Muon spin relaxation investigation of the spin dynamics of geometrically frustrated antiferromagnets $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$

S. R. Dunsiger
Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T-1Z1

R. F. Kiefl
Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T 1Z1 and Canadian Institute for Advanced Research, University of British Columbia, Vancouver, Canada V6T-1Z1

K. H. Chow
Clarendon Laboratory, Oxford University, Parks Road, Oxford, OX1 3PU, United Kingdom

B. D. Gaulin
Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1

M. J. P. Gingras*
TRIUMF, 4004 Wesbrook Mall, Vancouver, Canada, V6T 2A3

J. E. Greedan
Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

A. Keren, K. Kojima, and G. M. Luke
Department of Physics, Columbia University, New York, New York 10027

W. A. MacFarlane
Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T 1Z1

N. P. Raju
Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

J. E. Sonier
Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T 1Z1

Y. J. Uemura and W. D. Wu
Department of Physics, Columbia University, New York, New York 10027

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The spin dynamics of geometrically frustrated pyrochlore antiferromagnets $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ have been investigated using muon spin relaxation. A dramatic slowing down of the moment fluctuations occurs as one approaches the spin freezing temperatures ($T_F=22$ and 25 K, respectively) from above. Below T_F there is a disordered magnetic state similar to that found in a spin glass but with a residual muon spin relaxation rate at low temperatures. These results show that there is a large density of states for magnetic excitations in these systems near zero energy. [S0163-1829(96)07438-3]

Antiferromagnets which are frustrated or diluted can exhibit novel electronic and magnetic behavior. Recently, there has been considerable interest in the behavior of systems where the natural antiferromagnetic coupling between ions is frustrated by the geometry of the lattice. In two dimensions, Heisenberg spins on triangular and corner sharing triangular (*kagomé*) lattices are simple examples of geometric frustration, while in three dimensions, the most well studied systems have a pyrochlore structure, in which the magnetic ions occupy a lattice of corner sharing tetrahedra. A system of Heisenberg spins interacting via nearest-neighbor antiferromagnetic couplings on the pyrochlore lattice displays a classical ground state with macroscopic degeneracy, since the lowest energy spin configuration requires only that $\Sigma_{i=1}^{4}\mathbf{S}_i=\mathbf{0}$ for each tetrahedron. This feature led Villain to argue that these systems remain in a *cooperative paramagnetic* state with only short-range spin-spin correlations for all $T>0$ (Ref. 1) and this has been confirmed by Monte Carlo simulations.[2] Possibly, the most interesting feature of the ground state of pyrochlore[3] and *kagomé*[4,5] lattice antiferromagnets is the prediction of a dispersionless spin-wave branch (''zero modes''). These zero modes manifestly effect the thermodynamics of these classical systems as demonstrated by Monte Carlo simulations, where the low tempera-

ture specific heat, C_v, falls below the classical value k_B expected from equipartition of energy.[2,5,6] Also, again because of these zero modes, the *kagomé* and pyrochlore antiferromagnets display large spin fluctuations down to $T=0^+$.[7] However, further nearest-neighbor exchange,[3] magnetic anisotropy and fluctuations[8] may lift this classical ground-state degeneracy.

A wide variety of interesting magnetic behavior has been observed in real systems. Neutron scattering results on FeF_3 (Ref. 9) show a transition to a noncollinear long-range ordered (LRO) state, in which the spins on a tetrahedron point away from the center. However, a large number of oxide pyrochlores do not show Néel LRO. Bulk magnetic susceptibility measurements[10] on the pyrochlore $Y_2Mo_2O_7$ show strong irreversible behavior below $T_F=22$ K, characteristic of spin glass ordering, even though the level of disorder is immeasurably small. Recent measurements of the dc magnetization of $Y_2Mo_2O_7$ show a divergent nonlinear susceptibility at $T\approx 22$ K,[11] which is a signature of a true thermodynamic spin glass phase transition. Inelastic neutron scattering data[12] on $Tb_2Mo_2O_7$ confirm there is rapid slowing down of the Tb spins as one approaches $T_F=25$ K from above and the absence of LRO below T_F. The observed strong diffuse scattering in $Tb_2Mo_2O_7$ indicates the presence of short-range correlations between the moments, which are frozen on a time scale of about 10^{-11} s.

In this article we report an investigation of the low-temperature magnetic properties of pyrochlores $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ using the technique of muon spin rotation and/or relaxation (μSR), which is sensitive to spin fluctuation rates in the range 10^4–10^{11} s^{-1},[13] below that detectable with neutron scattering. We find that, despite its nominally disorder free structure, the magnetic behavior in $Y_2Mo_2O_7$ is close to that observed in conventional random spin glasses. Specifically, a large static internal magnetic field with a very broad distribution develops below T_F, such that no coherent muon spin precession is observed. At the same time, the muon spin relaxation rate $1/T_1$ decreases according to a power law with decreasing temperature. A similar magnetic transition occurs in $Tb_2Mo_2O_7$. The most remarkable feature in the data is the presence of a sizeable residual spin relaxation rate at low temperatures, which is not evident from previous data on conventional metallic spin glasses such as CuMn (Ref. 14), AuMn (Ref. 15), and amorphous-FeMn.[16] This is direct evidence for a larger density of magnetic excitations near zero energy than in conventional random spin glasses.

Details on the preparation of the $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ samples are given elsewhere.[10] Pyrochlores crystallize with an fcc structure containing eight formula units per conventional unit cell and space group $Fd3m$. The ions on the 16*d* site form a network of corner sharing tetrahedra; the 16*c* sites constitute an identical sublattice, displaced by $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Mo^{4+} ions occupy the 16*c* site, Y^{3+} or Tb^{3+} ions the 16*d* site. The Tb^{3+} ion has a large magnetic moment of $\sim 9\mu_B$, roughly nine times larger than that of Mo^{4+}, whereas Y^{3+} is diamagnetic. $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ are semiconductors with small band gaps of 0.013 and 0.007 eV, respectively.[17] The samples in this study were characterized by magnetic susceptibility and x-ray diffraction. Sharp irreversibilities in the magnetization were observed at spin freezing temperatures of 22 and 25 K, respectively, consistent with that seen in other highly stoichiometric samples of $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$. From Rietveld profile refinements of neutron diffraction measurements,[12] one can say the concentration of oxygen vacancies, likely the main source of crystalline disorder in these materials, is below the detectable limit of 1%. Since the ionic radii of Y^{3+} and Mo^{4+}, as well as that of Tb^{3+} and Mo^{4+} are very different, there should be no admixing between the 16*c* and 16*d* cations. This is confirmed by analysis of x-ray data.

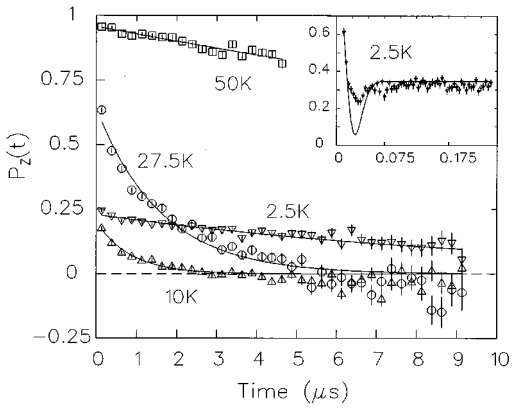

FIG. 1. The muon spin relaxation function, $P_z(t)$ at various temperatures in $Y_2Mo_2O_7$. The inset shows the early time behavior at $T=2.5$ K.

μSR measurements were made 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. For the DR measurements the pressed polycrystalline pellets were varnished onto an Ag plate and covered in thin Ag foil, which was bolted to the cold finger. 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 and their temporal fluctuations. In a longitudinal field (LF) geometry an external magnetic field is directed along the initial polarization direction. The present measurements were made in a small longitudinal field to quench any spin relaxation from static nuclear dipolar fields in the sample holder. Further details on the μSR technique may be found in Ref. 13.

Fig. 1 shows several typical μSR spectra in $Y_2Mo_2O_7$. Above $T_F=22$ K the observed spin relaxation is attributed to rapid fluctuations of the internal magnetic field due to Mo^{4+} moments in the paramagnetic phase. When the fluctuation rate $\nu \gg \Delta$ (defined below), the relaxation function [see $P_z(t)$ in Fig. 1] for each magnetically equivalent muon site i can be described by a single exponential $e^{-\lambda_i t}$ with a relaxation rate:[14]

$$\lambda_i = 2\Delta_i^2 \nu_i / (\nu_i^2 + \nu_L^2), \tag{1}$$

where $\Delta_i = \gamma_\mu B_i$ is the gyromagnetic ratio of the muon $[2\pi \times 135.54\ (10^6\ \text{rads s}^{-1}\ \text{tesla}^{-1})]$ times the rms internal magnetic field B_i at site i. ν_i is the fluctuation rate of the internal field and $\nu_L = \gamma_\mu B_{\text{ext}}$ is the Larmor frequency of the muon in the external magnetic field. Note that λ_i is only weakly dependent on the applied field provided $\nu_i \gg \nu_L$; this

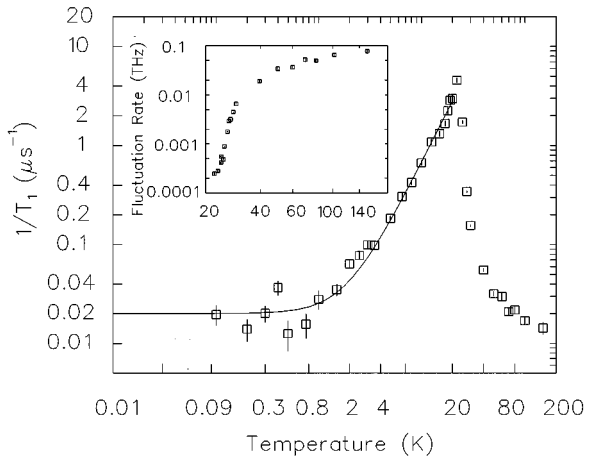

FIG. 2. The muon spin relaxation rate $1/T_1$ vs temperature for $Y_2Mo_2O_7$ in a small applied field of 0.02 T. The solid line is the best fit to the data assuming a power-law functional form. The Mo^{4+} spin fluctuation rate vs temperature above T_F is shown in the inset.

is consistent with the absence of any field dependence observed in the spectra for T above T_F. Figure 2 shows the average muon spin relaxation rate in $Y_2Mo_2O_7$ obtained from fits to a single exponential relaxation function $P_z(t) \sim e^{-t/T_1}$ over a restricted time interval of 0.05 to 6 μs, where $\lambda = 1/T_1$. In the paramagnetic phase one may use Eq. (1) to estimate the average fluctuation rate of the moments. For example, with $B_i = 0.066$ T (see below) one obtains fluctuation rates shown in the inset of Fig. 2. Note the sharp rise in the average $1/T_1$ and corresponding decrease in the Mo^{4+} fluctuation rate as one approaches $T_F = 22$ K.

Just above T_F, $P_z(t)$ deviates somewhat from a single exponential (see, for example, $T = 27.5$ K spectrum in Fig. 1) and is better described by a stretched exponential of the form $e^{-(\lambda t)^\beta}$, with β near 0.4. Similar behavior has recently been observed in other dense spin glasses AgMn and AuFe.[18]

The muon spin polarization function below T_F (see inset in Fig. 1) is characterized by rapid depolarization of $\frac{2}{3}$ of the initial polarization, followed by slow relaxation of the remaining $\frac{1}{3}$ component. This is a characteristic signature of a highly disordered magnetic state in which the moments are quasi-static on the time scale of the muon lifetime. For example, the muon polarization function for a single magnetic site with a Gaussian distribution of static internal fields is given by the Kubo-Toyabe function:[13]

$$P_z(t) = [\tfrac{1}{3} + \tfrac{2}{3}(1 - \Delta^2 t^2) e^{[-(1/2)\Delta^2 t^2]}], \qquad (2)$$

The curve in the inset of Fig. 1 shows a fit of the early time data at 2.5 K to Eq. (2), modified slightly to include the small external field of 0.02 T. The best fit gives a value $\Delta/\gamma_\mu = 0.066(3)$ T, which corresponds to an average field strength $\sqrt{8/\pi}\,(\Delta/\gamma_\mu) = 0.105(5)$ T. Note however that the dip in $P_z(t)$ at 0.032 μs is not as deep as predicted by the modified Eq. (2), indicating the distribution of internal fields is more complicated than a single Gaussian. One can generalize Eq. (2) to include a fluctuating component to the internal field, which results in relaxation of the $\frac{1}{3}$ tail seen in Fig. 1.

Muon spin relaxation results from the exchange of energy with magnetic excitations. A first order process, in which the muon absorbs or creates an excitation with an energy equal to the muon Zeeman energy, is normally suppressed in conventional systems with LRO, where the density of states $\rho(E) \to 0$ as $E \to 0$, since it requires excitations near zero energy. In a second order (Raman magnon scattering) process involving inelastic scattering of an excitation, application of Fermi's Golden rule gives

$$1/T_1 \propto \int_0^\infty dE\; n\left(\frac{E}{k_B T}\right)\left[n\left(\frac{E}{k_B T}\right) + 1\right] M^2(E)\rho^2(E), \qquad (3)$$

where the muon Zeeman energy has been neglected and $M(E)$ is the matrix element for inelastic scattering of an excitation of energy E causing a muon spin flip. In a spin glass, $n(E/k_BT)$ is the probability distribution (assumed to be Bose) for ''intravalley'' excitations, i.e., spin excitations within one of the macroscopic number of metastable states or valleys. From Eq. (3), the temperature-dependent behavior of $1/T_1$ is primarily determined by the energy dependence of $\rho(E)M(E)$. The low-temperature linear specific heat observed in $Y_2Mo_2O_7$ (Ref. 10) suggests $\rho(E)$ is flat or at least weakly dependent on energy. If $\rho(E)$ and $M(E)$ have power-law dependences with powers l and m, respectively, then Eq. (3) implies that $1/T_1$ varies as $T^{2(l+m)+1}$ below T_F. In other words, below T_F, $1/T_1$ decreases gradually as the magnetic excitations freeze out. The curve in Fig. 2 shows the best fit of the data below 12 K to a simple power-law form $\lambda = \lambda_0 + AT^n$ with exponent $n = 2.1(3)$. This power law behavior and the small value of n indicate that $M(E)\rho(E)$ in Eq. (3) has a very weak energy dependence (i.e., $l+m$ is less than 1). Intervalley transitions, involving reorientations of finite-sized spin clusters, are thought to be important only in the mK range,[19] where $1/T_1$ is independent of temperature in this sample. There is a small residual relaxation rate ($\lambda_0 = 0.02\ \mu s^{-1}$) at the lowest temperatures, which implies there is a nonzero density of excitations close to zero energy. Such relaxation is just above the resolution limit of the μSR technique.

A similar spin freezing transition is observed in $Tb_2Mo_2O_7$, but the residual $1/T_1$ at low temperatures is much larger. Figure 3 shows the muon spin relaxation rate measured in a small longitudinal field of 5 mT. As in $Y_2Mo_2O_7$, a critical slowing down of the moment fluctuations occurs as one approaches $T_F = 25$ K from above. Using a value for $B_i = 0.7$ T (see below) we obtain the spin fluctuation rates (ν) above T_F shown in the inset of Fig. 3. For comparison, we include some of the corresponding Tb^{3+} spin fluctuation rates determined from inelastic neutron scattering.[12] Considering the fluctuation rates measured by neutron scattering are at the lower experimental limit and the systematic errors in both measurements, the agreement is reasonable. From this we can conclude that both techniques are sensitive to the same quantity in this sample, i.e., the Tb^{3+} moment fluctuation rates. The fact that T_F is about the same in $Tb_2Mo_2O_7$ and $Y_2Mo_2O_7$ supports the proposal that the spin freezing temperature in $Tb_2Mo_2O_7$ is determined mainly by the Mo^{4+} ions, which provide an effective coupling between the larger but more localized rare earth Tb^{3+} moments.

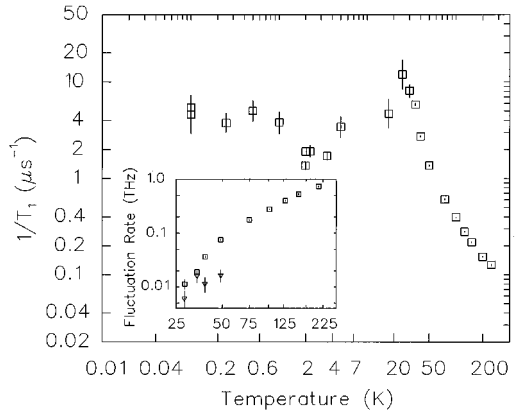

FIG. 3. Dynamical muon spin relaxation rate $1/T_1$ vs temperature for $Tb_2Mo_2O_7$ in an applied field of 5 mT. The inset shows the Tb^{3+} moment fluctuation rate vs temperature above T_F. The inverted triangles indicate neutron scattering data (Ref. 8).

Figure 3 shows that $1/T_1$ initially begins to decrease as T falls below T_F but recovers below 1 K and stays constant at a relatively large value of 5 μs^{-1}. The initial amplitude of the relaxing $\frac{1}{3}$ component increases as the ratio between the external magnetic field and internal static field. This dependence was used to estimate the magnitude of the static component of the internal magnetic field $B_i = 0.70(6)$ T which is about an order of magnitude larger than in $Y_2Mo_2O_7$,[20] as expected from the ratio of Tb^{3+} and Mo^{4+} magnetic moments. This confirms that the Tb^{3+} moments are involved in the 25 K freezing transition. Note the ratio of residual relaxation rates in $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ is roughly equal to the ratio of the square of the respective internal fields. The large residual $1/T_1$ in $Tb_2Mo_2O_7$ establishes there is a nonzero density of low energy excitations, which cause relaxation either by a first or second order process. Computer simulations by Ching *et al.*[21] on insulating Heisenberg spin glasses $Eu_xSr_{1-x}S$ ($x = 0.54$ and 0.40) have indicated the density of states $\rho(E)$ may be peaked at low energies and $\rho(0)$ finite.

We emphasize here that we find convincing evidence for a limiting temperature independent $1/T_1$ in $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ only in the temperature range $T/T_F < 0.05$. Previous μSR experiments[14–16] found a strong temperature dependence of $1/T_1$ in the temperature range $T/T_F \in [0.1-1.0]$, with no sign that $1/T_1$ was approaching a limiting and temperature independent value $\lim_{T\to 0}[1/T_1(T)]$ above the experimental μSR resolution limit and in any case, did not probe the temperature range $T/T_F < 0.1$. It is interesting to note that other spin glasses such as $Cd_{1-x}Mn_xTe$ ($0.27 \leqslant x \leqslant 0.65$) (Ref. 22) and $La_{1.94}Sr_{0.06}CuO_4$ (Ref. 23) show indications of low-temperature spin dynamics but again, these insulating Heisenberg spin glasses have not been studied in the important region below $0.1T_F$. The geometrically frustrated *kagomé* lattice system $SrCr_8Ga_4O_{19}$ has also recently been studied using μSR. Dynamics spin fluctuations are observed without static freezing, even at 100 mK, well below $T_F = 3.5$ K.[24] There is however some controversy over $SrCr_8Ga_4O_{19}$,[25,26] as it has been suggested that this material does not show a thermodynamic freezing transition at T_F.[26] In this case, one would expect to find spin dynamics persisting down to zero temperature. This is not the case for $Y_2Mo_2O_7$ where we have strong evidence for a *collective freezing transition* at T_F as seen in the critical slowing down seen in μSR and the divergent nonlinear susceptibility.[11]

In conclusion, despite the nominal absence of disorder, the freezing process in $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ appears similar to that expected for a dense spin glass. In particular we observe a critical slowing down of the spin fluctuations and nonexponential muon spin relaxation near T_F, while below T_F there is evidence for a highly disordered magnetic structure. The most striking feature in both systems is the presence of a residual, temperature independent spin relaxation which persists down to very low temperatures. This shows there is an appreciable density of states for low energy magnetic excitations which is much larger in these systems than in conventional randomly frustrated spin glasses. It is possible that the residual low-temperature dynamics in these systems are ''remnants'' of the zero modes predicted theoretically for nearest-neighbor Heisenberg spins on a pyrochlore lattice.[3–6]

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*Present address: Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

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