I. INTRODUCTION

The rare-earth pyrochlore magnets, with chemical formula \(R_2\text{Ti}_2\text{O}_7\), exhibit a variety of low-temperature phenomena, from magnetic ordering in Er\(\text{Ti}_2\text{O}_7\)\cite{1}, to spin ice states in H\(\text{O}_7\) \(\text{Ti}_2\text{O}_7\)\cite{2} and D\(\text{y}_3\text{Ti}_2\text{O}_7\)\cite{3}, and possible spin liquid behaviour in Tb\(\text{Ti}_2\text{O}_7\)\cite{4}. In each case, the magnetic properties are due to the magnetic moments of the rare earth ions, which are proportional to \(J\), the total angular momentum of the ion, and to interactions between them. In spite of rather large values of \(J\) derived from Hund’s rules, the rare-earth pyrochlores are essentially quantum magnets: a strong crystal electric field (CEF) lowers the \(2J+1\)-fold degeneracy of the rare earth ions into singlets and doublets, with rather large energy differences between the levels. In many cases, the CEF ground state is a doublet, which is treated as a basic two-level quantum mechanical system.

Recently, there has been a great deal of effort to describe these various rare earth pyrochlores within the same phenomenological model, the spin-1/2 nearest-neighbour exchange interaction. This modeling process is straightforward for materials such as Er\(\text{Ti}_2\text{O}_7\) and Yb\(\text{Ti}_2\text{O}_7\), whose CEF ground state doublets are in fact spin-1/2 single tetrahedron states. The exchange models is given in Section V. Section VI contains concluding remarks.

The rare earth ions in pyrochlore crystals are located at the 16d Wyckoff position of the space group \(Fd\bar{3}m\). There are 16 sites in the \(primitive\) unit cell, located on the vertices of a tetrahedron. The local site symmetry (CEF symmetry) is \(D_{3d}\). The 3-fold \((C_3)\) axes point in different directions for the different sites: [111], [1\(\bar{1}\)1], [11\(\bar{1}\)] and [1\(\bar{1}\)1] for sites #1, 2, 3 and 4 respectively. These directions define a local \(z\)-axis for each site on a tetrahedron. For non-Kramers ions (such as \(\text{Tb}^{3+}\) or \(\text{Ho}^{3+}\)), the CEF states are singlets or doublets belonging to the \(A_1\), \(A_2\) or \(E\) representations of \(D_3\). For Kramers ions (such as \(\text{Er}^{3+}\), \(\text{Yb}^{3+}\) or \(\text{Dy}^{3+}\)), the CEF states are doublets belonging to either the \(\Gamma_4\) or \(\Gamma_5\) representations of \(D_3\), the double group of \(D_3\). The CEF ground states for \(\text{Er}^{3+}\) in \(\text{Er}_2\text{Ti}_2\text{O}_7\) and \(\text{Yb}^{3+}\) in \(\text{Yb}_2\text{Ti}_2\text{O}_7\) belong to \(\Gamma_4\), which is isomorphic to spin-1/2. Therefore CEF ground state doublets of \(\text{Er}^{3+}\) and \(\text{Yb}^{3+}\) can be easily mapped to a spin-1/2 spinor by an appropriate renormalisation of the matrix elements for the operators \(J_z\) and \(J_\perp\). Here we are concerned with finding a map between the non-Kramers (\(E\)) doublet and a spin-1/2 (\(\Gamma_4\)) doublet. Because these two kinds of doublets transform differently under rotations, such a map must be constructed with care. In fact, a symmetry-preserving map exists if these doublets are considered in groups of 4 (the four vertices of a tetrahedron in the pyrochlore lattice).

In the following section, we describe the CEF ground state of \(\text{Tb}_2\text{Ti}_2\text{O}_7\), and the map between \(\text{Tb}_2\text{Ti}_2\text{O}_7\) and spin-1/2 single tetrahedron states is defined. The exchange interaction is treated in Section III, for the general case, the spin-1/2 case, and for \(\text{Tb}_2\text{Ti}_2\text{O}_7\). A map between spin-1/2 and \(\text{Tb}_2\text{Ti}_2\text{O}_7\) exchange models is given in Section IV. The magnetisation is discussed in Section V. Section VI contains concluding remarks.

II. QUANTUM MECHANICAL STATES FOR \(\text{Tb}_2\text{Ti}_2\text{O}_7\)

A. CEF ground state for \(\text{Tb}^{3+}\) in \(\text{Tb}_2\text{Ti}_2\text{O}_7\)

The CEF Hamiltonian for the rare earth sites in \(\text{R}_2\text{Ti}_2\text{O}_7\) is given by

\[
H_{\text{CEF}} = B_{1}^{0}O_{2}^{0} + B_{1}^{0}O_{4}^{0} + B_{3}^{0}O_{6}^{0} + B_{5}^{0}O_{6}^{0} + B_{6}^{0}O_{6}^{0} \tag{1}
\]

where \(O_{j}^{0}\) are Stevens operators, \(j\)-th order polynomials of the operator \(\bar{J}\), the total angular momentum. \(B_{j}^{0}\) are constants determined experimentally. There have been several determinations of \(B_{j}^{0}\) for \(\text{Tb}_2\text{Ti}_2\text{O}_7\); all\cite{5} but the most recent\cite{6} are consistent with each other. The differences in these constants do not affect the symmetries...
of the CEF states, but they are eventually reflected in
the exchange constants (see Section V).
According to Hund’s rules, the total angular momentum
of the Tb\(^{3+}\) ion is \(J = 6\). The CEF lifts the 13-fold
degeneracy into singlets and doublets. The CEF ground
state of Tb\(^{3+}\) in Tb\(_2\)Ti\(_2\)O\(_7\) is a doublet,
\[
|\pm\rangle = \pm 0.263|\pm 5\rangle - 0.131|\pm 2\rangle \mp 0.128|\mp 1\rangle - 0.947|\mp 4\rangle
\]
where the quantisation axis points along the \(C_3\) axis,
which points in a different direction at each site. The
quantisation axis defines a local \(z\)-axis. In this way, a
different set of local axes is defined for each site on a
tetrahedron (see Appendix A for a detailed description).

The matrix elements for the operators \(J_\pm \equiv J_x \pm iJ_y\)
within the \(|\pm\rangle\) doublet are zero, while
\[
j_1 \equiv \langle +|J_2|+\rangle = -3.21. \quad (3)
\]
Here \(x, y, z\) subscripts are used to denote local axes, while
superscripts will be used to denote global axes.

### B. The first excited CEF state for Tb\(^{3+}\) in Tb\(_2\)Ti\(_2\)O\(_7\)

In Tb\(_2\)Ti\(_2\)O\(_7\), the first excited CEF state (also a dou-
blet) lies only \(\Delta = 17.90\) K above the ground state.
Therefore, as was recognised long ago, there is a sig-
nificant admixture of this excited state to the lowest en-
ergy states. However, the symmetry of the lowest energy
states cannot be affected by this admixture.

The first excited CEF state is
\[
|\uparrow/\downarrow\rangle = \mp 0.923|\pm 5\rangle + 0.251|\pm 2\rangle \mp 0.082|\mp 1\rangle - 0.280|\mp 4\rangle
\]
The matrix element for \(J_2\) within this doublet is
\[
j_2 \equiv \langle \uparrow|J_2|\uparrow\rangle = 4.05, \quad (4)
\]
and the matrix elements for \(J_x\) are again zero. The mixing
of the first CEF excited state to the ground state will
depend on the matrix elements
\[
j_3 \equiv \langle \uparrow|J_2|\uparrow\rangle = -2.37 \quad (5)
\]
and
\[
t \equiv \langle \uparrow|J_2|\uparrow\rangle = 4.72. \quad (6)
\]

### C. Map between states

With four sites per tetrahedron, there are sixteen
Tb\(_2\)Ti\(_2\)O\(_7\) tetrahedron states of the form
\(|\pm\pm\pm\pm\rangle_{Tb} = |\pm\rangle_1 \otimes |\pm\rangle_2 \otimes |\pm\rangle_3 \otimes |\pm\rangle_4\),
where \(|\pm\rangle_i\) is a non-Kramers doublet on the \(i\)th site. In a similar fashion, we can also
define sixteen spin-1/2 tetrahedron states, which will be
denoted as \(|\pm\pm\pm\rangle_{1/2}\). Each of these kets represents a
classical state where each spin can be visualised as point-
ing into or out of the tetrahedron. There are two anti-
ferromagnetic states, |\(-\cdots\rangle\) and |\(+\cdots\rangle\), with
all four spins pointing into (\(-\)) or out of (\(+\)) the tetra-
hedron ("all-in/all-out" states), while the six states of the
form |\(+\cdots\rangle\) are ferromagnetic, with two spins
pointing in and two spins pointing out of the tetra-
hedron ("2-in-2-out" spin ice states). In addition, there are
eight "3-in-1-out/1-in-3-out" states.

The symmetry group of a tetrahedron in the pyrochlore
lattice is \(T_d\), with representations \(A_1, A_2, E, T_1\) and \(T_2\).
Both the Tb\(_2\)Ti\(_2\)O\(_7\) and the spin-1/2 tetrahedron states
can be used as basis functions to generate a (reducible)
representation of \(T_d\). In both cases, in spite of different transformation properties of the individual site states,
the decomposition is \(A_1 \oplus 3E \oplus 2T_1 \oplus T_2\).
This finding allows us to define a map between the Tb\(_2\)Ti\(_2\)O\(_7\) (non-Kramers)
tetrahedron states and spin-1/2 tetrahedron states. The map
between the Tb\(_2\)Ti\(_2\)O\(_7\) and spin-1/2 tetrahedron ba-
sis states is
\[
|\pm\pm\pm\rangle_{Tb} \sim (-1)^\eta \mathcal{K} |\pm\pm\pm\rangle_{1/2} \quad (7)
\]
where \(\mathcal{K}\) stands for time reversal (represented in the stan-
dard way as \(-i\sigma_y K_0\), where \(K_0\) is complex conjugation)
and the exponent \(\eta = 0\) for the 2-in-2-out states and the
3-in-1-out spin-1/2 states (but not the 1-in-3-out states);
\(\eta = 1\) otherwise. The phase \((-1)^\eta\) is a reflection of
the non-triviality of the map.

It is worth noting that the tetrahedron states formed
from the third kind of doublet (belonging to the \(\Gamma_5\)
representation of \(D_3^7\)) generate a representation with decom-
position \(3A_1 \oplus 2A_2 \oplus E \oplus 2T_1 \oplus T_2\). Therefore there is no
map between \(\Gamma_5\) tetrahedron states and spin-1/2 tetra-
hedron states that is generally valid. The CEF ground
state of Dy\(^{3+}\) in Dy\(_2\)Ti\(_2\)O\(_7\) belongs to this case.

### III. THE EXCHANGE INTERACTION

#### A. Nearest neighbour exchange interaction: general

The exchange interaction is a phenomenological model
that describes the energy dependence of different relative
orientations of neighbouring magnetic moments. The
general form of the exchange Hamiltonian is governed by
the symmetry of the crystal. In a highly symmetric crys-
tal, the number of free parameters of the Hamiltonian is
small.

The most general form of the of the nearest neighbour
exchange interaction on the pyrochlore lattice is
\[
H_{\text{ex}} = J_1 X_1 + J_2 X_2 + J_3 X_3 + J_4 X_4 \quad (8)
\]
where \(J_i\) are four independent exchange constants. It is
convenient to express the exchange terms \(X_i\) using the
local axes introduced in the previous section and described
in detail in Appendix A,

\[ X_1 = -\frac{1}{3} \sum_{ij} J_{1z} J_{2z} \]  
(9)

\[ X_2 = -\frac{\sqrt{2}}{3} \sum_{ij} [\Lambda_{i,i,j} (J_{1z} J_{2z} + J_{2z} J_{1z}) + \text{H.c.}] \]  
(10)

\[ X_3 = \frac{1}{3} \sum_{ij} (\Lambda_{i,i,j}^* J_{i+} J_{j+} + \text{H.c.}) \]  
(11)

\[ X_4 = -\frac{1}{6} \sum_{ij} (J_{i+} J_{j-} + \text{H.c.}) \]  
(12)

where H.c. stands for “Hermitian conjugate,” \( \Lambda_{12} = \Lambda_{24} = 1 \) and \( \Lambda_{13} = \Lambda_{23} = \varepsilon = \exp(\frac{2\pi i}{4}) \). The sums are over pairs of nearest neighbours and are infinite; the phases \( \Lambda_{i,i,j} \) depend on the site numbers of the neighbouring spins. When \( i \) and \( j \) are nearest neighbours, the site numbers \( s_i \) and \( s_j \) are always different. Note that in the special case when \( J_1 = J_2 = J_3 = J_4 \equiv J \), the exchange interaction is isotropic, \( H_{\text{ex}} = H_{\text{iso}} = J \sum_{i,j} \vec{J}_i \cdot \vec{J}_j \).

The simplest case is when \( J_{2,3,4} = 0 \). Then the eigenstates of \( H_{\text{ex}} \) are classical states in which every spin is parallel to its local z-axis, pointing either into or out of each tetrahedron. Since each spin sits on the vertex of one tetrahedron necessarily points into the other. When \( J_1 > 0 \), the ground state is doubly degenerate; all four spins point into or out of each tetrahedron in the lattice. When \( J_1 < 0 \), the ground state is the highly degenerate 2-in-2-out “spin ice” state.

The coupling constants \( J_i \) will be reserved for effective spin-1/2 models. The coupling constants for \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) will be denoted \( I_i \),

\[ H_{\text{ex}}^{\text{Tb}} = I_1 X_1 + I_2 X_2 + I_3 X_3 + I_4 X_4 \]  
(13)

\( H_{\text{ex}} \) and \( H_{\text{ex}}^{\text{Tb}} \) have exactly the same form, but with different coupling constants. Also, \( H_{\text{ex}} \) acts on spin-1/2 states, while \( H_{\text{ex}}^{\text{Tb}} \) acts on \( J = 6 \) states. Our goal is to replace \( H_{\text{ex}}^{\text{Tb}} \) by effective spin-1/2 model, which we will call \( H_{\text{eff}}^{\text{Tb}} \). The exchange constants \( J_i \) in \( H_{\text{eff}}^{\text{Tb}} \) will be expressed in terms of the constants \( I_i \) in \( H_{\text{ex}}^{\text{Tb}} \).

We will now analyse the models \( H_{\text{ex}} \) and \( H_{\text{ex}}^{\text{Tb}} \) in more detail. Pairs of nearest neighbours can be visualised as lines that connect nearest neighbour sites on the lattice. In the pyrochlore lattice, these lines are precisely the edges of the tetrahedra. The tetrahedra occur in two orientations, \( A \) and \( B \) (see Fig. 1). Thus the sum over nearest neighbours can be split into two parts: the set of all \( A \) tetrahedra and the set of all \( B \) tetrahedra. Then the exchange Hamiltonian can be written as

\[ H_{\text{ex}} = H^A + H^B \]  
(14)

Let \( n \) index the \( A \) tetrahedra. For example, \( J_{niz} \) is the \( J_z \) operator (using the local z-axis) for the \( i \)th \((i=1,2,3,4)\) site on the \( n \)th \( A \) tetrahedra. Using this notation, we have

\[ H^A = \sum_n H_n^A = \sum_n J_1 X_{1n}^A + J_2 X_{2n}^A + J_3 X_{3n}^A + J_4 X_{4n}^A \]  
(15)

where, for example, \( X_{1n}^A \) is the first exchange term for nearest neighbours on the \( n \)th tetrahedron,

\[ X_{1n}^A = -\frac{1}{3} (J_{n1z} J_{n2z} + J_{n1z} J_{n3z} + J_{n1z} J_{n4z} + J_{n2z} J_{n3z} + J_{n2z} J_{n4z} + J_{n3z} J_{n4z}) \]  
(16)

\[ H_{\text{ex}}^{\text{Tb}} = H_{\text{ex}}^{A,\text{Tb}} + H_{\text{ex}}^{B,\text{Tb}} \]  
(20)
B. The spin-1/2 independent tetrahedra model

First we consider a simple model involving the exchange paths on a single tetrahedron (the n-th A tetrahedron),

\[ H^A_n = J_1 X_{1n}^A + J_2 X_{2n}^A + J_3 X_{3n}^A + J_4 X_{4n}^A. \]  

(21)

This can be represented as a 16 × 16 matrix, which can be block diagonalised using the keys described in Appendix B. Exact eigenfunctions can easily be found. The solutions to \( H^A \) \( (13) \) are the direct product of the single tetrahedron solutions of \( H^A_n \) \( (21) \), which is why it is called the “independent tetrahedra model”. Because it is exactly solvable, \( H^A \) is often used to model experiments instead of the full Hamiltonian \( H_{\text{ex}} \). We also note that \( H^A \) has a lower symmetry than \( H_{\text{ex}} \), and the solutions to \( H^A \) are approximately twice as large as those of \( H_{\text{ex}} \). We also note that \( H^A \) has a lower symmetry than \( H_{\text{ex}} \), which suggests that the exchange constants of \( H^A \) are approximately twice as large as those of \( H_{\text{ex}} \). We also note that \( H^A \) has a lower symmetry than \( H_{\text{ex}} \). Instead of the full space group \( I_4 \), we will study the simpler independent tetrahedra model.

C. The exchange interaction for Tb$_2$Ti$_2$O$_7$

1. The exchange interaction for non-Kramers spins restricted to the CEF ground state

When non-Kramers spins are restricted to the CEF ground state, the exchange interaction is greatly simplified because the matrix elements for \( J_\pm \) vanish within this restriction. Then the eigenvectors are the classical states \(| ± ± ± ± ± ± \). The ground state is either the doubly degenerate all-in-all-out state (\( I_1 > 0 \)) or a highly degenerate spin ice state (\( I_2 < 0 \)). This model maps to a spin-1/2 model with \( J_1 = 4 J_1 J_2 \) and \( J_2 = 0 \). This model describes the spin ice material Ho$_2$Ti$_2$O$_7$, but it is insufficient for Tb$_2$Ti$_2$O$_7$, for which higher CEF levels must be included.

2. The exchange interaction for non-Kramers spins restricted to the CEF ground state and first excited state

Perturbation theory is used to determine the mixing of the first excited CEF level to the CEF ground state manifold. The unperturbed Hamiltonian is \( H_{\text{CEF}} \) \( (11) \) restricted to the CEF ground state manifold, while the exchange interaction \( H_{\text{ex}} \) \( (13) \) is the perturbation. Second order perturbation theory yields an effective exchange Hamiltonian restricted to the CEF ground state:

\[ H_{\text{ex}}^{\text{Tb}} = PH_{\text{ex}}^{\text{Tb}} P + PH_{\text{ex}}^{\text{Tb}} Q H_{\text{ex}}^{\text{Tb}} P \]  

(22)

where \( P \) is the projector to the CEF ground state and \( Q \) is the projector that is supplementary to \( P \) i.e. it projects states that have one or more spins in the CEF first excited state. The denominator \( a \) is the energy difference between the ground and excited states. \( P \) is the direct product of projectors \( P_n \) which operate on single tetrahedra. \( Q \) can also be expressed in terms of single tetrahedron operators: on the n-th tetrahedron, one, two, three or four spins can be excited, corresponding to the projections \( Q_{n,\text{one}}, Q_{n,\text{two}}, \text{etc.} \). However, for second order perturbation theory, we need only consider contributions to \( Q \) where one or two spins are excited because \( H_{\text{eff}}^{\text{Tb}} \) is bilinear in the spin operators and can only excite up to two spins at a time via the operators \( J_\pm \) and \( J_z \). Therefore,

\[ Q \left( \frac{a}{4} \right) = \sum_n \frac{Q_{n,\text{one}}}{-\Delta} + \sum_n \frac{Q_{n,\text{two}}}{-2\Delta} + \sum_{n,m<n} \frac{Q_{n,\text{one}} Q_{m,\text{one}}}{-2\Delta} \]  

(23)

where the first term has one spin excited on one tetrahedron, the second term has two spins excited on one tetrahedron and the third term has two spins excited on two different tetrahedra. The operators \( Q_{n,\text{one}} \) and \( Q_{n,\text{two}} \) can be further expanded as

\[ Q_{n,\text{one}} = P_n Q_{n,\text{one}} P_n + \text{etc.} \]  

(24)

In Section IV, we show that \( H_{\text{eff}}^{\text{Tb}} \) \( (22) \) has the same matrix representation as \( H_{\text{ex}} \). However, before considering the full lattice exchange \( H_{\text{eff}}^{\text{Tb}} \), we will study the simpler independent tetrahedra model.

3. The exchange interaction for non-Kramers spins in the independent tetrahedra model

In the independent tetrahedra model, the Hamiltonian for Tb$^{3+}$ spins is \( H^{A,\text{Tb}} \). Perturbation theory yields

\[ H_{\text{eff}}^{A,\text{Tb}} = PH^{A,\text{Tb}} P + PH^{A,\text{Tb}} Q H^{A,\text{Tb}} P \]  

(26)

\[ = \sum_n P H_n^{A,\text{Tb}} P + \sum_{n,m} P H_n^{A,\text{Tb}} Q H_n^{A,\text{Tb}} P \]  

(27)

\[ = \sum_n \left[ P H_n^{A,\text{Tb}} P + \sum_{n,m} P H_n^{A,\text{Tb}} Q H_n^{A,\text{Tb}} P \right] \]  

(28)

In the second last line we make use of the fact that \( H_n^{A,\text{Tb}} \) acts only within the n-th tetrahedron, so the only non-zero contribution in the sum over \( n \) and \( m \) is when \( m = n \). Therefore this calculation reduces to a single tetrahedron Hamiltonian \( H_{\text{eff}}^{A,\text{Tb}} \).
IV. MAP BETWEEN SPIN-1/2 AND TB$^{3+}$ EXCHANGE MODELS

The results of the single tetrahedron calculation were found previously. By comparing a matrix representation of $H_{n,\text{eff}}$ to a matrix representation of the spin-1/2 single tetrahedron $H_{ex}^{n}$, a map between the Tb$^{3+}$ exchange constants and the spin-1/2 exchange constants was found. The basis functions that were used to find the matrix representations are given in Appendix B. Here we follow a slightly different approach to the same result: instead of representing $H_{ex}^{n}$ and $H_{ex}$ in the basis given by $P J_{a} \rightarrow -j_{i} \sigma_{z}$ and $P J_{a} \rightarrow 0$,

\[ P J_{a} \rightarrow -j_{i} \sigma_{z} \]

\[ P J_{a} \rightarrow 0 \]

Using the replacements (29-31), the independent tetrahedra model can be inferred and previous results are reproduced:

The 2 × 2 identity matrix is assumed when no matrix is

1. Exchange interaction for Tb$^{3+}$ spins in the independent tetrahedra model

Using the substitutions $P J_{a} \rightarrow -j_{i} \sigma_{z}$, the independent tetrahedra exchange Hamiltonian for Tb$^{3+}$ spins $H_{ex}^{A,Tb}$ can be expressed as a matrix. By direct comparison to the matrix representation of the spin-1/2 independent tetrahedra Hamiltonian $H_{ex}$, the following map between the exchange constants of spin-1/2 and the Tb$^{3+}$ independent tetrahedra models can be inferred and previous results are reproduced:

\[ J_{1} = 4I_{1}j_{1}^{2} + \frac{(4I_{1}j_{1}j_{3})^{2}}{3\Delta} - \frac{(4I_{1}j_{1}t)^{2}}{3\Delta} + \frac{(I_{1}t^{2})^{2}}{3\Delta} \]

\[ -\frac{(I_{1}t^{2})^{2}}{12\Delta} \]

\[ J_{2} = -\frac{4I_{1}I_{2}j_{1}j_{3}^{2}}{3\Delta} \]

\[ J_{3} = \frac{2(I_{2}j_{3}t)^{2}}{3\Delta} - \frac{I_{1}I_{2}j_{3}^{2}t^{2}}{3\Delta} \]

\[ J_{4} = \frac{(2I_{2}j_{3}t)^{2}}{3\Delta} + \frac{I_{1}I_{2}j_{3}^{2}}{3\Delta} \]

A constant offset was also found:

\[ C = -\frac{(2I_{1}j_{1}j_{3})^{2}}{3\Delta} - \frac{(I_{1}j_{3}^{2})^{2}}{3\Delta} - 2\frac{(2I_{1}j_{1}t)^{2}}{3\Delta} - \frac{(2I_{2}j_{3}t)^{2}}{6\Delta} - \frac{(I_{3}t^{2})^{2}}{3\Delta} - \frac{(I_{4}t^{2})^{2}}{24\Delta} \]
2. The full lattice exchange interaction for Tb$^{3+}$ spins

We now consider the full exchange model $H_{\text{eff}}^{\text{Tb}}$ for Tb$^{3+}$ spins. We shall show that $H_{\text{eff}}^{\text{Tb}}$ is equivalent to the spin-1/2 exchange Hamiltonian $H_{\text{ex}}$ plus additional next-nearest-neighbour and fourth order in $\vec{J}$ interactions.

Both of the operators $H^{A,Tb}$ and $H^{B,Tb}$ appear in the expression for $H_{\text{eff}}^{\text{Tb}}$, which is expanded as:

$$H_{\text{eff}}^{\text{Tb}} = PH^{A,Tb}P + PH^{A,Tb}Q \frac{H_{\text{eff}}^{A,Tb}P}{a} + PH^{B,Tb}P + PH^{B,Tb}Q \frac{H_{\text{eff}}^{B,Tb}P}{a} + PH^{A,Tb}Q \frac{H^{B,Tb}P}{a}$$

The first two terms were already considered in the discussion of independent tetrahedra model $H_{\text{ex}}^{A,Tb}$, and they correspond to the term $H^{A}$ in $H_{\text{ex}}$. The third and fourth terms correspond to $H^{B}$ in $H_{\text{ex}}$. It is obvious from symmetry considerations that the constants of the effective spin-1/2 model for $H_{\text{ex}}$ should be the same as those found for $H^{A}$. The sum of the first four terms therefore corresponds to $H_{\text{ex}}$, with effective coupling constants as given by (42-46).

The last two terms of (47) yield additional next-nearest-neighbour (n.n.n.) interactions, and some unusual fourth order in $\vec{J}$ interactions. Symmetry considerations determine the most general form of these interactions. When the two interacting spins are at different site numbers then the interaction takes the same general form as $H_{\text{ex}}$ except that the sum is over pairs of next-nearest-neighbours with different site numbers, $s_i \neq s_j$. These four contributions will be denoted $X'_{i}$, $i = 1, 2, 3, 4$. In addition, there are two interaction terms between spins that are next-nearest-neighbours with the same site number ($s_i = s_j$), for a total of 6 n.n.n. exchange coupling constants:

$$H_{\text{ex,n.n.n.}} = J'_i X'_i + J'_2 X'_2 + J'_3 X'_3 + J'_4 X'_4 + J'_5 X'_5 + J'_6 X'_6$$

where

$$X'_5 = \sum_{\langle i,j \rangle} J_{i\perp} J_{j\perp} \ (s_i = s_j)$$

$$X'_6 = \sum_{\langle i,j \rangle} J_{i\perp} J_{j\perp} \ (s_i = s_j)$$

Among the many different fourth order in $\vec{J}$ terms which may appear in $H_{\text{eff}}^{\text{Tb}}$, the ones that are produced by the last two terms of (17) are

$$H_{\text{ex,4-order}} = J'_7 X'_7 + J'_8 X'_8$$

where

$$X'_7 = \sum_{\langle i,j,k,l \rangle} \Lambda_{ijkl} J_i J_j J_k J_l + J_i J_j J_k J_l$$

$$X'_8 = \sum_{\langle i,j,k,l \rangle} \Lambda_{ijkl} J_i J_j J_k J_l$$

In $X'_7$, the sites $i, j, k, l$ have different site numbers. Three of the sites ($i, j, k$) form a triangle, and the fourth site $l$ is connected to the triangle by a nearest neighbour bond (but it does not complete a tetrahedron). In $X'_8$, the sites $i, j, k$ have different site numbers. They are arranged in a triangle, while the fourth site $l$ has the same site number as the site $i$ and is connected to the triangle by a nearest neighbour bond. Examples of arrangements of ions involved in these interactions are shown in Fig. 2. Similar to the expressions for $X'_2$ and $X'_3$, the phases $\Lambda_{ijkl}$ are fixed by symmetry considerations with values of either 1, ε or $\varepsilon^2$.

Matrix representations for $H_{\text{ex,n.n.n.}}$ and $H_{\text{ex,4-order}}$ can be written using the substitutions (48-51). By comparing these with the matrix representation of $H_{\text{eff}}^{\text{Tb}}$, the constants $J'_i$ can be inferred:

$$J'_{2,3,4,6} = 0$$

$$J'_1 = \frac{2(2J_1 J_1 J_1)}{3\Delta} - \frac{2(2J_2 J_1 J_1 J_1)}{3\Delta}$$

$$J'_5 = -\frac{2(2J_1 J_1 J_1)}{9\Delta} - \frac{2(2J_2 J_1 J_1 J_1)}{9\Delta}$$

$$J'_7 = \frac{32\sqrt{2}}{9\Delta}$$

$$J'_8 = -\frac{16\sqrt{2}}{9\Delta}$$

In summary, we have considered two different exchange models for Tb$^{3+}$ spins in Tb$_2$Ti$_2$O$_7$, the independent
Recent magnetisation measurements on $\text{Tb}_2\text{Ti}_2\text{O}_7$ have been performed by a few groups [16–18]. In the presence of a magnetic field, the Hamiltonian for $\text{Tb}_2\text{Ti}_2\text{O}_7$ is

$$H(\vec{B}) = H_{\text{CEF}} + H_{\text{ex}} + \sum_i \mu_B g_J \vec{J}_i \cdot \vec{B}$$  \hfill (59)

where $g_J = \frac{3}{2}$ is the Landé $g$-factor for $\text{Tb}^{3+}$ and $\mu_B$ is the Bohr magneton. Being unsolvable, $H(\vec{B})$ is normally handled using either a self-consistent mean field approximation or by using the independent tetrahedron model. Both of these methods involve considerable simplifications of $H(\vec{B})$. In the former, nearest neighbour exchange interactions are replaced by an effective mean field, and the problem is reduced to the solution of a single ion Hamiltonian. In the latter, a single tetrahedron is solved but correlations between tetrahedra are omitted.

Using the mean field approach, approximate values for the exchange constants for $\text{Tb}_2\text{Ti}_2\text{O}_7$ were obtained. The relation between the exchange constants used in Ref. [18] and those defined by (8,9-12) is given in Appendix C. Using our definitions, the constants are (in kelvin)

$$I_1 = -0.128 \quad (60)$$
$$I_2 = -0.083 \quad (61)$$
$$I_3 = -0.1595 \quad (62)$$
$$I_4 = -0.281 \quad (63)$$

It should be noted that in Ref. [18], a constraint was applied in determining these numbers (it was assumed that the anti-symmetric exchange term was absent), such that in effect only three parameters within the four parameter space were explored. Nevertheless, these numbers can provide estimates of the exchange constants for the effective spin-1/2 model. Ref. [18] uses CEF states derived from the CEF Hamiltonian in Ref. [6] with matrix elements $j_1 = -3.4, j_2 = 4.3, j_3 = -2.0, t = 4.65$ (defined by Eqs. (30)) and $\Delta = 18.24$ K. Among all the exchange constants for the spin-1/2 model, only $J_1$ has a first order in perturbation theory correction; the rest are non-zero only in second order. Using Eq. (42) and the numbers given above, we calculate $J_1 \approx -6.1$. The other constants are calculated using (43-45), which yields $J_2 \approx 0.085, J_3 \approx -0.011$ and $J_4 \approx 0.10$; however, without more accurate knowledge of the $\text{Tb}_2\text{Ti}_2\text{O}_7$ exchange constants, these values are likely not very meaningful. The values obtained in Ref. [14], also highly approximate, are in rough agreement, $J_1 \approx -5.1, J_2 \approx 0.2, J_3 \approx 0.1$ and $J_4 \approx 0.3$.

The negative sign of $J_1$ indicates that $\text{Tb}_2\text{Ti}_2\text{O}_7$ is a spin-1/2 spin ice, with quantum fluctuations arising from the other terms in $H_{\text{ex}}$, in agreement with recent observations of spin ice-like correlations in $\text{Tb}_2\text{Ti}_2\text{O}_7$. It will be interesting to see how magnetic monopoles, which are postulated to exist as excitations in spin ices, may be manifested in $\text{Tb}_2\text{Ti}_2\text{O}_7$.

Using either set of estimates for the exchange constants given above to locate the position of $\text{Tb}_2\text{Ti}_2\text{O}_7$ in the phase diagrams presented in Refs. [22 and 23], the ground state of $\text{Tb}_2\text{Ti}_2\text{O}_7$ is predicted to be a “quantum spin liquid” (QSL), or possibly a “Coulomb ferromagnet” (CFM) close to the QSL boundary. Both of these are highly entangled quantum mechanical states, with the CFM state distinguishable from the QSL state by a non-zero magnetisation. However, a complete description of $\text{Tb}_2\text{Ti}_2\text{O}_7$ is almost certainly more complicated due to interactions with lattice structure or elastic strain.
Appendix A: Local axes for rare earth ions in pyrochlore crystals

For site #1, the local z-axis is parallel to the [111] direction and the local x- and y-axes are chosen to be perpendicular to z and to obey the right hand rule. These local axes define a set of magnetic operators

\[ J_{1x} = (J_{1}^x + J_{1}^y - 2J_{1}^z)/\sqrt{6} \]  
\[ J_{1y} = -(J_{1}^x + J_{1}^y)/\sqrt{2} \]  
\[ J_{1z} = (J_{1}^x + J_{1}^y + J_{1}^z)/\sqrt{3} \]

where subscripts are used for operators using local axes and superscripts for global axes.

Local axes for site #2 are defined by rotating the #1 axes by \( C_{2z} \) (this operation also exchanges sites #1 and #2):

\[ J_{2x} = (J_{2}^x - J_{2}^y + J_{2}^z)/\sqrt{6} \]  
\[ J_{2y} = (J_{2}^x - J_{2}^y + J_{2}^z)/\sqrt{2} \]  
\[ J_{2z} = (J_{2}^x - J_{2}^y + J_{2}^z)/\sqrt{3} \]
Similarly, local axes for site #3 are defined by rotating the #1 axes by $C_{2y}$:

\begin{align}
J_{3x} &= (-J_3^x + J_3^y + 2J_3^z)/\sqrt{6} \\
J_{3y} &= (J_3^x + J_3^y)/\sqrt{2} \\
J_{3z} &= (-J_3^x + J_3^y - J_3^z)/\sqrt{3}.
\end{align}

(7)
(8)
(9)

Finally, local axes for site #4 are defined by rotating #1 axes by $C_{2x}$:

\begin{align}
J_{4x} &= (J_4^x - J_4^y + 2J_4^z)/\sqrt{6} \\
J_{4y} &= (-J_4^x - J_4^y)/\sqrt{2} \\
J_{4z} &= (J_4^x - J_4^y - J_4^z)/\sqrt{3}.
\end{align}

(10)
(11)
(12)

**Appendix B: Tetrahedron basis functions**

A suitable set of basis functions for the non-Kramers doublet that transform according to the irreducible representations $A_1 \oplus 3E \oplus 2T_1 \oplus T_2$ is:

\begin{align}
|A_1\rangle &= (|+++-\rangle + |++++-\rangle + |+-+-+\rangle + |--++-\rangle + |--+-+\rangle + |++++-\rangle)/\sqrt{6} \\
|E^{(1)}_+\rangle &= -|---++\rangle, \quad |E^{(1)}_-\rangle = -|+++-\rangle \\
|E^{(2)}_+\rangle &= (|+++-\rangle + |+++--\rangle + |+-+-+\rangle + |--++-\rangle)/2 \\
|E^{(2)}_-\rangle &= (|--+-+\rangle + |---++\rangle + |+++-\rangle + |++++-\rangle)/2 \\
|E^{(3)}_+\rangle &= (|+++-\rangle + |+++--\rangle + |--++-\rangle + |++++-\rangle)/\sqrt{6} \\
|E^{(3)}_-\rangle &= (|--+-+\rangle + |---++\rangle + |+++-\rangle + |++++-\rangle)/\sqrt{6} \\
|T^{(1)}_{1z}\rangle &= (|+++-\rangle + |+++--\rangle + |--++-\rangle + |++++-\rangle)/\sqrt{2} \\
|T^{(2)}_{1z}\rangle &= (|--+-+\rangle + |+++--\rangle + |+++-\rangle + |++++-\rangle)/\sqrt{2} \\
|T_{2x}\rangle &= -(|+++--\rangle + |+++-\rangle - |--++-\rangle - |++++-\rangle)/\sqrt{2}.
\end{align}

(13)
(14)
(15)

The states $|T_{1,2x}\rangle$ and $|T_{1,2y}\rangle$ can be found by rotating $|T_{1,2z}\rangle$. The corresponding spin-1/2 tetrahedron states can be found using (7). They are:

\begin{align}|A_1\rangle &= (|+++-\rangle + |+++--\rangle + |--++-\rangle + |++++-\rangle)/\sqrt{6} \\
|E^{(1)}_+\rangle &= |+++-\rangle, \quad |E^{(1)}_-\rangle = -|---++\rangle \\
|E^{(2)}_+\rangle &= (|--+-+\rangle + |---++\rangle + |+++-\rangle + |++++-\rangle)/2 \\
|E^{(2)}_-\rangle &= (|+++-\rangle + |+++--\rangle + |+-++-\rangle + |++++-\rangle)/2 \\
|E^{(3)}_+\rangle &= (|+++-\rangle + |+++--\rangle + |--++-\rangle + |++++-\rangle)/\sqrt{6} \\
|E^{(3)}_-\rangle &= (|+++-\rangle + |+++--\rangle + |+-++-\rangle + |++++-\rangle)/\sqrt{6} \\
|T^{(1)}_{1z}\rangle &= (|+++-\rangle + |+++--\rangle + |--++-\rangle + |++++-\rangle)/\sqrt{2} \\
|T^{(2)}_{1z}\rangle &= (|--+-+\rangle + |+++--\rangle + |+++-\rangle + |++++-\rangle)/\sqrt{2} \\
|T_{2x}\rangle &= (|+++--\rangle + |+++-\rangle - |--++-\rangle - |++++-\rangle)/\sqrt{2}.
\end{align}

(16)
(17)
(18)
As described elsewhere, using the spin-1/2 single tetrahedron states, $H^A$ can be represented as a block matrix, with the eigenvalues $J_1/6 - 2J_3/3$ and $2J_3/3 + J_4/6$ in the $A_1$ and $T_2$ sectors, and the matrices
\[
\begin{pmatrix}
-\frac{J_2}{2} & 0 & \frac{\sqrt{2}J_4}{3} \\
0 & -\frac{J_2}{2} & \frac{\sqrt{2}J_4}{3} \\
\frac{\sqrt{2}J_4}{3} & -\frac{\sqrt{2}J_4}{3} & J_4/6 + \frac{\sqrt{2}}{3}
\end{pmatrix}
\]
in the $E$ and $T_1$ sectors. The $E$ sector is doubly degenerate while the $T_1$ and $T_2$ sectors are triply degenerate.

Appendix C: Alternate definitions of the exchange constants

Several different choices of definitions of the four anisotropic nearest neighbour exchange constants have appeared in the literature. This article uses the same definitions as in [11,13,33] with exchange constants denoted as $J_1$, $J_2$, $J_3$ and $J_4$.

The constants used in [22,34,35], denoted $J_{zz}$, $J_{z\pm}$, $J_{\pm\pm}$ and $J_{\pm}$, are proportional to the constants used in this work:

\[
\begin{align*}
J_1 &= -3J_{zz} \quad \text{(C1)} \\
J_2 &= 3J_{z\pm}/\sqrt{2} \quad \text{(C2)} \\
J_3 &= 3J_{\pm\pm} \quad \text{(C3)} \\
J_4 &= 6J_{\pm} \quad \text{(C4)}
\end{align*}
\]

The constants used in the magnetisation study by Sazonov et al. (Ref. 18), denoted $J^u$, $J^v$, $J^w$ and $D$, are defined in Ref. 36. The relation between them and the constants used in this work is

\[
\begin{align*}
J_1 &= -J^u + 2J^w - 2\sqrt{2}D \quad \text{(C5)} \\
J_2 &= J^u/2 + J^w/2 + D/(2\sqrt{2}) \quad \text{(C6)} \\
J_3 &= J^u/2 + 3J^v/4 - J^w/4 - D/\sqrt{2} \quad \text{(C7)} \\
J_4 &= -J^u + 3J^v/2 + J^w/2 + \sqrt{2}D. \quad \text{(C8)}
\end{align*}
\]

Since $J_i$ are reserved for spin-1/2 models, the constants $I_1$, $I_2$, $I_3$ and $I_4$ are used instead for Tb$_2$Ti$_2$O$_7$. Using the results obtained in [18,36], $(J^u, J^v, J^w, D) = (-0.068, -2, -0.098, 0)$ K, we calculate the results given in (60)-(63).

For completeness, we also include the constants used in [37,38], denoted $J_{zz}$, $J_{z\perp}$, $J_{\perp}$ and $J_{\perp}^a$:

\[
\begin{align*}
J_1 &= -3J_{zz} \quad \text{(C9)} \\
J_2 &= -\sqrt{3}J_{z\perp}/(2\sqrt{2}) \quad \text{(C10)} \\
J_3 &= J_{\perp} - J_{\perp}^a/4 \quad \text{(C11)} \\
J_4 &= J_{\perp} + J_{\perp}^a/2. \quad \text{(C12)}
\end{align*}
\]