Magnetic field dependence of muon spin relaxation in geometrically frustrated $Gd_2Ti_2O_7$

S. R. Dunsiger,[1,*] R. F. Kiefl,[2,3] J. A. Chakhalian,[4] J. E. Greedan,[5] W. A. MacFarlane,[6,3] R. I. Miller,[3] G. D. Morris,[3] A. N. Price,[7] N. P. Raju,[8] and J. E. Sonier[9]

[1]*Los Alamos National Laboratory, MST-10, MS K764 Los Alamos, New Mexico 87545, USA*
[2]*Department of Physics and Astronomy, University of British Columbia, British Columbia, Canada V6T 1Z1*
[3]*TRIUMF, Vancouver, British Columbia, Canada V6T 2A3*
[4]*Max Planck Institute for Solid State Research, D-70569 Stuttgart, Heisenbergstrasse 1, Germany*
[5]*Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1*
[6]*Department of Chemistry, University of British Columbia, British Columbia, Canada V6T 1Z1*
[7]*Physikalisches Institut III, Universitaet Erlangen-Nuernberg, 91058 Erlangen, Germany*
[8]*Department of Physics, Ohio State University, Columbus, Ohio, USA*
[9]*Department of Physics, Simon Fraser University, British Columbia, Canada V5A 1S6*

(Received 7 June 2005; revised manuscript received 3 February 2006; published 31 May 2006)

Muon spin relaxation has been investigated in the geometrically frustrated antiferromagnet $Gd_2Ti_2O_7$ as a function of magnetic field and temperature. Well above the magnetic ordering temperature of $T_c=1$ K, the field dependence of the muon spin relaxation rate (T_1^{-1}) originates from field-induced changes in the spectral density of Gd fluctuations. This allows one to determine both the autocorrelation time and magnitude of the fluctuating local magnetic field at the muon. Well below T_c a coherent precession signal is observed, corresponding to a much smaller quasistatic local magnetic field. At low temperatures T_1^{-1} levels off, at a constant value which is much larger than reported recently for a single crystal of $Gd_2Ti_2O_7$ [Yaouanc *et al.*, Phys. Rev. Lett. **95**, 047203 (2005)]. A magnetic field of 2 T completely quenches the low-temperature spin relaxation in the present sample. These results indicate that the ordered state is characterized by low-frequency dynamics which are most likely due to residual crystalline disorder.

DOI: 10.1103/PhysRevB.73.172418 PACS number(s): 75.25.+z, 76.75.+i, 77.84.Dy

Since Anderson considered the problem of antiferromagnetic ordering on the pyrochlore lattice[1] in 1956, there has been a great deal of interest in systems where the magnetic ions occupy the vertices of edge or corner sharing triangular units.[2] In such systems the natural magnetic coupling will be *geometrically* frustrated if it is not possible for the spins to satisfy the dominant magnetic interaction. In pyrochlore metal oxides, with a general formula $A_2B_2O_7$, the magnetic ions (A and/or B) occupy a network of corner-sharing tetrahedra. The curiosity about these systems stems from the possibility that if conventional magnetic order is highly frustrated then one may find novel low temperature behavior. There is now considerable evidence that the low-temperature state depends sensitively on a variety of factors such as anisotropy,[3] the range of the spin-spin interactions,[4,5] thermal,[6] and quantum[7–9] fluctuations and residual disorder.[3,10] Novel properties, such as cooperative paramagnetism,[11] unusual first-order phase transitions,[12] and dipolar "spin-ice" behavior,[13–15] have all been observed in rare earth titanate pyrochlores.

Recent theoretical efforts have focused on geometrically frustrated systems with competing superexchange and dipolar interactions, assuming either Ising[15,16] or Heisenberg spins.[4,17,18] Calculations by Del Maestro *et al.*[19] predict several ordered structures at low temperature depending on further neighbor interactions. $Gd_2Ti_2O_7$ is an excellent approximation to such a model system characterized by a Heisenberg antiferromagnetic coupling with the dipole-dipole interaction as the leading perturbation. The Gd^{3+} ion ($4f^7$) has an $^8S_{7/2}$ ground state with no orbital contribution to its angular momentum. Thus, crystal field splittings and anisotropy are expected to be relatively unimportant. Experimentally, measurements of the heat capacity, ac and dc susceptibility[17] show evidence of long-range ordering at 0.97 K, with several ordered phases as a function of temperature and applied magnetic field.[20,21] Initial neutron diffraction[22] data at 50 mK suggested a partially ordered noncollinear antiferromagnetic ground state, while more recent measurements[23] suggest rather that three of the four spins on a tetrahedron are fully ordered, while the fourth is weakly ordered with a reduced moment of $1.9\mu_B$. Recently μSR data have also been reported in a single crystal of $Gd_2Ti_2O_7$,[24] which show a sharp second transition at 0.7 K in specific heat measurements and where the low-temperature muon spin relaxation rate is very small but finite even at 20 mK. The nature of the 0.7 K transition is not known for certain but the authors suggest that it may be structural.

In this paper we report a μSR investigation as a function of magnetic field of a polycrystalline sample of $Gd_2Ti_2O_7$ with a single transition at $T_c=1$ K. The pressed polycrystalline samples were prepared in a manner similar to that of Ref. 17. In particular, Gd_2O_3 and TiO_2 were mixed in stoichiometric quantities and heated in alumina crucibles for 12 h at 1400 °C. The absence of the second transition at 0.7 K has been attributed to residual disorder.[20] The μSR measurements were carried out at TRIUMF in a ^{4}He gas flow cryostat for temperatures above 2 K and in an Oxford Instruments model 400 top-loading dilution refrigerator (DR) for lower temperatures. In a μSR experiment the observed quantity is the time evolution of the muon spin polarization, which depends on the distribution of internal magnetic fields

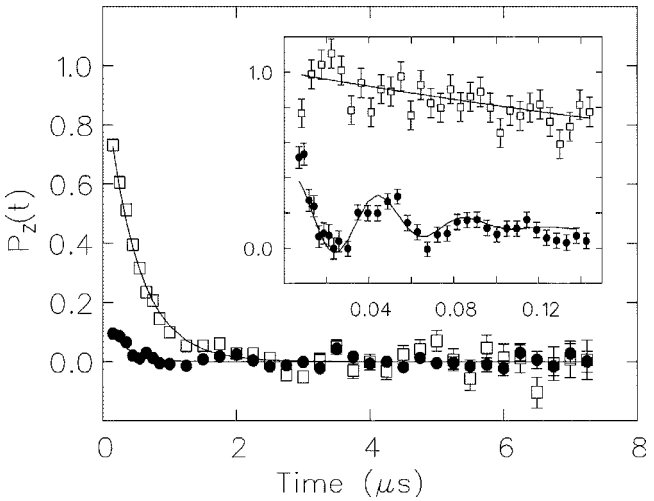

FIG. 1. Time evolution of the muon spin polarization in $Gd_2Ti_2O_7$ in a longitudinally applied field of 0.005 T at $T=2$ and 0.05 K (open squares and filled circles, respectively). The inset shows the behavior at early times on the same vertical scale.

and their temporal fluctuations.[25] Figure 1 shows the time evolution of the muon polarization above and below the magnetic ordering transition at $T_c=1$ K in a small applied field of 5 mT.[26] Above T_c (open squares) single exponential behavior of the entire signal is observed. On cooling below T_c a high-frequency oscillation develops (filled circles in the inset), indicating a quasistatic internal field with a component perpendicular to the initial muon polarization direction ($\hat{z}$). In addition, there is a smaller, slowly relaxing part of the signal which is observable on a longer time scale (filled circles in the main figure) and which is attributed to the $\hat{z}$ component of the internal field. Ideally, in a randomly oriented powder the amplitude for the precessing and nonprecessing components should be 2/3 and 1/3, respectively. The observed amplitudes extrapolated to $t=0$ are close to this ratio but account for only about half of the signal amplitude seen above T_c, indicating there is an unresolved fast-relaxing signal.

Figure 2 shows the average muon spin relaxation rate in $Gd_2Ti_2O_7$ obtained from fits to a single exponential relaxation function over the time interval of 0.05 or 0.1 to 7.5 μs above and below T_c, respectively. The oscillatory component has been omitted from the analysis as it became too highly damped in the neighborhood of T_c. The muon spin relaxation rate at 5 mT is almost temperature independent for $T \gg T_c$, as the spin fluctuation rate is then determined by the exchange coupling $\mathcal{J}$. The rise in T_1^{-1} below 10 K is attributed to critical slowing down of the fluctuations as one approaches T_c. The low field results above T_c are in good agreement with Ref. 24. Similar behavior is observed in a large applied field of 4 T except the relaxation rates are slightly smaller. Below T_c the magnetic field has a much more dramatic effect. In *low* field the relaxation rate falls sharply immediately below T_c but levels off at a constant value below 500 mK. In *high* field T_1^{-1} continues to fall below 500 mK and is too small to measure below 100 mK. The latter is more typical of conventional magnetic order where the magnetic excitations die off rapidly at low temperatures.[27]

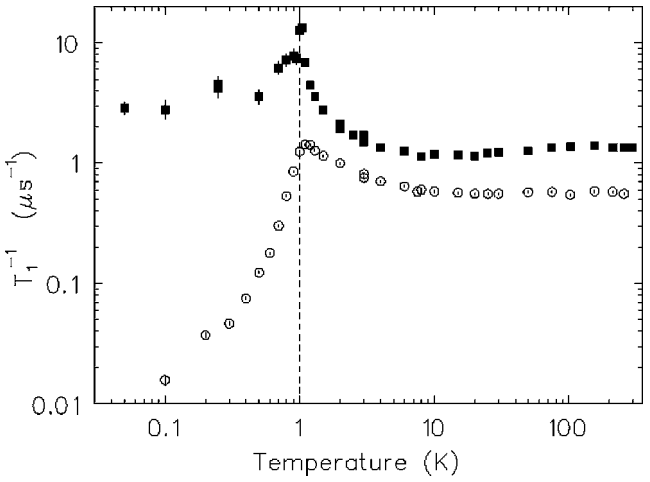

FIG. 2. Spin relaxation rate in $Gd_2Ti_2O_7$ as a function of temperature in longitudinally applied magnetic fields of 5 mT (filled squares) and 4 T (open circles).

We first discuss the spin dynamics in the paramagnetic phase. A detailed field dependence of the muon spin relaxation rate is shown in Fig. 3 at 100 and 7.5 K. Note T_1^{-1} falls off gradually above a few Tesla. Following conventional theory for nuclear spin relaxation from fluctuating electronic moments,[28] one can express T_1^{-1} in terms of the autocorrelation functions for the components of the electron spin parallel (S_z) and perpendicular (S_x) to the magnetic field direction ($\hat{z}$): $\langle S_z(t)S_z(0)^*\rangle = 1/3S(S+1)\exp(-t/\tau)$ and $\langle S_x(t)S_x(0)^*\rangle = 1/3S(S+1)\exp(i\omega_e t)\exp(-t/\tau)$, where $\omega_e=\gamma_e B$ is the electronic Zeeman frequency and τ is the correlation time for fluctuations. For simplicity, we have assumed exponential correlation functions with the same correlation times for S_z and S_x. Note the transverse component of an electron spin precesses in the field at ω_e as it relaxes, whereas the longitudinal component relaxes without precession. The muon spin relaxation rate is proportional to the spectral density $J(\omega)$ of the effective fluctuating field at the muon, evaluated

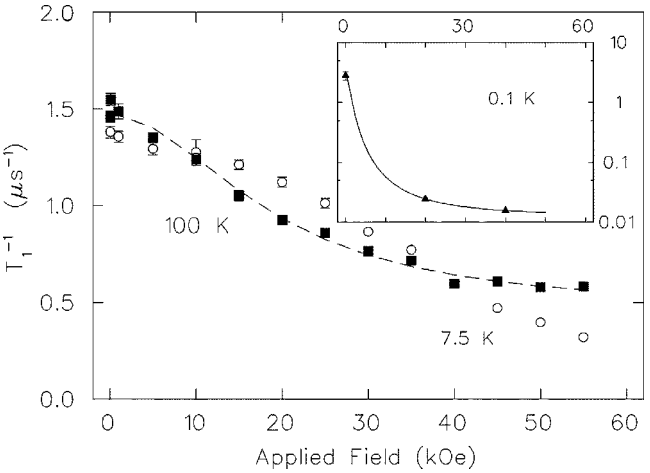

FIG. 3. Spin relaxation rates T_1^{-1} in $Gd_2Ti_2O_7$ as a function of longitudinal magnetic field at 100, 7.5, and 0.1 K (see the inset). Note the logarithmic scale on the inset. The solid line is a guide to the eye.

at the muon Larmor frequency $\omega_\mu = \gamma_\mu B$. Calculation of $J(\omega_\mu)$ involves Fourier transforms of the electron correlation functions and knowledge of the muon-electron magnetic interaction. The field dependence of T_1^{-1} is a sum of three Lorentzian functions,[28]

$$1/T_1 = \frac{2\Delta_1^2\tau}{1+\omega_\mu^2\tau^2} + \frac{2\Delta_0^2\tau}{1+(\omega_e+\omega_\mu)^2\tau^2} + \frac{2\Delta_2^2\tau}{1+(\omega_e-\omega_\mu)^2\tau^2}, \tag{1}$$

where Δ_i depends on the form of the muon-electron coupling. For an isotropic hyperfine coupling only Δ_0 is nonzero, whereas for dipolar coupling all three may be nonzero with amplitudes which depend on the orientation between the muon-electron direction and the magnetic field. Using the fact that $\omega_e \gg \omega_\mu$, one can simplify Eq. (1),

$$1/T_1 = f\frac{2\Delta^2\tau}{1+\omega_\mu^2\tau^2} + (1-f)\frac{2\Delta^2\tau}{1+\omega_e^2\tau^2}, \tag{2}$$

where Δ is measure of the total coupling strength and $f = \Delta_1^2/\Delta^2$ is the fractional contribution from the first term, which is almost field independent when $\omega_\mu\tau \ll 1$. Note the first term originates from fluctuations in S_z (i.e., along the magnetic field), whereas the second comes from fluctuations in S_x. Most of the observed field dependence comes from the second term, arising from peaks in the spectral density at $\pm$ the electron spin resonance (ESR) transition frequency. This term becomes small when the *electronic* Zeeman frequency (ω_e) exceeds the fluctuation rate ($1/\tau$). It is interesting to note that the relaxation rate decreases due to the field-induced change in the shape of the spectral density function rather than a change in the muon Larmor frequency. In earlier works on spin glasses it has been assumed that the spectral density does not depend on magnetic field in the paramagnetic state.[29] The data at 100 K in Fig. 3 were fit to Eq. (2), yielding $\tau = 3.0(1)\times 10^{-12}$ s, $\Delta = 4.94(9)\times 10^8$ s^{-1}, and $f = 0.31(1)$. The fitted value of τ can be used to estimate the exchange constant $|\mathcal{J}| = 0.29(2)$ K using $(\hbar/\tau)^2 = 2Z\mathcal{J}^2S(S+1)/3$,[30] with a coordination number $Z=6$, and spin $S=7/2$. This is close to the value of $\mathcal{J} = -0.30(1)$ K deduced from measurements of the Curie-Weiss temperature $\theta_{CW} = Z\mathcal{J}S(S+1)/3 = -9.6$ K.[17] One can also estimate the total magnitude of the effective fluctuating magnetic field at the muon as $\sqrt{3}\Delta/\gamma_\mu = 1.00(2)T$,[31] which is reasonable for such large moments. It is clear from Fig. 3 that the field dependence at 7.5 K is no longer well described by Eq. (2), indicating there are significant changes in the spectral density as one approaches θ_{CW}, where short-range correlations become important. The low-frequency contributions to the spectral density are particularly sensitive to further neighbor interactions,[32] which become increasingly important as the phase transition is approached.

We now turn to the behavior in the ordered state below $T_c = 1$ K. As can be seen from Fig. 1, the muon spin polarization function in low field shows a heavily damped oscillation at early times and a slowly relaxing component at later times. The spontaneous precession signal at 23 MHz is a characteristic signature of an ordered magnetic state in which the moments are quasistatic on the time scale of the muon lifetime. Considering the complex crystal structure and the possibility of multiple muon sites with a corresponding distribution of internal fields, the damping rate is reasonable. The signal is very similar to that reported in Ref. 24 where the precession signal was fit to a sum of two frequencies with an average equal to that observed here. In both samples the average internal field at the muon is 0.17 T, which is six times smaller than the fluctuating internal field measured above the transition temperature. It is also substantially smaller than the internal field strength of 1.2 T observed in the ordered state of the isostructural compound $Tb_2Mo_2O_7$, where the Tb^{3+} ion has a similarly sized moment.[33] While some reduction in an ordered state could be anticipated due to cancellation effects from neighboring moments, such a large difference is surprising in a complicated structure with many low-symmetry interstitial sites. (The muon is expected to occupy a low-symmetry site about an O–H bond length from an oxygen.) This suggests there may also be some reduction in the ordered moment relative to the paramagnetic state. Recent neutron scattering measurements find an ordered moment of only 1.9 μ_B on one of the four spins comprising a tetrahedron[23] below the lower phase transition. By comparison, measurements of the susceptibility in the paramagnetic state are consistent with a free-ion value for Gd^{3+} equal to $7.94\mu_B$.

There is a significant difference in the low-temperature spin relaxation rate in the present sample compared to that reported in Ref. 24. While the relaxation rates depend somewhat on how the data are analyzed, the differences are apparent even in the raw time spectra. For example, the time for the polarization to relax to half its initial value is ~ 0.3 μs or a factor of 10 shorter than reported for the crystal. This suggests that low-temperature spin relaxation originates from residual structural disorder since the present sample was not annealed extensively at low temperature. Off-stoichiometry in the Gd to Ti ratio has been reported in $Gd_2Ti_2O_7$ which has been synthesized at high temperature.[34] Such disorder would act to dilute the magnetic species on the *A* site, introducing paramagnetic-like spins.[10]

Application of a large magnetic field of 4 T dramatically alters the temperature dependence of the relaxation rate below T_c. As seen in Fig. 2, T_1^{-1} drops rapidly below a slightly shifted $T_c = 1.1$ K and is too small to measure below 100 mK. Thus, the magnetic field completely quenches the low-temperature spin relaxation. This is in sharp contrast to the much smaller effect of the 4 T field observed above T_c. On general grounds, we expect terms in the spectral density centered at $\pm\omega_e$, arising from transverse fluctuations [second and third terms in Eq. (1)], will evolve to much higher frequencies in the ordered state *even in low applied field*, since at low temperatures any electron spin transition will be on the order of any spin gap. In this case only the first term from the longitudinal fluctuations should contribute significantly to the terms in the spectral density relevant to the muon spin relaxation rate. In order to completely quench the relaxation one must only satisfy that $\omega_\mu\tau \gg 1$, implying the fluctation rates at low temperatures are much less than 1 GHz, several orders of magnitude slower than the paramagnetic regime.

In conclusion, we have performed a detailed investigation

of the spin dynamics in a polycrystalline sample of $Gd_2Ti_2O_7$ as function of magnetic field and temperature. Well above the magnetic phase transition the muon spin relaxation rate is weakly field dependent. This behavior is attributed to field-induced changes in the spectral density from the transverse spin fluctuations. We show that this field dependence may be used to directly measure both the correlation time for Gd spin fluctuations and the magnitude of the fluctuating magnetic field at the muon. Well below $T_c = 1.0$ K a coherent oscillation is observed corresponding to a quasistatic internal field much smaller than the fluctuating field seen above T_c. Finally, the residual spin relaxation at low temperatures is much greater than has been reported recently on a single crystal with a second phase transition at 0.7 K.[24] The enhanced low-temperature relaxation is quenched by the application of a magnetic field, suggesting that the low-temperature relaxation arises from low-frequency dynamics, possibly due to residual structural disorder. Such residual disorder may be a more widespread feature of the rare earth titanate pyrochlores,[35] despite their nominally stoichiometric composition. This phenomenon may explain the differing low-temperature behavior reported in the related compound $Tb_2Ti_2O_7$ (Ref. 36) and once again highlights the fragile nature of the ground state in these geometrically frustrated materials.

ACKNOWLEDGMENTS

Work at Los Alamos National Laboratory was performed under the auspices of the U.S. Department of Energy. It is a pleasure to acknowledge the support of the TRIUMF μSR facility, National Sciences and Engineering Research Council of Canada and the Canadian Institute for Advanced Research.

*Present address: Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada.

[1] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).
[2] A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier Science, Amsterdam, 2001), Vol. 13, p. 423.
[3] J. Villain, Z. Phys. B **33**, 31 (1979).
[4] J. N. Reimers, A. J. Berlinsky, and A.-C. Shi, Phys. Rev. B **43**, 865 (1991).
[5] J. N. Reimers, Phys. Rev. B **45**, 7287 (1992).
[6] S. T. Bramwell, M. J. P. Gingras, and J. N. Reimers, J. Appl. Phys. **75**, 5523 (1994).
[7] A. B. Harris, A. J. Berlinsky, and C. Bruder, J. Appl. Phys. **69**, 5200 (1991).
[8] B. Canals and C. Lacroix, Phys. Rev. Lett. **80**, 2933 (1998).
[9] B. Canals and C. Lacroix, Phys. Rev. B **61**, 1149 (2000).
[10] R. Moessner and A. J. Berlinsky, Phys. Rev. Lett. **83**, 3293 (1999).
[11] J. S. Gardner *et al.*, Phys. Rev. Lett. **82**, 1012 (1999).
[12] J. A. Hodges *et al.*, Phys. Rev. Lett. **88**, 077204 (2002).
[13] M. J. Harris, *et al.*, Phys. Rev. Lett. **79**, 2554 (1997); S. T. Bramwell and M. J. Harris, J. Phys.: Condens. Matter **10**, L215 (1998).
[14] A. P. Ramirez, *et al.*, Nature (London) **399**, 333 (1999).
[15] R. Siddharthan *et al.*, Phys. Rev. Lett. **83**, 1854 (1999).
[16] B. C. den Hertog and M. J. P. Gingras, Phys. Rev. Lett. **84**, 3430 (2000).
[17] N. P. Raju *et al.*, Phys. Rev. B **59**, 14489 (1999).
[18] S. E. Palmer and J. T. Chalker, Phys. Rev. B **62**, 488 (2000).
[19] A. G. Del Maestro and M. J. P. Gingras, J. Phys.: Condens. Matter **16**, 3339 (2004).
[20] A. P. Ramirez, *et al.*, Phys. Rev. Lett. **89**, 067202 (2002).
[21] O. A. Petrenko *et al.*, Phys. Rev. B **70**, 012402 (2004).
[22] J. D. M. Champion *et al.*, Phys. Rev. B **64**, 140407(R) (2001).
[23] J. R. Stewart *et al.*, J. Phys.: Condens. Matter **16**, L321 (2004).
[24] A. Yaouanc *et al.*, Phys. Rev. Lett. **95**, 047203 (2005).
[25] A. Schenck, *Muon Spin Rotation Spectroscopy* (Adam Hilger Ltd., Bristol, 1985).
[26] The small external magnetic field of 5 mT is negligible compared to the large internal fields in the sample. However, it suppresses depolarization from nuclear moments.
[27] For example see V. Jaccarino, in Magnetism **2**, 307 (1965), and references therein.
[28] I. J. Lowe and D. Tse, Phys. Rev. **166**, 279 (1968).
[29] A. Keren *et al.*, Phys. Rev. Lett. **77**, 1386 (1996); A. Keren *et al.*, Phys. Rev. B **64**, 054403 (2001).
[30] T. Moriya, Prog. Theor. Phys. **16**, 23 (1956).
[31] The factor of $\sqrt{3}$ arises because there are three components contributing to the rms internal field whereas Δ is a measure of only one component.
[32] G. Reiter and F. C. Barreto, Phys. Rev. B **8**, 1935 (1973).
[33] S. R. Dunsiger *et al.*, Phys. Rev. B **54**, 9019 (1996).
[34] J. L. Waring and S. J. Schneider, J. Res. Natl. Bur. Stand., Sect. A **69**, 255 (1965).
[35] P. Bonville *et al.*, J. Phys.: Condens. Matter **15**, 7777 (2003).
[36] J. S. Gardner, *et al.*, Phys. Rev. Lett. **82**, 1012 (1999); Y. Yasui, *et al.*, J. Phys. Soc. Jpn. **71**, 599 (2002); J. S. Gardner *et al.*, Phys. Rev. B **68**, 180401(R) (2003).