Muon spin relaxation investigation of frustrated antiferromagnetic pyrochlores $A_2B_2O_7$

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In a system where magnetic ions occupy the vertices of edge or corner sharing triangular units, the natural antiferromagnetic coupling between ions is *geometrically* frustrated. A wide variety of interesting magnetic behaviour has been observed in pyrochlores, where magnetic ions form a network of corner sharing tetrahedra. The low temperature spin dynamics of a number of pyrochlores $A_2B_2O_7$ have been investigated using the technique of μSR. For example, $Y_2Mo_2O_7$ shows a transition to a disordered magnetic state similar to a spin glass at $T_F = 22$ K. However, unlike conventional metallic spin glasses, a non-zero muon spin depolarization rate is observed to persist well below $0.1\,T_F$. These results suggest that there is a finite density of states for magnetic excitations in this system near zero energy.

Recently, there has been a considerable interest in the behaviour of systems where the natural antiferromagnetic coupling between ions is frustrated by the geometry of the lattice. In three dimensions, the most well studied systems have a pyrochlore structure. Frustrated systems are characterized by a suppression of the ordering temperature T_c relative to the Curie–Weiss temperature, θ. Within the mean field theory, T_c is given by $T_c = \frac{2}{3}zS(S+1)k_B|J|$ for both ferromagnets and two sublattice antiferromagnets, where z is the number of nearest neighbours, S the spin and J is the exchange interaction. In a ferromagnetic or unfrustrated antiferromagnetic system, the high temperature susceptibility is then

$$\chi = \frac{\mu_B^2 g^2 S(S+1)}{3k_B(T-\theta)}, \tag{1}$$

where $|\theta| = T_c$, g is the Landé g factor and μ_B the Bohr magneton. This no longer holds for frustrated systems and allows the definition of an empirical level of frustration $f = -\theta/T_c$.

We report here an investigation of the low temperature magnetic properties of pyrochlores $Y_2Mo_{2-x}Ti_xO_7$ ($x = 0, 0.4, 0.8, 1$). We find that a large static internal magnetic field with a very broad distribution develops below T_F, such that no coherent muon spin precession is observed. However, the most remarkable feature in the data is the presence of a sizeable residual spin relaxation rate at low temperatures. This is direct evidence for a large density of magnetic excitations near zero energy.

Pyrochlores crystallize with an fcc structure and space group $Fd\bar{3}m$. The ions on the 16c and 16d sites each form networks of corner sharing tetrahedra. Mo^{4+} ions occupy the 16c site, Y^{3+} ions the 16d site. The Mo^{4+} ion has a magnetic moment of $1.7\,\mu_B$, whereas Y^{3+} and Ti^{4+} are diamagnetic.

μSR measurements were made at TRIUMF in a ^{4}He gas flow cryostat for temperatures above 2 K and in an Oxford Intruments Model 400 top loading dilution refrigerator (DR) for lower temperatures. The measurements were made in a small longitudinal field of 0.02 T to quench any spin relaxation from static nuclear dipolar fields. Figure 1 shows several typical μSR spectra in $Y_2Mo_2O_7$. Above $T_F = 22$ K

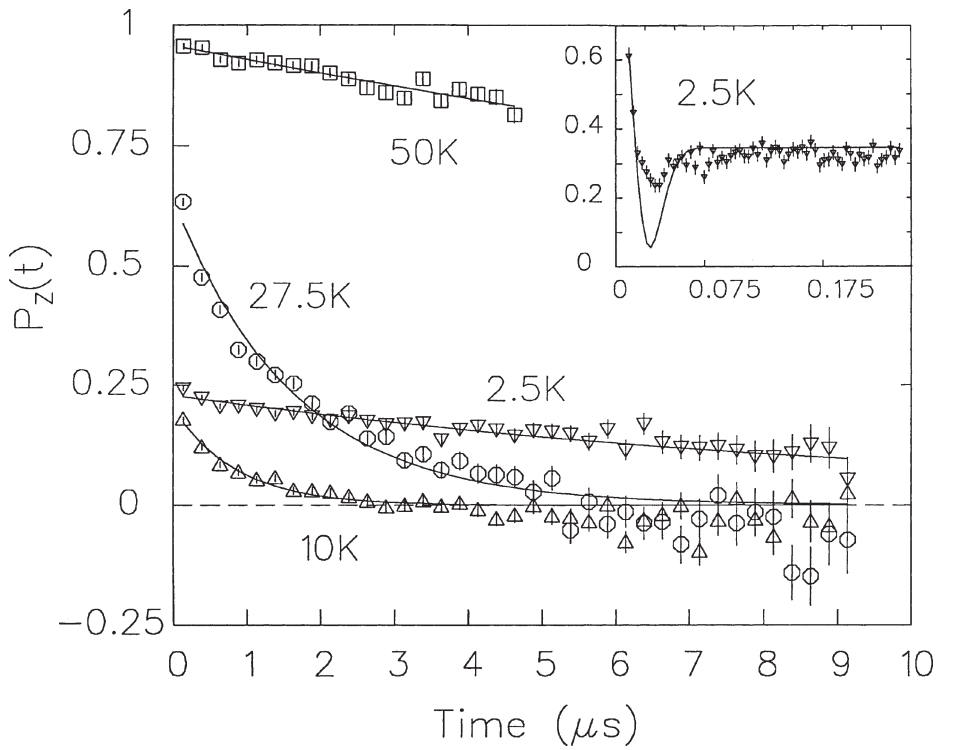

Fig. 1. The muon spin relaxation function, $P_z(t)$, at various temperatures in $Y_2Mo_2O_7$. The inset shows the early time behaviour at $T = 2.5$ K.

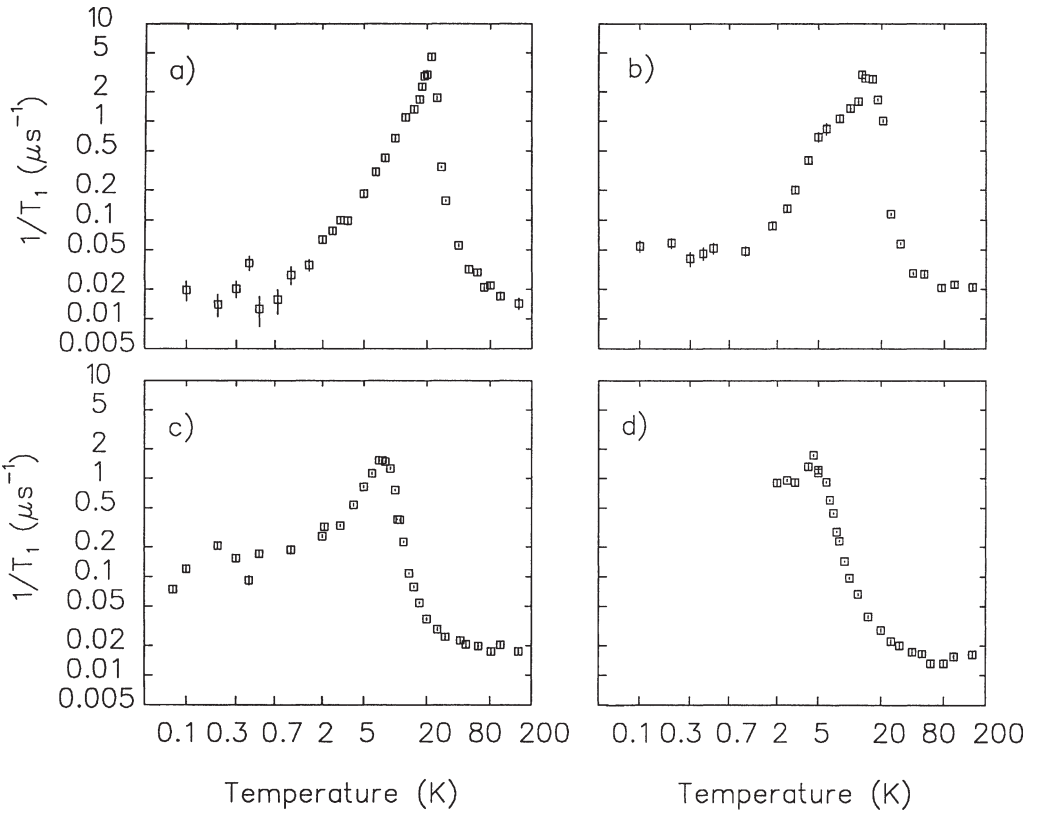

Fig. 2. The muon spin relaxation rate $1/T_1$ vs. temperature for (a) $Y_2Mo_2O_7$, (b) $Y_2Mo_{1.6}Ti_{0.4}O_7$, (c) $Y_2Mo_{1.2}Ti_{0.8}O_7$ and (d) Y_2MoTiO_7 in an applied field of 0.02 T.

the observed spin relaxation is attributed to rapid fluctuations of the internal magnetic field due to Mo^{4+} moments in the paramagnetic phase. Figure 2(a) shows the average muon spin relaxation rate in $Y_2Mo_2O_7$ obtained from fits to a single exponential relaxation function e^{-t/T_1} over a restricted time interval of 0.05 to 6 μs. Just above T_F, $P_z(t)$ deviates somewhat from a single exponential (see for example $T = 27.5$ K spectrum in fig. 1). This behaviour possibly originates from a distribution of correlation times τ associated with different finite spin clusters.

Below T_F, $1/T_1$ decreases gradually as the magnetic excitations freeze out. The muon spin polarization function below T_F (see inset in fig. 1) is characterized by rapid depolarization of $2/3$ of the initial polarization, followed by slow relaxation of the remaining $1/3$ component. This is a characteristic signature of a highly disordered magnetic state in which the moments are quasi-static on the timescale of the muon lifetime. The curve in the inset of fig. 1 shows a fit of the early time data at 2.5 K to a Gaussian Kubo–Toyabe function [3]. The best fit gives a value of the average field strength of $\sqrt{8/\pi}(\Delta/\gamma_\mu) = 0.105(5)$ T, where $\Delta = \gamma_\mu B$ is the gyromagnetic ratio of the muon times the rms internal magnetic field B. Note however that the dip in $P_z(t)$

Table 1
Transition temperatures and levels of frustration in various $Y_2Mo_{2-x}Ti_xO_7$ compounds.

	θ (K)	T_F (K)	f
$Y_2Mo_2O_7$	-28.0	21.8	1.3
$Y_2Mo_{1.6}Ti_{0.4}O_7$	$-38(2)$	15.0	2.5
$Y_2Mo_{1.2}Ti_{0.8}O_7$	$-26(3)$	5.84	4.5
Y_2MoTiO_7	$-33(6)$	3.10	10.6

at 0.032 μs is not as deep as predicted, indicating the distribution of internal fields is more complicated than a single Gaussian.

There is a small but finite residual relaxation rate ($\lambda_0 = 0.02\ \mu s^{-1}$) at the lowest temperatures, which implies there are excitations close to zero energy. Note however that this is just slightly above the resolution limit of the μSR technique. The low temperature linear specific heat observed in $Y_2Mo_2O_7$ [2] suggests the density of states for excitations $\rho(E)$ is flat or at least weakly dependent on energy and is reminiscent of a spin glass. Irreversible behaviour in field and zero field cooled bulk dc magnetic susceptibility measurements [2] is observed below $T_F = 22$ K. Recent measurements of the dc magnetization of $Y_2Mo_2O_7$ also show a divergent non-linear susceptibility at $T \approx 22$ K [4], which is a signature of a true thermodynamic spin glass phase transition [7]. Hence, despite its nominally disorder free crystalline structure, the magnetic behaviour in $Y_2Mo_2O_7$ is similar to that observed in conventional random spin glasses like CuMn [8] and AuMn [9]. The data are not consistent with superparamagnetism, where no discontinuity in the dc susceptibility is expected [5]. Nor is a spin liquid a possible explanation, where the ground state is a fluid of spin pairs correlated together into singlets [6]. In this case we expect no large internal magnetic fields to be present for $T \ll T_F$.

μSR spectra for $Y_2Mo_{1.6}Ti_{0.4}O_7$, $Y_2Mo_{1.2}Ti_{0.8}O_7$ and Y_2MoTiO_7 are shown in figs. 2(b), 2(c) and 2(d), where the diamagnetic Ti^{4+} ions are substitutional impurities on the B site, introducing random disorder. The level of frustration *increases* with increasing Ti substitution (see table 1). The spin freezing temperatures, as seen by a peak in $1/T_1$, are in agreement with magnetic susceptibility measurements, summarized in table 1 [10]. As shown, there is a decrease in the transition temperature with increasing impurity concentration. While this is observed universally in conventional magnets [11], as T_c scales with the number of nearest neighbours, it is not clear that this approach is appropriate for describing spin glasses, where the order parameter is not a simple quantity.

The muon spin depolarization rate is roughly temperature independent below 1 K, at values which increase with increasing impurity concentration. We suggest that the mechanism giving rise to this behaviour is enhanced by the addition of random disorder. In principle, both first and second order muon spin depolarization processes are present in spin glasses, since $\rho(E)$ is thought to be only weakly dependent on energy.

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 long range ordered systems, where the density of states $\rho(E) \to 0$ as $E \to 0$. In a second order (Raman magnon scattering) process inelastic scattering of an excitation is accompanied by a muon spin flip. The frustrated spinel $ZnCr_{1.6}Ca_{0.4}O_4$ shows evidence of a paramagnetic contribution to the dc susceptibility below its spin glass ordering temperature [12]. This behaviour is attributed to unfrozen "entropic" clusters of spins which experience zero effective local field. Susceptibility measurements at millikelvin temperatures might indicate whether a similar mechanism is present in the pyrochlores.

We emphasize here that we find convincing evidence for a limiting temperature independent $1/T_1$ in $Y_2Mo_{2-x}Ti_xO_7$ only in the temperature range $T/T_F < 0.05$. Previous μSR experiments [8,9] found a strong temperature dependence of $1/T_1$ in the temperature range $T/T_F \in [0.1-1.0]$, with no sign of a 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 $T/T_F < 0.1$.

The geometrically frustrated Kagomé lattice system $SrCr_8Ga_4O_{19}$, where there is also a large amount of disorder, has recently been studied using μSR. Dynamic spin fluctuations are observed without static freezing, even at 100 mK, well below $T_F = 3.5$ K [13]. The level of frustration is substantially higher ($f = 150$) and in contrast with the pyrochlores studied T_F *increases* on increasing substitution of diamagnetic Ga ions [14].

In conclusion, despite the nominal absence of disorder, the freezing process in $Y_2Mo_2O_7$ appears similar to that expected for a dense spin glass. In particular we observe a critical slowing down of the spin fluctuations and non-exponential muon spin relaxation near T_F, while below T_F there is evidence for a highly disordered magnetic structure. The most striking feature in these systems is the presence of a residual, temperature independent spin relaxation which persists down to very low temperatures. This indicates 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.

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