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Neutron scattering investigations of the partially ordered pyrochlore $Tb_2Sn_2O_7$

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Abstract
Neutron scattering measurements have been performed on polycrystalline $Tb_2Sn_2O_7$ at temperatures above and below that of the phase transition, $T_N = 0.87$ K, to investigate further the spin dynamics in the magnetically ordered state. In particular, new neutron spin echo results are presented showing a dependence on Q in the dynamics. We show evidence of the coexistence of static ferromagnetism and dynamically fluctuating spins down to 30 mK and we make a comparison of this partially ordered system to the spin liquid $Tb_2Ti_2O_7$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Geometric frustration is by no means a new area of condensed matter research: the first frustrated magnets were investigated more than 50 years ago [1, 2]. However, studies of frustrated systems have greatly increased during the last ten years due to the many diverse ground state properties that have been revealed. Structures involving triangular units such as the kagome (2D) or pyrochlore (3D) lattices offer a particularly rich variety of low temperature ground states.

One such group of materials which have been consistently studied are the rare earth (RE) pyrochlores with general formula unit $RE_2X_2O_7$ where X can be Ti^{4+} or Sn^{4+}. In these materials only the RE ion is magnetic, forming a network of corner sharing tetrahedra. The low temperature ground state properties in these families are extremely diverse, including spin ice freezing in $Dy_2Ti_2O_7$ [3] and $Ho_2Ti_2O_7$ [4], cooperative paramagnetism in $Tb_2Ti_2O_7$ [5] and partial ordering in the Heisenberg system $Gd_2Ti_2O_7$ [6]. The stannates also exhibit varying ground states with $Gd_2Sn_2O_7$ entering a classical long range ordered state [7] with a gapped excitation spectrum [8] while the magnetism of $Tm_2Sn_2O_7$ has been explained by a van Vleck susceptibility (that is, a magnetic ground state singlet) [9]. $Pr_2Sn_2O_7$ has recently been described as a ‘dynamical spin ice’ compound showing properties of a traditional spin ice combined with a highly dynamic spin component [10]. In each of these materials the magnetism is governed by a delicate balance of competing interactions, including single-ion anisotropy, near neighbour exchange and dipolar interactions [12].

$Tb_2Ti_2O_7$ and $Tb_2Sn_2O_7$ demonstrate somewhat different low temperature properties despite having the same magnetic ion. The magnetic moment was determined to be $\approx 5\ \mu_B$ in $Tb_2Ti_2O_7$ [13, 14] and 5.9 μ_B in $Tb_2Sn_2O_7$ [15, 16]. The magnetization of both pyrochlores follows a Curie–Weiss law for temperatures above ~ 100 K. $Tb_2Ti_2O_7$ remains paramagnetic down to 15 mK despite the large antiferromagnetic (afm) Curie–Weiss constant of $\theta_{CW} \approx -19$ K [17]. $Tb_2Sn_2O_7$ has a similarly large negative $\theta_{CW} \approx -12.5$ K implying strong afm interactions between Tb^{3+} ions [9]. However unlike $Tb_2Ti_2O_7$, powder neutron diffraction measurements indicate a strong increase in ferromagnetic correlations below 1.3 K and static long range canted ferromagnetic order sets in below $T_N = 0.87$ K [15].

The ordered magnetic structure was found to involve Tb^{3+} moments oriented at an angle of 13.3° to the local $\langle 111\rangle$ anisotropy axes [15, 16]. The structure obeys the '2-in 2-out' spin ice rule [12]. Because of this, $Tb_2Sn_2O_7$ has been described as an 'ordered spin ice' since the combination of the afm exchange interactions and the ferromagnetic dipolar coupling result in magnetic order with $\boldsymbol{k} = 0$. Mirebeau *et al* also found sizeable diffuse scattering in their diffraction data at low temperature, and a significant difference between the ordered moment as determined by neutron diffraction and by specific heat enabled them to put a timescale of 10^{-4}–10^{-5} s on spin fluctuations coexisting with the static magnetic order.

Subsequent muon spin relaxation (μSR) measurements have demonstrated that such magnetic fluctuations truly exist and persist down to the lowest temperature that is experimentally accessible. However, complicating the magnetic picture of $Tb_2Sn_2O_7$, these measurements were initially interpreted as showing the absence of static long range order [16, 18]. Since evidence to the contrary was available from neutron diffraction, these reports proposed for the ground state a rather exotic scenario of large spin clusters undergoing rotations of their magnetization vector on a timescale that would fit the μSR results, between $\sim 10^{-8}$ and $\sim 10^{-10}$ s. Only in a later μSR experiment reported by a different group it was shown, by implanting the muon at the sample exterior and thus separating near and far contributions to the magnetic field at the muon stopping site, that the muon results are in fact compatible with static order on a timescale from 1 to $\sim 10^{-9}$ s [19].

Due to the apparently contradictory results from different techniques, the nature of the magnetic correlations in $Tb_2Sn_2O_7$ was subsequently re-examined with polarized inelastic neutron scattering with the time-of-flight (TOF) [20] and spin echo (NSE) [21] spectroscopic methods. In the former study it was found that at 0.04 K static correlations (slower than $\sim 10^8$ Hz) giving rise to Bragg peaks coexisted with a liquid-like structure factor arising from correlated near neighbours fluctuating faster than 4×10^{10} Hz. The data also showed two bands of low lying excitations around 0.3 and 1.2 meV in the ordered phase. The lower of the two bands, originating from the crystal field, partially softens at the phase transition, $T \approx 0.8$ K and below. The NSE study [21] found a static spin ensemble at base temperature, ~330 mK, and spin fluctuations at $\sim 10^{10}$ Hz at elevated temperatures. Unfortunately only data in the small angle scattering regime at $Q = 0.08$ Å^{-1} were reported, thus probing a length scale of $2\pi/0.08 \sim 80$ Å or 8 unit cells. This length scale is typical for ferromagnetic short range order, but much longer than where one expects to see the signatures of geometric frustration of near neighbours.

More recently, very high resolution neutron scattering measurements revealed the presence of 3 different correlation length scales in $Tb_2Sn_2O_7$ [22]. Here it was shown that the long range ordered (LRO) moments were correlated over a length scale of 190 Å while the short range ordered moments were correlated over a distance comparable to the Tb–Tb neighbour distance. This confirmed that multiple correlation lengths and fluctuation rates coexist in $Tb_2Sn_2O_7$ at low temperatures.

In this paper, we present new NSE data with emphasis on the Q-dependence of the spin dynamics. The aim was to consolidate the neutron scattering data [15, 20–22] and to come to a coherent picture of the low temperature magnetic behaviour of $Tb_2Sn_2O_7$ in view of the μSR results. The strength of the NSE technique [23] lies in the intrinsic separation of magnetic and nuclear scattering, and its sensitivity to fluctuations over a broad range of timescales (10^{-11}–10^{-8} s are usually accessible).

2. Experimental method

Stoichiometric quantities of Tb_4O_7 and SnO_2 were thoroughly mixed and fired in air at 1375 °C. This produced a homogeneous polycrystalline sample of $Tb_2Sn_2O_7$ which has been tested for quality and phase purity using high resolution powder neutron and x-ray diffraction. This sample conformed to the cubic space group of $Fd\bar{3}m$ with lattice parameter $a = 10.426(3)$ Å at 300 K. In each of our neutron experiments reported here, about 30 g of polycrystalline $Tb_2Sn_2O_7$ was loaded into a Cu sample can and mounted in a low temperature insert capable of reaching temperatures below the ordering temperature of 0.87 K.

TOF spectroscopy measurements were performed using the disk chopper spectrometer (DCS) at NIST [24]. DCS can measure a wide range of (Q, ω) space simultaneously with a resolution between 1.97 and 0.017 meV for incident neutron wavelengths between 1.8 and 9 Å. The data were corrected in a standard manner using measurements of an empty container and a vanadium standard sample.

NSE measurements were taken at the SPAN spectrometer [25] at Helmholtz Zentrum Berlin (HZB), with an incident wavelength of 4.5 Å and a wavelength spread of $\Delta\lambda/\lambda \sim 15\%$. Three wide angle detector banks covered the Q-range from ~0.1 to 2.4 Å^{-1} simultaneously and data were collected at 30 and 820 mK. Since the Q resolution in such an experiment is coarse, care was taken to avoid the ranges around the magnetic Bragg peaks [15] in the analysis, which would otherwise overwhelm the data with elastic magnetic scattering. To account for instrumental effects, a standard elastic sample was also measured.

3. Experimental results

Figure 2 shows the $S(|Q|, \omega)$ maps of the lowest crystal field (CF) levels in $Tb_2Sn_2O_7$. Measurements were taken at 10 K (figure 2(a)) and 0.04 K (figure 2(b)) using DCS. It is clear from these maps that the system is gapped both in the collective paramagnetic phase (10 K) as well as the ordered phase (0.04 K). The first excited state doublet visibly softens toward the ground state at a wave vector of ≈ 1.1 Å^{-1} which corresponds to the first maximum in the afm wave vector. As in the cooperative $Tb_2Ti_2O_7$, this softening is thought to result from paramagnetic ions becoming correlated with their neighbours in some way. Although weak, softening of the modes around 1.2 and 0.3 meV is also present in the $T = 0.04$ K data, implying that the system retains some dynamic moments within the ordered phase at very low temperatures.

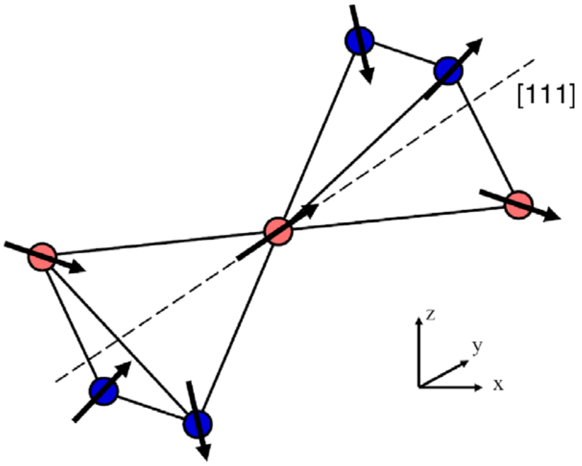

Figure 1. Magnetic ions in $RE_2X_2O_7$ reside on the corners of tetrahedra in the cubic pyrochlore lattice. The arrows are oriented in the '2-in 2-out' spin ice structure and the three-fold symmetry axis (or [111]) is also shown. The red (light) and blue (dark) circles differentiate between α and β sites [11] which form chains orthogonal to each other (see the text for details).

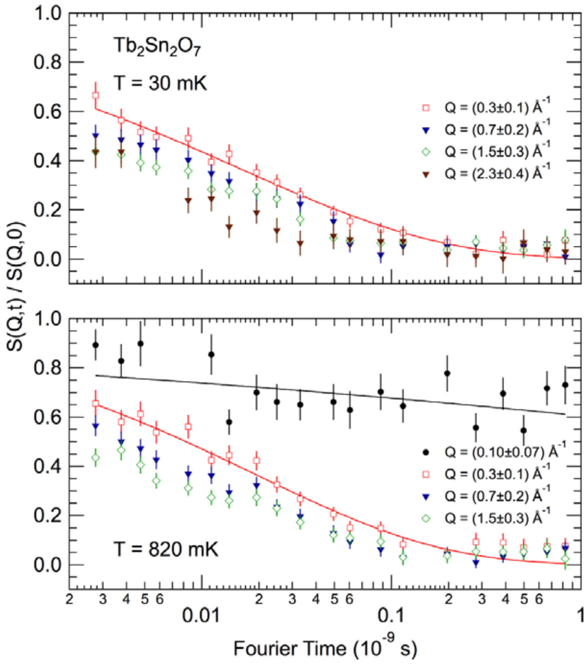

Figure 3. SPAN neutron spin echo data taken at 30 and 820 mK. Solid lines are fits to the data using the function $\exp[-(t/\tau)^{\beta}]$. The data at $|Q| \sim 0.1$ Å^{-1} and 30 mK are consistent with $S(Q,t)/S(Q,0) = 1$ but the error bars arising from counting statistics are too large to draw meaningful conclusions which is why this data set has been omitted from the figure.

These results from the ordered state in $Tb_2Sn_2O_7$ are remarkably similar to the TOF data of $Tb_2Ti_2O_7$ in an applied magnetic field [26]. The splitting of both the ground state doublet and the first excited doublet is a clear indication that the molecular field from the canted ferromagnetic order in $Tb_2Sn_2O_7$ has a similar effect on the system as an applied external field to $Tb_2Ti_2O_7$. This indicates that the magnetic field at the Tb^{3+} ion in both materials is sufficient to lift the degeneracy of the low lying CF doublets [27]. This leads us to believe that not only are the spin liquid regimes of the two materials similar [28], but the ordered state in $Tb_2Sn_2O_7$ is also very similar to the low field induced state in $Tb_2Ti_2O_7$. Thus if static and dynamic spins coexist in the ordered phase in $Tb_2Sn_2O_7$, there may be similar dynamics still present in the induced ordered state in $Tb_2Ti_2O_7$.

NSE results for the normalized intermediate scattering function, $S(Q,t)/S(Q,0)$, of $Tb_2Sn_2O_7$ are shown in figure 3 illustrating the temporal spin correlations at 30 and 820 mK. Again, note that these data are taken at positions in momentum space between Bragg peaks to avoid contamination from elastic scattering. Groups of 7 detectors were binned together to give an average $|Q|$ as indicated in the figure. A data set at $|Q| = 2.3$ and $T = 820$ mK was omitted as it is virtually indistinguishable from data at lower $|Q|$ at this temperature. These measurements show that there is an initial, fast relaxation of the $S(Q,t)/S(Q,0)$ signal which occurs outside the time window of the NSE measurement (at $t < 2 \times 10^{-12}$ s), which is consistent with the observation of inelastic scattering due to CF transitions as discussed above. With the exception of the lowest Q, within the time window of our NSE measurements (2×10^{-12} s $< t < 1 \times 10^{-9}$ s) we see a full relaxation of the $S(Q,t)/S(Q,0)$ signal from ≈60% of its $t = 0$ value to zero.

For a phenomenological description, these data were fitted with a stretched exponential function, $S(Q,t)/S(Q,0) = \exp[-(t/\tau)^{\beta}]$, to reveal a spin relaxation with a similar timescale to that observed in $Tb_2Ti_2O_7$ [29]. In this equation,

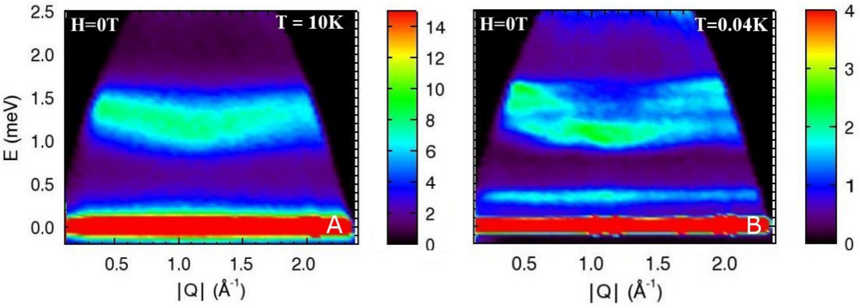

Figure 2. DCS data showing the lowest crystal field levels of polycrystalline $Tb_2Sn_2O_7$ within the frustrated, afm state at 10 K (A) and in the ordered state at 0.04 K (B).

β does not refer to any physical property of the system but simply the stretched exponent ranging from 0 to 1. In the limit of $\beta = 1$ the system is governed by a single relaxation time and equilibrium is achieved by overcoming a well defined energy barrier. Many systems ranging from glasses to dielectrics to thermal responses in complex systems have been parametrized by the stretched exponential or Kohlrausch–Williams–Watts function as it is formerly known. The parameter τ is a direct measure of the relaxation rate of the magnetic spins. With the exception of the lowest Q, we obtain $\tau = (2 \pm 0.1) \times 10^{-11}$ s and $\beta = 0.4 \pm 0.02$. At the lowest Q where we could take reliable data, $Q \sim 0.1$ Å^{-1}, the spin relaxation is considerably slower and more stretched—here we obtain $\tau \sim 4 \times 10^{-8}$ s and $\beta \sim 0.08$. This is consistent with the earlier NSE result [21] which showed *only* low-Q dynamics.

Figure 4 cuts across the data set at a constant relaxation time in the middle of our dynamic range at $t = 0.05$ ns, showing the data for four detector bank positions. Up to $Q \sim 0.2$ Å^{-1}, the data steeply drop with increasing Q to $S(Q, 0.05\ \mathrm{ns})/S(Q, 0) \sim 0.2$, and then reach a plateau with weak Q dependence. This demonstrates clearly how the dynamics in $Tb_2Sn_2O_7$ varies across the different length scales—a fact that was briefly touched on in [22]. It also highlights that the static moments only contribute to the scattering at very low $|Q|$ (ferromagnetic forward scattering), and at the Bragg peaks. The remainder of Q-space is dominated by the diffuse scattering due to the dynamic fluctuations.

4. Discussion and conclusions

The voluminous body of experimental work published on $Tb_2Sn_2O_7$, using neutron scattering, μSR and bulk techniques, all point to a coexistence of static and dynamic magnetic moment components in the ground state. This is a highly unconventional finding ($Gd_2Ti_2O_7$ is a similar case, see [6]), and while the main characteristics appear to be experimentally established, a theoretical understanding is missing. The system presents a very delicate balance between the nearest neighbour exchange, dipolar and crystal field interactions, putting the low temperature ground state sort of half way between the static spin ice state found in $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ on one hand and the spin liquid state in $Tb_2Ti_2O_7$ on the other hand.

The TOF data presented here reveal strong similarities between the ordered state in $Tb_2Sn_2O_7$ and the field induced spin ice state in $Tb_2Ti_2O_7$ [26, 27]. When a field is applied along the [110] direction in $Tb_2Ti_2O_7$, one can differentiate between two sublattices of Tb^{3+} ions: those moments which point with a component along the applied field and those orthogonal to this (see figure 1) [11]. A neutron study on the induced spin ice state in $Tb_2Ti_2O_7$ also showed that not only were the α and β sites independent from each other, but even the magnitude of the β sites was also modulated [22, 30]. It is therefore possible that at low applied fields, dynamics may still be present since $Tb_2Ti_2O_7$ has not yet reached saturation. Thus it is likely that if the spins can be differentiated between in the spin ice state in $Tb_2Ti_2O_7$, then the same classification may exist in $Tb_2Sn_2O_7$. The different α and β sites may then provide an explanation for the proportion of static to dynamic spins in $Tb_2Sn_2O_7$. Further comparisons of the dynamics in $Tb_2Sn_2O_7$ and those in the induced ordered state of $Tb_2Ti_2O_7$ will clarify this.

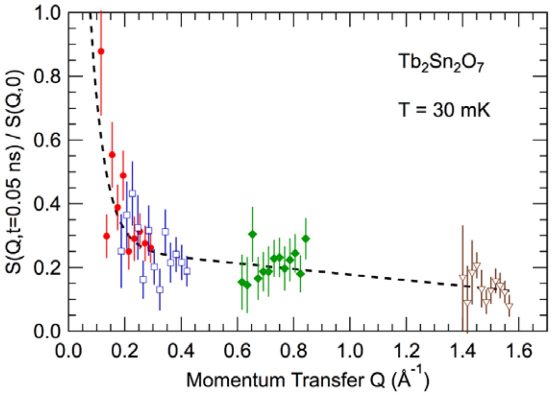

Figure 4. Q-dependence of spin echo data at base temperature. The different symbols correspond to data taken from different detector banks on SPAN. The line is a guide to the eye. Two magnetic Bragg peaks occur in the 'gap' between 0.9 and 1.3 Å^{-1}.

There is also a strong similarity between the spin echo data of $Tb_2Sn_2O_7$ and $Tb_2Ti_2O_7$ which both show a spin relaxation function that is very stretched on the time axis. For $Tb_2Ti_2O_7$ the spin relaxation was not measured at very low Q since no forward scattering was expected for an antiferromagnet [29, 31]. In both systems, at $Q > 0.3$ where any short and intermediate range correlations between frustrated moments would appear, there is very little Q dependence of the dynamics. This strongly indicates that NSE observes primarily single-ion dynamics in both materials. The single-ion anisotropy leads to some preferential alignment of the spins with a local $\langle 111 \rangle$ axis, giving a Q-dependent scattering function with at least two maxima when only nearest neighbour interactions are considered. Nevertheless, there is no signature of dynamic correlations in a Q-dependent timescale of the dynamics.

In $Gd_2Ti_2O_7$ the situation is a little different in that only a sub-set (1/4) of the magnetic moments fluctuate while the others are static in the ground state. These fluctuations however are much faster, by several orders of magnitude, and would be observed outside the NSE window. Their presence is only revealed by an initial loss of polarization at short Fourier times (complete relaxation by $t = 10^{-11}$ s) [32].

In this paper we have presented new neutron spin echo data demonstrating the Q-dependence of the fluctuation rate for the dynamic moments of $Tb_2Sn_2O_7$ at low temperatures. The spin echo technique enabled a precise measurement of the decay of the spin correlations in time, and our result for the timescale is consistent with earlier estimates. At the same time, through the Q-dependence of the scattering, it was possible to unambiguously identify the scattering as due to the near neighbour spin–spin correlations. Thus it is clear that $Tb_2Sn_2O_7$ contains static components to the magnetic moments which are responsible for the observed magnetic Bragg peaks, as well as dynamic components coexisting at the lowest temperatures.

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