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Dynamic frustrated magnetism in $Tb_2Ti_2O_7$ at 50 mK

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The low temperature ($T<1$ K) properties of the cooperative paramagnet $Tb_2Ti_2O_7$ have been studied by ac susceptibility, neutron diffraction and neutron spin echo techniques. Like several other frustrated magnets, $Tb_2Ti_2O_7$, is believed to remain paramagnetic down to $\sim$0.07 K. However, recent studies [Yasui *et al.*, J. Phys. Soc. Jpn. **71**, 599 (2002), for example] suggest that $Tb_2Ti_2O_7$ enters an ordered, albeit glassy, state at a relatively high temperature, $\sim$1.5 K. Our results confirm that the majority of the spins in $Tb_2Ti_2O_7$ fluctuate very rapidly, even at 50 mK and that static, spatial correlations do not develop beyond nearest neighbor at similar temperatures. We suggest that the observation of a partial freezing of this magnetic system, at finite temperature, is a result of a small fraction of spins freezing around defects in the stoichiometric crystal structure.

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Geometrically frustrated magnetic materials[1] have been of intense interest recently.[2–7] In these cooperative systems, the combination of the local structure with the nature of the magnetic interactions facilitates the possibility of interesting magnetic ground states. This phenomenon is often displayed in materials containing antiferromagnetically coupled magnetic moments which reside on geometrical units which cannot form a bipartite lattice, such as triangles and tetrahedra. A well known example occurs for the two-dimensional triangular framework of unidirectional, classical, antiferromagnetically coupled magnetic moments.[8] In such a system, any two moments can align in a spin-up, spin-down arrangement, but the third cannot satisfy both its nearest neighbor interactions simultaneously. In a three-dimensional system of corner sharing tetrahedra, a similar situation ensues, wherein at least two antiferromagnetic ''bonds'' are always frustrated. The only constraint on the ground state of such systems is that the vector sum of the spins on a frustrated unit (the triangle or tetrahedron) is zero.

The pyrochlore lattice is made up of a three-dimensional network of corner sharing tetrahedra. Such a sublattice of exchange coupled spins occurs in the oxide pyrochlore family with chemical composition $A_2B_2O_7$. The sublattice of each of the two metal ions (A and B) form infinite, interpenetrating, networks of such corner-sharing tetrahedra.

Anderson's proposal of the resonant valence bond model for spin $\frac{1}{2}$ moments and the triangular lattice,[9] focused significant attention on structures which can support frustration in the search for higher dimensional spin-liquid-like ground states. That is to say, the absence of any magnetically ordered phases on lattices in two or more dimensions. Such magnets are particularly rare since, like the chemical lattice, the magnetic moments in materials usually freeze into ordered and sometimes disordered structures,[10] but do not typically remain fluctuating as the temperature is lowered. Theoretical arguments for large ground state degeneracies, in an antiferromagnetically coupled spin system on a pyrochlore lattice, have been made for both discrete[11] and continuous[12] spin symmetries. Long-range order is suppressed and an incoherent, local order occurs in systems with near neighbor interactions only. More recent studies of classical antiferromagnetic Heisenberg spins on such a lattice show no transition to a Néel state at any temperature.[13,14] Numerical calculations for quantum mechanical $S=\frac{1}{2}$ moments produce similar results.[15] These low temperature states have been referred to as either ''collective paramagnets'' or ''spin liquids'' depending on whether one is referring to classical or quantum mechanical states, respectively. Generally speaking, these terms are used to describe a fluctuating spin system with strong, short-range spatial correlations as $T\rightarrow 0$ K.

Significant experimental interest has focused on $Tb_2Ti_2O_7$.[6,16–22] In this material, antiferromagnetically coupled Tb^{3+} ions reside on the A-site sublattice. In this paper we report low temperature ($T<1$ K) neutron scattering studies of $Tb_2Ti_2O_7$ in both single crystal and polycrystalline forms. These measurements significantly extend earlier data[6,17–21] and probe both static and dynamic magnetic correlations. We conclusively show an absence of long range magnetic order in this system as the temperature approaches zero; indeed, we show that the system remains dynamic at least on the nanosecond timescale. Moreover, we discuss the

occurrence of static short range magnetic correlations that have previously been reported.

$Tb_2Ti_2O_7$ is an insulator which crystallizes in the cubic, face centered space group $Fd\bar{3}m$ with lattice parameter $a = 10.15(1)$ Å at 300 K. The paramagnetic Tb^{3+} ions possess almost the full magnetic moment expected for the free $^7F_6$ Tb^{3+} ion ($9.6\mu_B$), as determined by Curie-Weiss fits to the high temperature susceptibility. Crystalline electric field calculations, in full agreement with experimental data, show the ground and first excited states to both be doublets, separated by roughly 18 K.[21] Both these doublets display very anisotropic *g* tensors with the principal eigenvalues directed along [111] directions. The ground state moment is large, estimated to be $\sim 5\mu_B$ with an exchange interaction of ~ -13 K.

Polycrystalline and single crystal samples were prepared as described elsewhere.[6,22] The phase purity, room temperature lattice parameters and crystal structure of the samples were confirmed by x-ray diffraction. Static magnetization results are consistent, as are the structural parameters, with those previously published.[6,16–22]

The neutron spin-echo experiment was performed at the IN11c spectrometer at the Institut Laue Langevin with incident neutrons of 5.5 Å. Data were taken in the $|\mathbf{Q}|$ range between 0.5 and 1.6 $Å^{-1}$. To maintain neutron polarization, the polycrystalline sample was kept in a low magnetic field of about 5 G. *XYZ* polarization analysis was performed for each individual scan in order to relate the echo amplitude to the elastic magnetic-scattering intensity. This analysis distinguishes between the magnetic, spin incoherent, nuclear incoherent, and isotope incoherent scattering in the total signal. The data were corrected for instrumental resolution by normalizing each scan to a reference sample with a similar structure that is known to be static[23] at low temperatures.

Neutron diffraction from a single crystal of $Tb_2Ti_2O_7$ was measured on the PRISMA spectrometer at ISIS. The single crystal was oriented with the $[1\ \bar{1}\ 0]$ vertical so that the (*hhl*) plane was the horizontal scattering plane.

Magnetic ac susceptibility from a single crystal was measured in a custom designed susceptometer. Measurements were taken with a driving frequency between 16 and 800 Hz and the [111] axis parallel to the small field. In all experiments the sample was mounted on a dilution refrigerator and the measurements were taken at the base temperature, 50 mK, and higher.

We present detailed measurements of the diffuse magnetic scattering from a single crystal of $Tb_2Ti_2O_7$. These measurements extend previous studies which were performed at temperatures above 400 mK only. The color contour plot in Fig. 1 is the energy integrated $S(\mathbf{Q})$ at 60 mK. Compared with high temperature scans (>1 K, not shown), it reveals no additional Bragg-like scattering in this plane of reciprocal space at these low temperatures. Significant diffuse scattering was found, around the (0,0,2) position, similar to that reported earlier at 4.2 K (Ref. 17) and 400 mK.[18] The broad, in $\mathbf{Q}$, nature of the scattering is indicative of very short ($<\frac{1}{2}$ nanometer) spin correlations extending across only one tetrahedra, even at 60 mK.

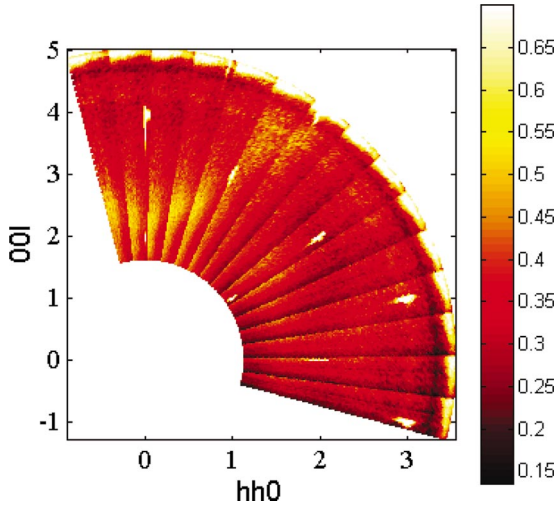

FIG. 1. (Color) Color contour plot of the Bragg scattering over several Brillouin zones at 60 mK. Nuclear Bragg reflections are seen as expected at the all even or all odd reciprocal lattice points. There is no indication of magnetic Bragg-like scattering, but extensive diffuse scattering is seen around the (0,0,2) position.

The neutron spin echo (NSE) technique was used to probe spin dynamics at relatively long times (high energy resolution) in polycrystalline $Tb_2Ti_2O_7$. The NSE directly measures the intermediate scattering function, $S(\mathbf{Q},t)$, which contains information on both spatial and temporal spin correlations. These data are very sensitive to fluctuating spins with dynamics faster than $t \sim 10^{-8}$ s. This technique has proved very useful for magnetic systems without long-range spatial order, such as spin glasses and superparamagnetic particles, and in quasistatic, glassy systems such as polymer melts and structural glasses.[24–27]

The NSE experiment requires a full *XYZ*-polarization analysis. The results of this diffraction experiment are shown in Fig. 2. The magnetic scattering is extracted directly from the *XYZ* polarization analysis, in contrast to previous measurements wherein the magnetic scattering were obtained by subtracting a high temperature, nonmagnetic data set from a low temperature data set. Our results show a broad peak as a function of $|\mathbf{Q}|$ in the magnetic structure factor, $S(\mathbf{Q})$, near 1.1 $Å^{-1}$ at 0.05 K, consistent with measurements at higher temperatures.[6,17,18] As shown previously,[6,17,18] the diffuse magnetic scattering evolves on a temperature scale of about 100 K, and we show here that it increases only slightly between 10 K and 50 mK.

Since the magnetic scattering is diffuse in $|\mathbf{Q}|$ we summed data over several detectors thereby increasing counting statistics in the echo measurement without significant loss of wavevector resolution. The normalized intermediate scattering function, $S(\mathbf{Q},t)/S(\mathbf{Q},0)$ for $|\mathbf{Q}| = 0.8$ $Å^{-1}$, is shown in the top panel of Fig. 3 at several temperatures between base temperature and 600 mK. These measurements show an initial fast relaxation of the $S(\mathbf{Q},t)/S(\mathbf{Q},0)$ signal to 20% of its $t=0$ value outside of the time window of the NSE measurement. Much slower relaxation occurs within the NSE time window as is seen in the signal relaxing from $\sim 20\%$, and this much slower process shows definite temperature dependence below ~ 400 mK.

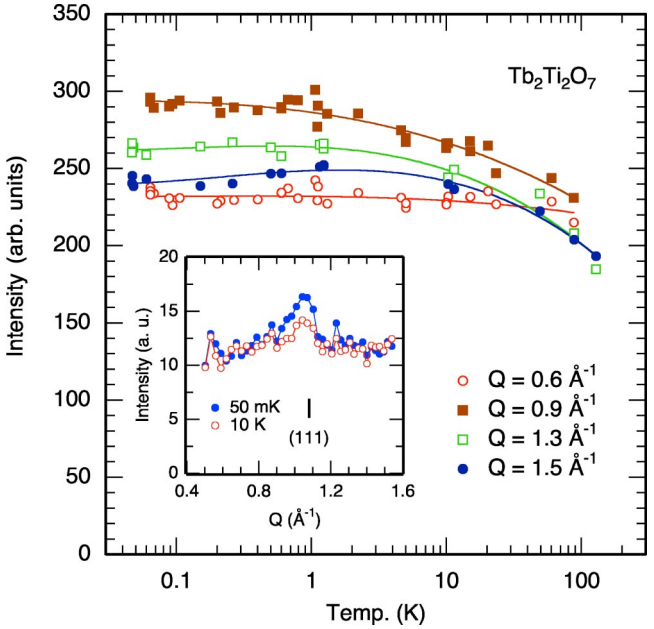

FIG. 2. (Color online) The temperature (main figure) and $|\mathbf{Q}|$ (inset) dependence of the elastic magnetic scattering, as measured by *XYZ* polarization analysis from $Tb_2Ti_2O_7$. Lines are a guide to the eye.

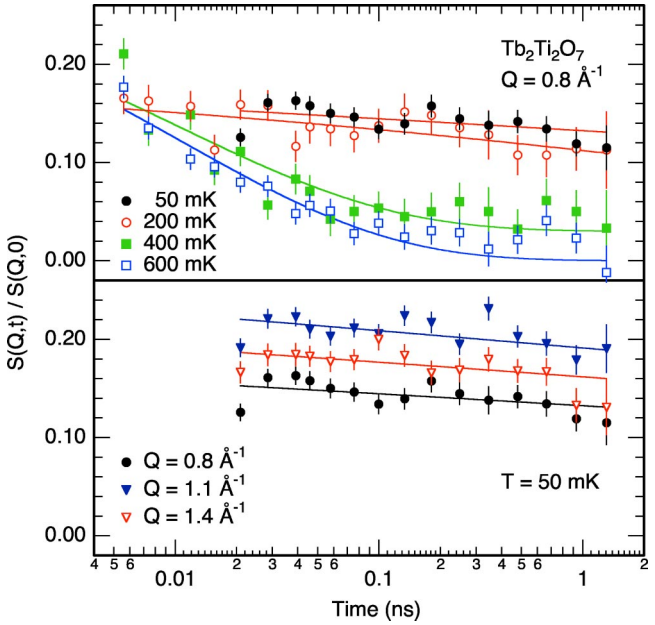

FIG. 3. (Color online) The echo signal at various $|\mathbf{Q}|$'s and temperatures from $Tb_2Ti_2O_7$. Lines are a guide to the eye.

These general features in $S(\mathbf{Q},t)/S(\mathbf{Q},0)$ are very different from that observed in other pyrochlore magnets which have been studied by NSE, such as the concentrated spin glass $Y_2Mo_2O_7$ (Ref. 26) as well as the spin ice magnet $Ho_2Ti_2O_7$.[27] In both cases at sufficiently low temperatures $S(\mathbf{Q},t)/S(\mathbf{Q},0)$ is approximately time independent and close to 1 across the full NSE time window, indicating that the vast majority of the spins are static on time scales $<10^{-9}$ s. The comparison with $Y_2Mo_2O_7$ is particularly interesting as this material is well characterized as having a spin glass phase transition near $T_g \sim 22$ K, with conventional critical exponents describing the divergence of its nonlinear susceptibility.[28] By roughly $T_g/2$, its $S(\mathbf{Q},t)/S(\mathbf{Q},0) \sim 1$ for the NSE time window.

The $S(\mathbf{Q},t)/S(\mathbf{Q},0)$ data on $Tb_2Ti_2O_7$ at 400 and 600 mK are much more typical of spin relaxation only observed in the paramagnetic regime (high temperature) of a magnet. At all temperatures and all $|\mathbf{Q}|$'s measured in the NSE experiment, some relaxation was observed. Indeed above 600 mK the system is too dynamic for this technique, and uncorrelated spin dynamics completely depolarizes the neutron beam. Between 400 and 600 mK significant relaxation can be seen in the spin echo time window. Below 400 mK the long time baseline increases to ~ 0.1; however it is still apparent that $S(\mathbf{Q},t)$ continues to decreases slowly with time, indicative of very slow dynamics within the roughly 10% volume fraction of spins that are almost static and that this occurs to temperatures as low as 50 mK.

It is interesting to note that Hodges *et al.*[29] have investigated an abrupt change in the fluctuation rate of the Yb^{3+} ion in $Yb_2Ti_2O_7$ at 0.24 K. Using muon spin relaxation and Mössbauer spectroscopies they determined that the Yb^{3+} spin slows down by more than three orders of magnitude to several megahertz, without freezing completely. The dramatic but incomplete freezing seen in a small fraction of $Tb_2Ti_2O_7$ is somewhat reminiscent of that seen in $Yb_2Ti_2O_7$ and maybe a characteristic seen in many dense spin liquids.

The bottom panel of Fig. 3 shows the $|\mathbf{Q}|$ dependence of $S(\mathbf{Q},t)/S(\mathbf{Q},0)$ at 50 mK. Unlike the single ion relaxation process seen in $Ho_2Ti_2O_7$,[27] there is a clear $|\mathbf{Q}|$ dependence to this data with the magnitude of the signal peaking around ~ 1 Å^{-1}. However the relaxation rate ($\propto$ slope) is similar at all $|\mathbf{Q}|$'s.

Lou *et al.*[20] recently reported a history dependence in the low temperature magnetization of $Tb_2Ti_2O_7$. They reported a splitting from field-cooled and zero-field-cooled magnetization near ~ 300 mK reminiscent of a spin-glass state. Our frequency dependence measurements of χ_{ac} confirm this

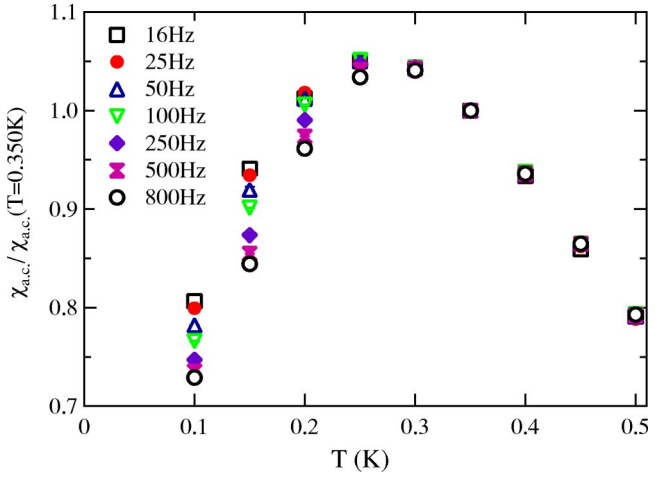

FIG. 4. (Color online) Temperature dependence of the magnetic susceptibility as a function of frequency from a single crystal of $Tb_2Ti_2O_7$.

glassy like transition at 350 mK, as seen in Fig. 4. However our neutron data show the vast majority of the spins to be dynamic on NSE time scales, 10^{-9} s and shorter. We therefore surmise that the partial freezing of the spin system is associated with a few spins around defects in the stoichiometric crystal structure.

Our studies on both polycrystalline and single crystal $Tb_2Ti_2O_7$ conclusively show the pyrochlore antiferromagnet remains dynamic with short range (~ 5 Å) spatial correlations to temperatures as low as 50 mK. Below 400 mK the long time baseline of the NSE signal raises from zero, wherein $S(\mathbf{Q},t)/S(\mathbf{Q},0)$ is completely dephased due to randomly fluctuating moments, to roughly 0.1. This suggests that a 10% volume fraction the magnetic system is quasistatic on the timescale of the experiment at these temperature, but remains slowly relaxing. This behavior is very different from that seen in other magnets, especially those with spin glass ground states. These new results reinforce the enigmatic position which $Tb_2Ti_2O_7$ occupies among magnetic materials with dynamic short range spin correlations down to 50 mK.

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