Thermodynamic and single-ion properties of Tb$^{3+}$ within the collective paramagnetic-spin liquid state of the frustrated pyrochlore antiferromagnet Tb$_2$Ti$_2$O$_7$

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In a recent paper [J. S. Gardner et al., Phys. Rev. Lett. 82, 1012 (1999)] it was found that the Tb$^{3+}$ magnetic moments in the Tb$_2$Ti$_2$O$_7$ antiferromagnetic pyrochlore lattice of corner-sharing tetrahedra remain in a collective paramagnetic state down to 70 mK. In this paper we present results from dc magnetic susceptibility, specific-heat data, inelastic neutron-scattering measurements, and crystal-field calculations that strongly suggest that i) the Tb$^{3+}$ ions in Tb$_2$Ti$_2$O$_7$ possess a moment of approximately $5 \mu_B$, and ii) the ground state $g$-tensor is extremely anisotropic below a temperature of $O(10^1)$ K, with Ising-like Tb$^{3+}$ magnetic moments confined to point along a local cubic $\langle 111 \rangle$ diagonal (e.g., towards the middle of the tetrahedron). Such a very large easy-axis Ising-like anisotropy along a $\langle 111 \rangle$ direction dramatically reduces the frustration otherwise present in a Heisenberg pyrochlore antiferromagnet. The results presented herein underpin the conceptual difficulty in understanding the microscopic mechanism(s) responsible for Tb$_2$Ti$_2$O$_7$ failing to develop long-range order at a temperature of the order of the paramagnetic Curie-Weiss temperature $\theta_{CW} \sim 10^1$ K. We suggest that dipolar interactions and extra perturbative exchange coupling(s) beyond nearest neighbors may be responsible for the lack of ordering of Tb$_2$Ti$_2$O$_7$.

I. INTRODUCTION

In magnetic systems, competition between magnetic interactions, combined with certain local lattice symmetries involving triangles, give rise to the notion of geometric frustration. Geometrically frustrated antiferromagnets are currently attracting much interest within the condensed-matter community. The main reason for this interest is that geometric frustration can cause sufficiently large zero-temperature quantum spin fluctuations as to drive a system into interesting types of intrinsically quantum-mechanical magnetic ground states with no classical equivalent.

Among three-dimensional systems, the pyrochlore lattice of corner-sharing tetrahedra (see Fig. 1) with antiferromagnetic nearest-neighbor exchange interaction is particularly interesting. For this system, theory and Monte Carlo simulations show that for classical Heisenberg magnetic moments interacting with a nearest-neighbor antiferromagnetic coupling, there is no transition to long-range magnetic order at finite temperature. This is unlike the two-dimensional kagomé lattice antiferromagnet where a thermally driven order-by-disorder of spin nematic order occurs. Villain coined the name “collective paramagnet” to describe the classical state of the pyrochlore lattice at low temperatures.

Because of their low propensity to order even for classical spins, antiferromagnetic materials based on a pyrochlore lattice appear to be excellent systems in which to seek exotic quantum-mechanical ground states. For example, numerical calculations suggest that the $S = 1/2$ pyrochlore Heisenberg antiferromagnet may be fully quantum disordered, giving rise to a state that is commonly referred to as “spin liquid.” Both terms “collective paramagnet” and “spin liquid” are

FIG. 1. Pyrochlore lattice of corner-sharing tetrahedra. The magnetic moments occupy the corners of the tetrahedra.
meant to emphasize that despite such a system remaining in a paramagnetic phase down to absolute zero temperature, the properties of such a state involve very strong and nontrivial short-range spin correlations, analogous to the nontrivial position-position correlations present in an ordinary atomic or molecular fluid.

A number of experimental studies on insulating pyrochlore materials have been reported in the past ten years. Interestingly, it has been found that such systems do not typically form such a spin liquid state that remains paramagnetic down to zero temperature. Most often, these systems either display long-range antiferromagnetic order: such as FeF$_3$, Gd$_2$Ti$_2$O$_7$, ZnFe$_2$O$_4$, and ZnCr$_2$O$_4$, or enter a spin-glass-like state below some nonzero spin-freezing temperature as exhibited by Y$_2$Mo$_2$O$_7$, Y$_2$Mo$_2$O$_7$, Y$_2$Mo$_2$O$_7$, Y$_2$Mo$_2$O$_7$, and CsNiCrF$_6$ pyrochlore. Recently, several studies of the pyrochlore rare-earth titanates, RE$_2$Ti$_2$O$_7$, have been published. In these compounds, the trivalent rare-earth ions, RE$^{3+}$, occupy the 16$d$ sites of the Fd$ar{3}$m space group and form a pyrochlore lattice (Fig. 1). The behaviors displayed in this family of pyrochlores are much varied indeed. Gd$_2$Ti$_2$O$_7$ develops true long-range order at a critical temperature of about 1 K; Tb$_2$Ti$_2$O$_7$ possesses a trivial nonmagnetic (i.e., spin singlet) ground state separated by an energy gap of about 120 K to the next crystal-field level. Ho$_2$Ti$_2$O$_7$ is well described by an Ising doublet. In that system, it was originally argued that the nearest-neighbor exchange interaction is weakly ferromagnetic, and that the strong Ising-like single ion anisotropy along (111) directions frustrates the development of long-range ferromagnetic order. This material also exhibits low-temperature thermodynamic properties reminiscent of Pauling’s “ice model,” an equivalence proposed by Harris and co-workers. Recently, it has been found that Dy$_2$Ti$_2$O$_7$ (Refs. 31 and 36) is also a very good example of “spin ice,” and that the application of a magnetic field can restore much of the ground-state entropy and drive magnetic phase transitions. Most recently, den Hertog and Gingras have argued that the spin ice physics in both Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ is not driven by nearest-neighbor ferromagnetic exchange, but is rather due to the long-range $1/r^3$ nature of magnetic dipole-dipole interactions.

In contrast to the long-range ordered, spin ice, or spin glass states mentioned above, strong evidence for collective paramagnetism, or spin liquid behavior, was recently observed in the insulating pyrochlore Tb$_2$Ti$_2$O$_7$. It was found using neutron scattering and muon relaxation methods that this material remains paramagnetic down to (at least) 70 mK despite the fact that the paramagnetic Curie-Weiss temperature $\theta_{CW}$ is $\sim 19$ K, and that short-range antiferromagnetic correlations begin to develop at $\sim 50$ K. At first sight, one could argue that it is “pleasing” to have found at last the spin liquid state anticipated by theory for Tb$_2$Ti$_2$O$_7$. However, the situation for Tb$_2$Ti$_2$O$_7$ is not as simple as it might naively appear.

In Tb$_2$Ti$_2$O$_7$ the Tb$^{3+}$ ions have a partially filled $7F_g$ shell, and one must first understand their crystal-field level scheme and, in particular, the nature of the single-ion magnetic ground state before constructing a correct effective spin-spin Hamiltonian for Tb$_2$Ti$_2$O$_7$. Indeed, we show below that crystal-field anisotropy renders the description of Tb$_2$Ti$_2$O$_7$ in terms of an isotropic Heisenberg antiferromagnetic model completely inappropriate.

If one neglects the axial oxygen distortion around the Tb$^{3+}$ sites, and assumes that the local environment of the Tb$^{3+}$ is perfectly cubic, one would expect, based on point-charge calculations, that the ground state of both Tb$^{3+}$ and Tm$^{3+}$ should either be a singlet or a nonmagnetic doublet. For example, as mentioned above, experimental evidence for a nonmagnetic singlet ground state has been found in Tm$_2$Ti$_2$O$_7$. Based on this naive picture, one can see that the experimental evidence of a moment for Tb$^{3+}$ in Tb$_2$Ti$_2$O$_7$ is therefore a nontrivial issue that needs to be understood.

A simple possibility is that corrections beyond the point-charge approximation and/or the known axial oxygen distortions around each of the 16$d$ sites cause the Tb$^{3+}$ cations to acquire a permanent magnetic moment. Another and more interesting possibility is that the moment on the Tb$^{3+}$ site in Tb$_2$Ti$_2$O$_7$ is induced by a collective bootstrapping of the magnetic (exchange and/or dipolar) interactions as occurs in the tetragonal LiTbF$_4$ material. In Tb$_2$Ti$_2$O$_7$, a priori, it is theoretically possible that there could be no moment on the Tb$^{3+}$ site for a concentration $x$ of Tb$^{3+}$ less than some critical concentration $x_c$, less than some critical concentration $x_c$, or $x_c < x < x_c$, or $x_c < x < x_c$. This is an important issue. Indeed, one could imagine that for the highly frustrated pyrochlore lattice, the collective development of a permanent ground-state moment would not give rise to homogeneous moments on the Tb$^{3+}$ sites, but to a kind of “modulated moment structure” (MMS). This idea is conceptually similar to what is found in the frustrated tetragonal TbRu$_2$Ge$_2$ material, but where for Tb$_3$Ti$_2$O$_7$ there might be instead a quantum-disordered state, possibly an MMS state, “intervening” between a trivial single-gluon state and a long-range ordered one, with the quantum-disordered state extending all the way to $x = 1$.

In the case where a permanent moment does exist on Tb$^{3+}$ even in absence of interaction [i.e., the limit $x \rightarrow 0$ in (Tb$_{1-x}$Y$_{1-x}$)$_2$Ti$_2$O$_7$], the important issue is to determine the wave-function decomposition of the ground state in terms of $|J,M_J\rangle$ states and the symmetry, Heisenberg or otherwise, of the resulting effective spin variable. The goal of such a program is to construct a low-energy effective spin Hamiltonian in order to tackle theoretically why Tb$_2$Ti$_2$O$_7$ does not order at nonzero temperature. Consequently, it is very important to understand in more detail the magnetic nature of the Tb$^{3+}$ single-ion ground state in Tb$_2$Ti$_2$O$_7$.

The main purpose of this paper is to examine the magnetic nature of the Tb$^{3+}$ ion in the Tb$_2$Ti$_2$O$_7$ pyrochlore in order to assess whether or not there is indeed a permanent moment at the Tb site as the temperature goes to zero, and to determine the nature of this moment (e.g., level of effective spin anisotropy). We present in Sec. II experimental evidence, based on results from dc susceptibility, heat capacity, and powder inelastic neutron studies that show there is a permanent moment at the Tb site, but that its approximate $5 \mu_B$ value is less than the value of $9.6 \mu_B$ estimated from the dc susceptibility measurements above 200 K, or the $9.72 \mu_B$ free ion value. To complement the experimental work, results from ab initio crystal-field calculations that take into
account covalent and electrostatic effects are presented in Sec. III and Appendix B. We discuss in Sec. IV the possibility that dipole-dipole interactions and extra perturbative exchange couplings beyond nearest neighbor may be responsible for the lack of ordering in Tb₂Ti₂O₇.

II. EXPERIMENTAL METHOD AND RESULTS

A. Sample preparation

Samples of Tb₂Ti₂O₇ and (Tb₀.₀₂Y₀.₉₈)₂Ti₂O₇ were prepared in the form of polycrystalline pellets by high-temperature solid-state reaction. Starting materials, Tb₂O₃, Y₂O₃, and TiO₂ were taken in stoichiometric proportions, mixed thoroughly, pressed into pellets, and heated in an alumina crucible at 1400°C for 12 h in air. Tb₂O₃ was prepared by hydrogen reduction of Tb₄O₇. The powder x-ray-diffraction patterns of the samples, obtained with a Guinier-Hagg camera, indicate that they are single phase with cubic unit-cell constants a = 10.149 Å for Tb₂Ti₂O₇ and 10.104 Å for (Tb₀.₀₂Y₀.₉₈)₂Ti₂O₇. The value for the concentration of Tb³⁺ in Tb₂Ti₂O₇ measured at an applied field of 0.01 T is shown in Fig. 2. A fit of the data to the Curie-Weiss (CW) law above 200 K gives an effective paramagnetic moment, 9.6 μB/Tb³⁺. For the diluted sample, (Tb₀.₀₂Y₀.₉₈)₂Ti₂O₇, was also studied. The data for this sample are shown in Fig. 3 along with a Curie-Weiss fit giving again a value close to the free ion value for the effective paramagnetic moment, 9.6μB/Tb³⁺, and θCW = −6 K. This finite value is in contrast to the essentially zero θCW value obtained for a similarly diluted sample of Gd₂Ti₂O₇ which contains the isotropic “spin only” $^{8}s_{7/2}$Gd³⁺ ion, and therefore indicates that a significant crystal-field contribution to θCW exists in the Tb³⁺-based material. Thus to a first approximation one can estimate that the portion of θCW for Tb₂Ti₂O₇ which can be attributed to magnetic interactions is

$$\theta_{CW}(\text{Tb}_2\text{Ti}_2\text{O}_7) = \theta_{CW}((\text{Tb}_{0.02}\text{Y}_{0.98})_2\text{Ti}_2\text{O}_7) \approx -13 \text{ K},$$

a value similar to the θCW ≈ −10 K found for Gd₂Ti₂O₇. This approach can be made more rigorous by noting that in a high-temperature series expansion, one finds that the magnetic susceptibility is

$$\chi = C_1/T + C_2/T^2$$

where $C_2 = \theta_{CW}$ can be “decomposed” as a simple sum of terms that are ascribed to exchange interactions, dipolar interactions, and crystal-field terms (see Appendix A). Note also that, down to a temperature of T = 2 K, neither Fig. 2 nor Fig. 3 show any sign of a singlet ground state which would manifest itself as an approach to a constant susceptibility with decreasing temperature, as found in the single ground state of the Tm₃Ti₂O₇. A more detailed analysis concerning this issue is presented in Sec. III.

While it is tempting to use the magnetic interaction contribution ($\theta_{CW} - \theta_{CW}^{eff}$)≈ −13 K (with $\theta_{CW} = -19$ K and $\theta_{CW}^{eff} = -6$ K), to extract the approximate value of the nearest-neighbor exchange, an estimate of the nearest-
neighbor dipole-dipole interaction for Tb$^{3+}$ ions indicates an energy scale of about 1 K. Given the long-range nature of dipolar forces, it becomes clear that the classical nearest-neighbor exchange constant cannot be obtained from a measurement of the Curie-Weiss temperature until the effects of long-range dipolar interactions on $\theta_{\text{CW}}$ have been understood. We find via a high-temperature series expansion analysis of the long-range dipolar contributions $\theta_{\text{CW}}^{\text{dip}}$ to the Curie-Weiss temperature (see Appendix A), that the estimated upper bound on $\theta_{\text{CW}}^{\text{dip}}$ is ferromagnetic and $\sim 1.2$ K (for needle-shaped powder crystallites), while the lower bound is antiferromagnetic and $\sim -2.4$ K (for slab-shaped powder crystallites). Consequently, we find that antiferromagnetic exchange interactions are predominantly responsible for the ($\theta_{\text{CW}}^{\text{dip}} - \theta_{\text{CW}}^{\text{dip}}$) $= -13$ K value determined above $T \gtrsim 200$ K, with a resulting $\theta_{\text{CW}}^{\text{dip}} \in [-14.2, -10.6]$ K.

C. Neutron-scattering experiments

Inelastic neutron scattering allows us to determine with reasonable precision the energy value of the crystal-field energy levels of Tb$_2$Ti$_2$O$_7$. The inelastic neutron-scattering measurements were carried out on a 50-g sample of polycrystalline Tb$_2$Ti$_2$O$_7$, loaded in a sealed Al cell with a helium exchange gas present. The cell was mounted in a closed cycle helium refrigerator with a base temperature of 12 K. The sample was the same as used in Ref. 37. Measurements were performed on the C5 triple axis spectrometer at the Chalk River Laboratories in constant scattered neutron energy mode. Two spectrometer configurations were employed, appropriate for relatively high- and low-energy resolution, respectively. Both configurations employed pyrolitic graphite (PG) as both monochromator and analyzer. The low-resolution measurements, appropriate for relatively high-energy transfers, were performed using $E'/h = 3.52$ THz (1 THz = 48 K), open-60-80-open collimation, and a PG filter in the scattered beam. The high-resolution configuration used $E'/h = 1.2$ THz, open-40-60-open collimation, and a cooled Be filter in the scattered beam. These results clearly indicate excitations at $E \approx 0.36$ and 2.5 THz and a broadband neutron group centered at 3.5 THz (corresponding to 16.8, 120, and 168 K, respectively).

The low-energy-resolution inelastic neutron-scattering measurements at 12 K with $E'/h = 3.52$ THz revealed the presence of two $Q$-independent modes with frequencies $\nu \sim 2.5$ and 3.5 THz. Representative neutron groups, as well as the dispersion relation for these two excitations are shown in the top panel of Fig. 4. These excitations are identified as being magnetic in origin due to the temperature and $Q$ dependence of their intensity. Their flat dispersion ($Q$ independence of their energies) indicates that they are crystal electric-field levels for Tb$^{3+}$ in the environment appropriate for Tb$_2$Ti$_2$O$_7$.

The high-energy-resolution inelastic neutron measurements at 12 K with $E'/h = 1.2$ THz shows the presence of a low-lying magnetic excitation near $\nu \sim 0.36$ THz. This mode is also dispersionless above a temperature of $\sim 25$ K, but partially softens in energy at the wave vector which characterizes the very short-range spin correlations, which develop below 50 K. The development of this interesting dispersion has been described previously. The dispersion of the low-lying excitation is shown in the lower panel of Fig. 4. One can see that this partial softening of the excitation branch occurs only for the lowest lying mode. As we show in the next section, this is manifested in the heat-capacity measurements as broad features that result of a broadening of the single-ion energy levels via these short-range magnetic correlation effects.

These measurements place constraints on any calculations for the energy eigenstates of Tb$^{3+}$ as they set both the energy spacing of the levels, and require that magnetic dipole matrix elements must connect the ground state with these levels in order that they be visible in the inelastic neutron-scattering experiment. In particular, this indicates nonzero $\langle 0 | J^+ | 1 \rangle$, $\langle 0 | J^- | 1 \rangle$, or $\langle 0 | F^\dagger | 1 \rangle$ matrix elements connecting the ground state |0\rangle and the first excited state |1\rangle at an energy $\sim 0.36$ THz $\approx 18$ K above the ground state. In other words, there must be large $| J,M_J \rangle$ components in |0\rangle and |1\rangle where some of the $M_J$ involved for the ground state and the excited state differ by 0, $\pm 1$.

D. Specific-heat measurements

Low-temperature specific-heat measurements on Tb$_2$Ti$_2$O$_7$ were performed using a thermal-relaxation microcalorimeter. The single-crystal sample was mounted on a sapphire holder which was isolated from the bath by four copper-gold alloy wires. The relative precision and absolute accuracy of the calorimeter were confirmed by measuring copper and gold standards. In principle, specific-heat measurements on a dilute (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ sample would be useful. Unfortunately, this is not technically easily feasible as the magnetic contribution to the total specific heat would be too small to be determined accurately.

The total specific heat $C_p$ of Tb$_2$Ti$_2$O$_7$ was measured from 0.4 to 30 K at applied fields of 0, 2, and 5 T (see Fig.
The zero-field data exhibits two broad peaks centered at about 1.5 and 6 K. The data are in agreement with those of Ref. 28, above a temperature of 0.4 K. Hyperfine contributions to the specific heat become important below 0.4 K for Tb-based compounds, as found for example in the Tb$_2$(GaSn)$_2$O$_7$ pyrochlore, and this is presumably the reason for the sharp increase of $C_p(T)/T$ found in Fig. 4 of Ref. 28 below 0.5 K. The solid line in Fig. 5 corresponds to the estimated lattice heat capacity $C_l$ for Tb$_2$Ti$_2$O$_7$, determined by scaling the heat capacity for Y$_2$Ti$_2$O$_7$, which is insulating, nonmagnetic, and is isotructural to Tb$_2$Ti$_2$O$_7$ (Ref. 47).

The magnetic specific heat $C_m$ obtained by subtracting $C_l$ from $C_p$ is shown in Fig. 6 for the three applied fields. With the application of a 2-T field the magnitude of the lower temperature peak diminishes and moves to a slightly higher temperature. In contrast, the position of the second peak does not change but increases in magnitude as the lower temperature feature begins to overlap with it. At 5 T the low-temperature feature disappears completely and the remaining peak is shifted to higher temperatures.

The crystal-field calculations described in Sec. III and Appendix B (see Table II) indicate a level scheme consisting of a ground-state doublet with another doublet as the first excited state. Attempts to fit the $C_m$ data to Schottky anomalies using a unique doublet-doublet level scheme for the Tb$^{3+}$ ions and varying the ground-state–excited-state energy splitting failed, since important magnetic short-range correlations are present in this system as observed in neutron scattering, and discussed above. Consequently, we interpret the anomaly at $\sim 6$ K as a remnant of the excited doublet that is “broadened” by exchange correlation fields, while the 1.5 K anomaly is presumably due to these same correlation effects, but now acting on the single-ion ground-state doublet. In other words, the buildup of short-range correlations in the low-temperature sector of the effective Hamiltonian for Tb$_2$Ti$_2$O$_7$ results in a specific heat anomaly at 1.5 K. This low-temperature anomaly at 1.5 K that results from correlations is akin to the broad specific heat bump at $\sim 2$ K found in Gd$_2$Ti$_2$O$_7$. However, Gd$_2$Ti$_2$O$_7$ is an $8^{5/2}$ spin-only ion, and there are no crystal-field levels at high energy, nor are there correlation remnants of crystal-field levels above the ground state such as those that cause the specific-heat anomaly at 6 K in Tb$_2$Ti$_2$O$_7$. Another distinction between Tb$_2$Ti$_2$O$_7$ and Gd$_2$Ti$_2$O$_7$ is that the latter shows a very sharp specific heat anomaly at 0.9 K, and therefore presumably a transition to long-range order at that temperature as suggested by recent theoretical calculations and neutron-scattering experiments.

Down to 0.4 K, no such sharp specific-heat anomaly is found in Tb$_2$Ti$_2$O$_7$. From the fit of the dc susceptibility and the crystal-field calculations presented in Sec. III and Appendix B, good evidence is obtained that the magnetic moment in the ground state and the first excited state is $\sim 5\mu_B$ and $\sim 6\mu_B$, respectively. Given a doublet-doublet energy gap of about 18 K, we can estimate the strength of the magnetic field where the separation between the doublets is equal to the magnetic-field energy, and find a magnetic field of about 5 T. For an applied field of that strength, the ground state and excited states merge and are strongly mixed. This explains the disappearance of the low-temperature specific-heat anomaly in Fig. 6 for a field $H \sim 5$ T.

It is usual to estimate the magnetic entropy $S_m(T)$ in a system by integrating $C_m(T)/T$ between the lowest temperature reached and the temperature $T$ of interest. Although it is straightforward to integrate $C_m(T)/T$, the interpretation of the results for Tb$_2$Ti$_2$O$_7$ is difficult. The main reasons for this are:

• The hyperfine interaction is large for Tb$^{3+}$ and the nuclear specific-heat contribution becomes significant with respect to the magnetic contribution below a temperature of 0.4 K. As one can hardly integrate $C_m(T)/T$ above 5 K without “already” embedding in the resulting entropy a contribution from excitations to the first excited doublet.

FIG. 5. Specific heat $C_p$ of Tb$_2$Ti$_2$O$_7$ as function of temperature for the indicated magnetic fields of 0, 2, and 5 T. The solid line corresponds to the lattice specific heat of Tb$_2$Ti$_2$O$_7$, $C_l$, estimated from the measurements on the nonmagnetic Y$_2$Ti$_2$O$_7$ that is isotructural to Tb$_2$Ti$_2$O$_7$ (Ref. 47).

FIG. 6. Magnetic specific heat $C_m$ of Tb$_2$Ti$_2$O$_7$ as function of temperature for the indicated magnetic fields of 0, 2, and 5 T. The solid lines are guides to the eye.
As discussed in the Introduction, it is very important to determine whether the existence of a moment at the Tb\textsuperscript{3+} site in Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} is intrinsic, or driven by magnetic interactions. Consequently, we have investigated in detail the problem of single-ion properties of Tb\textsuperscript{3+}, both theoretically and via dc susceptibility measurements, of Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, and of the dilute (Tb\textsubscript{0.02}Y\textsubscript{0.98})\textsubscript{2}TiO\textsubscript{7} material where the Tb-Tb interactions should be negligible. The main conclusion from this investigation is that the Tb\textsuperscript{3+} cation does indeed carry an intrinsic moment inherent to its environment in Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, and that moment is not due to a bootstrapping effect from magnetic exchange and/or dipole-dipole interactions.

The results from inelastic neutron-scattering and specific-heat measurements presented in the previous section already provide some evidence for a doublet ground state and an excited doublet state at an energy of ~18 K. The purpose of this section is to investigate further from a theoretical point of view the question of the existence of a magnetic ground-state doublet for Tb\textsuperscript{3+} in Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}. In short, both a simple point-charge calculation and a more sophisticated \textit{ab initio} method confirm that a doublet-doublet scheme is the most likely low-energy level structure for Tb\textsuperscript{3+}. We have constructed a van Vleck equation based on such a doublet-doublet scheme in order to parametrize the dc susceptibility of the dilute (Tb\textsubscript{0.02}Y\textsubscript{0.98})\textsubscript{2}TiO\textsubscript{7} powder sample, and to extract the value of the magnetic moment for both the ground-state and excited-state doublets. We find that experimental results for the dc susceptibility of (Tb\textsubscript{0.02}Y\textsubscript{0.98})\textsubscript{2}TiO\textsubscript{7} are in reasonably good agreement with the \textit{ab initio} calculations.

A. Crystal-field effects

Experimental evidence of a doublet-doublet structure for the low-temperature crystal-field levels of Tb\textsuperscript{3+} in Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} can be understood by considering the crystal-field environment surrounding the ion. Pyrochlore oxides \textit{A}_{2}B\textsubscript{2}O\textsubscript{7} are described by the space group \textit{Fd\bar{5}m} with A\textsuperscript{3+}, the trivalent rare-earth in 16\textit{d}, B\textsuperscript{4+}, the tetravalent transition-metal ion, in 16\textit{c}, O1 in 48\textit{e} and O2 in 8\textit{b}. The A\textsuperscript{3+}, or Tb\textsuperscript{3+} site in this case, is coordinated to six O1 ions at about 2.5 Å in the form of a puckered ring and to two O2 ions at a distance of 2.2 Å in the form of a linear O2-Tb-O2 chain oriented normal to the mean plane of the O1 ring. The O2-Tb-O2 units are parallel to the (111) directions within the cubic unit cell. Overall, the local geometry at the Tb\textsuperscript{3+} site can be described as a severe trigonal compression along the body diagonal of a simple cube.

Based on symmetry considerations, the cubic plus axial distortion surrounding the Tb\textsuperscript{3+} ion may be expressed by a crystal-field Hamiltonian of the general form

\[ H^{C} = B_{0}^{C}C_{0}^{C} + B_{4}^{C}C_{4}^{C} + B_{2}^{C}(C_{2}^{C} - C_{-2}^{C}) + B_{0}^{C}C_{0}^{C} + B_{2}^{C}(C_{2}^{C} - C_{-2}^{C}) + B_{0}^{C}(C_{0}^{C} + C_{-6}^{C}) \]

(3.1)

where the \( B_{k}^{C} \)'s are yet to be determined crystal-field parameters, and the \( C_{k}^{C} \)'s are tensorial operators defined as \( C_{k}^{C} = (4\pi/(2k+1))^{1/2}Y_{k}^{C} \), where \( Y_{k}^{C} \) is a normalized spherical harmonic. In general, the \( B_{k}^{C} \)'s represent an effective one-body potential which lifts the degeneracy of the angular mo-
mentum states in question. In practice, they may be determined experimentally by spectroscopic or thermodynamic probes, or theoretically within various levels of approximation.

In the simplest approximation of the crystal-field interactions, one often uses the so-called point-charge (PC) approximation where the crystal field is simply assumed to be caused by the Coulomb field of point charges situated at neighboring sites. In such a picture, the crystal-field eigenstates and eigenvalues have been determined for a number of rare earths by Lea et al. for systems with cubic symmetry (i.e., without trigonal distortion).\(^{39}\) For Tb\(^{3+}\), the lowest three energy levels in a cubic environment are a \(\Gamma_3\) singlet, a nonmagnetic \(\Gamma_2\) doublet and a \(\Gamma_5^{(2)}\) triplet, with their precise ordering in terms of lowest energy states dependent upon variation of the point-charge crystal-field parameters.\(^{39}\) In general, the addition of the trigonal distortion splits the \(\Gamma_5^{(2)}\) triplet into a singlet and doublet, while the \(\Gamma_3\) and \(\Gamma_2\) states are preserved. Hence we expect that the crystal-field ground state of the Tb\(^{3+}\) ion in Tb\(_2\)Ti\(_2\)O\(_7\) will be a competition between two doublets and two singlets.

Some notion regarding the difficulty of determining the precise ordering of these states and the size of their associated magnetic moments may be obtained by diagonalizing the crystal-field Hamiltonian \(H^{\text{cf}}\) using Stevens’ operator equivalents\(^{48}\) of the \(C_k\) within a fixed \(J\) manifold,\(^{49}\) and by using the point-charge approximation for the Coulomb effects of the surrounding oxygen ions. The resulting crystal-field point-charge Hamiltonian \(H^{\text{pc}}\) with quantization axis along the appropriate \(\langle 111 \rangle\) direction can be expressed as

\[
H^{\text{cf}}_{\text{pc}} = \alpha J B_2^0 (r^{-3} - 1) O_2^0 + \beta J B_4^0 \left[ \frac{27 r^3 + 1}{28} O_4^0 - 20 \sqrt{2} O_4^1 \right] + \gamma J B_6^0 \left[ \frac{188 + 324 r^7}{512} O_6^0 + \frac{35 \sqrt{2}}{4} O_6^3 + \frac{77}{8} O_6^6 \right],
\]

(3.2)

where \(r = R_1/R_2\) and \(R_1, R_2\) are the Tb-O distances for oxygen ions situated on the puckered ring and on the distortion axis, respectively. The \(O_m^k\) represent crystal-field operators as discussed by Hutchings,\(^{30}\) while \(\alpha J, \beta J, \) and \(\gamma J\) are the Stevens’ coefficients.\(^{48,50}\) Trivalent Tb\(^{3+}\) is an \(7\)\(F_6\) ion and thus the fixed \(J\) manifold is \(J = 6\) \((L = S = 3 J = L + S = 6)\) for the operator equivalent point-charge calculation. The precise relationship between the point charge parameter set \(\{B_k^{(i)}\}\) and the more general \(\{B_k\}\) is discussed by Kassman.\(^{49}\)

Although a point-charge estimation of the crystal-field parameters is in most cases unreliable in predicting the actual crystal-field level spacing of rare-earth ions, we find that varying the point-charge parameter set \(\{B_k^{(i)}\}\) indicates that the ground state can be confirmed to be a competition between two singlets close in energy and two magnetic doublets, which are well separated from the other crystal-field states. These levels are indeed the remnants of the \(\Gamma_2, \Gamma_3,\) and \(\Gamma_5^{(2)}\) states of the cubic environment eluded to earlier.

In general, we find that in a large region of the crystal-field parameter space, the two doublets form the lowest energy levels, although their precise ordering may change. Although the weight of each angular momentum component

\[\frac{M_J}{4\pi}
\]

of a crystal-field eigenstate varies with the values of the crystal-field parameters, some other general features do emerge. In particular, one singlet contains only \(|\pm 6\rangle\) and \(|\pm 3\rangle\) states while the other is a combination of \(|\pm 6\rangle, |\pm 3\rangle, \) and \(|0\rangle\). On the other hand, both sets of doublets are magnetic (e.g., they have a nonzero quantum expectation value of \(J^z\)), and also contain components of exclusively different \(J^z\) values (the \(J^z\) operator does not connect the ground state to the excited state). One doublet has large \(|\pm 4\rangle\) and \(|\pm 1\rangle\) components, while the other has large \(|\pm 5\rangle\) and \(|\pm 2\rangle\) components. Hence the two doublets have \(M_J\) components that differ by \(\pm 1\), and a neutron spin-flip-induced transition from one to the other is allowed, consistent with what is found in the inelastic neutron-scattering results presented above.

We have confirmed these conclusions based on our point-charge analysis by performing a more sophisticated first-principles calculation that take into account both electrostatic and covalency effects as well as the intra-atomic and configurational interactions. This approach, described in Appendix B, does not restrict the decomposition of the electronic energy levels into a fixed \((J, M_J)\) manifold as is usually done using the Steven’s operator equivalents, as discussed above. In the results presented in Appendix B, we find that the two lowest energy doublets have a leading \(M_J = \pm 4\) and \(M_J = \pm 5\) components, respectively (close to 90% of the weight). Table II in Appendix B lists three very similar energy level structures given for slightly different constraints on the crystal-field parameters. The theoretically determined energy levels with mean values: 0, 13, 60, and 83 cm\(^{-1}\), that is, 0, 19, 86, and 119 K, respectively, can be favorably compared with the experimental levels determined by inelastic neutron diffraction: 0, 18, 115, and 168 K. The corresponding wave functions allow for a good estimate of the magnetic susceptibility of the diluted and concentrated compounds as shown by Table III and Fig. 8.

From these results, a picture of the low-temperature single-ion properties of Tb\(^{3+}\) can be deduced. Considering the structure of the eigenstates of the two lowest doublets, a calculation of their \(g\) tensors indicates extremely strong
Ising-like anisotropy along the appropriate (111) axes (the axis formed by joining the two centers of the tetrahedra to which the ion belongs) for each Tb$^{3+}$ ion at low temperatures. In summary, based on both point-charge and ab initio calculations, we have strong evidence of a doublet-doublet scheme for Tb$^{3+}$, and a substantial single-ion anisotropy in Tb$_2$Ti$_2$O$_7$, making the the Tb$^{3+}$ moment effectively Ising like for $T \lesssim O(10^5)$ K. The consequences of this result will be discussed in Sec. IV.

B. Susceptibility

The zero-field susceptibility measurements of the Tb-diluted powder compound (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ shown in Fig. 3 enables us to gain a more concise understanding of the nature of the crystal-field levels of Tb$^{3+}$ in Tb$_2$Ti$_2$O$_7$, and the single ion properties of Tb$^{3+}$. Indeed, the dilute concentration of Tb$^{3+}$ ions in the system removes the effect of magnetic interactions and, in principle, leaves only crystal-field contributions to the magnetic susceptibility. Having obtained strong evidence for a doublet-doublet scheme for the Tb$^{3+}$ ions we now proceed further and analyze the dc magnetic susceptibility by constructing a phenomenological expression for the susceptibility based on a van Vleck equation for such a doublet-doublet energy level structure. This allows us to extract the size of the magnetic moments of both doublets from experiment, as well as check for consistency with the conclusions based on our crystal-field calculations of Appendix B.

Due to the powder nature of our (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ sample, the random orientation of the grains can lead to both parallel and transverse contributions to the susceptibility at first and second order. For the doublet-doublet structure at low temperature eluded to earlier, the van Vleck equation for the susceptibility has the general form

$$\chi = \frac{g^2 e^2 N_{\text{B}}^2}{3 k_B} \left( \frac{a/T + b + e^{-\Delta_T/c(T - d)}}{1 + e^{-\Delta_T}} \right),$$

where $g$ is the Landé factor, equal to $3/2$ for Tb$^{3+}$, $\mu_B$ is the Bohr magneton and $N_{\text{B}}=0.04 N_0$, where $N_0$ is Avogadro’s constant. The adjustable parameters $a, b, c, d$ are defined through second-order perturbation theory to be

$$a = \sum_{\alpha, \alpha', m_0} \left| \langle n_0 | J^\alpha | m_0 \rangle \right|^2,$$

$$b = 2 \sum_{\alpha, \alpha', m_0} \left| \langle n_1 | J^\alpha | m_0 \rangle \right|^2,$$

$$c = \sum_{\alpha, \alpha', m_1} \left| \langle n_1 | J^\alpha | m_1 \rangle \right|^2,$$

$$d = 2 \sum_{\alpha, \alpha', m_1} \left| \langle n_1 | J^\alpha | m_1 \rangle \right|^2,$$

where $n_0, m_0$ label states within the ground-state doublet, $n_1, m_1$ label states in the excited doublet while the index $i$ defines any state from the $i$th crystal-field level. The $\Delta$’s represent crystal-field energy level differences (in K) and $\alpha = x, y, z$. The fitting parameters $a$ and $c$ are due to first-order terms in perturbation theory while $b$ and $d$ are from second-order terms and give rise to temperature independent van Vleck paramagnetism contributions to $\chi$.

We have performed a least-squares fit to the susceptibility data of (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ up to a temperature $\sim 30$ K, which is approximately where thermal contributions from a crystal-field level at $\sim 100$ K become non-negligible. Because of the narrow energy spacing between the ground-state and excited-state doublet, all four adjustable parameters $a, b, c, d$ are important in fitting the susceptibility data. Based on the crystal-field calculations of the previous section, the specific-heat analysis of the doublet-doublet gap in the concentrated Tb$_2$Ti$_2$O$_7$ sample, and the evidence of an anisotropy gap of $\sim 18$ K observed in inelastic neutron measurements on the same sample, we have carried out the fit of the low-temperature behavior of the susceptibility using a doublet-doublet gap $\Delta$ ranging from 12$\sim 24$ K. We find that the goodness of fit is quite flat in this range for $\Delta$. However, the magnitude of the adjustable parameters do not deviate strongly and can be determined to a reasonable degree of accuracy over this interval. Using values of the gap outside of this interval yields a noticeably poorer goodness of fit. In Fig. 8, we show our best fit to susceptibility data for the dilute (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ sample using an anisotropy gap of 18 K as well as the results for the ab initio crystal-field calculations.

We can interpret the fitted results for the susceptibility data by making use of our crystal-field results and Eq. (3.3). Due to the strong Ising like nature of the $g$ tensors of the two theoretically calculated doublets, transverse terms such as $\langle n_1 | J^z | n_0 \rangle$ between two states within a doublet are negligible compared to $\langle n_0 | J^x | n_0 \rangle$. Thus we expect that $a = (\langle n_0 | J^x | n_0 \rangle)^2$ and $c = (\langle n_1 | J^x | n_1 \rangle)^2$ and, consequently, both the $a$ and $c$ terms represent permanent moment contributions to the susceptibility. For the same reason, the $g$ tensors characterizing the ground state is extremely anisotropic with essentially only a $g_{||}$ component along the local (111) direction with very little $g_\perp$ component. As a result, and this is the most important point of the paper: At a temperature $T < O(10^4)$ K, Tb$^{3+}$ ions can be considered to a very good approximation as (classical) Ising magnetic moments confined to point parallel or antiparallel to their local (111) directions.

Over the range mentioned above for the doublet-doublet gap $\Delta$, we have found that the magnitude of the moment in the doublet ground state to be $5.10 \pm 0.3 \mu_B$. Overall, we find that our best fit for the susceptibility data gives $a = 11.6 \pm 0.1, b = 1.53 \pm 0.04$ K$^{-1}, c = 15.7 \pm 4.0$, and $d = 0.71 \pm 0.05$ K$^{-1}$. The value of $c$ gives a magnitude for the moment of the first excited doublet of $5.9 \pm 0.8 \mu_B$. These results are consistent with our crystal-field results. In particular, from the $J^x$ components of our calculated low-energy doublet and singlet eigenstates, there will be predominant contributions to $b$ and $d$ coming from transverse angular momentum matrix elements connecting the two doublets, as well as additional contributions involving transverse matrix elements between the doublets and the higher energy singlet.
states at \(\approx 100\) K. The doublet-doublet coupling will give equal (in magnitude) contributions to \(b\) and \(d\) while coupling to the singlets will give further positive contributions to \(b\) while reducing the value of \(d\). This can be simply understood in terms of the signs of the denominators for each of these virtual excitation processes in our definitions of \(b\) and \(d\).

In summary, we are able to successfully fit the \((\text{Th}_{0.02}\text{Y}_{0.98})\text{Ti}_2\text{O}_7\) susceptibility measurements at low temperature using a doublet-doublet picture consistent with our crystal-field calculations. We find reasonable agreement in terms of calculated moments and paramagnetic contributions between that expected from theory and our fitted values. In particular, we find a permanent moment in the ground state of approximately 5.1\(\mu_B\). This moment is intrinsic to the \(\text{Tb}^{3+}\) ion and is not driven by exchange and/or dipolar interactions as occurs in \(\text{LiTbF}_4\). This value is also compatible to the singlets will give further positive contributions to \(d\) in terms of the signs of the denominators for each of these interactions.

To what is estimated from the limiting low-temperature muon spin-relaxation rate \(1/T_1\) found in Ref. 37, assuming a dipole coupling between a positive muon \(\mu^+\) bounded to an oxygen at \(\approx 2.5\) Å away from a \(\approx 5\mu_B\) \(\text{Tb}^{3+}\) moment (see Appendix C).

IV. DISCUSSION

Combining together our results from dc susceptibility measurements, specific-heat data, inelastic neutron-scattering data, and crystal-field calculations, the following picture emerges:

- The \(\text{Tb}^{3+}\) ion in \(\text{Th}_2\text{Ti}_2\text{O}_7\) carries a permanent magnetic moment of approximately 5\(\mu_B\). That moment is intrinsic to the \(\text{Tb}^{3+}\) ion and is not driven by magnetic correlation from exchange and/or dipolar interactions.

- The ground state is well described as an Ising doublet with extremely anisotropic \(g\) tensor. In other words, the moments in the single-ion ground state are predominantly confined to point along the (111) directions.

- The first excited state is at an energy of approximately 15–20 K above the ground state, which is also characterized by a very anisotropic Ising-like \(g\) tensor.

- Consequently, in the absence of interactions, the \(\text{Tb}^{3+}\) ions should be very well modeled below \(T \leq O(10^3)\) K by effective classical Ising spins confined to point along the local (111) directions.

From dc susceptibility measurements at high temperature, we know that the magnetic interactions are predominantly antiferromagnetic, with \(J_{\text{exchange}} \approx -13\) K. Although the interactions are not small compared to the first excitation energy gap of 18 K, let us momentarily ignore the exchange coupling between the ground state and the excited doublet, and consider only the Ising-like ground-state doublet. We then have a classical model with effective Ising spins pointing along their local (111) directions. In other words, spins that can only point either inward or outward on a tetrahedron.

Because of the open structure of the pyrochlore lattice, we expect that the nearest-neighbor exchange interactions predominate. If we make the further approximation that only nearest neighbors contribute to the antiferromagnetic interactions, we arrive at a scenario where \(\text{Th}_2\text{Ti}_2\text{O}_7\) is effectively described by classical Ising spins pointing along the (111) directions and coupled via nearest-neighbor antiferromagnetic exchange. As discussed in Refs. 32, 52, and 53, such a model is not frustrated. Indeed, if we pick one spin, and choose either an “in” or “out” orientation for it, then the three other spins on the same tetrahedron must also take the same in or out configuration to minimize the exchange interactions.

The observation that \(\text{Tb}_2\text{Ti}_2\text{O}_7\) remains paramagnetic down to at least 70 mK, while sustaining important short-range magnetic correlations, is therefore very puzzling. We believe that a plausible explanation is that the exchange interactions in \(\text{Tb}_2\text{Ti}_2\text{O}_7\) involve those at distances beyond further nearest neighbor \(J_{nn}\). The presence of these interactions, as well as the long-range dipolar interactions, could “reintroduce” sufficiently large frustration in the spin Hamiltonian describing \(\text{Tb}_2\text{Ti}_2\text{O}_7\), and conspire to destroy the “would-be” long-range Neél order.

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V. CONCLUSION

In conclusion, we have presented results from dc susceptibility, specific-heat, inelastic neutron-scattering, and crystal-field calculations for the pyrochlore lattice antiferromagnet \(\text{Tb}_2\text{Ti}_2\text{O}_7\). We have obtained strong evidence that the \(\text{Tb}^{3+}\) magnetic moment on the 16\(d\) site at \(T < 2\) K is intrinsic and is not induced by magnetic (exchange and/or dipolar) interactions or correlation effects such as found in \(\text{LiTbF}_4\) and is of the order of 5\(\mu_B\). All evidence points towards a very strong Ising-like anisotropy for the doublet ground state which forces the resulting classical \(\text{Tb}^{3+}\) Ising moments to point either parallel or antiparallel to their local (111) direction. For antiferromagnetic exchange interactions, such strong anisotropy largely removes all local ground-state spin degeneracy, and should naïvely force the system to possess an Ising-like long-range-order ground state with all
spins in or out on a tetrahedron basis cell. The reason for the failure of Tb$_2$Ti$_2$O$_7$ to order at a temperature $\sim 10^4$–$10^5$ K set by the exchange part of the Curie-Weiss temperature remains unresolved at this time. The results presented here point towards the need to consider the role that exchange interactions beyond nearest-neighbor and dipolar interactions play in Tb$_2$Ti$_2$O$_7$.

We have recently become aware of two publications which report evidence for single ion anisotropy for the Tb$^{3+}$ ion in Tb$_2$Ti$_2$O$_7$. Rosenkranz et al.$^{77}$ have found by rescaling appropriately the set of crystal field parameters deduced for Ho$^{3+}$ in Ho$_2$Ti$_2$O$_7$, that Tb$^{3+}$ shows Ising-like anisotropy with a doublet-doublet gap of $\sim 10$ K, in general agreement with the conclusions of this work. Kanada et al.$^{78}$ using inelastic neutron scattering measurements, have also detected a finite single-ion anisotropy energy.

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APPENDIX A: DIPOLE CONTRIBUTIONS TO $\theta_{CW}$

The contribution from dipolar interactions to $\theta_{CW}$ may be determined from a high-temperature series expansion of the long-range dipole-dipole Hamiltonian to first order in $\beta$. That is to say, given the additive property of crystal-field effects, exchange, and dipolar interactions to $\theta_{CW}$, i.e., $\theta_{CW} = \theta_{CW}^{iso} + \theta_{CW}^{el} + \theta_{CW}^{dip}$, we may determine $\theta_{CW}^{dip}$ from an expansion of

$$\chi = \frac{g^2 \mu_B^2 N J (J+1)}{3 k T} \left( 1 - \frac{g^2 \mu_B^2 J (J+1)}{3 N k T} \Lambda \right),$$

and consequently that

$$\theta_{CW}^{dip} = - \frac{g^2 \mu_B^2 J (J+1)}{3 N k} \Lambda,$$  \hspace{1cm} (A1)

where

$$\Lambda = \sum_{ij} \frac{1}{|r_{ij}|^3} \frac{3 |r_{ij}|^2}{|r_{ij}|^5}.$$  \hspace{1cm} (A2)

We see from the above analysis that the evaluation of $\theta_{CW}^{dip}$ involves the summation of a conditionally convergent series (a lattice sum), and thus special care must be taken in its evaluation. In general, it can be treated in a controlled manner by the use of a rapid convergence factor via the Ewald method.$^{55,56}$ Within the Ewald approach, the sum is split into two rapidly converging sums, one over the real-space lattice and one in reciprocal space. Additionally, a surface (shape dependent) term also arises (which is interpreted as a demagnetization factor$^{56,57}$).

Indeed, if we approximate the powder grains of the (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ as spherical, then the sum, Eq. (A2) is identically zero. This can be understood by imagining Eq. (A2) as a sum over parallel (along the $z$ axis) dipoles moments of magnitude unity. For a spherical object, it can be shown that such a sum must be identically zero for a system with cubic symmetry.$^{58,59}$ Accordingly, there would be no dipolar contribution to the measured value of $\theta_{CW}$. On the other hand, we do not expect that the geometry of the powder grains is, in fact, spherical (additionally, there is also the possibility of effects from intergranular interactions). Therefore to gain an estimate on the upper bound of the dipolar contribution, we carry out the lattice sum Eq. (A2) for an infinitely long cylinder (needle shape) along the $z$ direction where surface effects are zero. This allows us to gain an approximate upper bound on the dipolar contribution as there are effectively no demagnetization effects. This calculation can be carried out rather simply by noting that for a spherical sample, Eq. (A2), can be written using the Ewald method as$^{58}$

$$\Lambda_{sphere} = \Lambda^{bulk} + \Lambda^{surface}$$  \hspace{1cm} (A3)

where

$$\Lambda^{bulk} = \frac{M}{L^3} \sum_{r_{ij}} \sum_n \left[ \frac{\alpha H(n|\mathbf{R}_{ij}(n)|) + (2\alpha/\sqrt{\pi}) e^{-\alpha^2|\mathbf{R}_{ij}(n)|^2}}{|\mathbf{R}_{ij}(n)|^2} - \frac{3\alpha|\mathbf{R}_{ij}(n)|^2 H(n|\mathbf{R}_{ij}(n)|) e^{-\alpha^2|\mathbf{R}_{ij}(n)|^2}}{|\mathbf{R}_{ij}(n)|^4} \right]$$

$$- \sum_n \frac{(2\alpha/\sqrt{\pi})|\mathbf{R}_{ij}^2(n)|^2 (3 + 2\alpha^2|\mathbf{R}_{ij}(n)|^2) e^{-\alpha^2|\mathbf{R}_{ij}(n)|^2}}{|\mathbf{R}_{ij}(n)|^4} + \sum_{n=0} \frac{4\pi n^2 |\mathbf{n}|^2 e^{-\alpha^2|\mathbf{n}|^2/\alpha^2} e^{2\pi n r_{ij}/L}}{|\mathbf{R}_{ij}(n)|^4}. \hspace{1cm} (A4)$$
The $\mathbf{R}_i(n) = r_i/L + n_i, i,j$ label the dipole (Ts$^{3+}$) sites within the cubic unit cell, $L$ is the length of the conventional cubic cell for Tb$_2$Ti$_2$O$_7$, and $M$ is the number of cells in the sample. The function $H(\gamma) = (2\gamma \sqrt{\pi}) f^n \phi^n e^{-y^2} dx$ while $n = (k,l,m)$ such that $k,l,m$ are integers and $\alpha$ is suitably chosen to rapid convergence of the summations over $n$. Based on the previously mentioned result that $\Lambda_{sphere}$ should vanish for a spherical sample, this implies that the first four terms in the above expression, $\Lambda^{bulk}$, must sum to the opposite value of the last term ($\Lambda^{surface}$, the surface term), and indeed we have verified that this is the case numerically. For an infinitely cylindrical sample, the surface term, $\Lambda^{surface}_{cylinder} = 0$, and thus one finds

$$\Lambda^{cylinder}_{cylinder} = \Lambda^{bulk} + \Lambda^{surface}_{cylinder} = \Lambda^{bulk} = \frac{M}{L^3} \sum_{i \neq j} \frac{4\pi}{3}$$

$$= -\frac{M}{L^3} \frac{4\pi}{3} (16 \times 15) \sim -105 \frac{M}{L^3}. \quad (A6)$$

On the other hand, for a slab geometry, we have

$$\Lambda_{slab} = \Lambda^{bulk} + \Lambda^{surface}_{slab} \quad (A7)$$

where

$$\Lambda^{surface}_{slab} = \frac{M}{L^3} \sum_{i \neq j} \frac{4\pi}{3},$$

thus arriving at

$$\Lambda_{slab} = \frac{M}{L^3} \sum_{i \neq j} \frac{8\pi}{3}. \quad (A8)$$

Combining Eqs. (A1), (A6), and (A8), and using a cubic cell length of $L \sim 10.104$ Å, we arrive at upper and lower bounds for dipolar contributions to the Curie-Weiss temperature, namely, $-2.4 \leq \theta^{slab}_{CW} \leq +1.2$ K.

**APPENDIX B: CRYSTAL-FIELD CALCULATIONS**

Our aim in this appendix is to pursue in further details using a more sophisticated (ab initio) approach the calculations of the magnetic susceptibilities of Tb$_2$Ti$_2$O$_7$ and (Ts$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$. To do so, we need to determine the electronic structure of the ground $^7F_6$ level of the Tb$^{3+}$ ($4f^8$ configuration) in these two compounds, deduce the wave functions and from there infer the value of the magnetic moment of the ground-state level. The determination of the $4f^8$ electronic configuration is obtained by diagonalizing the following Hamiltonian for a generic $f^n$ configuration without making the fixed $J$ manifold approximation used in Sec. III A:

$$H(f^n) = \sum_k F^k(f) f^k + \zeta(f) A_{so} + \alpha J(L+1) + \beta G(G2) + \gamma G(R7) + \sum_{kq} B^k_q C^k_q. \quad (B1)$$

Let us explain first what are the different terms in $H(f^n)$:

- The $F^k$’s $(k = 2, 4, 6)$ are the electrostatic integrals (Slater’s parameters) which split the $4f^n$ configurations into terms $2S + 1L$, where $S$ is the total spin and $L$ is the total orbital angular momentum. The $f^k$’s are the associated two-electron operators.\(^{61}\)

- $\zeta(f)$ is the spin-orbit interaction integral which splits the terms into $2S + 1L$ levels. $A_{so}$ is the associated one-electron spin-orbit operator.\(^{61}\)

- $\alpha$, $\beta$, and $\gamma$ are parameters associated with effective two-body correction terms for interconfiguration interaction.\(^{52}\) $G(G2)$ and $G(R7)$ are the Casimir’s operators for groups $G2$ and $R7$. When $2 < n < 12$, there can be several terms $2S + 1L$ with the same $S$ and $L$ values in the $f^n$ configuration. For instance there are three $5G$ terms in $4f^8$ while there exists only one term $7F$. The states may differ by the way they are built from the parent configuration $f^{n-1}$. An additional classification of the states is therefore necessary. It is done according to the irreducible representations of the groups $G2$ and $R7$ and bestows additional quantum numbers to the states.

- The $B^k_q$ are the coefficients of the one-electron crystal-field interaction which acts between $|2S + 1L_{J}M_J\rangle$ sublevels. They can be theoretically predicted or extracted from fits of the energy levels from experiments. In the point-charge electrostatic model, their expression is

$$B^k_q = (4 \pi/2k + 1)^{1/2} \langle r^k \rangle \sum_{i} (Q_{i}/R_{i}^{k+1}) Y_{k}^{i*} (\theta_{i}, \phi_{i}),$$

where $\langle r^k \rangle$ is a 4f electron radial integral, $Q_{i}$ is the point charge of ligand $j$, and $R_{i}$, $\theta_{i}$, and $\phi_{i}$, are the polar coordinates of ligand $j$. The derivation of the $B^k_q$ for the covalent interactions is more involved.\(^{63}\) The $C^k_q = (4 \pi/2k + 1)^{1/2} Y_{k}^{q*}$, are the tensorial one-electron crystal-field operators.

The evaluation of the matrix elements of (i) the electrostatic interaction, (ii) the spin-orbit interaction, (iii) the free-ion configuration interaction, and (iv) the crystal-field interaction, between the states of the basis set chosen for the $f^n$ configurations is necessary in order to determine the eigenvalues and eigenvectors of the latter. The matrix elements are calculated by the means of tensorial algebra.\(^{61}\) Besides, if coupled $|2S + 1L_{J}M_J\rangle$ states are chosen as the basis set, the one- or two-electron operators which are involved in the Hamiltonian cannot act directly on them. The calculation requires intermediate mathematical quantities known as reduced matrix elements which are tabulated for standard $f^n$ configurations.\(^{64}\) Once evaluated, the complete matrix elements are multiplied by the associated parameters before diagonalization. The parameters are then determined by trial and error by successive diagonalizations and comparison of the eigenvalues with experimental energy levels. In the present case our main concern is the structure of the Tb$^{3+}$ ground level, so that the only specific material dependent parameters which have to be determined before diagonaliz-
ing $H(f^\sigma)$ are the $B^6_\sigma$ crystal-field interaction parameters. As already mentioned, the most convenient way to deduce the electronic structure of a rare-earth ion in a solid compound, and hence determine the crystal-field parameters, is usually via analysis of its electronic spectrum by fitting the $B^6_\sigma$ to match the frequency of the observed transitions. The strongest lines are due to electronic transitions partly allowed by the mixing of the ground-state configuration with opposite parity configurations (Judd-Ofelt mechanism).\cite{55,66} However, in the case of pyrochlores, the site symmetry at the rare-earth site is centrosymmetrical. The odd parity crystal-field parameters vanish, the mixing of opposite parity configurations is impossible, hence no electric dipole transitions are detectable in the spectrum. Indeed, only the weak $^7F_1 \rightarrow ^5D_0$ and $^7F_0 \rightarrow ^7D_0$ magnetic dipole transitions were observed previously in the absorption spectra of the pyrochlore compounds Eu$_2$Ti$_2$O$_7$ and Eu$_2$Sn$_2$O$_7$.\cite{66} Hence a complete set of ‘phenomenological’ crystal-field parameters (CFP) cannot be determined from optical absorption or emission spectra. However, recent inelastic neutron-scattering experiments have been able to give information on the lowest electronic levels of Ho$_2$Ti$_2$O$_7$.\cite{27} From these neutron results, some CFP’s can be deduced. CFP’s can also be calculated \textit{ab initio} from the compound structure and the atomic data of the constituents. Therefore, in what follows, two different approaches (discussed in paragraphs IA and IB) have been used to determine the CFP’s of Tb$_2$Ti$_2$O$_7$ and (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$.

IA A full \textit{ab initio} calculation of the CFP’s utilizing the structural data of the compounds.

IB The fit of the CFP’s from the Ho$_2$Ti$_2$O$_7$ (Ref.~27) and Eu$_2$Ti$_2$O$_7$ (Ref.~67) data and a transposition to the Tb$_2$Ti$_2$O$_7$ and (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ compounds.

The next two steps for the calculations of the magnetic susceptibility are

II The calculation of the $4f^8$ electronic configuration utilizing plausible free ion parameters, and the fitted or calculated \textit{ab initio} values of the CFP’s.

III The calculation of the magnetic susceptibility of Tb$_2$Ti$_2$O$_7$ and (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ utilizing the wave functions derived from the previous step II.

These steps are detailed in the following:

\begin{itemize}
  \item IA \textit{Ab initio} calculation of the CFP’s.
  \item An \textit{ab initio} determination of the CFP’s is obtained by adding an electrostatic and a covalent contribution along lines similar to the ones developed in Refs. 63 and 68 for oxygen ligands. The crystal structure, the ionic charges, and the ionization energies of the ligands are used. In Ref.~69, experimental and predicted values of the parameters calculated by the ‘‘covaloelectrostatic’’ model were compared for ten compounds. The mean deviation between experimental and calculated values is

$$
\Delta B^k/B^k = \left[ 1 + 1/(S^k)^2 - 2 \cos(R^k)/S^k \right]^{1/2},
$$

where $S^k$ and $R^k$ are the scale and reliability factors listed in Table 7 of Ref.~69. $\Delta B^k/B^k$ is found to be equal to 52, 30, and 23% for $k = 2$, $k = 4$, and $k = 6$, respectively. Such is the uncertainty which can be expected from a ‘‘blind eyed’’ prediction of the CFP’s of Tb$_2$Ti$_2$O$_7$.

As mentioned earlier, the space group of rare-earth titanates with the pyrochlore structure is $Fd\bar{3}m$. The eight oxygen first neighbors form a distorted cubic polyhedron. Two oxygens occupy ideal positions on opposite summits of the cubic threefold axis. The three sides of the cube originating from each of these two summits are equally elongated. The $a$ cubic lattice parameter is equal to 10.15 and 10.09 Å, and $x$ the positional parameter for the six displaced oxygens to 0.3 and 0.2968 for the dense and dilute compound, respectively.\cite{43}

The site symmetry at the rare-earth site is reduced from $O_h$ (cubic) to $D_{3d}$. The remaining threefold order symmetry axis imposes for the crystal-field parameters the condition $q = 0$, modulo 3, so that the nonzero even $k$ CFP’s are $B^6_0$, $B^4_0$, $B^4_3$, $B^6_0$, $B^6_3$, and $B^6_6$. The predicted CFP values are re-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
 & $B^2_0$ & $B^4_0$ & $B^4_3$ & $B^6_0$ & $B^6_3$ & $B^6_6$ \\
\hline
Tb$_2$Ti$_2$O$_7$ & 471 & 708 & $-187$ & 610 & 1599 & $-227$ & 1261 & 314 & 482 \\
\hline
 & PCEM & Cov. & & & & & & & \\
\hline
Total & 1081 & 2307 & $-414$ & 1261 & 314 & 482 \\
\hline
(Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ & 407 & 731 & $-210$ & 609 & 1711 & $-288$ & 1324 & 389 & 571 \\
\hline
 & PCEM & Cov. & & & & & & & \\
\hline
Total & 1016 & 2442 & $-498$ & 1324 & 389 & 571 \\
\hline
Experimental & 622$^a$ & 3691$^b$ & $-1698^b$ & 1731$^b$ & 1665$^b$ & 784$^b$ \\
\hline
\end{tabular}
\caption{Empirical CFP’s deduced by the covaloelectrostatic model for Tb$_2$Ti$_2$O$_7$ and (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$. The latter are obtained using two approaches. All values are in K. (PCEM = point-charge electrostatic model.)
\footnote{Value of $B^6_0$ obtained by transposing to Tb$^{3+}$. Value of $B^6_0$ determined from spectroscopic data of Eu$_2$Ti$_2$O$_7$.}
\footnote{Values $B^k_{q\neq4}$ obtained by transposing to Tb$^{3+}$. Value of $B^k_{q\neq4}$ determined from inelastic neutron data on Ho$_2$Ti$_2$O$_7$.}}
\end{table}
TABLE II. Lowest energy levels (in K), irreducible representations in (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ and Tb$_2$Ti$_2$O$_7$, and leading compositions of the corresponding eigenvectors. Lines labeled (a) and (b) are for the predicted projections for the dilute (Tb$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ and dense Tb$_2$Ti$_2$O$_7$, respectively, using the CFP’s listed in Table I. Lines labeled (c) are for the predicted projections for the dense Tb$_2$Ti$_2$O$_7$ using the experimental CFP’s listed in the last line of Table I.

<table>
<thead>
<tr>
<th>(E)</th>
<th>En</th>
<th>$7F_{6} - +/ -4$</th>
<th>$7F_{6} - +/ +4$</th>
<th>$7G_{6}(1) - +/ +4$</th>
<th>$7G_{6}(3) - +/ +4$</th>
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</thead>
<tbody>
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<td>(a)</td>
<td>0</td>
<td>$-0.97$</td>
<td>$+/-0.05$</td>
<td>$-/+0.06$</td>
<td>$+0.15$</td>
</tr>
<tr>
<td>(b)</td>
<td>0</td>
<td>$-0.97$</td>
<td>$+/-0.05$</td>
<td>$-/+0.06$</td>
<td>$+0.15$</td>
</tr>
<tr>
<td>(c)</td>
<td>0</td>
<td>$-0.95$</td>
<td>$+/-0.05$</td>
<td>$-/+0.06$</td>
<td>$+0.14$</td>
</tr>
</tbody>
</table>

ported in Table I. The distances between the Tb$^{3+}$ ion and the oxygens on the threefold axis is short (2.20 and 2.18 Å for the dense and the dilute compound, respectively) while the distances to the six peripheral oxygens are much larger (2.52 and 2.49 Å, respectively). This explains why the “axial” $B_{q}^{0}$ parameters are much larger than the “azimuthal” $B_{q}^{1}$’s.

(IB) Experimental determination of the CFP’s.

The CFP’s can be determined by fitting the energy levels of the $f^{n}$ configuration either using spectroscopic or inelastic neutron-scattering data from other pyrochlore compounds. Here, we can use the $B_{v}^{0}$ from spectroscopic data on Eu$_2$Ti$_2$O$_7$ (Ref. 67) and the other $B_{q}^{0}$ from neutron-scattering data on Ho$_2$Ti$_2$O$_7$.28

- Determination of $B_{v}^{0}$ from spectroscopic data on Eu$_2$Ti$_2$O$_7$.

The $7^{2}F_{1} - 5D_{0}$ and $7^{2}F_{0} - 5D_{1}$ magnetic dipole transitions were observed previously in the electronic absorption spectrum of Eu$_2$Ti$_2$O$_7$.67 In the latter, the $7^{2}F_{1}$ and $5^{2}D_{1}$ splittings amount to 291 and 51.9 K, respectively. A fit in 4$^{f^{6}}$ (Eu$^{3+}$) yields $B_{v}^{0}$ = 684 K. The transposition to Tb$^{3+}$ is made assuming the crystal-field parameter is scaled by the ratio of radial integrals: $B_{v}^{0}(\text{Tb}^{3+}) = B_{v}^{0}(\text{Eu}^{3+}) \times \langle r^{2} \rangle(\text{Tb}^{3+}) \langle r^{2} \rangle(\text{Eu}^{3+}) \times 0.91 = 622$ K. This “experimental” value, listed in Table I, and referred to as (a), has the same sign, but it is about half of the predicted value. As pointed out above, the uncertainty on the calculated $k=2$ parameters is large.

- CFP determination in Ho$_2$Ti$_2$O$_7$.

Siddharthan et al.28 recently reported results from inelastic neutron scattering at low temperature on Ho$_2$Ti$_2$O$_7$. They determined the six lowest $E$ irreducible representations of the $5I_{6}$ ground-state level. Utilizing their experimental values, we fitted the CFP’s of Ho$^{3+}$ while maintaining the ratio between CFP’s with the same $k$ value close to the theoretical ratio. The program ATOME was used for the refinement.70 In this program, the basis set is composed of Slater determinants which makes unnecessary the use of tables of reduced matrix elements.64 The evaluation of the matrix elements is straightforward, but the configuration cannot be truncated. Indeed, each eigenvector being a linear combination of a large number of Slater determinants, none of the latter can be computed. As a consequence, all the 1001 states of 4$^{f^{10}}$ configuration are included in the diagonalization matrix. The basis is large (1001) but still tractable. The final mean deviation between experimental and calculated levels was equal to 7.8 K. The fitted CFP’s are: $B_{v}^{0} = 3173$ K, $B_{q}^{0} = -1459$ K, $B_{q}^{0} = 1343$ K, $B_{q}^{0} = 1292$ K, and $B_{q}^{0} = 609$ K. As pointed out above, the CFP’s were then scaled according to the ratio between the radial integrals of Ho$^{3+}$ and Tb$^{3+}$ to give the experimental CFP’s for Tb$_2$Ti$_2$O$_7$. Namely, $B_{v}^{0}(\text{Tb}^{3+}) = B_{v}^{0}(\text{Ho}^{3+}) \times (\langle r^{2} \rangle(\text{Tb}^{3+}) / \langle r^{2} \rangle(\text{Ho}^{3+}))$. These “experimental” values are as listed in Table I, and referred to as (b). The experimental $k=4$ and $k=6$ CFP’s are 1.7 and 1.9 times larger than the theoretical values which is somewhat unusual.

(II) Calculation of 4$^{f^{6}}$ electronic configuration.

The calculation of the 4$^{f^{6}}$ electronic configuration is done by the means of program $^{\text{F}}$ (Ref. 71) utilizing the Hamiltonian $H(f^{n})$ in Eq. (B1) acting on coupled states $2^{5+1}L_{J}$. Contrary to program ATOME previously mentioned, program $^{\text{F}}$ can work on a truncated basis, which is necessary to resolve the 4$^{f^{6}}$ configuration of Tb$^{3+}$ with a large number of states (3003 states). The interaction matrix is built on a 387 $\times$ 387 basis set comprising the following $2^{5+1}L$ terms of the Tb$^{3+}(4f^{6})$ configuration: $7F$, $5D (1,2,3)$, $5F (1,2)$.
$^5G(1,2,3)$, $^3P(1,2,3,4,5,6)$, and $^1S(1,2,3,4)$. The conjugate configuration of $^{2}E_3^+$ is that of $^{4}I_{15/2}$ with $4I + 2 - 8 = 6$ electrons. The $^{4}I^{n}$ ($n = 6$) configuration of $^{4}I^{15/2}$ contains exactly the same number of basis states (e.g., $[4I + 2 - n]/[n!]) = 3003$ states) as $^{2}E_3^+$, the same terms, and the same levels. The interactions involving an odd number of electrons have a reverse sign in $^{4}I^{n}$ and $^{4}I^{o}$. For instance the $^{25+1}L_J$ levels appear in a reverse order, and so do the crystal-field sublevels. In addition, the terms determined by the electrostatic interaction (two electron interaction) appear up in the same order for $^{4}I^{15/2}$ and $^{2}E_3^+$.

For $^{4}I^{15/2}$ the above quoted basis had proved large enough to allow a simulation of the levels up to $^{2}D_2$ ($30,219$ K) without drastic truncation effects.$^{72}$ The $F^k$’s were assigned the $Gd^{15/2}$ values given in Ref. 73, that is $147,289$, $102,479$, and $55,868$ K for $k = 2$, $4$, and $6$, respectively. $\alpha$, $\beta$, $\gamma$ were ascribed the Nd$^{15/2}$ values fitted in Ref. 74, that is, $30.98$ K, $-1005.03$ and $2510.48$ K, respectively. The spin-orbit coupling constant $\zeta(f)$ was set equal to $2446.30$ K which is a standard value for $^{2}E_3^+$. $^{75}$ $B^c_\ell$ was assigned the transposed value quoted hereabove, and the other CFP’s the values listed in Table I obtained after rescaling the $B^c_\ell$ extracted from fits to the levels of $Ho^{15/2}$. The diagonalization of the interaction matrix gives the energy levels and the corresponding leading eigenvectors listed in Table II. The lowest levels are two doublets. Both states are rather Ising-like, with nearly exclusive ($-0.95$) $M_J = \pm 4$ and $M_J = \pm 5$ components. This is caused by the very “axial” crystal-field parameters. In other words, the $M_J = \pm 4$ and $M_J = \pm 5$ carry, respectively, about $90\%$ of the weight of the ground-state and first excited-state doublet wave functions.

(III) Calculation of the magnetic susceptibility of $Tb_2Ti_2O_7$ and $(Tb_{0.02}Y_{0.98})_2Ti_2O_7$.

The magnetic susceptibility is by van Vleck’s formula,$^{76,51}$ using the eigenvectors determined in the previous step,

$$\chi = \frac{N\mu_B^2}{\sum_i e^{-\epsilon_i^{(0)}/k_B T}} \left[ \sum_i \left( \frac{\epsilon_i^{(1)}}{k_B T} - 2 \epsilon_i^{(2)} \right) e^{-\epsilon_i^{(0)}/k_B T} \right],$$

where $N$ is the number of moles of $^{2}E_3^+$, $\mu_B$ is the Bohr magneton, $k_B$ is the Boltzmann constant, $E_i^{(0)}$ is the energy of the $i$th level. Besides,

$$\epsilon_i^{(1)} = \langle \psi_i | \vec{L} + 2\vec{S} | \psi_i \rangle,$$

$$\epsilon_i^{(2)} = \sum_{j \neq i} \left( \frac{\langle \psi_i | \vec{L} + 2\vec{S} | \psi_j \rangle^2}{E_i^{(0)} - E_j^{(0)}} \right).$$

The results as a function of the temperature are given in Table III. The values for $\langle \mu(T) \rangle$ are very similar for the $Tb_2Ti_2O_7$ and $(Tb_{0.02}Y_{0.98})_2Ti_2O_7$ compounds. Therefore any large experimentally stated difference between the two compounds at low temperature cannot be accounted for by a difference in the individual characteristics of $^{2}E_3^+$ in the dense $Tb_2Ti_2O_7$ and the dilute $(Tb_{0.02}Y_{0.98})_2Ti_2O_7$.

**APPENDIX C: MAGNETIC MOMENT IN $Tb_2Ti_2O_7$ ESTIMATED FROM MUON SPIN RELAXATION**

In Ref. 37 a temperature-independent muon spin-lattice relaxation rate $1/T_1$ of approximately 2 MHz was observed between 70 mK and 1 K for $Tb_2Ti_2O_7$. Usually, a temperature-independent muon spin lattice relaxation rate is a measure of the magnetic spin-fluctuation rate, $1/\tau$ where $\tau$ is the mean-correlation time for spin fluctuations. In the fast fluctuation limit, the spin-lattice relaxation rate is

$$1/T_1 = \Delta^2/\tau,$$

where $\Delta^2/\tau = \langle H_{\text{int}} \rangle$. Here $\langle H_{\text{int}} \rangle$ is the second moment of the local internal magnetic field experienced by the muon, and $\gamma_\mu$ is the muon gyromagnetic ratio, $\gamma_\mu/(2 \pi) = 135.5$ MHz. The mean-correlation time for spin fluctuations can be described by an effective Tb-Tb magnetic spin interactions $J_{\text{int}}$, with $\tau \sim 1/J_{\text{int}}$. Assuming that the muon $\mu$ is located at a nearby oxygen site of a $^{2}E_3^+$ moment, that is at a distance, $r_{\text{TB}-\mu}$ of about 2.5 Å, and that the muon is coupled via magnetic dipole interactions to the $\approx 5\mu_B$ $^{2}E_3^+$ moment, we get for $H_{\text{loc}}$

$$H_{\text{loc}} \approx \frac{\mu_0}{4\pi} \frac{\mu_{TB}}{r_{\text{TB}-\mu}^3} \sim 1.5 \text{ T.}$$

Using $J_{\text{int}} \sim O(10^0)$ K, an effective low-temperature exchange/dipole energy scale suggested by the magnetic specific-heat and inelastic neutron-scattering data, we obtain $1/T_1 \sim 1 - 10$ MHz, which is the correct order of magnitude of $1/T_1$ found experimentally. Thus we conclude that a magnetic moment of $\approx 5\mu_B$ is consistent with the temperature-independent muon spin-lattice relaxation measured in $Tb_2Ti_2O_7$ below 2 K.$^{37}$

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$^1$Present address: Department of Physics, The Ohio State University, Columbus, Ohio, 43210-1106.


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<th>$T$ (K)</th>
<th>$\langle \mu \rangle$ (mole/emu)</th>
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<tr>
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<td>5.8</td>
<td>0.11</td>
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<tr>
<td>5</td>
<td>6.84</td>
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<tr>
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<td>3.48</td>
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<tr>
<td>15</td>
<td>7.97</td>
<td>4.73</td>
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<tr>
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<tr>
<td>300</td>
<td>9.22</td>
<td>706</td>
<td>14.09</td>
</tr>
</tbody>
</table>


Strictly speaking, ZnFe$_2$O$_4$ and ZnCr$_2$O$_4$ are


Strictly speaking, ZnFe$_2$O$_4$ and ZnCr$_2$O$_4$ are $B$-site spinels with no, or little, inversion. However, the magnetic lattice of the $B$-site spinel is identical to the lattice of corner-sharing tetrahedra in pyrochlores (Ref. 6).


In Ref. 28, Siddharthan *et al.* argued that the nearest-neighbor interaction is antiferromagnetic in Ho$_2$Ti$_2$O$_7$. This possibility is also discussed in two other recent papers (Refs. 30 and 31). In Ref. 28, Siddharthan *et al.* also considered the role of dipolar effects in Ising pyrochlores. However, in their work, the dipole-dipole interaction was truncated beyond five nearest-neighbor distances, and a sharp transition between paramagnetism and a partially ordered phase (where rapid freezing occurs) was observed for interaction parameters believed appropriate for Ho$_2$Ti$_2$O$_7$. From their simulation results, they argue that the Ho$_2$Ti$_2$O$_7$ material is not a spin ice, but shows partial ordering. However, it was recently argued that there is no experimental evidence for partial freezing in Ho$_2$Ti$_2$O$_7$ down to 50 mK (Ref. 30). As well, there is numerical evidence that the truncation of dipole-dipole interactions can be misleading, and introduce spurious features in various thermodynamic properties and, in particular, gives rise to a transition to a partially ordered phase (Ref. 30).


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