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Citation for published version:

Digital Object Identifier (DOI):
10.1103/PhysRevLett.113.267205

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Physical Review Letters

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Incipient Ferromagnetism in Tb$_2$Ge$_2$O$_7$: Application of Chemical Pressure to the Enigmatic Spin-Liquid Compound Tb$_2$Ti$_2$O$_7$


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(Received 24 April 2014; published 31 December 2014)

After nearly 20 years of study, the origin of the spin-liquid state in Tb$_2$Ti$_2$O$_7$ remains a challenge for experimentalists and theorists alike. To improve our understanding of the exotic magnetism in Tb$_2$Ti$_2$O$_7$, we synthesize a chemical pressure analog: Tb$_2$Ge$_2$O$_7$. Substitution of titanium by germanium results in a lattice contraction and enhanced exchange interactions. We characterize the magnetic ground state of T$_2$Ge$_2$O$_7$ with specific heat, ac and dc magnetic susceptibility, and polarized neutron scattering measurements. Akin to Tb$_2$Ti$_2$O$_7$, there is no long-range order in T$_2$Ge$_2$O$_7$ down to 20 mK. The Weiss temperature of $19.2(1)$ K, which is more negative than that of T$_2$Ti$_2$O$_7$, supports the picture of stronger antiferromagnetic exchange. Polarized neutron scattering of T$_2$Ge$_2$O$_7$ reveals that liquidlike correlations dominate in this system at 3.5 K. However, below 1 K, the liquidlike correlations give way to intense short-range ferromagnetic correlations with a length scale similar to the Tb-Tb nearest neighbor distance. Despite stronger antiferromagnetic exchange, the ground state of T$_2$Ge$_2$O$_7$ has ferromagnetic character, in stark contrast to the pressure-induced antiferromagnetic order observed in T$_2$Ti$_2$O$_7$.

DOI: 10.1103/PhysRevLett.113.267205 PACS numbers: 75.40.-s, 75.25.-j, 75.30.Cr

Geometrically frustrated pyrochlores $R_2M_2O_7$ exhibit a diverse array of exotic magnetic behaviors [1]. The ground states in these materials are dictated by a complex, and often delicate balance of exchange, dipolar, and crystal field energies. T$_2$Ti$_2$O$_7$ is one of the most remarkable of these frustrated pyrochlores; strong antiferromagnetic exchange and Ising-like spins led to predictions of an antiferromagnetic Néel state below $\sim 1$ K for this material [2]. However, experimental studies revealed a lack of static order or spin freezing in T$_2$Ti$_2$O$_7$ down to 70 mK [3,4], and more recently 57 mK [5]. Subsequently, enormous efforts have been undertaken to uncover the origin of the spin-liquid state in T$_2$Ti$_2$O$_7$.

A further complication in T$_2$Ti$_2$O$_7$ is the coupling of the magnetic and lattice degrees of freedom [6–9]. It has been suggested that hybridized magnetoelastic excitations may be responsible for the suppression of magnetic order in T$_2$Ti$_2$O$_7$ [10]. Another theoretical construct that attempts to account for the lack of static order in T$_2$Ti$_2$O$_7$ is a quantum spin ice state [11–15]. A third proposed scenario is that the non-Kramers doublet ground state of T$_2$Ti$_2$O$_7$ is split into two nonmagnetic singlets through a symmetry reducing structural distortion [16–18].

Other studies sought to uncover the origin of the spin-liquid state in T$_2$Ti$_2$O$_7$ by focusing on mechanisms of its destruction, such as external pressure [19], magnetic fields [18,20,21], and a combination of the two [22]. Partial antiferromagnetic order is induced in T$_2$Ti$_2$O$_7$ with external hydrostatic pressures of 8.6 GPa, resulting in a 1% compression of the lattice [19]. Another means of destroying the spin-liquid state is chemical pressure: substitution of the nonmagnetic titanium cation for a valence isoelectronic cation with a different ionic radius. Substitution of titanium in T$_2$Ti$_2$O$_7$ for the larger tin cation allowed exploration of negative chemical pressure [23]. In T$_2$Sn$_2$O$_7$, reduced antiferromagnetic exchange results in an “ordered spin ice” state at 0.87 K [23,24]. In this two-in, two-out state, the spins are oriented $13.3^\circ$ to the local $\langle 111 \rangle$ axes. This ground state can be partially understood by a model of Heisenberg spins with finite ferromagnetic exchange and $\langle 111 \rangle$ anisotropy [25]. However, this can only be reconciled with the apparent antiferromagnetic nearest neighbor
exchange in Tb$_2$Sn$_2$O$_7$ if a tetragonal distortion is considered [26], for which there is currently no evidence.

More recently, the study of chemical pressure in the pyrochlores has focused on substitution of Ti$^{4+}$ for the much smaller Ge$^{4+}$. Germanium substitution results in a lattice contraction and enhanced exchange interactions [27]. Study of the germanate pyrochlores has revealed that some frustrated ground states are stable against the application of chemical pressure while others are not. For example, the spin ice state is robust in the holmium pyrochlores Ho$_2$B$_2$O$_7$ ($B$ = Ge, Ti, Sn) [27–29]. Conversely, quantum fluctuations in the effective $S = 1/2$ Yb$^{3+}$ cation are very sensitive to chemical pressure. Consequently, the ytterbium pyrochlores Yb$_2$B$_2$O$_7$ ($B$ = Ge, Ti, Sn) each have markedly different magnetic ground states [30].

To gain a better understanding of the exotic magnetism in Tb$_2$Ti$_2$O$_7$ we synthesized a positive chemical pressure analog: Tb$_2$Ge$_2$O$_7$. We characterized the magnetic ground state of Tb$_2$Ge$_2$O$_7$ with specific heat, magnetic susceptibility, and polarized neutron scattering measurements. Akin to Tb$_2$Ti$_2$O$_7$, there is no long-range order in Tb$_2$Ge$_2$O$_7$ down to 20 mK. However, the liquidlike correlations in Tb$_2$Ge$_2$O$_7$ give way to intense short-range ferromagnetic interactions below 1 K.

When reacted under ambient pressure, Tb$_2$Ge$_2$O$_7$ has a tetragonal pyrogermanate structure [31]. We prepared Tb$_2$Ge$_2$O$_7$ in the cubic pyrochlore phase using a high-temperature, high-pressure technique. Stoichiometric quantities of Tb$_2$O$_3$ and GeO$_2$ were reacted at 1000°C and 8 GPa using a multianvil press. Batches of approximately 60 mg, prepared from a common precursor, were heated in rhenium capsules to produce a total of 320 mg of polycrystalline sample. Room temperature powder neutron diffraction measurements were made on the general materials diffractometer at the ISIS neutron facility. Rietveld fits to the diffraction pattern of Tb$_2$Ge$_2$O$_7$ with GSAS confirmed the Fd$^3$m pyrochlore phase and the absence of pyrogermanate impurities [Fig. 1(a)]. The room temperature lattice parameter was refined to a value of 9.68 1.91 Å. This corresponds to a reduction from Tb$_2$Ti$_2$O$_7$ and Tb$_2$Sn$_2$O$_7$ of ~2% and ~5%, respectively (Table I).

Off stoichiometry and site mixing are known to have a significant impact on the magnetic properties of Tb$_2$Ti$_2$O$_7$ [33,34] and other pyrochlores [35]. These issues are most severe in the case of single crystals grown with the optical floating zone technique [35]. A key advantage of the study of germanium pyrochlores is that the large size mismatch between the rare earth and germanium cations should preclude the possibility of site mixing. Rietveld refinement of the powder neutron diffraction pattern indicates ideal stoichiometry and the absence of site mixing in Tb$_2$Ge$_2$O$_7$. The $A$ and $B$ sites of the lattice have an occupation of 1.00(5) by Tb$^{3+}$ and Ge$^{4+}$, respectively.

The inverse dc susceptibility of Tb$_2$Ge$_2$O$_7$ provides no evidence of long-range order down to 0.5 K [Fig. 1(b)]. A Curie-Weiss fit between 100 and 300 K yields an antiferromagnetic Weiss temperature of $\theta_{CW} = -17.5(2)$ K. Fits over an identical temperature range for Tb$_2$Ti$_2$O$_7$ [32] and Tb$_2$Sn$_2$O$_7$ [23] give Weiss temperatures of $-17.5$ and $-12.5$ K, respectively. The more negative Weiss temperature for Tb$_2$Ge$_2$O$_7$ is indicative of stronger antiferromagnetic exchange that results from a reduced Tb-Tb distance. The susceptibility of Tb$_2$Ge$_2$O$_7$ begins to deviate from Curie-Weiss behavior below 70 K. This is similar to Tb$_2$Ti$_2$O$_7$ [32], in which the deviation is attributed to the onset of developing short-range magnetic correlations [3].

The heat capacity of Tb$_2$Ge$_2$O$_7$ contains two low temperature anomalies centered at 5.5 and 1.2 K

<table>
<thead>
<tr>
<th>$\alpha$ (Å)</th>
<th>$\theta_{CW}$ (K)</th>
<th>$\rho_{eff}$ ($\mu_B$)</th>
<th>$D_{an}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$_2$Sn$_2$O$_7$</td>
<td>10.426</td>
<td>$-12.5$</td>
<td>9.68</td>
</tr>
<tr>
<td>Tb$_2$Ti$_2$O$_7$</td>
<td>10.149</td>
<td>$-17.5(3)$</td>
<td>9.56</td>
</tr>
<tr>
<td>Tb$_2$Ge$_2$O$_7$</td>
<td>9.961(1)</td>
<td>$-19.2(1)$</td>
<td>9.87(3)</td>
</tr>
</tbody>
</table>
These features bear a significant qualitative resemblance to the low temperature heat capacity of Tb$_2$Ti$_2$O$_7$, which exhibits two peaks centered at 6 and 1.5 K (inset of Fig. 2). Gingras et al. interpret the peak at 6 K in Tb$_2$Ti$_2$O$_7$ as a remnant of the first excited state doublet [32]. The anomaly at 1.5 K in Tb$_2$Ti$_2$O$_7$ is attributed to the buildup of short-range magnetic correlations. While the corresponding peak in Tb$_2$Ge$_2$O$_7$ is sharper, there is no evidence for the onset of long-range order at 1.2 K. We thus speculate that Tb$_2$Ge$_2$O$_7$ has a crystal field scheme that resembles that of Tb$_2$Ti$_2$O$_7$, resulting in similar heat capacity anomalies. In Tb$_2$Ti$_2$O$_7$, approximately −6 K of the Weiss temperature is due to crystal field effects [32], 2 K is related to long-range dipolar contributions, and the remaining −13.5 K is due to magnetic exchange. The dipolar interaction, approximated as $D_{nn} = 5/3 (\mu_0/4\pi) \mu^2/r_{nn}^3$, in pyrochlores, does not significantly vary with lattice parameter (Table I).

Given that the crystal fields and dipolar contributions are similar to those of Tb$_2$Ti$_2$O$_7$, we suggest that the increased magnitude of the Weiss temperature in Tb$_2$Ge$_2$O$_7$ results from enhanced antiferromagnetic exchange. However, a definite conclusion on this matter will require a detailed investigation of the crystal electric field of Tb$_2$Ge$_2$O$_7$.

We measured the ac susceptibility of Tb$_2$Ge$_2$O$_7$ down to 20 mK with frequencies ranging from 41 to 511 Hz and in dc fields up to 0.05 T. In zero field, the real component of the susceptibility $\chi'$ contains no evidence of an ordering transition down to 20 mK in Tb$_2$Ge$_2$O$_7$ [Fig. 3(a)]. The imaginary component of the susceptibility $\chi''$ is also free of anomalies and has an increasing magnitude with decreasing temperature [Fig. 3(b)]. The application of external dc fields as small as 0.01 T to Tb$_2$Ge$_2$O$_7$ induces a broad peak in $\chi'$ [Fig. 3(a)]. As the external dc field is increased, the peak flattens and shifts to higher temperatures. At constant field strength, this feature is independent of frequency [Fig. 3(c)]. There is no corresponding peak or significant difference in $\chi''$. If this field-induced feature in Tb$_2$Ge$_2$O$_7$ had antiferromagnetic origins, an increasing field would suppress the peak to lower temperature. The field enhancement of this peak combined with its frequency independence suggest that it is ferromagnetic in character. This feature may be related to the formation of short-range spin correlations in Tb$_2$Ge$_2$O$_7$.

The related pyrochlores Tb$_2$Ti$_2$O$_7$ and Tb$_2$Sn$_2$O$_7$ have been extensively characterized with ac susceptibility [14,36–38]. In Tb$_2$Ti$_2$O$_7$, frequency dependent peaks at 350 and 140 mK are attributed to defect freezing [4] and a quantum spin ice state [14], respectively. In Tb$_2$Sn$_2$O$_7$, the ordering transition at 850 mK is marked by a frequency independent feature in both the real and imaginary parts of the ac susceptibility [38]. With an external magnetic field, this feature of Tb$_2$Sn$_2$O$_7$ is reduced in magnitude while shifting to higher temperatures. Although no peak is observed in the zero-field susceptibility of Tb$_2$Ge$_2$O$_7$, the behaviors otherwise more closely resemble Tb$_2$Sn$_2$O$_7$. It is possible that at the lowest temperatures Tb$_2$Ge$_2$O$_7$ is approaching an ordering transition that is not accessible experimentally. A further similarity between Tb$_2$Sn$_2$O$_7$ and Tb$_2$Ge$_2$O$_7$ is the increasing magnitude of the imaginary

![Image](image_url)
susceptibility below 1 K, which has been attributed to increasing ferromagnetic correlations in Tb$_2$Sn$_2$O$_7$ [38].

We carried out polarized neutron scattering measurements on Tb$_2$Ge$_2$O$_7$ using the DNS spectrometer, which is operated by the Heinz Maier-Leibnitz Zentrum at Garching. Measurements were taken at 100 mK, 3.5 K, 25 K, and 100 K using a dry-type dilution insert and a top-loading closed cycle refrigerator with an incident wavelength of 4.2 Å. XYZ-polarization analysis allows the magnetic scattering to be separated from the nuclear-coherent and spin-incoherent components. The scattering of Tb$_2$Ge$_2$O$_7$ at 25 and 100 K is well fit by the square of the magnetic form factor for Tb$^{3+}$ [Fig. 4(a)]. Thus, the scattering at these temperatures is mainly paramagnetic. However, the deviations from the magnetic form factor are more pronounced at 25 K compared to 100 K due to the development of short-range correlations.

At 3.5 K, the magnetic diffuse scattering in Tb$_2$Ge$_2$O$_7$ strongly deviates from the magnetic form factor. There is an upturn in the scattering at low $Q$ and a hump in the scattering centered at 1.1 Å$^{-1}$ [Fig. 4(a)]. These two features have competing origins. The upturn at low $Q$ is related to short-range ferromagnetic correlations. The hump at 1.1 Å$^{-1}$ is related to liquidlike correlations. A coexistence of short-range ferromagnetic and liquidlike correlations has also been observed in Tb$_2$Sn$_2$O$_7$ at 1.2 K, above its ordering temperature [24]. The fit to the data was achieved by combining a Lorentzian function and an antiferromagnetic nearest-neighbor spin correlation function. The Lorentzian function $I(Q) = (A/\pi)(\kappa/(\kappa^2 + Q^2))$ fits the short-range ferromagnetic correlations [39]. The liquidlike scattering is modeled by $I(Q) \approx \sin(Qr_{ij})/Qr_{ij}$, where $r_{ij}$ is the distance between spins at sites $i$ and $j$ [3]. The value of $r_{ij}$ was refined to 3.65(6) Å, which agrees well with the Tb-Tb nearest neighbor distance of 3.52 Å in Tb$_2$Ge$_2$O$_7$. The antiferromagnetic contribution to the scattering, which is responsible for the maximum at $Q = 1.1$ Å$^{-1}$ and the minimum at $Q = 2.1$ Å$^{-1}$, is strongly reminiscent of the scattering in Tb$_2$Ti$_2$O$_7$ at 2.5 K [3].

The $Q$ dependence of the magnetic diffuse scattering changes significantly between 100 mK and 3.5 K [Fig. 4(b)]. The decreased error bar size at 100 mK is due to significantly longer counting times. The spectral weight at 100 mK is increasing at low-$Q$ values, towards $Q = 0$. The contribution from the liquidlike correlations, which were prominent at 3.5 K, are dwarfed by the low-$Q$ scattering. Thus, at 100 mK the magnetism in Tb$_2$Ge$_2$O$_7$ is dominated by short-range ferromagnetic correlations. This low-$Q$ scattering is fit to a Lorentzian function between 0.3 and 0.7 Å$^{-1}$. From this fit, a mean correlation length can be estimated by $\kappa^{-1}$ as 3.6(9) Å, close to the Tb-Tb distance. Another feature at 100 mK is the presence of developing intensity at 1.08 and 3.6(9) Å, close to the Tb-Tb distance. The spectral weight at 100 mK is increasing at low-$Q$ values, towards $Q = 0$. The contribution from the liquidlike correlations, which were prominent at 3.5 K, are dwarfed by the low-$Q$ scattering. Thus, at 100 mK the magnetism in Tb$_2$Ge$_2$O$_7$ is dominated by short-range ferromagnetic correlations. This low-$Q$ scattering is fit to a Lorentzian function between 0.3 and 0.7 Å$^{-1}$. From this fit, a mean correlation length can be estimated by $\kappa^{-1}$ as 3.6(9) Å, close to the Tb-Tb distance. Another feature at 100 mK is the presence of developing intensity at 1.08 and 3.6(9) Å, close to the Tb-Tb distance.

At 1.2 K, the scattering at 25 and 100 K has been offset 6 and 12 counts/s respectively for clarity. The ferromagnetic Bragg peak positions (111) and (200) are indicated by the dashed lines. The black lines are the fits to data, as described in the text.

![FIG. 4 (color online). Magnetic diffuse scattering of Tb$_2$Ge$_2$O$_7$ at (a) 100 K, 25 K, 3.5 K, and (b) 100 mK. The scattering at 25 and 100 K has been offset 6 and 12 counts/s respectively for clarity. The ferromagnetic Bragg peak positions (111) and (200) are indicated by the dashed lines. The black lines are the fits to data, as described in the text.](267205-4)
further emphasizes the delicate balance of exchange, dipolar, and crystal field interactions in these pyrochlores. Consideration of the similarities and differences between Tb$_2$Ti$_2$O$_7$ and Tb$_2$Ge$_2$O$_7$ should be useful for achieving a complete understanding of the origin of their collective paramagnetic states. To that end, a thorough study of Tb$_2$Ge$_2$O$_7$’s crystal field scheme will prove valuable. The local oxygen environment of terbium, which dictates the crystal electric field, is altered by germanium substitution. Our heat capacity measurements indicate qualitative similarities in the crystal fields of Tb$_2$Ge$_2$O$_7$ and Tb$_2$Ti$_2$O$_7$. However, it is possible that the significant differences in the magnetism of these two materials are related to subtle differences in the crystal field scheme and, consequently, the single ion anisotropy.

In conclusion, our results reveal a lack of long-range order in Tb$_2$Ge$_2$O$_7$ down to 20 mK. Magnetic diffuse neutron scattering measurements reveal that Tb$_2$Ge$_2$O$_7$ does not share a spin-liquid ground state with Tb$_2$Ti$_2$O$_7$. Instead, Tb$_2$Ge$_2$O$_7$ is dominated by short-range ferromagnetic correlations with a length scale characteristic of the Tb-Tb distance. A field induced peak with ferromagnetic character is observed in the ac susceptibility. Tb$_2$Ge$_2$O$_7$ represents an exciting new avenue to probe the exotic phase diagram of the terbiyum pyrochlores. Characterization of the crystal field scheme of Tb$_2$Ge$_2$O$_7$ and a muon spin relaxation investigation of its dynamics will allow additional valuable comparisons to be drawn.

We are appreciative of helpful comments from M. J. P. Gingras and B. D. Gaulin. We gratefully acknowledge the support received from staff at the Heinz Maier-Leibnitz Zentrum (MLZ), especially Kirill Nemkovskiy and Heinrich Kolb. We thank Dr. W. Kockelmann (ISIS) for assistance with diffraction measurements. A. M. H. acknowledges support from the Vanier Canada Graduate Scholarship Program. This work was supported by NSERC, the CRC program, and CFI. We acknowledge support from EPSRC, STFC, and the Royal Society. A portion of this work was performed at the NHMFL, which is supported by NSF Cooperative Agreement No. DMR-1157490, the State of Florida, and the U.S. DOE. J. G. C. acknowledges support from NSFC (Grant No. 11304371) and the Chinese Academy of Sciences (Grant No. Y2K5016X51).


