Transition to Long Range Magnetic Order in the Highly Frustrated Insulating Pyrochlore Antiferromagnet Gd$_2$Ti$_2$O$_7$

N.P. Raju$^1$, M. Dion$^{2,*}$, M. J.P. Gingras$^{3,†}$, T.E. Mason$^{4,‡}$, and J.E. Greedan$^1$

$^1$Brookhouse Institute for Materials Research and Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada
$^2$Department of Physics, University of Waterloo, Waterloo, Ontario, N2L-3G1, Canada
$^3$Laboratoire Louis Néel, Centre National de la Recherche Scientifique, B.P. 166, 38042, Grenoble, Cedex, France
$^4$Department of Physics, University of Toronto, Toronto, Ontario, M5S 1A7, Canada

Experimental evidence from measurements of the a.c. and d.c. susceptibility, and heat capacity data show that the pyrochlore structure oxide, Gd$_2$Ti$_2$O$_7$, exhibits short range order that starts developing at 30K, as well as long range magnetic order at $T \sim 1K$. The Curie-Weiss temperature, $\theta_{CW} = -9.6K$, is largely due to exchange interactions. Deviations from the Curie-Weiss law occur below $\sim 10K$ while magnetic heat capacity contributions are found at temperatures above 20K. A sharp maximum in the heat capacity at $T_c = 0.97K$ signals a transition to a long range ordered state, with the magnetic specific accounting for only $\sim 50\%$ of the magnetic entropy. The heat capacity above the phase transition can be modeled by assuming that a distribution of random fields acts on the $^8S_{7/2}$ ground state for Gd$^{3+}$. There is no frequency dependence to the a.c. susceptibility in either the short range or long range ordered regimes, hence suggesting the absence of any spin-glassy behavior. Mean field theoretical calculations show that no long range ordered ground state exists for the conditions of nearest-neighbor antiferromagnetic exchange and long range dipolar couplings. At the mean-field level, long range order at various commensurate or incommensurate wave vectors is found only upon inclusion of exchange interactions beyond nearest-neighbor exchange and dipolar coupling. The properties of Gd$_2$Ti$_2$O$_7$ are compared with other geometrically frustrated antiferromagnets such as the Gd$_3$Ga$_5$O$_{12}$ gadolinium gallium garnet, RE$_2$Ti$_2$O$_7$ pyrochlores where RE = Tb, Ho and Tm, and Heisenberg-type pyrochlore such as Y$_2$Mo$_2$O$_7$, Tb$_2$Mo$_2$O$_7$, and spinels such as ZnFe$_2$O$_4$.

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I. INTRODUCTION

There has been in the past eight years an enormous amount of theoretical and experimental activity devoted to the study of highly geometrically frustrated antiferromagnetic materials [1]. The main reason for this interest stems from the suggestion that a high degree of frustration can induce sufficiently large zero-temperature quantum spin fluctuations as to destroy long range Neél order even in three dimensions. This could give rise to new exotic and intrinsically quantum mechanical ground states such as dimerized ground states, “spin nematics”, or fully disordered states (e.g. RVB-like) with no broken spin or lattice symmetries [1][2]. Frustration arises when a magnetic system cannot minimize its total classical ground-state energy by minimizing the bond energy of each spin-spin interaction individually [2]. This is the case, for example, in systems where antiferromagnetically coupled spins reside on a network made of basic units such as triangles or tetrahedra. On a triangular plaquette, vector (i.e. XY or Heisenberg) spins can manage the frustration better than Ising moments by adopting a noncollinear structure with the spins making an angle of 120° from each other. Triangular or tetrahedral units can be put together to form a regular lattice such that they are either edge sharing or corner sharing. For example, the space-filling arrangements of edge-sharing triangles and tetrahedra form the well-known triangular and face-centered cubic lattices in two and three dimensions, respectively. In two dimensions, a network of corner-sharing triangles forms the kagomé lattice [1][2]. In three dimensions, a lattice of corner-sharing tetrahedra forms the structures found in spinels, Lave phases, and pyrochlore crystals [1][2][3], while corner-sharing triangles give the familiar garnets [2][3].

Among highly frustrated antiferromagnets, the three-dimensional pyrochlore lattice of corner-sharing tetrahedra is a particularly interesting system (see Fig. 1). Theory [1][2][3] and Monte Carlo simulations [4][5] show that classical Heisenberg spins residing on the vertices of the pyrochlore lattice and interacting only via nearest-neighbor antiferromagnetic exchange do not show a transition to long range magnetic order at nonzero temperature. This is very different from the, also frustrated, classical nearest-neighbor fcc Heisenberg antiferromagnet where long range order occurs at finite-temperature via a 1st order transition driven by thermally-induced order-by-disorder [6][7][8]. Because of their failure to order even at the classical level, the high-frustration present in pyrochlore antiferromagnets would appear to make these systems excellent candidates to search for novel three-dimensional quantum disordered magnetic ground states.
Indeed, recent numerical calculations suggest that the quantum $S = 1/2$ pyrochlore Heisenberg antiferromagnet may be a quantum spin-liquid [1].

In all real systems there exist perturbations, $\{H'\}$, beyond the nearest-neighbor Heisenberg Hamiltonian such as further than nearest-neighbor exchange, single-ion and exchange anisotropy, and magnetic dipolar couplings. For a classical system, one generally expects that such perturbations will select a unique classical ground state to which a transition at nonzero temperature can occur. It is also possible that the energetic perturbations $\{H'\}$ can sufficiently reduce the classical degeneracy such that “additional” order-by-disorder via thermal [19, 20] and/or weak quantum fluctuations [21], such as occur in the fcc antiferromagnet [14, 18], can “complete” the ground-state selection and give rise to a transition to conventional long range Néel order at nonzero temperature. However, in presence of quantum fluctuations (i.e. finite S spin value), one expects that for small spin value $S$ and/or sufficiently weak $\{H'\}$, a quantum disordered phase may occur [12].

What is perhaps one of the most interesting issues in geometrically frustrated antiferromagnet systems, is that a large number of highly frustrated antiferromagnetic insulators exhibit spin-glass behavior rather spin-liquid behavior. For example, in a number of antiferromagnetic insulators exhibit spin-glass behavior rather spin-liquid behavior, such as occur in the fcc antiferromagnet [14, 18], can “complete” the ground-state selection and give rise to a transition to conventional long range Néel order at nonzero temperature. However, in presence of quantum fluctuations (i.e. finite S spin value), one expects that for small spin value $S$ and/or sufficiently weak $\{H'\}$, a quantum disordered phase may occur [12].

Pyrochlores oxides, of which two examples have just been cited, present a number of opportunities for studying geometrically frustrated antiferromagnets. In this structure both cation sites in Fd3m, the 16c site normally occupied by a transition element and 16d normally occupied by a lanthanide, have the same “pyrochlore” topology, i.e., the three dimensional network of corner sharing tetrahedra shown in Figure 1. Thus materials exist with only the 16c site magnetic (Y$_2$Mo$_2$O$_7$) [22–24] and with only the 16d site magnetic, the RE$_2$Ti$_2$O$_7$ materials for example. This latter series has a number of interesting aspects with studies for RE= Tm, Ho and Tb [20]. The RE$_2$Ti$_2$O$_7$ materials are generally quite well-ordered crystallographically, with oxygen non-stoichiometry and 16c/16d site cation admixing at or below the limit of detection by neutron diffraction [25].

Gd$_2$Ti$_2$O$_7$ has not yet been studied in detail and there exist some compelling reasons to do so [26]. Previous reports for Gd$_2$Ti$_2$O$_7$ indicate no long range order down to 1K [27]. The Gd$^{3+}$ ion (4$f^7$) is spin-only with a 8$S_{7/2}$ ground state and thus, crystal field splittings and anisotropy, which play a large role in the properties of the aforementioned Tm$^{3+}$, Ho$^{3+}$ and Tb$^{3+}$ materials, as will be discussed later, are expected to be relatively unimportant. Gd$_2$Ti$_2$O$_7$ then, should be an excellent approximation to a classical Heisenberg antiferromagnetic system with dipole-dipole interactions as leading perturbations $\{H'\}$. In addition it is important to compare this material to the Gd$_3$Ga$_5$O$_{12}$, gadolinium gallium garnet (GGG), where the Gd$^{3+}$ ions reside on a three-dimensional sublattice of corner-sharing triangles [8–12]. GGG has been found to possess a very unusual set of thermodynamic properties with anomalous specific heat behavior, spin glass magnetic properties and no true long range order [13], but incommensurate short range order developing at very low temperatures [11]. Interesting properties are also observed for applied magnetic fields in the range [0.1 – 0.7] Tesla [12].

In this work a detailed study of Gd$_2$Ti$_2$O$_7$ has been carried out including both a.c. and d.c. susceptibility and heat capacity studies. To complement the experimental work, results from mean-field theoretical calculations are presented which take into account exchange and dipolar interactions.

II. EXPERIMENTAL METHOD

A. Sample Preparation

A polycrystalline sample of Gd$_2$Ti$_2$O$_7$ was prepared by high temperature solid state reaction. Starting materials, Gd$_2$O$_3$ and TiO$_2$, were taken in stoichiometric proportions and mixed thoroughly. The mixture was pressed into pellets and heated in an alumina crucible at 1400°C in air for 12 hours. The powder x-ray diffraction pattern of the sample obtained using a Guinier-Hagg camera indicate that the sample formed is single phase with the cubic pyrochlore structure. The size of the conventional cubic unit cell is $a_0 = 10.184(1)$ Å.

B. DC & AC Magnetic Susceptibility Measurements

The DC magnetic susceptibility, $\chi$, was measured using a SQUID magnetometer (Quantum Design, San Diego) in the temperature range 2–300K. The AC susceptibility, $\chi_{AC}$, was measured at different frequencies by the mutual inductance method. The primary coil of the mutual inductor is energized by a frequency generator (DS 335, Stanford Research Systems) and the output across
the two identical secondary coils, wound in opposite directions, was measured using a lock-in-amplifier (SR-830 DSP, Stanford Research Systems). The sample susceptibility was determined from the difference in the outputs with the sample in the middle of the top secondary coil and without the sample. The cryostat used for the temperature variation is described in the section below.

C. Specific Heat Measurements

The specific heat of the sample in the form of a pellet (≈100 mg) was measured in the temperature range 0.6–35K using a quasiadiabatic calorimeter and a commercial Heliox sorption pumped $^3$He cryostat supplied by Oxford Instruments. The sample was mounted on a thin sapphire plate with apiezon for better thermal contact. Underneath the sapphire plate a strain gauge heater and a RuO$_2$ temperature sensor were attached with G-E varnish. The temperature of the calorimetric cell was controlled from the $^3$He pot on the Heliox. The sample temperature was measured using an LR-700 AC resistance bridge at a frequency of 16Hz. The specific heat of the sample was obtained by subtracting the contribution of the addendum, measured separately, from the total measured heat capacity.

III. EXPERIMENTAL RESULTS

The DC susceptibility, Fig. 2a, $\chi$, measured at an applied field of 0.01 Tesla vs temperature is found to obey the Curie-Weiss behavior in the range 10K–300K. An effective magnetic moment of 7.7$\mu_B$/Gd$^{3+}$ obtained from the Curie-Weiss fit is close to the expected value of 7.94$\mu_B$/Gd$^{3+}$ for the free ion, $^8S_7/2$, and a paramagnetic Curie temperature, $\theta_{CW}$, of -9.6(3)K indicates antiferromagnetic interactions between the Gd$^{3+}$ spins. It is worth noting that $\chi$ starts deviating at a temperature of the order of $\theta_{CW}$ as it ought to be for a “conventional” system undergoing a transition to long range order. That $\theta_{CW}$ is predominantly due to exchange interactions as opposed to crystal field effects is confirmed by measurements on the magnetically diluted system (Gd$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$, for which $\theta_{CW}$ is much reduced and of the order of $\sim -0.9$K (Fig. 2b). The absence of any magnetic ordering down to 2K in the concentrated system, even though $\theta_{CW}$ is about five times larger than this temperature, suggests the presence of important magnetic frustration inhibiting the occurrence of magnetic long range order.

In search of a possible magnetic ordering below 2K, AC susceptibility, $\chi_{AC}$, was measured down to 0.3K. The temperature variation of $\chi_{AC}$ for different frequencies, Fig. 3, exhibits two features, a broad peak centered at about 2K and a sharp down turn below about 1K, the latter possibly signaling a transition to long range antiferromagnetic order. $\chi_{AC}(\omega)$ appears to be independent of frequency which would seem to rule out a spin glass state, as opposed to what has been found in other pyrochlore oxides such as Y$_2$Mo$_2$O$_7$ [22,23], T$_2$Mo$_2$O$_7$ [22,24] and the frustrated Gd$_2$Ga$_5$O$_{12}$ garnet [10,12].

The specific heat, $C_p$, as a function of temperature is shown in Fig. 4. There is a broad peak centered around 2K and a very sharp peak slightly below 1K indicating the presence of short range correlations and, in agreement with the AC susceptibility data, the development of long range magnetic order via a sharp transition at 1K. The solid line corresponds to the estimated lattice specific heat, $C_l$, of Gd$_2$Ti$_2$O$_7$ determined by scaling the specific heat for Y$_2$Ti$_2$O$_7$, which is insulating, non-magnetic, and isostructural to Gd$_2$Ti$_2$O$_7$. The magnetic specific heat, $C_m$, was obtained by subtracting $C_l$ from $C_p$ and its temperature variation is shown in Fig. 5. The Gd$^{3+}$ ion has an isotropic spin of $S = 7/2$ with no orbital magnetic moment contribution and the degeneracy of the $8$–level ground state cannot be lifted by the crystal electric field beyond a fraction of a Kelvin. The presence of $C_m$ up to about 30K clearly indicates that the ground state degeneracy is lifted by magnetic interactions.

The magnetic entropy, $S_m$, was obtained by extrapolating the $C_m/T$ behavior to 0K and numerically integrating it vs temperature. The total magnetic entropy is 33.8 J mol$^{-1}$K$^{-1}$ which is close to the expected 2Rln(8) = 34.6 J mol$^{-1}$K$^{-1}$ for an $S = 7/2$ system. The entropy recovered at the long range order temperature is about 50% of the total value which indicates that a sizeable fraction of the entropy is due to the short range correlations present above $T = 1K$.

An attempt was made to fit the $C_m$ data above 1K. A zeroth order model consisting of a simple Schottky anomaly based on a splitting scheme of 8 equally spaced discrete levels, i.e., assuming a unique value for the internal magnetic field at each Gd$^{3+}$ site, gives a poor fit, as might be expected. A much better fit is obtained by assuming a continuous range of energy level splittings with a truncated Gaussian distribution. The probability distribution is normalized such that the area under the curve is unity. The resulting fit is shown in Fig. 5. This model is equivalent to assuming a distribution of internal magnetic fields, i.e., an array of random fields as appropriate to a thermal regime dominated by quasi-static short range magnetic order. A similar approach has been used before to model the specific heat anomaly due to the Gd sublattice in Gd$_2$Mo$_2$O$_7$ [13]. In this pyrochlore structure material the Mo$^{4+}$ sublattice undergoes a spin glass type of order at 60K while the Gd$^{3+}$ specific heat contribution is also a broad peak centered about 9K.

In summary, experimental results obtained from AC and DC susceptibility measurements as well as specific heat measurements reported in Section III give strong compelling evidence for a single sharp transition to a long range ordered state at $T_c = 0.97$K preceded by
a short range ordered regime which extends to approximately 30Tc ≈ 30CW. The heat capacity in this regime can be modelled in terms of a distribution of random exchange fields acting on the 5S7/2 ground state of Gd3+.

IV. MEAN-FIELD THEORY

A. Model and Method

Our aim in this section is to determine, within mean-field theory, what the expected magnetic properties and type of magnetic ordered phase(s) for a classical spin model of Gd2Ti2O7 are.

We first consider the following classical spin Hamiltonian for Gd2Ti2O7:

\[ H = \frac{1}{2} \sum_{(i,j)} -J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{2} \sum_{(i,j)} \left( \frac{\mu_i \cdot \mu_j}{r_{ij}^3} - 3 \frac{\mu_i \cdot \mathbf{r}_{ij} \cdot \mu_j}{r_{ij}^5} \right) \]  

(4.1)

The first term is the isotropic Heisenberg exchange interaction, and the second term is the dipolar coupling between the Gd magnetic moments. For the open pyrochlore lattice structure, we expect very small second and further nearest-neighbor exchange coupling, \( J_{n \geq 2} \), compared to the nearest-neighbor \( J_1 \) (\( J_{n \geq 2} < 0.05J_1 \)). Hence, we first consider the case where the sum in the first (exchange) term of Eq.(4.1) above is restricted to the nearest-neighbor exchange \( J_1 \) only.[33]

Gd3+ has a spin \( S = 7/2 \), which gives an effective dipole moment of \( \mu(Gd^{3+}) = g \mu_B \sqrt{S(S+1)} = 7.94 \mu_B \), with \( g = 2 \), in good agreement with the Curie constant determined in Section III. This gives an estimate for the nearest-neighbor strength of the dipole-dipole interaction \( D_{dd} = 63\mu_0^2/(4\pi r_{nn}^3) \), where \( \mu_0 \) is the magnetic permeability. With a Gd3+ at \( r = (0,0,0) \) and a nearest-neighbor at \( r_{nn} = (a/4,a/4,0) \), where \( a = 10.184 \AA \) is the size of the conventional cubic unit cell, we find \( D_{dd} \approx 0.84 K \).

An estimate of the nearest-neighbor exchange \( J_1 \) can be found from the measured Curie-Weiss temperature (see below). We have \( \theta_{CW} \sim -9.6 K \). This gives for the effective classical nearest-neighbor exchange, \( J_1 = J_1 S(S+1) \sim -4.8 K \) using \( \theta_{CW} = zJ_1 S(S+1)/3 \), where \( z = 6 \) is the number of nearest neighbors. We henceforth use a classical approximation of Eq. (2.1) above, where we use unit length vectors \( \mathbf{S}_i \), and replace \( \mu_i \) by \( \mathbf{S}_i \langle D_{dd} \rangle^{1/2} \), and express \( r_{ij} \) in units of the nearest-neighbor distance. We set \( J_1 = -4.8 K \) and a strength of 0.84K for the nearest-neighbor dipole coupling. Below, we take \( D_{dd}/J_1 = 0.2 \). Hence, unlike in the transition metal pyrochlores, dipole-dipole interactions is the major perturbation at play beyond the nearest-neighbor Heisenberg exchange coupling in Gd2Ti2O7.

We now proceed along the lines of Reimers, Berlinisky and Shi in their mean-field study of Heisenberg pyrochlore antiferromagnets,[13] where we consider the mean-field order parameters, \( \mathbf{B}^m(r_i) \) at site \( r_i \), in terms of Fourier components. The pyrochlore lattice is a non-Bravais lattice, and we use a rhombohedral basis where there are four atoms per unit cell located at \((0, 0, 0), (1/4, 1/4, 0), (1/4, 0, 1/4), \) and \((0, 1/4, 1/4) \) in units of the conventional cubic unit cell. We relabel the spins, \( \mathbf{S}(r_i) \), in terms of unit cell coordinates, and a sublattice index within the unit cell, and take advantage of the translational symmetry of the lattice, and expand the order parameters \( \mathbf{B}^m(r_i) \) in terms of Fourier components. In this case \( \mathbf{B}^m(r_i) \) on the \( a \)’th sublattice site of the unit cell located at \( r_i \) can be written as

\[ \mathbf{B}^m(r_i) = \sum_q \mathbf{B}^m(q) \exp(iq \cdot r_i) . \]  

(4.2)

The spin-spin interaction matrix, \( \mathcal{J}_{\alpha\beta}(|r_{ij}|) \), including both exchange and dipolar interactions, reads:

\[ \mathcal{J}_{\alpha\beta}^ab(|r_{ij}|) = J_1 \delta_{\alpha\beta} \delta_{rij} \delta_{r\alpha\beta} + D_{dd} \left\{ \delta_{\alpha\beta} \left( \frac{r_{ij}}{r_{ij}} \right)^2 - 3 \frac{r_{ij,\alpha} r_{ij,\beta}}{(r_{ij})^5} \right\} , \]  

(4.3)

where \( \delta_{\alpha\beta} \) is the Kronecker delta, and \( \alpha \) and \( \beta \) refer to the \( x, y, z \) cartesian components of \( \mathbf{S} \), and \( r_{ij,\alpha} \). \( r_{ij,\alpha} \) denotes the \( \alpha \) components of the interspin vector \( r_{ij} \) that connects spin \( \mathbf{S}_i^a \) to spin \( \mathbf{S}_j^b \). We write \( \mathcal{J}_{\alpha\beta} \) in terms of its Fourier components as

\[ \mathcal{J}_{\alpha\beta}^ab(|r_{ij}|) = \frac{1}{n} \sum_q \mathcal{J}_{\alpha\beta}^ab(q) \exp(-iq \cdot r_{ij}) . \]  

(4.4)

where \( N \) is the number of unit cells with 4 spins per unit cell.

The quadratic part of the mean-field free-energy, \( F^2 \), then becomes,[13]

\[ F^2(T)/N = \frac{1}{2} \sum_{q,(\alpha\beta),(\alpha\beta)} B^m(q) \left\{ 3T \delta_{\alpha\beta} \delta_{\alpha\beta} \mathcal{J}_{\alpha\beta}^ab(q) \right\} B^m(-q) . \]  

(4.5)

Diagonalizing \( F^2(T) \) requires transforming to normal modes of the system

\[ B^m(q) = \sum_i \sum_\beta U^m_{\alpha\beta} \Phi^m_{\beta}(q) \]  

(4.6)

where \( \Phi^m_{\beta}(q) \) are the eigenmodes, and \( U(q) \) is the unitary matrix that diagonalizes \( \mathcal{J}(q) \) in the spin–sublattice space, with eigenvalues \( \lambda(q) \).

\[ \sum_b \sum_{\beta} F_{ab}^{\alpha\beta}(q) U_{\beta\gamma}(q) = \lambda_i(q) U_{i\gamma}(q) \]  

Henceforth we will use the convention that indices (ab) label sublattices, that indices (ijk) label the normal modes, and that (\alpha\beta\gamma) label spin components. We express \( F^{(2)}(T) \) in terms of normal modes

\[ F^{(2)}/N = \frac{1}{2} \sum_q \sum_i \sum_\gamma \Phi_i(q)\Phi_i(-q) \left\{ 3T - \lambda_i(q) \right\} \]

The first ordered state of the system occurs at the temperature

\[ T_c = \frac{1}{3} \max_{q,i}\{\lambda_i(q)\} \]

where \( \max_{q,i}\{\lambda_i(q)\} \) indicates a global maximum of the spectrum of \( \lambda_i(q) \) for all \( q \).

Let us briefly explain how we proceed using the above set of equations to determine the “soft mode(s)” of the system at \( T_c \). Firstly, the Fourier transform of \( F_{ab}^{\alpha\beta}(r_{ij}) \) is calculated using Eq. (4.3). For the rhombohedral basis used above, the space is of dimension \( D_S = D_{st} \), where the spin-component subspace, \( D_S \), is of dimension 3×3 and the sublattice subspace, \( D_{st} \), is of dimension 4×4. The eigenvalues, \{\lambda_i(q)\}, and eigenvectors \( \Phi_i(q) \) are determined by reshaping \( F_{ab}^{\alpha\beta}(q) \) into a 12×12 array. The pyrochlore lattice has a symmetry of inversion with respect to a lattice point and this implies that \( F_{ab}^{\alpha\beta}(q) \) is real and symmetric. The eigenvalues and eigenvectors are found using a standard numerical packages for eigen problems of real symmetric matrices.

B. Results

For \( D_{dd} = 0 \), we recover the results of Ref. [13]. Before we present the results with the dipolar interactions, we review what the mean-field results found for the isotropic pyrochlore class Heisenberg antiferromagnet depending on the values of the second, \( J_2 \) and third, \( J_3 \) nearest-neighbor exchange couplings are [13]. For \( J_2 = J_3 = 0 \) there are two dispersionless unstable or critical modes throughout the Brillouin zone. There are therefore no selected wavevector for long range order. Numerical work has shown that no long range order occurs at nonzero temperature in the nearest-neighbor classical Heisenberg pyrochlore antiferromagnet [12,13]. For \( J_3 = 0 \), ferromagnetic \( J_2 > 0 \) gives rise to an ordering at an incommensurate wavevector, while for antiferromagnetic \( J_2 < 0 \), the system orders at \( q^* = 0 \). For \( J_2 = 0 \), and ferromagnetic \( J_3 > 0 \), the system also orders at \( q^* = 0 \), while there are dispersionless (degeneracy lines) along certain symmetry directions for \( J_2 = 0 \) and antiferromagnetic \( J_3 < 0 \). In the overall parameter space \{\( J_2/J_1, J_3/J_1 \}\), long range order is always expected to occur at nonzero temperature within mean-field theory, except for \( J_2 = 0 \) and antiferromagnetic \( J_3 \leq 0 \) (Fig. 6 in Ref. [13]).

We now consider the case where \( D_{dd}/J_1 = 0.2 \), and first set \( J_2 = J_3 = 0 \). Naively, one might have thought that (i) the long range and (ii) anisotropic nature of the dipolar interactions would lift all macroscopic ground state degeneracies that occur in the isotropic nearest-neighbor \( (J_1 < 0) \) Heisenberg antiferromagnet and give rise to a unique selected wavevector \( q^* \), at which long range order would occur [13]. This is not the case. We find that the largest eigenvalue \( \lambda_i(q) \) that controls the mean-field \( T_c \) (Eq. 4.9) is dispersionless along the star of the [111] direction in the cubic basis (Fig. 6). The figure shows \( \lambda_{max}(q) \) as a function of \( q_1 \) in the [110] and \( q_2 \) in the [001], where \( \lambda_{max}(q) \) is the largest eigenvalue of \( \lambda_i(q) \) at a given \( q \). Hence, no-long range order is to be expected in this system within the mean-field approximation [11]. In this context, it is interesting to note that the combined long range dipolar and RKKY interactions in the problem of nuclear magnetism in Cu and Ag do not lead either to a full selection of a unique classical long range ordered state below the mean-field \( T_c \). Such “degeneration lines” as found in the present system also occur in other frustrated systems such as the nearest-neighbor Heisenberg fcc antiferromagnet where there are degeneration lines along the \( \pi/a(1,q,0) \) direction [13, 14]. Degeneration (spiral) lines also occur in the more complicated case of the rhombohedral antiferromagnet [13]. By analogy with the work on the frustrated fcc [13, 14, 15, 16] and rhombohedral [13] antiferromagnets, we expect that for degeneration lines (as opposed to degeneration zone as in the case of the nearest-neighbor pyrochlore antiferromagnet [14,15]), Thermal and/or quantum fluctuations will restore long range order at finite temperature via a process of order-by-disorder. Work in that direction is in progress and will be reported elsewhere [17].

We find that for either nonzero ferromagnetic or antiferromagnetic, \( |J_2| \ll D_{dd} \) and/or \( |J_3| \ll D_{dd} \), that the line-degeneracy along the [111] direction is lifted and that a specific value \( q^* \) along that direction is picked up, giving rise to an absolute maximum of \( \lambda_i(q) \). For sufficiently large \( |J_2| \) and/or \( |J_3| \) compared to \( D_{dd} \), a different selected wavevector direction is chosen as found by Reimers et al. [13], except that here, there is no degeneration line occurring for \( J_2 = 0 \) and \( J_3 < 0 \), as found in Ref. [13] when \( D_{dd} \neq 0, D_{dd} \ll |J_2| \) and \( D_{dd} \ll |J_3| \). In other words, all non-global degeneracies are lifted in the case where \( D_{dd} \neq 0, J_2 \neq 0, \) and \( J_3 \neq 0 \). In summary, we would expect that long range order should occur in \( \text{Gd}_2\text{Ti}_2\text{O}_7 \), either via an order-by-disorder mechanism, or via energetic selection of an ordering wavevector via superexchange couplings beyond \( J_1 \) and dipolar interactions, \( D_{dd} \).
V. DISCUSSION

It is useful to compare Gd$_2$Ti$_2$O$_7$ with related systems such as the remaining RE$_2$Ti$_2$O$_7$ materials, Gd$_3$Ga$_5$O$_{12}$ (GGG), Gd$_2$O$_3$, cubic-Gd$_2$O$_3$ (C–Gd$_2$O$_3$) and also GdAlO$_3$ for reasons which should soon become clear.

C-Gd$_2$O$_3$ crystallizes in the so-called bixbyte structure, Ia$\bar{3}$, with two distinct crystallographic sites. However, the sublattice of the two sites taken together is an excellent approximation to that for GGG. The heat capacity whether C-Gd$_2$O$_3$ or quasi degenerate dispersion lines or surfaces of zero magnitude [39].

Returning to the RE$_2$Ti$_2$O$_7$ series, as mentioned, Gd$_2$Ti$_2$O$_7$ offers the opportunity to study a system in which the crystal field and anisotropy perturbations are minimized. As this is certainly not the case for RE=Tb, Ho and Tm, some comment on the symmetry of the local environment at the RE site is in order. The 16d rare-earth site is coordinated by two sets of oxygen atoms, six O1(48f) and two O2(8b), giving eight-fold coordination overall. It is important to note that the RE site symmetry is strongly distorted from cubic, which would imply eight equal RE-O distances (for RE=Gd the sum of the ionic radii give 2.42 \( \AA \) and O-RE-O angles of 70.5°, 109.5° and 180°. In RE$_2$Ti$_2$O$_7$, the six O1 atoms form a puckered ring about the RE (Gd-O distance of 2.55\( \AA \)) and the two O2 atoms a linear O2-RE-O2 unit oriented normal to the mean plane of the puckered ring with extremely short RE-O2 distances(Gd-O distance is 2.21\( \AA \)). This Gd-O distance is among the shortest, if not the shortest, such distance known in Gd oxide chemistry and implies a very strong interaction. This observation suggests that a crystal field of axial symmetry might be an even better approximation than cubic. The O2-Gd-O2 angle is of course 180°, while the O1-Gd-O1 angles are 62.7°, 117° and 180°. Thus, it is best, when thinking about the RE site crystal field, to consider the true symmetry, i.e., 3m(D$_3d$) and if the RE site crystal field, to consider the true symmetry, -3m(D$_3d$).

The known situation with respect to the presence or absence of long range order in the RE$_2$Ti$_2$O$_7$ pyrochlores is summarized in Table 1.

One obvious correlation is that those RE$_2$Ti$_2$O$_7$ pyrochlores which contain a Kramers (odd electron) ion nearly always show long range order (Dy being the exception) while those with a non-Kramers (even electron) ion do not. A “zeroth order” interpretation of the trends in Table 1. is then, that the action of the relatively low symmetry crystal field induces a true singlet ground state in the non-Kramers ions and this is the explanation of the absence of long range order (LRO). There is good evidence that such is the case for RE=Tm from a combination of susceptibility [29,30], inelastic neutron scattering [31], and crystal field calculations (using the correct -3m symmetry) [32]. Experimentally [31], the singlet state is well-separated by 120K from the nearest excited state which is in remarkable agreement with the aforementioned crystal field calculations which predict 118K [30].

The other two non-Kramers ions are not so simple. For Ho$_2$Ti$_2$O$_7$, the ground state is thought to be a singlet [32], in agreement with crystal-field calculations [30], and the nearest neighbor exchange is weakly ferromag-
spin glass material with a well-known geometrically frustrated antiferromagnet nearest-neighbor Heisenberg pyrochlore antiferromagnetic exchange is responsible for the behavior observed in Ho$_2$Ti$_2$O$_7$ [19]. This material also exhibits spin dynamics and spin freezing reminiscent of the disorder-free, intrinsic glassy behavior exhibited by the “ice model” [21,31] with an exponential decrease of the spin lattice relaxation rate suggestive of Orbach processes [33]. In contrast Gd$_2$Ti$_2$O$_7$ exhibits no apparent dynamics or spin-glassiness at any temperature even above $T_c$

A detailed study of Tb$_2$Ti$_2$O$_7$ will be described in a subsequent publication [15]. The salient facts are that the Tb$^{3+}$ ground state also appears to be a doublet but not so well isolated from several other levels within 15K–100K. The exchange interactions are relatively strongly antiferromagnetic, comparable to Gd$_2$Ti$_2$O$_7$, and short range magnetic correlations persist up to at least 30K, also similar to what is found in Gd$_2$Ti$_2$O$_7$. Tb$_2$Ti$_2$O$_7$ does not order down to 70 mK [24]. The lack of LRO in this system is difficult to understand [35]. Indeed, as argued in refs [20,22] a nearest-neighbor Heisenberg antiferromagnet with a [111] easy axis is a trivial problem with an effectively non-frustrated and unique (two-fold Ising-like globally degenerate) classical ground state, and should therefore show a phase transition at nonzero temperature in the limit of sufficiently strong crystal-field level splitting compared to the superexchange $J$.

From the above discussion we can conclude that each RE$_2$Ti$_2$O$_7$ material presents its own special set of circumstances where details of the finely tuned relative strength of crystal field parameters, exchange and dipolar couplings play a crucial role, and a blanket explanation for the apparent systematics of Table 1 will not be found. It is worth noting an interesting paradox. Gd$_2$Ti$_2$O$_7$ represents the case for which some of the perturbations which might be thought to aid in the selection of an unique ground state, i.e., crystal fields and anisotropy, are largely absent, yet it orders. On the other hand, Tb$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ in which crystal fields and anisotropy are clearly important, do not order and it is likely that these perturbations in fact inhibit the occurrence of long range order by competing with important interactions other [19] than nearest-neighbor Heisenberg antiferromagnetic exchange [20,32]. Some other interesting recent results have been found in the Y$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ pyrochlores [18].

It is also useful to compare Gd$_2$Ti$_2$O$_7$ with other Heisenberg pyrochlores such as Y$_2$Mo$_2$O$_7$ [23] and Heisenberg spinels such as ZnFe$_2$O$_4$ [31]. Y$_2$Mo$_2$O$_7$ is a well-known geometrically frustrated antiferromagnet spin glass material with $\theta_{CW}/T_f \approx 10$, $T_f$ being the spin freezing temperature of 21K [28]. Here too, only a speculation can be offered for the differences as follows. Because of the high level of degeneracy across the zone, the nearest-neighbor Heisenberg pyrochlore antiferromagnet is expected to be fragile against a small, random disorder level, $x$, and will have a propensity to develop a disorder-driven spin glass ground state the smaller the perturbations $\{H'\}$ beyond the nearest-neighbor exchange interaction is [20]. We expect that the critical disorder level for the Néel to spin-glass transition, $x_c$, will go to zero as $\{H'\}$ goes to zero [6]. For example, in Y$_2$Mo$_2$O$_7$, there is preliminary evidence that the second neighbor exchange parameter, $J_2$, is only a few percent of $J_1$. In Gd$_2$Ti$_2$O$_7$ on the other hand the leading corrections $\{H'\}$ are dipolar interactions, $D_{dd}$, and of order 20% of $J_1$. In other words $\{H'\}/J_1$ is not small in Gd$_2$Ti$_2$O$_7$ and the anisotropy of the dipolar interactions will possibly introduce sizeable stabilizing anisotropy gaps to the spin-wave excitations out of the selected long range ordered ground state. Both the relative size of $D_{dd}/J_1$ and the “spin-holding” effect of the anisotropy of dipolar interactions will result in a much increased $x_c$ compared to more isotropic Heisenberg systems with small $\{H'\}$ [6]. In summary in this picture weak disorder drives the spin glass transition in Y$_2$Mo$_2$O$_7$ while the strong and anisotropic dipolar interactions “helps” stabilize long range order in Gd$_2$Ti$_2$O$_7$. In this context the existence of a very weakly dispersive line along [111] restored by order-by-disorder, or perturbative $J_2$ and $J_3$, would suggest that, as in the fcc antiferromagnet [10], weak random disorder would rapidly drive Gd$_2$Ti$_2$O$_7$ into a spin glass state.

Finally, it is interesting to compare the behavior of Gd$_2$Ti$_2$O$_7$ with the frustrated ZnFe$_2$O$_4$ antiferromagnet spinel where Fe$^{3+}$ is a $^6S_{5/2}$ closed shell ion for which single-ion anisotropy should be negligible as is the case for the $^8S_{7/2}$ Gd$^{3+}$ ion in Gd$_2$Ti$_2$O$_7$. In the insulating normal Heisenberg spinel ZnFe$_2$O$_4$, where the Fe$^{3+}$ magnetic moments occupy a lattice of corner-sharing tetrahedra, muon spin relaxation and neutron studies have revealed that long range antiferromagnetic order (LRO) develops below $T_N = 10.5$K. However, already at temperatures of about $T \approx 10T_N$ a short range antiferromagnetic order (SRO) develops which extends through $\approx 70\%$ of the sample volume just above $T_N$. Below $T_N$ antiferromagnetic SRO and LRO coexist. At 4.2K still $\approx 20\%$ of the sample are short range ordered. The regions exhibiting SRO are very small $\approx 30\%$. The physical origin of the SRO as well as partial glassy behavior in ZnFe$_2$O$_4$ remains an enigma. Hence, while it appears that Gd$_2$Ti$_2$O$_7$ displays conventional antiferromagnetic long range order and Y$_2$Mo$_2$O$_7$ shows full-blown spin-glass behavior, ZnFe$_2$O$_4$ exhibits a combination of both short and long range antiferromagnetic order, as well as spin-glassy behavior. The origin of the difference between the Gd and Fe based pyrochlore lattice antiferromagnets in terms of their coexistence of long range order and spin-glassy behavior is not known. Possibly different range of interactions, presence of strong dipolar anisotropy in Gd$_2$Ti$_2$O$_7$ compared to a much more overall isotropic spin-spin interaction in ZnFe$_2$O$_4$ may play some role. In
light of this, it would be interesting to study in further detail the magnetic properties of Gd$_2$Ti$_2$O$_7$ using muon spin relaxation and neutron scattering methods.

VI. CONCLUSION

Evidence has been presented from a.c. and d.c. susceptibility and specific heat measurements, that the frustrated Gd$_2$Ti$_2$O$_7$ insulating pyrochlore exhibits a transition to a long range ordered state at 0.97K as opposed to a spin glass or spin liquid state as often observed in other pyrochlore materials. From specific heat measurements, short range magnetic correlations have been found to extend to $T > 30T_c$ and the entropy removal below $T_c$ is only about 50%. From a mean field theoretical study it is concluded that no long range order should exist for the pyrochlore lattice for nearest neighbor antiferromagnetic interactions, $J_1$, only, even upon inclusion of long range, anisotropic dipolar couplings, $D_{dd}$. Long range order at various commensurate or incommensurate wave vectors is predicted to occur only upon including a finite second, $J_2$, and/or third, $J_3$, nearest-neighbor exchange interactions beyond $J_1$ and $D_{dd}$. Long range order could also be driven by thermal and/or quantum fluctuations via an order-by-disorder mechanism. The exact wave vector depends on the relative signs and magnitudes of $J_2$, $J_3$ and $D_{dd}$. It would be of interest to investigate further the nature of the ordered state in zero and applied fields in Gd$_2$Ti$_2$O$_7$ by neutron scattering and muon spin relaxation methods. Finally, we argued above that the related fcc antiferromagnet material, cubic-Gd$_2$O$_3$, should be reconsidered as a geometrically frustrated antiferromagnet and is worthy of further study.

VII. ACKNOWLEDGEMENTS

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* Present Address: Serin Physics Laboratory, Rutgers University, Piscataway, NJ 08555-0849
† Permanent Address: Department of Physics, University of Waterloo, Waterloo, Ontario,N2L-3G1, Canada

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[39] To obtain a more reliable estimate of $D_{dd}/J_1$, one should determine the Curie-Weiss contribution from dipole-dipole interactions to the high-temperature limit of $\chi$, and hence $\theta_{CW}$, in order to extract a more precise estimate of $J_1$. The results of such calculations will be produced elsewhere. Note that the specific value chosen for $D_{dd}/J_1$ with $J_2 = J_3 = 0$ does not affect the results of a line of degeneracy along the star of [111] (Ref. [33]).

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TABLE I
Presence or Absence of Long Range Order in $\text{RE}_2\text{Ti}_2\text{O}_7$
Pyrochlores.

| Rare Earth | $n$ in 4th | Long Range Order ($T_c$) | Ref.          |
|------------|-----------|--------------------------|---------------|
| Gd         | 7         | YES, (0.97K)             | This work     |
| Tb         | 8         | NO                       | Ref. [34,35]  |
| Dy         | 9         | NO                       | Ref. [34,35]  |
| Ho         | 10        | NO                       | Ref. [34,35]  |
| Er         | 11        | YES, (1.25K)             | Ref. [34,35]  |
| Tm         | 12        | NO                       | Ref. [34,35]  |
| Yb         | 13        | YES, (0.21K)             | Ref. [34,35]  |

![Pyrochlore lattice](image1)

FIG. 1. Pyrochlore lattice of corner-sharing tetrahedra.

![Gd$_2$Ti$_2$O$_7$](image2)

FIG. 2. (a) Inverse molar susceptibility, $1/\chi$, of Gd$_2$Ti$_2$O$_7$ against temperature in the temperature range $T = [2 - 25]$ K, and in the temperature range $T = [2 - 300]$ K in the inset.
(b) Inverse molar susceptibility, $1/\chi$, of (Gd$_{0.02}$Y$_{0.98}$)$_2$Ti$_2$O$_7$ against temperature in the temperature range $T = [2 - 25]$ K, and in the temperature range $T = [2 - 300]$ K in the inset.
FIG. 3. Real part of the ac susceptibility, $\chi'$, vs. temperature measured at different frequencies.

FIG. 4. Specific heat, $C_p$, of $Y_2Ti_2O_7$ as function of temperature. The solid line corresponds to the lattice specific heat, $C_l$, estimated from the measurements on the non-magnetic $Y_2Ti_2O_7$.

FIG. 5. Magnetic specific heat, $C_m$, (obtained by subtracting $C_l$ from $C_p$) against temperature. The solid line represents the theoretical fit (see text for details). The inset shows a blown-up region of $C_m$ in the low-temperature regime.
FIG. 6. Largest eigenvalue $\lambda_{\text{max}}(q)$ as a function of wavevector $q$ for $D_{dd}/J_1 = 0.2$ and $J_2 = J_3 = 0$. A degeneration line occurs for $q$ in the star of the [111] direction. The small “ripples” seen on the degeneration lines along (111) and (11$\bar{1}$) directions are due to the finite number (500) nearest-neighbors considered in the dipolar interactions. When considering more than 10 nearest-neighbors, the maximum of $\lambda(q)$ always occurs on the star of [111] with the amplitude of the modulations due to the dipolar cut-off continuously decreasing as the number of nearest-neighbors is increased to infinity.