Muon spin relaxation investigation of the spin dynamics of geometrically frustrated antiferromagnets $\text{Y}_2\text{Mo}_2\text{O}_7$ and $\text{Tb}_2\text{Mo}_2\text{O}_7$

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The spin dynamics of geometrically frustrated pyrochlore antiferromagnets $\text{Y}_2\text{Mo}_2\text{O}_7$ and $\text{Tb}_2\text{Mo}_2\text{O}_7$ 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. [S0163-1829/96/10-9019-$\$10.00]
ture specific heat, $C_v$, falls below the classical value $k_B$ expected from equipartition of energy.\textsuperscript{2,5,6} Also, again because of these zero modes, the \textit{kagome} and pyrochlore antiferromagnets display large spin fluctuations down to $T=0\,^\circ\text{C}$.\textsuperscript{7} However, further nearest-neighbor exchange,\textsuperscript{8} magnetic anisotropy and fluctuations\textsuperscript{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\textsubscript{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 pyrochloro do not show Néel LRO. Bulk magnetic susceptibility measurements\textsuperscript{10} on the pyrochlore $Y_2\text{Mo}_2\text{O}_7$ 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 $Y_2\text{Mo}_2\text{O}_7$ show a divergent nonlinear susceptibility at $T=22$ K,\textsuperscript{11} which is a signature of a true thermodynamic spin glass phase transition. Inelastic neutron scattering data\textsuperscript{12} on $\text{Tb}_2\text{Mo}_2\text{O}_7$ 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 $\text{Tb}_2\text{Mo}_2\text{O}_7$ 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 pyrochloro $\text{Y}_2\text{Mo}_2\text{O}_7$ and $\text{Tb}_2\text{Mo}_2\text{O}_7$ using the technique of muon spin rotation and/or relaxation ($\mu$SR), which is sensitive to spin fluctuation rates in the range $10^{-4}-10^{-11}$ s$^{-1}$\textsuperscript{13} below that detectable with neutron scattering. We find that, despite its nominally disorder free structure, the magnetic behavior in $\text{Y}_2\text{Mo}_2\text{O}_7$ 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 $\text{Tb}_2\text{Mo}_2\text{O}_7$. 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.\textsuperscript{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 $\text{Y}_2\text{Mo}_2\text{O}_7$ and $\text{Tb}_2\text{Mo}_2\text{O}_7$ samples are given elsewhere.\textsuperscript{10} Pyrochloro crystals crystallize with an fcc structure containing eight formula units per conventional unit cell and space group $Fd\bar{3}m$. The ions on the $16d$ site form a network of corner sharing tetrahedra; the $16c$ sites constitute an identical sublattice, displaced by $(\pm \frac{1}{2}, \pm \frac{1}{2})$. Mo\textsuperscript{4+} ions occupy the $16c$ site, Y\textsuperscript{3+} or Tb\textsuperscript{3+} ions the $16d$ site. The Tb\textsuperscript{3+} ion has a large magnetic moment of $\sim 9 \mu_B$, roughly nine times larger than that of Mo\textsuperscript{4+}, whereas Y\textsuperscript{3+} is diamagnetic. $\text{Y}_2\text{Mo}_2\text{O}_7$ and $\text{Tb}_2\text{Mo}_2\text{O}_7$ are semiconductors with small band gaps of 0.013 and 0.007 eV, respectively.\textsuperscript{17} The samples in this study were characterized by magnetic susceptibility and x-ray diffraction. Sharp irre-

![FIG. 1. The muon spin relaxation function, $P_\mu(t)$ at various temperatures in $\text{Y}_2\text{Mo}_2\text{O}_7$. The inset shows the early time behavior at $T=2.5$ K.](image)

versibilities 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 $\text{Y}_2\text{Mo}_2\text{O}_7$ and $\text{Tb}_2\text{Mo}_2\text{O}_7$. From Rietveld profile refinements of neutron diffraction measurements,\textsuperscript{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\textsuperscript{3+} and Mo\textsuperscript{4+}, as well as that of Tb\textsuperscript{3+} and Mo\textsuperscript{4+} are very different, there should be no admixing between the $16c$ and $16d$ cations. This is confirmed by analysis of x-ray data.

$\mu$SR 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 $\mu$SR 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 $\mu$SR technique may be found in Ref. 13.

Fig. 1 shows several typical $\mu$SR spectra in $\text{Y}_2\text{Mo}_2\text{O}_7$. Above $T_F=22$ K the observed spin relaxation is attributed to rapid fluctuations of the internal magnetic field due to Mo\textsuperscript{4+} moments in the paramagnetic phase. When the fluctuation rate $\nu \gg \Delta$ (defined below), the relaxation function $P_\mu(t)$ in Fig. 1 for each magnetically equivalent muon site $i$ can be described by a single exponential $e^{-\nu_\mu t}$ with a relaxation rate:\textsuperscript{14}

$$\lambda_i = 2\Delta_i^2 \nu / (\nu_i^2 + \nu_\mu^2),$$

where $\Delta_i = \gamma_i B_i$ is the gyromagnetic ratio of the muon [$2\pi \times 135.54 (10^6 \text{ rads} \text{s}^{-1} \text{tesla}^{-1})$] times the rms internal magnetic field $B_i$ at site $i$. $\nu_i$ is the fluctuation rate of the internal field and $\nu_\mu = \gamma_B B_{\text{ext}}$ is the Larmor frequency of the muon in the external magnetic field. Note that $\lambda_i$ is only weakly dependent on the applied field provided $\nu_\mu \gg \nu_L$; this
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 $\rho(E)\to0$ as $E\to0$, 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

$$1/T_1 \approx \int_0^\infty dE \ n(E/k_BT) \left[ n\left(\frac{E}{k_BT}\right) + 1 \right] M^2(E)\rho^2(E), \quad (3)$$

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 $\mu$SR 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 ($\nu$) 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.
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 $\mu$s$^{-1}$. The initial amplitude of the relaxing $\frac{1}{2}$ 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 $Y_2Mo_2O_7$ 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 rate vs temperature above $T_F$ is initially begins to decrease as $T$ falls below $T_F$. The geometrically frustrated kagomé lattice system SrCr$_8$Ga$_4$O$_{19}$ has also recently been studied using $\mu$SR.

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 $\mu$SR experiments 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 $\mu$SR 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$_x$Te ($0.27 \leq x \leq 0.65$) (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$_8$Ga$_4$O$_{19}$ has also recently been studied using $\mu$SR. Dynamics spin fluctuations are observed without static freezing, even at 100 mK, well below $T_F=3.5$ K. There is however some controversy over SrCr$_8$Ga$_4$O$_{19}$ as it has been suggested that this material does not show a thermodynamic freezing transition at $T_F$. 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 $\mu$SR and the divergent nonlinear susceptibility.

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.

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