will be relatively uncorrelated (i.e., that they will behave like free spins), since the majority of surrounding spins are correlated into approximately momentless clusters. We fit the intermediate temperature $\chi^{-1}(T)$ data under the assumption that each spin belongs to either a population of correlated spins or of orphan spins which are excluded from the correlated clusters. The resulting form is

$$\chi^{-1}(T)=[C_1/(T+\Theta_{w1})+C_2/(T+\Theta_{w2})]^{-1},$$

where C_1 and C_2 are the Curie constants which depend on the size and fraction of the spins in the correlated and orphan spin populations, respectively. The constants Θ_{w1} and Θ_{w2} ($|\Theta_{w1}| \gg |\Theta_{w2}|$) are the effective values of Θ_w which reflect the effective exchange field for the spins in the correlated and orphan spin populations, respectively. The resultant fit is remarkably exact as shown by the solid lines in Figs. 1 and 2 (the parameters are given in Table I). In all cases, we find $C_2 \ll C_1$ as expected. For SCGO, $NaTiO_2$, and GGG, we fix $\Theta_{w2}=0$ so *the fit contains only three free parameters*. In the cases of $CsMnFeF_6$ and $Cd_{1-x}Mn_xSe$, a small nonzero $\Theta_{w2}(|\Theta_{w2}| < |\Theta_{w1}|/20)$ was required to describe the data. These materials are the most disordered and multiply connected of those studied here, so it is perhaps not surprising that the orphan spins would be subject to small effective exchange fields. Within this model, the universal downturn in $\chi^{-1}(T)$ results from the relatively large low-temperature susceptibility of the orphan spins compared to the correlated spins (see inset to Fig. 3).

To test the model further, we compared the fit parameters to the data taken on the different samples of SCGO. One would expect under this model that the parameter C_2, which is proportional to the number of orphan spins, would scale

TABLE I. The parameters from the fits in Figs. 1 and 2.

Material	C_1	Θ_{w1} (K)	C_2	Θ_{w2} (K)
SCGO ($p=0.89$)	2.21 (3)	639 (12)	0.0279 (6)	0 (fixed)
SCGO ($p=0.79$)	1.96 (2)	438 (8)	0.055 (2)	0 (fixed)
SCGO ($p=0.61$)	2.14 (2)	487 (8)	0.121 (1)	0 (fixed)
SCGO ($p=0.54$)	1.99 (2)	406 (9)	0.164 (1)	0 (fixed)
SCGO ($p=0.39$)	1.71 (1)	263 (5)	0.190 (3)	0 (fixed)
GGG	7.6 (2)	2.4 (2)	0.81 (5)	0 (fixed)
$NaTiO_2$	14.0 (2)	1670 (20)	0.0129 (4)	0 (fixed)
$CsMnFeF_6$	17 (1)	1000 (90)	0.68 (1)	−31.6 (2)
$Cd_{0.55}Mn_{0.45}Se$	5.05 (5)	352 (6)	0.011 (2)	−15.1 (9)
$Cd_{0.65}Mn_{0.35}Se$	4.47 (4)	248 (5)	0.062 (6)	−9.3 (6)

with the percentage of nonmagnetic Ga ions on the Cr sites which break up the clusters. As shown in Fig. 3, we find this to be precisely the case and the scaling to be linear. That only three free parameters are required to describe the data and that these data were taken on samples synthesized by three different methods adds further credence to the validity of this relation. Notice also that Θ_{w2} is linear in p with a zero intercept as predicted to be the case in the high-temperature limit for any diluted magnet.[20] The data are not available to make similar tests in $Cd_{1-x}Mn_xSe$ in which the spins within the clusters are ordered antiferromagnetically[21] or in the case of GGG where the defects are excess spins rather than dilution with nonmagnetic ions, but the model of a correlated and an orphan spin population seems to describe the data rather well in each case.

One cannot expect from the Curie-Weiss law that $\chi^{-1}(T)$ for the correlated spins in the clusters should be linear for $T<|\Theta_w|$ since the Curie-Weiss law is a high-temperature and mean-field result. To test the assumption that $\chi^{-1}(T)$ would be linear for these spins, we therefore calculated the longitudinal susceptibility[20] from Monte Carlo simulations of correlated clusters of three and four classical Heisenberg spins ($S=1$) with frustrated antiferromagnetic interactions (J is constant and antiferromagnetic between all spin pairs in the clusters). As expected in our model, such clusters show nearly linear $\chi^{-1}(T)$ at temperatures $T \ll J/k_B$ with a slope ~4% less than that for free spins (Fig. 4). There is a slight upward curvature, as the slope approaches the high-temperature free-spin value $[d\chi^{-1}(T)/dT=3]$. Such nearly linear behavior has previously been demonstrated in Monte Carlo simulations on defect-free pyrochlore and *kagomé* lattices,[4,7] suggesting that $\chi^{-1}(T)$ will be linear for $T<J/K_B$ in a geometrically frustrated cluster of spins regardless of the cluster size.

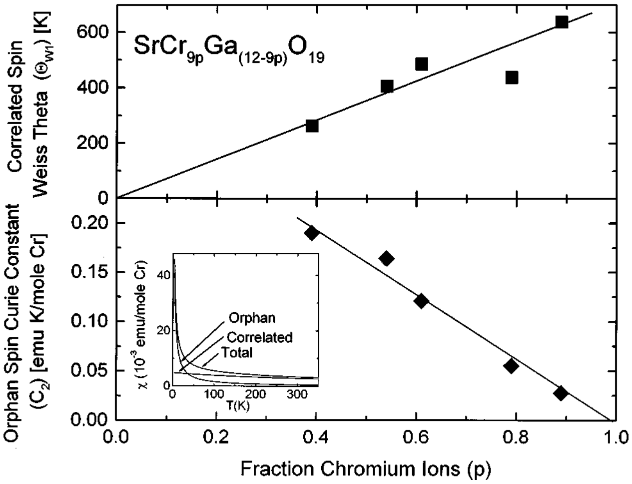

FIG. 3. The parameters C_2 and Θ_{w1} plotted as a function of Cr concentration, from the fits in Fig. 1 (lines are merely guides for the eye). The inset shows the relative contribution of the correlated and ''orphan'' spins for $p=0.54$.

This phenomenological model leads to relatively simple explanations for some outstanding characteristics of SCGO which have been the subject of much recent attention.[11–13,15,23] Since the orphan spins are responsible for most of the susceptibility as $T \rightarrow T_c$, the observation of spin freezing at T_c could be only indicating the behavior of the orphan spins. The majority of the spins, which are within correlated clusters, could presumably continue to fluctuate down to $T \ll T_c$. This would explain why the scattering and μSR experiments see spin fluctuations for $T \ll T_c$, while the bulk magnetization measurements observe a spin freezing. Given that the spins which are freezing are the orphan spins and not the correlated spins, we can also understand why the anomalous thermal properties are rather robust against dilution with nonmagnetic ions,[11] since the correlated clusters retain their spin-liquid-like nature even when the frustrated lattice is strongly diluted by nonmagnetic ions. This model does suggest a reexamination of some of the conclusions of a recent paper[15] on single crystals of SCGO, since the observed anisotropy is presumably due primarily to the orphan spins in the model.

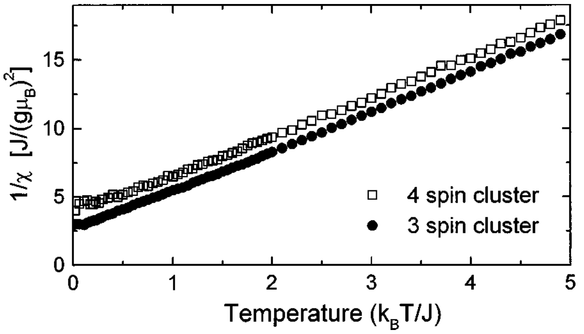

FIG. 4. The inverse magnetic susceptibility per spin of three and four spin clusters from Monte Carlo calculations demonstrating Curie-Weiss-like behavior at low temperatures.

In conclusion, we have shown that strongly geometrically frustrated magnets display a common behavior in their intermediate temperature magnetic susceptibility, and that this behavior can be understood within a simple phenomenological model. This model is by no means a complete description of the behavior of such systems and must certainly be extended considerably, incorporating the characteristics of each material, in order to fully understand the low-temperature properties of geometrically frustrated magnets. In particular the exact nature of the orphan spins is unclear, and it is somewhat surprising that a model which assumes such spins to be isolated should work so well when there are no physically isolated magnetic ions in these materials. This model does, however, reproduce the features of the data exceedingly well, and it also provides a possible explanation for several of the outstanding features in the data.

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