Low Temperature Spin Dynamics of the Geometrically Frustrated Antiferromagnetic Garnet $Gd_3Ga_5O_{12}$

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The low temperature spin dynamics of the geometrically frustrated antiferromagnet $Gd_3Ga_5O_{12}$ (GGG) have been investigated using muon spin relaxation. No evidence for static order is seen down to a temperature of 25 mK or a few percent of the Curie-Weiss temperature. Instead there is a linear decrease in the Gd spin fluctuation rate below 1 K which extrapolates to a small but finite value of 2 GHz at zero temperature. In terms of the spin fluctuations the system appears essentially to remain dynamic at low temperatures ($T > 0.02$ K) and magnetic fields up to 1.8 T.

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Magnetic materials where the lattice symmetries are based on triangles or tetrahedra may exhibit a phenomenon known broadly as *geometrical frustration* [1]. Recently, there has been considerable interest in the behavior of systems where the natural magnetic coupling between ions is frustrated by the constraints placed upon the spins by the lattice, since they can exhibit novel electronic and magnetic behavior. In two dimensions, Heisenberg spins on corner-sharing triangular (Kagomé and garnet) lattices are simple examples of geometrically frustrated systems, while in three dimensions geometric frustration occurs in the pyrochlore structure where the magnetic ions occupy a lattice of corner-sharing tetrahedra. A system of Heisenberg spins interacting via nearest-neighbor antiferromagnetic (AF) couplings on the pyrochlore lattice displays a classical ground state with macroscopic degeneracy, since the lowest energy spin configuration requires only that the net spin for each tetrahedron is zero, $\sum_i \mathbf{S}_i = 0$. This feature led Villain to argue that these systems remain in a *cooperative paramagnetic* state with only short-range spin-spin correlations for all $T > 0$ K (Ref. [2]), and this has been confirmed by Monte Carlo simulations [3]. Experimentally, such behavior has been realized in the pyrochlore $Tb_2Ti_2O_7$ (Ref. [4]), where large Tb spins are observed to fluctuate rapidly down to 75 mK with little or no temperature dependence below 1 K.

The classical ground state degeneracy is fragile and may be lifted when further nearest-neighbor exchange [5], magnetic anisotropy, fluctuations [6], or impurities are considered. This is probably responsible for the variety of novel and mostly unpredictable behavior observed in real systems. Neutron scattering results on the pyrochlore FeF_3 (Ref. [7]) show a transition to a noncollinear long-range-ordered (LRO) state, in which the spins on a tetrahedron point towards or away from the center. However, the majority of frustrated systems do not show Néel LRO. Bulk magnetic susceptibility measurements on the pyrochlore, $Y_2Mo_2O_7$ (Ref. [8]), show strong irreversible behavior below $T_F = 22.5$ K, characteristic of spin glass ordering, even though the level of crystalline disorder is immeasurably small by diffraction techniques [9]. Neutron scattering and muon spin rotation/relaxation (μSR) data on $Y_2Mo_2O_7$ (Refs. [10,11]) and $Tb_2Mo_2O_7$ (Refs. [10,12]) confirm that there is rapid slowing down and freezing of the magnetic moments as one approaches and goes through T_F from above and the absence of LRO down to 0.1 T_F. The most striking feature in many of these systems is the temperature independent dynamic spin relaxation which persists down to very low temperatures. This shows that there is an appreciable density of states for low energy magnetic excitations which is larger in these systems than in conventional chemically disordered spin glasses.

A remarkable feature of many geometrically frustrated systems is the suppression of long-range magnetic ordering and in some cases a high sensitivity to the presence of an external magnetic field. $Gd_3Ga_5O_{12}$ (GGG) is perhaps the best known example of a field induced phase transition. In GGG (space group $Ia\overline{3}d$) the Gd^{3+} ions occupy two interpenetrating, corner-sharing triangular sublattices, with Heisenberg spins which are only weakly coupled through second and third nearest-neighbor interactions. The single ion anisotropy is estimated to be less than 0.04 K (Ref. [13]). Specific heat and magnetic susceptibility in zero field indicate there is no long-range magnetic ordering down to at least $T = 0.14$ K, which is more than an order of magnitude below the Curie-Weiss temperature of $\Theta_{CW} \sim -2$ K (Ref. [14]). Similar measurements on a [100] needlelike single crystal have shown that the application of an external field ($0.6 < H < 1.4$ T) can induce long-range AF order [15]. A spin glass transition below 150 mK has been reported in a single crystal of GGG,

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where the site disorder from Gd on Ga sites is estimated at 1%. In a powdered sample where such disorder is estimated at only 0.1%, the transition is lowered by 50 mK, indicating that this magnetic transition is controlled by the amount of site disorder. Recently, neutron diffraction measurements [16] have found that short-range magnetic ordering can occur at temperatures as high as 5 K and that correlations of up to ~100 Å can exist below 140 mK.

In this paper we report the first study of the local magnetic properties of GGG using the technique of muon spin relaxation, which is well suited to studying slow spin fluctuations in geometrically frustrated magnets. We find that in both powdered and single crystal GGG samples there is no sign of static ordering down to at least 25 mK, or $0.013\Theta_{CW}$. Instead, below 1 K there is a linear drop in the Gd fluctuation rate. Furthermore, the muon spin relaxation rate is only weakly dependent on magnetic field, indicating that there is no true static LRO induced by the magnetic field. It appears the system remains dynamic, albeit with slow fluctuations, as in some other geometrically frustrated magnets.

The powder sample was prepared from a stoichiometric mixture of Gd_2O_3 and Ga_2O_3 by a solid state diffusion reaction at $T = 1350$ K for 36 h. The slab shaped single crystal was acquired from Escete B. V. Single Crystal Technology, where it was grown using the Czochralski method. A small piece of the crystal was chipped off and ground into powder for room temperature x-ray powder diffraction measurements, which confirmed the garnet crystal structure, lattice parameters, and high purity of the sample. Specific heat data were collected with a quasiadiabatic technique [17]. The low temperature μSR measurements were made using an Oxford Instruments top-loading dilution refrigerator. The single crystal was oriented with the [111] direction parallel to the muon beam and perpendicular to the slab face and attached to a silver cold finger using low temperature grease. Both samples were covered with a thin Ag foil which was bolted to the sample holder to ensure a well-defined and uniform sample temperature.

Low temperature specific heat measurements were performed in order to compare our sample with those used in other studies [15]. In zero field, a broad feature centered at 0.75 K (see Fig. 1), indicative of short-range correlations, is similar to that reported by Schiffer *et al.* [15]. An additional feature centered at 0.17 K is clearly seen in C/T (inset of Fig. 1). The total entropy recovered by 2 K is 47.7 J/mol K, close to $3R \ln(2S + 1) = 51.8$ J/mol K expected for the full degeneracy of Gd ($S = 7/2$). Approximately one-fifth is recovered by 250 mK. In applied fields of 0.9 and 1 T, specific heat measurements on the powder sample also show the sharp peak associated with the transition to LRO.

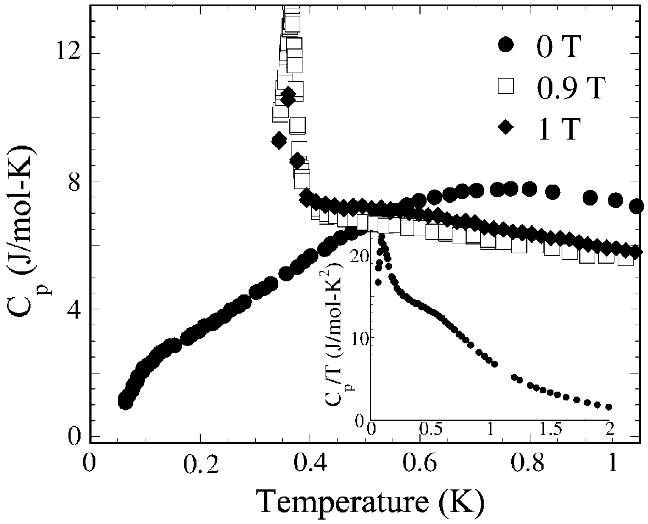

FIG. 1. Specific heat capacity C of GGG as a function of temperature in magnetic fields of 0, 0.9, and 1 T. The inset shows the temperature dependence of C/T in zero field.

The μSR measurements were performed on the M15 beam line at TRIUMF. Spin polarized muons are implanted into the sample, and one records the time evolution of the muon spin polarization. In the longitudinal field geometry used in this experiment, an external magnetic field is directed along the initial polarization direction. The muon acts as a sensitive probe of static and/or slowly fluctuating magnetic moments in magnetic systems and is sensitive to moment fluctuations in a frequency window of 10^4–10^{11} s^{-1} (Ref. [18]).

Figure 2 shows the muon spin relaxation functions $P_z(t)$ in GGG at several temperatures in a small applied field of 0.005 T. In the fast fluctuation limit, when the fluctuation rate ν of the Gd^{3+} moments is much greater than Δ (defined below), the muon spin polarization at each inequivalent muon site i should relax according to a single exponential $P_z^G(t) = e^{-t/T_1}$ with a relaxation rate [19] $1/T_1 = 2\Delta_i^2/\nu$, where $\Delta_i = \gamma_\mu B_i$ is the gyromagnetic

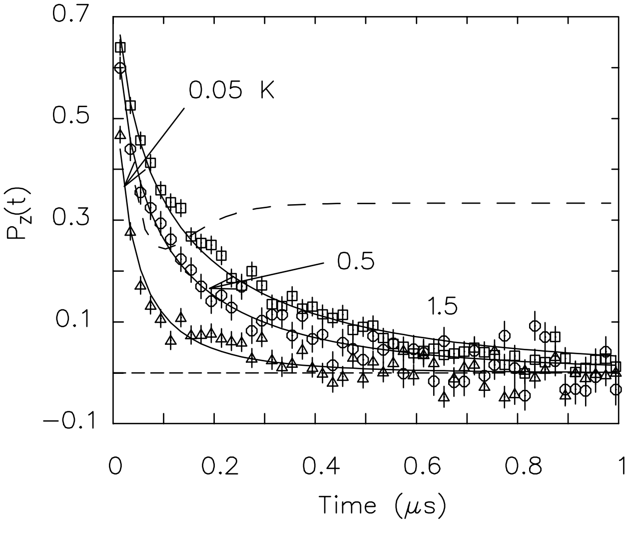

FIG. 2. The muon spin relaxation function, $P_z(t)$, at various temperatures in a powder sample of GGG in an applied field of 0.005 T. The dashed curve is the expected behavior for static spins.

ratio of the muon $[2\pi \times 135.54(10^6 \text{ rads s}^{-1} \text{T}^{-1}]$ times the rms value of the fluctuating internal field B_i. The data in Fig. 2 are well described by a root-exponential relaxation function $P_z(t) \sim e^{-(t/T_1)^\beta}$ with $\beta = 0.5$. In dilute alloys this is explained by the fact that the muon stops at different distances from the magnetic ion. For example, if one assumes a Gaussian distribution of Δ_i's,

$$\rho(\Delta_i) = \sqrt{\frac{2}{\pi}}\frac{a}{\Delta_i^2}\exp\left(-\frac{a^2}{2\Delta_i^2}\right), \tag{1}$$

and then

$$P_Z^L(t) = \int_0^\infty P_Z^G(t)\rho(\Delta)d\Delta = \exp\left(-\left[\frac{4a^2t}{\nu}\right]^{1/2}\right). \tag{2}$$

It is remarkable that we observe the same root-exponential relaxation in GGG which has a dense system of magnetic ions, where one expects much less variance in the distance between the muon and the magnetic ion. This suggests that in the system the spin-spin autocorrelation function itself is nonexponential, as in dilute spin glasses [20].

The temperature dependence of the muon spin relaxation rate is shown in Fig. 3 for both single crystal and powdered GGG samples. Note that $1/T_1$ increases monotonically below 2 K, demonstrating the slowing down of the Gd moments as short-range correlations develop. However, no freezing of the spins is seen on the time scale of our measurement, as would be evidenced by the development of a 1/3 static component (see the dashed curve in Fig. 2). From this we may conclude that the system is close to ordering but remains slowly fluctuating, at least down to 25 mK. The same conclusion holds for both the powdered and the crystalline samples. Note that there is a small scaling factor between the powder and the crystalline samples, but otherwise the same result is obtained.

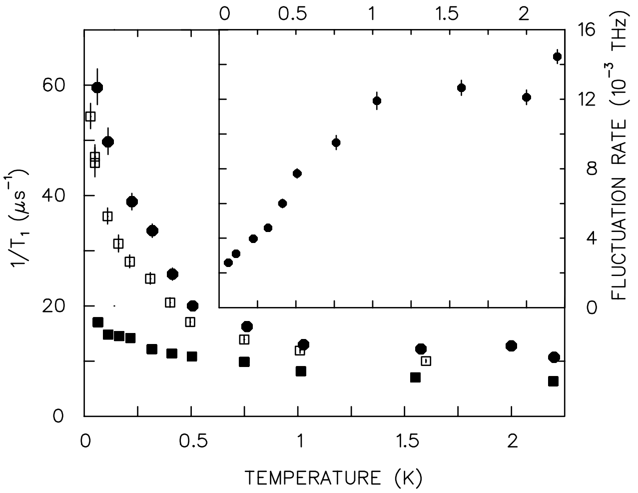

FIG. 3. The root-exponential muon spin relaxation rate $1/T_1$ versus temperature in GGG. The filled circles and squares are for single crystal GGG in fields of 0.0011 T and 1 T, respectively. The open squares are for GGG powder in a small field of 0.005 T. The inset shows the temperature dependence of the Gd spin fluctuation rate.

One can use Eq. (2) and the observed muon spin relaxation rates to obtain the temperature dependence of the Gd spin fluctuation rate (see Fig. 3). The high temperature limit of ν can be estimated from Moriya's expression [21], $\nu^2 = \frac{2}{3\hbar^2}J^2 zS(S+1)$, using a value for $J = 0.107$ K, obtained from specific heat [22]. This gives $\nu = 14$ GHz which will give rise to the spectrum taken at 2.2 K if $a = 196$ MHz in Eqs. (1) and (2). The use of $1/T_1 = 2\Delta_i^2/\nu$ in $P_Z^G(t)$, valid for rapid spin fluctuations, is thus justified. Note the linear drop in the fluctuation rate as the temperature falls below 1 K which extrapolates to a value of about 2 GHz at 0 K. These fluctuation rates are remarkably slow for a paramagnet, but nevertheless finite. Moessner and Chalker [23] studied the precessional dynamics of classical vector spins on geometrically frustrated lattices and predicted such linear behavior below roughly 0.1 J_{cl}, where $J_{\text{cl}} = JS(S+1)$ is the effective classical exchange energy. We find no evidence of a spin glass freezing transition, similar to that seen in other frustrated systems [8–12]. Thus only a small fraction of the moments or a small fraction of each moment is involved. It is estimated from neutron diffraction measurements [16] that only 15% of the volume is made up of regions correlated over ~100 Å. Together with the present results this suggests that the system remains paramagnetic in the sense that most of the moments are fluctuating with an average rate of a few GHz, albeit with short-range correlations. This implies that a truly frozen state, if it occurs, happens at much lower temperatures than previously thought.

We have also studied the field dependence of $1/T_1$ to search for the field induced AF transition reported by Schiffer *et al.* [15]. Figure 4 is a plot of $1/T_1$ at 100 mK as a function of external magnetic field, applied along a [111]

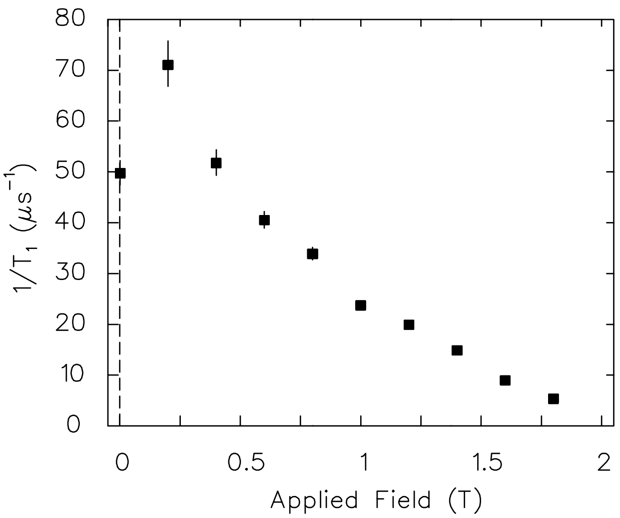

FIG. 4. The root-exponential muon spin relaxation rate in GGG as a function of applied magnetic field at $T = 100$ mK.

direction. The region between 0.8 and ~1.4 T represents the AF phase previously reported [24,25] for a spherical sample, in which the phase boundaries were not corrected for demagnetization effects. No features are seen in $1/T_1$ in this region; instead there is a gradual dropoff in $1/T_1$ above 0.2 T. This decrease is more dramatic than expected in an isotropic paramagnet, when the electronic Zeeman energy becomes comparable to J and k_BT. There remains a large dynamic component of the internal field through the AF region. The field dependence is qualitatively similar to the behavior of the diffuse scattering observed in recent neutron diffraction measurements in an applied magnetic field [26]. Note, however, that there is a small anomalous increase in $1/T_1$ between 0.005 T and 0.2 T. This low field anomaly implies the spin fluctuation rate decreases slightly in the presence of the magnetic field. This is consistent with the results of measurements by Tsui *et al.* [27] at 85 mK, which show that the specific heat decreases with field in this so-called "spin liquid" regime and there is a decrease in the density of states of spin fluctuations with field.

In conclusion, we have shown that GGG remains in a partially dynamic state down to 25 mK. The Gd spin fluctuation rate starts to decrease below 1 K. This is consistent with the onset of short-range correlations, as evidenced by a broad peak in the specific heat of about 0.75 K. Surprisingly, there is no evidence for static magnetic order at low temperatures down to 20 mK. In this sense GGG is similar to other geometrically frustrated systems where true static order is suppressed down to temperatures less than a few percent of Θ_{CW}. The finite $1/T_1$ is evidence for residual entropy even at 25 mK. Similar partial freezing has been observed in hydronium and deuteronium jarosites [28], which form Kagomé lattices with 95% coverage of spins or greater.

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