Spin Fluctuations in Frustrated Kagomé Lattice System $SrCr_8Ga_4O_{19}$ Studied by Muon Spin Relaxation

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(Received 16 May 1994)

We have performed muon spin relaxation measurements of the frustrated kagomé lattice spin system $SrCr_8Ga_4O_{19}$. Our results demonstrate the slowing down of the Cr spin fluctuations when cooling toward the susceptibility-cusp temperature $T_g \sim 3.5$ K. The saturation of the relaxation rate below T_g, together with its weak dependence on longitudinal field (LF) between 0 and 2 kG, indicates the presence of dynamic spin fluctuations persisting even at $T \sim 100$ mK without static order parameter. We propose a spin-liquid type ground state to explain an undecouplable Gaussian shape of the relaxation function observed at $T \leq T_g$.

PACS numbers: 75.40.Gb, 75.50.Lk, 76.75.+i

Magnetic moments on the kagomé lattice, coupled with a nearest neighbor antiferromagnetic exchange interaction, are a prototypical example of geometrically frustrated spin systems which could possibly have a novel ground state and exhibit unconventional low-temperature behavior [1]. For classical spins coupled by the Heisenberg interaction, a macroscopic number of different spin configurations compose the highly degenerate ground state. The system can move between different ground state configurations without passing through an energy barrier. These features lead to strong spin fluctuations persisting at low temperatures and to the suppression or even total elimination of long range magnetic order [2]. Quantum studies on $S = 1/2$ systems predict a dynamic disordered ground state [3,4]. Specifically, formation of disordered singlet spin pairs [4] is reminiscent of the resonating valence bond (RVB) picture first proposed for frustrated spins on a triangular lattice [5].

Although it includes alternating kagomé lattice and triangular lattice planes, and about 10% [more precisely, $(9 - x)/9$] of the kagomé lattice Cr ($S = 3/2$) sites are randomly substituted by nonmagnetic Ga atoms, $SrCr_xGa_{12-x}O_{19}$ (SCGO) has been studied most extensively by various experimental methods [6–8], as an example of a kagomé lattice Heisenberg antiferromagnet. The high-temperature susceptibility shows a Curie-Weiss behavior with a Weiss temperature $\Theta_W \sim 400$ K, indicating an antiferromagnetic exchange interaction J with an energy scale of a few hundred kelvin [6,7]. When the Cr concentration x is above the percolation threshold $p_c \sim 6.0$, a spin-glass-like cusp of the susceptibility is observed at $T_g \sim 2$–5 K, with increasing T_g for increasing x [7]. History dependence of the susceptibility is seen below T_g, similar to ordinary spin glasses. In neutron scattering measurements [8] for $x = 7.1$, quasielastic scans show short-range spin correlations, without magnetic Bragg peaks, which slow down over a broad temperature range. At $T \sim \frac{1}{2}T_g$, more than 80% of the spectral weight was found to remain in the inelastic channel ($\Delta E \geq 0.2$ meV), indicating the strong spin fluctuations. There has, however, been no detailed experimental information on static order parameter nor on the behavior at truly low temperatures.

In this Letter, we report muon spin relaxation (μSR) measurements on a sintered ceramic specimen of SCGO ($x = 8.0$) [9]. Dynamic spin fluctuations and static magnetic order can be detected by μSR, even in systems with very small ordered moment and/or random spin configurations, as demonstrated in the conventional spin glass systems *Cu*Mn and *Au*Fe [10] and in some heavy fermion systems [11]. In SCGO we observe the slowing down of Cr spin fluctuations which occurs over a wide temperature range when cooling towards $T_g \sim 3.5$ K. Unlike the case in conventional spin glasses, we detect no signature of static spin freezing below T_g; dynamic spin fluctuations persist even at $T = 100$ mK. Detailed analysis of the observed relaxation function and its longitudinal field (LF) dependence reveals an unconventional time evolution of the local fields below T_g, which may be related to the formation of singlet spin pairs.

The specimen of SCGO was prepared using $SrCO_3$, Cr_2O_3, and Ga_2O_3 with 99.9% purity, heated at 1350 °C in air for 24 h. X-ray analysis confirmed the single-phase nature of the specimen, while the susceptibility cusp observed at $T = 3.5$ K indicates a Cr concentration $x \sim 8.0$ [7], as expected from the nominal concentration. The μSR measurements were performed at TRIUMF using an Oxford dilution refrigerator (covering 50 mK–10 K) and a conventional He gas flow cryostat (covering above 2.5 K). Data taken in these two cryostats agree very well in the overlapping temperature region.

Discussion of the μSR technique can be found in Refs. [10,12]. In zero-field (ZF) and longitudinal field

 0031-9007/94/73(24)/3306(4)$06.00 © 1994 The American Physical Society

(LF) measurements, the positive muon beam, polarized parallel to the beam direction, is stopped in a specimen, and the time histograms of muon decay positrons are recorded by forward (F) and backward (B) counters as a function of residence time t for each μ^+ within the specimen. Since a positron is emitted preferentially toward the muon spin direction, the asymmetry $A(t) = (F - B)/(F + B)$ of the two histograms (after correction for solid-angle effects) reflects the time evolution of muon spin polarization.

In Fig. 1(a), we plot the muon relaxation function $G(t) = A(t)/A_0$ ($A_0 \sim 0.2$ is the initial asymmetry at $t = 0$) observed in LF = 100 G. The relaxation rate increases gradually with decreasing temperature. Above T_g, the observed spectra do not depend much on the applied longitudinal fields up to LF = 5 kG. This indicates that the relaxation is caused by dynamic local fields at the muon site, originating from the surrounding $S = 3/2$ Cr moments via dipolar and/or hyperfine interactions. We fit the observed spectra to a phenomenological power-law function $G(t) = \exp[-(t/T_1)^\beta]$, which gives satisfactory agreement with the data as shown by the solid lines in Fig. 1(a). Figure 2 shows the relaxation rate $1/T_1$ and the power β thus obtained for the data in LF = 100 G. Upon cooling from $T = 20$ K toward $T_g \sim 3.5$ K, $1/T_1$ increases over 2 orders of magnitude, demonstrating the slowing down of the Cr spin fluctuations. The wide temperature range of this slowing down reflects the large ratio $J/kT_g \sim 100$ in SCGO. In usual spin glasses with $J \sim kT_g$, the slowing down occurs in a much narrower region $T_g \leq T \leq 2T_g$ [10].

When the distribution of magnetic moments is dense in real space, the random local fields $H_{\rm loc}$ at the muon sites can be approximated by a Gaussian distribution with a width $\Delta \sim \gamma_\mu \sqrt{(H_{\rm loc} - \langle H_{\rm loc}\rangle)^2}$ ($\gamma_\mu = 2\pi \times 13.55$ MHz/kG is the μ^+ gyromagnetic ratio) [12]. For rapid fluctuations of $H_{\rm loc}$ with a rate $\nu \geq 5\Delta$ (the "narrowing limit"), we expect an exponential shape of $G(t)$. In contrast, if the origin of the random fields is dilute [10], $G(t)$ has a root-exponential shape ($\beta = 1/2$) in the narrowing limit. Therefore, the observed power $\beta \sim 1.0$, shown in Fig. 2(b) above T_g, indicates a dense source of magnetic fields, suggesting that the majority of Cr moments, rather than dilute moments related to defects, are responsible for the depolarization above T_g. Above $T \sim 15$ K, $1/T_1$ showed almost no temperature dependence, indicating that the relaxation at high temperatures is likely due to exchange fluctuations of the Cr spins. Using $k_B\Theta_W = 2zS(S+1)J_{ij}/3$ with $z = 4$ the nearest neighbor coordination number of kagomé lattice and $S = 3/2$, we obtain the exchange fluctuation rate $\nu = \sqrt{z}J_{ij}S/\hbar \sim 3 \times 10^{13}\ {\rm s}^{-1}$. Combined with the relation $1/T_1 = 2\Delta^2/\nu$ in the narrowing limit, $1/T_1(T = 75\ {\rm K}) = 0.03\ \mu{\rm s}^{-1}$ implies a width $\Delta/\gamma_\mu \sim 8$ kG of the random field distribution.

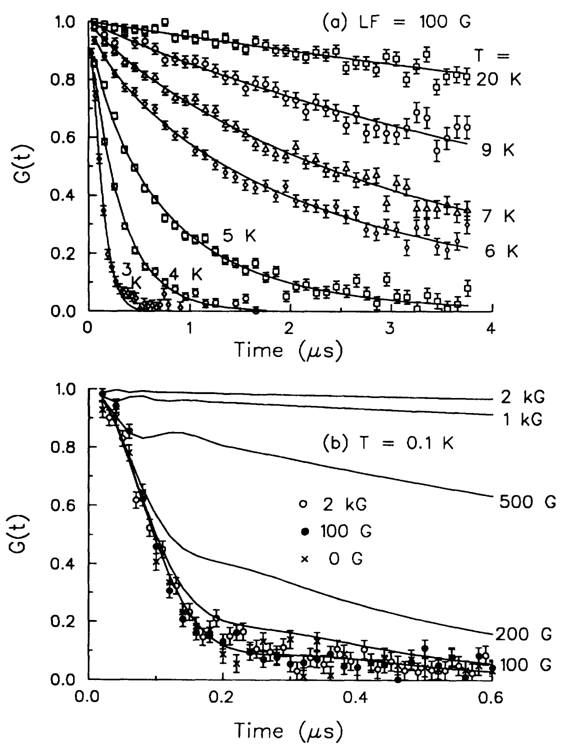

FIG. 1. Muon spin relaxation function $G(t)$ observed in a sintered ceramic specimen of $SrCr_8Ga_4O_{19}$: (a) above $T = 3$ K in LF = 100 G, and (b) at $T = 100$ mK in zero field, LF = 100 G and 2 kG. The solid lines in (a) represent the fit to a power law $\exp[-(t/T_1)^\beta]$, while in (b) represent the expected decoupling in LF if the initial depolarization were due mainly to static random fields (with a small dynamic effect).

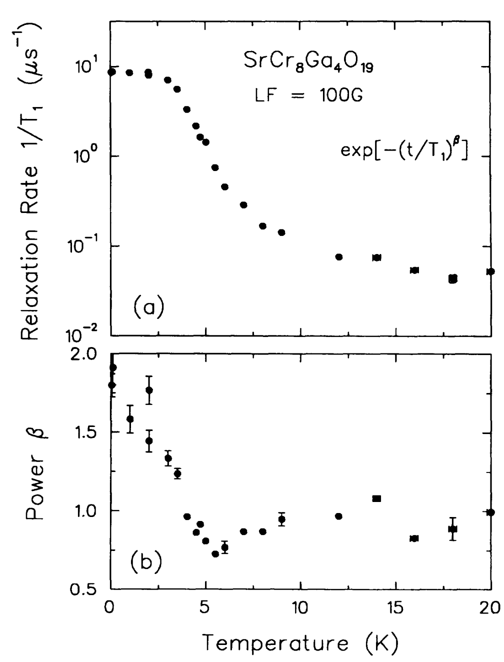

FIG. 2. (a) Muon spin relaxation rate $1/T_1$, and (b) the power β obtained by fitting the μSR spectra in $SrCr_8Ga_4O_{19}$ observed in LF = 100 G to a generalized power-exponential function $\exp[-(t/T_1)^\beta]$.

Below T_g, the relaxation rate in LF = 100 G exhibits saturation as shown in Fig. 2(a). In the entire temperature region below T_g, we found essentially no field dependence up to LF = 2 kG, as shown in Fig. 1(b). This is a clear signature of dynamic relaxation due to fluctuating fields. In fact, if the observed relaxation at $T = 100$ mK were due to static random fields, we should have observed decoupling in LF as illustrated by the solid lines in Fig. 1(b). Further evidence against the existence of static random fields comes from the lack of a characteristic recovery of the asymmetry to 1/3 in zero-field measurements. In dilute alloy spin glasses, for example, clear decoupling in LF and a 1/3 recovery in zero field were both observed below T_g, demonstrating development of the static order parameter [10]. In contrast, we observe no signature of static spin freezing in SCGO, even at $T = 100$ mK. In SCGO, with a dynamic relaxation of $1/T_1 \sim 10\ \mu s^{-1}$, a static random field greater than 100 G would be easily detectable. This value corresponds to a static component of about $\sim 0.1\mu_B$ per Cr atom, providing an upper limit for the static order parameter. In view of the complicated crystal structure of SCGO, it is unlikely that μ^+ selectively chooses a site where the local field from the Cr moments cancels completely by symmetry. Even in such an unlikely case, we would still expect that the presence of nonmagnetic Ga sites would lead to static fields larger than 100 G. Therefore, the present results below T_g essentially rule out static spin freezing in SCGO.

In view of this dynamic nature below T_g, it was surprising to find the line shape below T_g in SCGO approaching a Gaussian shape, as indicated by the power $\beta \to 2$ at $T \to 0$. If the Gaussian shape arises from a static random field persisting at the muon site, the initial damping rate of the observed spectra $G_z(t)$ is far too small to account for the large LF required to cause a decoupling effect. On the other hand, dynamic field modulation usually leads to an exponential (root-exponential) shape of $G_z(t)$ in dense (dilute) magnetic systems [10,12]. The present results represent the first example of an "undecouplable Gaussian" line shape observed in μSR. We note that the electron Zeeman level due to the applied field LF ~ 1 kG is 4 orders of magnitude smaller than J and is comparable to or smaller than kT in most of the temperature region below T_g, where the observed results show little dependence on temperature. Therefore, it is unlikely that the application of LF has significantly affected the spin dynamics.

This mystery of the line shapes can be resolved if we assume that a local field of significant magnitude exists at each muon site, not persistently, but sporadically. Figure 3(a) illustrates the simplest example of such a situation: Here a local field $H_{\text{loc}} \sim \Delta/\gamma_\mu$ exists only during a fraction ft ($f \ll 1$) of the total muon residence time t, and otherwise $H_{\text{loc}} = 0$. The finite field is assumed to persist during a time $\sim 1/\nu = dt$ and then randomly change its direction and magnitude (or change to 0). In this case, the observed relaxation function $G_z(t)$ can be given by $G_z^G(ft, \Delta, H_{\text{LF}}, \nu)$, which is calculated using a standard μSR fitting function for a Gaussian random local field characterized by a width Δ/γ_μ. From a trivial scaling argument [12], we expect $G_z^G(ft, \Delta, H_{\text{LF}}, \nu) = G_z^G(t, f\Delta, fH_{\text{LF}}, f\nu)$. This leads to a much smaller relaxation (effective random field reduced by a factor f) and much smaller effect of longitudinal fields H_{LF} (reduced by a factor f). Furthermore, a Gaussian-like line shape can be expected for $f\Delta > f\nu$ (i.e., $\Delta \geq \nu$), yet the decoupling starts around the field $H_{\text{LF}} \geq \Delta$, a field much larger than that estimated from the initial damping rate $\sim f\Delta$ of $G_z(t)$. These features agree well with the observed data.

This model successfully reproduces the qualitative features observed at $T = 100$ mK, as shown in Fig. 3(b). Here the solid lines represent $G_z^G(t, f\Delta, fH_{\text{LF}}, f\nu)$ with $f = 0.037$, $\Delta = 257\ \mu s^{-1}$, $\nu = 194\ \mu s^{-1}$, obtained by fitting the results at LF = 0.1, 2, and 5 kG. The value of the instantaneous field $\Delta/\gamma_\mu = 3.0$ kG is roughly consistent with the magnitude of local field ~ 8 kG estimated from the exchange fluctuations at high temperatures, while $\nu \sim 200$ MHz indicates slow but still dynamic fluctuations. Both the Gaussian shape and the lack of recovery to 1/3 in zero field originate from these fluctuations with $\nu \sim \Delta$.

The most likely origin of this "zero-field time" is the formation of local spin singlet pairs, as illustrated

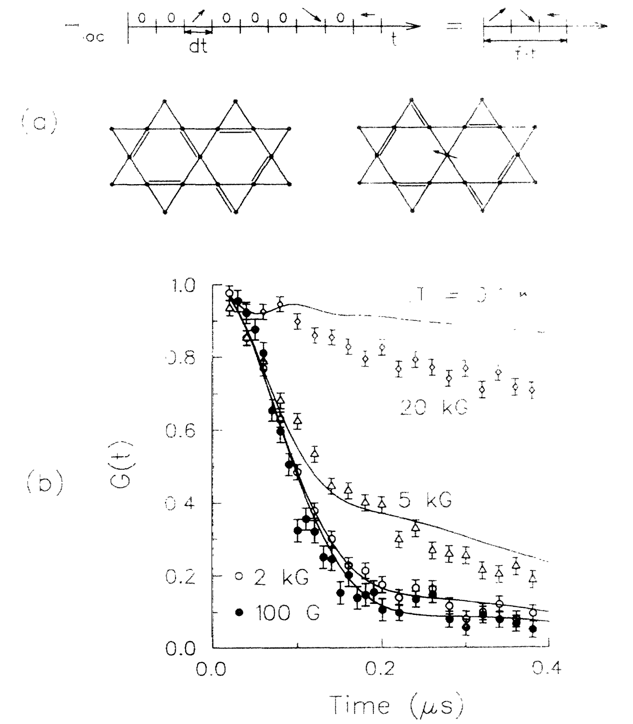

FIG. 3. (a) Schematic illustration of proposed time evolution of random local field at a muon site and local singlet spin pairs on kagomé lattice (indicated by double line) in the case with and without an unpaired spin. (b) A fit of μSR spectra at $T = 100$ mK in LF = 0.1, 2, and 5 kG to the model function $G_z^G(t, f\Delta, fH_{\text{LF}}, f\nu)$. For LF = 20 kG, the model function is compared to the observed data.

schematically in Fig. 3(a). When all the neighboring Cr spins around a muon site form such pairs, the local field at the muon site will be very small, originating only from more distant unpaired spins. In contrast, an unpaired spin adjacent to the muon site can produce a local field of significant magnitude. In view of the randomness due to nonmagnetic Ga sites, it is conceivable that a small number (~ a few %) of Cr moments remain unpaired. If such unpaired spins migrate from site to site through alternation of the pair bonding, we can expect a time sequence of local fields as observed in our measurements. If, however, these dilute moments are spatially fixed and do not migrate, then we expect $\beta \sim 1/2$ in the fluctuating case and $\beta \sim 1$ in static case, inconsistent with the observed results. The Gaussian distribution of local fields is realized when a dilute source of magnetic field spatially migrates, resulting in a rather homogeneous magnitude of local fields at different muon sites.

In frequency space, local singlet spin pairs would correspond to an inelastic response associated with a spin gap at an energy $\hbar\omega \sim J$. Involvement of more than two spins (larger singlet clusters) would lower the gap energy, while randomness in the system would smear the sharp gap, leading to a broad inelastic response as was observed in neutron scattering from SCGO [8]. This inelastic response would take away most of the spectral weight from the low frequency region around $\omega = 0$, which is detected by μSR. This feature explains the reduction of the muon relaxation rate at low temperatures from the values expected from the bare amplitude Δ of the local fields.

Compared to the Curie susceptibility calculated for free $S = 3/2$ paramagnetic Cr moments, the susceptibility χ observed in our specimen of SCGO $x = 8.0$ is about 30 times reduced near T_g. For migrating unpaired spins embedded in a sea of local singlet pairs, we would expect that the "unpaired time fraction f" would roughly represent the ratio of unpaired versus singlet spins at any given time. Since the singlet pairs do not respond to the uniform field, we expect χ to be reduced from the Curie value by a factor of $\sim f$. Thus the observed reduction of χ is consistent with our μSR results with $f \sim 0.04$.

Instead of this quantum picture, it is possible, in principle, to attribute the zero-field time to the correlated Cr spin directions (each Cr spin having 120° direction from neighboring ones) [1,2] around a muon site which possibly eliminates the field through symmetry. Such a coincidental cancellation of $H_{\rm loc}$ is, however, unlikely in a system with the complicated crystal structure of SCGO.

As shown in Figs. 2(a) and 2(b), the observed results show little temperature dependence below $T \sim 2$ K, despite the clear dynamic characteristics discussed above. This suggests that the dynamics mainly reflect quantum fluctuations rather than classical thermal fluctuations. A classical numerical simulation of spins on kagomé lattice [13], which exhibited dynamic behavior at $T \rightarrow 0$, resulted in decreasing $1/T_1$ with decreasing temperature without saturation, as expected for thermal fluctuations. In contrast, a numerical work on $S = 1/2$ antiferromagnets on the kagomé lattice [4] found a disordered spin liquid ground state consistent with the present work. In the SCGO system with $S = 3/2$ spins, spin fluctuations may reflect both quantum and classical character.

Recently, we obtained μSR results with similar undecouplable Gaussian line shapes in the doped Haldane gap system $(Y,Ca)_2BaNiO_5$ (Ca 5%–10%) [14]. Doped carriers on the 1D NiO chain, created by Ca substitution, cut the $S = 1$ Haldane chain. If the unpaired spins associated with such carriers migrate along the chain, we would expect a situation similar to the spin liquid picture of SCGO, i.e., mobile unpaired spins embedded in a background sea of singlet spins. Indeed, not only μSR but also neutron [15] and susceptibility results [14] from this doped Haldane system are qualitatively similar to those in SCGO.

In summary, we observed Cr spin fluctuations in $SrCr_8Ga_4O_{19}$ and found dynamic fluctuations persisting even at $T \rightarrow 0$ without the formation of a static order parameter. We have proposed a picture of a dynamic spin liquid ground state with a small number of unpaired spins migrating in a sea of singlet spin pairs. Further theoretical and experimental work is required to clarify how the spin-glass-like behavior can arise from such a dynamic spin liquid state.

We would like to acknowledge I. Affleck, S. M. Girvin, and G. M. Kalvius for useful discussions, and Packard, Mitsubishi, and Yamada Foundations, Mrs. I. I. Rabi, and Japan Society for Promotion of Science (JSPS) for financial support.

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