Entropy Balance and Evidence for Local Spin Singlets in a Kagomé-Like Magnet

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We have measured the specific heat $C(T)$ of the $S = \frac{3}{2}$ Kagomé-lattice-containing compound $SrCr_{9p}Ga_{12-9p}O_{19}$. We find little field dependence of the low-temperature $C(T)$, consistent with a low-energy spectrum dominated by many-body singlet excitations. At high temperatures, we recover only $\sim$50% of the total R ln4 entropy.

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Geometrically frustrated magnets (GFMs) provide a simple setting in which to study the combined effects of symmetry incompatibility between local and extended degrees of freedom [1], and Maxwellian underconstraint [2]. In particular, the magnetism of Kagomé and pyrochlore lattices continues to yield surprising low-energy properties [3]. These properties include spin-glass (SG) ground states in the virtual absence of disorder [4], spin-liquid behavior [5,6], cooperative paramagnetism [7], and icelike zero-point entropy [8]. One experimental signature of strong frustration is downward shift in spectral weight, a direct result of local degeneracy—this is the key feature that distinguishes geometric frustration from other effects that serve to reduce the freezing temperature T_c to values well below that predicted by mean-field theory. Unlike conventional antiferromagnets, where phase diagrams depict the competition between long-range order and Zeeman energy at low temperature, little is known about how the reduced energy scale for spin freezing in GFMs changes with applied field. This energy scale can be up to 2 orders of magnitude lower than the mean-field energy, which motivates the question of whether the Zeeman energy competes with the exchange interaction on the mean-field scale or at this reduced scale.

We chose to address this question by studying the field and temperature dependence of the low-energy excitations in $SrCr_{9p}Ga_{12-9p}O_{19}$. This material is a quasi-2D insulator with the magnetoplumbite structure [9], where $\frac{2}{3}$ of the Cr^{3+} ($S = \frac{3}{2}$) ions lie in Kagomé planes. Despite a large (mean-field) Weiss temperature, $\theta_w \sim -500$ K [9], no long-range order is seen down to temperatures as low as 0.05 K [10]. A spin-glass state occurs at about $T_g \sim 3$–4 K for concentrations $p = 80$–90% but the dynamics of the majority of the spins is nontrivial in this low-temperature regime: The specific heat varies as T^2, instead of the usual T dependence found in spin glasses, and there is a peak in C/T at 6 K [5]; the Q and ω-integrated neutron scattering places the ratio of fluctuating to frozen moments below the spin-glass transition at $\sim$4 [11]; muon spin rotation (μSR) also reveals a fluctuating moment below T_g [10]. Both the fluctuating moment studies and the specific heat indicate a large ground state degeneracy. From existing measurements, one finds that approximately 15% of the total R ln4 entropy of the Cr^{3+} ions is lost below 10 K, an energy scale about 2 orders of magnitude lower than θ_w. We are interested specifically in whether or not the peak in C/T is affected by a Zeeman energy in a way similar to that of a conventional ordering transition.

We have studied $SrCr_{9p}Ga_{12-9p}O_{19}$ by means of specific heat and susceptibility measurements over a broad range of both magnetic fields and temperatures, and find two main results. The first is that only $\sim$50% of the total entropy is removed below 100 K, implying substantial singlet formation at a still higher temperature. Second, we find that $C(T,H)$ has very little field dependence in the low-temperature regime. This latter result suggests that the low-energy state of $SrCr_{9p}Ga_{12-9p}O_{19}$ is a correlated spin liquid, where the fundamental degrees of freedom are not moment-carrying spins but rather moment-free singlets. A physical picture that emerges is one where triangles (or tetrahedra) of spins formed at a high energy are still fluctuating at a much reduced energy scale. This picture is supported by the exact diagonalization studies accompanying this paper.

The structural and local atomic properties of $SrCr_{9p}Ga_{12-9p}O_{19}$ have been studied extensively. There are three distinct sites for the Cr^{3+} ions, and the majority of these ions ($\frac{7}{9}$) lie in a trilayer sandwich comprised of two outer Kagomé layers [5] and one inner layer with triangular coordination and $\frac{1}{3}$ the 2D spin density of the Kagomé layers, as shown in Fig. 1. The trilayer structure can also be thought of as (111) slabs of the spinel structure. The Cr^{3+} ion in $SrCr_{9p}Ga_{12-9p}O_{19}$ has been shown by high-field ESR to have a single-ion anisotropy of only 0.08 K, and so is Heisenberg-like at the temperatures of interest [12]. Most of the $\frac{2}{9}$ of the spins residing between the Kagomé layers have been shown to form singlet pairs with a binding energy of 18.6 meV and are isolated from the trilayer structure. Thus, at the temperatures of interest

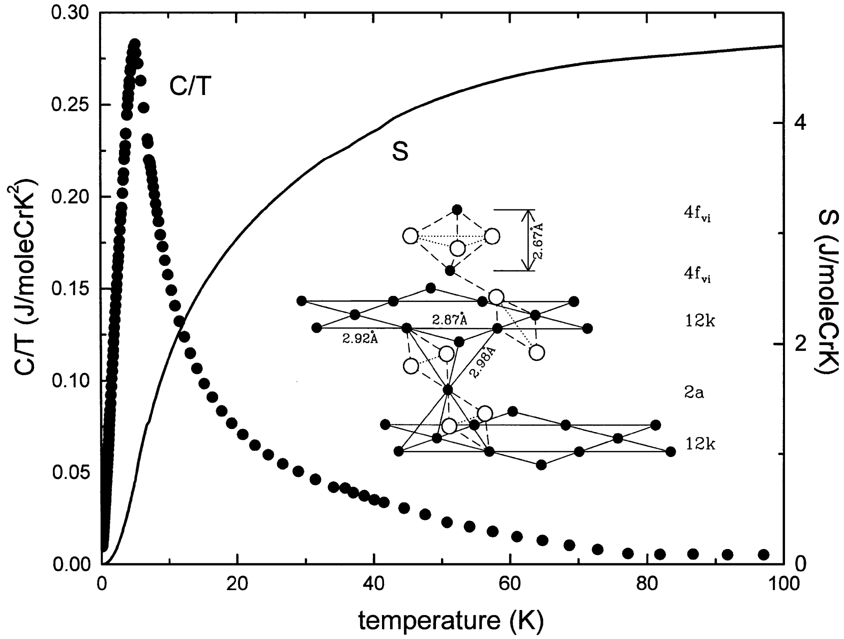

FIG. 1. The magnetic specific heat, divided by temperature, $C(H,T)/T$, for $SrCr_{9p}Ga_{12-9p}O_{19}$, $p = 0.89$, as a function of temperature. Also shown is the integral of these data, the entropy, expressed as a fraction of the total Cr^{3+} entropy. The inset shows the magnetic sites of the magnetoplumbite structure, where the Kagomé planes are labeled $12k$ (reproduced from [13].)

in this paper, we can consider $SrCr_{9p}Ga_{12-9p}O_{19}$ as an underconstrained 2D antiferromagnetic(AF)-coupled spin system [13].

The samples were made using standard solid-state synthesis techniques such as described in Ref. [5]. Magnetization measurements were made in a commercial SQUID magnetometer. The susceptibility was determined by numerically differentiating isothermal $M(H)$ data. Specific heat measurements were made using a standard semi-adiabatic heat pulse technique. The magnetic part of $C(T,H)$ was determined by subtracting the measured heat capacity of $SrGa_{12}O_{19}$, thus eliminating the phonon contribution.

In Fig. 1 we show the magnetic contribution to $C(T, H = 0)/T$ from 3 to 100 K of a sample with $p = 0.98$. The integrated entropy is also shown in Fig. 1, and it is seen that $S(100\ \mathrm{K}) \sim 4.7$ J/mol Cr K, or 41% of $R\ln 4$. Since $\frac{2}{9}$ of the spins have formed pairs above 100 K, the measured entropy represents 52% of the total entropy within the spinel slab. We note that the ground state entropy for the $S = \frac{1}{2}$ Ising-Kagomé lattice is $S(0)/k_B \cong 0.5018$, or 72.4% of the available entropy. This is in good agreement with Pauling's method estimate of $\ln 2 + \frac{2}{3}\ln\frac{3}{4} = 0.5014$, an indication that correlations do not extend far beyond a triangle in the Ising-Kagomé system. Because the present system is closer to Heisenberg than Ising, we view the measured shortfall of entropy to be a result of entropy already lost at a higher temperature, rather than due to finite ground state entropy. A division of energy scales for entropy removal is a common feature of numerical studies of Kagomé antiferromagnets. For instance, Zheng and Elser [14] show that, for the Heisenberg case, the entropy is removed in two separate $C(T)$ peaks. The present result, together with the entropy shortfall, suggests a distinct low-energy process, and the T^2 dependence of the low-T $C(T)$ argues against a Schottky, or single-ion origin for this process. In general, a peak in $C(H,T)/T$ results from a peak in the density of states, $g(\omega)$, defined as $U = \int d\omega\, g(\omega) n(\omega)\omega$, where U is the internal energy, $n(\omega)$ the Bose population factor, and the integral is taken over the excitation bandwidth. For optical and Schottky modes, the temperature of the $C(H,T)/T$ peak is roughly half the mode energy. Because of the short correlation length, we expect such a rule of thumb to apply here as well, suggesting a peak in $g(\omega)$ at $\hbar\omega_0/k_B \sim 10$ K.

Although specific heat can provide only limited detailed information about the excitations giving rise to the peak in $g(\omega)$, it can resolve between two qualitatively different scenarios. Either the low-T entropy arises from degrees of freedom associated with (1) short-range order among weakly interacting individual spins or (2) short-range order among groups of spins. To address this question we measured the field dependence of $C(T)$. In Fig. 2 we show $C(H,T)/T$ in the low-temperature region at several values of fixed magnetic fields from 0 to 11 T for a $p = 0.92$ sample, and for 0, 1, and 6 T for a $p = 0.98$ sample. The most surprising aspect of the data in Fig. 2 is the insensitivity of $C(H,T)/T$ to magnetic field. In isotropic unfrustrated antiferromagnets, a peak in $C(H,T)/T$ signals a transition to long-range order. This feature is suppressed to zero temperature by a field of order $H_c(0) \sim k_B\theta_w/g\mu_B$.

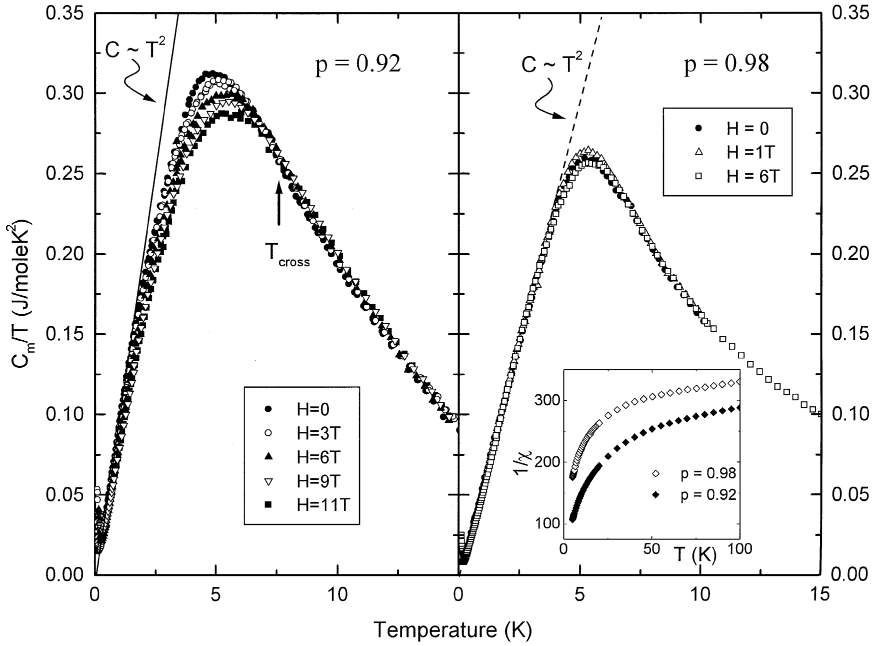

FIG. 2. The magnetic specific heat, divided by temperature, $C(H,T)/T$, for $SrCr_{9p}Ga_{12-9p}O_{19}$, $p = 0.92$ (left) and $p = 0.98$ (right), as a function of temperature, at several different values of fixed magnetic field. The inset shows the crossing temperature, T_{cross}, for the $p = 0.92$ sample. The inset also shows the inverse susceptibility $1/\chi$ ($H = 50$ G) for the two samples.

Thus, if the present feature in $SrCr_{9p}Ga_{12-9p}O_{19}$ were due to a simple smearing out of a long-range-order feature, one would expect it to be completely suppressed by a field of $k_B T_{peak}/g\mu_B \sim 5$ T. Instead, even at fields twice this value, 11 T, the peak in $C(H,T)/T$ for $p = 0.92$ has been reduced in magnitude by only 10% and T_{peak} has increased by only 20%. In addition, the peak has moved up slightly in temperature, instead of down, as would be expected for an inhomogeneously broadened antiferromagnetic transition. If the $C(H,T)/T$ peak were due to defect spins, as suggested to explain the SG ordering [15], then there is a large discrepancy between the measured entropy, ~40%, and defect densities, ~1%, extracted from susceptibility measurements [15].

A clear physical picture of the low-energy spectrum of $SrCr_{9p}Ga_{12-9p}O_{19}$ has yet to emerge. However, one can draw important conclusions from the field dependence of $C(H,T)/T$. The main conclusion is that the peak in the generalized $g(\omega)$ and, indeed, the corresponding spin states are only weakly affected by a magnetic field. It seems unlikely, then, that the components of such states are individual spins, such as Bloch spin waves—because the neutron experiments indicate no long-range order, the low-energy scale of these states would need to originate from shallow local potentials which might occur from a mean-field-like reduction of the internal field due to frustration. However, in this case, the spin would then couple to an external field, producing a clear Schottky anomaly, which is not observed. A more compelling picture of the low-energy spectrum is one of excitations among magnetic singlets. It is appealing to think of these singlets as triangular clusters with reduced moment, although the structure of $SrCr_{9p}Ga_{12-9p}O_{19}$ makes tetrahedral clusters a likely possibility. In either case, the singlets would form at temperatures close to θ_w, and, in the temperature range of interest, become strongly interacting. Sindzingre *et al.* discuss field dependence of $C(H,T)$ for the $s = \frac{1}{2}$ Kagomé system determined by exact diagonalization of finite-size lattices and find a similar insensitivity to that found for $s = \frac{3}{2}$ $SrCr_{9p}Ga_{12-9p}O_{19}$ [16]. The spectra of such systems have been previously found to be dominated at low energy by a large density of states in the singlet excitation channel [17], which supports our experiment-based picture.

The low-field magnetic response in $SrCr_{9p}Ga_{12-9p}O_{19}$ is that of a conventional spin glass with a freezing temperature of $T_g = 3.5$ K [5], yet we see that the high-field $C(H,T)/T$ suggests a different type of state, one where spin singlets are fluctuating, a type of spin-singlet liquid (SSL) state. Using high-field susceptibility $\chi(H,T)$, measurements, we can show that the SSL state coexists with the SG state at low fields. We note that the $C(H,T)/T$ curves cross at $T_{cross} = 7 \pm 0.5$ K. Therefore, all field derivatives of $C(H,T)/T$ vanish at T_{cross}. Since $\partial^2(C/T)/\partial H^2 = \partial^2\chi/\partial T^2$, the first partial temperature derivative of the contribution of $\chi(H,T)$ from the same excitations as probed in $C(H,T)/T$ should have an extremum at T_{cross}. Figure 3 shows $\partial\chi/\partial T$ at various values of fixed field for the $p = 0.92$ sample (the $p = 0.98$ sample shows the same qualitative behavior). We see that, at a low field of 0.02 T, the minimum temperature, T_{min}, in $\partial\chi/\partial T$ corresponds to T_g for this

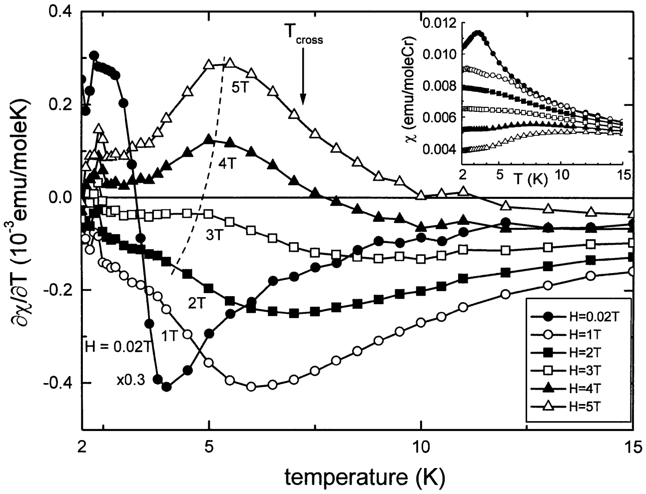

FIG. 3. The first partial temperature derivative of the susceptibility, $\chi(H,T)/T$, versus temperature for various values of fixed field for the $p = 0.92$ sample. The minimum temperature of $\partial\chi/\partial T$ is much less than the crossing temperature for the specific heat isochores, T_{cross}, at high fields. The inset shows that susceptibility data at the same fields.

composition, but, at higher fields, $T_{\min}$ is significantly less than T_{cross}. This indicates that the low-field spin-glass signature is destroyed by large fields, as also shown by Martinez *et al.* [18]. Since the peak in $C(H,T)/T$ is evidence for an SSL, and doesn't change with field, we conclude that the SSL coexists with the SG state at low field, as distinct low-temperature ground states. A possible mechanism for this unusual coexistence is suggested by the "orphan spin" picture [15], where a small density of defect spins is responsible for most of the low-T, low-H susceptibility, including the spin-glass-like response, while the background, which yields an AF-like response, is an SSL. The spins contributing to these behaviors can exist in distinct spatial regions. However, since $C(H,T)$ is more sensitive to small wavelength excitations than $\chi(H,T)$, another explanation is that the physical description demanded by the two different measurements is actually the momentum-space limits of the same ground state. Since SG behavior is usually associated with quenched defects, it is hard to imagine such a scenario, except if SG is a possible ground state in the absence of disorder, as proffered by Greedan *et al.* [4] for the pyrochlore compound $Y_2Mo_2O_7$ and discussed theoretically by Chandra and Coleman [19]. Clearly, further $C(H,T)/T$ experiments on $SrCr_{9p}Ga_{12-9p}O_{19}$ in the low-defect limit $p = 1$ are required to resolve this question.

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