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FAST TRACK COMMUNICATION

Proposal for a [111] magnetization plateau in the spin liquid state of $Tb_2Ti_2O_7$

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Abstract

Despite a Curie–Weiss temperature $\theta_{CW} \sim -14$ K, the $Tb_2Ti_2O_7$ pyrochlore magnetic material lacks long range magnetic order down to at least $T^* \approx 50$ mK. It has recently been proposed that the low temperature collective paramagnetic or spin liquid regime of this material may be akin to a spin ice state subject to both thermal and quantum fluctuations—a *quantum spin ice* (QSI) of sorts. Here we explore the effect of a magnetic field $\boldsymbol{B}$ along the [111] direction on the QSI state. To do so, we investigate the magnetic properties of a microscopic model of $Tb_2Ti_2O_7$ in an independent tetrahedron approximation in a finite field $\boldsymbol{B}$ along [111]. Such a model describes semi-quantitatively the collective paramagnetic regime where nontrivial spin correlations start to develop at the shortest length scale, that is over a single tetrahedron, but where no long range order is yet present. Our results show that a magnetization plateau develops at low temperatures as the system develops $\boldsymbol{B} = 0$ ferromagnetic spin ice like 'two-in/two-out' correlations at the shortest length scale. From these results, we are led to propose that the observation of such a [111] magnetization plateau in $Tb_2Ti_2O_7$ would provide compelling evidence for a QSI at $\boldsymbol{B} = 0$ in this material and help guide the development of a theory for the origin of its spin liquid state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The spin liquid (SL) is the state of a magnetic system characterized by short range spin–spin correlations down to temperatures much lower than the Curie–Weiss temperature, θ_{CW}, which is set by the magnetic interactions. While the SL concept was originally proposed in 1973 in the context of a spin-1/2 Heisenberg antiferromagnet on a triangular lattice [1], it is only in recent years that its systematic experimental search in highly frustrated magnetic systems has really taken off [2]. A number of quasi-two-dimensional [3] and three-dimensional (3D) [4, 5] materials with SL behavior have been tentatively identified. Yet, the $Tb_2Ti_2O_7$ insulator is perhaps one of the 3D highly frustrated magnetic systems with SL behavior that has been attracting interest for the longest time [5]. In $Tb_2Ti_2O_7$, the magnetic Tb^{3+} ions reside on a pyrochlore lattice of corner-sharing tetrahedra. Despite $\theta_{CW} \approx -14$ K [6], $Tb_2Ti_2O_7$ does not develop conventional magnetic long range order down to at least $T^* = 50$ mK [5, 7–9].

It is unclear why $Tb_2Ti_2O_7$ fails to order [10]. It was originally thought that the Tb^{3+} magnetic moments could be described by classical Ising spins that can only point in or out of a given tetrahedron [6, 11], similar to the Ho^{3+} and Dy^{3+} moments in the $Ho_2Ti_2O_7$ [12] and $Dy_2Ti_2O_7$ [13] spin ice materials [14]. However, such an Ising model for $Tb_2Ti_2O_7$ predicts a transition to a four sublattice Néel ordered state at a temperature around 1 K [11], in dramatic disagreement with experiments [5, 8]. The microscopic justification for depicting the Tb^{3+} moments as Ising spins stems from considering only the single ion crystal field (CF) ground state doublet of Tb^{3+} and neglecting higher excited levels when describing the system at temperatures $T \lesssim 10$ K [6]. However, a

number of experimental [7, 9, 15] and theoretical [16, 17] results argue against such an Ising description. For example, an Ising model fails to explain, even at a qualitative level, the symmetry of the neutron scattering intensity pattern, $I(\boldsymbol{q})$, even in the paramagnetic phase [7, 16]. Interestingly, $I(\boldsymbol{q})$ remains largely unaltered from 4 K [7] down to 50 mK, never extending much beyond the size of a tetrahedron primitive basis [8]. One must therefore incorporate the excited CF states when constructing an effective low-energy Hamiltonian, $H_{\rm eff}$, describing $Tb_2Ti_2O_7$ at $T \lesssim 10$ K. The main reason for this necessity is that, unlike in spin ices [18], the exchange and dipolar interactions in $Tb_2Ti_2O_7$ are not much smaller than the energy gap $\Delta \approx 18$ K separating the ground and first excited CF doublets [6, 7, 19]. Also, when described as a classical $\langle 111 \rangle$ Ising model, $Tb_2Ti_2O_7$ is found to be close to the boundary between an 'all-in/all-out' four sublattice Néel ordered ground state and a spin ice state [6, 11]. Hence, perturbations, such as those introduced by virtual excitations to the excited crystal field states [20], can in principle give rise to new ground states, and these excitations must therefore be considered at the very outset.

A recent work [20] argued, on the basis of perturbation theory calculations that consider an independent tetrahedra approximation (ITA) to model the SL state of $Tb_2Ti_2O_7$, that exchange and magnetic dipole–dipole interactions induce significant admixing between the ground and excited CF states. Most importantly, this admixing renormalizes the Ising (longitudinal) part of $H_{\rm eff}$ from that of a non-frustrated $\langle 111 \rangle$ Ising antiferromagnet [21] to that of a frustrated $\langle 111 \rangle$ Ising ferromagnet, in essence turning the system into a spin ice [12, 14, 21, 22][3]. Interaction-induced admixing of the CF states also generates effective off-diagonal (transverse) spin–spin interactions in $H_{\rm eff}$ [20, 22]. As a result, $Tb_2Ti_2O_7$ may possibly be described by an effective frustrated $\langle 111 \rangle$ Ising ferromagnet model with additional quantum fluctuations transverse to the local $\langle 111 \rangle$ directions [22]. In other words, $Tb_2Ti_2O_7$ may be viewed in the temperature range (50 mK $\lesssim T \lesssim$ 10 K) as being in a thermally and quantum mechanically fluctuating spin ice state where frustrated ferromagnetic correlations in the $\langle 111 \rangle$ Ising components exist at the shortest length scale—a *quantum spin ice* (QSI) of sorts[4]. Hence, $Tb_2Ti_2O_7$ may constitute an exciting playground to explore quantum effects in a spin ice system with the QSI proposal providing a long awaited and useful theoretical perspective to rationalize $Tb_2Ti_2O_7$ [10]. The possibility of a QSI in $Tb_2Ti_2O_7$ is also of somewhat fundamental interest as it may relate to the topical problem of fractionalized spin excitations and emerging photon-like excitations in theoretical models of frustrated quantum Ising antiferromagnets on the pyrochlore lattice [24].

[3] The ground state of an isolated single tetrahedron [20] is an entangled quantum variant of the 6-fold degenerate 'two-in/two-out' classical ice-like spin configurations [12, 21].

[4] The $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ spin ice materials are well described by a model of classical Ising spins [14] (see also [23]). By quantum spin ice, we merely aim to emphasize that both thermal longitudinal spin fluctuations (that break the ice-rules) as well as thermal and quantum *transverse* spin fluctuations perpendicular to the local $\langle 111 \rangle$ directions are concomitantly at play in the collective paramagnetic/spin liquid regime (50 mK $\lesssim T \lesssim$ 10 K) of $Tb_2Ti_2O_7$.

Because of the accidental quasi-cancelation of the exchange and dipolar energy scales at the nearest-neighbor level, the zero-frequency QSI correlations in $Tb_2Ti_2O_7$ may be masked by strong dynamical fluctuations and difficult to detect via neutron scattering [5, 7–9] and muon spin relaxation experiments [5]. From this perspective, the behaviors exhibited by $Tb_2Ti_2O_7$ may be viewed as an interesting example of the spectral weight downshift expected in highly frustrated magnetic systems [25]. We believe that this phenomenology is an important part of the physics of $Tb_2Ti_2O_7$ and at the origin of the stumbling blocks in developing a microscopic theoretical understanding of $Tb_2Ti_2O_7$ [10]. With this in mind, we explore here whether low temperature bulk magnetization, $\boldsymbol{M}(T)$, measurements may be used to expose whether the nearest-neighbor part of the longitudinal (Ising) sector of $H_{\rm eff}$ describing $Tb_2Ti_2O_7$ is indeed that of a frustrated $\langle 111 \rangle$ ferromagnet [21] and, therefore, whether a QSI description of this system is correct. Perhaps one of the clearest tell-tale bulk magnetic signatures of frustrated ferromagnetic 'two-in/two-out' ice-rule correlations [14] in a spin ice material is the emergence of a magnetization plateau for a magnetic field $\boldsymbol{B}$ along the [111] direction (diagonal of the conventional cubic unit cell) at low temperatures once the ice-rule obeying spin correlations have become established [26, 27]. Motivated by this magnetization plateau phenomenon in classical Ising spin ices, we therefore ask here whether a plateau-like feature in the [111] magnetization can also develop in the collective paramagnetic regime of $Tb_2Ti_2O_7$ as the frustrated ferromagnetic $\langle 111 \rangle$ spin correlations develop at the shortest (single tetrahedron) length scale.

The suggestion that $Tb_2Ti_2O_7$ may be described at low energies and low temperatures by an effective Hamiltonian, $H_{\rm eff}$, whose longitudinal Ising components are frustrated by effective nearest-neighbor couplings was motivated by perturbation theory calculations carried out over a single tetrahedron of interacting Tb^{3+} ions [20]. The coupling between the $\langle 111 \rangle$ Ising components for a pair of interacting Tb^{3+} ions is in principle renormalized by the interactions with all the other Tb^{3+} ions in the system. Therefore, an important question that arises is whether the frustrated 'two-in/two-out' spin ice like correlations are preserved in a perturbation theory extended to a thermodynamically large lattice and, in particular, in the presence of the long range magnetostatic dipole–dipole interactions between Tb^{3+} ions [6, 11, 16]. Our preliminary perturbation theory calculations carried over the whole lattice show that the system remains in an ice-rule obeying ground state with competing states with a 'three-in/one-out' spin configuration having a slightly higher energy [20, 22]. Consequently, we would expect that, in an 'exact' treatment of $H_{\rm eff}$ at nonzero temperature, spin ice 'two-in/two-out' correlations would develop at low temperatures. The important question is therefore whether such correlations actually develop in real $Tb_2Ti_2O_7$ at low temperatures and if they can be evinced by the observation of a [111] magnetization plateau.

To get a preliminary handle on the relevant temperature and magnetic field scale where QSI physics may become experimentally discernable in $Tb_2Ti_2O_7$, we consider the

same ITA used in [20] to describe the SL state of that material since, as stated above, interactions beyond a single tetrahedron do not spoil the existence of an ice-rule obeying semi-classical ground state [22]. The merit of the ITA to describe the collective paramagnetic state of $Tb_2Ti_2O_7$ was discussed in [20, 22][5]. In the context of the work presented here, one may interpret the ITA as a self-consistent cluster mean-field theory (SCMFT) [29] where the considered cluster is a tetrahedron, *but* where the self-consistency conditions that incorporate the inter-clusters (inter-tetrahedra) interactions have been set to zero. This is because we are describing the collective paramagnetic/spin liquid regime of the model where the correlations extend solely over the smallest cluster length scale where no global symmetry is (yet) spontaneously broken. The experimental observation that spin correlations in $Tb_2Ti_2O_7$ never develop beyond the size of a single tetrahedron from a temperature of $\sim 10^0$ K down to 50 mK [5, 7–9] would seem to further provide a post-factum justification to this 'constrained' paramagnetic description of a SCMFT of the $H_{\rm eff}$ of $Tb_2Ti_2O_7$.[6] In other words, the ITA should be qualitatively valid for sufficiently small field and temperatures such that long range spin–spin correlations are not induced [15]. Finally, for the proposed experiment seeking to expose a magnetization plateau for $\boldsymbol{B}$ along [111], symmetry considerations play a crucial role [26, 27], and the ITA does capture that symmetry aspect of the problem. Below, we find that for parameter values for which the model exhibits a QSI, and which are appropriate for $Tb_2Ti_2O_7$ [20], the low temperature magnetization $M(T)$ ($T \lesssim 100$ mK) does indeed exhibit a plateau for $B \equiv |\boldsymbol{B}| \sim 0.1$ T.

2. Model and results

Within the ITA, the Hamiltonian for $Tb_2Ti_2O_7$ reads

$$H = \sum_{a=1,b>a}^{4} (H_{ab}^{\rm ex} + H_{ab}^{\rm dip}) + \sum_{a=1}^{4} (H_a^{\rm Z} + H_a^{\rm cf}). \qquad (1)$$

$H_{ab}^{\rm dip} = \mathcal{D} R_{\rm nn}^3 [\mathbf{J}_a \cdot \mathbf{J}_b - 3(\mathbf{J}_a \cdot \hat{r}_{ab})(\mathbf{J}_b \cdot \hat{r}_{ab})] |\mathbf{R}_{ab}|^{-3}$ and $H_{ab}^{\rm ex} = \mathcal{J} \mathbf{J}_a \cdot \mathbf{J}_b$ describe, respectively, the dipole–dipole and the exchange interactions for a pair ab. $H_a^{\rm Z} = -g\mu_{\rm B} \mathbf{J}_a \cdot \boldsymbol{B}$ is the Zeeman Hamiltonian and $H_a^{\rm cf}$ is the crystal field (CF) Hamiltonian, both for ion a [6, 19]. $\mathbf{R}_{ab} \equiv \mathbf{R}_b - \mathbf{R}_a = |\mathbf{R}_{ab}| \hat{r}_{ab}$ where $\mathbf{R}_a$ is the position vector of ion a, and $R_{\rm nn} = 3.59$ Å is the nearest-neighbor distance. $\mathcal{D} = \mu_0 (g\mu_{\rm B})^2 / (4\pi R_{\rm nn}^3) = 0.0315$ K is the dipole–dipole coupling and $\mathcal{J} = 0.167$ K is the exchange coupling, with the convention that $\mathcal{J} > 0$ is antiferromagnetic [20][7]. $\mu_{\rm B}$ is the Bohr magneton, $g = \frac{3}{2}$ is the Landé factor of Tb^{3+} and $\mathbf{J}_a$ ($|\mathbf{J}_a| = 6$) is the total angular momentum operator of Tb^{3+} ion a. Calculations considering a single (non-interacting) Tb^{3+} ion in nonzero $\boldsymbol{B}$ show that the six lowest-energy CF states describe well the exact $\boldsymbol{M}$ when compared with calculations that consider all $2J + 1 = 13$ CF states for $\boldsymbol{B} \lesssim 30$ T with an error less than 1%. Henceforth, we use the six lowest CF states of Tb^{3+} to calculate $\boldsymbol{M}$ within the ITA. The basis states of the system are taken as the tensor product of the CF states of the four non-interacting Tb^{3+} ions on a tetrahedron. We denote the two states of the CF ground state by $|\uparrow\rangle$ and $|\downarrow\rangle$. These correspond, respectively, to the 'out' and 'in' degenerate (Ising) CF ground states of $H^{\rm cf} \equiv \sum_a H_a^{\rm cf}$ on an 'upward pointing' tetrahedron primitive basis [6, 11, 26] when referring to the [111] direction along which $\boldsymbol{B}$ points. The CF ground doublet and first excited doublet are given in [20] and the two other excited states, determined as in [20], are $|\psi^{(3)}\rangle = a_6(|6\rangle + |-6\rangle) + a_3(|3\rangle - |-3\rangle)$ and $|\psi^{(4)}\rangle = b_6(|6\rangle + |-6\rangle) + b_3(|3\rangle - |-3\rangle) + b_0|0\rangle$ with energies $E_3 = 142.1$ K and $E_4 = 212.4$ K, respectively[8]. Here we express $|\psi^{(3)}\rangle$ and $|\psi^{(4)}\rangle$ in terms of the eigenstates $|J = 6, m_J\rangle$ of J^z within the fixed $J = 6$ manifold. The local $\hat{z}$ easy axes for sublattices 1 to 4 on an individual tetrahedron primitive unit cell are along [111], $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}]$ and we maintain this sequence of labeled spins/sites throughout the paper, with $|ijkl\rangle \equiv |ijkl\rangle_{1234} \equiv |i\rangle_1 \otimes |j\rangle_2 \otimes |k\rangle_3 \otimes |l\rangle_4$.

We determine the matrix elements of the full H in equation (1) in the CF basis, find the eigenvalues and eigenstates of H using a numerically exact diagonalization method and use these to calculate $\boldsymbol{M}$ given by the standard formula

$$M^\alpha = \frac{g\mu_{\rm B}}{4} \sum_{i=1}^{N_s} \sum_{a=1}^{4} u_a^{\alpha\beta} \langle \phi_i | J_a^\beta | \phi_i \rangle n_{\rm B}(E_i), \qquad (2)$$

where M^α is the α component of the total $\boldsymbol{M}$ per ion. $|\phi_i\rangle$'s are the eigenstates of Hamiltonian (1), $u_a^{\alpha\beta}$ is the $\alpha\beta$ component of the rotation matrix from the local quantization frame, aligned along the local cubic [111] direction at site a, to the global axis. J_a^α is the α component of $\mathbf{J}$ expressed in the local xyz quantization frame with $\hat{z}$ aligned with the local [111] axis. $n_{\rm B}(E_i) = \exp(-E_i/k_{\rm B}T)$ is the Boltzmann population of state i with energy E_i at temperature T. The sum over i in equation (2) is carried over the $N_s = 6^4 = 1296$ eigenstates retained in $H^{\rm cf}$ and the sum on a is over the four sites of a tetrahedron.

We calculate $\boldsymbol{M}$ within the ITA for $\boldsymbol{B}$ along [111] and for $T = 20$, 50 and 100 mK. The result of this calculation is shown in figure 1. As in spin ices [26], a magnetization plateau occurs, becoming apparent only below the temperature at which the ice-rules are well established [20]. That is, when the temperature drops below the very small energy gap separating the manifold of 'two-in/two-out' states from the manifold of 'three-in/one-out' states. In the present model, the spin ice phenomenology is 'hidden' at low temperature because of the accidental location of the system near the phase boundary

[5] It has been suggested [28] that the very slight departure from perfect $Fd\bar{3}m$ space group symmetry in $Tb_2Ti_2O_7$, as indicated by a nonzero neutron scattering intensity at $\boldsymbol{q} = 002$ [15], and compatible with $F\bar{4}3m$ symmetry, may lead to a (partial) decoupling of the tetrahedron primitive unit cells. This could provide a simple physical justification for the semi-quantitative validity of the independent tetrahedron approximation (ITA) to describe $Tb_2Ti_2O_7$ [20].

[6] That said, further theoretical work aimed to understand this bottlenecked growth of spin correlations in $Tb_2Ti_2O_7$ below $\sim 10^0$ K is most definitely warranted.

[7] A recent work [19] reports a smaller (less antiferromagnetic) exchange $\mathcal{J}$.

[8] The values of coefficients a_m and b_n are $a_6 = 0.25$, $a_3 = 0.66$, $b_6 = 0.33$, $b_3 = 0.62$ and $b_0 = 0.12$.

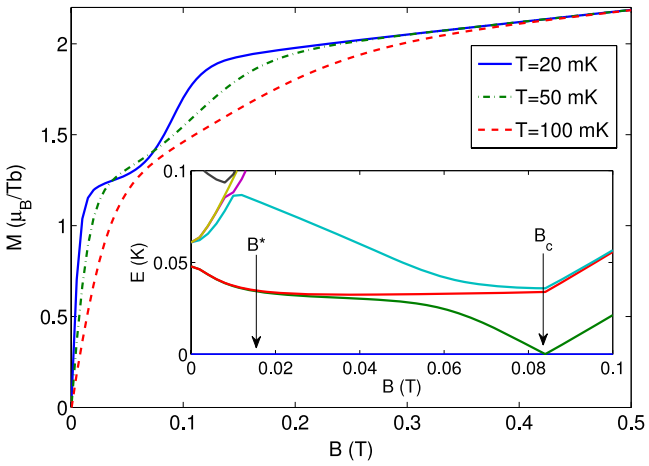

Figure 1. Magnetization M of $Tb_2Ti_2O_7$ in the ITA as a function of magnetic field $\boldsymbol{B}$ applied along the [111] direction. In the magnetization plateau regime, where $M(B)$ flattens out for $T = 20$ mK, the system is in a 'quantum kagome ice' state (see text). Inset: energy of the lowest states as a function of B which which shows a level crossing at $B_c = 0.082$ T.

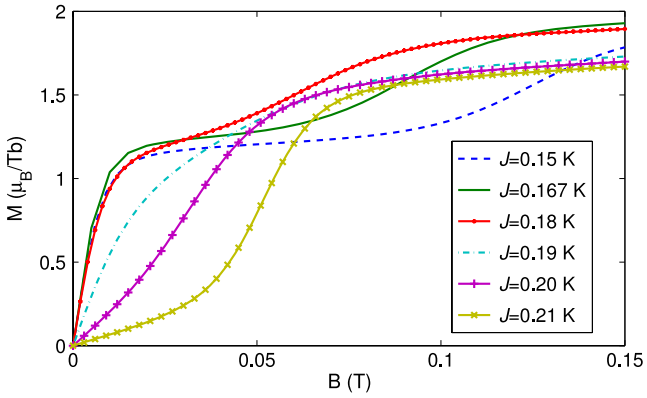

Figure 2. [111] magnetization M of $Tb_2Ti_2O_7$ in the independent tetrahedron approximation as a function of $\boldsymbol{B}$ in the [111] direction. Here the temperature is 20 mK.

between the 'all-in/all-out' (doublet) Néel state and the 'two-in/two-out'spin ice state [20]. The plateau develops only at low temperature because the QSI state in H in equation (1), and possibly in $Tb_2Ti_2O_7$, is inherited by perturbative virtual quantum mechanical crystal field excitations renormalizing the already accidentally almost vanishing classical (longitudinal Ising) interactions in $H_{\rm eff}$ [20]. Hence, the manifold of low-energy states at $\boldsymbol{B} = 0$, which descend from the $2^4 = 16$ parent Ising CF ground doublet states, span a small energy bandwidth $\delta\Omega \sim 0.5$ K [20], with the six lowest-energy spin ice states spanning an even smaller bandwidth $\delta\omega \sim 0.06$ K (see the six lowest (singlet $\oplus$ doublet $\oplus$ triplet) states at $\boldsymbol{B} = 0$ in the inset of figure 1) [20]. Consequently, the plateau in M only emerges at quite low temperature. This constitutes a prime example where high frustration is caused by naturally accidentally fine-tuned microscopic interactions (here $H^{\rm ex}$ and $H^{\rm dip}$) and where the relevant low-energy physics is pushed down to an exceedingly small scale [25]. For small B, M starts to increase even at a very low T (e.g. 20 mK). The reason for this is that, despite the ground state being a singlet at the ITA level, there exist a second order (van Vleck like) susceptibility originating from the excited states which leads to $M \neq 0$ for $B > 0$.

The value of the exchange $\mathcal{J}$ in $Tb_2Ti_2O_7$ is not fully agreed upon [6, 19] (see footnote 7). It is therefore worthwhile to explore how $M(B)$ changes as $\mathcal{J}$ is varied. We plot in figure 2 M as a function of B for $T = 20$ mK and exchange couplings $\mathcal{J} = 0.15, 0.167, 0.18, 0.19, 0.20$ K. These results show that a magnetization plateau is manifest only when the system displays a QSI state at $\boldsymbol{B} = 0$ for $\mathcal{J} < \mathcal{J}_c$ [20]. Here $\mathcal{J}_c = 0.187$ K delineates the transition between the QSI and the 'all-in/all-out' (doublet) state [20], with the plateau disappearing for $\mathcal{J} > \mathcal{J}_c$. For $\mathcal{J} = 0.18$ K, the system is barely beyond the threshold for exhibiting a QSI state and one finds that the plateau is poorly formed even at $T = 20$ mK. Our calculations also show that, although a rescaling of $\mathcal{J}$ and $\mathcal{D}$ changes the magnetization plateau value and the B range over which a magnetization plateau arises, it does not change the generic qualitative behavior seen in figure 1 as long as the model, and presumably the real system, displays a QSI state for $\boldsymbol{B} = 0$ or, in other words, as long as the system possesses frustrated ferromagnetic interactions in the nearest-neighbor Ising part of $H_{\rm eff}$.

3. Field dependence of energy levels on a single tetrahedron

The ITA results above can be interpreted as describing the behavior of the system in the temperature range where no long range order exists except for the field-driven global [111] magnetization, but where spin correlations extend over the shortest length scale characteristic of a collective paramagnetic/spin liquid regime (i.e. over a tetrahedron). Yet, it is interesting, for completeness, to consider the evolution of the energy levels over a single tetrahedron as this evolution would ultimately need to be taken into account in a SCMFT [29] going beyond a single tetrahedron to describe the possible spontaneously broken symmetry states of the model.

To understand $M(B)$ at 20 mK within the ITA, we scrutinize the ground state of the system as a function of B. We first note that the ground state, $|\Psi\rangle$, in the B range considered in figure 1, can be generically and compactly written as $|\Psi\rangle = \alpha|\omega\rangle + \bar{\alpha}|\bar{\omega}\rangle + \beta|\uparrow\downarrow\downarrow\downarrow\rangle + \epsilon|\chi\rangle$. Here $|\omega\rangle = |\uparrow\uparrow\downarrow\downarrow\rangle + |\uparrow\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\uparrow\rangle$ and $|\bar{\omega}\rangle$ is the time conjugate of $|\omega\rangle$. α, $\bar{\alpha}$, β, ϵ and $|\chi\rangle$ are B-dependent and ϵ is much smaller than at least one of the coefficients α, $\bar{\alpha}$, or β. Notice that in $|\omega\rangle$, ion #1 is in the $|\uparrow\rangle$ ('out') state. We denote the QSI state with $\boldsymbol{B} = 0$ in equation (1) as $|\text{QSI}\rangle \equiv |\Psi\rangle$ above with $\alpha = \bar{\alpha}$, $\beta = 0$ and $|\epsilon| \ll |\alpha|$.

The evolution of the ground state with B can be explained from the competition between $H^{\rm Z}$ and $H^{\rm ex} + H^{\rm dip}$ in equation (1). For weak B, $\langle\text{QSI}|H^{\rm Z}|\varphi\rangle \neq 0$, where $|\varphi\rangle$ refers to any of the six pure 'two-in/two-out' states (e.g. $|\uparrow\uparrow\downarrow\downarrow\rangle$, $|\uparrow\downarrow\uparrow\downarrow\rangle$, etc). Among these, the three states with ion #1 in $|\uparrow\rangle_1$ (i.e. polarized along [111]) have a lower Zeeman energy than the other three two-in/two-out states. Hence, with $B \neq 0$, a

state with larger weight from these components, i.e. with ion #1 $|\uparrow\rangle_1$, has lower energy than the $\boldsymbol{B} = 0$ $|\mathrm{QSI}\rangle$ state and become the ground state. As a result, for nonzero and sufficiently weak B, the ground state evolves from $|\mathrm{QSI}\rangle$ to a state $|\Psi\rangle$ with $\alpha > \bar{\alpha}$ and with $\beta = 0$ ($\beta = 0$ because H^Z does not admix $|\mathrm{QSI}\rangle$ with $|\uparrow\downarrow\downarrow\downarrow\rangle$ at any order in H^Z).

As B is increased, α grows and $\bar{\alpha}$ decreases until $B^* \approx 0.016$ T where $\delta E^Z \equiv \langle \mathrm{QSI}|H^Z|\mathrm{QSI}\rangle \approx 0.06$ K. For $B \sim B^*$, all six lowest-energy states with a predominant two-in/two-out weight spanning the small energy bandwidth $\delta\omega \approx 0.06$ K (see inset of figure 1) fall within the energy range δE^Z. Hence, for $B > B^*$, the system adopts a ground state with $\alpha \gg \bar{\alpha}$, where ion #1 is polarized towards [111], while the three other ions are in an entangled state which is a symmetric linear combination of two-in/one-out states. This partially spin polarized (PSP) state, $|\mathrm{PSP}\rangle$, is analogous to the kagome ice state in classical spin ice systems [26, 27]. By increasing B beyond B^*, up to B_c, the ground state remains $|\mathrm{PSP}\rangle$ (i.e. $\beta = 0$ because H^Z does not admix $|\mathrm{PSP}\rangle$ with $|\uparrow\downarrow\downarrow\downarrow\rangle$ at any order in H^Z), until a level crossing occurs for $B_c \approx 0.082$ T (see inset of figure 1).

One must consider the evolution of the first excited energy level with B in order to understand the above level crossing. For $\boldsymbol{B} = 0$, one of the two states from the first excited doublet has a small $|\uparrow\downarrow\downarrow\downarrow\rangle$ 'three-in/one-out' component. As a result, the matrix elements of H^Z between this state and the higher-energy excited states which have a three-in/one-out component is nonzero. Hence, by increasing B, the $|\uparrow\downarrow\downarrow\downarrow\rangle$ weight in the first excited state increases and its energy decreases and, by the time $B \sim 0.08$ T, this state is almost pure $|\uparrow\downarrow\downarrow\downarrow\rangle$. This state then crosses the PSP state at $B_c \approx 0.082$ T and becomes the ground state (see inset of figure 1), with the system exiting the PSP state characterized by a magnetization plateau.

4. Conclusion

We calculated the magnetization $\boldsymbol{M}$ of $Tb_2Ti_2O_7$ for a field $\boldsymbol{B}$ along the [111] direction within a single tetrahedron approximation (ITA). For weak $\boldsymbol{B}$ in this direction, a magnetization plateau is found to occur for a temperature range where the system is in a collective paramagnetic/spin liquid regime. Within this regime, the correlations extend solely over the size of a tetrahedron and each tetrahedron primitive basis is in a state predominantly weighted by $|\uparrow\rangle_1 \otimes (|\uparrow\downarrow\downarrow\rangle_{234}|\downarrow\uparrow\downarrow\rangle_{234}|\downarrow\downarrow\uparrow\rangle_{234})$, where the three spins on the vertices of the triangle perpendicular to the [111] direction, i.e in the kagome plane, form a linear combination of two-in/one-out states [26, 27]. This partially spin polarized state (PSP) is reminiscent of the classical kagome ice state in classical Ising spin ices [26, 27] which one may label *quantum kagome ice* to distinguish it from the degenerate kagome ice state. From a microscopic level point of view, both the zero field quantum spin ice (QSI) and the PSP states originate from virtual crystal field excitations and quantum many-body effects [20]. At this time, low temperature experiments are needed to test the proposals of QSI and PSP states in $Tb_2Ti_2O_7$. From the results presented here, we propose that an experiment based on measurements of $\boldsymbol{M}$ along the [111] direction would help to ascertain the possibility of a QSI state in $Tb_2Ti_2O_2$. Furthermore, the observation of a QSI and a PSP in $Tb_2Ti_2O_7$ would confirm the status of this material as a unique opportunity to explore quantum effects in a spin ice system. It may also open an experimental avenue to explore some of the exciting physics proposed to be at play in frustrated pyrochlore Ising systems with perturbative quantum fluctuations [24]. We hope that this work will motivate such investigations which would help shed some light on the microscopic origin of the enigmatic spin liquid state in $Tb_2Ti_2O_7$ [5, 10].

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