Long-Range Order at Low Temperatures in Dipolar Spin Ice

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It has recently been suggested that long-range magnetic dipolar interactions are responsible for spin ice behavior in the Ising pyrochlore magnets $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$. We report here numerical results on the low temperature properties of the dipolar spin ice model, obtained via a new loop algorithm which greatly improves the dynamics at low temperature. We recover the previously reported missing entropy in this model, and find a first order transition to a long-range ordered phase with zero total magnetization at very low temperature. We discuss the relevance of these results to $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$.

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Competing or frustrated interactions are a very common feature of condensed matter systems. In some cases, the frustration can be so intense that it induces novel and complex phenomena, often causing extensive degeneracy in the ground state of the system and preventing any ordering down to absolute zero temperature, a situation referred to as "zero-point entropy." Because of the availability of a large variety of magnetic materials that can be described by rather simple theoretical models, magnetic systems offer themselves as the ideal benchmark for generic concepts pertaining to collective phenomena in nature. In this context, the term *spin ice* was recently coined by Harris and co-workers [1] to describe the analogy that exists between the statistical physics of certain geometrically frustrated Ising pyrochlore magnets, and proton ordering in the hexagonal phase of ice (I_h) [2–4]. For the Ising pyrochlore systems $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$, the Ho^{3+} and Dy^{3+} rare earth magnetic moments reside on a network of corner sharing tetrahedra (Fig. 1). Each moment is forced by single-ion anisotropy to lie along the axis joining the centers of the two tetrahedra that it belongs to [1,5]. For a simple theoretical model considering only nearest neighbor ferromagnetic (FM) exchange, the ground state is macroscopically degenerate, but is required to have two moments pointing in and two pointing out of every tetrahedron, a constraint that maps exactly the two short and long proton bonds and the ice rules for their arrangement in I_h [6,7]. This nearest neighbor FM model shows no ordering and is characterized by a broad Schottky-like peak in the magnetic specific heat [7].

Both $Ho_2Ti_2O_7$ [1,8] and $Dy_2Ti_2O_7$ [5,9] show qualitative properties roughly consistent with the basic spin ice picture of the simple nearest neighbor FM model [6,7]. However, it has been shown recently that, rather than nearest neighbor FM exchange, it is surprisingly the large dipolar interaction present in these materials that is responsible for their spin ice behavior [8–12]. For a model which we call *dipolar spin ice,* with the long-range nature of the dipolar interaction properly handled using Ewald summation techniques, numerical results show a lack of magnetic ordering down to very low temperatures [8,9]. Furthermore, the dipolar spin ice model agrees quantitatively very well with specific heat data for $Dy_2Ti_2O_7$ [5] and $Ho_2Ti_2O_7$ [8], as well as neutron scattering measurements on the latter material [8]. In other words, while the nearest neighbor FM model provides a simple and qualitative understanding of the spin ice phenomenon, there is now strong evidence that the dipolar spin ice model with its long-range dipolar interactions provides a quantitatively accurate description of experimental results on real materials [8,9]. As in the case of I_h, for dipolar spin ice, it

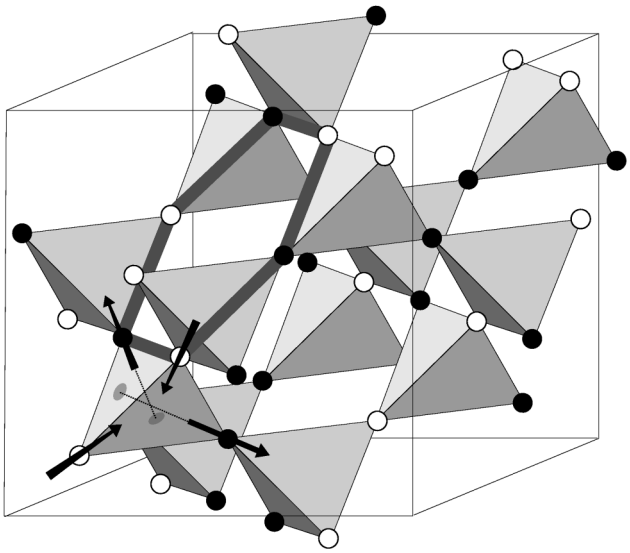

FIG. 1. The lower left "downward" tetrahedron of the pyrochlore lattice shows Ising spins (arrows). Each spin axis is along the local $\langle 111 \rangle$ quantization axis, which goes from one site to the middle of the opposing triangular face (as shown by the disks) and meets with the three other $\langle 111 \rangle$ axes in the middle of the tetrahedron. For clarity, black and white circles on the lattice points denote other spins. White represents a spin pointing into a downward tetrahedron while black is the opposite. The entire lattice is shown in an ice-rules state (two black and two white sites for every tetrahedron). The hexagon (thick grey line) shows a minimal loop move, which corresponds to reversing all colors (spins) on the loop to produce a new ice-rules state.

is unclear whether the interactions which cause the quasidegeneracy (here the long-range magnetic dipolar interaction [9]), should at the same time prevent any ordering down to zero temperature and cause zero-point entropy. The dipolar interaction is itself FM at nearest neighbor, and is thus prone to spin ice correlations. However, *a priori* one might expect that its longer range component should lift the nearest neighbor degeneracy and induce the selection of an ordered state within the ice-rules manifold. We show in this Letter that this is precisely the case. Specifically, the dipolar spin ice model with long-range interactions does possess a unique ground state (apart from trivial global symmetry operations) which develops at very low temperature. However, for local dynamical processes (such as single spin fluctuations), the development of this ground state is completely dynamically inhibited because of high energy barriers separating quasidegenerate ice-rules states. We explore here the low temperature ordering properties of dipolar spin ice by taking advantage of "loop moves" incorporated into a standard Metropolis Monte Carlo algorithm, a method considered previously for two-dimensional square ice models [13]. Such moves allow one to explore degeneracy lifting effects within the ice-rules manifold in an efficient manner, something which is not possible via single spin flip dynamics. We present here strong numerical evidence for a phase transition at low temperature in the dipolar spin ice model in zero field that recovers the entire low temperature residual magnetic entropy of the system.

For the pyrochlore lattice with Ising spins defined by local axes, the Hamiltonian with nearest neighbor exchange and long-range dipolar interactions is [8–10]

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

where the spin vector $\mathbf{S}_i^{z_i}$ labels the Ising moment of magnitude $|S| = 1$ at lattice site i and *local* Ising $\langle 111 \rangle$ axis z_i discussed earlier. Here, J represents the exchange energy and $D = (\mu_0/4\pi) g^2 \mu^2 / r_{nn}^3$. However, because of the local Ising axes, the effective nearest neighbor energy scales are $J_{nn} \equiv J/3$ and $D_{nn} \equiv 5D/3$.

As described in Ref. [9], the long-range nature of the dipolar interactions can be handled by the Ewald method. In that Letter, extensive numerical analysis via single spin flip Monte Carlo simulations found no evidence of a transition to long-range order. Rather, short-range order dominated by ice-rules correlations was observed down to low temperatures, similar to that found in the nearest neighbor FM model [12].

Qualitatively, the dynamics of both models appear to be very similar. As the temperature is lowered, significant thermal barriers are created by the energy cost involved in fluctuating *out* of the ice-rules manifold. With single spin flips, fluctuations *between* states *within* the ice-rules manifold are also reduced, as it is impossible to do so without first breaking the two-in/two-out ice rules. Such thermal barriers produce nontrivial and extremely slow dynamics. If a unique ground state exists within the plethora of ice-rules states [$\sim (3/2)^{N/2}$] of the dipolar spin ice model [Eq. (1)], these thermal barriers make the probability of reaching it in a numerical simulation using conventional spin flips exceedingly small. Consequently, the question concerning the nature of the ground state becomes difficult to answer using standard numerical techniques, and a different procedure must be applied [13]. Since we found in Ref. [9] that long-range dipolar interactions do give rise to spin ice behavior, we take as a starting point for identifying the low energy states and excitations of Eq. (1) the exactly degenerate ice-rules states of the nearest neighbor FM model. In Fig. 1 we denote each site of the pyrochlore lattice by a white or a black circle which represents a spin pointing into or out of a "downward" facing tetrahedron, respectively. In this particular example, the spin configuration shown forms an ice-rules state that can be transformed into another ice-rules state by reversing all the colors (spins) on the loop denoted by the grey hexagon. In general, six spins form the shortest loop, while larger loops are also possible. A loop can be constructed by simply choosing a starting lattice site and tracing out a closed path that involves tetrahedra which have exactly two spins on the path. Each pair of spins which are neighbors on the path are such that one is pointing into and the other pointing out of their shared tetrahedron, with such a loop constructed from alternating black and white circles.

For our numerical study of the dipolar spin ice model, this type of loop move was utilized in conjunction with conventional single spin flip dynamics. Specifically, such loops are identified by allowing a wandering path to form a loop whenever it encounters any previously visited site and ignoring any "dangling" spins in the path. This allows for a large number of short loops to be created, with an average length that tends to a finite value as the system size is increased. As explained above for the dipolar system, such "loop reversal" moves are not true zero modes, but involve a small gain or lowering of the energy (small compared to $J_{nn} + D_{nn}$) which is handled by a standard Metropolis algorithm [14].

Our numerical simulations for the dipolar spin ice model were carried out on system sizes up to 2000 spins (of cubic unit cell length $L = 5$) with $O(10^5)$ spin flips per spin and $O(10^5)$ loop moves. For all interaction parameters J_{nn} and D_{nn} which show spin ice behavior using single spin flip dynamics only ($J_{nn}/D_{nn} \gtrsim -0.91$) [9], we find that the acceptance ratio of the loop moves increases at low temperature as the system enters the spin ice regime, before dropping to zero just below the temperature at which the system undergoes a transition to a long-range ordered state obeying the ice rules.

In Fig. 2 we present specific heat data obtained for a system with interaction parameters J_{nn} and D_{nn} identified

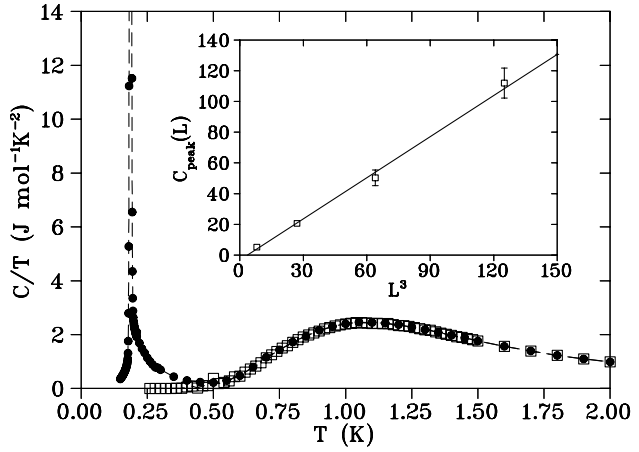

FIG. 2. Specific heat data from simulations using single spin flips (squares) and combined single spin flips and loop moves (filled circles) for a system size $L = 4$. Interaction parameters are Dy_2Ti_2O7 values $J_{nn} = -1.24$ K and $D_{nn} = 2.35$ K (as in Ref. [9]). Inset: Finite size scaling of the specific heat peak height as a function of system size $L = 2, 3, 4, 5$. The scaling behavior $C_{\text{peak}}(L) = a + bL^3$ is consistent with that expected for a first order phase transition.

in Ref. [9] for the spin ice material $Dy_2Ti_2O_7$. Using a single spin flip Monte Carlo algorithm, spin ice correlations develop over a large temperature regime (signified by the broad peak around 1.1 K), before the system dynamically freezes into a disordered ice-rules state at low temperature. Using the loop algorithm in combination with single spin flips, the higher temperature data is reproduced before a very sharp transition at $T_c \simeq 0.18$ K. The energy probability distribution displays a double-peak feature in a narrow temperature region close to T_c, a strong indicator that the transition is first order. To assess more quantitatively the nature of the phase transition, a finite size scaling study was done (see inset of Fig. 2). Because of the extremely sharp nature of the specific heat at T_c, the method of slowly cooling in a Monte Carlo simulation with discrete temperature steps could not give sufficiently accurate data to resolve C_{peak} within reasonable computer time. To avoid this problem, simulations were performed in a multicanonical ensemble [15] at a single temperature near T_c. This data was then reweighted using Ferrenberg and Swendsen's technique [16]. This allows us to obtain the appropriate thermodynamic quantities to any degree of temperature resolution required. The latent heat ΔE determined from the slope of $C_{\text{peak}}(L)$ vs L [$C_{\text{peak}}(L) \propto 16\Delta E L^3/(4T_c^2)$] is $\Delta E = 0.246 \pm 0.002\ \text{J mol}^{-1}$, in excellent agreement with the discontinuity of the internal energy at T_c, $0.245 \pm 0.003\ \text{J mol}^{-1}$. As well, on integration of C/T and taking into account the entropy associated with the latent heat at T_c, we recover a magnetic entropy within 4% of the total possible value of $k_B \ln 2$ per spin.

The ordered phase we observe is similar to that found in the order by disorder transition in the antiferromagnetic fcc Ising model where an ordering of antiferromagnetically stacked FM planes occurs [17]. Here, the ordering vector $\mathbf{q}$ lies parallel to one of the cubic axes directions, specifically $\mathbf{q} = (0, 0, 2\pi/a)$ or its starred directions. To construct the ordered state, first consider a starting tetrahedron with its six possible ice-rules states. For a given ordering vector $\mathbf{q}$, this tetrahedron selects one of the four possible spin configurations (two independent configurations and their spin reversals, $\mathbf{S}_i \rightarrow -\mathbf{S}_i$), with a total magnetic moment for the tetrahedron perpendicular to $\mathbf{q}$. The entire ordered state may then be described by planes (perpendicular to $\mathbf{q}$) of such tetrahedra. The wavelength defined by $\mathbf{q}$ physically corresponds to antiferromagnetically stacked planes of tetrahedra, where a given plane has tetrahedra of opposite configuration to the plane above and below it. In Fig. 3 we show one such ground state with ordering vector $\mathbf{q} = (0, 0, 2\pi/a)$.

The transition to such a ground state structure can be characterized by the multicomponent order parameter,

$$\Psi_\alpha^m = \frac{1}{N}\left|\sum_{j=1}^{N/4}\sum_{a=1}^{4}\sigma_a^j e^{i\phi_a^m} e^{i\mathbf{q}_\alpha\cdot\mathbf{r}_j}\right|. \qquad (2)$$

Such a labeling is natural given that the pyrochlore lattice can be viewed as an fcc lattice with a downward tetrahedral basis (see Fig. 1). Thus, j labels the fcc lattice points of the pyrochlore lattice, and the index a sums over the four spins comprising the basis attached to each j. The index α labels the three possible symmetry related $\mathbf{q}$ ordering vectors. For a given $\mathbf{q}_\alpha$, as described above, there are two ice-rules configurations and their reversals which can each form a ground state. Thus $m = 1, 2$ labels these possibilities with the phase factors $\{\phi_a^m\}$ describing the given configuration m. Each Ising variable σ_a^j has value 1 (-1) when a spin points into (out of) its downward tetrahedron labeled by j.

As written in Eq. (2), Ψ_α^m has six degenerate components, each of which can take on a value between 0 and

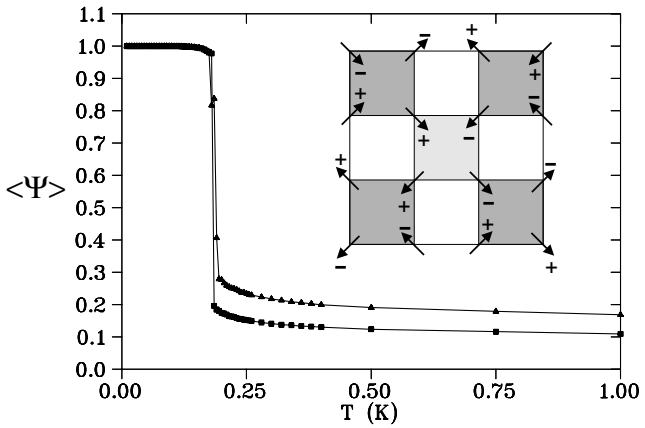

FIG. 3. Temperature dependence of the order parameter $\langle\Psi\rangle$ defined above for system sizes $L = 3$ (triangles) and $L = 4$ (squares). Inset: The $\mathbf{q} = (0, 0, 2\pi/a)$ ground state projected down the z axis. The four tetrahedra making up the cubic unit cell appear as dark grey squares. The light grey square does not represent a tetrahedron; however, its diagonally opposing spins occur in the same plane. The component of each spin parallel to the z axis is indicated by a + and a − sign.

1. Upon cooling through the transition, the system selects a unique ordered configuration, causing the corresponding component of Ψ_α^m to rise to unity and all others to fall to zero. The component selected by the ordering is equally likely to be any one of the six. Figure 3 is a plot of $\langle\Psi\rangle$ for two system sizes, where $\langle\Psi\rangle = \sqrt{\sum_{m=1}^{2}\sum_{\alpha=1}^{3}(\Psi_\alpha^m)^2}$ is the magnitude of the multicomponent order parameter. For $T < T_c$ the two lattice sizes produce identical order parameters. By contrast, $\langle\Psi\rangle$ for the smaller lattice shows a somewhat more pronounced rounding near T_c, and an increased residual value for large T. These results show a clear discontinuity of the order parameter at T_c, and, hence, a first order transition to the long-range ordered phase we have identified.

For all values of J_{nn}/D_{nn} within the dipolar spin ice regime [9], we find a low temperature phase transition to the state discussed above. We find that the transition is independent of the strength of the nearest neighbor exchange J ($T_c/D_{nn} \sim 0.08$), consistent with the idea that the transition is solely driven by the long-range dipolar interactions. The observation of a finite ordering temperature using the algorithm presented here demonstrates that long-range dipolar interactions between Ising spins on the pyrochlore lattice have no special exact symmetry that allow for a macroscopically degenerate ground state. This conclusion is also found within a mean field analysis [10], which shows that, as the truncation of long-range dipolar interactions is pushed out to further distances (up to 10^4 nearest neighbors), the maximal eigenvalues of the normal mode spectrum become only *quasidegenerate* throughout the Brillouin zone, as opposed to the completely flat spectrum (and macroscopic degeneracy) we find for the nearest neighbor spin ice model [10]. Furthermore, the quasidegenerate eigenvalues of the mean field theory have a very weak dispersion and predict the same ordering wave vector $\mathbf{q}$ found here.

The question remains as to what extent our conclusions apply to the real spin ice materials $Ho_2Ti_2O_7$ [1] and $Dy_2Ti_2O_7$ [5]. The dipolar spin ice model may be an accurate description of these materials even at extremely low temperatures, while it is also possible that perturbations, H', exist beyond Eq. (1) which could induce another type of ground state selection. Similar to I_h, however, irrespective of the origin of any ordering, its actual observation may depend critically on the dynamical behavior of the materials. The inability of single spin fluctuations to connect different ice-rules states in phase space shows that at low temperatures relaxation via local dynamics is extremely slow. For both $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$, the transition temperature for the ordered phase observed in our simulations is well below the temperature at which single spin fluctuations over extended length scales (and out of the ice-rules manifold) are thermally frozen out. Thus, while theoretically an ordered phase induced by long-range dipolar interactions between Ising spins on the pyrochlore lattice does exist, its experimental observation will depend acutely on the dynamical processes of the real materials. Furthermore, one requires that perturbations H' are negligible, i.e., that $H'/D_{nn} \lesssim T_c/D_{nn} \lesssim 0.08$.

In conclusion, we predict that, for the dipolar spin ice model, which is in quantitative agreement with experimental data on real systems in the temperature regime investigated so far [8,9], there exists a unique long-range ordered ground state with zero total magnetization per cubic unit cell. If dynamical equilibrium is achieved, this state is arrived at via a first order transition with recovery of all residual "zero-point" entropy.

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