Dipolar Interactions and Origin of Spin Ice in Ising Pyrochlore Magnets

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Recent experiments suggest that the Ising pyrochlore magnets $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ display qualitative properties of the nearest-neighbor "spin ice" model. We discuss the dipolar energy scale present in both these materials and discuss how spin-ice behavior can occur *despite* the presence of long-range dipolar interactions. We present results of numerical simulations and a mean field analysis of Ising pyrochlore systems. Based on our quantitative theory, we suggest that the spin-ice behavior in these systems is due to long-range dipolar interactions, and that the nearest-neighbor exchange in $Dy_2Ti_2O_7$ is *antiferromagnetic*.

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An exciting development has occurred in the last two years with the discovery of an apparent analogy between the low temperature physics of the geometrically frustrated Ising pyrochlore compounds $Ho_2Ti_2O_7$ [1] and $Dy_2Ti_2O_7$ [2] (so called "spin ice" materials), and proton ordering in real ice [3]. The magnetic cations Ho^{3+} and Dy^{3+} of these particular materials reside on the pyrochlore lattice of corner sharing tetrahedra. Single-ion effects conspire to make their magnetic moments almost ideally Ising-like, but with their own set of local axes. In particular, each moment has its local Ising axis along the line connecting its site to the middle of a tetrahedron to which it belongs (see inset of Fig. 1).

In a simple model of nearest-neighbor ferromagnetic (FM) interactions, such a system has the same "ice rules" for the construction of its ground state as those for the ground state of real ice [3,4]. In both cases, these rules predict a macroscopically degenerate ground state, a feature that a number of geometrically frustrated systems possess [5–8].

In $Ho_2Ti_2O_7$, muon-spin rotation (μSR) data indicate a lack of ordering down to $\sim$50 mK despite a Curie-Weiss temperature $\theta_{\mathrm{cw}} \sim 1.9$ K, while single crystal neutron scattering data suggest the development of short-range FM correlations, but the absence of ordering down to at least 0.35 K [1]. $Ho_2Ti_2O_7$ also displays field dependent behavior consistent with a spin-ice picture [9]. Quite dramatically, thermodynamic measurements on $Dy_2Ti_2O_7$ [2] show a lack of any ordering feature in the specific heat data, with the measured ground state entropy within 5% of Pauling's prediction for the entropy of ice [3].

However, both spin-ice materials contain further interactions additional to the nearest-neighbor exchange. Often, rare earth cations can have appreciable magnetic moments and, consequently, magnetic dipole-dipole interactions of the same order as, if not larger than, the exchange coupling can occur. Furthermore, it has been suggested that the nearest-neighbor exchange interaction in $Ho_2Ti_2O_7$ is actually *antiferromagnetic* (AF) [10], which by itself should cause a phase transition to a long-range ordered ground state. Thus, *how* these systems actually display spin icelike behavior is most puzzling. For example, one might naively expect that the long-range and anisotropic spin-space nature of the dipolar interactions would introduce so many constraints that a large degree of the degeneracy present in the simple nearest-neighbor FM spin-ice model [1] would be removed, and consequently, induce long-range order. It is this issue that we wish to address in this Letter.

A previous attempt to consider dipolar effects in Ising pyrochlores was made by Siddharthan *et al.* [10]. In that work, the dipole-dipole interaction was truncated beyond five nearest-neighbor distances, and a sharp transition between paramagnetism and a partially ordered phase (where rapid freezing occurs) was observed for interaction parameters believed appropriate for $Ho_2Ti_2O_7$ [10]. However, we argue that the truncation of dipole-dipole interactions can be misleading, and may introduce spurious

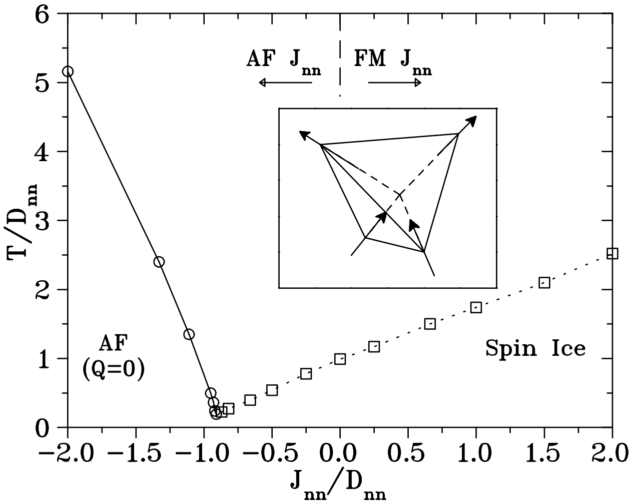

FIG. 1. Phase diagram of Ising pyrochlore magnets with nearest-neighbor exchange and long-range dipolar interactions. D_{nn} and J_{nn} are the Ising parameters for the nearest-neighbor dipolar and exchange energies, respectively (see text). Inset: An ice rule configuration of a tetrahedral unit. The four local $\langle 111 \rangle$ Ising axes meet in the middle of the tetrahedron [4].

features in various thermodynamic properties. For example, we find that the sharp feature observed in the specific heat for truncation beyond five nearest-neighbor distances [10] is softened and rounded for truncation beyond the tenth nearest-neighbor shell, and the observed dynamical freezing is pushed to lower temperatures. As we show below, in the limit of infinite range dipoles, the interaction parameters of Siddharthan *et al.* [10] yield spin ice.

In this Letter, we consider the interplay between nearest-neighbor exchange and dipolar interactions by taking into account the long-range (out to infinity) nature of the dipolar interactions through the use of Ewald summation techniques [11,12]. Our Monte Carlo simulations and mean field results show that dipolar forces are remarkably adept at producing spin-ice physics over a large region of parameter space.

Some of our main conclusions are shown in Fig. 1. For Ising pyrochlores, the dipole-dipole interaction at nearest neighbor is FM, and therefore favors frustration. Beyond nearest neighbor, the dipole-dipole interactions can be FM or AF, or interestingly, even multiply valued [13], depending on the neighbor distance. Defining the nearest-neighbor dipole-dipole interaction as D_{nn} and the nearest-neighbor exchange as J_{nn}, our Monte Carlo results indicate that spin-ice behavior persists in the presence of AF exchange up to $J_{\mathrm{nn}}/D_{\mathrm{nn}} \sim -0.91$. For $J_{\mathrm{nn}}/D_{\mathrm{nn}} < -0.91$ we find a second order phase transition to the globally doubly degenerate $\mathbf{Q} = 0$ phase of the nearest-neighbor AF exchange-only model [14], where all spins point either in or all out of a given tetrahedron.

Our Hamiltonian describing the Ising pyrochlore magnets is as follows:

$$H = -J\sum_{\langle ij\rangle} \mathbf{S}_i^{z_i}\cdot\mathbf{S}_j^{z_j} + Dr_{\mathrm{nn}}^3\sum_{j>i}\frac{\mathbf{S}_i^{z_i}\cdot\mathbf{S}_j^{z_j}}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i}\cdot\mathbf{r}_{ij})(\mathbf{S}_j^{z_j}\cdot\mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5}, \qquad (1)$$

where the spin vector $\mathbf{S}_i^{z_i}$ labels the Ising moment of magnitude $|S| = 1$ at lattice site i and *local* Ising axis z_i. Because the local Ising axes belong to the set of $\langle 111\rangle$ vectors, the nearest-neighbor exchange energy between two spins i and j is $J_{\mathrm{nn}} \equiv J/3$. The dipole-dipole interaction at nearest neighbor is $D_{\mathrm{nn}} \equiv 5D/3$ where D is the usual estimate of the dipole energy scale, $D = (\mu_0/4\pi)g^2\mu^2/r_{\mathrm{nn}}^3$. For both $\mathrm{Ho_2Ti_2O_7}$ and $\mathrm{Dy_2Ti_2O_7}$, $D_{\mathrm{nn}} \sim 2.35$ K.

It is well known in the field of electrostatic interactions that the dipole-dipole interaction is difficult to handle due to its $1/r^3$ nature. In general, a lattice summation of dipole-dipole interactions is conditionally convergent, and must be considered with care. In order to include the important long-range nature of the dipole-dipole interaction, we have implemented the well known Ewald method within our simulation technique, in order to derive an *effective* [15] dipole-dipole interaction between spins within our simulation cell [12]. A standard Metropolis algorithm was used in our Monte Carlo simulations. We used a conventional cubic cell for the pyrochlore lattice, which contains 16 spins. In general, we found it sufficient to simulate up to $4 \times 4 \times 4$ cubic cells (i.e., $L = 4$, and 1024 spins) with up to $\sim 10^6$ Monte Carlo steps per spin when necessary. Thermodynamic data were collected by starting the simulations at high temperatures and cooling very slowly.

Referring to Fig. 1, the characterization of a system as having spin-ice behavior was carried out by determining the entropy, via numerical integration of the specific heat divided by temperature data. Pauling's argument for the entropy of ice yields $R[\ln 2 - (1/2)\ln(3/2)]$ or $4.07\ \mathrm{J\,mol^{-1}\,K^{-1}}$ [2,3]. We find for $J_{\mathrm{nn}}/D_{\mathrm{nn}} = -0.91$ (our spin-ice data point closest to the phase boundary in Fig. 1), this value for the entropy to within 3%, using a system size $L = 4$.

Our thermodynamic data indicate that when the nearest-neighbor exchange is AF and large compared to the dipolar interactions, the system undergoes a second order phase transition to an all in or all out $\mathbf{Q} = 0$ ground state as alluded to earlier. This AF phase persists slightly beyond the point where the nearest-neighbor dipolar interaction (FM) is stronger than nearest-neighbor AF exchange.

In the spin-ice regime, our specific heat data have a number of interesting features which help shed light on the effect of long-range dipole-dipole interactions. In general, each data set shows qualitatively the same broad peak as observed in the nearest-neighbor FM exchange model, and vanishes at high and low temperatures [9,10]. We detect very little system size dependence upon comparison of data from $L = 2, 3, 4$ simulation sizes. In particular, there is no noticeable size dependence of the specific heat maximum, nor its position. As the AF/spin-ice phase boundary is approached from the spin-ice side, the specific heat peak begins to narrow and, more importantly, both the peak height and peak position begin to vary. As we discuss below, this has important ramifications for the interpretation of experimental data.

In Fig. 2 we plot the dependence of the specific heat peak height (C_{peak}) and the temperature at which it occurs (T_{peak}) on the ratio of the nearest-neighbor exchange and dipole-dipole energies, $J_{\mathrm{nn}}/D_{\mathrm{nn}}$. Note that in the regime of large nearest-neighbor FM coupling, the peak height plateaus to the value one observes in the nearest-neighbor FM exchange-only model [1,9,14].

When the exchange becomes FM, the nearest-neighbor effective bond energy, $J_{\mathrm{eff}} = J_{\mathrm{nn}} + D_{\mathrm{nn}}$ is large enough to dominate the excitations of the system, and the broad specific heat peak occurs at $T_{\mathrm{peak}} \sim O(J_{\mathrm{eff}})$. Hence, in terms of an effective energy scale, the medium- to long-range effects of the dipolar interactions are "screened" by the system, and one recovers qualitatively the short-range physics of the nearest-neighbor spin-ice model [1,14]. As the nearest-neighbor exchange interaction becomes AF, the nearest-neighbor energy scale becomes less dominant, and

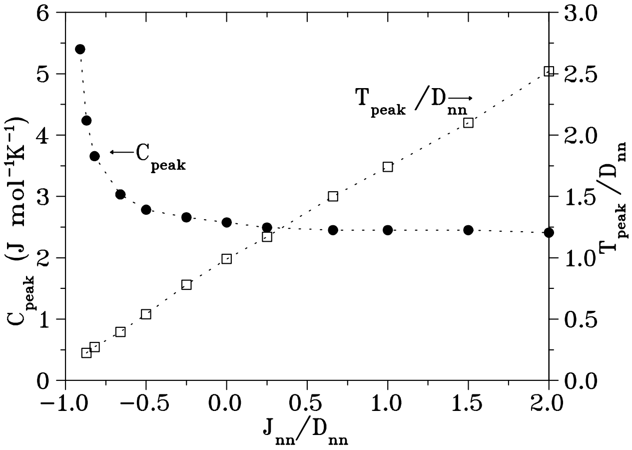

FIG. 2. Dependence of the specific heat peak height C_{peak} and temperature location T_{peak} on exchange and dipole-dipole interaction parameters.

the broad feature in the specific heat becomes dependent on $J_{\mathrm{nn}}/D_{\mathrm{nn}}$ in a more complicated manner. It is within this regime that we believe that both $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ exist.

Since D_{nn} is a quantity which can be calculated once the crystal field structure of the magnetic ion is known, the nearest-neighbor exchange J_{nn} is the only adjustable parameter in our theory. Figure 2 enables us to test in two independent ways the usefulness of our approach to the long-range dipole problem in spin-ice materials.

If we consider $Dy_2Ti_2O_7$, for example, specific heat measurements by Ramirez *et al.* [2] indicate a peak height, $C_{\mathrm{peak}}^{\mathrm{Dy}}$ of $\sim$2.72 J mol^{-1} K^{-1}. Given that $D_{\mathrm{nn}} \approx 2.35$ K for this material, the left hand plot of Fig. 2 indicates a nearest-neighbor exchange coupling $J_{\mathrm{nn}} \sim -1.2$ K. The same experimental specific heat data show that this peak occurs at a temperature of $T_{\mathrm{peak}}^{\mathrm{Dy}} \sim 1.25$ K. Using the plot of T_{peak} in Fig. 2, we independently arrive at approximately the same conclusion for the value of the nearest-neighbor exchange. Thus, we predict that AF exchange is present in $Dy_2Ti_2O_7$ with $J_{\mathrm{nn}} \sim -1.2$ K. If there was no AF exchange present in this system, our results in Fig. 1 imply that there would be a peak in the specific heat at a temperature of at least $\sim$2.3 K, which is not observed experimentally [2]. Our best fit for the specific heat data of $Dy_2Ti_2O_7$ by Ramirez *et al.* [2] is shown in Fig. 3, where we find good agreement between theory and experiment for $J_{\mathrm{nn}} = -1.24$ K.

Specific heat measurements on a powdered sample of $Dy_2Ti_2O_7$ in a magnetic field were also reported in Ref. [2]. Three field independent peaks were observed at low temperature. For a large field in the $\langle 110 \rangle$ direction, two spins on each tetrahedron are pinned by the field, while the other two remain free, since their Ising axes are perpendicular to the applied field. Because of the dipolar interaction, there will be a coupling between the fluctuating spins on these two sublattices. Our preliminary simulations on small lattice sizes suggest a field independent ordering at low temperature as observed in experiment.

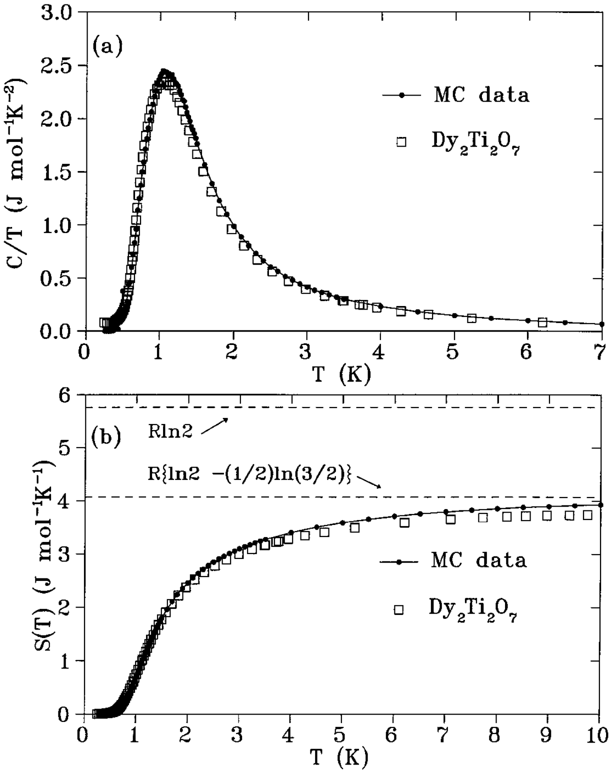

FIG. 3. Comparison of (a) specific heat and (b) entropy data between $Dy_2Ti_2O_7$ [2] and Monte Carlo simulation with $J_{\mathrm{nn}} = -1.24$ K, $D_{\mathrm{nn}} = 2.35$ K, and system size $L = 4$.

Considering $Ho_2Ti_2O_7$, experimental data on its thermodynamic properties are not so categorical. The specific heat data of Siddharthan *et al.* [10] indicate a feature at $\sim$0.8 K, although it has been suggested that this could be due to an additional contribution in this temperature range from an anomalously large hyperfine coupling in Ho^{3+} [16]. Nevertheless, using the plot of T_{peak} in Fig. 2, we find substantial AF exchange coupling of the same order of magnitude as in the Dy compound. We note that Siddharthan *et al.* [10] and den Hertog *et al.* [16] find from analysis of magnetization measurements a similar order of magnitude for J_{nn}. Furthermore, our numerical simulations within this region of parameter space indicate a Curie-Weiss temperature of $\sim$2 K, in agreement with an experimental estimate by Harris *et al.* of $\theta_{\mathrm{cw}} \sim 1.9$ K [1].

$Tb_2Ti_2O_7$ is an Ising pyrochlore system of similar type to the Ho^{3+} and Dy^{3+} based materials [7,8], but the Ising anisotropy is reduced to much lower temperature due to narrowly spaced crystal field levels [8]. While this makes the interpretation of experimental data more difficult, initial estimates of the nearest-neighbor exchange and dipole moment [8] yield $J_{\mathrm{nn}}/D_{\mathrm{nn}} \sim -1$, placing this system very close to the phase boundary of Fig. 1. Indeed, μSR measurements suggest that $Tb_2Ti_2O_7$ fails to order down to

70 mK [7], and thus it would appear that a spin-ice picture for this material cannot be *a priori* ruled out.

While we believe our approach yields a reasonably successful quantitative theory of spin-ice behavior in Ising pyrochlores, there still remains the question of why long-range dipolar interactions do not appear to lift the macroscopic degeneracy associated with the ice rules, and select an ordered state.

Mean field theory provides a more quantitative basis for examining this issue. Following the approach used in Refs. [17–19], we find that the soft modes for Ising pyrochlore systems described by Eq. (1) consist of two very weakly dispersive branches (less than 1% dispersion) over the whole Brillouin zone (except at $\mathbf{Q} \equiv 0$). Such a set of quasidispersionless branches is very similar to the two completely dispersionless soft branches of the nearest-neighbor FM spin-ice model [1,14]. Consequently, both nearest-neighbor FM and dipolar spin-ice behave almost identically over the whole temperature range spanning $O(w) \leq T < \infty$ where w is the bandwidth of the soft branch of dipolar spin ice. We note that this near dispersionless behavior is recovered only *asymptotically* as the long-range dipoles are included out to infinity. The lifting of degeneracy at the 1% level in the apparent absence of any small parameters in the theory is at this point not completely understood. We do not believe it is due to numerical or computational error. A partial explanation may be that the $\langle 111 \rangle$ Ising anisotropy, the $1/r^3$ long-range nature of dipolar interactions, and the specific relationship between the topology of the pyrochlore lattice and the anisotropic (spin-space) coupling of dipolar interactions combine in a subtle manner to produce a spectrum of soft modes that *approximate* very closely the spectrum of the nearest-neighbor FM spin-ice model [1,14]. In other words, there must be an almost exact symmetry fulfilled in this system when long-range dipolar interactions are taken into account. However, the same long-range nature of these interactions renders it difficult to construct a simple and intuitive picture of their effects, and we have not been able to identify such an "almost exact" symmetry.

Also in these systems, the absence of soft fluctuations (Ising spins) combined with the macroscopic degeneracy associated with the ice rules may be such that correlations associated with a "true" ground state are dynamically inhibited from developing. For energetic reasons, states obeying the ice rules are favored down to low temperature, by which time such large energy barriers exist that evolution towards the true ground state is never achieved. In simulation terms, at low temperature the Boltzmann weights for local spin flips "towards" this state are simply too small.

In conclusion, using Ewald summation techniques we have considered the effects of long-range dipole-dipole interactions on the magnetic behavior of Ising pyrochlore systems. Our results show that spin-ice behavior is recovered over a large region of parameter space, and we find quantitative agreement between our approach and experimental data on spin-ice materials.

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