Strong Frustration and Dilution-Enhanced Order in a Quasi-2D Spin Glass

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The interactions in the magnetoplumbite isomorph $SrCr_8Ga_4O_{19}$ are highly frustrated. Thermodynamic data are presented and show the existence of a transition from paramagnetic to spin-glass ordering but only at $T_c = 3.3$ K, despite the high Curie-Weiss temperature of 515 K. Other unusual properties include a low-temperature specific heat varying as T^2 and an inverse relationship of T_c to magnetic-ion concentration for a set of differently prepared crystals. The latter result is conjectured to arise from competition between 2D frustration and a tendency toward 3D order, controlled by preferential site substitution.

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Frustration, that is, a structural prohibition against satisfying the lowest-energy state of each bipartite bond,[1,2] exists in many types of magnetic systems and leads to different phenomena depending on the degree of site disorder present in the crystal. In computer simulations of periodic site-ordered systems, frustration leads to a variety of unusual topological excitations and ordering phenomena.[3,4] In real compounds, however, there usually exist additional interactions which relieve the frustration and allow the system to order at a temperature comparable to the dominant interaction strength. On the other hand, in systems which possess site disorder, frustration often leads to a spin-glass (SG) state. Although all SG materials exhibit some frustration, two of the most highly frustrated compounds—the cubic *B*-site spinels $Zn(Cr,Ga)_2O_4$ (Ref. 5) and $CsNiFeF_6$ (Ref. 6)—display some unconventional SG behavior. This behavior might be due to an overriding influence of frustration relative to disorder in raising the ground-state degeneracy. If so, then compounds capable of supporting even higher degrees of frustration than those mentioned above might yield phenomena similar to that found in simulations or at least distinct from conventional SG behavior.

In this paper we describe magnetothermal measurements on such a highly frustrated system, $SrCr_{8-x}Ga_{4+x}O_{19}$ (Sr-Cr-Ga-O), first described by Obradors *et al.*[7] We have studied the ordering into a SG state and find several unusual effects, including a quadratic temperature dependence of the specific heat below the SG transition and the novel result of an enhancement of this transition temperature with decreasing magnetic-ion concentration.

For the present study, three different types of samples were synthesized. The Cr content, which varies over quite a wide range, was inferred afterwards from both the high-temperature susceptibility and x-ray fluorescence spectroscopy (XFS). The most highly Cr-concentrated specimen, $x=0$, was a ceramic prepared using the appropriate amounts of 99.999% $SrCO_3$, Cr_2O_3, and Ga_2O_3. Microcrystalline ($x=1.0$) material was grown from a SrO-B_2O_3 solvent and single crystals ($x=4.5$) were grown from a Bi_2O_3-V_2O_5 solvent. Although a large amount of Bi was found by XFS in the single crystals (no V was detected), the Debye-Scherer powder photographs exhibited single-phase material with highly resolved back reflections for all samples. Since the Bi^{3+} ion will presumably occupy the Sr^{2+} site, its incorporation will lead to Cr or Ga site vacancies in order to maintain charge balance in this insulating material. In the worst case of full Bi substitution, this will lead to only a 5% overestimate of the Cr content. The hexagonal lattice parameters were $a=5.792\pm0.01$ Å and $c=22.677\pm0.004$ Å for the ceramic and microcrystallites, and $a=5.798\pm0.001$ Å and $c=22.713\pm0.004$ Å for the single crystals. Attempts were made to synthesize $x<0$ material but resulted in finite amounts of a second phase, most likely due to a steric hindrance effect operative during growth.

All susceptibility data were taken with a Quantum Design SQUID magnetometer. The high-temperature data were taken in an applied field of 0.1 T, and the low-temperature data were taken in a 5 ± 0.2-mT field. Specific-heat data were taken in a ^{3}He-^{4}He dilution refrigerator, using a standard semiadiabatic heat-pulsed method.

The structure of Sr-Cr-Ga-O showing only the octahedral Cr^{3+} sites for half of the *c* dimension of the unit cell is drawn in Fig. 1. There are three sites which are structurally segregated into three distinct layers. The Cr occupation is 86%, 100%, and 86% for the 12*k*, 12*a*, and 4*f* sites of the $P6_3/mmc$ space group, respectively, in the $x=0$ samples, with the remaining sites filled with Ga^{3+}. However, the 12*k* sites contain 65% of all the Cr ions and form a lattice of corner-sharing triangles, the Kagomé lattice, with nearest-neighbor distances as shown in Fig. 1. The close proximity and high density of Cr ions within the Kagomé lattice is the main evidence for quasi-two-dimensionality of the magnetic behavior. The spin dimensionality is inferred from the single-crystal susceptibility data. These show an enhancement in the *c* direction starting to appear below 100 K; thus the spin correlations appear to be weakly Ising-like with *c* the easy axis.

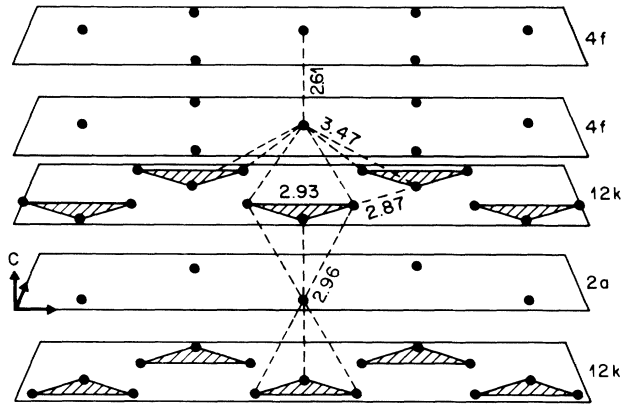

FIG. 1. Structure of $SrCr_9Ga_3O_{19}$ showing only the Cr sites. The $2a$ layer is fully occupied, and the $12k$ and $4f$ layers are only 86% occupied. The relevant nearest-neighbor bond distances are shown in angstroms.

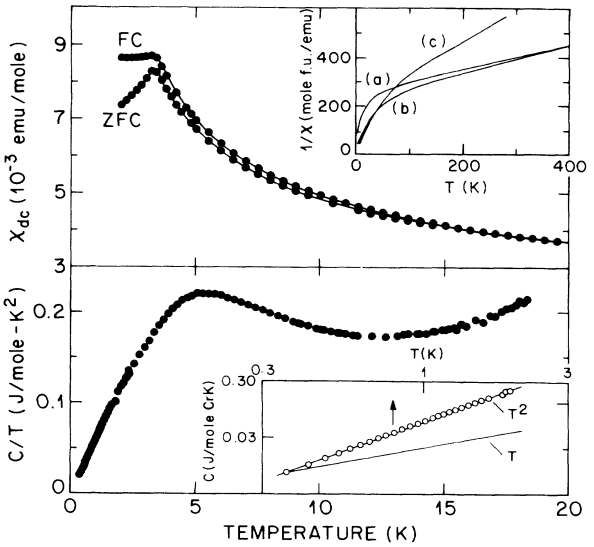

FIG. 2. dc susceptibility, χ_{dc}, in the zero-field-cooled (ZFC) and field-cooled (FC) states, and specific heat, $C(T)$, divided by temperature for $SrCr_8Ga_4O_{19}$. Upper inset: The inverse susceptibility, normalized to the $x=0$ formula-unit mole weight, vs temperature for the three $SrCr_{8-x}Ga_{4+x}O_{19}$ samples studied: (curve *a*) $x=0$ ceramic, (curve *b*) $x=1.0$ microcrystalline, and (curve *c*) $x=4.5$ single crystal. Lower inset: The low-temperature $C(T)$ data on an expanded log-log scale with lines drawn to show linear and quadratic power-law behavior.

The main evidence for a frustrated state comes from the disparity between the expected ordering temperature, Θ_{CW}, and the actual temperature, T_c, where an ordering-like anomaly is observed. Here, Θ_{CW} is extracted from a high-temperature Curie-Weiss law $\chi_{dc}^{-1}=A(T+\Theta_{CW})$, which the data are found to obey above 150 K. For $x=0$, $\Theta_{CW}=515$ K (the effective moment is $4.07\mu_B$, a typical value for Cr^{3+}), yet no ordering anomaly is seen until $T_c=3.5$ K, so that $\Theta_{CW}/T_c=150$. Such a large disparity between the expected and eventual T_c suggests a cooperative hindrance for ordering arising from an unusual coordination of interaction neighbors. The particular structure of Sr-Cr-Ga-O further suggests that bond frustration plays a major role for the magnetic disorder. For reference, the next most highly frustrated system, to our knowledge, is $CsNiFeF_6$ (Ref. 6) with $\Theta_{CW}/T_c=45$. It is intriguing that at temperatures above the uniaxial anisotropy energy but still well below Θ_{CW}, the spins do not order. This is, perhaps, a manifestation of the two-dimensional character of the dominant interaction for Heisenberg spins.[8] As the temperature is lowered and the anisotropy becomes more influential, the frustration inherent to the Kagomé lattice further inhibits the tendency to order. Thus, the extremely low value found for the ordering anomaly seems to be a direct result of the two dimensionality of the crystal structure.

The anomaly seen at 3.5 K for the $x=0$ specimen can be shown to result from a SG type of transition. This is first indicated by $\chi_{dc}(T)$ and the specific heat, $C(T)$, shown in Fig. 2. The susceptibility at 5 mT shows a cusp at 3.5 K and a marked difference below this temperature depending on whether the sample was zero-field cooled (ZFC) or field cooled (FC). A small amount of irreversibility is seen above the cusp and can perhaps be attributed to blocking of superparamagnetic clusters. Such short-range-ordered regions are expected to exist at these temperatures, given the extremely large interaction strengths implied by Θ_{CW}. The specific heat is smoothly varying at the temperature where χ_{dc} peaks and exhibits a broad maximum peaking at a 60% higher temperature. This behavior, namely, the discrepancy between $C(T)$ and $\chi(T)_{dc}$ peak temperatures and the difference between FC and ZFC susceptibility, is typical for SG and is usually ascribed to the absence of a well-defined equilibrium state. Well below the maximum, $C(T)$ obeys a T^2 law. This contrasts sharply with the linear dependence expected of SG. Hence, the density of states for magnetic excitations is more strongly temperature dependent than in most spin glasses. This implies that the blocking of spins in this strongly frustrated system has a different dynamic nature than in a SG dominated by configurational disorder. It is interesting to note that T^2 is the expected form for two-dimensional antiferromagnetic spin waves, implying the existence of large 2D correlated regions.

Although the cusp in $\chi(T)_{dc}$ would seem to indicate a SG transition, it is alternatively conceivable, especially in light of the irreversibility discussed above, that it results from a blocking, or dynamical freezing transition, of a collection of superparamagnetic clusters.[9,10] Such a system cannot be characterized by an order parameter and a diverging correlation length. This explanation can be ruled out by the observed behavior of the nonlinear susceptibility, a_3, defined in terms of the magnetization, M, and applied field, H, in the usual way:[10]

$$M=a_1H-a_3H^3+a_5H^5-\cdots. \quad (1)$$

Mean-field SG theory predicts the divergence of a_3 at the SG freezing temperature[11,12] with the form $a_3 \propto (T-T_f)^{-\gamma}$, where γ is typically between 1 and 4 (Ref. 10) for most SG. The data shown in Fig. 3 were obtained by measuring M vs H at fixed temperatures, at a rate of 0.2 T/(30 min), after cooling in a finite field (0.2 T). The data were then fitted by an odd-order polynomial plus a constant offset term and a $1/H$ term to reduce systematic errors while maintaining a reasonable χ^2 statistic. Both of these modifications to the expected form of Eq. (1) are significant only at low fields and have little effect on the derived values of a_3. The nonlinear part of the magnetization, $-M_{\mathrm{NL}}$, is plotted in Fig. 3 for several temperature values and shows the qualitative effect near the transition. The full set of a_3 data is shown in the inset. Of the two sets of data, a_3 is most severely flattened around T_c for the dense data set which was obtained in roughly twice the time, ~36 h, as the sparse set. If one takes for the transition temperature the middle of the flattened region, $T_c = 3.3 \pm 0.05$ K, and fits the data for both sets outside this region, then a value of $\gamma = 2.1$ is found for the critical exponent. Alternatively, if one assumes $T_c = 0$, γ is found to be ~13. A similar peaking of a_3 was also found in the diluted crystals for both directions of applied field. The divergence of a_3 at a finite temperature with a reasonable exponent thus constitutes strong evidence that the peak in χ_{dc} not only corresponds to a spin-glass transition but that the ordering is three dimensional, since two-dimensional spin glasses are not expected to order at a finite temperature.[13]

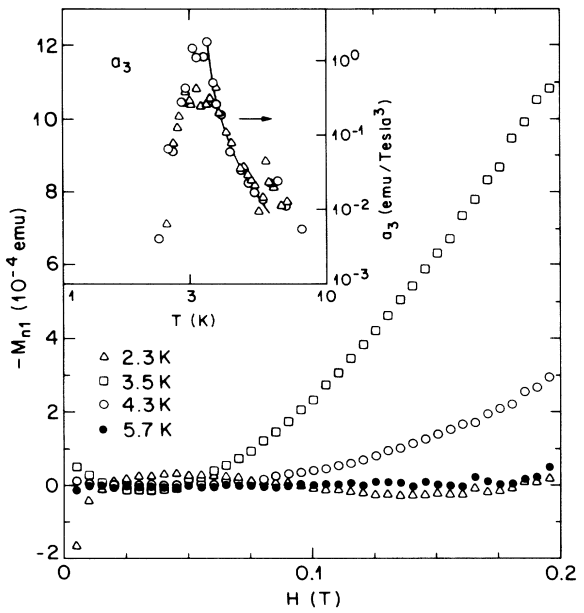

FIG. 3. Nonlinear magnetization, $-M_{\mathrm{NL}}$, for $SrCr_8Ga_4O_{19}$ at selected temperatures above and below the ordering temperature. Inset: The temperature dependence of the a_3 coefficient (defined in the text). The behavior above the peak has been fitted by a power-law divergence with $T_c = 3.3$ K and exponent $\gamma = 2.1$, and is shown by the solid line.

The existence of SG order in Sr-Cr-Ga-O is, by itself, quite unusual. There are very few materials which possess a small amount of site disorder ($x = 0$ corresponds to 89% occupation on the Cr sites), yet still become SG.[14] In none of these compounds, however, is the frustration as strong as in Sr-Cr-Ga-O. It is, therefore, of interest to study the effect of additional site disorder by dilution on the magnetic site. The variation of Cr concentration in the three crystal types studied here is indicated by the differing slopes of χ^{-1}, as shown in the inset of Fig. 1, and confirmed by XFS. By scaling the concentration as the inverse of the slope, starting from the known value for the $x = 0$ (Ref. 7) compound, we find the Cr occupancy on the Cr-octahedral sites to be 0.89, 0.77, and 0.38 for the ceramic, microcrystalline, and single-crystal specimens, respectively. In addition, we find $\Theta_{\mathrm{CW}} = 515$, 393, and 187 K for the three specimens. Normally, one would expect Θ_{CW} to scale with the number of nearest neighbors, via the concentration, in a mean-field model. The observed deviation from strict scaling (187 is 15% less than expected) might be a sign of preferential Cr removal from the sites with the strongest bonds, i.e., the $12k$ sites. Such site disorder is also indicated by a 40% reduction in the quadratic specific-heat term and the appearance of a linear term of 0.10 J/mol-Cr K^2 on going from $p = 0.89$ to 0.38. This transferral of entropy from spin-wave to tunneling-type modes is most easily explained by the presence of large additional disorder among the sites containing the most strongly interacting Cr ions.

The most unusual effect of dilution, however, is the increase of the SG ordering temperature. SG order is a collective effect and one might naively expect T_c to be proportional to the number of nearest neighbors. While such behavior is observed universally in conventional magnets,[15] it is not obvious that it should always be seen in SG where the order parameter is not a simple quantity like the magnetization (and not always well understood for specific compounds). It is, in fact, the case that nearly all SG T_c's increase with increasing concentration in the dilute limit.[16] On further increasing the concentration, the paramagnetic- (PM-) to-SG boundary merges with a PM-ferromagnetic (or antiferromagnetic) boundary. Therefore, the behavior shown in Fig. 4 seems to be novel. It is seen that the particular type of SG order developed in Sr-Cr-Ga-O is actually enhanced when magnetic ions are removed from the lattice. Since 65% of the ions sit in a 2D layer thought to be frustrated and since a_3 seems to diverge at a finite temperature, unlike a 2D system,[12] it is possible that dilution actually increases the effective dimensionality of the magnetic system from two to three. This would happen if, for instance, Cr is removed preferentially from the $12k$ layers, as conjectured above for the Θ_{CW} variation, having the dual effect of relieving the frustration within the layer and decreasing the ratio of intraplane to interplane bonds.

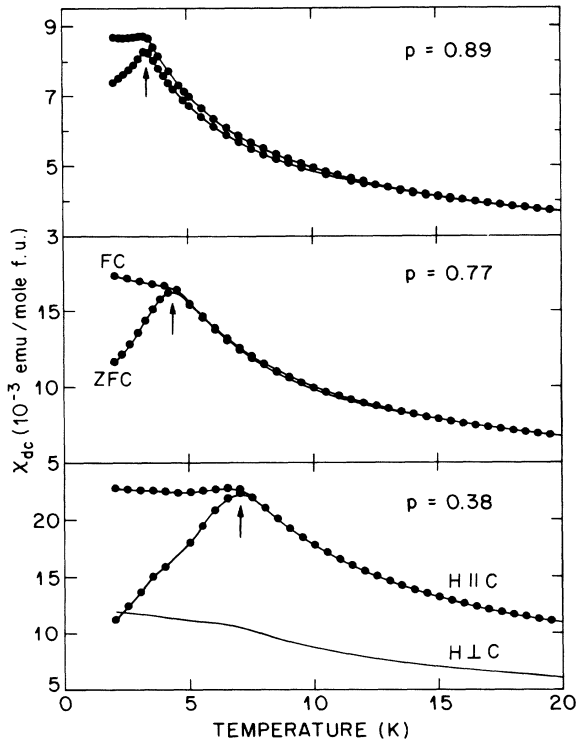

FIG. 4. dc susceptibility vs temperature, in the FC and ZFC states for the three samples studied. The label p is the magnetic site occupancy. The increase of T_c, indicated by an arrow, with decreasing p is a result of strong frustration. The data for the $p=0.38$ single crystal show a marked difference for fields parallel and perpendicular to the c axis, demonstrating the weak Ising-like anisotropy.

In conclusion, we have shown that the novel effect of increasing SG ordering temperature on dilution occurs in large crystals of Sr-Cr-Ga-O. In addition, the low-temperature specific heat has the temperature dependence of spin waves in a long-range-ordered 2D antiferromagnet, thus differing significantly from the usual SG behavior. These results seem to arise from the dominating influence of frustration relative to site disorder in this compound. Further work will involve microscopic structural and magnetic probes to determine the fractional occupancy of the Cr sites and the interaction strengths between these sites.

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Note added.—Chandra and Coleman[17] have recently explained how a T^2 specific heat can coexist without an ordered moment in a 2D frustrated Heisenberg system. In their theory, it arises from a double-spin-flip Goldstone mode in a quantum spin liquid with tensorial long-range order.

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