Neutron Studies of $Tb_2Mo_2O_7$

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We have used the new high energy resolution spectrometer (BaSiS), at the Spallation Neutron Source in Oak Ridge, to conclusively prove the existence of a low energy mode at 0.34(1) meV in the spin glass $Tb_2Mo_2O_7$. This mode is reminiscent of the excitation observed in the ordered phases of both $Tb_2Ti_2O_7$ and $Tb_2Sn_2O_7$. The dynamical nature of the transition seen in the magnetization at ~ 25 K suggests that this frustrated magnet shows a dynamic crossover between a high-temperature phase of poorly correlated, quickly relaxing spins to a low-temperature regime with much slower, short ranged spin correlations extending no further than to the next nearest neighbor. Existing theories explain the spin glass transition in terms of a phase transition and order parameters, and assume the existence of a distinct spin glass phase. There is no evidence for such a phase in $Tb_2Mo_2O_7$.

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I. INTRODUCTION

$Tb_2Mo_2O_7$ crystallizes in the Fd-3m cubic space group with a lattice parameter of ~ 10.3 Å where both the Tb and Mo sublattices are magnetic and form three-dimensional networks of corner sharing tetrahedra. This makes it likely that *geometrical frustration* is relevant for this system at low temperature. Such frustration is the consequence of the geometric arrangement of the magnetic spins on an underlying crystal lattice that prevents the system from minimizing the energy of all near neighbor bonds simultaneously [1]. The low-temperature magnetic properties of many rare-earth titanate pyrochlores have been studied for this reason [2], however $Tb_2Mo_2O_7$ is complicated further by the presence two different magnetic species in the unit cell.

$Tb_2Mo_2O_7$ was first prepared and characterized by J. E. Greedan's group over 25 years ago [3]. They found that the magnetic spin system froze below $T_g \sim 25$ K and later went on to study the short range magnetic correlations using neutron scattering and muon spin relaxation on a powder sample [4, 5]. Spin-spin correlations were seen to develop below 50 K, with diffuse magnetic scattering peaking near $|Q| = 1.1$ Å^{-1} and 1.7 Å^{-1}, consistent with short range order of Tb^{3+} with a $< 111 >$ wave vector. From the width of these diffuse peaks the authors also obtained a temperature independent correlation length of (5 ± 1)

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Å, similar to that later found in $Tb_2Ti_2O_7$ [6]. Remarkably, residual spin dynamics was found down to 100 mK, the lowest temperature measured in the muon study. These data suggested that the glass-like anomaly seen in magnetization is a dynamical transition with a change in the characteristic relaxation times at 25 K.

More recently the authors of this paper, and others, have revisited $Tb_2Mo_2O_7$ [7–9]. Neutron powder diffraction, extended x-ray absorption fine structure and inelastic neutron scattering were used to characterize a new polycrystalline sample of $Tb_2Mo_2O_7$. The local and long-range structure has been extensively studied and reported in Ref. [8]. During synthesis it is important to stabilize the Mo^{4+} state, which appears to be successful when the cubic lattice constant is approximately 10.309(1) [10] Å at room temperature. As discussed in Ref. [11], if the oxygen stoichiometry is off, creating defects and/or a different molybdenum valence, the lattice will expand and reveal the stoichiometry in the cubic lattice parameter. The room temperature lattice constant, of our sample, determined by X-ray diffraction was 10.312(5) Å indicating nearly ideal stoichiometry. A.c. susceptibility revealed a frequency dependent, glass-like transition consistent with earlier work. Analyzing low temperature elastic neutron scattering we were able to confirm that the near neighbor Tb-Tb correlations are ferromagnetic and do not reach beyond 10 Å. The Tb-Mo correlations are predominantly ferromagnetic [7, 12], but are strongly antiferromagnetic in the second shell, in agreement with the earlier analysis [4]. Mo-Mo correlations could not be measured due to the much smaller Mo^{4+} moment. The analysis of the spin-spin correlations in Ref. [7] accounted for the entire magnetic scattering from 100 K to 8 K. A significant amount of spectral weight was observed in the inelastic channels. A signature of a low energy excitation at ~ 0.28 meV was seen in the inelastic data, but the instrumental resolution was insufficient for a detailed analysis. In this paper we investigate this spectral weight with an instrument with better energy resolution.

Young Lee's group at MIT has been successful in growing a single crystal of this material [9]. This remarkable feat has allowed for a more detailed examination of both the static and dynamic magnetic behavior of $Tb_2Mo_2O_7$. Measurements of $S(\mathbf{Q},\omega)$ were made, with directional dependencies on $\mathbf{Q}$ revealed directly, as opposed to being averaged out, as in the measurements on polycrystalline samples mentioned above. Unfortunately the room temperature lattice constant or a chemical analysis of the stoichiometry were not reported, and therefore more work may be needed to characterize this sample [13]. However, the elastic neutron scattering data could be analyzed in terms of a canted, spin-ice like local structure with approximately 4 μ_B per Tb spin. In addition, a relatively large $\mathbf{Q}$ independent background was ascribed to scattering from uncorrelated Tb^{3+} spins. Thus the overall picture was somewhat inconsistent with the results that emerged from the analysis of the powder data, where spin-spin correlations between all magnetic ions were considered [7]. Singh *et al.* [9] also reported that inelastic scattering was observed at 4.5 meV and 15 meV, the latter almost definitely being dominated by phonon scattering (compare to the $Tb_2Ti_2O_7$ system, Ref. [14]).

Since the local environment of the Tb^{3+} ions in $Tb_2Ti_2O_7$, $Tb_2Sn_2O_7$, $Tb_2Ru_2O_7$and $Tb_2Mo_2O_7$ are very similar, the latter two having a magnetic B-site, one would expect their single ion properties to be similar. It is well established that there are 4 levels within the

first 2 meV ($\sim$ 25 K) of the first 3 Tb based pyrochlores listed above [14–18], but very little spectral weight has been observed in $Tb_2Mo_2O_7$ at such low energy [7, 9]. In order to get a better handle on the spin Hamiltonian, we have performed more inelastic neutron scattering experiments at the BaSiS spectrometer at the Spallation Neutron Source in Oak Ridge, concentrating on the lower energy range.

II. EXPERIMENT

Polycrystalline $Tb_2Mo_2O_7$ samples were prepared using the same method as reported in reference [3]. For the study reported here, the same sample was used as in reference [7]. Earlier experiments were performed on the time-of-flight (TOF) Disk Chopper Spectrometer (DCS) and the Neutron Spin Echo Spectrometer (NSE) at NIST in Gaithersburg, as well as the IN11 Spin Echo Spectrometer at the Institute Laue-Langevin in Grenoble. Experimental details can be found in reference [7]. New high energy resolution, neutron backscattering experiments were performed at the beam line 2 instrument, BaSiS at the Spallation Neutron Source (SNS) [19]. In backscattering one uses a polychromatic incident neutron beam and Si(111) analyzer crystals to select the final energy of 2.08 meV for scattered neutrons. In the experiment reported here, the center of the incident energy band was shifted between 1.97 meV and 2.58 meV, at a chopper frequency of $f = 30$ Hz, allowing measurements in the energy transfer range between -0.20 meV (neutron energy gain) and $+0.80$ meV (neutron energy loss).

III. RESULTS AND DISCUSSION

Fig. 1 shows data obtained with NSE (upper panel) at 10 K, 20 K and 40 K and TOF (lower panel) with simultaneous fits to the same dynamical scattering function, which consisted of three terms: (i) strictly elastic scattering, (ii) quasielastic scattering (stretched exponential in the time domain), and (iii) a low intensity inelastic mode at 0.28 meV (marked by arrows in the lower panel).

The analysis showed that, within the precision of the measurement, the dynamics was independent of Q. The low intensity inelastic mode is almost irrelevant for the spin echo data, because its Fourier Transform has decayed to zero by about 10^{-11} seconds, that is, in the time window accessed in this experiment it only leads to a small initial drop of the normalized signal below 1. In the time domain it is easy to see that at the lowest temperature the system is still relaxing with time and thus the transition observed by bulk susceptibility is not to a static state. This dynamical type transition is seen in many spin-glass-like materials where the meaning of a "freezing" temperature depends on the frequency one uses to probe the system [20].

Not immediately apparent, but the data in Fig. 1 could only be fitted satisfactorily to a model that included a small amount of spectral weight at finite energy (marked by arrows in the figure). The DCS instrument response to an elastic scatterer is known to be nearly

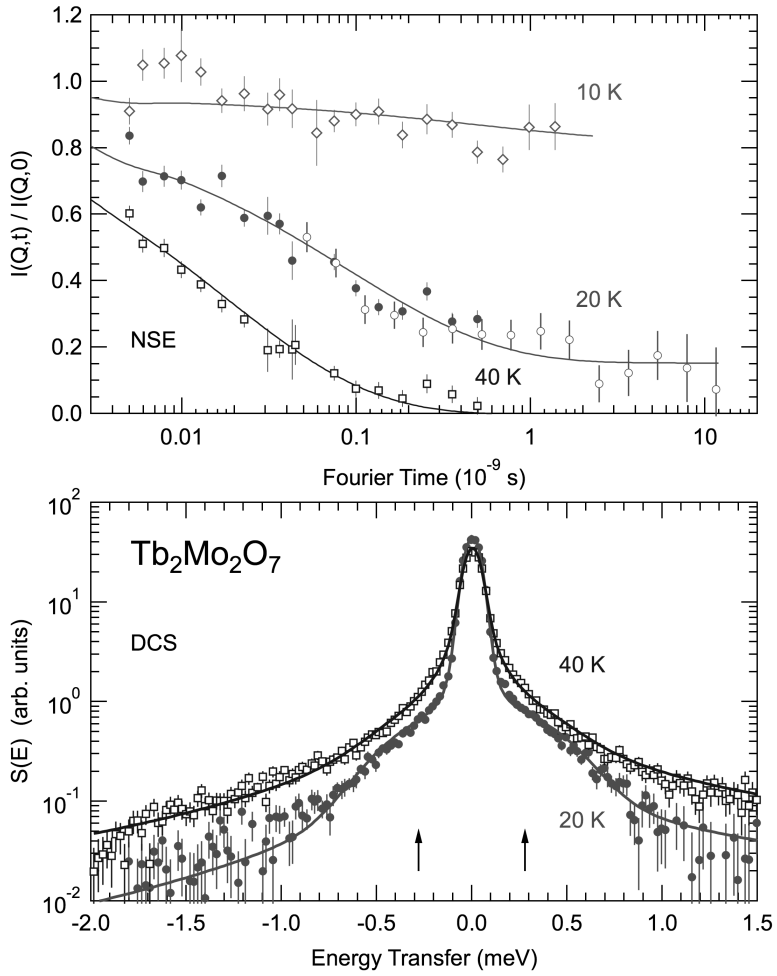

FIG. 1: Quasi-elastic neutron scattering above and below $T_g \sim 25$ K. Top panel: Neutron spin echo (data from ILL and NIST). Bottom Panel: Time-of-flight data (DCS). The lines in both panels are the results from a simultaneous fit assuming a superposition of elastic scattering, a main relaxation process and a low intensity inelastic mode centered at the arrows in the bottom panel.

Gaussian in shape, without low energy shoulders as observed here. To confirm the presence of a low energy mode, we have recently performed a measurement of S($|\mathbf{Q}|$,ω) with much better energy resolution. Fig. 2 shows the data summed over all $|\mathbf{Q}|$ between 0.2 Å^{-1} to 2 Å^{-1} on BaSiS. A more detailed analysis again showed that the dynamics was independent of $|\mathbf{Q}|$. With the better resolution, the low lying excitation is now clearly separated from the elastic line and can be fitted with much more certainty. In fact the best fit reveals that the small inelastic feature is centered at 0.34(1) meV. These data also suggest that there is still a significant amount of inelasticity to the sample at 1.4 K ($T_g/20$) with spectral weight (quasielastic scattering) stretching out over the entire dynamic range measured in Fig. 2.

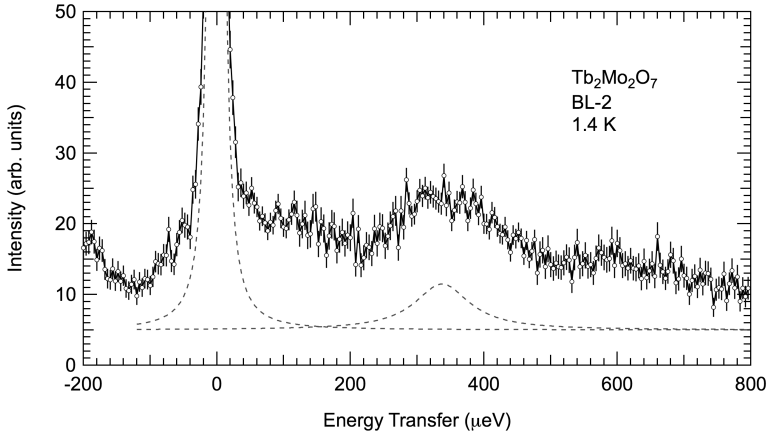

FIG. 2: High energy resolution neutron scattering data taken on the backscattering spectrometer at the SNS. A small peak (0.34(1) meV) can now clearly be seen on top of a significant amount of spectral weight that extends over the entire energy transfer shown.

IV. CONCLUSIONS

The spin glass character of $Tb_2Mo_2O_7$, as well as that in the simpler but related system $Y_2Mo_2O_7$ [21, 22] needs to be studied further. For the first time, we have conclusively revealed the presence of a low energy mode that has the character of a crystalline electric field excitation. Modeling this and other data and calculating the full crystal field Hamiltonian should be performed to determine the Tb^{3+} single ion properties. It is clear however that the energy levels associated with Tb^{3+} are significantly different to those seen in other Tb-based pyrochlores. This excitation, approximately 3.5 K above the ground state and will be thermally excited at all temperatures studied. With the temperature independent nature to the correlation length below 100 K and the observation of several spin relaxation processes at 1.4 K, one might consider modeling the transition as a dynamical crossover and not the crossover into a distinct state.

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