Theory of Two-Step Magnetic Ordering Phenomena in a Geometrically Frustrated
Heisenberg Pyrochlore Antiferromagnet with Long Range Dipolar Interactions

Matthew Enjalran$^1$ and Michel J.P. Gingras$^{1,4}$

$^1$Department of Physics, University of Waterloo, Ontario, N2L 3G1, Canada
$^2$Canadian Institute for Advanced Research, 180 Dundas Street West, Toronto, Ontario, M5G 1Z8, Canada
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A model for a Heisenberg antiferromagnet on a pyrochlore lattice with exchange and dipole-dipole interactions is studied via mean-field theory. In treating the dipoles by use of the Ewald method, a soft (critical) mode with a unique ordering wave vector is selected for all strengths of the dipole-dipole coupling. For weak dipoles a partially ordered, three sublattice spin structure (P state), with $q_{ord} = \frac{\pi}{2} \pm \frac{\pi}{2}$, is selected. A fully ordered, four sublattice spin structure (F state), with $q = 000$, competes with the P state and becomes the stable structure as the temperature is reduced. Our results are compared against other theoretical calculations and connection to recent experimental results for Gd$_2$Ti$_2$O$_7$ are discussed.

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Frustration is ubiquitous in condensed matter and arises whenever a system cannot minimize its total classical ground state energy by minimizing the energy of its pairwise interactions, pair by pair. In the context of magnetism, frustration commonly occurs in triangular or tetrahedral unit based lattice structures with anisotropic antiferromagnetic (AFM) interactions, geometric frustration, and prevents the magnetic moments (spins) from pointing antiparallel to each other. Two and three dimensional lattices of corner sharing triangles or tetrahedra with nearest neighbor AFM Heisenberg exchange are highly frustrated and are particularly interesting. There, mean-field theory (MFT) finds a massive degeneracy of soft (critical) modes with no unique preferred state chosen at some critical temperature $T_c$. As a consequence, frustrated systems exhibit a propensity for thermal and quantum fluctuations. The possibility that exotic novel quantum states arise in frustrated quantum spin systems is currently attracting much attention.

It is generally expected that perturbations to the nearest neighbor spin Hamiltonian select a unique ordered state. In the insulating pyrochlore systems R$_2$M$_2$O$_7$, where R$^{3+}$ is a magnetic trivalent rare earth ion (R=Gd, Tb, Ho, Dy), and M=Ti$^{4+}$ or Sn$^{4+}$, non-magnetic (Fig. 11), the leading perturbation to the nearest-neighbor Hamiltonian is the long-range magnetic dipole-dipole interaction. Due to its (i) long-range $1/r^3$ and (ii) anisotropic $r \cdot S$ spin-space coupling nature, one would naively expect dipolar interactions to select a unique and robust soft magnetization density (mode) at an ordering wave vector $q_{ord}$. However, explicit calculations in two specific cases have found dramatically different behavior.

In the Ho$_2$(Ti,Sn)$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ pyrochlores with local $\langle 111 \rangle$ Ising spins, it has been found that the $1/r^3$ dipolar interactions are to a very large extent self-screened. As a result, the system does not develop long-range order at a critical temperature $T_c \sim D_{nn}$, where $D_{nn} \sim 2$ K is the dipolar energy scale at nearest-neighbors. Instead, the system develops an extensive quasi-degenerate “spin ice” state at $T \sim D_{nn}$ analogous to the proton disordered state in common ice water with the same residual extensive Pauling entropy. Interestingly, detailed calculations (mean-field $^2$ and Monte Carlo $^3$) find that the dipolar interactions do not produce an exact symmetry and thus allows for the weak selection of an ordered state at ordering wave vector $q_{ord} = 001$. Monte Carlo simulations employing nonlocal loop dynamics find a first order transition, removing all residual entropy, to the $q_{ord} = 001$ long-range ordered state at the critical temperature $T_c/D_{nn} \approx 0.07 \ll 1^4$. In the Gd$_2$(Ti,Sn)$_2$O$_7$ pyrochlores, the Gd$^{3+}$ ions have $S = 7/2$ and $L = 0$, hence negligible single-ion anisotropy. They are, therefore, good realizations of antiferromagnetically coupled Heisenberg spins with weak long-range magnetic dipole-dipole interactions (20% of nearest-neighbor AFM exchange). Here too, the effect of dipolar interactions is far from obvious. Two independent mean-field (Gaussian approximation) calculations have found that long-range dipole-dipole interactions truncated at large distance (i.e., 100 nearest-neighbors) gives rise to a line of degenerate soft modes along the cubic $\langle 111 \rangle$ direction. Palmer and Chalker argued that including quartic terms in the theory leads to the selection of a four sublattice Néel ordered state at $q_{ord} = 000$, see Fig. 15. Experiments provide a different picture: (i) Neutron diffraction measurements at $T = 50$ mK find a partially ordered phase at $q = \frac{1}{2} \pm \frac{1}{2}$, see Fig. 15; with one disordered sublattice. (ii) Mössbauer experiments find strong evidence for a paramagnetic (PM) fluctuating spin down to 35 mK, too. (iii) Specific heat measurements find two transitions at $T = 0.7$ K and $T = 1.0$ K. All these experimental results are seemingly incompatible with the prediction of Ref. 4. In view of these perplexing results from theory and experiments, we have revisited the mean-field calculations of Refs. 3 and 4. We have found that the degeneracy of...
soft modes along the $q = 111$ direction reported in \[8\] and \[9\] is only approximate. Instead, we find that long-range dipolar interactions, when properly re-summed to infinite distance, give rise to a weakly selected unique soft mode at $q_{\text{ord}} = \frac{111}{222}$ with one disordered sublattice, similar to what is found in experiments (Fig. 1b) \[10\]. Just 0.7% below that first transition, we find a second transition to the $q = 000$ state of Fig. 1b. We also find that weak second and third nearest neighbor exchange only acts to suppress or enhance the transition temperature of the $q = 000$ mode relative to that of the $q_{\text{ord}} = \frac{111}{222}$ state.

We consider a model for large $S$-spins on a pyrochlore lattice with exchange and dipolar interactions but negligible single-ion anisotropy. The appropriate Heisenberg Hamiltonian, $H$, is given by $H = -\frac{1}{2} \sum_{i,j} \sum_{a,b} \sum_{u,v} \mathcal{J}_{uv}^{ab}(i,j)S_{iu}^a S_{jv}^b$, where indices $(i,j)$ denote fcc Bravais lattice points, $(a,b)$ describe the tetrahedral basis, and $(u,v)$ define the components of classical Heisenberg spins, $S_{ij}^{a,u}$. The $\mathcal{J}_{uv}^{ab}(i,j)$ interaction matrix contains exchange and dipolar contributions and is given by $\mathcal{J}_{uv}^{ab}(i,j) = J_{N}^{\delta_{ij,N_{nn}}^{uv} - D_{dd}^{uv}|R_{ij}^{ab}|^3 - 3R_{ij}^{ab,u} R_{ij}^{ab,v}|R_{ij}^{ab}|^{-5}]$, where $J_{N}^{\delta_{ij,N_{nn}}}$ restricts the exchange to the $N$-th nearest neighbor distance, $D_{dd}^{uv} = D R_{nn}^{uv}$ with $D = \mu_{0} \mu_{R}^2 / 4 \pi R_{nn}^3$, $\mu$ is the magnetic moment occupying the pyrochlore lattice site, $R_{nn}$ is the nearest neighbor distance, and $R_{ij}^{ab}$ is the vector separation between spins $S_{i}^a$ and $S_{j}^b$. The nearest neighbor exchange, $J_1$, sets the energy scale ($J_1 < 0$ is AFM). The effects of weak long-range exchange ($J_2$ and $J_3$) are also considered.

We first investigate the soft-mode spectrum of $H$ by studying the momentum dependence of the static susceptibility, $\chi(q)$ within MFT \[13\] \[14\]. The field free energy is $F = \text{Tr} \{ \rho H \} + T \text{Tr} \{ \rho \ln \rho \} \[1\] \[2\]$, where $\text{Tr}$ is a trace over spin configurations and $\rho$ is the mean-field (one-particle) density matrix. The expression for $F$ is expanded to quadratic order in $m_{i}^{a}$, the vector order parameter, Fourier transformed, and then diagonalized by a normal mode transformation. The diagonal form of $F$ is used to calculate the correlation function $(S_{i}^a \cdot S_{j}^b)$ in the definition of $\chi(q)$,

$$\chi(q) = (\beta/N_{\text{cell}}) \sum_{(a,b) \neq (1,2)} (S_{i}^{a} \cdot S_{j}^{b}) e^{i\vec{q} \cdot \vec{R}_{ij}^{ab}}, \quad (1)$$

where $\beta = 1/T$ in units of $k_{B} = 1$ and $N_{\text{cell}}$ is the number of Bravais lattice points, and $q$ is wave vector in the first Brillouin zone. The final form for the $q$-dependent susceptibility is $\chi(q)/N_{\text{cell}} = (\beta/3) \sum_{\alpha, \mu} (F_{\mu}^{\alpha}(q))^2(1 - \lambda_{\alpha}^{\mu}(q)/3T)^{-1}$, where the Greek indices label the normal modes ($\alpha = 1, 2, 3, 4$ and $\mu = 1, 2, 3$) at each value of $q$, and $F_{\mu}^{\alpha}(q) = \sum_{\gamma, \mu} U_{\gamma, \mu}^{\alpha}(q) = U_{\mu}^{\gamma}(q)$ is a 3-component vector. $U(q)$ is the unitary matrix that diagonalizes $\mathcal{J}(q)$ in the sublattice space with eigenvalues $\lambda_{\alpha}^{\mu}(q)$. The static susceptibility is a maximum at the ordering wave vector, $q_{\text{ord}}$, which also defines the maximum eigenvalue, i.e., $\lambda_{\text{max}}(q_{\text{ord}}) = \max_{q} \{ \lambda_{\text{max}}(q) \}$, where $\lambda_{\text{max}}(q)$ is the maximum eigenvalue at $q$ and $\max_{q}$ selects the global maximum for all $q$. The mean-field critical temperature is given by $T_{c}^{\text{MF}} = \lambda_{\text{min}}(q_{\text{ord}})/3$.

To find $q_{\text{ord}}$ for our model, we search for the maximum in the soft mode spectrum ($\lambda_{\text{max}}(q)$). We consider AFM first neighbor exchange, $J_1 = -1.0$, and a variable dipole-dipole interaction strength, $D$. The dipolar interactions in $\mathcal{J}(q)$ are summed directly to a cut off separation distance, $R_{c}$, measured in units of the nearest neighbor distance and to the infinite range limit through the use of the Ewald method \[13\]. The regime of weak dipole-dipole interactions is of greatest interest to us because the value $D/|J_1| = 0.20$ faithfully approximates Gd$_2$Ti$_2$O$_7$ \[8\] \[9\]. At this point, we find a spectrum in the $(hhl)$ plane that appears degenerate along the $(hhh)$ diagonal, in agreement with earlier works \[8\] \[9\] (Fig. 6 in Ref. \[8\]). However, when we examine the spectrum along the $(hhh)$ diagonal in greater detail, we observe the selection of a global maximum as one increases the cut off distance of the dipole lattice sum. Figure \[9\] displays results for several values of $R_{c}$ and the Ewald limit. An ordering wave vector occurs at $q_{\text{ord}} = \frac{111}{222}$ (in units of $2\pi/a$),
and emerges from a smoothly varying spectrum along (hhh) in the Ewald limit. We note that for dipole-dipole interactions summed to \( R_c < 500 \), \( \lambda_{\text{max}}(q) \) displays substantial variations making it difficult to ascertain the existence of a critical ordering wave vector. These fluctuations are dampened with increasing \( R_c \) and approach the Ewald limit for \( R_c > 1000 \). A similar sensitivity of the soft-mode spectrum to the dipole-dipole cut off has been observed in the spin ice materials [13]. In a broader expance of phase space, we find three regions for an ordering wave vector: (i) \( q_{\text{ord}} = \frac{1}{11} \) for \( D/|J_1| \leq 5.60 \), (ii) \( q_{\text{ord}} = 001 \) for \( 5.60 < D/|J_1| < 5.85 \), (iii) \( q_{\text{ord}} = 000 \) for \( D/|J_1| \geq 5.85 \). Earlier work that imposed a cut off on the dipole-dipole lattice sum found a degenerate spectrum along the (hhh) diagonal for \( D/|J_1| \leq 5.70 \), with the selection of an ordering wave vector near (000) for larger values of \( D \), (see Fig. 2 in Ref. [10]).

The spin structure for \( q_{\text{ord}} = \frac{1}{11} \) can be obtained from the corresponding eigenvectors, \( U^u_{i,m}(\frac{1}{11}) \). About a single tetrahedron one infers that three sublattices have equal moments with all spins confined to a plane and a fourth sublattice that is PM, i.e., zero moment, see Fig. [11]. When this configuration is extended over the pyrochlore lattice and modulated by \( q_{\text{ord}} \), one has ordered kagomé planes along the [111] direction with a reversal of spin direction in alternating planes, all interstitial sites are PM. This partially ordered three sublattice structure (P state) has been observed in neutron scattering experiments [11] and is supported by Mössbauer [11] experiments on Gd$_2$Ti$_2$O$_7$. The mean-field transition temperature to this state is \( T_c^F = \lambda_{\text{max}}(\frac{1}{11})/3 = 0.94008|J_1| \) \( D/|J_1| = 0.2 \).

The mode \( q = 000 \) corresponds to a fully ordered (four sublattice) equal moment structure (F state) initially predicted to be the ground state of a \( D/|J_1| = 0.20 \) model [10]. We find the limit of stability for the paramagnetic state against an ordering to the F state occurs at \( T_c^F = \lambda_{\text{max}}(000)/3 = 0.93923|J_1| \), which is very close to \( T_c^P = 0.94008|J_1| \) [12]. Given the close proximity of \( T_c^P \) and \( T_c^F \) at the Gaussian level, we study the evolution of the respective free energies as a function of temperature below both values of \( T_c \).

The real-space mean-field theory (RSMFT) begins with the mean-field decomposition \((S^{a,u}_{i} - m_{i}^{a})(S^{b,v}_{j} - m_{j}^{b,v}) = 0\) applied to \( H \). The free energy is determined from \( f = -(1/\beta)\ln Z_{\text{MF}} \), where \( Z_{\text{MF}} \) is the RSMFT partition function. For our model, one obtains

\[
f = \frac{1}{2} \sum_{i,j} \sum_{a,b} S_{i}^{a} S_{j}^{b} - \sum_{i,a} \ln Z_{i}^{a} - \sum_{i,a} \ln m_{i}^{a} - \frac{1}{\beta} \sum_{i,a} \ln Z_{i}^{a},
\]

where \( Z_{i}^{a} = (4\pi/\beta|B_{i}^{a}|) \text{sinh}(\beta|B_{i}^{a}|) \) is the single-site partition function and \( B_{i}^{a} \) is the local field. The sublattice magnetization \( m_{i}^{a} \) (order parameter) is obtained from differentiation of \( f \) with respect to local \( B_{i}^{a} \) field. One finds \( m_{i}^{a} = \frac{B_{i}^{a}}{|B_{i}^{a}|} \left[ \text{coth}(\beta|B_{i}^{a}|) - \frac{1}{\beta|B_{i}^{a}|} \right] \), where the field at site \((i,a)\) is due to all other moments in the system acting at site \((i,a)\), i.e., \( B_{i}^{a} = \sum_{j} B_{i}^{a,b} = \sum_{j,b,v} J^{ab}(i,j) m_{j}^{b,v} \). It is convenient to factor out the magnitude of the order parameter and write, \( B_{i}^{a} = m_{i}^{a} \hat{b}_{i}^{a} \), where \( m_{i}^{a} = m_{i}^{f} \) and \( \hat{b}_{i}^{a} \) is a unit vector that defines the orientation of the order parameter at site \((i,a)\). Using this form for \( B_{i}^{a} \), one expands the right-hand-side of the above expression for \( m_{i}^{f} \) for small \( m \) to obtain \( T_c \) for RSMFT, \( T_c^{MF} = |\hat{b}_{i}^{a}|/3 \).

We work on a lattice of \( L \times L \times L \) cubic cells, or \( 16L^{3} \) spins, with periodic boundary conditions and \( D/|J_1| = 0.20 \). The lattice is tiled with one of the above order parameters. We consider systems of size \( L = 4, 6 \) and calculate the dipole-dipole interactions via the Ewald method in real-space [14]. Our procedure is to solve self-consistently for the sublattice magnetization, \( m_{i}^{a} \), at temperature \( T/|J_1| \) and then calculate the corresponding free energy from Eq. [2] i.e., \( f/|J_1| \). The real-space transition temperatures are \( T_c^{F} = |b_{i}^{a}(F)|/3 = 0.94002|J_1| \) and \( T_c^{P} = |b_{i}^{a}(P)|/3 = 0.93917|J_1| \) for \( L = 6 \), in good agreement with the above \( q \)-space results. For \( L = 8 \), the real-space and \( q \)-space results for \( T_c^{F} \) and \( T_c^{P} \) agree within

FIG. 2: Soft-mode spectrum along (hhh) as a function of dipolar cut off, \( R_c \), with \( D/|J_1| = 0.20 \). (a) The spectrum develops \( R_c \) dependent maxima for \( R_c > 1 \). (b) The fluctuations in \( \lambda_{\text{max}}(hhh) \) are smoothed out as \( R_c \) increases with the \( R_c \to \infty \) limit obtained with the Ewald method. In the Ewald limit, the critical mode falls at \( q_{\text{ord}} = \frac{1}{11} \).
$10^{-7}$. Free energy versus temperature curves for the F and P ordered states on a $L = 4$ lattice are displayed in Fig. 3. At high temperatures, near either $T_F^P$ or $T_F^E$, the free energy curves appear degenerate. However, the insets to Fig. 3 demonstrate that the respective curves actually cross. We performed linear fits to points from the two curves about the crossing temperature. Solving these equations we find the temperature $T_{\text{cross}} \approx 0.93358|J_1|$. Above $T_{\text{cross}}$, the P state has a lower free energy and is thus the preferred state. Below $T_{\text{cross}}$, the free energy of the F state drops below that of the P state and eventually becomes the stable ground state of the system. We find $T = 0$ energies per spin of $E_F^P = -1.40586|J_1|$ and $E_F^P = -1.65737|J_1|$. Hence, in this very simple mean-field picture, the three sublattice P state is the initially preferred structure at high temperatures, but the nearby four sublattice F state competes with it and very rapidly wins out as the temperature is lowered.

The proximity of the P and F states in MFT suggests it would be difficult to realize their experimental differentiation (or in Monte Carlo simulations). However, the inclusion of weak long-range exchange in our model separates the transition temperatures of these two states effectively and reduces their competition. We note that a $J_2$ or $J_3$ has no effect on the transition temperature of the P state [17]. In the Fourier transform of the $J_2$ and $J_3$ matrices, the particular combination of the lattice symmetry and the $q = \pi \pi \pi$ phase yields zero matrix elements for $J_2(\pi \pi \pi)$ and $J_3(\pi \pi \pi)$ in the above calculation of $\chi(q)$ at $q = \pi \pi \pi$. Hence, we find that $J_3 = 0.02J_1$ (AFM) suppresses the F state to $T_F^P \approx 0.859237|J_1|$ ($L = 4$). A small FM $J_2$ has a similar effect but of reduced magnitude. Conversely, a small AFM $J_2$ or FM $J_3$ enhances the F state by raising its transition temperature above $T_F^P$.

Hence, experimentally reasonable values for long-range exchange could allow for the detection of two well-separated transitions in Gd$_2$Ti$_2$O$_7$. Although two transitions have been observed in specific heat measurements at $T \approx 1$ K and $T \approx 0.7$ K, neutron scattering results only find the three sublattice P state down to $T \approx 50$ mK [18]. We note that a 1-$k$ structure is pursued experimentally for the P state, but a 4-$k$ spin state is a possibility. In our RSMFT, a 4-$k$ spin structure corresponds to a unit cubic cell in which one of the tetrahedra is fully disordered [19]. It is unclear at this time whether it is a material (sample) specific effect or something else that causes the P state to freeze out in the neutron experiments as the material is cooled from $T \gtrsim 1$ K down to 50 mK [19]. Recent ESR results have also found peculiar behavior in Gd$_2$Ti$_2$O$_7$, where a large [111] anisotropy develops spontaneously below 80 K [20]. Clearly, more experimental and theoretical work is needed to elucidate the peculiar thermodynamic properties of Gd$_2$Ti$_2$O$_7$.

In conclusion, our calculations above have identified another system, apart from spin ice, where the long-range $1/r^3$ nature of dipolar interactions cause a large degree of symmetry restoration on the $q$-dependent susceptibility. However, this symmetry restoration is incomplete, and gives rise ultimately to a well defined ordering state upon cooling from the fully disordered paramagnetic state.

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\* Electronic address: enjalran@gandalf.uwaterloo.ca
\textsuperscript{1} Electronic address: gingras@gandalf.uwaterloo.ca

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Errors in the reported numerical values arise from finite size effects and round off errors associated with double precision floating point calculations and are less than $10^{-7}$.

The selection of and ordered state for $J_2$ and $J_3$ of sizeable strength compared to $J_1$ has recently been discussed by O. Cépas and B. S. Shastry, cond-mat/0306638, (unpublished).

Neutron scattering on a single crystal would be needed to distinguish between a single-$k$ and a multiple-$k$ structure.

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