Interaction-Induced Spin Coplanarity in a Kagomé Magnet: $SrCr_{9p}Ga_{12-9p}O_{19}$

P. Schiffer*
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

A. P. Ramirez, K. N. Franklin,† and S-W. Cheong
Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974
(Received 2 October 1995)

We report the first detailed magnetic measurements on single crystals of the frustrated kagomé magnet $SrCr_{9p}Ga_{12-9p}O_{19}$. Significant anisotropy develops in the linear susceptibility at low temperatures, providing experimental evidence for coplanar spin states. In a magnetic field, the anisotropy is suppressed and displays a peak (unreported in other spin-glass-like materials) at temperatures well above the spin-glass-like transition. The signatures of the spin-glass-like transition also show strong anisotropy, suggesting that the component of the system's magnetization which is normal to the kagomé planes freezes completely, while the component parallel to the planes does not. [S0031-9007(96)01104-0]

PACS numbers: 75.50.Lk, 75.30.Gw, 75.50.Ee

There has been much recent interest in magnetic materials which have antiferromagnetic exchange interactions frustrated by the intrinsic geometry of the magnetic sublattice [1]. The high degeneracy of states due to frustration is expected to lead to spin-liquid-like collective behavior where the spins fluctuate at low temperatures despite interacting strongly with each other. The nature of the ground states of pure frustrated systems is the subject of much theoretical work, and real frustrated magnetic materials do display low-temperature behavior not observed in other magnets [2–5].

The geometrically frustrated magnetic material which has received the most attention is $SrCr_{9p}Ga_{12-9p}O_{19}$ (SCGO), in which (for $p = 1$) 67% of the spin 3/2 Cr^{3+} ions are arranged on a two-dimensional (2D) kagomé lattice consisting of corner-sharing triangles [3–6]. Although the antiferromagnetic Weiss theta (Θ_W) is between -200 and -500 K depending on the Cr concentration, no long range order is observed in this system above $T = 1$ K [4]. This indicates that the antiferromagnetic interactions are highly frustrated by the kagomé geometry of the lattice. SCGO does undergo a transition into a novel magnetic state [3], but only at $T \ll |\Theta_W|(T_c \sim 5$ K). In this low temperature state, SCGO has the bulk magnetic properties of a spin glass, but thermal properties which are usually associated with a two dimensional antiferromagnet (specific heat $\sim T^2$). Neutron scattering [4] and muon spin rotation (μSR) [5] data indicate that the spins are not strictly frozen in this low-temperature state, but rather continue to fluctuate down to very low temperatures, which is consistent with spin-liquid-like behavior. The anisotropic structure of SCGO suggests that these fluctuations are likewise anisotropic, and understanding this anisotropy is crucial to the goal of understanding the novel ground state. Indeed much theoretical work has addressed the idea of an anisotropic spin liquid in a kagomé spin system [7–9]. A common feature of these theories is the prediction that the spins have a coplanar ground state configuration (assuming the presence of either thermal or quantum mechanical fluctuations), a prediction which can be tested in single crystal samples.

In this paper we report measurements on macroscopic singe crystals of SCGO. We find that as spin correlations develop upon cooling, the dc magnetic susceptibility ($\chi = M/H$) develops significant ($\sim$160%) anisotropy, providing the first experimental evidence of the theoretically predicted development of spin coplanarity. In the presence of a strong magnetic field, the anisotropy is suppressed but displays a peak at temperatures well above T_c. The peak in the anisotropy, indicative of a dimensionality crossover as $T \to T_c$, has never before been reported in any anisotropic spin-glass-like material. The spin freezing at T_c is also anisotropic in both χ and the nonlinear susceptibility (χ_3). The results suggest that the component of the magnetization normal to the kagomé planes ($M_\perp$) freezes much more completely than the component in the planes ($M_\parallel$), which our data show continuing to fluctuate to $T < T_c/3$. The existence of anisotropic freezing provides a physical model for the coexistence of spin freezing and spin-liquid-like behavior which has been observed in previous studies.

The magnetic Cr^{3+} ions in SCGO are arranged in a repeating pattern of five stacked 2D layers in which the second and fourth layers have the kagomé structure and the others have a much less dense triangular structure in registry with the kagomé [3,6]. The excess Ga ions on the Cr sites have been found to be distributed randomly on those sites [6]. Single crystals of SCGO with dimensions large enough to allow measurements of a single grain possessing a hexagonal crystal habit were grown for the first time from Bi_2O_3 and B_2O_3 based flux with slow cooling in the temperature range between 1350 and 900 °C. The crystals have typical size $\sim$5 mm wide $\times$ 1 mm thick with weight $\sim$0.05 g. The x-ray powder

diffraction pattern at room temperature was consistent with the hexagonal magnetoplumbite structure of SCGO.

The concentration of Cr atoms (p) was determined from high temperature and high field ($4T$) fits of χ^{-1} vs T to Curie-Weiss behavior: $\chi^{-1}(T) = (T - \Theta_W)/N\mu^2$ where μ is the effective moment and N is the number of spins. The ratio of μ to the expected value for 100% Cr concentration gives the actual concentration in the samples. We label the samples studied as A, B, and C which had values for p of 0.42, 0.50, and 0.56; masses of 9.7, 27.0, and 20.4 mg; values for Θ_W of -203, -271, -312 K; and transition temperatures (based on the separation of field-cooled and zero-field-cooled data) of 7.2, 6.5, and 4.8 K for A, B, and C, respectively. The heat capacity of our samples had low temperature behavior consistent with that seen in previously studied ceramic samples, confirming that their magnetic properties are governed by the same physics. Sample A was actually four crystals grown by a different method (which produced much smaller crystals) [10]. The data shown below were all taken from sample B, but the results were equivalent to those in all of the other samples.

The measurements were performed on a commercial magnetometer (Quantum Design) using a carefully machined epoxy sample holder to orient the crystals within $\pm 2°$ of the intended orientation. The data have been corrected for the small diamagnetic magnetization of the sample holder. The samples all displayed effects of ferromagnetic impurities equivalent to $\sim$10 ppm of the Cr ions, the magnetization of which was saturated in fields above 0.5 T and which had a negligible ($\sim$1%) effect on the data.

The linear high temperature Curie-Weiss behavior, $\chi^{-1} \sim T - \Theta_W$, is seen in the inset to Fig. 1. That this behavior extends to temperatures well below $|\Theta_W|$ is a measure of the high level of frustration in the system [1] since one expects linear temperature dependence of χ^{-1} from only nearest neighbor correlations. The absence of deviations from linearity at $T \sim |\Theta_W|$ indicates that further neighbor correlations are suppressed by the frustration. At $\sim$120 K, however, $\chi^{-1}(T)$ deviates below linearity, as seen in the inset to Fig. 1, which suggests a decrease in both the effective moment and in the effective $|\Theta_W|$. This deviation suggests the formation of dynamic spin clusters with moments smaller than the sum of the constituent spins (as expected given the strong antiferromagnetic interaction) and that the dynamic clusters do not interact strongly with each other. This behavior is consistent with the kagomé spins forming coplanar correlated antiferromagnetic triangles with zero moment as predicted theoretically [7]. These data are also consistent with neutron scattering results suggesting that the frozen moments at the lowest temperatures are substantially less than the full moment of the Cr ions [4]. As shown in Fig. 1, significant anisotropy and nonlinearity in $\chi(H)$ develop by $T \sim 20$ K, although the temperature is still well above $T_c = 6.5$ K.

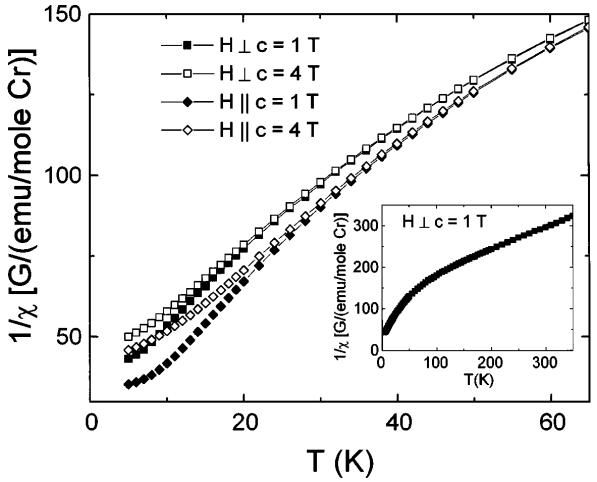

FIG. 1. The inverse susceptibility of an SCGO crystal as a function of temperature with the applied field both parallel and perpendicular to the c axis ($H \perp C$ and $H \parallel c$).

As shown in the inset to Fig. 3, the anisotropy ($A = M_\parallel/M_\perp$) begins to deviate from unity at a temperature $\sim$100 K, $\sim$20% lower than that where $\chi^{-1}(T)$ deviates from linearity. This anisotropy grows with decreasing temperature to as much as 160% at $T = 7$ K and $H = 0.01$ T. Since the anisotropy develops in the same temperature range as further neighbor correlations, we attribute the anisotropy to these multispin correlations. The anisotropy is probably not due to single-ion effects since the energy scale (<1 K) of single ion anisotropy for Cr^{3+} ions in the octahedral O^{2-} environment [11] is much smaller than the temperatures where we observe significant deviations of A from unity. Chemical disorder could possibly be responsible for the anisotropy either through crystalline field or bond anisotropy, but this possibility is strongly discounted by the correlation of features in $A(T)$ with many-body effects such as the nonlinearity of $\chi^{-1}(T)$ and the development of spin-glass-like order. Furthermore disorder-induced anisotropy with $A > 1$ would give an Ising-like character to the spins which in turn lead to formation of a gap at the lowest temperatures. No such gap has been observed, however, in ceramic samples of SCGO with similar levels of disorder. These factors lead us to conclude that the observed anisotropy in SCGO is due to the formation of a correlated spin state at low temperatures and that the behavior of $A(T)$ reflects that of the correlated spins.

The sense of the anisotropy ($M_\parallel > M_\perp$) and the development of correlations imply that the moments are oriented preferentially in the planes of the lattice, since one expects to find a larger χ normal to the preferred spin direction in an antiferromagnet. These data are experimental evidence for the theoretically predicted coplanar spin orientation in a kagomé spin system. They further indicate that the spins preferentially choose to lie in the a-b crystal plane in SCGO. The selection of the a-b plane (for which there is no justification in a pure kagomé system) implies that the correlations with nonkagomé spins (i.e., those in the triangular layers)

influence the kagomé spins. This is consistent with lower temperature magnetization and nonlinear susceptibility [3] data which show that all of the spins (including those in the triangular layers) freeze.

Particularly interesting are the temperature dependences of the magnetization and anisotropy as the sample approaches T_c from above. As seen in Fig. 2, A actually begins to decrease at a temperature as high as $2T_c$ in a few tesla field. This effect is even more visible in Fig. 3 where we have plotted the temperature derivatives of A and χ^{-1}, both of which show pronounced peaks at a temperature well above T_c. As seen in Fig. 2, the temperature of the peak in $A(T)$ *increases* with applied field. Note that the peak in $A(T)$, which has not been reported in other anisotropic spin-glass-like materials, has field dependence opposite to that of T_c. (Based on the branching temperatures between field-cooled and zero-field-cooled data, T_c in SCGO decreases sharply with field as expected for an ordinary spin glass [12]). It is clear from the data at 0.01 and 1.0 T in Fig. 3 that the maximum in A corresponds to the same physical process (discussed below) responsible for the maximum in the slope of $\chi^{-1}(T)$. As shown in Fig. 2, application of a magnetic field also strongly suppresses the high degree of anisotropy at low temperatures. The decrease of the anisotropy with a field which is small relative to the exchange energy ($|J| \sim 100$ K based on Θ_W) implies that the energy scale of the anisotropy is of order $\mu gH \sim 10$ K.

The magnetic signatures of the spin-glass-like transition also show significant anisotropy. Plotted in Fig. 4(a) is the difference between the field-cooled (FC) and the zero-field-cooled (ZFC) susceptibility at $H = 100$ G. There is a clear qualitative difference between the susceptibility measured in the two orientations of the crystal ($\chi_{\parallel/\perp} = M_{\parallel/\perp}/H$). The freezing with $H \| c$ results in a sharp decrease of the ZFC $\chi_\parallel$ below T_c and the virtual leveling of FC data at temperatures below the transition. By contrast, the ZFC $\chi_\perp$ data show only a weak decrease below T_c, with a slope that is more than 5 times smaller than the $\chi_\parallel$ data. Furthermore, the FC susceptibility continues to increase monotonically to our lowest temperature (1.8 K). These results suggest that the coplanar components of the spins are not completely frozen, but that the noncoplanar components are. This makes qualitative sense since the noncoplanar spins do not form the $S = 0$ correlated coplanar triangles and thus interact more strongly with spins in other planes and are more susceptible to freezing. The freezing of only noncoplanar components of the spins is consistent with the results of neutron and μSR experiments which demonstrate spin fluctuations down to very low temperatures despite the spin freezing observed in bulk measurements (recently Lee *et al.* showed that ~40% of the spins do not freeze [4]). The anisotropy in χ cannot be explained by preferential domain formation in a particular field orientation since the spin correlation length is ~10 Å in the planes and 2 Å out of the planes [4].

The nonlinear susceptibility also shows strong anisotropy as seen in Fig. 4(b). We determine χ_3 in the same manner as previous authors [2,3,6] by fitting M vs. H to a polynomial in odd powers of H and taking the cubic term to be χ_3. The much larger peak seen in $-\chi_3$ measured with $H \| c$, confirms the above conclusion that spin freezing is more complete with the field in that orientation. One might argue that the anisotropy in χ_3 is a result only of the anisotropy in χ and not indicative of anisotropy in the spin freezing, since $\chi_3 \sim \chi^2/T$ in the absence of a spin-glass-like transition [7]. This reasoning is, however, incorrect since the ratio $(\chi_3)_\perp/(\chi_3)_\parallel$ is more than 3 times $(\chi_\perp/\chi_\parallel)^2$ at temperatures slightly above T_c (where rounding effects are not significant). This confirms that the difference in χ_3 is not due to the anisotropy in the linear susceptibility, but reflects the anisotropic development of an Edwards-Anderson-like order parameter.

The anisotropy in spin freezing and the resultant anisotropy in χ_3 suggest that the maximum in $A(T)$

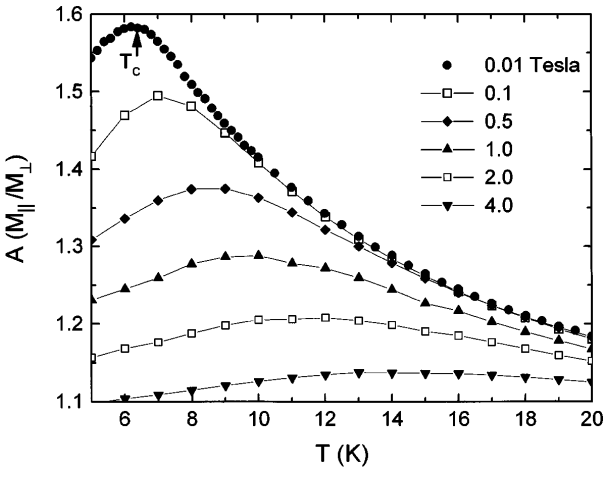

FIG. 2. The anisotropy of the magnetization as a function of temperature at various magnetic fields. Note that application of a strong field suppresses the peak in $A(T)$ and moves it to a higher temperature.

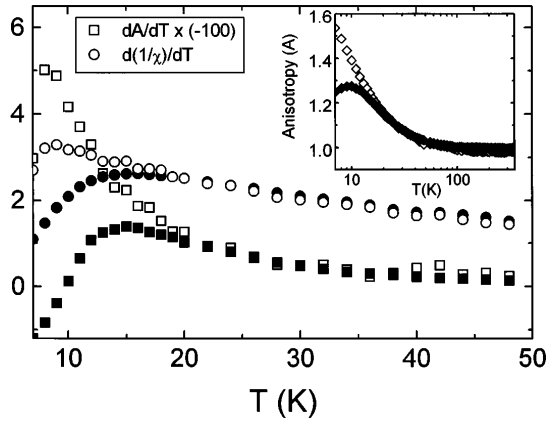

FIG. 3. The temperature derivatives of A and of the inverse susceptibility in G/(emu/mole Cr)/K with $H \| c$. Inset: The temperature dependence of $A(T)$. Data were taken at 0.01 T (open symbols) and 1.0 T (closed symbols).

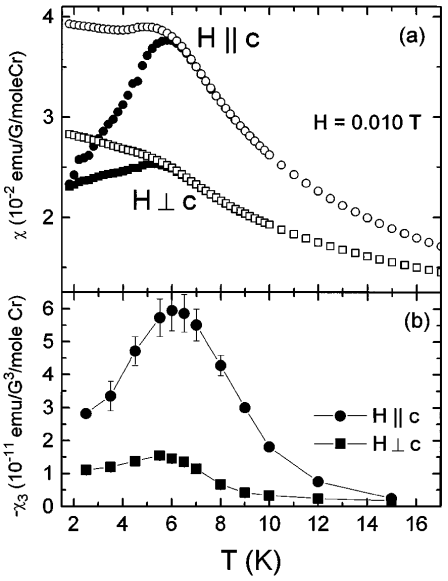

FIG. 4. The anisotropy of the spin freezing in SCGO. (a) The FC (open symbols) and ZFC (closed symbols) linear susceptibility at 0.010 T in the two orientations ($H \perp c$ and $H \parallel c$). (b) The nonlinear susceptibility in the two orientations.

results from a crossover from 2D to 3D behavior as the system approaches the 3D spin-glass-like transition [3]. Since $-\chi_3$ is growing much more quickly for $H \parallel c$, $M_{\parallel}$ in a strong field is suppressed relative to $M_{\perp}$. This suppression grows and extends to a higher temperature with increasing field, leading to the field dependence of temperature of the peak in A. The negative divergence of χ_3 also explains the field dependence of the low temperature change in slope of $\chi^{-1}(T)$ shown in Fig. 3. Physically, this crossover corresponds to the spins in the kagomé planes (which have strong in-plane correlations [4]) developing correlations with spins out of the planes. These out-of-plane correlations then lead to the 3D spin freezing observed at T_c. The anisotropic behavior in SCGO, induced by the correlations between frustrated spins, is rather different in origin from that of other 2D spin-glass-like systems where the reduced dimensionality is usually due to single-ion effects and the spins are hence Ising-like or the samples are made of microscopically thin films [13]. Also the observed behavior is qualitatively different from that in bulk 2D spin-glass-like systems of similar (Heisenberg) spin dimensionality without strong geometrical frustration (e.g., $La_{1.96}Sr_{0.04}CuO_4$ [14]).

Our data provide new insight into the nature of the low-temperature state in SCGO. The result that the spins prefer to be coplanar provides an important link between SCGO, a somewhat disordered system of spins which are not all within kagomé planes, and theoretical models of the behavior of SCGO which have concentrated on ideal or nearly ideal kagomé systems. The anisotropic freezing suggests that at T_c the spin component in the planes does not freeze completely, while the component normal to the planes does. This is consistent with theoretical suggestions that defects in SCGO lead to noncoplanarity [8] since the disorder induced by these defects is probably responsible for the spin-glass-like freezing.

The coplanarity within the kagomé plane does not, however, appear to be requisite for the anomalous ground states since the T^2 dependence of the heat capacity is observed even in fields as high as 12 T [15], which our data show to be sufficient to dominate the anisotropy. This suggests that the primarily two-dimensional nature of the spin correlations [which is responsible for the deviation of $\chi^{-1}(T)$ from linearity and the T^2 specific heat dependence at $T < T_c$] has a much higher energy scale ($\sim$100 K) than the three dimensional interplanar interactions (leading to the spin-glass-like freezing) which have energies $\sim$10 K.

We gratefully acknowledge discussions with G. Aeppli, C. Broholm, and D. A. Huse, and we thank P. Chandra and P. Coleman for their critical reading of the manuscript.

*Work performed while at AT&T Bell Laboratories.
†Permanent address: Physics Department, Southern University, Baton Rouge, LA 70813.

[1] A. P. Ramirez, Annu. Rev. Mater. Sci. **24**, 453 (1994); P. Schiffer and A. P. Ramirez, Commun. Cond. Mater. Phys. **18**, 21 (1996).
[2] P. Schiffer *et al.*, Phys. Rev. Lett. **74**, 2379 (1995); **73**, 2500 (1994); M. J. Harris *et al.*, Phys. Rev. Lett. **73**, 189 (1994); Phys. Rev. B **52**, R707 (1995).
[3] A. P. Ramirez *et al.*, Phys. Rev. Lett. **64**, 2070 (1990); Phys. Rev. B **45**, 2505 (1992).
[4] C. Broholm *et al.*, Phys. Rev. Lett. **65**, 3173 (1990); G. Aeppli *et al.*, J. Magn. Magn. Mater. **90–91**, 225 (1990); S.-H. Lee *et al.*, Phys. Rev. Lett. **76**, 4424 (1996); Europhys. Lett. **35**, 127 (1996).
[5] Y. J. Uemura *et al.*, Phys. Rev. Lett. **73**, 3306 (1994).
[6] B. Martinez *et al.*, Phys. Rev. B **50**, 15 779 (1994); **46**, 10 786 (1992); X. Obradors *et al.*, Solid State Commun. **65**, 189 (1988).
[7] P. Chandra *et al.*, J. Phys. I (France) **3**, 591 (1993), and references therein; P. Chandra (private communication).
[8] E. F. Shender *et al.*, Phys. Rev. Lett. **70**, 3812 (1993).
[9] I. Ritchey *et al.*, Phys. Rev. B **47**, 15 342 (1993); J. T. Chalker *et al.*, Phys. Rev. Lett. **68**, 855 (1992); R. R. P. Singh and D. A. Huse, Phys. Rev. Lett. **68**, 1766 (1992); P. Chandra and P. Coleman, Phys. Rev. Lett. **66**, 100 (1991).
[10] G. P. Espinosa (unpublished). Limited data taken on crystals from this batch have been published previously [3].
[11] For specific examples, see A. Abragam and B. Bleany, *Electron Paramagnetic Resonance of Transition Ions* (Dover Publications Inc., New York, 1986).
[12] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[13] For example, P. Granberg *et al.*, Phys. Rev. B **44**, 4410 (1991); C. Dekker *et al.*, J. Appl. Phys. **63**, 4334 (1988); A. Ito *et al.*, J. Phys. Soc. Jpn. **59**, 829 (1990).
[14] F. C. Chou *et al.*, Phys. Rev. Lett. **75**, 2204 (1995); A. Fert *et al.*, Phys. Rev. B **26**, 5300 (1962).
[15] A. P. Ramirez (unpublished).