Lack of Evidence for a Singlet Crystal Field Ground State in the Tb$_2$Ti$_2$O$_7$ Magnetic Pyrochlore

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We present new high resolution inelastic neutron scattering data on the candidate spin liquid Tb$_2$Ti$_2$O$_7$. We find that there is no evidence for a zero field splitting of the ground state doublet within the 0.2 K resolution of the instrument. This result contrasts with a pair of recent works on Tb$_2$Ti$_2$O$_7$ claiming that the spin liquid behavior can be attributed to a 2 K split singlet-singlet single-ion spectrum at low energies. We also reconsider the entropy argument presented in Chapuis et al. as further evidence of a singlet-singlet crystal field spectrum. We arrive at the conclusion that estimates of the low temperature residual entropy drawn from heat capacity measurements are a poor guide to the single ion spectrum without understanding the nature of the correlations.

Introduction — In some magnetic systems, the lattice geometry or the competition between different interactions can dramatically inhibit, or frustrate, the development of long range order. The failure of a frustrated magnetic system to exhibit magnetic order down to zero temperature, giving rise to a so-called spin liquid state, is one of the most sought after phenomena among strongly interacting condensed matter systems. Despite two decades of experimental searches, the number of candidate materials that display a spin liquid state remains small.

The Tb$_2$Ti$_2$O$_7$ insulating material, where magnetic Tb$^{3+}$ ions sit on a pyrochlore lattice of corner-sharing tetrahedra, is one of these candidates. Despite a Curie-Weiss temperature, $\theta_{\text{CW}} \approx -14$ K set by the magnetic interactions, Tb$_2$Ti$_2$O$_7$ does not develop long range order down to at least 50 mK. The microscopic mechanism by which Tb$_2$Ti$_2$O$_7$ fails to develop long range order at a temperature scale of approximately 1 K is not understood. Compounding the difficulty in understanding why Tb$_2$Ti$_2$O$_7$ does not order, one notes that Tb$_2$Sn$_2$O$_7$, seemingly closely related at the microscopic level to Tb$_2$Ti$_2$O$_7$, develops long range order at 0.87 K.

Since Tb$^{3+}$ is an even electron system (electronic configuration $7^3F_6$, $L = 3$, $S = 3$, $J = 6$), the existence of a magnetic ground state for an an isolated (i.e. assumed non-interacting) Tb$^{3+}$ ion in Tb$_2$Ti$_2$O$_7$ is not guaranteed by Kramers’ theorem. To investigate whether Tb$^{3+}$ is magnetic, the so-called single-ion crystal field (CF) problem must first be solved.

For example, for a perfect cubic ionic environment, theory predicts that Tb$^{3+}$ would either have a singlet or non-magnetic doublet single-ion CF ground state. However, in Tb$_2$Ti$_2$O$_7$, with its Fd3m symmetry, the Tb$^{3+}$ environment displays a large enough trigonal distortion away from cubic symmetry. Early investigations found that this distortion endows Tb$^{3+}$ with a magnetic CF doublet characterized by two mutually time-reversed conjugate states, $|\psi^+_0\rangle$ and $|\psi^-_0\rangle$. The states, $|\psi^+_0\rangle$ and $|\psi^-_0\rangle$, are such that all matrix elements of the raising and lowering angular momentum operator, $J^\pm$, vanish while $\langle \psi^0_0 | J^z | \psi^0_0 \rangle = \pm \langle J^z \rangle \approx 3.4$ K. Since $\langle \psi^0_0 | J^\mu | \psi^0_0 \rangle = \pm \langle J^\mu \rangle \delta_{\mu z}$, $\mu \neq z$, the Tb$^{3+}$ moment within its CF ground state can be described by a classical Ising spin with a moment that points “in” or “out” of the reference primitive tetrahedral unit cell to which it belongs. This makes Tb$_2$Ti$_2$O$_7$ a relative of the Ising spin ice compounds.

The lowest excited CF state is also a doublet, $|\psi^\pm_q\rangle$, at an energy approximately 1.6 meV $\sim 18$ K above the ground doublet. Recent theoretical work has argued that the proximity of Tb$_2$Ti$_2$O$_7$ to the zero temperature transition from an “all-in/all-out” $q = 0$ Néel to a spin ice state, along with the exchange and dipole-dipole interaction-induced admixing of $|\psi^0_0\rangle$ and $|\psi^\pm_q\rangle$, constitute two key ingredients as to why Tb$_2$Ti$_2$O$_7$ does not develop long range order.

In conventional (unfrustrated) magnets, spin-lattice couplings typically play an insignificant role in the development of long range order. In highly frustrated magnetic systems, however, spin-lattice couplings can lead to a combined magnetic-lattice (“spin-Peierls”) transition to long range magnetic order that reduces the magnetic frustration, as observed in the highly frustrated antiferromagnet ZnCr$_2$O$_4$ spinel compound.

In Tb$_2$Ti$_2$O$_7$, Mamsurova and co-workers long ago reported an unusually large anomalous field-dependent thermal expansion, indicating an important spin-lattice coupling in this material. In more recent x-ray diffraction experiments, Ruff et al. found evidence for a tendency of the Tb$_2$Ti$_2$O$_7$ lattice to undergo a cubic tetragonal deformation but, down to 300 mK and in zero field, no equilibrium cubic to tetragonal transition was observed. Only in the presence of very high magnetic fields ($\sim 29$ T), does the system show any evidence for such a structural phase transition. In contrast, Chapuis and co-workers very recently argued that a tetragonal deformation does actually exist in...
Tb$_2$Ti$_2$O$_7$ in zero field that splits the above $|\psi_{1,0}^{+}\rangle$ doublet into two non-magnetic singlets separated by an energy scale, $\delta$, with $\delta \approx 1.8$ K [13]. They invoke previously published inelastic neutron scattering (INS) data [12] to suggest that such a large splitting of the ground doublet compared to the exchange and dipolar interactions between Tb$^{3+}$ ions is responsible for inhibiting the spontaneous development of long range order. Reference [18] also present data for the temperature dependence of the magnetic entropy, $S(T)$, which, they claim, by falling below Rh2 at low temperature, further supports the evidence for a split doublet. Very recently, Bonville and collaborators [19] have built further on Chapuis et al.’s split doublet picture to advocate that the failure of Tb$_2$Ti$_2$O$_7$ to order is due to the sub-critical value of the interactions compared to the singlet-singlet gap $\delta$.

In this paper, we argue that the evidence for a split doublet of energy scale as large as $\delta \sim 1.8$ K in Tb$_2$Ti$_2$O$_7$ as proposed in Refs. [18,19] is not compelling. Using new high resolution INS data, we show that there is no evidence for a split doublet in this material with an energy splitting greater than 0.2 K, a factor 10 or so smaller than the proposed [18,19] singlet-singlet gap $\delta$. Secondly, we argue that by neglecting correlations that develop in the collective paramagnetic (spin liquid) phase of Tb$_2$Ti$_2$O$_7$, the authors of Ref. [18] are in principle unable to draw any conclusion about the nature of the CF state of Tb$^{3+}$ in Tb$_2$Ti$_2$O$_7$ on the basis of a measurement of $S(T)$. We illustrate that point via the calculation of $S(T)$ for a toy model which, while possessing a ground state doublet and lacking a transition to long range order, does display an $S(T)$ that falls below Rh2 at low temperature.

Inelastic neutron scattering results – We first proceed to show that a singlet-singlet gap $\delta \sim 1.8$ K is inconsistent with high-energy-resolution inelastic neutron scattering data and that, in fact, Tb$_2$Ti$_2$O$_7$ displays quasielastic magnetic spectral weight down to energies of at least 0.02 meV, approximately an order of magnitude lower in energy than the value $\delta \sim 1.8$ K reported in Refs. [13,19].

Time-of-flight neutron scattering data was obtained on single crystal Tb$_2$Ti$_2$O$_7$ in zero and finite magnetic field applied along the [110] (vertical) direction at T=0.4 K. These measurements used the Disk Chopper Spectrometer (DCS) at NIST and employed incident neutrons of wavelength $\lambda=4.8$ Å resulting in an energy resolution of 0.1 meV. The $H=0$, zero magnetic field data set, after integration along the [HH0] direction, perpendicular to the (00L) direction and within the horizontal scattering plane, is plotted in Fig. 1 a). The quasi-elastic magnetic scattering peaks at $Q=0.02$ (Q=1.2 Å$^{-1}$). Previous work [4,11] has shown that the corresponding diffuse scattering is distributed in reciprocal space into a well known checkerboard pattern. Figure 1 b) shows cuts in energy of this zero magnetic field data set and also of a data set with a $H = 3$ T magnetic field applied along the [110] direction. These cuts simulate constant-$Q$ scans, although they integrate the scattering data in the [HH0] direction (shown in Fig.1 a) and also in the [00L] direction between L=1.6 and 1.8. Two features are noteworthy: while there is a shoulder to this particular cut of the zero field quasi-elastic scattering near $E \sim 0.2$ meV, there is a continuous and monotonically increasing distribution of magnetic spectral weight as the energy decreases down to zero energy. The nature of this shoulder near 0.2 meV is subtle for the zero magnetic field data set. Indeed, low energy quasi-elastic magnetic scattering is obscured by relatively strong nuclear incoherent elastic scattering which dominates the elastic signal within the 0.1 meV energy resolution of this measurement. However, this nuclear incoherent contribution to the elastic scattering can be estimated and removed by examination of the $H = 3$ T data set (in Fig. 1 b). Field-induced long range order [20] leads to a splitting-off of the quasi-elastic magnetic scattering from the resolution-limited nuclear incoherent elastic scattering. Thus the strength of the nuclear incoherent contribution can be determined. Consider the two, otherwise identical cuts shown in Fig. 1 b), both at T=0.4 K, and taken at $H = 0$ (top) and at $H = 3$ T (bottom). One observes scattering at $E = 0$ with an intensity of $\sim 9$ for $H = 0$ where the zero energy scattering has contributions from both nuclear incoherent elastic scattering and quasi-elastic magnetic scattering. In the bottom of panel b), for $H = 3$ T, an $E = 0$ intensity of $\sim 3.5$ is measured, which has contributions from nuclear incoherent scattering alone. Hence the intensity of the elastic magnetic scattering at $H = 0$ is $\sim 5.5$ in the intensity units employed in Figs 1 b); at least a factor of two higher than the intensity associated with the shoulder near $\sim 0.2$ meV. Therefore, the distribution of magnetic scattering intensity does indeed peak at zero energy and extends out to $\sim 0.3$ meV at low temperatures in $H = 0$. In other words, there is no obvious mode centred at an energy of 1.8 K (0.16 meV) in the $H = 0$ data.

![FIG. 1: a) High energy-resolution inelastic neutron scattering data taken with $\lambda=4.8$ Å on DCS [20]. b) Energy cuts of the data shown in a) as described in the text. Quasi-elastic magnetic scattering at T=0.4 K and zero applied magnetic field peaks at zero energy. The crystal field excitation in zero field (top right panel) is anomalously broad in energy, compared with resolution-limited spin waves seen in the bottom right panel within the field-induced ordered phase.](image-url)
same single crystal of Tb$_2$Ti$_2$O$_7$, in zero magnetic field, as well with several different magnetic field strengths applied along the [110] direction. This data, taken with $\lambda = 9$ Å incident neutrons on DCS, is shown in Fig. 2. The scattering data shown in Fig. 2 integrates the raw inelastic scattering data over all Q surveyed, which extends out in reciprocal space to the centre of the aforementioned diffuse magnetic scattering checkerboard at $Q = 002$. This very high energy-resolution data clearly shows the quasi-elastic magnetic scattering to increase continuously with decreasing energy down to the energy resolution of the measurement, $\sim 0.02$ meV $\sim 0.2$ K, an order of magnitude lower than the singlet-singlet gap $\delta \sim 1.8$ K invoked in Refs. [18, 19].

Figure 2 also shows that application of a sufficiently strong [110] magnetic field ($H \sim 4$ T) moves the quasi-elastic magnetic scattering out of the field of view of the figure, revealing a low background which is energy-independent. As a function of increasing applied magnetic field, the quasi-elastic scattering is strongly depleted at low energies, and an inelastic feature is observed for field strengths above $H \sim 1$ T. This excitation moves to higher energies with increasing field strength. However, and crucially significant for our argument, we see that even with an applied field of $H = 1$ T (red curve), the broad inelastic peak is at an energy of $\sim 0.1$ meV $\sim 1$ K, roughly a factor of 2 lower in energy than the gap $\delta \sim 1.8$ K invoked in Refs. [18, 19] in zero field.

One could speculate that the quasi-elastic distribution of magnetic scattering in zero field out to $\sim 0.3$ meV is a dispersive singlet-singlet excitation with a band width of twice the mean separation between the two states, such that its density-of-states fills in the quasi-elastic energy range. However, the intensity would then be the largest for the top of this band, as the density-of-states would be high where the dispersion is flat. This is not observed – the quasi-elastic scattering (Fig. 2) decreases monotonically with increasing energy.

One could also speculate a static and random Jahn-Teller distortion in which a broad distribution of singlet-singlet gaps is present in the spin liquid state. This could lead to a distribution of gaps and induce monotonically-decreasing (as a function of energy) quasielastic scattering in zero field as seen in Figs. 1 and 2. However, with decreasing temperature, these static gaps would get progressively frozen out, resulting in a larger and larger fraction of the system being in a non-magnetic state. The $1/T_1$ muon spin relaxation rate is large and flat in temperature from $\sim 1$ K down to 0.05 K [2]. This would seem to rule out this scenario since, at 0.05 K, excited singlets with an energy gap larger than 0.005 meV would be frozen out. Similarly, neutron spin echo (NSE) results in Ref. [4] rules out a large 1.8 K gap in the system. NSE with sub-μeV resolution and polarised neutron diffraction [4] both show an increase in the magnetic scattering below 300 mK suggesting a magnetic ground state or an extremely small gap that is thermally active at 50 mK.

Taken altogether, we conclude there is no compelling evidence for a well-defined singlet-singlet gap in Tb$_2$Ti$_2$O$_7$ in zero field at low temperatures. Its quasi-elastic, magnetic spectrum is not substantially different from that displayed by Ho$_2$Ti$_2$O$_7$ just above its frozen spin ice ground state, albeit with a higher energy scale.

**Residual entropy** — Having established that there is no direct evidence for a split doublet with an energy gap larger than 0.02 meV $\sim 0.2$ K in Tb$_2$Ti$_2$O$_7$, we now address the interpretation given in Ref. [18] of low temperature magnetic entropy data determined from the heat capacities of Tb$_2$Sn$_2$O$_7$ and Tb$_2$Ti$_2$O$_7$. The magnetic entropy results for Tb$_2$Sn$_2$O$_7$ are given in Fig. 2 of Ref. [18]. In this data, the nuclear and phonon contributions have been subtracted. One sees that roughly Rln 4 is lost upon cooling the sample from 20 K down to 40 mK. This is consistent with having no extensive residual entropy and with magnetic ions having four states lying beneath 20 K. The data for Tb$_2$Ti$_2$O$_7$ also indicate a similar loss of magnetic entropy of Rln 4 below 20 K [18]. The authors of Ref. [18] proceed to make the following argument: Suppose that there is a doublet-doublet crystal field scheme with a gap $\Delta$. Then, at high temperatures exceeding the scale of the gap, the entropy would be Rln 4 whereas at low temperatures, $T \ll \Delta$, the entropy would saturate at Rln 2. Therefore, in this scheme, the total entropy variation should be Rln 2. Since the entropy variation is observed to be Rln 4 in both Tb$_2$Sn$_2$O$_7$ and Tb$_2$Ti$_2$O$_7$, Ref. [18] concludes that the doublet-doublet energy level scheme must be incorrect.

In an attempt to support their argument, the authors present a calculation of the entropy for a crystal field scheme consisting of a pair of low-lying singlets separated by a tuneable energy gap of $\delta$ and one excited doublet at energy $\Delta > \delta$ above the ground singlet. Upon increasing $\delta$ from zero, the lowest temperature entropy drops to zero for $T \lesssim \delta$ and exhibits a plateau at Rln 2 for $\delta \lesssim T \lesssim \Delta$ (see Fig. 3 of Ref. [13]). The width of the plateau decreases as $T$ increases and for $\delta \approx 1.8$ K, the entropy variation for this model roughly matches that for Tb$_2$Ti$_2$O$_7$ (the fit is shown in Fig. 4 of Ref. [18]). This is presented as evidence for a singlet-singlet crystal field scheme in Tb$_2$Ti$_2$O$_7$. A similar conclusion is reached for Tb$_2$Sn$_2$O$_7$. 

![FIG. 2: Very high energy-resolution inelastic neutron scattering data employing $\lambda = 9$ Å incident neutrons with DCS, as described in the text. The zero field measurement shows the quasielastic magnetic distribution of scattering to extend down to at least 0.02 meV.](image-url)
However, the authors of Ref. [18] have not ruled out the possibility that the magnetic entropy is lost through the effects of interactions and the concomitant build-up of correlations as the temperature is decreased below 20 K. This is particularly evident in Tb$_2$Sn$_2$O$_7$ which exhibits a phase transition at 0.87 K to a long range ordered phase. This implies that the residual entropy for $T < 0.87$ K K should have no extensive contribution, as appears to be borne out by the analysis of the specific heat capacity data in Ref. [18]. It follows that one must account for the details of the transition in order to extract information about the single ion level structure from entropy data obtained from the magnetic heat capacity while no attempt was made to carry out such an analysis in Ref. [18].

Switching on the exchange $J$ causes FM correlations to build up. There is no transition, but there is a peak in $C_{\text{mag}}$ beneath the Schottky anomaly at $T/J \sim 0.1$. This is reflected in the magnetic entropy, $S_{\text{mag}}$, dropping below the Rln 2 value. The Rln 2 plateau gradually shrinks as $J$ increases [Fig. 3(b)]. We conclude that the disappearance of an Rln 2 entropy plateau can occur when interactions are introduced even in the absence of a phase transition and, therefore, cannot be attributed definitively to a splitting of the doublet ground state without interactions.

Conclusion — We have reconsidered the scenario advanced in Refs. [18,19] whereby long range order for Tb$_2$Ti$_2$O$_7$ is evaded because the single ion crystal field states are split in zero field, ostensibly due to a tetragonal distortion breaking the Fd3m symmetry. We have presented high energy resolution neutron scattering data to re-examine the case for a singlet-singlet splitting, finding no evidence for excitations that would indicate a splitting greater than 0.2 K. We have also argued that measurements determining the residual entropy cannot be used to draw conclusions about the single ion spectrum without considering the build-up of short-range correlations at low temperatures. In conclusion, the nature of the low temperature state of Tb$_2$Ti$_2$O$_7$ remains a remarkable and unsolved problem in the field of frustrated magnetism. One may anticipate further progress in light of the constraints that we and others are placing on possible scenarios to explain the spin liquid behavior in this material.

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