Low temperature specific heat and possible gap to magnetic excitations in the Heisenberg pyrochlore antiferromagnet \( \text{Gd}_2\text{Sn}_2\text{O}_7 \)

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The \( \text{Gd}_2\text{Sn}_2\text{O}_7 \) pyrochlore Heisenberg antiferromagnet displays a phase transition to a four sublattice Néel ordered state at a critical temperature \( T_v \sim 1 \) K. The low-temperature state found via neutron scattering corresponds to that predicted by a classical model that considers nearest-neighbor antiferromagnetic exchange and long-range dipolar interactions. Despite the seemingly conventional nature of the ordered state, the specific heat \( C_v \) has been found to be described in the temperature range \( 350 \) mK \( \leq T \leq 800 \) mK by an anomalous power law, \( C_v \sim T^2 \). A similar temperature dependence of \( C_v \) has also been reported for \( \text{Gd}_2\text{Ti}_2\text{O}_7 \), another pyrochlore Heisenberg material. Such behavior is to be contrasted with the typical \( T^3 \) behavior expected for a three-dimensional antiferromagnet with conventional long-range order which is then generally accompanied by an \( \exp(-\Delta/T) \) behavior at lower temperature where anisotropy effects induce a gap \( \Delta \) to collective spin excitations. Such anomalous \( T^2 \) behavior in \( C_v \) has been argued to be correlated to an unusual energy-dependence of the density of states which also seemingly manifests itself in low-temperature spin fluctuations found in muon spin relaxation experiments. In this paper, we report calculations of \( C_v \) that consider spin wave like excitations out of the Néel order observed in \( \text{Gd}_2\text{Sn}_2\text{O}_7 \) via neutron scattering. We argue that the parametric \( C_v \propto T^2 \) does not reflect the true low-energy excitations of \( \text{Gd}_2\text{Sn}_2\text{O}_7 \). Rather, we find that the low-energy excitations of this material are antiferromagnetic magnons gapped by single-ion and dipolar anisotropy effects, and that the lowest temperature of \( 350 \) mK considered in previous specific heat measurements accidentally happens to coincide with a crossover temperature below which magnons become thermally activated and \( C_v \) takes an exponential form. We argue that further specific heat measurements that extend down to at least \( 100 \) mK are required in order to ascribe an unconventional description of magnetic excitations out of the ground state of \( \text{Gd}_2\text{Sn}_2\text{O}_7 \) or to invalidate the standard picture of gapped excitations proposed herein.

I. INTRODUCTION

A. Persistent spin dynamics in pyrochlores

A magnetic system with Heisenberg spins that sit on the vertices of a three-dimensional pyrochlore lattice of corner sharing tetrahedra and interact among themselves via nearest-neighbor antiferromagnetic exchange interactions is highly geometrically frustrated. Such a system is theoretically predicted to not develop conventional magnetic long range order at finite temperature for either classical or quantum spins. As a result of this frustration, real magnetic materials with antiferromagnetically coupled spins on this pyrochlore structure are highly sensitive to weak perturbative interactions beyond nearest-neighbor exchange which dramatically affect the nature of the low temperature state. It is partially for this reason that the insulating \( \text{R}_2\text{M}_2\text{O}_7 \) magnetic pyrochlore oxides have attracted such a great deal of attention in recent years. Indeed, this family of materials has been found to display a variety of magnetic states and exotic low temperature behaviors that strongly depend on the specific elements \( \text{R} \) and \( \text{M} \) considered.

In \( \text{R}_2\text{M}_2\text{O}_7 \), the \( \text{R} \) site is occupied by a trivalent ion, such as diamagnetic \( \text{Y}^{3+} \) or a magnetic rare earth ion (\( \text{R} = \text{Gd}^{3+}, \text{ Tb}^{3+}, \text{ Dy}^{3+}, \text{ Ho}^{3+}, \text{ Er}^{3+}, \text{ Tm}^{3+}, \text{ Yb}^{3+} \)) while the \( \text{M} \) site is occupied by a tetravalent ion which can be diamagnetic, such as \( \text{Ti}^{4+} \) or \( \text{Sn}^{4+} \), or magnetic, such as \( \text{Mo}^{4+} \) or \( \text{Mn}^{4+} \). Both the \( \text{R} \) and \( \text{M} \) sites form disordered materials like \( \text{Gd}_2\text{Ti}_2\text{O}_7 \) and \( \text{Gd}_2\text{Sn}_2\text{O}_7 \), spin ices such as \( \text{Ho}_2\text{Ti}_2\text{O}_7 \) and \( \text{Dy}_2\text{Ti}_2\text{O}_7 \), conventional long range ordered materials like \( \text{Gd}_2\text{Ti}_2\text{O}_7 \) and \( \text{Gd}_2\text{Sn}_2\text{O}_7 \) and even possible spin liquids as in the case of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) and \( \text{R}_2\text{Sn}_2\text{O}_7 \).

One common thread throughout these various materials is that several experimental studies have found that, almost without exceptions, all insulating rare-earth pyrochlore materials \( \text{R}_2\text{Ti}_2\text{O}_7 \) and \( \text{R}_2\text{Sn}_2\text{O}_7 \) display temperature-independent spin dynamics down to \( T_0 \sim 0(10^4) \) mK. Indeed, residual low temperature dynamics has been found in pyrochlore magnetic materials with low temperature states that range from not understood whatsoever to seemingly conventional long range ordered. We note in passing that persistent low-temperature spin dynamics has also been found in the \( \text{Gd}_3\text{Ga}_5\text{O}_{12} \) garnet (GGG) and in the \( \text{SrCr}_2\text{Ga}_4\text{O}_{19} \) kagome antiferromagnet. We now briefly review the various experimentally observed behaviors of the \( \text{R}_2\text{Ti}_2\text{O}_7 \) and \( \text{R}_2\text{Sn}_2\text{O}_7 \) pyrochlore oxides.
Strong evidence for fluctuating spins down to extremely low temperatures has been observed in Tb$_2$Ti$_2$O$_7$ where Ti$^{4+}$ at the M site is non-magnetic. The reason for the failure of Tb$_2$Ti$_2$O$_7$ to develop long-range magnetic order above 50 mK despite a Curie-Weiss temperature, $\theta_{C\text{-}W} \sim -14$ K remains to this day largely unexplained. Yb$_2$Ti$_2$O$_7$ is perhaps just as intriguing, with specific heat measurements revealing a sharp first order transition at $T_c \approx 0.24$ K\textsuperscript{6,25,26}, but with the spins not appearing static below $T_c$ since muon spin relaxation ($\mu$SR) and Mössbauer spectroscopy find significant spin dynamics down to the lowest temperature.\textsuperscript{28} Hence, the observed first order transition in Yb$_2$Ti$_2$O$_7$ seems rather unconventional.

Ho$_2$Ti$_2$O$_7$\textsuperscript{12,13,14} and Dy$_2$Ti$_2$O$_7$\textsuperscript{15,16} are frustrated ferromagnets\textsuperscript{12} and possess an extensive low-temperature magnetic entropy\textsuperscript{14,15} similar to that of the common hexagonal $I_h$ phase of water ice.\textsuperscript{14,15} As such, the (Ho,Dy)$_2$(Ti,Sn)$_2$O$_7$ materials are referred to as spin ice.\textsuperscript{25} Theoretical and numerical studies have shown that the spin ice behavior originates from the long range nature of magnetic dipole-dipole interactions.\textsuperscript{26,27} Numerical Monte Carlo studies using non-local loop dynamics predict that those interactions should lead to long range order at low temperatures.\textsuperscript{25} Yet, at variance with the numerical predictions, experimental studies of the Dy$_2$Ti$_2$O$_7$\textsuperscript{28} and Ho$_2$Ti$_2$O$_7$\textsuperscript{12,40,41} have not found a transition to long range order down to 60 mK. In particular, muon spin relaxation ($\mu$SR)\textsuperscript{41} and neutron spin echo\textsuperscript{42} experiments find evidence for Ho$^{3+}$ spin dynamics well below $T_{SI}$ in Ho$_2$Ti$_2$O$_7$. Interestingly, a recent neutron scattering study on Tb$_2$Sn$_2$O$_7$ found a transition to a long-range ordered state at $T_c \approx 0.87$ K with an analysis of the scattering intensity indicating that the observed state is a long-range spin ice state.\textsuperscript{42} However, even more recent $\mu$SR studies find that the state at $T < T_c$ in Tb$_2$Sn$_2$O$_7$ remains dynamic down to the lowest temperature.\textsuperscript{43,44} Er$_2$Ti$_2$O$_7$, like Tb$_2$Sn$_2$O$_7$, was found via neutron scattering to display long range order below 1.2 K.\textsuperscript{45} Yet, $\mu$SR found persistent spin dynamics down to the lowest temperature.\textsuperscript{45}

Gd$_2$Ti$_2$O$_7$ displays two consecutive transitions at $T^+_c \sim 1$ K and $T^-_c \sim 0.7$ K.\textsuperscript{16,17} Neutron scattering experiments\textsuperscript{18} found that the magnetic state between $T^-_c$ and $T^+_c$ has one site out of four on a tetrahedral unit cell that is paramagnetic and fluctuating. At $T < T^-_c$, the fourth site orders, but remains much more dynamic than the three other sites. The microscopic mechanism giving rise to the two experimentally observed states is still not understood. Here too, in Gd$_2$Ti$_2$O$_7$, $\mu$SR finds considerable spin dynamics persisting down to 20 mK.\textsuperscript{16,17} A phenomenological model for the density of states, $g(\epsilon)$, has been proposed for the low-temperature state of Gd$_2$Ti$_2$O$_7$. Most significantly, the proposed model for $g(\epsilon)$ was shown to describe the peculiar temperature dependence of the magnetic specific heat, $C_v(T)$, in Gd$_2$Ti$_2$O$_7$ which was found to be $C_v(T) \propto T^2$ below $T^-_c$. Such $C_v \propto T^2$ behavior is rather unconventional. Indeed, in a conventional long-range ordered three-dimensional antiferromagnet, $C_v \sim T^3$ down to a temperature where the temperature dependence turns to $C_v \sim \exp(-\Delta/T)$ because of a gap $\Delta$ in the excitation spectrum induced by single ion anisotropy or anisotropic spin-spin interactions.

In all the pyrochlore systems reviewed above, Tb$_2$Ti$_2$O$_7$, Yb$_2$Ti$_2$O$_7$, (Ho,Dy)$_2$Ti$_2$O$_7$, Tb$_2$Sn$_2$O$_7$, Er$_2$Ti$_2$O$_7$, and Gd$_2$Ti$_2$O$_7$, some theoretical lapses exist in our understanding of the equilibrium thermodynamic low-temperature state. Hence, it is perhaps not completely surprising that the spin dynamics appears unconventional in these materials with, in particular, a temperature independent $\mu$SR spin polarization relaxation rate down to a baseline temperature $T_0 \sim 10^4$ mK. However, that tentative self-reassured standpoint is put on shaky ground by the $\mu$SR and specific heat measurements on Gd$_2$Sn$_2$O$_7$ that we now discuss.

B. The case of Gd$_2$Sn$_2$O$_7$

It was first proposed that the aforementioned Gd$_2$Ti$_2$O$_7$ material would be a good candidate for a classical Heisenberg pyrochlore antiferromagnet with leading perturbations coming from long-range magnetic dipole-dipole interactions.\textsuperscript{16} The reason for this is that Gd$^{3+}$ is an S-state ion with half-filled 4f shell, hence orbital angular moment $L = 0$, and spin $S = 7/2$. Spin anisotropy is therefore expected to be much smaller than for the above Ho, Dy and Tb based rare earth materials.\textsuperscript{18} In that context, Gd$_2$Sn$_2$O$_7$ should be similar to Gd$_2$Ti$_2$O$_7$; the main difference being that Gd$_2$Sn$_2$O$_7$ displays only one phase transition observed from a paramagnetic to a long-range ordered phase at $T_c \sim 1$ K.\textsuperscript{29} Perhaps most interestingly, unlike Gd$_2$Ti$_2$O$_7$, the experimentally observed long-range ordered phase in Gd$_2$Sn$_2$O$_7$ corresponds to the one predicted by Palmer and Chalker for the classical Heisenberg pyrochlore antiferromagnet model with perturbative long-range dipolar interactions.\textsuperscript{29} It is possible that the experimentally observed transition in Gd$_2$Sn$_2$O$_7$ corresponds to two very close transitions\textsuperscript{30,31} that are not resolved.\textsuperscript{32}

From our perspective, Gd$_2$Sn$_2$O$_7$ is an exemplar of the intriguing behavior discussed above. Yet, it offers itself as a crucial system to understand. The reasons are as follows: (i) as in Gd$_2$Ti$_2$O$_7$, and all the materials previously described, persistent low-temperature spin dynamics have been observed\textsuperscript{25} and (ii) again similarly to Gd$_2$Ti$_2$O$_7$, unconventional power-law temperature dependence of the magnetic specific heat has been found, specifically, $C_v \sim T^2$. So here too, there may exists the possibility to relate a dynamical response and a bulk thermodynamic measurements to an unconventional density of states $g(\epsilon)$ — a possible manifestation of the spectral down-shift that corresponds to the hallmark of highly frustrated systems. We see the experimental results on Gd$_2$Sn$_2$O$_7$ as a crucial paradox to contend
This is the question that we ask, and aim to answer in this paper. Since the observed ordered state in Gd$_2$Sn$_2$O$_7$ corresponds to the one predicted by the model of Palmer and Chalker\cite{54}, or a more refined model that includes Gd$^{3+}$ single-ion anisotropy\cite{55,56} and exchange interactions beyond nearest-neighbor\cite{20,25,52}, one could in principle follow the well-trodden road of solid state physics and conventional magnetism: with the Hamiltonian and consequent ground state known, identify the long wavelength excitations and, by second-quantizing them, calculate the low-temperature thermodynamic quantities. It turns out that this program was carried out in a prior work\cite{27} for a quantum version of a simple pyrochlore lattice model with nearest-neighbor antiferromagnetic exchange plus long-range dipolar interactions\cite{16,49}. What was found in Ref. \cite{55} is that all spin wave excitations of the Heisenberg pyrochlore antiferromagnet are pushed up in energy by the dipolar interactions and, as a result, all thermodynamic quantities show exponential temperature dependence, \( \sim \exp(-\Delta/T) \), at low temperatures\cite{55}. The following question thus arises:

Do the \( C_v \approx T^2 \) results of Ref. \cite{24} for Gd$_2$Sn$_2$O$_7$ contradict the theoretical prediction of Ref. \cite{54}, and are the magnetic excitations of Gd$_2$Sn$_2$O$_7$ truly unconventional?

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To spell out the question above more specifically, we show in Fig. 1 the specific heat data on Gd$_2$Sn$_2$O$_7$ reproduced from Ref. \cite{27}. The \( T^2 \) behavior (dashed line in main panel) ranges from \( T_{low} \approx 0.5 \) K to \( T_{up} \approx 0.8 \) K. The \( T_{up} \) is very close to the critical temperature, and one does not expect on general grounds (non-critical) power-law behaviors reflecting excitations out of the ground state to extend so close to the phase transition. Secondly, the temperature \( T_{low} \), when compared with the results of Ref. \cite{55}, is \textit{high} compared to the temperature regime where we expect second-quantized (spin wave) excitations to describe this system. Finally, and this is the key aspect of the data that prompted the present work, we note that the \( C_v \) data at \( T \lesssim 0.5 \) K progressively droop below the dashed \( C_v \sim T^2 \) behavior. This is emphasized in the inset of Fig. 1. Incidentally, we note from this plot that the \( C_v \sim T^2 \) behavior does not provide a particularly good fit of the data for \( T \in [350, 800] \) mK. The crux of the argument presented in this paper is that (i) the \( T^2 \) power law between \( T_{low} \) and \( T_{up} \) is not a reflection of the low-energy properties of Gd-based antiferromagnetic pyrochlores and, most importantly, (ii) the behavior exhibited by \( C_v \) below \( T_{low} \approx 0.5 \) K (inset of Fig. 1) is a signature that the system is progressively entering a low-temperature regime characterized by exponentially activated spin excitations over a gap originating from both magnetic dipole-dipole interactions and single-ion anisotropy. We show below via calculations that expand on the authors’ previous work, Ref. \cite{55}, that the specific heat data of Fig. 1 can be reasonably well described by such gapped magnetic excitations. In other words, we assert that the bulk thermodynamic properties of Gd$_2$Sn$_2$O$_7$, revealed by data like that shown in Fig. 1, are compatible with a conventional semi-classical long-range ordered phase. We suggest that specific heat measurements below \( T_{low} \) and down to 100 mK could be used to confirm or disprove our proposal. The rest of the paper is organized as follows. We first present a model for exchange and dipole coupled spins on the pyrochlore lattice in the presence of a crystal field inducing single ion spin anisotropy. The Hamiltonian is decoupled via linear spin wave theory, and expressions for the quantum fluctuations and low temperature thermodynamic properties are calculated. We then investigate the effects of second and third nearest neighbor magnetic exchange on the gap to spin wave excitations. Comparing the specific heat calculated in spin wave theory for Gd$_2$Sn$_2$O$_7$ to that measured in the experiments of Bonville \textit{et al} \cite{27}, we use a maximum likelihood estimator to determine a set of further neighbor couplings which may be present in the material. Finally, we identify the zero temperature quantum fluctuations and present a schematic phase diagram of Gd$_2$Sn$_2$O$_7$.

II. MODEL HAMILTONIAN

As reviewed in the previous section, the pyrochlore lattice has evinced much experimental and theoretical interest due to the large degree of geometrical frustration arising from a structure consisting of corner sharing tetrahedra. The cases of Gd$_2$Ti$_2$O$_7$ and Gd$_2$Sn$_2$O$_7$ are somewhat special, in that the \( S = \frac{7}{2} \) Gd$^{3+}$ S-state ion should

![FIG. 1: (Color online) The specific heat of Gd$_2$Sn$_2$O$_7$ as a function of temperature, with an inset showing an enlargement of the low temperature region from Bonville \textit{et al} \cite{27}, plotted on a logarithmic scale. The dashed line shows the result of a relatively successful \( T^2 \) fit below 0.75 K. [Data were generously provided by P. Bonville].](image-url)
have a relatively small intrinsic anisotropy when compared to other $\mathrm{R_2\mathrm{Ti}_2\mathrm{O}_7}$ pyrochlore oxides. It is known that the titanate (Gd$\mathrm{2}\mathrm{Ti}_2\mathrm{O}_7$) has a complicated low temperature multi-$\mathbf{k}$ magnetic structure\cite{58}. However, recent neutron scattering\cite{59,20} and electron spin resonance\cite{60} experiments performed on gadolinium stanate (Gd$\mathrm{2}\mathrm{Sn}_2\mathrm{O}_7$) indicate that this material exhibits a $\mathbf{k} = 0$ long range ordered state below $\sim 1$ K. As such, Gd$\mathrm{2}\mathrm{Sn}_2\mathrm{O}_7$ should be reasonably well described by a general two-body spin interaction Hamiltonian which includes predominant isotropic magnetic exchange interactions up to at least third nearest neighbor and anisotropy in the form of interactions with the local crystal field as well as long range dipole-dipole interactions\cite{16,20,54,55,56,57,21,27,18,24,25,26}.

Such a Hamiltonian can be written as

$$H = H_{\text{ex}} + H_{\text{dd}} + H_{\text{cf}},$$

where the exchange, dipole-dipole and crystal field terms are given by

$$H_{\text{ex}} = -\frac{1}{2} \sum_{i,a} \sum_{j,b} J_{ab}(\mathbf{R}_{ab}^i) \cdot \mathbf{S}_a(\mathbf{R}^i) \cdot \mathbf{S}_b(\mathbf{R}^j),$$

$$H_{\text{dd}} = \frac{D_{\text{dd}}}{2} \sum_{i,a} \sum_{j,b} \left\{ \frac{\mathbf{S}_a(\mathbf{R}^i) \cdot \mathbf{S}_b(\mathbf{R}^j)}{|\mathbf{R}_{ab}^i|^3} - \frac{3}{|\mathbf{R}_{ab}^j|^5} \right\},$$

$$H_{\text{cf}} = \sum_{i,a} \sum_{\ell,m} B_{\ell m}^m \hat{O}^m_{\ell} [\mathbf{S}_a(\mathbf{R}^i)].$$

with the factors of $1/2$ having been included to avoid double counting. The various conventions used in Eqs. (2a) to (2c) are as follows: $\mathbf{S}_a(\mathbf{R}^i)$ is the spin located on one of $N$ tetrahedra identified by the face centered cubic (FCC) Bravais lattice vector $\mathbf{R}^i$ and the site by one of four tetrahedral sublattice vectors $\mathbf{r}_a$. $\mathbf{S}_a(\mathbf{R}^i)$ is assumed to be a full $O(3)$ operator satisfying $\mathbf{S}_a(\mathbf{R}^i) \cdot \mathbf{S}_b(\mathbf{R}^j) = S(S+1)$. $J_{ab}(\mathbf{R}_{ab}^i)$ gives the value of the isotropic Heisenberg exchange interaction between two spins separated by $\mathbf{R}_{ab}^i = \mathbf{R}^i + \mathbf{R}^j - \mathbf{r}_a$, with a negative sign corresponding to antiferromagnetic interactions. In this study, we focus on the Gd$\mathrm{2}\mathrm{Sn}_2\mathrm{O}_7$ material, and thus consider a fixed value of $J_1 = 3\Theta_{\text{CW}}/|\varepsilon S(S+1)| = -0.273$ K where the Curie-Weiss temperature is $\Theta_{\text{CW}} = -8.6$ K and $z = 6$ is the coordination number on the pyrochlore lattice. We treat the exchange interactions $J_2$ and $J_3$ beyond nearest neighbors as parameters to be adjusted below to produce agreement with experimental (specific heat) measurements on Gd$\mathrm{2}\mathrm{Sn}_2\mathrm{O}_7$. Following the approach of Wills et al.\cite{20} we treat the two possible third nearest neighbor (NN) exchange paths $J_3$ and $J_{32}$, known to be present in the pyrochlores,\cite{26,22} separately (see Fig. 2). With the expectation that $J_{32} \ll J_{31}$, we henceforth set $J_{32} = 0$. The strength of the dipole interaction is given by $D_{\text{dd}} = \mu_0(\mu_0)^2/4\pi$. At nearest neighbor distance, $R_{\text{nn}} = a\sqrt{2}/4 = 3.695$ Å, where $a = 10.45$ Å is the size of the cubic unit cell, $D_{\text{dd}}/R_{\text{nn}}^3$ is approximately 15% of the exchange energy $J_1$. The crystal field Hamiltonian is written as an expansion of Stevens operators, $\hat{O}^m_{\ell}$, that transform like the real tesseral harmonics.\cite{58} The number of terms in the expansion is strongly constrained by symmetry and, from recent electron spin resonance (ESR) measurements,\cite{60} the values of $B_{20}^2$ and $B_{40}^2$ have been estimated at $(47 \pm 1)$ mK and $(0.05 \pm 0.02)$ mK, respectively. Here, we only consider the dominant lowest order term in the expansion of $H_{\text{cf}}$, $B_{20}^2$, which contributes energetically on equal footing with the dipole interactions, and leave the inclusion of higher order corrections to a future study. Writing the Stevens’s operators in terms of angular momentum operators,\cite{58} the crystal field part of the Hamiltonian $H$, $H_{\text{cf}}$, is:

$$H_{\text{cf}} = -4N B_{20}^0 S(S+1) + 3B_{40}^0 \sum_{\ell,a} [\mathbf{S}_a(\mathbf{R}^i) \cdot \hat{z}_a]^2,$$

where the four unit vectors $\hat{z}_a$ describe the local (111) direction for each site on a tetrahedron. The conventions and definitions used in this study for all vectors and lengths on the pyrochlore lattice are given in Table 1 of a previous work by one of the authors.\cite{58}

We are interested in the effects of the low energy excitations (spin waves) on the thermodynamic properties of a real material described by Eq. (1). At zero temperature, we assume that the system is in one of the six discrete Palmer-Chalker (PC) $\mathbf{k} = 0$ ground states depicted in Fig. 3. We have confirmed by direct numerical simulations that the classical zero temperature ground state in a model with nearest-nearest neighbor antiferromagnetic exchange and long-range dipolar interactions at the level of 10 – 20% of the exchange is the PC ground state. See also Refs. [51,52,53]. The use of the PC state for Gd$\mathrm{2}\mathrm{Sn}_2\mathrm{O}_7$ is supported by recent powder neutron scattering experiments,\cite{20} where the magnetic diffraction pattern was compared to the expected result from multiple

![FIG. 2: (Color online) A schematic portion of the pyrochlore lattice, detailing the paths which correspond to second nearest neighbor and two types of third nearest neighbor exchange interactions.](image-url)
on the pyrochlore lattice via a Holstein-Primakoff spin wave expansion to order $1/S$, through the introduction of bosonic spin deviation (magnon) creation (annihilation) operators $c_{\alpha}^\dagger$ ($c_{\alpha}$). The Ewald summation technique was used to calculate the Fourier transform of the infinite range dipole-dipole interaction matrix. The calculations of DG can be straightforwardly generalized to include the effects of the crystal field by shifting the diagonal spin interaction matrix elements ($A_{\alpha\alpha}(k)$ and $B_{\alpha\alpha}(k)$ of Eq. (16) in DG) by a term proportional to $B^2_2$ (see Eq. (6)). The result, after the usual Bogoliubov diagonalization procedure, is a Bose gas of non-interacting spin waves described by

$$\mathcal{H} = \mathcal{H}^{(0)} + \sum_{k} \sum_{\alpha} \varepsilon_{\alpha}(k) \left[ a_{\alpha}^\dagger(k) a_{\alpha}(k) + \frac{1}{2} \right],$$

where the summation is over all wavevectors in the first Brillouin zone (BZ) of the FCC lattice. The dispersion relations for the spin wave modes, $\varepsilon_{\alpha}(k)$, are calculated from the spectrum of the Bogoliubov transformation. Physically, they are identical to $\varepsilon_{\alpha}(k) = \hbar \omega_{\alpha}(k)$ where $\omega_{\alpha}(k)$ are the classical excitation frequencies obtained by linearizing the classical equations of motion for interacting magnetic dipoles or rotors.

In a real magnet, spin wave fluctuations with dispersion $\varepsilon_{\alpha}(k)$ raise the classical ground state energy and reduce the staggered magnetic moment per spin from its classical value of $S$. From Eq. (7), the contribution to the ground state energy is given by

$$\Delta \mathcal{H}^{(0)} = \frac{1}{2} \sum_{k} \sum_{\alpha} \varepsilon_{\alpha}(k).$$

The full spectrum of the Holstein-Primakoff transformation can be used to calculate the reduction in the staggered magnetization

$$\Delta S = \frac{1}{2} \left( \frac{1}{8N} \sum_{k} \text{Tr}[Q^\dagger Q] - 1 \right),$$

where $Q$ is the $8 \times 8$ hyperbolically normalized matrix of eigenvectors such that $\text{Tr} (Q^\dagger HQ) = \sum_{\alpha} \varepsilon_{\alpha}(k)$ and $H$ is the $8 \times 8$ block matrix Hamiltonian [see DG Eqs. (16) and (19)]. $N$ is the number of tetrahedra on a pyrochlore lattice with periodic boundary conditions.

At low temperatures ($k_B T < \varepsilon_{\alpha}(k)$) expressions for the specific heat at constant volume, $C_v$, and staggered magnetization, $m = S - \Delta S$, can be derived from the classical partition function $Z = \text{Tr} [\exp(-\beta \mathcal{H})]$ corresponding to Eq. (7). Using Eqs. (7) to (9), we find (see DG)

$$C_v = \beta^2 \sum_{k} \sum_{\alpha} [\varepsilon_{\alpha}(k) n_B(\varepsilon_{\alpha}(k))]^2 \exp[\beta \varepsilon_{\alpha}(k)],$$

$$m = S + \frac{1}{2} \left( \frac{1}{8N} \sum_{k} \sum_{\alpha} [Q^\dagger Q]_{aa} [1 + n_B(\varepsilon_{\alpha}(k))] \right),$$

where $\beta$ is the inverse temperature and $n_B(\varepsilon_{\alpha}(k)) = 1/(e^{\beta \varepsilon_{\alpha}(k)} - 1)$ is the Bose distribution function.

III. LINEAR SPIN WAVE THEORY

In a previous study, which we henceforth refer to as DG, we presented the diagonalization of $\mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{dd}}$...
confirm the naive expectation that even perturbatively behavior of ε along high symmetry path described in Fig. 4. We do indeed for soft modes (the pyrochlore lattice can be investigated by searching stability of the proposed PC classical ground states on perturbative lattice, we may now study the quantitative effects of perturbative second and third NN exchange interactions ∆S (Eq. (9)) is shown in Fig. 7. Here we observe the underlying presence of a finite wavevector instability as J2 and J31 are tuned away from J2 = J31 = 0.

The spin wave energy gap can be analyzed more quantitatively by defining

\[
\Delta(k) = \min_{a} \{\varepsilon_a(k)\},
\]

\[
\Delta = \min_{k} \{\Delta(k)\}. \tag{12b}
\]

The value of Δ(k) can be investigated as a function of J2 and J31 at each of the high symmetry points described above. As we vary J2 and J31 through some critical values, instabilities first appear at these wavevectors of high symmetry. The resulting gap values are shown in Fig. 5. Although Δ(Γ) > 0 for all values of J2 and J31 studied here, the region of stability of the PC states is defined by the observed appearance of soft modes, at k = K = 2π/a(3/4, 3/4, 0) for ferromagnetic (positive) J2 and antiferromagnetic (negative) J31. Performing a search for the minimum value of the gap over the entire Brillouin zone (Δ) at each value of J2 and J31 confirms that the instability first appears at the K-point. The effect of perturbative second and third NN exchange interactions on the global minimum energy gap (Eq. (12b)) along with the corresponding magnitude of spin fluctuations ∆S/S (Eq. (9)) is shown in Fig. 7. Here we observe that upon reaching a pair of critical values for J2/J1 and J31/J1, the excitation gap is suppressed to zero.
The values of $J_{31}$, and divergent spin fluctuations ensue (bottom panel). A soft mode instability occurs only for antiferromagnetic third NN coupling $J_{31}$ (top panel), and divergent spin fluctuations ensue (bottom panel). The values of $J_2$ and $J_{31}$ corresponding to $\Delta \to 0$ can be identified, and are best described by the linear relationship $J_{31} = 0.750J_2 - 0.077|J_1|$. This line defines the phase boundary between a sector of stability for the $k = 0$ PC ground states, and a region characterized by instabilities at finite wavevector. In addition, this line corresponds to the white regions in Fig. 6 where $\Delta \to 0$, and thus defines the limit of applicability of the spin wave calculation around the PC ground state described in Section III.

Plotting $\Delta(k)$ along $\Gamma \to X \to W \to L \to K \to \Gamma$ with $J_{31}$ pinned to this phase boundary leads to the spectrum shown in Fig. 6. It is apparent from this result, that once the value of the third NN exchange constant has been set at a suitably antiferromagnetic value, altering the second NN exchange constant, has a relatively limited effect on the gap and on the consequential proliferation of quantum fluctuations about the classical ground state.

To summarize, the effects of perturbative second and third NN exchange interactions on the appearance of soft modes and their accompanying quantum fluctuations in a model of a dipolar coupled antiferromagnetic Heisenberg pyrochlore with single-ion anisotropy is globally illustrated in Figs. 6 and 7. Such a model should well characterize the low temperature behavior of Gd$_2$Sn$_2$O$_7$, and we next apply these tools with the goal of searching for the unconventional spin excitations believed to be present in this material on the basis of the unconventional $C_v \propto T^2$ specific heat in the temperature range [350, 800] mK.

### B. The case of Gd$_2$Sn$_2$O$_7$

As described in the Introduction, recent studies of Gd$_2$Sn$_2$O$_7$ have reported, on the basis of $\mu$SR measurements, evidence for Gd$^{3+}$ spin dynamics well below 0.9 K, as well as suggesting that the low temperature specific heat is accurately described by an anomalous $T^2$ power law. This is in stark contrast with the expected $T^3$
behavior for a three dimensional antiferromagnet, with possible exponential suppression at a temperature below a characteristic excitation gap.

On the other hand, the long-range ordered state found by neutron scattering in Gd$_2$Sn$_2$O$_7$ is that predicted by the simple model of Eq. 1 in Section III and discussed in Refs. [49,50,51,52] and, consequently, the low-temperature behavior of this material should be well described by linear spin wave theory. Thus, in an attempt to resolve the paradox offered by the $C_v \sim T^2$ behavior, we have calculated the low temperature specific heat via Eq. (10) within the $J_2 - J_{31}$ plane, and have performed a search for the parameters which best reproduce the reported low temperature specific heat. This was accomplished by performing least squares linear fits of $\log C_v$ vs $1/T$ for $T < 0.5$ K between the experimental data and the spin wave specific heat for approximately 500 values of $J_2$ and $J_{31}$. A characteristic subset of the large number of performed fits are displayed in Fig. 9. The values of $J_2$ and $J_{31}$ which provided the best fit to the experimental data can be quantified by defining a maximum likelihood estimator $\chi^2$ which is shown in Fig. 10. It is important to note that the fits of the specific heat, $C_v$, discussed here, were done with an absolute dimensionfull scale, and thus no vertical adjustment of the experimental data was allowed. The comparisons allow only for adjustments of $J_2$ and $J_{31}$ which are therefore fine-tuning effects. As such, it appears that a model which possesses solely nearest-neighbor exchange, long-range dipolar interactions and single-ion anisotropy already leads to a reasonable semi-quantitative description of the $C_v$ data below 500 mK. This indicates that the temperature $T \sim 500$ mK corresponds to the upper temperature below which magnetic excitations become thermally activated.

The minimum of $\chi^2$ in the $J_2 - J_{31}$ plane falls along the straight line $J_{31} = 0.760 J_2 - 0.014 |J_1|$. This line of best fit also falls in a region of large stability (highly gapped spin wave excitations) for the classical PC ground states.
FIG. 11: (Color online) The low temperature specific heat (data from Ref. [27]) versus temperature on a logarithmic scale. The calculated specific heat is plotted for the parameter set $J_2 = 0.02$, $J_{31} = 0.0$ which had the smallest $\chi^2$, although any values close to the line mentioned in the text give a qualitatively very similar result. The agreement is quite good at low temperatures, where spin wave theory should be applicable. The low temperature suppression of $C_v$ is characteristic of gapped excitations, in contrast with previously reported power law behavior\cite{53}. The inset displays the temperature dependence of the Gd$^{155}$ moment calculated using a Bose gas of excitations along with the value measured from$^{155}$Gd Mössbauer measurements\cite{53}.

with respect to quantum fluctuations (see Fig. [11]).

The poorness of fit for simultaneously strong ferromagnetic second NN and antiferromagnetic third NN interactions or vice versa (top left, or lower right of Fig. [10]), seems to indicate that is quite unlikely that Gd$_2$Sn$_2$O$_7$ resides in these portions of the phase diagram. The parameters $J_2 = 0.02$ and $J_{31} = 0.0$ provide the best empirical fit to the experimental specific heat data, although qualitatively similar fits are seen for all parameters which satisfy $J_{31} = 0.760J_2 - 0.014|J_1|$. Setting the parameters to these particular values, we display the spin wave specific heat, as well as the temperature dependence of the order parameter $m$ in Fig. [11]. Again, as shown in Fig. [8] it is clear that at low temperatures, $(T < 370$ mK), the experimental specific heat data systematically falls below the gapped spin wave results. This behavior is tentatively consistent with the fact that spin wave theory produces a smaller value for the magnetization $m$ than what is measured from Mössbauer experiments. However, we note that due to the intrinsic short dynamical time scale probed by Mössbauer measurements, the experimental data in the inset of Fig. [11] may not reflect the true value of the infinite-time order parameter.

It is perhaps worthwhile to make a few comments on the physical meaning of the above fits. Firstly, we note that because of the weakly dispersive nature of the two lowest lying gapped magnon excitations (see Fig. [8]), the temperature dependence of thermodynamics quantities in the pyrochlore Heisenberg antiferromagnet plus dipolar interactions do not display the typical $C_v \sim T^3$ behavior as the temperature reaches approximately 0.5 K and exits its characteristic low-temperature exponential behavior. In fact, such an observation was already made in Ref. [53] independently of any attempt to describe $C_v$ for Gd$_2$Sn$_2$O$_7$. Secondly, the calculations presented here constitute a standard procedure for a system with conventional long range magnetic order. In this context, it is therefore interesting to note that, contrary to the reported $T^2$ behavior, the experimental specific heat data are not only relatively well fit using the exponential spin wave form of Eq. (10), but it appears to fall off even faster than the exponentials considered at low temperatures. This would lend credence to the view that analyzing experimental data on a log-log scale over a limited range, can lead to spurious power law fits. Hence, and on the basis of specific heat measurements alone (i.e. without consideration of the $1/T_1 \mu$SR spin-lattice relaxation rate), it would therefore appear that the suggestion of unconventional excitations in Gd$_2$Sn$_2$O$_7$ should be challenged by the principle of “Ockham’s razor”. We are therefore led to suggest that the description of the specific heat $C_v$ in terms of an anomalous power law, $C_v \sim T^2$, in a reduced and intermediate temperature range $T \in [350, 800]$ mK does not provide a convincing indicator for anomalous excitations out of the ground state of Gd$_2$Sn$_2$O$_7$. Unlike the suggestion made in Ref. [53] on the basis of the temperature independence of the $1/T_1$ muon spin relaxation rate below $T_c \sim 1$ K, we have found a fully gapped spin wave spectrum with no density of states at zero energy. Hence, at this time, the microscopic origin of the temperature independence of $1/T_1$ found below $T_c$ in Gd$_2$Sn$_2$O$_7$ remains to be understood.

C. Ground state properties

In the previous section, we have identified a relationship between the second $J_2$ and third $J_{31}$ NN exchange constants which best reproduce the low temperature thermodynamic behavior in Gd$_2$Sn$_2$O$_7$. We now investigate the role of quantum fluctuations. Fig. [12] displays both the minimum spin wave energy gap $\Delta$ and the reduction in the staggered moment $\Delta S/S$ along the line of best fit $J_{31} = 0.760 J_2 - 0.014|J_1|$. This result details the complicated relationship between the value of the gap, and the stability of the ground state, i.e. a decrease in the global spin wave energy gap (which may only occur at a single $k$-point) does not immediately trigger an increase of moderate quantum fluctuations. Indeed, the opposite behavior is seen in Fig. [12] In an exchange coupled Heisenberg antiferromagnet on a non-Bravais lattice, the specifics of all relative energy scales come into play, and one must not neglect the effects of weakly dispersing optical modes. All the results presented here can be
The ground state of this system, as found by neutron scattering experiments, corresponds to the (classical, antiferromagnetic exchange and long-range dipolar couplings) compiled into an effective schematic phase diagram for Gd$_2$Sn$_2$O$_7$. Fig. 13 depicts the separatrix in the $J_2 - J_{31}$ plane (solid line) that delineates the limit of stability of the $k = 0$ PC state against a soft mode characterized by wavevector $2\pi/a(3/4,3/4,0)$, i.e. the $K$-point. Possibly relevant values of $J_2$ and $J_{31}$ for which $\chi^2$ reaches it minimum value are shown as the parametric dashed line $J_{31} = 0.760 J_2 - 0.014 |J_1|$. We note that Fig. 13 shows a zero temperature phase diagram that delineates the limit of stability of the $k = 0$ Palmer-Chalker ground state against an instability at $2\pi/a(2\pi/a,2\pi/a,0)$.

### V. DISCUSSION

We have considered a Heisenberg model that includes isotropic exchange interactions up to third nearest-neighbors, single-ion anisotropy and long-range magnetic dipole-dipole interactions to describe the long-range ordered state of the Gd$_2$Sn$_2$O$_7$ pyrochlore antiferromagnet. The ground state of this system, as found by neutron scattering experiments, corresponds to the (classical, PC) ground state described by Palmer and Chalker for the classical Heisenberg pyrochlore with nearest-neighbor antiferromagnetic exchange and long-range dipolar coupling. We used a long wavelength $(1/S \text{ spin wave})$ expansion to describe the low-energy excitations about the PC ground state and to calculate the low-temperature behavior of the specific heat, $C_v$, and order parameter, $m$, for this material.

By fitting the available specific heat data in the low-temperature range ($0.35 \text{ K} < T < 0.5 \text{ K}$), we were able to procure an estimate of the exchange interactions beyond nearest neighbors. We obtained evidence that Gd$_2$Sn$_2$O$_7$ is in a region of exchange coupling with large stability against quantum fluctuations. Our main result (which does not rely on excruciatingly fine-tuned exchange constants beyond nearest-neighbor) is that the experimental temperature range $0.35 \text{ K} < T < 0.5 \text{ K}$ corresponds to the upper temperature range below which the thermodynamic quantities become thermally activated above an excitation gap $\Delta \sim 1 \text{ K}_{\text{mag}}$. In other words, the independently experimentally determined microscopic nearest-neighbor exchange (on the basis of DC magnetic susceptibility), single-ion anisotropy (on the basis of ESR) and dipolar coupling strength already predict a temperature dependence for $C_v$ in Gd$_2$Sn$_2$O$_7$ that is in rough agreement with the experiment without significant adjustment.

The excitation gap takes its origin from the combination of single-ion anisotropy and magnetic dipolar anisotropy. From our fits of the experimental specific heat, we tentatively conclude that the real gap is actually even larger than the one we have determined. Specifically, considering the lower temperature range in Fig. 9 and Fig. 11 (and the inset of Fig. 11 for $m$), it appears that the specific heat is dropping faster in the lower temperature range than the calculations predict. We speculate that this may indicate that the sub-leading anisotropy terms neglected in $\mathcal{H}_{\text{el}}$ in Eq. (5) (and which correspond to crystal field terms $B_{l,m}$ with $l = 4,6$) would further increase the effective gap. In particular,
those corrections would resign to further limit the spin fluctuations perpendicular to the local three-fold axis. However, at this time, experimental measurements of $C_v$ below 0.3 K are required to ascertain quantitatively the detail of the microscopic parameters for Gd$_2$Sn$_2$O$_7$ and to determine with better precision the exchange parameters $J_1$, $J_2$ and $J_{31}$. As in other Gd$^{3+}$–based insulating magnetic materials\textsuperscript{63,64}, it is also possible that anisotropic exchange interactions ultimately need to be included in a complete description of Gd$_2$Sn$_2$O$_7$.

It therefore appears that a rejoinder to the question posed in the Introduction is that the low temperature specific heat observed in gadolinium stanate (Gd$_2$Sn$_2$O$_7$) may possibly be well described by the conventional gapped spin wave excitations of Ref. 15. We believe that either a confirmation or rebuttal of our suggestion of gapped excitations in Gd$_2$Sn$_2$O$_7$ via specific heat ($C_v$) measurements down to $\sim$ 100 mK would tremendously help focus the discussion about the pervasive low energy excitations in insulating magnetic rare-earth pyrochlore oxides. However, a possible confirmation of such gapped excitations in Gd$_2$Sn$_2$O$_7$ via specific heat measurements would ultimately have to be rationalized within the context of the perplexing and persistent temperature-independent spin dynamics found in muon spin relaxation studies on this, and other geometrically frustrated pyrochlores.

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