# Static Magnetic Order in $Tb_2Sn_2O_7$ Revealed by Muon Spin Relaxation with Exterior Muon Implantation

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$Tb_2Sn_2O_7$ has been proposed as an ordered spin ice, but the precise nature of the low temperature magnetic state remains uncertain. Recent independent muon spin relaxation ($\mu$SR) investigations suggest the possibility of exotic ground states with static order precluded on time scales longer than $10^{-6}$ s. Here the more conventional hypothesis of canted ferromagnetism is tested by means of $\mu$SR with the muons stopped *outside* the sample, as well as ultralow field bulk magnetization measurements. The field cooled state shows conventional static order, while the zero field cooled state may be interpreted in terms of conventional closed domains. These results rule out purely dynamical ground states and illustrate the value of exterior muon implantation as a complement to the conventional technique.

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A system is said to be frustrated when it is not possible to simultaneously minimize every pairwise interaction [1]. Among magnetic materials, frustration plays an important role in the physics of spin glasses [2], frustrated antiferromagnets [3], and spin ice [4,5], but the general importance of frustration is not limited to the sphere of magnetism: it also plays a crucial role in such diverse problems as the zero point entropy of crystalline ice, the formation of stripe phases in ''high-$T_c$'' oxides and the folding of proteins to give biological functionality.

The magnetic rare earth pyrochlores exhibit a wealth of phenomena driven by magnetic frustration, including spin glass, spin liquid, and spin ice behavior. This is particularly well illustrated by the series of rare earth titanate pyrochlores $R_2Ti_2O_7$, in which, by altering the rare earth, a wide variety of magnetic behavior can be realized at low temperatures (typically $<1$ K). For example, $R =$ Ho, Dy, which have effectively ferromagnetic (FM) coupling, form spin ice states with zero point entropy [4,6], $R =$ Tb, with antiferromagnetic (AF) coupling, forms a spin liquid [7] and $R =$ Er forms an ordered AF state, which has been argued to be stabilized by quantum fluctuations [8]. The delicate energy balance that is a feature of these materials is further illustrated by a comparison between the rare earth titanates and their analogous stannates $R_2Sn_2O_7$, an apparently innocuous substitution of one nonmagnetic spectator ion for another. While $R =$ Ho, Dy remain spin ices, the low temperature behavior of the AF $R =$ Er, Tb systems is radically altered by the substitution [9]. With $R =$ Er, the magnetic order is strongly suppressed; with $R =$ Tb, rather than forming an AF spin liquid, a canted ferromagnet order is observed [10].

On the basis of neutron diffraction and ac susceptibility measurements, $Tb_2Sn_2O_7$ has been described as an ''ordered spin ice''[10]. In a spin ice, the magnetic ions sit on corner sharing tetrahedra with two spins pointing into the tetrahedron, along a local $\langle 111 \rangle$ direction, and the other two pointing out [11]. This condition is degenerate, and equivalent to the ice rule that controls proton arrangements in water ice, so spin ices form a low temperature state with ice-type disorder and consequent residual entropy. If every ''up'' tetrahedron has the same ''two-in two-out'' configuration, then an ordered state is obtained that may be described as a canted ferromagnet. In the spin ice materials this state is statistically excluded (in the absence of an applied field) but in $Tb_2Sn_2O_7$ a state similar to this forms at $T_C < 1$ K, despite an AF Curie-Weiss temperature of $-11$ K [9]. Analysis of the specific heat suggests residual fluctuating dynamics on a short time scale [10].

Further interest in the low temperature state of $Tb_2Sn_2O_7$ stems from the independent $\mu$SR studies of Refs. [12,13], which conclude that rather than being truly ordered, the magnetic ground state in fact remains fully dynamic. However, the dynamics must be consistent with the spin correlation functions deduced from neutron diffraction, which imply order at length scales of hundreds of Ångstroms. Both studies therefore propose exotic ground states in which the dynamics are due to the fluctuations of large volumes of spins. Suggested mechanisms involve either coherent rotations or tunneling of the *macroscopic*

 

magnetization vector (Ref. [12]), or very low energy barriers separating the sixfold degenerate ground states, allowing collective reorientation of large static clusters of spins (Ref. [13]). In both cases, these fluctuations would occur on a time scale sufficiently slow that neutron scattering observes apparent long range order (a relaxation time of $10^{-10}$ s for the magnetization would be consistent with this scenario [12]). However, current understanding of condensed matter considers the reorientation of such large numbers of spins to be immeasurably slow [14], so the proposed ground states present a challenge to the current paradigm. It is therefore of great interest to examine the ground state of $Tb_2Sn_2O_7$ using different techniques.

In this Letter the magnetic ground state of $Tb_2Sn_2O_7$ is examined further using an unconventional $\mu$SR method, with the muons stopped outside the sample, as well as ultralow field dc-magnetization measurements. The experimental modification of the $\mu$SR method ensured that the muons could not perturb the sample and provided complementary information to that gained by the standard technique. In any standard $\mu$SR experiment the magnetic field at a muon site arises from the applied field, the sum of dipolar fields from the magnetic moments in the sample and any additional contact hyperfine fields [15]. With muons stopped inside the sample, nearby moments and distant moments contribute roughly equally to the dipolar sum so it is generally tricky to distinguish their contribution. With muons stopped outside the sample, all moments are (to within an order of magnitude) equally distant, and the $\mu$SR effectively isolates the contribution arising from the bulk magnetization of the sample [16]. The muons act as a bulk magnetometer, but with precisely the $\mu$SR time scale (i.e., much faster than any conventional magnetometer). Combined with ultralow field dc magnetization this method allowed the sample magnetization to be measured over a large dynamical range between $10^{-9}$ s and 1 s.

Polycrystalline samples of $Tb_2Sn_2O_7$ were prepared by mixing stoichiometric amounts of $Tb_4O_7$ and $SnO_2$ and then firing in air at 1375 °C. Powder x-ray diffraction patterns confirm the sample as single phase. Magnetization measurements were performed between 1.8 and 300 K using a commercial SQUID in static fields of 1 and 0.2 mT. Field cooled (FC) and zero field cooled (ZFC) magnetization measurements were also performed in the milli-Kelvin regime by combining a commercial d.c SQUID and $He^3$ probe, enabling an active temperature regime between 350 mK and 5 K with a sensitivity of $10^{-12}$ J $T^{-1}$ [17]. All of these measurements were performed in 10 $\mu$T; the field applied for the cooling stage of the FC measurement was 50 mT.

Magnetic characterization of the sample between 1.8 and 300 K demonstrates a Curie-Weiss behavior with a $\theta$ parameter of $-9.8(0.4)$ K, as expected for $Tb_2Sn_2O_7$. Figure 1 shows the temperature dependence of the magnetization (expressed as a susceptibility) between 350 mK and 4 K for the ZFC/FC measurements. Although the $\theta$ parameter suggests AF order should occur at relatively

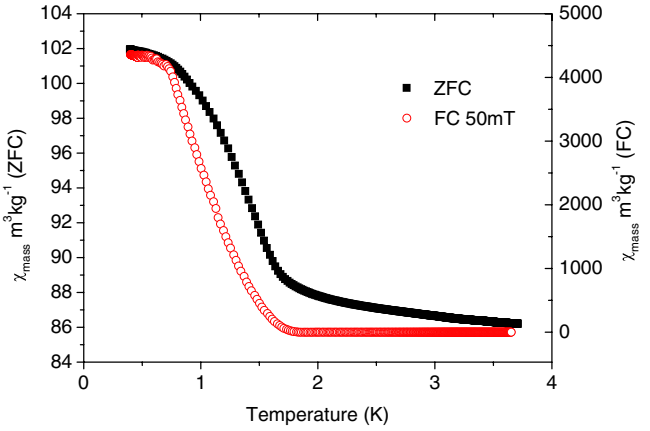


FIG. 1 (color online). The temperature dependence of the magnetization of $Tb_2Sn_2O_7$ expressed as a mass susceptibility between 350 mK and 4 K (note the two scales). The field cooled (FC) and zero field cooled (ZFC) histories result in a drastically different magnetization when measured in 10 $\mu$T.

high temperatures, Fig. 1 demonstrates instead that FM ordering is observed below 1 K. It is not possible to fit the FC or ZFC data to a standard Brillouin function or a single critical exponent. The relative change of the mass susceptibility through the transition between the FC and ZFC data is a factor of $10^2$. This is a significant observation as it implies that the sample moment is being enhanced by the process of field cooling and it is static on the time scale of the measurement (1 s). Hysteretic behavior is characteristic of either a conventional FM or a spin ice [18], where a field of 50 mT is sufficient to provide irreversibility in the isothermal magnetization loops.

Figure 2 shows the temperature dependence of the moment per $Tb^{3+}$ ion, obtained from the FC data. The ordering temperature ($T_c$) as detected by a change in slope of the derivative of the magnetic susceptibility is shown in the inset of Fig. 2. The value of 0.87 K is in agreement with the $T_c$ obtained from specific heat measurements [10,13]. The moment of $3.5\mu_B$ per $Tb^{3+}$ ion can only be obtained once a demagnetization factor has been accounted for. It is very close to that obtained by neutron diffraction [10]. The order observed in neutron scattering is therefore static on the 1 s time scale, after field cooling.

Because the sample appears to be static on the time scale of both magnetization and neutron scattering measurements, a technique sensitive to magnetization fluctuations in the time scale window between neutron scattering and magnetization is required. Muon spectroscopy has a time scale of $10^{-9}$–$10^{-6}$ s, but, as described above, in the normal experimental configuration the muons probe in part the local magnetic environment [19]. In the present investigation our goal was to probe the *bulk* magnetization of $Tb_2Sn_2O_7$ in the muon time window. Using the MuSR spectrometer at the ISIS pulsed muon source (of the Rutherford Appleton Laboratory, UK), muons were implanted into a 0.25 mm thick silver plate which was

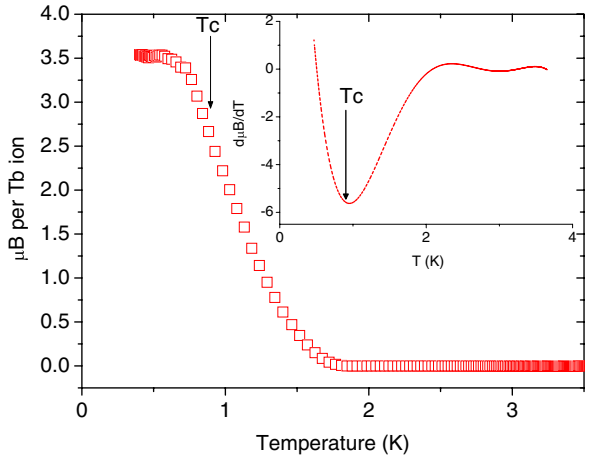


FIG. 2 (color online). The temperature dependence of the FC magnetization for $Tb_2Sn_2O_7$ between 350 mK and 5 K expressed as a moment per Tb ion. The inset shows the derivative of the FC data with respect to temperature, clearly demonstrating the FM transition at 0.87 K.

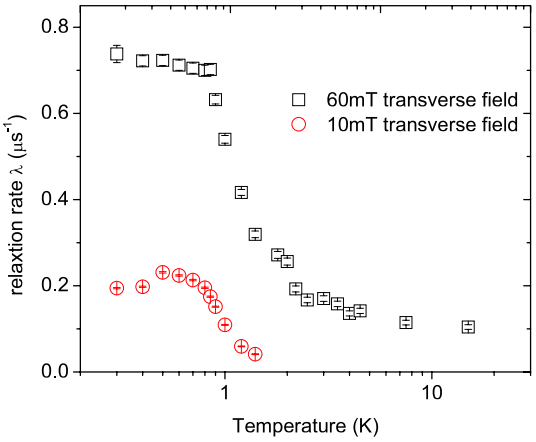


FIG. 3 (color online). The temperature dependence of the relaxation rate ($\lambda$) of the muon precession frequency in an applied TF of 60 and 10 mT, measured in Ag which is mounted on $Tb_2Sn_2O_7$. The FM ordering temperature is clearly visible for both applied fields as a plateau in the relaxation rate.

attached directly to a 2 mm thick, 30 mm diameter disc of $Tb_2Sn_2O_7$. Muons implanted into silver have a negligible relaxation. Any modification of the muon relaxation must therefore be a direct consequence of the magnetic dipolar fields in the $Tb_2Sn_2O_7$, the result of an externally applied field or a combination of both effects. The muons do not observe local magnetic fluctuations, but the bulk magnetic signal, from the field lines of the magnetic sample penetrating the silver.

Initial transverse field (TF) measurements were performed in fields of 10 and 60 mT. The oscillatory signal can be fitted with a function of the form

$$G_x(t) = A\exp(-\lambda t)\cos(2\pi\upsilon_i t) + A_{bg} \qquad (1)$$

where $\lambda$ is the envelope relaxation rate, $\upsilon_i$ is the frequency of local precession at the $i$th muon site and $A$ is the initial asymmetry of the signal and background term, respectively. The frequency of oscillations is related to the local magnetic field $B_i$ by $\upsilon_i = \gamma_\mu B_i/2\pi$ where $\gamma_\mu$ is the muon gyromagnetic ratio ($=2\pi \times 135.5$ MHz T$^{-1}$). Figure 3 shows the temperature dependence of the $\lambda$ parameters for both applied TF. The form of the relaxation rate demonstrates a temperature dependence similar to the magnetization of Fig. 1 and to those found in the independent muon investigations [12,13]. This measurement therefore confirms that the muons implanted into the silver observe the $Tb_2Sn_2O_7$. Because the muons are implanted into the silver, outside the sample, the temperature dependence of the relaxation rate is independent of local magnetic fluctuations. Therefore the similarity of the present data with the previous bulk $\mu$SR data suggests the importance of macroscopic static fields when considering muons implanted into the sample.

Figure 3 shows that $\lambda$ of the 60 mT data is a factor of 3.5 greater than the 10 mT data. The difference in $\lambda$ can be associated with the magnetic field from the $Tb_2Sn_2O_7$. The applied TF is homogeneous across both the silver and the sample space [20]. Therefore, it is a nonuniform field from the sample that causes the coherent precession of the muons to dephase resulting in the observed relaxation. This field distribution is strongly perturbed by the application of a magnetic field.

If static long range magnetic order is present in $Tb_2Sn_2O_7$, the muons implanted in the silver will precess about the static field due to the magnetization of $Tb_2Sn_2O_7$, resulting in an oscillating signal in zero applied field [21]. After cooling in zero field from 10 K to 350 mK no oscillations were observed. However, significantly different properties were observed after cooling in a TF of

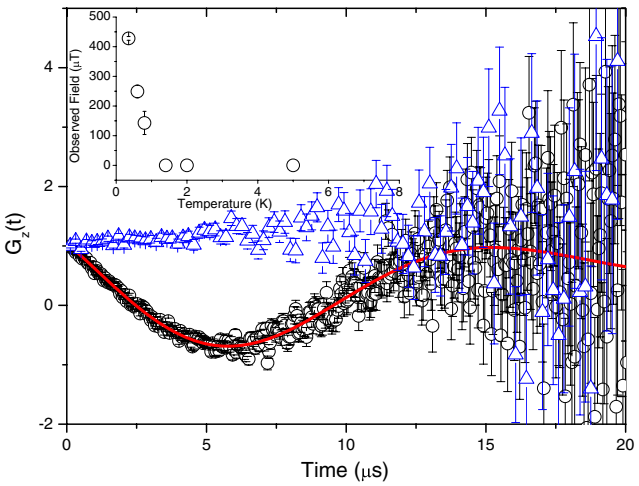


FIG. 4 (color online). The muon signal of the observed field in the silver above (triangles) and below (circles) $T_c$ in $Tb_2Sn_2O_7$, oscillations are clearly observed. The red line is a fit from Eq. (1). The inset shows the temperature dependence of the observed field.

250 mT, and then measuring with active field compensation and zero applied field (active field compensation screens the Earth's magnetic field). Figure 4 shows the time dependent muon signal at temperatures of 0.35 (circles) and 1.4 K (triangles). At 0.35 K oscillations indicative of precession are observed and the data can be fitted with Eq. (1). Above the FM transition, the signal becomes nonoscillatory (Fig. 4, triangles). This strongly suggests that the muons are indeed precessing about a static field distribution due to canted ferromagnet order in the $Tb_2Sn_2O_7$ sample. However, cooling in a TF is required to enhance the uncompensated static component. The inset shows the temperature dependence of the observed field as measured in the silver plate from a fit to Eq. (1). No signal is observed above 1.4 K, in agreement with the FM transition initially observed by Mirebeau *et al.* [10]. The field-cooling process was repeated twice to ensure reproducibility.

The observations presented above unambiguously demonstrate that there is static magnetization observable from the nanosecond to the second time scale. This is clearly shown by the enhancement of the magnetization in the FC/ZFC measurements (Fig. 1) and by the oscillating muon signal in zero field obtained from the magnetized state (Fig. 4). The reduced ordered moment in Fig. 2 is then readily explained by the formation of conventional closed domains to minimize the dipolar energy. The domains can be pinned at low temperatures when cooled in an applied field. This accounts for the enhanced FC magnetization, and the need to cool in applied field in order to subsequently observe a significant static component in zero applied field $\mu$SR. Such domains should be visible using small angle neutron scattering.

The strong static component of magnetization on the muon time scale below the FM transition suggests that the previous ground state propositions are not entirely accurate. The interpretation of both previous results were based upon the observation of a purely dynamical form of the relaxation that would preclude any static component [12]. Moreover, the proposed coherent rotations of spin clusters would not account for the magnetization observed in Fig. 1 nor the change in relaxation shown in Fig. 4, as the rotating spin clusters would not conserve the density of the field lines exiting the sample when field cooled. This leaves open the question of how to interpret the relaxation observed below the FM transition in Refs. [12,13]. As mentioned above, the interior implanted muons do sense the static macroscopic dipolar field in the sample. The full relaxation of the signal observed in Refs. [12,13] is therefore unlikely to be a consequence of electronic dipolar fields. For example, the electron spin dynamics in recent neutron inelastic scattering studies [22] would add a dynamic component to the local electronic dipolar field, but not cause complete relaxation. Possible causes of the relaxation that should be considered in future work are a strong hyperfine contribution [15], or an unusual muon environment. The latter might be provided, for example, by grain boundaries, proved relevant in the case of $Gd_2Ti_2O_7$ [23]. The physical origin of the muon depolarization in $Tb_2Sn_2O_7$ remains an interesting problem for future investigation.

In conclusion, detailed bulk measurements and a modified muon technique have been used to confirm a static magnetization of $Tb_2Sn_2O_7$ over a time scale of $10^{-9} - 1$ s. The results rule out purely dynamical ground states and illustrate the value of complementing conventional $\mu$SR with the exterior implantation technique described here, which provides crucial extra information by which to interpret the $\mu$SR signal.

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