Spin Liquid Ground State in the Frustrated $J_1$-$J_2$ Zigzag Chain System BaTb$_2$O$_4$

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We have investigated polycrystalline samples of the zigzag chain system BaTb$_2$O$_4$ with a combination of magnetic susceptibility, heat capacity, neutron powder diffraction, and muon spin relaxation measurements. Despite the onset of Tb$^{3+}$-short-range antiferromagnetic correlations at $|J_{CW}| = 18.5$ K and a very large effective moment, our combined measurements indicate that BaTb$_2$O$_4$ remains paramagnetic down to 0.095 K. The magnetic properties of this material show striking similarities to the pyrochlore antiferromagnet Tb$_2$Ti$_2$O$_7$, and therefore we propose that BaTb$_2$O$_4$ is a new large moment spin liquid candidate.

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Spin liquids are exotic ground states of frustrated magnets in which local moments are highly correlated but still fluctuate strongly down to zero temperature.$^1$ In principle, the fluctuations of a spin liquid can be quantum or classical in nature. Several types of spin liquids have been proposed theoretically, including Anderson’s resonating valence bond state,$^2$ spin icos[3]$^4$ and others characterized by either gapped or gapless low-energy excitations.$^5$ The experimental search for new spin liquid candidates is an ongoing area of interest since this state of matter remains largely unexplored in the laboratory. Some well-known examples of quantum spin liquid candidates include ZnCu$_3$(OH)$_6$Cl$_2$(herbertsmithite)$^6$[7], BaCu$_3$V$_2$O$_8$(OH)$_2$(vesignieite)$^8$, and Ba$_3$NiSb$_2$O$_9$,$^9$ while their classical counterparts are the pyrochlore magnets Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$.$^1$[10,11]

Magnetic systems characterized by frustration and low-dimensionality have proven to be useful starting points in the quest for uncovering additional spin liquids, but particular complications have severely limited the number of viable candidates. For example, although one-dimensional (1D) magnets and two-dimensional Heisenberg systems are not expected to order due to the Mermin-Wagner theorem$^12$, most real low-dimensional materials are governed by weak exchange interactions in the other spatial dimensions and therefore exhibit magnetic order at low temperatures. Furthermore, while magnetic frustration can drastically suppress leading terms in the Hamiltonian that would be responsible for magnetic order, there are instances in which the sub-leading terms can still drive the system to an ordered ground state.$^13$ To overcome these obstacles and find new spin liquid candidates, it is important to perform detailed studies on a wide variety of frustrated, low-dimensional magnets.

The family of materials AR$_2$O$_4$ ($A =$ Ba, Sr; $R =$ rare earth)$^{14,15}$ satisfy the two criteria described above. Two crystallographically-inequivalent $R$ sites independently form two different types of zigzag chains running along the $c$-axis, and therefore quasi-1D magnetic behavior may be expected. Bulk characterization studies have also shown that most members of the family have dominant antiferromagnetic (AFM) exchange interactions and relatively large frustration indices. Geometric frustration can arise in this structure type if the $J_2$ exchange interactions are AFM and the $J_1$ couplings are of comparable strength.

The general trend for the AR$_2$O$_4$ family is that a small (large) ionic radius$^{17}$ $r$ for the $R$ atom shortens (lengthens) the $J_1$ bonds and induces Néel (double Néel) order on the chains. Schematics of these two magnetic ground states are shown in Fig. 1(a). The Néel and double Néel long-range ordered states are consistent with predictions for the large AFM $J_1$ and $J_2$ limits of the classical Ising $J_1$-$J_2$ chain$^{13}$, and have been realized in SrYb$_2$O$_4$ ($r =$ 0.87 Å)$^{19}$ and BaNd$_2$O$_4$ ($r =$ 0.98 Å)$^{20}$ respectively. By tuning the ionic radii of the $R$ atoms with different rare earths, the intermediate regime between these two limits has also been explored in detail. A variety of magnetic ground states have been observed, including coexisting long-range Néel and short-range double Néel order in SrEr$_2$O$_4$ ($r =$ 0.94 Å)$^{21,22}$, coexisting short-range Néel and short-range double Néel order in SrHo$_2$O$_4$ ($r =$ 0.90 Å)$^{23-25}$, incommensurate magnetic order in SrTb$_2$O$_4$ ($r =$ 0.92 Å)$^{26}$, and no magnetic ordering of any kind down to 0.065 K in SrTm$_2$O$_4$ ($r =$ 0.88 Å)$^{29}$. It is also interesting to note that any long-range order observed in this family has been found to arise from only one rare earth site (except for SrYb$_2$O$_4$)$^{19}$, and therefore the two types of zigzag chains are often characterized by different magnetic ground states. Since the $J_1$ and $J_2$ bond lengths are essentially equal for the two chain types, this behavior may be a consequence of the inequivalent, distorted oxygen octahedral local environments of the rare earths comprising each chain.

In this Letter, we investigate polycrystalline BaTb$_2$O$_4$ ($r =$ 0.92 Å) with a combination of magnetic susceptibility, heat capacity, neutron diffraction, and muon spin relaxation
measurements. The magnetic species in this system is Tb$^{3+}$, which is a non-Kramers ion with a large angular momentum $J = 6$. Despite the onset of antiferromagnetic correlations at the Curie-Weiss temperature $\theta_{CW} = -18.5$ K, there is no evidence for long-range magnetic ordering or spin freezing in any of the measurements down to 0.095 K. However, neutron diffraction reveals that incredibly short-ranged magnetic correlations exist between $J_2$ bonds. These findings provide strong evidence that BaTb$_2$O$_4$ is a new large moment spin liquid candidate.

Polycrystalline BaTb$_2$O$_4$ samples were synthesized by a standard solid-state reaction method from high-purity starting materials of BaCO$_3$ and Tb$_4$O$_7$. First, Tb$_2$O$_3$ was obtained by reducing Tb$_4$O$_7$ in Ar (4% H$_2$). Next, a stoichiometric mixture of BaCO$_3$ and Tb$_2$O$_3$ (with 10% excess BaCO$_3$) were ground, pressed into pellets, and then sintered in Ar (4% H$_2$) at 1150°C for 8 hours. The final product was confirmed to be single phase by laboratory x-ray powder diffraction.

The magnetic susceptibility of polycrystalline BaTb$_2$O$_4$ was measured in an applied field $\mu_0 H = 0.1$ T under the zero-field-cooled condition using a Quantum Design Magnetic Properties Measurement System. The data are presented in Fig. 1(b), plotted as $1/\chi$, i.e. $\mu_0 H/M$, vs. $T$, and the results are in good agreement with previous work [15]. The high temperature data is well-described by a Curie-Weiss law, with a fit between 40 and 100 K yielding $\theta_{CW} = -18.50(3)$ K and an effective moment $\mu_{eff} = 9.95(1) \mu_B$. The effective moment is close to the expected value of 9.72 $\mu_B$ for Tb$^{3+}$. Despite the onset of AFM correlations around 20 K, there is no evidence for long-range magnetic order from the susceptibility measurements down to 2 K.

The specific heat ($C_p$) below 2 K was measured with a home-built probe based on the adiabatic heat-pulse technique in a He-3/He-4 dilution refrigerator from Oxford Instruments. Data at higher temperatures were taken in a Quantum Design Physical Properties Measurement System equipped with a 12 T superconducting magnet. Fig. 1(c) shows $C_p$ data in selected applied fields. No evidence for magnetic order is found, while observed field dependence is likely indicative of crystal field splitting that changes with $\mu_0 H$.

The zero field $C_p$ data show a sharp upturn for $T < 0.3$ K that can be attributed to nuclear Schottky contributions of Tb nuclei, as discussed for other Tb compounds [30, 31]. A broad maximum is also observed at $T^* = 1.5$ K, which likely corresponds to a low-lying crystal field level. Integrating $C_p/T$ from 0.5-6 K over the broad peak (assuming a negligible lattice contribution in this range) yields an entropy of just over $R\ln(3/2)/\text{mol-Tb}$. This finding could imply a doublet ground state for the Tb$^{3+}$ ions with a small energy gap to a low-lying singlet excited state. However, we note that $C_p$ measurements on the AR$_2$O$_4$ family provide limited quantitative information on the crystal field level schemes, due to the monoclinic site symmetries and the inequivalence of the local environments for the two different R sites. The build-up of short-range magnetic correlations with decreasing $T$ can also complicate analysis of the magnetic entropy extracted from $C_p$ data [32].

Neutron powder diffraction was performed with 5 g of polycrystalline BaTb$_2$O$_4$ between 0.3-100 K at Oak Ridge National Laboratory using the HB-2A powder diffractometer of the High Flux Isotope Reactor with a collimation of 12'-open-6'. Data with a neutron wavelength of 2.41 Å is depicted in Fig. 2(a) and (d) with $T = 0.3$ K and 10 K respectively. Successful Rietveld refinements were performed using FullProf [33] with the known room temperature space group $Pnma$ [15], indicating that there are no structural phase transitions down to 0.3 K. The lattice constants at 0.3 K refined as $a = 10.423(1)$ Å, $b = 12.178(1)$ Å, and $c = 3.497(1)$ Å.

No evidence was found for long-range order in the diffraction data of BaTb$_2$O$_4$. However, magnetic diffuse scattering was observed instead in both the 0.3 and 10 K datasets. This contribution is modeled as background in Fig. 2(a) and (d), and most clearly seen in Fig. 2(b) and (e). The $Q$-dependence of the diffuse scattering remains almost unchanged up to 10 K. These findings indicate that there are significant magnetic correlations that persist well above the onset of any possible long-range order. We note that the combined diffraction and sus-
FIG. 2: (a) HB-2A neutron diffraction data with $\lambda = 2.41$ Å at 0.3 K for polycrystalline BaTb$_2$O$_4$. The solid curve is a fit generated from a structural Rietveld refinement using the space group $Pnma$. (b) An enlarged version of the data shown in panel (a), emphasizing the magnetic diffuse scattering. (c) A 0.3-100 K difference plot, with the intensity normalized by the Tb$^{3+}$ magnetic form factor squared. The dashed and solid curves are fits to models incorporating only Tb$^{3+}$ magnetic correlations between $J_1$ and $J_2$ bonds respectively. (d)-(f) Similar plots to those shown in panels (a)-(c), but with $T = 10$ K.

cceptibility data rule out a well-isolated crystal field singlet ground state as found for Tm$_2$Ti$_2$O$_7$[34] and possibly applicable to SrTm$_2$O$_4$[29], since the signatures for such a scenario are a constant low-$T$ magnetic susceptibility and the absence of any elastic magnetic scattering, in contrast to observations.

0.3-100 K and 10-100 K difference plots are shown in Fig.2(c) and (f), with the data normalized by the Tb$^{3+}$ form factor squared. Similar oscillatory scattering patterns are clearly evident in both datasets, therefore no drastic change is found in the magnetic correlations through $T^*$. This observation confirms that the $C_p$ anomaly at $T^*$ is not associated with any form of magnetic ordering, but can likely be attributed to a low-lying crystal field level. The intensity of the difference plots is well-described by the function:

$$I(Q) = \sum_{ij} A_{ij} \frac{sin(Qd_{ij})}{Qd_{ij}}$$  \hspace{1cm} (1)

This equation represents the expected polycrystalline response for a local magnetic structure with the spins at sites $i$ and $j$ correlated over distances of $d_{ij}$ only. Antiferromagnetic (ferromagnetic) correlations are inferred from $A_{ij} < 0$ ($A_{ij} > 0$). In BaTb$_2$O$_4$, the 0.3 K refinement discussed above yields a $J_1$ bond length of 3.50 Å, while the two types of zigzag chains are found to have inequivalent $J_2$ bond lengths of 3.59 Å and 3.60 Å. The best fits of the BaTb$_2$O$_4$ data, shown by the solid curves in Fig.2(c) and (f), require only one term with $A < 0$ and $d = 3.58(4)$ Å at 0.3 K (3.61(3) Å at 10 K). Fits with $d_{ij}$ fixed to 3.50 Å are also shown for comparison purposes by the dashed curves, but they do simulate the data as accurately. Therefore, the analysis described above is consistent with AFM correlations extending only between $J_2$ bonds, with $d$ representing an average bond length between the two types of chains. Furthermore, the incredibly short-range nature of the correlations is reminiscent of the magnetic behavior in the large moment spin liquid candidate Tb$_2$Ti$_2$O$_7$, where the Tb$^{3+}$ spins were found to be correlated over a single tetrahedron only[35].

The neutron diffraction results discussed above do not allow one to determine whether the spins are static or dynamic in the magnetic ground state. For example, diffuse elastic magnetic scattering was observed for all three pyrochlore systems Y$_2$Mo$_2$O$_7$[36 37], Tb$_2$Mo$_2$O$_7$[38], and Tb$_2$T$_2$O$_7$[35], but the molybdates have been characterized as spin glasses while the titanate is best described as a spin liquid. Muon spin relaxation ($\mu$SR) measurements proved to be instrumental in unambiguously determining the nature of the ground states in these cases. More specifically, the $\mu$SR spectra for the two scenarios evolve quite differently in a longitudinal magnetic field configuration[40].

Therefore, to better understand the magnetic ground state of BaTb$_2$O$_4$, $\mu$SR was performed at the EMU (10-300 K) and MuSR (0.095-4 K) spectrometers in longitudinal field (LF) geometry at the ISIS Pulsed Neutron and Muon Source. Zero field data were collected at 0.095, 0.5, 2, and 4 K, and no fea-
A symmetry

0.050
0.100
0.125
0.150

/\(\text{MHz}\)

\(\lambda\)

dependence of the relaxation rate \(T\) which suggests that its origin is a dynamic mechanism.

(b) This \(T\)-dependence is consistent with dynamic behavior of the spins down to the lowest temperatures investigated.

These measurements, the presence of low-temperature short-range spin correlations from neutron diffraction, and the lack of any static magnetism detected by \(\mu\)SR down to 0.095 K provide strong evidence for a large moment spin liquid ground state in BaTb_2O_4. This exotic state likely arises from incredibly balanced \(J_1\) and \(J_2\) intrachain exchange interactions, which lead to a high degree of frustration. Single crystal inelastic neutron scattering and theoretical calculations are needed to help determine the crystal field level schemes and the evolution of the magnetic Hamiltonian throughout the AR_2O_4 series, as such work will lead to a deeper understanding of the origins of the exotic and varied magnetism in this family of materials.

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