Quantum spin fluctuations in the dipolar Heisenberg-like rare earth pyrochlores

Adrian G Del Maestro[1,2] **and Michel J P Gingras**[1,3]

[1] Department of Physics, University of Waterloo, Waterloo, ON N2L 3G1, Canada
[2] Department of Physics, Yale University, New Haven, CT 06520, USA
[3] Canadian Institute for Advanced Research, Toronto, ON M5G 1Z8, Canada

E-mail: adrian.delmaestro@yale.edu

Abstract

The magnetic pyrochlore oxide materials of general chemical formula $R_2Ti_2O_7$ and $R_2Sn_2O_7$ ($R \equiv$ rare earth) display a host of interesting physical behaviours depending on the flavour of rare earth ion. These properties depend on the value of the total magnetic moment, the crystal field interactions at each rare earth site and the complex interplay between magnetic exchange and long range dipole–dipole interactions. This work focuses on the low temperature physics of the dipolar isotropic frustrated antiferromagnetic pyrochlore materials. Candidate magnetic ground states are numerically determined at zero temperature and the role of quantum spin fluctuations around these states is studied using a Holstein–Primakoff spin wave expansion to order $1/S$. The results indicate the strong stability of the proposed classical ground states against quantum fluctuations. The inclusion of long range dipole interactions causes a restoration of symmetry and a suppression of the observed anisotropy gap leading to an increase in quantum fluctuations in the ground state when compared to a model with truncated dipole interactions. The system retains most of its classical character and there is little deviation from the fully ordered moment at zero temperature.

1. Introduction

Magnetic frustration arises when magnetic moments (spins) are unable to minimize their classical ground state energy by minimizing the two-body magnetic exchange interactions pair by pair. The simplest example of magnetic frustration is for antiferromagnetically coupled spins on a triangular lattice where the triangular coordination prevents the spins from pointing mutually antiparallel to each other and where, consequently, the spins adopt a non-collinear structure to minimize their energy. Due to the canted structure, the internal mean field is

much smaller in frustrated spin systems than in conventional collinear magnets. As a result, frustrated magnetic systems have an enhanced propensity for large zero-temperature quantum spin fluctuations allowing for the possibility of exotic quantum ground states [1, 2].

The pyrochlore lattice of corner-sharing tetrahedra where spins interact via nearest neighbour antiferromagnetic exchange interactions has attracted much interest over the past 15 years [3]. In particular, the $R_2Ti_2O_7$ and $R_2Sn_2O_7$ magnetic insulators (where R is a trivalent rare earth ion, R = Tb, Ho, Dy, Gd, Yb and Er, sitting on a regular pyrochlore lattice) have been found to display a multitude of magnetic phenomena. For example, the combination of the strong Ising anisotropy in $Dy_2Ti_2O_7$ [4, 5], $Ho_2Ti_2O_7$ [6, 7] and $Ho_2Sn_2O_7$ [8] gives rise to 'spin ice' behaviour where the system exhibits extensive magnetic entropy and maps onto the problem of proton disorder in common ice water [9, 10]. In $Yb_2Ti_2O_7$, a sharp first-order transition is observed in specific heat measurements, but with no obvious sign of long range order in neutron scattering [11]. The $Tb_2Ti_2O_7$ antiferromagnet is particularly interesting since it appears to be an excellent candidate for showing collective paramagnetism [12] or 'spin liquid' behaviour, as it fails to develop long range order down to 50 mK despite a Curie–Weiss temperature of $\theta_{CW} = -20$ K [13–15]. Finally, both $Er_2Ti_2O_7$ [16] and $Gd_2Ti_2O_7$ [17–19] display a transition to long range ordered states below 1 K.

In the $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$, $Tb_2Ti_2O_7$ and $Gd_2Ti_2O_7$ materials, the rare earth ion carries a large magnetic moment between five and ten Bohr magnetons and the dipolar energy scale at the nearest neighbour makes a sizable contribution to the total magnetic interaction. Indeed, in $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$, it has been shown that it is the dipolar interactions that cause the spin ice phenomenology [5, 9]. In $Tb_2Ti_2O_7$, the dipolar interactions play a very important role in frustrating the nearest neighbour exchange interactions and are significant players in the formation of a possible spin liquid state [15]. In $Gd_2Ti_2O_7$, the 4f orbital of Gd^{3+} is half-filled and crystal field single-ion anisotropy effects are negligible. This system, with $\theta_{CW} \sim -9.8$ K and spin quantum number $S = 7/2$, therefore constitutes a useful starting point as a real material which could be described by a nearest neighbour Heisenberg pyrochlore model [2, 20]. However, in this system the large dipolar interactions are important since they have been predicted to select a unique long range ordered classical ground state [18, 21].

Rare earth pyrochlores do not hold a monopoly on unusual phenomena among the insulating rare earth magnetic materials. Possibly one of the most interesting cases is that of the $Gd_3Ga_5O_{12}$ three-dimensional garnet of corner-sharing triangles [22]. In this material, experimental evidence of a magnetic field induced spin liquid has been found [22], as well as re-entrance from a long range ordered magnetic state to a spin liquid upon cooling [23, 24].

The discussion in the previous two paragraphs brings up the following question. In conventional exchange-coupled Heisenberg antiferromagnets the quantum fluctuations, ΔS, are governed by an integral over the Brillouin zone of $1/\omega(\mathbf{k})$ where $\omega(\mathbf{k})$ are the $\mathbf{k}$-dependent excitation frequencies. Weakly dispersive modes give rise to larger fluctuations and (anisotropy) gapped modes contribute smaller quantum fluctuations [25]. In the nearest neighbour Heisenberg pyrochlore, we have two zero-energy modes throughout the zone and any conventional perturbative spin wave calculation is therefore singular. In systems such as the rare earth pyrochlores above, we expect both single-ion anisotropy and dipolar interactions to lift the classical degeneracy and make the spin excitations dispersive. The leading effect of those perturbations will be to push the two zero modes throughout the zone to finite frequency. This is akin to the finite energy $\mathbf{k}$-independent resonance observed in inelastic neutron scattering in the $ZnCr_2O_4$ spinel [26]. In other words, in the isotropic Heisenberg antiferromagnet with conventional long range Néel order, it is the dispersion of the acoustic magnons ($\omega(\mathbf{k}) \sim |\mathbf{k}|$) that controls the leading $1/S$ quantum fluctuations. The question therefore concerns the magnitude of quantum fluctuations arising from gapped excitations with

negligible dispersion throughout the Brillouin zone in a highly frustrated system of the type considered here. This would seem particularly relevant to $Gd_2Ti_2O_7$ where the experimentally observed ground state seems to be at odds with classical predictions [19, 21].

The outline of the paper is as follows. In section 2 we discuss the general framework for calculating the quantum spin fluctuations in a non-Bravais lattice in the presence of combined exchange and long range dipolar interactions. In section 3, we apply the method discussed in section 2 to the specific case of the $Gd_2Ti_2O_7$ pyrochlore material. Section 4 contains a brief conclusion of our work.

2. $1/S$ formalism

In this section we introduce the Hamiltonian believed to describe our antiferromagnetic pyrochlore system and map out its low temperature excitations using linear spin wave theory. From the diagonalized form of the spin wave Hamiltonian we obtain expressions for the zero-point energy shift and reduction in the classical staggered moment due to spin fluctuations. Utilizing the partition function of the non-interacting Bose gas, the relevant thermodynamic quantities are given in terms of the calculated spin wave dispersion energies.

2.1. Model Hamiltonian

A general two-body spin interaction Hamiltonian including both pth-nearest neighbour anisotropic exchange and long range dipole–dipole interactions can be written as

$$\mathcal{H} = -\frac{1}{2} \sum_{\mu,\alpha} \sum_{\nu,\beta} \sum_{k,l} J_{\alpha\beta}^{kl}(\boldsymbol{R}_{\alpha\beta}^{\mu\nu}) S_\alpha^k(\boldsymbol{R}^\mu) S_\beta^l(\boldsymbol{R}^\nu)$$

$$+ \frac{1}{2} D_{dd} \sum_{\mu,\alpha} \sum_{\nu,\beta} \left[\frac{\boldsymbol{S}_\alpha(\boldsymbol{R}^\mu) \cdot \boldsymbol{S}_\beta(\boldsymbol{R}^\nu)}{|\boldsymbol{R}_{\alpha\beta}^{\mu\nu}|^3} - 3 \frac{(\boldsymbol{S}_\alpha(\boldsymbol{R}^\mu) \cdot \boldsymbol{R}_{\alpha\beta}^{\mu\nu})(\boldsymbol{S}_\beta(\boldsymbol{R}^\nu) \cdot \boldsymbol{R}_{\alpha\beta}^{\mu\nu})}{|\boldsymbol{R}_{\alpha\beta}^{\mu\nu}|^5} \right] \quad (1)$$

using $\boldsymbol{R}_{\alpha\beta}^{\mu\nu} = (\boldsymbol{R}^\nu + \boldsymbol{r}_\beta) - (\boldsymbol{R}^\mu + \boldsymbol{r}_\alpha)$, $J_{\alpha\beta}^{kl}(\boldsymbol{R}_{\alpha\beta}^{\mu\nu}) = \sum_{n=1}^{p} J_n^{kl} f_{\alpha\beta}^n \delta_{\boldsymbol{R}_{\alpha\beta}^{\mu\nu}, \mathcal{R}_{\alpha\beta}^n}$ ($\mathcal{R}_{\alpha\beta}^n$ is the set of nth-nearest neighbour connection vectors) and $D_{dd} = \mu_0(g\mu_B)^2/4\pi$ where the spins are full $O(3)$ operators satisfying $\boldsymbol{S}_\alpha(\boldsymbol{R}^\mu) \cdot \boldsymbol{S}_\alpha(\boldsymbol{R}^\mu) = S(S+1)$. A factor of $\frac{1}{2}$ has been included to avoid double counting. The anisotropic exchange tensor J_n^{kl} is the relative strength of the magnetic interaction for spin components k and l between nth-nearest neighbours. The factor $f_{\alpha,\beta}^n$ is equal to $1 - \delta_{\alpha,\beta}$ if the coupled spins are on different sublattices, or $\delta_{\alpha,\beta}$ if they are on the same sublattice. The symbols μ and ν index all primitive Bravais lattice vectors, α and β run over all basis vectors and k and l over the spin components x, y and z. We wish to consider the stability of some classical ground state by investigating the role of quantum fluctuations in reducing the fully polarized classical spin value $\boldsymbol{S} = (0, 0, S)$. This can be accomplished by changing the axis of quantization from the global z-direction (which is an arbitrary choice of the theory) to a local quantization axis which points in the direction of each spin. Let $\tilde{\boldsymbol{S}}_\alpha(\boldsymbol{R}^\mu)$ be the locally quantized spin which is related to the real spin operator defined in the crystallographic frame via the rotation

$$\boldsymbol{S}_\alpha(\boldsymbol{R}^\mu) = \mathsf{R}(\theta_\alpha, \phi_\alpha)\tilde{\boldsymbol{S}}_\alpha(\boldsymbol{R}^\mu). \quad (2)$$

This transformation can be implemented in an alternative way by defining an orthogonal triad of unit vectors $\boldsymbol{n}_{i,\alpha}$ for each sublattice α by

$$\boldsymbol{n}_{i,\alpha} = \mathsf{R}(\theta_\alpha, \phi_\alpha)\boldsymbol{e}_i \quad (3)$$

where $\{e_x, e_y, e_z\}$ are the usual Cartesian unit vectors and clearly $n_{z,\alpha}$ points in the direction of the spin $S_\alpha(R^\mu)$. In this form, we can re-express equation (2) as

$$S_\alpha(R^\mu) = \sum_i \tilde{S}_\alpha^i(R^\mu) n_{i,\alpha} \tag{4}$$

and substituting into our original Hamiltonian equation (1) we find

$$\mathcal{H} = -\tfrac{1}{2} \sum_{\alpha,\beta} \sum_{i,j} \sum_{\mu,\nu} \mathcal{J}_{\alpha\beta}^{ij}(R_{\alpha\beta}^{\mu\nu}) \tilde{S}_\alpha^i(R^\mu) \tilde{S}_\beta^j(R^\nu) \tag{5}$$

where

$$\mathcal{J}_{\alpha\beta}^{ij}(R_{\alpha\beta}^{\mu\nu}) = \sum_{k,l} J_{\alpha\beta}^{kl}(R_{\alpha\beta}^{\mu\nu}) n_{i,\alpha}^k n_{j,\beta}^l - D_{dd} \left[\frac{(n_{i,\alpha} \cdot n_{j,\beta})}{|R_{\alpha\beta}^{\mu\nu}|^3} - 3\frac{(n_{i,\alpha} \cdot R_{\alpha\beta}^{\mu\nu})(n_{j,\beta} \cdot R_{\alpha\beta}^{\mu\nu})}{|R_{\alpha\beta}^{\mu\nu}|^5} \right] \tag{6}$$

is the two-spin coupling matrix. Making use of the periodicity of the lattice we Fourier transform the spin operators via

$$\tilde{S}_\alpha^i(R^\mu) = \frac{1}{\sqrt{N}} \sum_k \tilde{S}_\alpha^i(k) \exp[ik \cdot (R^\mu + r_\alpha)] \tag{7}$$

where N is the number of Bravais lattice points, leading to

$$\mathcal{H} = -\tfrac{1}{2} \sum_{\alpha,\beta} \sum_{i,j} \sum_{\mu,\nu} \sum_{k,k'} \mathcal{J}_{\alpha\beta}^{ij}(R_{\alpha\beta}^{\mu\nu}) \tilde{S}_\alpha^i(k) \tilde{S}_\beta^j(k')$$
$$\times \exp[ik \cdot (R^\mu + r_\alpha)] \exp[ik' \cdot (R^\nu + r_\beta)] \tag{8}$$

and using the definition of the Dirac delta function $\delta_{q,q'} = \frac{1}{N} \sum_\nu \exp[i(q - q') \cdot R^\nu]$, we can write this as

$$\mathcal{H} = -\tfrac{1}{2} \sum_{\alpha,\beta} \sum_{i,j} \sum_k \tilde{S}_\alpha^i(k) \mathcal{J}_{\alpha\beta}^{ij}(k) \tilde{S}_\beta^j(-k) \tag{9}$$

where the Fourier transform of the spin–spin interaction matrix has been defined by

$$\mathcal{J}_{\alpha\beta}^{ij}(k) = \sum_\mu \mathcal{J}_{\alpha\beta}^{ij}(R_{\alpha\beta}^{\mu\nu}) \exp[-ik \cdot R_{\alpha\beta}^{\mu\nu}]. \tag{10}$$

The Holstein–Primakoff transformation [27] defined by

$$\tilde{S}_\alpha^+(R^\mu) = \sqrt{2S - c_\alpha^\dagger(R^\mu) c_\alpha(R^\mu)} \, c_\alpha(R^\mu) \tag{11a}$$

$$\tilde{S}_\alpha^-(R^\mu) = c_\alpha^\dagger(R^\mu) \sqrt{2S - c_\alpha^\dagger(R^\mu) c_\alpha(R^\mu)} \tag{11b}$$

$$\tilde{S}_\alpha^z(R^\mu) = S - c_\alpha^\dagger(R^\mu) c_\alpha(R^\mu) \tag{11c}$$

allows us to express our anticommuting fermionic spin operators in terms of commuting bosonic spin deviation annihilation and creation operators $c_\alpha(R^\mu)$ and $c_\alpha^\dagger(R^\mu)$ where $[c_\alpha(R^\mu), c_\beta^\dagger(R^\nu)] = \delta_{\alpha,\beta} \delta_{\mu,\nu}$. We wish to deal with a theory whose transverse terms are only linear in the boson operators, leading to a quadratic boson mode spin wave Hamiltonian—in other words, a harmonic theory where there exist only small deviations away from some stable minimum energy spin configuration. Identifying that the boson operators can be written in terms of their Fourier components:

$$c_\alpha(R^\mu) = \frac{1}{\sqrt{N}} \sum_k c_\alpha(k) \exp[-ik \cdot (R^\mu + r_\alpha)] \tag{12a}$$

$$c_\alpha^\dagger(R^\mu) = \frac{1}{\sqrt{N}} \sum_k c_\alpha^\dagger(k) \exp[ik \cdot (R^\mu + r_\alpha)] \tag{12b}$$

we can write the linearized Holstein–Primakoff transformation in reciprocal space as

$$\tilde{S}_\alpha^x(\boldsymbol{k}) = \sqrt{\frac{S}{2}} \left[c_\alpha^\dagger(\boldsymbol{k}) + c_\alpha(-\boldsymbol{k}) \right] + O\left(\frac{1}{S^2}\right) \tag{13a}$$

$$\tilde{S}_\alpha^y(\boldsymbol{k}) = \mathrm{i}\sqrt{\frac{S}{2}} \left[c_\alpha^\dagger(\boldsymbol{k}) - c_\alpha(-\boldsymbol{k}) \right] + O\left(\frac{1}{S^2}\right) \tag{13b}$$

$$\tilde{S}_\alpha^z(\boldsymbol{k}) = \sqrt{N} S \delta_{k,0} \ \exp[-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_\alpha] - \frac{1}{\sqrt{N}} \sum_{k'} c_\alpha^\dagger(\boldsymbol{k}') c_\alpha(\boldsymbol{k}' - \boldsymbol{k}) \tag{13c}$$

where the Fourier transformed boson operators satisfy $[c_\alpha(\boldsymbol{k}), c_\beta^\dagger(\boldsymbol{k}')] = \delta_{\alpha,\beta}\delta_{k,k'}$.

Performing this transformation on equation (9) and keeping only terms up to second order in the boson mode amplitudes, we obtain a form for the Hamiltonian to order $1/S$ which can be broken into three parts that are zeroth, first and second order in the boson operators:

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)} \tag{14}$$

with

$$\mathcal{H}^{(0)} = -\tfrac{1}{2} N S(S+1) \sum_{\alpha,\beta} \mathcal{J}_{\alpha\beta}^{zz}(0) \tag{15a}$$

$$\mathcal{H}^{(1)} = -S\sqrt{\frac{NS}{2}} \sum_{\alpha,\beta} \left[\mathsf{F}_{\alpha\beta}(0) c_\alpha^\dagger(0) + \mathsf{F}_{\alpha\beta}^*(0) c_\alpha(0) \right] \tag{15b}$$

$$\mathcal{H}^{(2)} = -\tfrac{1}{2} S \sum_{\alpha,\beta} \sum_{k} \left[\mathsf{A}_{\alpha\beta}(\boldsymbol{k}) c_\alpha^\dagger(\boldsymbol{k}) c_\beta(\boldsymbol{k}) + \mathsf{B}_{\alpha\beta}(\boldsymbol{k}) c_\alpha^\dagger(\boldsymbol{k}) c_\beta^\dagger(-\boldsymbol{k}) \right.$$
$$\left. + \mathsf{B}_{\alpha\beta}^*(-\boldsymbol{k}) c_\alpha(-\boldsymbol{k}) c_\beta(\boldsymbol{k}) + \mathsf{A}_{\alpha\beta}^*(-\boldsymbol{k}) c_\alpha(-\boldsymbol{k}) c_\beta^\dagger(-\boldsymbol{k}) \right] \tag{15c}$$

and

$$\mathsf{F}_{\alpha\beta}(0) = \mathcal{J}_{\alpha\beta}^{xz}(0) + \mathrm{i}\mathcal{J}_{\alpha\beta}^{yz}(0) \tag{16a}$$

$$\mathsf{A}_{\alpha\beta}(\boldsymbol{k}) = \tfrac{1}{2}\{\mathcal{J}_{\alpha\beta}^{xx}(\boldsymbol{k}) + \mathcal{J}_{\alpha\beta}^{yy}(\boldsymbol{k}) - \mathrm{i}[\mathcal{J}_{\alpha\beta}^{xy}(\boldsymbol{k}) - \mathcal{J}_{\alpha\beta}^{yx}(\boldsymbol{k})]\} - \sum_\gamma \mathcal{J}_{\alpha\gamma}^{zz}(0)\delta_{\alpha,\beta} \tag{16b}$$

$$\mathsf{B}_{\alpha\beta}(\boldsymbol{k}) = \tfrac{1}{2}\{\mathcal{J}_{\alpha\beta}^{xx}(\boldsymbol{k}) - \mathcal{J}_{\alpha\beta}^{yy}(\boldsymbol{k}) + \mathrm{i}[\mathcal{J}_{\alpha\beta}^{xy}(\boldsymbol{k}) + \mathcal{J}_{\alpha\beta}^{yx}(\boldsymbol{k})]\}. \tag{16c}$$

Here we note the manifestation of the equilibrium condition that, for a particular classical ground state to be stable, the effective magnetic field acting on each spin is parallel to that spin. This implies that there are no terms linear in the boson operators in equation (14), or $\sum_\beta \mathsf{F}_{\alpha\beta}(0) = 0$, showing that the $\mathcal{J}_{\alpha\beta}^{xz}(0)$, $\mathcal{J}_{\alpha\beta}^{yz}(0)$, $\mathcal{J}_{\alpha\beta}^{zx}(0)$ and $\mathcal{J}_{\alpha\beta}^{zy}(0)$ blocks of the interaction matrix are only responsible for determining the equilibrium configuration and do not play any dynamical role [28].

2.2. Diagonalization

If a stable ground state spin configuration exists, then the quadratic spin wave Hamiltonian in equation (15c) can be rewritten in terms of a general quadratic form by defining a vector which contains the boson creation and destruction operators:

$$\mathsf{X} = \left[c_1(\boldsymbol{k}) \cdots c_s(\boldsymbol{k}), \ c_1^\dagger(-\boldsymbol{k}) \cdots c_s^\dagger(-\boldsymbol{k}) \right]^\mathrm{T} \tag{17}$$

where s is the number of atoms in the basis. In matrix notation, this leads to the Hamiltonian

$$\mathcal{H} = \mathcal{H}^{(0)} + \sum_{k} \mathsf{X}^\dagger \mathsf{H} \mathsf{X} \tag{18}$$

where H is the $2s \times 2s$ matrix defined by

$$H = -\tfrac{1}{2}S \begin{bmatrix} A(\boldsymbol{k}) & B(\boldsymbol{k}) \\ B^*(-\boldsymbol{k}) & A^*(-\boldsymbol{k}) \end{bmatrix} \tag{19}$$

and $A(\boldsymbol{k})$ and $B(\boldsymbol{k})$ are the full matrix representations of equations (16b) and (16c). We now introduce the transformation $X = QY$ where Y is a column matrix of new boson operators $a_\alpha(\boldsymbol{k})$ and $a_\alpha^\dagger(\boldsymbol{k})$. It is clear that if we intend to diagonalize our spin wave Hamiltonian, the transformation law must satisfy $Q^\dagger H Q = \Lambda$ where Λ is the diagonal matrix of eigenenergies. The matrix Q constructed from the eigenvectors of the transformation must be normalized with respect to a metric which preserves proper boson commutation rules for our new operators. This requirement leads to the possibility of a non-unitary Q and in general forces us to perform a Bogoliubov transformation to diagonalize the spin wave Hamiltonian [29]. The details of the numerical construction of this transformation are included in the appendix and the result is given by

$$\mathcal{H} = \mathcal{H}^{(0)} + \sum_{\boldsymbol{k}} \sum_\alpha \varepsilon_\alpha(\boldsymbol{k}) + \sum_{\boldsymbol{k}} \sum_\alpha \varepsilon_\alpha(\boldsymbol{k}) \left[a_\alpha^\dagger(\boldsymbol{k}) a_\alpha(\boldsymbol{k}) + a_\alpha^\dagger(-\boldsymbol{k}) a_\alpha(-\boldsymbol{k}) \right]. \tag{20}$$

2.3. Zero-point effects

In a quantum mechanical antiferromagnet, there exist spin fluctuations at zero temperature with energy $\varepsilon(\boldsymbol{k})$ which raise the classical ground state energy and reduce the staggered magnetic moment per spin from its classical value of S. Examining equation (20) and noting the fact that, at zero temperature, $\langle a_\alpha^\dagger(\boldsymbol{k}) a_\alpha(\boldsymbol{k}) \rangle = 0$, the contribution to the ground state energy from quantum spin fluctuations to order $1/S$ will be given by

$$\Delta \mathcal{H}^{(0)} = \sum_{\boldsymbol{k}} \sum_\alpha \varepsilon_\alpha(\boldsymbol{k}). \tag{21}$$

Returning to the original Holstein–Primakoff bosons, the reduction in the classical spin polarization will be equivalent to the average number of activated magnons localized at each site:

$$\Delta S = \frac{1}{Ns} \sum_\mu \sum_\alpha \left\langle c_\alpha^\dagger(\boldsymbol{R}^\mu) c_\alpha(\boldsymbol{R}^\mu) \right\rangle \tag{22}$$

where $\langle \cdots \rangle$ indicates the expectation value with respect to the classical ground state. Upon moving to Fourier space, this becomes an average over the first Brillouin zone given by

$$\Delta S = \frac{1}{2Ns} \sum_{\boldsymbol{k}} \sum_\alpha \left\langle c_\alpha^\dagger(\boldsymbol{k}) c_\alpha(\boldsymbol{k}) + c_\alpha^\dagger(-\boldsymbol{k}) c_\alpha(-\boldsymbol{k}) \right\rangle = \frac{1}{2Ns} \sum_{\boldsymbol{k}} \left\langle X^\dagger X \right\rangle - \frac{1}{2}. \tag{23}$$

Recall that we have introduced new boson operators $a_\alpha(\boldsymbol{k})$ which diagonalize the spin wave Hamiltonian through the canonical Bogoliubov transformation $X = QY$, where it is convenient to note that the transformation can be written in component form as $X_\alpha = \sum_i Q_{\alpha,i} Y_i$ and $X_{\alpha+s} = \sum_i Q_{\alpha+s,i} Y_i$ with the convention that Greek indices run over $1, \ldots, s$ and Latin indices over $1, \ldots, 2s$. The inner product, $X^\dagger X$ can then be expanded as

$$X^\dagger X = \sum_i \sum_{\alpha,\beta} \left[Q_{\alpha,i}^\dagger Q_{i,\beta} a_\alpha^\dagger(\boldsymbol{k}) a_\beta(\boldsymbol{k}) + Q_{\alpha+s,i}^\dagger Q_{i,\beta+s} a_\beta^\dagger(-\boldsymbol{k}) a_\alpha(-\boldsymbol{k}) \right.$$
$$\left. + Q_{\alpha,i}^\dagger Q_{i,\beta+s} a_\alpha^\dagger(\boldsymbol{k}) a_\beta^\dagger(-\boldsymbol{k}) + Q_{\alpha+s,i}^\dagger Q_{i,\beta} a_\alpha(-\boldsymbol{k}) a_\beta(\boldsymbol{k}) + Q_{\alpha+s,i}^\dagger Q_{i,\beta+s} \delta_{\alpha,\beta} \right] \tag{24}$$

and at zero temperature there are no thermally activated spin deviations to destroy with $a_\alpha(\boldsymbol{k})$, so the expectation value of all quadratic boson terms tend to zero. Substituting equation (24)

into (23) and neglecting these terms we find the staggered moment at zero temperature due to quantum spin fluctuations to be

$$\Delta S = \frac{1}{2}\left(\frac{1}{Ns}\sum_{k}\sum_{\alpha}\left[\mathsf{Q}^{\dagger}\mathsf{Q}\right]_{\alpha\alpha} - 1\right). \tag{25}$$

At this point we may reflect upon the fact that beginning with equation (18) the form of the fully diagonalized spin wave Hamiltonian to O(1/S) in equation (20) could have been inferred with little or no calculation. Physically, to order 1/S, the Hamiltonian ought to describe a system of non-interacting bosons with energy dispersion equal to $\hbar\omega_{\alpha}(k)$ where $\omega_{\alpha}(k)$ are the classical spin wave frequencies obtained by linearizing the classical equations of motion for interacting magnetic dipoles. Self-contained approaches exist which begin from such a Hamiltonian and allow for the calculation of the staggered magnetic moment at zero temperature without any knowledge of the eigenvectors of the diagonalizing transformation embedded within the Q matrix discussed above. A staggered anisotropy field h_{α} is introduced which points along the local quantization (classical ground state) direction and the change in the ground state energy $\partial E/\partial h_{\alpha}$ is calculated giving the total magnetic moment on each sublattice at $T = 0\,\mathrm{K}$ [30]. In the discussion above, we have chosen not to follow this physically motivated approach and have instead utilized the full spectrum of our transformation matrix Q to compute the desired zero-point quantum effects.

2.4. Thermodynamic relations

We have decomposed our theory of spins on a lattice interacting via frustrated exchange and dipole–dipole interactions to that of non-interacting Bose gas (equation (20)). Beginning from the well known partition function

$$\mathcal{Z} = \mathrm{Tr}\,\exp[-\beta\mathcal{H}] = \exp[-\beta E]\prod_{k}\prod_{\alpha}\frac{1}{1 - \exp[-\beta\varepsilon_{\alpha}(k)]} \tag{26}$$

where $E = \mathcal{H}^{(0)} + \Delta\mathcal{H}^{(0)}$ and β is the inverse temperature, we have used the standard thermodynamic relations to derive equations for the free energy ($\mathcal{F}$), average internal energy ($\mathcal{U}$), specific heat at constant volume ($\mathcal{C}_v$) and entropy ($\mathcal{S}$) as a function of temperature. These expressions will be valid only for low temperatures where $T \ll \varepsilon_{\alpha}(k)$ and are given by

$$\mathcal{F} = E + \beta^{-1}\sum_{k}\sum_{\alpha}\ln(1 - \exp[\beta\varepsilon_{\alpha}(k)]) \qquad \mathcal{U} = E + \sum_{k}\sum_{\alpha}\varepsilon_{\alpha}(k)n_{\mathrm{B}}(\varepsilon_{\alpha}(k))$$

$$\mathcal{C}_v = \beta^2\sum_{k}\sum_{\alpha}[\varepsilon_{\alpha}(k)n_{\mathrm{B}}(\varepsilon_{\alpha}(k))]^2\exp[\beta\varepsilon_{\alpha}(k)] \qquad \mathcal{S} = \beta(\mathcal{U} - \mathcal{F}) \tag{27}$$

where $n_{\mathrm{B}}(\varepsilon_{\alpha}(k)) = (\exp[\beta\varepsilon_{\alpha}(k)] - 1)^{-1}$ is the Bose factor [31]. In order to calculate the magnetic order parameter as a function of temperature ($m^{\star}$), we must return to the general form for the reduction of the sublattice magnetization in equation (24). For suitably low temperatures, the expectation value of all non-number conserving quadratic boson terms will be negligible and we find

$$m^{\star} = S - \Delta S(T = 0) - \frac{1}{Ns}\sum_{k}\sum_{\alpha}\left[\mathsf{Q}^{\dagger}\mathsf{Q}\right]_{\alpha\alpha}n_{\mathrm{B}}(\varepsilon_{\alpha}(k)). \tag{28}$$

3. The Heisenberg-like dipolar pyrochlore

Having developed the formalism of linear spin wave theory for a multi-sublattice non-Bravais magnetic system we now map out the low temperature excitations of spins interacting via
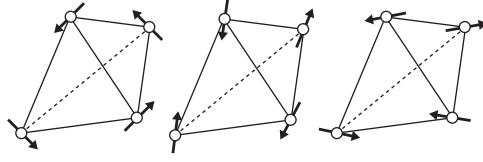
Figure 1. Six degenerate Palmer–Chalker (PC) ground states (reverse spins for the other three) for spins on a single tetrahedron.

Table 1. Vectors which define the six classical PC ground state spin configurations on the pyrochlore lattice.

PC_{xy} state	PC_{xz} state	PC_{yz} state
$S_1 = 1/\sqrt{2}(1, \bar{1}, 0)$	$S_1 = 1/\sqrt{2}(1, 0, \bar{1})$	$S_1 = 1/\sqrt{2}(0, 1, \bar{1})$
$S_2 = 1/\sqrt{2}(\bar{1}, 1, 0)$	$S_2 = 1/\sqrt{2}(1, 0, 1)$	$S_2 = 1/\sqrt{2}(0, 1, 1)$
$S_3 = 1/\sqrt{2}(1, 1, 0)$	$S_3 = 1/\sqrt{2}(\bar{1}, 0, 1)$	$S_3 = 1/\sqrt{2}(0, \bar{1}, \bar{1})$
$S_4 = 1/\sqrt{2}(\bar{1}, \bar{1}, 0)$	$S_4 = 1/\sqrt{2}(\bar{1}, 0, \bar{1})$	$S_4 = 1/\sqrt{2}(0, \bar{1}, 1)$

nearest neighbour Heisenberg exchange and long range dipole–dipole interactions on the pyrochlore lattice.

3.1. Classical ground states

It is known that when isotropic nearest neighbour exchange interactions alone are considered on the pyrochlore lattice, the system exhibits no global symmetry breaking and has soft modes at long wavelengths [2, 20]. The inclusion of a perturbation such as long range dipole–dipole interactions breaks the continuous $O(3)$ symmetry [18, 21] and leads to a gap in the excitation spectrum. The non-trivial coupling of the isotropic spin symmetry and translational lattice symmetry for a particular set of interaction parameters controls how these optical modes disperse. The details of this dispersion directly affect the stiffness of a given spin configuration and quantitatively determine the level of proliferation of quantum fluctuations in the ground state.

Palmer and Chalker [21] have investigated the classical Heisenberg model for spins residing on the pyrochlore lattice with long range dipolar interactions. They find that the dipolar perturbation fixes the two continuous internal degrees of freedom and leads to the energetic selection of the six degenerate $q = 0$ (Palmer–Chalker, PC) ground states shown in figure 1 where the total magnetic moment on each tetrahedron is zero. We have confirmed the six degenerate PC classical ground states numerically in real space using a field averaging approach by exploring the energy landscape at zero temperature as shown in table 1. The inclusion of long range dipole interactions does indeed break the global rotational symmetry and selects a crystallographic plane in which the spins are confined while still preserving a zero-moment structure on each tetrahedron. The discrete degeneracy of the PC ground states allows us to perform our spin wave calculation on just one state and the remainder of the results presented were calculated for the PC_{xy} state, but are identical (with the proper symmetry considerations) for the other five states.

3.2. Spin wave dispersion

The functional dependence of the normal modes of an oscillating system on the wavevector can be derived from classical mechanics. Treating each spin as a classical rotor, the rate of

change of the angular momentum in the local spin frame, $\hbar \partial \tilde{S}_\alpha(\mathbf{R}^\mu)/\partial t$, is equal to the torque, $\tilde{\mathbf{N}}_\alpha(\mathbf{R}^\mu) = \tilde{\mu}_\alpha(\mathbf{R}^\mu) \times \tilde{\mathbf{B}}_\alpha(\mathbf{R}^\mu)$, acting on $\tilde{S}_\alpha(\mathbf{R}^\mu)$, where $\tilde{\mathbf{B}}_\alpha(\mathbf{R}^\mu)$ is the total effective magnetic field experienced by a spin on site α in the local frame. Here we must take care to ensure that the vector product is carried out in a way that is independent of the local coordinate system. Following this procedure we use a plane-wave ansatz of the form $S_\alpha^j(\mathbf{R}^\mu) \sim \exp[i\vec{k} \cdot (\mathbf{R}^\mu + \mathbf{r}_\alpha) - i\omega t]$ to solve the resulting system of linear equations and obtain the excitation spectrum. The spin wave dispersion spectrum calculated using the Holstein–Primakoff bosons above can then be compared with the classical modes of excitation as an essential consistency check.

Armed with the knowledge of a set of candidate classical ground state spin configurations for the isotropic dipolar pyrochlore (which satisfy $\mathcal{H}^{(1)} = 0$) we may now attempt to apply this method to an actual material, the frustrated pyrochlore antiferromagnet gadolinium titanate. $Gd_2Ti_2O_7$ is a spin only $(S = 7/2)$ material with a parameter describing the isotropic magnetic exchange between nearest neighbours which can be estimated from the value of the Curie–Weiss constant $(\theta_{CW} = -9.8$ K$)$ using the relation $J_1 = 3\theta_{CW}/[zS(S + 1)] \simeq -0.304\,76$ K where z is the number of nearest neighbours. The dipolar energy scale is set at $D_{dd}/(a\sqrt{2}/4)^3 \simeq 0.053\,38$ K where $a = 10.184$ Å is the edge size of the cubic unit cell and $|\mathcal{R}^1| = a\sqrt{2}/4$ is the nearest neighbour distance leading to $(D_{dd}|\mathcal{R}^1|^{-3})/|J_1| \sim 1/5$ [17].

In order to map out the low temperature magnetic excitations of this material we are faced with the non-trivial task of calculating the Fourier transform of the 12×12 interaction matrix $\mathcal{J}_{\alpha\beta}^{ij}(\mathbf{R}_{\alpha\beta}^{\mu\nu})$ (equation (15c)) which contains the exchange contribution out to a finite number of nearest neighbours and the infinite range dipole–dipole interactions. This is accomplished via the Ewald summation method [32], and the final result for up to third-nearest neighbour isotropic exchange [33, 34] is given by

$$\mathcal{J}_{\alpha\beta}^{ij}(\mathbf{k}) = \mathcal{E}_{\alpha\beta}^{ij}(\mathbf{k}) - D_{dd}\mathcal{D}_{\alpha\beta}^{ij}(\mathbf{k}) \tag{29}$$

where

$$\begin{aligned}
\mathcal{E}_{\alpha\beta}^{ij}(\mathbf{k}) &= 2J_1(\mathbf{n}_{i,\alpha} \cdot \mathbf{n}_{j,\beta})\cos[\mathbf{k} \cdot (\mathbf{r}_\alpha - \mathbf{r}_\beta)](1 - \delta_{\alpha,\beta}) \\
&+ 2J_2(\mathbf{n}_{i,\alpha} \cdot \mathbf{n}_{j,\beta})\sum_{\gamma\neq\alpha,\beta}\cos[\mathbf{k} \cdot (\mathbf{r}_\alpha + \mathbf{r}_\beta - 2\mathbf{r}_\gamma)](1 - \delta_{\alpha,\beta}) \\
&+ 2J_3(\mathbf{n}_{i,\alpha} \cdot \mathbf{n}_{j,\beta})\sum_{\sigma<\rho}\cos[2\mathbf{k} \cdot (\mathbf{r}_\sigma - \mathbf{r}_\rho)]\delta_{\alpha,\beta}
\end{aligned} \tag{30}$$

and

$$\begin{aligned}
\mathcal{D}_{\alpha\beta}^{ij}(\mathbf{k}) &= -\frac{4\lambda^3}{3\sqrt{\pi}}(\mathbf{n}_{i,\alpha} \cdot \mathbf{n}_{j,\beta})\delta_{\alpha,\beta} + \frac{4\pi}{v}\sum_{\mathbf{G}}\mathcal{K}_{\alpha\beta}^{ij}(\mathbf{k} - \mathbf{G})e^{-|\mathbf{k}-\mathbf{G}|^2/4\lambda^2}\exp[-i\mathbf{G} \cdot \mathbf{r}_{\alpha\beta}] \\
&+ {\sum_\mu}'[\mathcal{U}1_{\alpha\beta}^{ij}(\mathbf{R}_{\alpha\beta}^{\mu\nu}) - \mathcal{U}2_{\alpha\beta}^{ij}(\mathbf{R}_{\alpha\beta}^{\mu\nu})]\exp[-i\mathbf{k} \cdot \mathbf{R}_{\alpha\beta}^{\mu\nu}]
\end{aligned} \tag{31}$$

with

$$\mathcal{K}_{\alpha\beta}^{ij}(\mathbf{k} - \mathbf{G}) = \frac{\left[\mathbf{n}_{i,\alpha} \cdot (\mathbf{k} - \mathbf{G})\right]\left[\mathbf{n}_{j,\beta} \cdot (\mathbf{k} - \mathbf{G})\right]}{|\mathbf{k} - \mathbf{G}|^2} \tag{32a}$$

$$\mathcal{U}1_{\alpha\beta}^{ij}(\mathbf{R}_{\alpha\beta}^{\mu\nu}) = (\mathbf{n}_{i,\alpha} \cdot \mathbf{n}_{j,\beta})\frac{1}{|\mathbf{R}_{\alpha\beta}^{\mu\nu}|^2}\left[\frac{2\lambda}{\sqrt{\pi}}e^{-\lambda^2|\mathbf{R}_{\alpha\beta}^{\mu\nu}|^2} + \frac{\mathrm{erfc}(\lambda|\mathbf{R}_{\alpha\beta}^{\mu\nu}|)}{|\mathbf{R}_{\alpha\beta}^{\mu\nu}|}\right] \tag{32b}$$

$$\begin{aligned}
\mathcal{U}2_{\alpha\beta}^{ij}(\mathbf{R}_{\alpha\beta}^{\mu\nu}) &= (\mathbf{n}_{i,\alpha} \cdot \mathbf{R}_{\alpha\beta}^{\mu\nu})(\mathbf{n}_{j,\beta} \cdot \mathbf{R}_{\alpha\beta}^{\mu\nu})\frac{1}{|\mathbf{R}_{\alpha\beta}^{\mu\nu}|^2} \\
&\times \left\{\frac{2\lambda}{\sqrt{\pi}}\left[2\lambda^2 + \frac{3}{|\mathbf{R}_{\alpha\beta}^{\mu\nu}|^2}\right]e^{-\lambda^2|\mathbf{R}_{\alpha\beta}^{\mu\nu}|^2} + 3\frac{\mathrm{erfc}(\lambda|\mathbf{R}_{\alpha\beta}^{\mu\nu}|)}{|\mathbf{R}_{\alpha\beta}^{\mu\nu}|^3}\right\}.
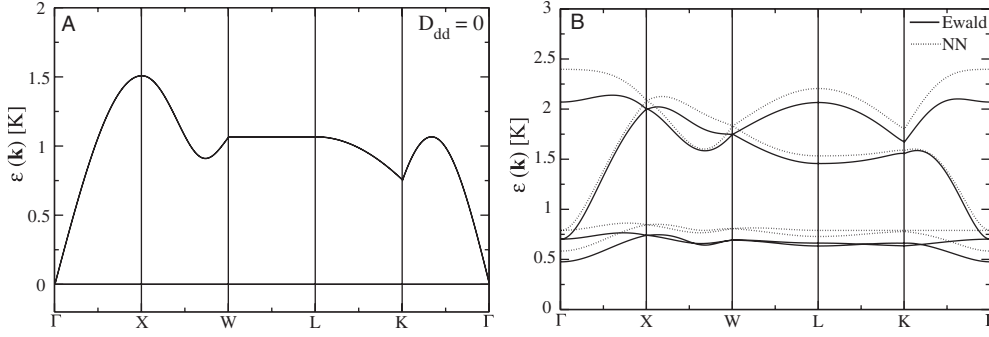\end{aligned} \tag{32c}$$

Figure 2. Spin wave energies, $\varepsilon_\alpha(\boldsymbol{k})$, in kelvins, for (A) the pure Heisenberg pyrochlore ($D_{dd} = 0$) with $J_1 = -0.304\,76$ K where both branches are doubly degenerate and (B) excitations from one of six discretely degenerate classical ground states for $Gd_2Ti_2O_7$ with nearest neighbour exchange and both nearest neighbour and long range dipole interactions, obtained using the Ewald method.

In these expressions $\lambda = \sqrt{\pi/v}$ is the Ewald convergence parameter, $\mathrm{erfc}(\cdots)$ is the complimentary error function, v is the volume of the primitive unit cell, $\boldsymbol{G}$ is a FCC reciprocal lattice vector and the primed summation indicates that the real space sum is over all FCC Bravais lattice vectors *except* $\boldsymbol{R}_{\alpha\beta}^{\mu\nu} = 0$.

If we completely ignore the effect of dipole interactions we expect the excitation spectrum of a system with massless Goldstone bosons seen in figure 2(A). There are two unfixed internal degrees of freedom associated with the spin isotropy and one time reversal degree of freedom. The ground state spin configuration can fluctuate with no cost in energy between states in its continuously degenerate manifold while maintaining a macroscopic zero-moment structure.

When the effects of dipole–dipole interactions are included, the internal degrees of freedom are fixed and the spins are able to minimize their energy by ordering in a non-collinear, planar configuration which satisfies a pairwise antiferromagnet constraint. This can be done in a number of ways, provided that each spin is parallel to an opposite edge of the tetrahedron (refer to figure 1) and we move from a continuously degenerate manifold to one with the six Palmer–Chalker discrete ground states.

Beginning from the PC_{xy} state with isotropic nearest neighbour exchange ($J_2 = J_3 = 0$) the spin wave dispersion spectrum for the parameter set of $Gd_2Ti_2O_7$ is shown in figure 2(B). We observe four optical modes indicating that all distortions from the chosen ground state are associated with a positive energy cost. As predicted, the introduction of anisotropy has broken a global symmetry and lifted the spectrum to finite frequency. The remnant soft modes from the pure Heisenberg model (figure 2(A)) have remained moderately degenerate and relatively dispersionless, while the acoustic modes have split and are dispersing to the point where one mode has changed curvature along $\Gamma \to X$ (for the PC_{xy} state). Once the system is in one of its stable classical ground states, it is unable to move between equivalent energy states through a low energy, long wavelength acoustic mode. This implies that we were justified in making our semi-classical approximations as it is likely that the $Gd_2Ti_2O_7$ may display very little quantum mechanical behaviour to asymptotically low temperatures.

The inclusion of truly long range dipole interactions using the Ewald technique, as opposed to truncating at nearest neighbours, leads to a restoration of some previously buried lattice symmetry. In figure 2(B) we observe promotion of quasi-degeneracy in the excitation spectrum between W and K and a slight suppression of the anisotropy gap throughout the Brillouin zone due to the global dipolar field being partially screened. It is interesting to note that when

interaction terms beyond nearest neighbour are neglected, quantum fluctuations are inhibited in the ground state as the local unscreened interaction leads to an increased anisotropy gap at the zone centre; $\varepsilon(\boldsymbol{k})$ obtained using the Ewald method is lower than $\varepsilon(\boldsymbol{k})$ obtained using only nearest neighbour interactions at Γ.

3.3. Quantum spin fluctuations

To form a quantitative picture of the role of spin fluctuations in the ground state we must calculate both the shift of the classical ground state energy and the reduction of the fully polarized $S = 7/2$ moment in $Gd_2Ti_2O_7$ at zero temperature. This is accomplished using the properly normalized eigenvectors of the numerically constructed Bogoliubov transformation in conjunction with equations (15a) and (21) for the energy of the system and equation (25) for the reduced moment. Performing averages over the first Brillouin zone of the FCC lattice, the main quantitative numerical results of this study, accurate to order $1/S$, are

$$E_{\mathrm{NN}} = E_0(1 + 0.1442/S) \qquad m^{\star}_{\mathrm{NN}} = S(1 - 0.1007/S) \qquad (33a)$$

$$E_{\mathrm{LR}} = E_0(1 + 0.3526/S) \qquad m^{\star}_{\mathrm{LR}} = S(1 - 0.1174/S) \qquad (33b)$$

where $E_0 = -1/2NS^2\sum_{\alpha,\beta}\mathcal{J}^{zz}_{\alpha\beta}(0)$ is the classical ground state energy, NN $\equiv$ nearest neighbour dipole and LR $\equiv$ long range dipole. In accordance with our naive expectation from an examination of the spin wave dispersion spectrum, we see a softening of the system and enhanced spin fluctuations in the ground state when long range dipole interactions are treated properly. The reduction of the fully polarized moment is almost 20% larger when the Ewald summation method is employed. These comparisons are overshadowed by the reality that the actual numerical values of the quantum corrections are negligible when the zero-point shifts above are divided by the large $S = 7/2$ moment of the Gd^{3+} ion. The ground state energy is shifted by less than 10% and the fully ordered moment is reduced by half of that. However, the S dependence of the numerical values for the quantum corrections in equations (33a) and (33b) has been explicitly removed and these numbers are set by J and $(\mu_0/4\pi)(g\mu_B)^2/|\mathcal{R}^1|^3$ for a given interacting system. It is apparent that one cannot *a priori* rule out the possibility of sizable quantum fluctuations ($\sim$5% for $S = 7/2$ here) in the ground state of the frustrated pyrochlore materials. $Yb_2Ti_2O_7$ falls into the category of an XY $S = 1/2$ system [11] and using equations (33a) and (33b) above we might expect quantum fluctuations of the order of 20%. Therefore, it is crucial to properly identify and include the variety of complex competing interactions which act as finite, non-zero perturbations of the isotropic Heisenberg exchange parameter J.

3.4. Thermodynamic properties

We have calculated the specific heat and staggered magnetization at finite temperatures and the results are shown in figure 3. At low temperatures, all four spin wave modes are gapped and we observe an exponentially vanishing specific heat as $T \to 0$ K, unlike the T^2 laws observed for both $Gd_2Ti_2O_7$ [18] and $Gd_2Sn_2O_7$ [37]. It appears that the energy scale set by the anisotropy gap corresponds to the peak position near 0.4 K in panel (A) and there exist some qualitative similarities with the experimentally measured value of $\mathcal{C}_v/T$ [18] where two peaks are observed at approximately 0.7 and 1.0 K. However, we have confined the system to a particular classical ground state and cannot probe the existence of multiple phase transitions in this study [18, 19, 35, 36].

The temperature dependence of the staggered magnetization shown in figure 3 panel (B) is also of interest and we find the behaviour $1 - \exp[-\Delta/T]T^3$, with $\Delta \sim$ gap, as expected for an antiferromagnet at low temperature [28].
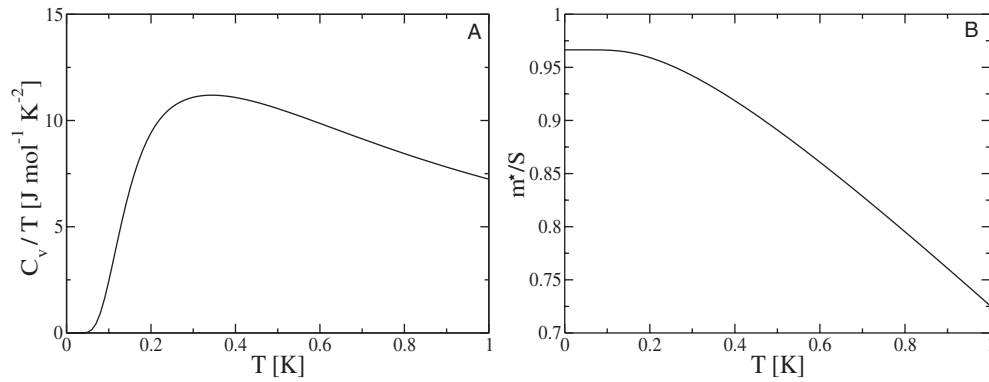
Figure 3. The specific heat at constant volume scaled by the temperature (A) and the staggered magnetic order parameter (B) as a function of temperature calculated using linear spin wave theory for gadolinium titanate.

4. Conclusions

We began by examining the energy landscape at zero temperature for the dipolar Heisenberg pyrochlore system and have confirmed the existence of the sixfold-degenerate Palmer–Chalker ground states. Beginning from one of these classical ground states we have employed the techniques of non-interacting spin wave theory. Using bosonic spin deviation operators and an analysis of the quantum mechanical equations of motion we have numerically constructed the canonical Bogoliubov transformation and diagonalized the spin wave Hamiltonian for the interaction parameter set of $Gd_2Ti_2O_7$. We have obtained the spin wave dispersion spectrum for nearest neighbour exchange and both nearest neighbour and long range dipole interactions using the Ewald summation technique and confirmed it classically, treating each spin as a rotor in its local frame. The spin wave excitation spectrum displays four non-degenerate modes and is gapped throughout the first zone. Ensuring that a proper bosonic transformation matrix has been found for each wavevector k, we have calculated the numerical contribution of zero-point quantum spin fluctuations to the ground state energy and the reduction of the classical staggered moment by performing a discrete average over the first Brillouin zone. The partition function was calculated using the fully diagonalized spin wave Hamiltonian and we obtained equations for the most relevant thermodynamic relations at low temperatures.

We have confirmed the stability of the PC ground states against quantum fluctuations and it appears that, due to the significant anisotropy gap present throughout the zone and the large value of the classical spin $S = 7/2$ of the gadolinium ion, quantum mechanical effects are small ($\sim$10%) in this system. The fully ordered spin polarization is reduced by less than 5% of its classical value and it should be well described by classical methods at low temperature. The physical system retains little 'quantum mechanical' knowledge of its fully disordered paramagnetic state after the effects of dipole interactions have been included in the Hamiltonian.

Small perturbations arising from exchange interactions beyond nearest neighbour may also be significant in this system and recent mean field theory studies of $Gd_2Ti_2O_7$ with $J_2 \neq J_3 \neq 0$ have identified another possible Kagomé-like ground state with ordering wavevector $q = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$. This state has one sublattice with a net moment of zero and it appears to be energetically selected over the PC states above some crossing temperature T_{cross} [35]. Powder neutron scattering results for $Gd_2Ti_2O_7$ [19] and recent theoretical work by Cépas

and Shastry [36] would tend to confirm the existence of this 1/4-disordered ground state at temperatures below 1 K. In contrast, an experimental study of the frustrated pyrochlore material $Gd_2Sn_2O_7$ [37] shows a single sharp first-order transition to a long range ordered magnetic state near 1 K which may be PC in character. It is therefore still under debate whether the real low temperature ordered phase of these Heisenberg-like dipolar pyrochlore materials is well described by the PC manifold. Nevertheless, the stability of the sixfold-degenerate classical PC states against quantum fluctuations in these systems is of considerable interest.

Although we have chosen to limit our calculation to one specific material, gadolinium titanate, we have presented the calculation in a general form with no real dependence on the structure of the lattice or the spin symmetry. It is therefore hoped that the theoretical techniques presented in this study can be employed to provide further understanding of the peculiar and interesting properties of highly frustrated antiferromagnets on non-Bravais lattices.

Acknowledgments

Appendix. Numerically constructed Bogoliubov transformation

The equations governing the construction of Q can be derived [38] by utilizing the vector commutator

$$\left[X, X^\dagger\right] \equiv X\tilde{X}^T - \left(\tilde{X}X^T\right)^T \tag{A.1}$$

where $\tilde{X}$ is the column vector of adjoint boson operators and T indicates the usual transpose operation. Using this definition we find

$$\left[X, X^\dagger\right] = g \tag{A.2}$$

where the metric of the transformation is

$$g = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{A.3}$$

and 1 is the $s \times s$ identity matrix where s is the number of magnetic sublattices. The required orthonormalization condition for the transformation matrix Q is found to be

$$QgQ^\dagger = g. \tag{A.4}$$

The Hermitian conjugate of Q can be expressed in terms of its inverse as $Q^\dagger = gQ^{-1}g$ and the diagonalization condition is now given by $Q^\dagger HQ = gQ^{-1}g = \Lambda$ leading to the more familiar eigenproblem

$$Q^{-1}gHQ = g\Lambda. \tag{A.5}$$

Defining $L = gH$ and $\Lambda_L = g\Lambda$ we can use a standard numerical package to solve for the eigenvectors and eigenvalues of the non-Hermitian matrix L, allowing us to write $Q_L \Lambda_L Q_L^{-1} = L$ where Q_L is the matrix whose columns are the eigenvectors of L subject to normalization with respect to the usual identity metric.

In order to find the proper diagonalizing transformation Q at each k-vector in the first Brillouin zone, three conditions must be met:

(I) $\quad Q\Lambda_L Q^{-1} = L$

(II) $\quad QgQ^\dagger = g$

(III) $\quad Q^\dagger HQ = \Lambda$.

These can be satisfied simultaneously, provided that we construct a Bogoliubov transformation which imposes the full *bosonic constraint* on our transformed operators. This amounts to properly grouping, organizing and then renormalizing the computed eigenvectors of L through a block transformation, ensuring that we always remain within only one eigenspace at a time [39].

Suppose L has m unique eigenvalues, each having degeneracy d_j for $j = 1, \ldots, m$. We assume that our eigenvector matrix Q_L is organized such that eigenvectors belonging to the same eigenspace are grouped together. Our goal is to construct a block diagonal transformation matrix dB consisting of m blocks of size $d_j \times d_j$ which will transform Q_L to our desired matrix Q via $Q = Q_L dB$. By performing this transformation we have simply formed new linear combinations of the eigenvectors within a given eigenspace and thus condition (I) will be satisfied. Condition (II) requires that

$$(Q_L dB)g(Q_L dB)^\dagger = g$$

and provided that there are only gapped spin wave excitations (no zero eigenvalues), Q_L is non-singular, so we can rearrange this as

$$dBgdB^\dagger = M \tag{A.6}$$

where we have defined the block diagonal matrix $M = \left(Q_L^\dagger g Q_L\right)^{-1}$. For each block dB we must solve an equation of the form

$$g_j dB_j dB_j^\dagger = M_j \tag{A.7}$$

where

$$g_j = \begin{cases} 1 & \text{if } \sum_{i<j} d_j < s \\ -1 & \text{otherwise} \end{cases} \tag{A.8}$$

$$M_j = \left(Q_{L,j}^\dagger g Q_{L,j}\right)^{-1} \tag{A.9}$$

and $Q_{L,j}$ is the $2s \times d_j$ block of vectors belonging to eigenspace j. An equation of this type can be solved by decomposing $M_j = V_j D_j V_j^{-1}$ where V_j is the unitary eigenvector matrix and D_j is the diagonal eigenvalue matrix corresponding to M_j. Substituting this into equation (A.7) we find that

$$dB_j = V_j \sqrt{g_j D_j} V_j^{-1} \tag{A.10}$$

is always a solution. Condition (III) is finally satisfied and we have arrived at an equation which can be used to numerically construct each block of dB yielding the proper transformation matrix Q for each k.

References

[1] Chandra P and Coleman P 1991 *New Outlooks and Old Dreams in Quantum Antiferromagnets* (*Les Houches Summer School Lectures*) ed B Douçot and J Zinn-Justin (Amsterdam: North-Holland)
[2] Canals B and Lacroix C 1998 *Phys. Rev. Lett.* **80** 2933
[3] Reimers J N, Berlisnky A J and Shi A-C 1991 *Phys. Rev.* B **43** 865
    Reimers J N, Greedan J E and Björgvinsson M 1992 *Phys. Rev.* B **45** 7295
    Ramirez A P 1994 *Ann. Rev. Mater. Sci.* **24** 453

[4] Ramirez A P, Hayashi A, Cava R J, Siddharthan R and Shastry B S 1999 *Nature* **399** 333
[5] den Hertog B C and Gingras M J P 2000 *Phys. Rev. Lett.* **84** 3430
[6] Harris M J, Bramwell S T, McMorrow D F, Zeiske T and Godfrey K W 1997 *Phys. Rev. Lett.* **79** 2554
[7] Bramwell S T *et al* 2001 *Phys. Rev. Lett.* **87** 047205
[8] Kadowaki H, Ishii Y, Matsuhira K and Hinatsu Y 2002 *Phys. Rev.* B **65** 144421
[9] Bramwell S T and Gingras M J P 2002 *Science* **294** 1495
[10] Bramwell S T and Harris M J 1998 *J. Phys.: Condens. Matter* **10** L215
[11] Hodges J A *et al* 2002 *Phys. Rev. Lett.* **88** 077204
[12] Villain J 1979 *Z. Phys.* B **33** 31
[13] Gardner J S *et al* 1999 *Phys. Rev. Lett.* **82** 1012
[14] Gardner J S, Gaulin B D, Berlinsky A J, Waldron P, Dunsinger S R, Raju N P and Greedan J E 2001 *Phys. Rev.* B **64** 224416
[15] Enjalran M, Gingras M J P, Kao Y-J, Del Maestro A and Molavian H R 2004 *J. Phys.: Condens. Matter* **16** S673
[16] Champion J D M *et al* 2003 *Phys. Rev.* B **68** 020401
[17] Raju N P, Dion M, Gingras M J P, Mason T E and Greedan J E 1999 *Phys. Rev.* B **59** 14489
[18] Ramirez A P, Shastry B S, Hayashi A, Krajewski J J, Huse D A and Cava R J 2002 *Phys. Rev. Lett.* **89** 067202
[19] Champion J D M, Wills A S, Fennel T, Bramwell S T and Green M A 2001 *Phys. Rev.* B **64** 140407
[20] Moessner R and Chalker J T 1998 *Phys. Rev. Lett.* **80** 2929
[21] Palmer S E and Chalker J T 2000 *Phys. Rev.* B **62** 488
[22] Schiffer P, Ramirez A P, Huse D A and Valentino A J 1994 *Phys. Rev. Lett.* **73** 2500
Schiffer P, Ramirez A P, Huse D A, Gammel P L, Yaron U, Bishop D J and Valentino A J 1995 *Phys. Rev. Lett.* **74** 2379
[23] Petrenko O A, Ritter C, Yethiraj M and Paul D M^c K 1998 *Phys. Rev. Lett.* **80** 4570
[24] Tsui Y K, Burns C A, Snyder J and Schiffer P 1999 *Phys. Rev. Lett.* **82** 3532
[25] Kittel C 1963 *Quantum Theory of Solids* (New York: Wiley)
[26] Lee S-H, Broholm C, Kim T, Ratcliff H W and Cheong S-W 2000 *Phys. Rev. Lett.* **84** 3718
[27] Holstein T and Primakoff H 1940 *Phys. Rev.* **58** 1098
[28] Rado G and Suhl H 1963 *Magnetism* vol 1 (New York: Academic) p 309
[29] Turov E A 1965 *Physical Properties of Magnetically Ordered Crystals* (New York: Academic)
[30] Corruccini L R and White S J 1993 *Phys. Rev.* B **47** 773
[31] Pathria R K 1996 *Statistical Mechanics* (Boston, MA: Butterworth-Heinemann)
[32] Ewald P P 1921 *Ann. Phys., Lpz.* **64** 253
[33] Del Maestro A G 2003 *MSc Thesis* University of Waterloo p 63 (for a copy, please contact the author)
[34] Enjalran M and Gingras M J P 2003 Theory of paramagnetic scattering in highly frustrated magnets with long-range dipole–dipole interactions: the case of 111 Ising pyrochlore systems *Preprint* cond-mat/0307151
[35] Enjalran M and Gingras M J P 2003 Theory of two-step magnetic ordering phenomena in a geometrically frustrated Heisenberg pyrochlore antiferromagnet with long range dipolar interactions *Preprint* cond-mat/0307152
[36] Cépas O and Shastry B S 2003 Field-driven transitions in the dipolar pyrochlore antiferromagnet $Gd_2Ti_2O_7$ *Preprint* cond-mat/0306638
[37] Bonville P *et al* 2003 Transition and spin dynamics at very low temperature in the pyrochlores $Yb_2Ti_2O_7$ and $Gd_2Sn_2O_7$ *Preprint* cond-mat/0306470
[38] White R M, Sparks M and Ortenburger I 1956 *Phys. Rev.* **139** A450
[39] Delannoy J-Y 2002 private communication