Elementary excitations in a diluted antiferromagnetic Kagomé lattice

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Thermodynamic studies as a function of dilution in the Heisenberg antiferromagnetic Kagomé spin glass $SrCr_{9p}Ga_{12-9p}O_{19}$ are presented. The unusual T^2 specific heat is found to be robust towards dilution, implying an origin intrinsic to the spin-glass state. The extremely small excitation stiffness and known correlation length indicate an unusual form of elementary excitation, with similarities to a hydrodynamic mode in a liquid.

It is well established that the two essential microscopic ingredients of a spin glass (SG) are site disorder and bond frustration.[1,2] The connection between these properties and the nature of the elementary excitations is usually made through the tunneling-level model.[3] In this model the lowest-energy excitations correspond to the populating of discrete levels which are predominantly localized and have a uniform spectrum, reflecting the separate influences of frustration and disorder, respectively. The model predicts a specific heat $C(T)$ with a linear temperature dependence for $T < T_g$ (the SG freezing temperature), a feature almost universally observed in SG materials.[1,2] Since frustration and disorder are physically quite different concepts, it is desirable experimentally to decouple them to study their individual effects on the low-energy spectrum. Of much current interest is the limit of strong frustration and low disorder, where spin-liquid excitations are expected to occur.[4] In most SG materials, however, frustration is actually induced by the disorder, making independent variation of either one technically impossible. It remains a challenging problem to find new materials where frustration is "built into" the underlying lattice and where disorder can be introduced trivially.

Recently, a layered SG compound[5,6] $SrCr_{9p}Ga_{12-9p}O_{19}$ [Sr-Cr-Ga-O(p)] was found to exhibit an unusually high degree of frustration, while possessing only a small amount of site disorder (magnetic concentration $p \leq 0.89$). While the magnetic response of Sr-Cr-Ga-O(p) displayed the usual field hysteresis and diverging nonlinear susceptibility,[6] $C(T)$ was found[6] to vary as T^2, and not as T. Since the T^2 form is suggestive of two-dimensional (2D) antiferromagnetic (AF) spin waves, it was speculated that this behavior might be extrinsic to the SG state, arising instead from finite-size AF regions. In this case blockage might occur between such regions, allowing different physical origins for the magnetic and thermal response of the material. If, however, the T^2 form is actually intrinsic to the SG state, it is a clear sign of a type of elementary excitation not yet observed in magnetism. One way of determining whether or not the T^2 behavior belongs to a SG or an AF state is to study its sensitivity to varying p through the percolation threshold p_c for the relevant excitation subspace. In the SG-extrinsic scenario, one would then look for a change from T^2 to T behavior of $C(T)$ as p_c is crossed, starting from the ordered state.

In the present work is described a study of the low-temperature $C(T)$ for Sr-Cr-Ga-O(p) over a wide range of Cr concentrations p. It is shown that the T^2 form of $C(T)$ is affected little by dilution and therefore represents the elementary excitations of the SG phase. The T^2 behavior itself is unusually free of additional contributions (e.g., phonons) which complicate the analysis in other nonfrustrated quasi-2D AF systems. The excitation stiffness is found to be only $\frac{1}{25}$ of the bare stiffness inferred from the nearest-neighbor interactions, illustrating the dominating influence of frustration on the low-energy spectrum. These results, combined with the known correlation length[7] of Sr-Cr-Ga-O(0.79) ($\xi_0 \simeq 7$ Å), imply the existence of a type of excitation suggestive of a hydrodynamic mode of a spin liquid.

The structure of Sr-Cr-Ga-O(p) is extremely two dimensional[5] and consists of layers of spinel blocks containing Cr^{3+} ($S=\frac{3}{2}$) ions. While there are three different sites for Cr occupancy, most of the ions lie in the 12k site of the $P6_3/mmc$ space group, forming a Kagomé lattice of corner-sharing triangles. The remainder of the ions also lie in layers, but at $\frac{1}{3}$ the density of the Kagomé layers. It is this difference in layer density which allows a seemingly complicated crystal structure to yield a very simple magnetic lattice. Direct evidence for lamellar magnetic behavior was found[7] in a broad, elastic neutron-diffraction feature which could be fit only by a model with strong 2D correlations. The single-ion properties of Cr^{3+} in an oxygen octahedral environment are well known[8] and described by a simple Heisenberg spin with possible anisotropy of order ≈ 0.1 K. The cooperative properties result from a large superexchange interaction, indicated by the Weiss constant $\Theta_{CW}=515$ K for $p=0.89$. Despite this large Θ_{CW}, the $p=0.89$ compound was found[6] to undergo a SG transition only at 3.5 K. The ratio $f=\Theta_{CW}/T_g$, a coarse indicator of the degree of frustration, is equal to 150 for Sr-Cr-Ga-O(0.89) and is typically less than 5 for usual spin-glass materials.

The Sr-Cr-Ga-O(x) specimens used in the present study are ceramics, except for the neutron-scattering sample ($p=0.79$), which was grown from a $SrO\text{-}B_2O_3$ solvent and formed into microcrystallites.[6] Five different Cr concentrations were studied, corresponding to $p=0$, 0.39,

0.72, 0.79, and 0.89. The largest structural change in the series was in the c-lattice constant, which varied by 0.1% among the Cr-containing members. The a-lattice constant varied by less than 0.03% over the same range, implying a negligible ($<1\%$) change of the in-plane exchange constant, the presumed dominant energy of the system.

The susceptibility measurements were obtained with a commercial superconducting quantum interference device (SQUID) magnetometer. The specific-heat measurements were performed using a semiadiabatic technique. All $C(T)$ data are shown with the contribution from the nonmagnetic $p=0$ isomorph subtracted and therefore represent only the magnetic contribution.

In Fig. 1 are presented $C(T)/T$ and inverse susceptibility $\chi^{-1}(T)$ data for the ceramic Sr-Cr-Ga-O(p) samples. The $\chi^{-1}(T)$ data exhibit a unique feature of highly frustrated systems, namely, the extended validity of the Curie-Weiss law to temperatures well below Θ_{CW}. In this region the slopes for each sample yield an effective moment of $4.0\mu_B$, in good agreement with the value $2\sqrt{S(S+1)}=3.87$ for $S=\frac{3}{2}$. The suppression of the Weiss constant (Table I), obtained by extrapolating only from the region of linearity, is in qualitative agreement with mean-field expectations based on reducing the number of nearest neighbors. More importantly, f remains fairly constant at $f\simeq 130$ as p is varied. This means that the cooperative SG transition scales with concentration as a normal Curie temperature might scale, away from p_c. It also implies that the distribution of Cr among the various sites is homogeneous.[9]

The $C(T)/T$ data in Fig. 1 show a rounded maximum occurring slightly above T_g for each specimen. This is similar to the behavior observed[1,2] in other SG's where a maximum is observed in $C(T)$ above T_g. Unlike the usual behavior, however, $C(T)/T$ continues to decrease below T_g. This is more clearly demonstrated in Fig. 2, where the low-temperature data are plotted in reduced units on a log-log scale. Also included in this plot are the data for the microcrystallites. For the three concentration values between $p=0.72$ and 0.89, the temperature dependence is well described by a T^{α} law where $\alpha=2.0$. For the $p=0.39$ sample, $\alpha=1.8$. The low-temperature specific heat in d dimensions of bosonic excitations with dispersion $\omega\sim k^{\nu}$ varies as $C(T)\sim T^{d/\nu}$. For 2D AF spin waves, therefore, $\alpha=2$.

For comparison to other SG systems, representative data for two well-characterized examples $Eu_pSr_{1-p}S$ [Eu-Sr-S(p) (Ref. 10)] and $Cd_{1-p}Mn_pTe$ [Cd-Mn-Te(p) (Ref. 11)] are also plotted in Fig. 2. Eu-Sr-S(p) and Cd-Mn-Te(p) are ferromagnetic and antiferromagnetic, respectively, at $p=1$, and both are insulators at low temperatures, with the moments interacting via superexchange, similar to Sr-Cr-Ga-O(p). These data exhibit the behavior usually associated with the tunneling-mode description of SG excitations, namely, a linear dependence upon T in the range $0.1T_g<T<0.9T_g$. The small deviation of the Cd-Mn-Te(0.3) sample below the $\alpha=1$ line can be attributed to the start of a smooth crossover towards the $C(T)\sim T^3$ form of a 3D AF as the SG-AF boundary at $x\simeq 0.7$ is approached.[11]

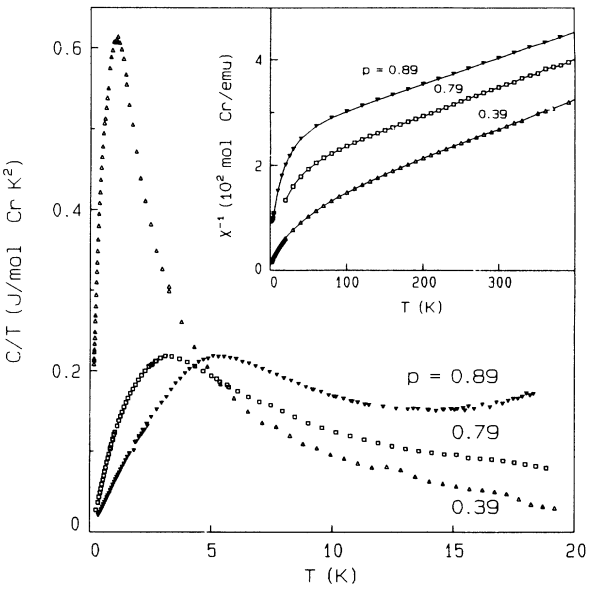

FIG. 1. Specific heat $C(T)$ and inverse susceptibility $\chi^{-1}(T)$ for the ceramic Sr-Cr-Ga-O(p) samples.

The data compared to Sr-Cr-Ga-O(p) in Fig. 2 were chosen for the similarity in concentration range with respect to p_c. Within this range the common feature of these three materials is the insensitivity of the $C(T)$ power law to dilution. Outside this range and depending on the temperature, SG-extrinsic effects are known to occur. These can include hyperfine contributions, single-ion anisotropy, or atomic clustering effects,[12] each of which will significantly alter $C(T)$. These effects are usually small, however, and there is no reason, *a priori*, to believe they are responsible for the difference in power law observed between Sr-Cr-Ga-O(p) and other SG's. Below we consider a different type of SG-extrinsic effect.

Since $C(T)\sim T^2$, it is natural to presume an origin in finite-size AF-ordered regions, especially in the $p=0.89$ material, since $p_c=0.6527$ for the Kagomé sublattice. In this scenario the SG behavior in the magnetization arises

TABLE I. Physical parameters for the Sr-Cr-Ga-O(p) samples studied.

Concentration (p)	Θ_{CW}(T) (K)	T_g (K)	f	c (Å)	a (Å)
0				22.84	5.796
0.39	−181	<2	>90	22.766	5.790
0.72	−341	2.5	136	22.714	5.791
0.79	−435	3.9	111	22.7	5.80
0.89	−515	3.5	147	22.677	5.792

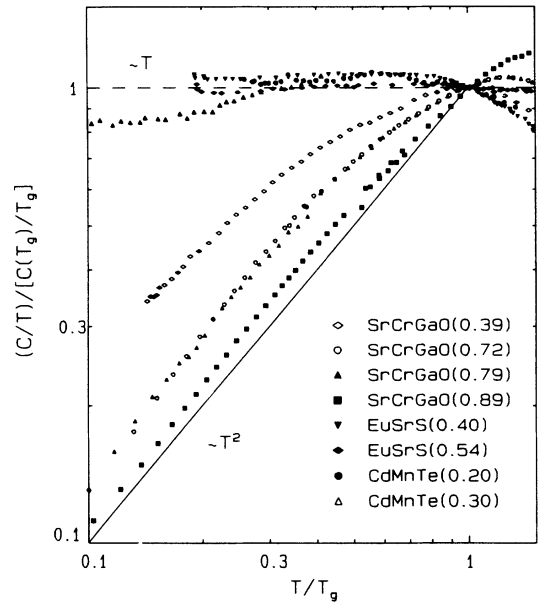

FIG. 2. Low-temperature specific heat $C(T)$ divided by T and normalized to the freezing temperature T_g for the ceramic and microcrystalline Sr-Cr-Ga-O(p) samples. Also shown are data for the well-characterized spin-glass compounds Eu_pSr_{1-p} (reproduced from Ref. 10) and $Cd_{1-p}Mn_pTe$ (reproduced from Ref. 11).

from intercluster blocking, and since no AF anomalies occur above T_g, then $T_{AF}=T_g$. $C(T)$ could easily be dominated by the AF phase, given its larger α, but one would expect large qualitative changes as p varies through p_c. This can be expressed through the concentration dependence of the spin-wave stiffness constant $D(p)$, where $\omega=D(p)k$ for long-wavelength excitations. It has been shown[13] that $D(p)$ decreases linearly with decreasing p until it vanishes at p_c. Since $D(p)$ is measured directly by $C(T)$, the effect of dilution should be readily apparent even above p_c. Although, for the sake of comparison, there exist no systematic studies of the effect of dilution on the low-temperature $C(T)$ for unfrustrated quasi-2D systems, one can draw from work on 3D systems. In particular, studies[14] of the simple cubic x-y magnet ($p_c=0.31$) $Co_pZn_{1-p}(C_5H_5NO)_6(ClO_4)_2$ not only confirm the expected decrease in $D(p)$, but also show that, at $p=0.34$, $C(T)\sim T$ instead of T^3, as found for larger p. For this value of p, the AF λ anomaly is unobservable, dominated instead by a broad short-range-order feature. In Sr-Cr-Ga-O(p) the situation is quite different. The observed change in α, even well below p_c for the Kagomé lattice (0.6527), is small. At $p=0.39$, $\alpha=1.8$, a decrease of only 20% of the possible change. Note that since the SG order has been shown[6] to be 3D, it will not necessarily be subject to the same percolation threshold as AF excitations. Therefore, the expectation within this two-phase scenario is that either of the phases SG or AF dominates the nature of the excitation spectrum at either end of the dilution range, with the crossover being the percolation boundary for the AF phase. In this region the low-temperature form of $C(T)$ has already changed qualitatively from that of the ordered phase to a form indicative of a distribution of clusters. In Sr-Cr-Ga-O(p), therefore, at and below the Kagomé p_c, $C(T)$ should be linear as in other SG's. In light of these expectations for a two-phase model, the observed T^2 form of $C(T)$ in Sr-Cr-Ga-O(p) is remarkably robust, being essentially the same at both $p=0.72$ and 0.39. It is concluded that the two-phase picture originally proposed is not applicable in this situation and, given the T^2 form, that the low-energy spectrum consists of long-wavelength (Goldstone) modes intrinsic to the SG state.

Since a common feature[1,2] of SG's is a small $T=0$ correlation length ξ_0, it is relevant to ask, precisely how long ranged are the excitations implied by the $C(T)$ data? This question can be addressed by examining the extension of the T^2 form to low temperatures on an absolute-temperature scale, using a standard finite-size analysis. One writes the internal energy as $U=\int d\omega\, g(\omega)n(\omega)\omega$, where ω is the spin-wave frequency, $g(\omega)$ the density of states, and $n(\omega)$ the Bose-Einstein factor, and the limits of integration are from a low-energy finite-size cutoff $\omega_0=2\pi D/L_0$ to the zone boundary. Here L_0 is the size of regions over which the excitations are well defined.[15] For $\omega_0 \ll T \ll \Theta_{CW}$,

$$C(T)=-(2\pi/L_0^2)k_B+2.3(k_B^3/h^2D^2)T^2 .$$

The second term of Eq. (1) is simply the quadratic form for 2D AF spin waves, while the first term is a uniform, size-dependent negative shift in $C(T)$ due to the finite-size gap. In Fig. 3 we show $C(T)$ for the same sample used for the neutron-diffraction studies of Broholm *et al.*,[7] the $p=0.79$ microcrystallites. A least-squares fit to these data yields an intercept less than the standard deviation for the fit, 0.9 mJ/mol Cr K. This corresponds, via Eq. (1), to 650 Å, to be taken as a lower limit on the region over which the excitations are well defined. Also plotted in Fig. 3 are lines calculated from Eq. (1) for representative values of L_0, with slope equal to the experimental value. This large value for a correlated region is in sharp contrast with the 2D correlation length found by

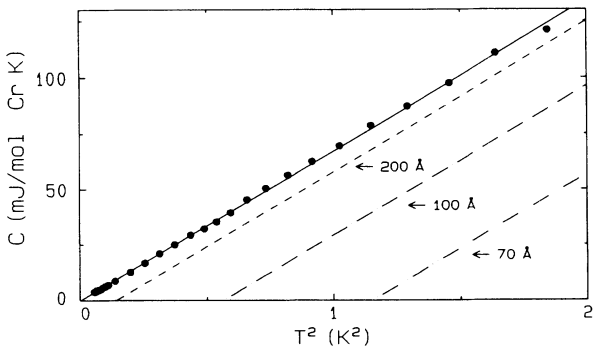

FIG. 3. Low-temperature specific heat $C(T)$ vs T^2 for the microcrystallite sample used in neutron-diffraction measurements of Ref. 7. The solid line is the result of a linear least-squares fit to the data. The three parallel lines below this correspond to the expected offset of the data due to finite-size corrections for correlated regions of the size L_0 as indicated.

neutron diffraction,[7] $\xi_0 = 7 \pm 2$ Å. Recall, however, that unpolarized neutron diffraction probes the two-spin correlation function,[16] whereas $C(T)$ probes excitations from all possible configurations. For a system where the geometry of the lattice inhibits the development of long-range order in the two-spin correlation function, one must consider the possibility of having longer-range order involving only multiple-spin correlations. the occurrence of excitations qualitatively different from those allowed in mean-field theory has been discussed for an Ising AF Kagomé system by Giordano and Wolf.[17]

The other aspect of $C(T)$, which implies a different type of excitation, is the magnitude of the spin stiffness below T_g. This can be estimated in the same way as for conventional magnets[18] by equating the full spin entropy with the integrated entropy up to an expected ordering temperature T^*, obtained from the bare nearest-neighbor interaction. For spin S and $C(T) = \mathcal{A} T^2$, one finds $\mathcal{A} = 2R \ln[S(S+1)]/T^{*2}$, where R is the gas constant. For the $p = 0.89$ sample, the bare stiffness can be calculated by substituting Θ_{CW} for T^*, resulting in $\mathcal{A}_{bare} = 9.0 \times 10^{-5}$ J/mol Cr K^3. By comparison, the measured value is $\mathcal{A} = 0.06$ J/mol Cr K$^3 \simeq 700 \mathcal{A}_{bare}$. Since $\mathcal{A} \sim D^{-2}$, this means that the excitations in Sr-Cr-Ga-O(0.89) are 25 times softer than the maximum allowed by the nearest-neighbor interaction. This extraordinary softening as a result of frustration places these modes quite clearly in a different category than the usual spin waves in an AF.

The T^2 dependence of $C(T)$ in Sr-Cr-Ga-O(p) implies the presence of long-wavelength Goldstone modes, which, in turn, implies an order parameter associated with the SG transition. Long-wavelength modes with linear dispersion were predicted to occur in x-y SG's by Edwards and Anderson.[19] An extension to more general spin arrangements in a hydrodynamic theory was made by Halperin and Saslow.[20] Recently, Chandra and Coleman[4] have considered the quantum dephasing effects on noncollinear spin configurations in a 2D spin-liquid model. They have postulated the existence of a spin-nematic state, which, though not possessing an ordered vector moment, will nevertheless have a Goldstone mode corresponding to the breaking of the twist-sense symmetry. The latter approach has validity for Sr-Cr-Ga-O(p) since the ground state seems not to be manifestly determined by site disorder, the T^2 specific heat and absence of moment occurring at high concentration. In this sense the observed behavior in Sr-Cr-Ga-O(p) resembles that of a spin liquid. These models might offer useful starting points for explaining the observed behavior. Further work is needed, however, to adapt these ideas to the specific microscopic conditions present in Sr-Cr-Ga-O(p), in order to formulate a description of the wave function of these unusual excitations. Further experimental work requires a microscopic probe that will allow direct coupling to the order parameter.

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