

## Spin ordering and partial ordering in holmium titanate and related systems

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We take another look at two compounds which have been discussed as possible realizations of “spin ice,” namely holmium titanate and dysprosium titanate. As we have earlier observed, holmium titanate does not display icelike behavior at low temperatures because the long-ranged dipolar interactions between spins are strong compared to the nearest-neighbor interactions. We show, exactly, that the true ground state of this system must be fully ordered, but simulations only reach partially ordered states because there are infinite energy barriers separating these from the true ground state. We also show that the true ground state of our model of dysprosium titanate is also fully ordered, and offer some explanations as to why simulations and experiments show icelike behavior. We discuss the effect on these systems of an applied magnetic field. Finally, we discuss several other models which show similar partial or full ordering in their ground states, including the well-known Ising model on the fcc lattice.

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### I. INTRODUCTION

With the wide interest in the physics of disorder and frustrated magnetism, pyrochlore magnets have attracted great attention in recent years,<sup>1</sup> and it is especially interesting to consider pyrochlores well approximated by the Ising model. We recently discovered<sup>2</sup> that dysprosium titanate, an Ising pyrochlore, exhibits a ground-state entropy very much like that of ice. Anderson<sup>3</sup> had long ago predicted that this should happen for a nearest-neighbor Ising pyrochlore. However, the story is not quite so simple here: the dominant interaction is really a long-ranged dipole-dipole interaction. There is no global Ising axis; instead each spin is constrained to point along the axis joining the centers of the two adjoining tetrahedra, so that there are local Ising axes in four possible directions. This leads to the interesting observation that, though for an effective Ising Hamiltonian an antiferromagnetic  $J$  ( $J > 0$ ) is frustrating, if we think of the Hamiltonian as a more physical-looking classical Heisenberg interaction  $\sum_{\langle ij \rangle} J \mathbf{S}_i \cdot \mathbf{S}_j$ , with the directions of the spins constrained to point along their respective Ising axes, it is the *ferromagnet* ( $J < 0$ , the state in which each tetrahedral unit has a net magnetic moment) which is frustrated. This observation was made by Harris and co-workers<sup>4</sup> who called the system “spin ice.” The presence of multiple Ising axes also has consequences for the effect of long-ranged interactions: there is heavy cancellation of interactions from distant spins, which would not happen with a uniform Ising axis. Moreover, the similar Ising pyrochlore holmium titanate has very different low-temperature behavior. We had explored the reasons for this in our earlier papers;<sup>2,5</sup> here we take those arguments further.

We observed earlier<sup>5</sup> that simulations of a model of the Ising pyrochlore holmium titanate suggest that it has a partially ordered ground state, which is degenerate but has no entropy per particle (the degeneracy being of the order  $2^L$  where  $L$  is the system length, rather than  $2^{L^3}$ ), and there appears to be a first-order phase transition from the high-

temperature paramagnetic phase to the above partially ordered phase. In this article we clarify the nature of this partial ordering, and explain it without recourse to simulations. Actually, we show that the ordering of the true ground state here is in fact complete, but there are numerous low-lying partially ordered metastable states which are separated from the true ground state by infinite energy barriers. It is easy for the simulation (and, presumably, the real compound) to get stuck in one of these states on cooling, and impossible to reach the true ground state in finite time thenceforth. Moreover, this is also the true ground state of our model of dysprosium titanate; but both the model and the experiments<sup>2</sup> suggest a finite ground-state entropy characteristic of nearest-neighbor spin ice. This, we suggest, is because this system has stronger nearest-neighbor interactions and settles into an icelike state at a higher temperature (over 1 K), and cannot then be easily dislodged from this into the true ground state. Our exact results, and also our simulations, support and substantiate our original suggestions of a transition to partial ordering, in contrast to recent suggestions to the contrary,<sup>6</sup> namely that that our model for holmium titanate should have an icelike ground state.

We also substantiate the major results and the underlying model from our earlier work,<sup>2</sup> namely that there is a low-temperature entropy observed in dysprosium titanate, it is decreased in the presence of a magnetic field, and the interactions in the system are dipole-dipole magnetic interactions and an isotropic superexchange. The fact that our simulations with a magnetic field reproduce experimental results quite well, qualitatively and quantitatively, confirms our calculation of the dipole moment (which is the only thing that couples with the field) and our estimate of the superexchange. Moreover, the ground state in the presence of a strong field is not the same as the zero-field ground state. While the experiments were done on powdered samples, simulations suggest that the behavior of dysprosium titanate in a magnetic field is very direction dependent. A strongly direction dependent ordering was initially suggested on the basis of the specific-heat measurement done on a powdered

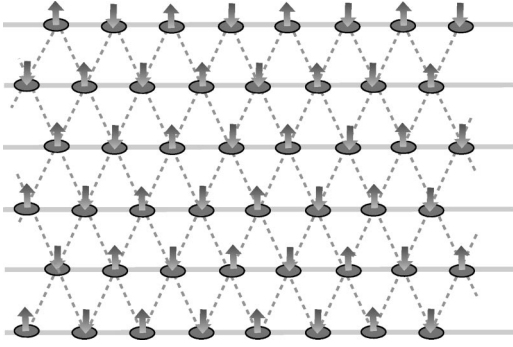


FIG. 1. Anisotropic triangular lattice, with antiferromagnetic Ising interaction  $J_1$  along solid lines and  $J_2 < J_1$  along dashed lines. In the ground state, each chain along the solid lines is ordered, but there is no order along the dashed lines.

sample.<sup>2</sup> We compare the experimental data on powder samples with simulations averaged over large numbers of directions, compare sharp features in both, and make important predictions for possible future experiments on single crystals.

Next, we use the insight from the ground-state analysis to progressively reduce the pyrochlore Ising model to a sequence of simpler models which display similar behavior: namely, a six-vertex model on the “diamond lattice” with nonlocal interactions, which reproduces all the essential behavior of holmium titanate, and has a fully ordered ground state and several metastable partially ordered low-lying states (Sec. IV); a six-state magnetic model on the fcc lattice, which actually has the sort of partially ordered ground state that the simulations had suggested for holmium titanate, and also reproduces the important behavior of holmium titanate (Sec. VI); and the well-known Ising model on the fcc lattice, which has been studied before<sup>7</sup> and is known to have exactly the same sort of partial ground-state ordering that concerns us here (Sec. VII). Along the way, we also introduce a square-lattice vertex model, by analogy with the above diamond-lattice model, which may be worthwhile to study in its own right.

Actually, the simplest example of partial ordering in an Ising system is perhaps the triangular lattice antiferromagnet, with interaction  $J_1$  along bonds in one direction (say parallel to the  $x$  axis),  $J_2 < J_1$  along bonds in other directions (Fig. 1), and  $J_1, J_2$  positive (antiferromagnetic). Then we have perfect antiferromagnetic order along a line of sites in the  $x$  direction, but each atom on an adjacent chain is frustrated so the adjacent chain (which also has perfectly antiferromagnetic order) has two possible configurations with respect to the first, and the system as a whole has a degeneracy  $2^L$  where  $L$  is the number of chains. This system is exactly solvable,<sup>8</sup> and has no finite-temperature phase transition. This situation is quite relevant to what happens in our system. The analogous model in three dimensions, the fcc Ising model, is discussed at the end of the paper and in the cited references.

## II. ORDERING IN OUR MODEL OF $\text{Ho}_2\text{Ti}_2\text{O}_7$

We briefly recapitulate our model of holmium titanate. The underlying lattice is the pyrochlore lattice, a lattice of

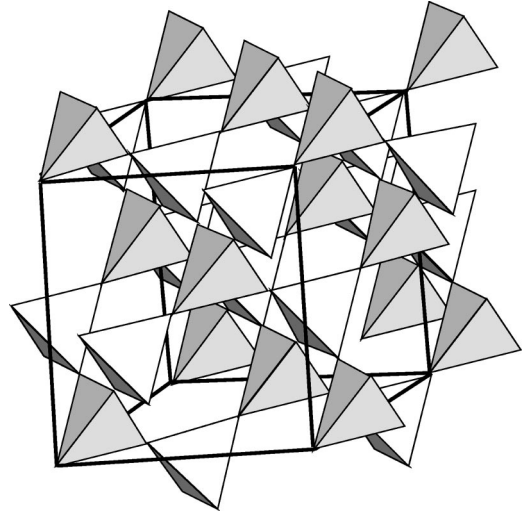


FIG. 2. The conventional unit cell of the pyrochlore, a lattice of corner-sharing tetrahedra with fcc symmetry.

corner-sharing tetrahedra of two possible orientations, which is well visualized as an fcc lattice of tetrahedra (Fig. 2). It may be generated by taking a single tetrahedron of one orientation and translating it by the primitive basis vectors of the fcc lattice (Fig. 3); the tetrahedra of the other orientation emerge automatically by this procedure—see Fig. 3. Thus we use the lattice vectors

$$\begin{aligned} \mathbf{a}_1 &= (r, \sqrt{3}r, 0), \\ \mathbf{a}_2 &= (-r, \sqrt{3}r, 0), \\ \mathbf{a}_3 &= (0, 2r/\sqrt{3}, -2r\sqrt{2/3}) \end{aligned} \quad (1)$$

with a basis of atoms located at

$$\begin{aligned} \mathbf{x}_0 &= (0, 0, 0) \\ \mathbf{x}_1 &= (r, 0, 0), \end{aligned}$$

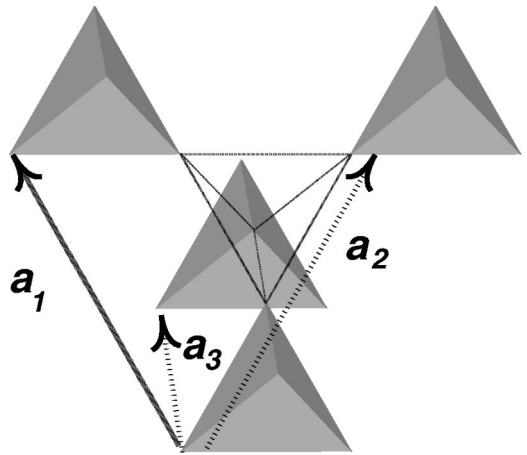


FIG. 3. The pyrochlore lattice can be generated by translating a tetrahedron along vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$ . Tetrahedra of the opposite orientation are formed from the corners of these (thin black lines).

$$\begin{aligned} \mathbf{x}_2 &= \left( \frac{1}{2}r, \frac{\sqrt{3}}{2}r, 0 \right), \\ \mathbf{x}_3 &= \left( \frac{1}{2}r, \frac{1}{2\sqrt{3}}r, \sqrt{\frac{2}{3}}r \right). \end{aligned} \quad (2)$$

In this system  $r$  is around  $3.54 \text{ \AA}$ .

We have Ising spins (the  $f$  electron states of the holmium atoms) located at these points. The local Ising axis is the line joining the centres of the two adjoining tetrahedra: thus each spin points directly out of one tetrahedron, and into the next one. The spins carry magnetic moments corresponding to  $J = 8$ ,  $g_s$  (the Landé factor) = 1.25. Based on this, the expected nearest-neighbor dipole-dipole interaction has an energy of  $\pm 2.35 \text{ K}$ , the sign depending on the alignment of the spins: one pointing out, one in is preferred. However, the experimental compound (unlike its cousin, dysprosium titanate) has properties which we can only explain by postulating a significant nearest-neighbor superexchange, which we estimate from high-temperature expansions for the susceptibility to be around  $1.9 \text{ K}$  with opposite sign to the dipolar interaction. So, with the convention that an Ising spin  $S = 1$  if it points out of an ‘‘up’’ tetrahedron and  $S = -1$  otherwise, we write the Hamiltonian as follows:

$$H = \sum_{i,j} J_{ij} S_i S_j, \quad (3)$$

$$J_{ij} = 0.45 \text{ K, for nearest-neighbor spins,} \quad (4)$$

$$J_{ij} = \frac{\mu_0}{4\pi} g_s^2 \mu_b^2 J^2 \left[ \frac{\mathbf{n}_i \cdot \mathbf{n}_j}{r_{ij}^3} - 3 \frac{(\mathbf{n}_i \cdot \mathbf{r}_{ij})(\mathbf{n}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (5)$$

further neighbors,

where  $\mathbf{n}_i$  is a unit vector pointing along the Ising axis at site  $i$  in the outward direction from an ‘‘up’’ tetrahedron. Thus this system has a drastically reduced nearest-neighbor interaction energy, which means the importance of the further-neighbor interactions increases. We saw that with only a long-ranged dipole-dipole interaction between these Ising spins, the behavior seems to change little from the nearest-neighbor Ising model which has a finite ground state entropy; we speculate that the substantially different behavior of holmium titanate is due to the significantly greater importance of further-neighbor interactions. As noted earlier, simulations of such a model do predict a freezing of the system at around  $0.7 \text{ K}$ , in agreement with experiment.

We now find the ground state (GS) for this system. For clarity we refer to the two different orientations of tetrahedra that occur as ‘‘up’’ and ‘‘down:’’ each ‘‘up’’ tetrahedron shares corners with only ‘‘down’’ tetrahedra, and vice versa. Consider a single tetrahedron: it has six possible ground states, each of which has two spins pointing out and two in. We label these states  $A, A', B, B', C, C'$  where  $A'$  is  $A$  with the directions of all spins reversed, and similarly  $B'$  and  $C'$  (Fig. 4). Consider a particular cluster of sites from the full lattice consisting of a single ‘‘up’’ tetrahedron and its trans-

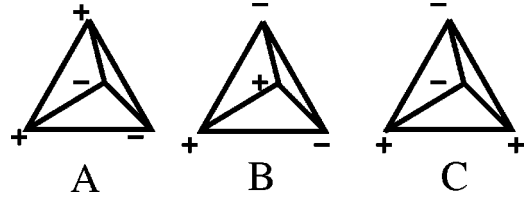


FIG. 4. Three possible ground-state configurations  $A, B, C$  of a tetrahedron. We will denote by  $A', B', C'$  these respective configurations with all spins reversed. ‘‘+’’ indicates a spin pointing out of the tetrahedron, ‘‘-’’ a spin pointing into the tetrahedron.

lation by the three primitive lattice vectors of the fcc lattice (as in Fig. 3), and long-ranged dipole-dipole interactions spanning the entire cluster plus a nearest-neighbor superexchange, as described above. We find the GS of this ‘‘tetrahedron of tetrahedra’’ by the unobjectionable method of enumerating each of the  $2^{16}$  allowed states on a computer, and picking out the lowest-energy ones.

We find that the GS of this cluster is 12-fold degenerate. Two are shown in Fig. 5. All others are rotations/reflections of these (which are reflections of each other). In each GS, as one might expect, only states satisfying the ice rule occur. Furthermore, only two kinds of icelike configurations occur:  $A$  and  $A'$ , or  $B$  and  $B'$ , or  $C$  and  $C'$ . They occur twice each. In the case shown in the figure, once the configuration of tetrahedron at the origin is fixed as  $C$ , the tetrahedron at  $\mathbf{a}_3$  must have the opposite configuration ( $C'$ ); and the tetrahedron at  $\mathbf{a}_2$  may have either configuration ( $C$  or  $C'$ ), but tetrahedron  $\mathbf{a}_1$  must have the opposite configuration to  $\mathbf{a}_2$ . With the previously quoted values for the dipole and superexchange interactions, the configurations in Fig. 5 have an energy  $-7.5 \text{ K}$ , and the next lower energy configurations have an energy  $-6.9 \text{ K}$ .

If we note that each tetrahedron in its ground state has a dipole moment, which is perpendicular to two possible lattice translation vectors, the rule is this: in every GS only configuration of two opposite kinds occur (say  $C$  and  $C'$ ), which therefore have antiparallel magnetic moments, and two tetrahedra separated by a vector perpendicular to these moments must have opposite configurations. These are the 12 ground states allowed for this cluster, but we are making no theoretical argument for this; this is what we learn from brute-force enumeration of states. In any of these states, moreover, the included ‘‘down’’ tetrahedron also has an icelike configuration.

Now consider the entire fcc lattice of tetrahedra (that is,

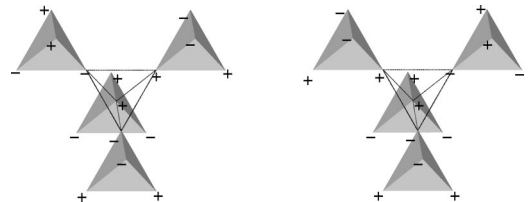


FIG. 5. Two of the 12 allowed ground states for a cluster of four tetrahedra. Each of the 12 states is related to the others by rotations or reflections. This consideration by itself leads to partial ordering in the ground state of the full system, as described in the text.

the pyrochlore lattice). Once we fix the configuration of a single “up” tetrahedron (say, as  $C$ ) each of its neighboring tetrahedra, with which it forms part of a cluster of the above sort, must have the same or opposite configuration (say  $C$  or  $C'$ ); and by extending further from each of these, this must be true for the entire lattice. We can also see that if we travel in either of the two lattice directions perpendicular to the magnetic moment of these tetrahedron configurations, we must have a perfectly alternating sequence (say  $C, C', C, C', \dots$ ); but when traveling in a third direction we have no ordering rule. So we get a ground-state ordering in two directions but not in the third, and a degeneracy exponential in  $L$  (the system length) rather than  $L^3$  (the system volume), precisely as the simulations suggested. Such a “partially ordered” state ensures that every cluster of tetrahedra is individually in its ground state, and any other arrangement would involve putting some local cluster of tetrahedra in a higher-energy state, suggesting that this is the true ground state for the whole lattice.

This is not the whole story, though. The system can be equally well described in terms of “down” tetrahedra, so the same sort of ordering should be evident if we describe a ground-state configuration using “down” tetrahedra. So only two configurations for these tetrahedra should be allowed, each of which is the other with all spins reversed. But we note immediately that the two “down” tetrahedra displayed as gray lines in the two clusters in Fig. 5 do not have opposite configurations. It follows that the two cluster configurations in that figure cannot both occur in the ground state: only one can. *This immediately implies that the ordering sequence in a third direction is not random, but constant* (say,  $C, C, C, \dots$ ).

So the true ground state for our model of holmium titanate is only 12-fold degenerate, and viewed in terms of configurations of either upward or downward tetrahedra, consists of alternating ordering of opposing configurations in two directions but a constant configuration in a third direction. However, the partially ordered states are also very low in energy, and, moreover, a system stuck in such a state can only get out by flipping entire planes of tetrahedron configurations, which is impossible in the thermodynamic limit. So simulations tend to get stuck in such states and in other “domainized” states and the chances of a given simulation actually hitting a true ground state are very small—unless we use some sort of specialised “cluster” algorithm which may not imitate the dynamics of the real system very well.

This is exact except for one thing: by only considering the energies of clusters of four adjacent tetrahedra, we have ignored interactions between further-neighbor tetrahedra, so effectively confined our interaction range to the fifth neighbor, which is the maximum separation of spins in two adjacent tetrahedra. Luckily, in the presence of long-ranged interactions, the nature of the system (with four different local  $z$  directions) is such that the effects of the more distant tetrahedra cancel heavily and have little effect on the energy of a single cluster. Thus if one take a particular “up” tetrahedron in the ground state, its energy turns out to be  $-21$  K because of interactions with the immediately neighboring “up” tetrahedra (to which the cluster argument applies), but

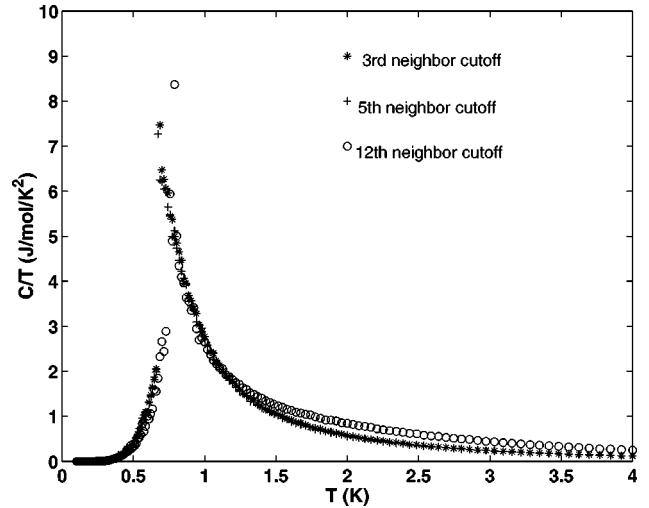


FIG. 6. The simulated specific heat when the interaction is cut off at the third ( $R \leq 2r$ ), fifth ( $R \leq 2.646r$ ), and 12th ( $R \leq 4r$ ) nearest neighbor distances ( $r = 3.54$  Å, roughly). The position of the phase transition and the plot of the specific heat near the transition hardly change at all on increasing the range of the interaction; but one needs longer equilibration times with increased interaction ranges. The simulations show a significant energy drop at the transition, suggesting that it is first order.

only  $-0.12$  K because of interactions with all other tetrahedra in the system. Thus the additional energy from the interactions we have ignored is not only negligibly small, but actually tends to stabilize this order. (With a random icelike configuration, this additional energy averages to zero, but fluctuates considerably from site to site.) Recall furthermore that the cost of disturbing a single four-tetrahedron cluster from its ground state (Fig. 5) is at least  $0.6$  K, and in fact much more since each tetrahedron is shared by four such clusters.

To provide an analogy: in a system with a nearest-neighbor ferromagnetic Heisenberg interaction, we would expect a uniform magnetization because each pair of spins would be satisfied, just as each cluster of tetrahedra is satisfied here. However, with such a uniformly magnetized state, the dipole-dipole interactions of infinitely far spins will in fact have a significant contribution, causing the system to break into domains; such a thing does not happen in our pyrochlore, because there is no net magnetization, and because there is large cancellation of the interactions from all spins beyond the fifth neighbor.

So we can be satisfied that the long-ranged interactions will not disturb our fully ordered ground state. In fact, the simulations too do not show much dependence on the range of the interaction, provided it extends to at least the third neighbor (Fig. 6), as indeed we had argued in our earlier paper, where we cut off the interaction at the fifth-neighbor distance.<sup>5</sup> The suggestion<sup>6</sup> that icelike behavior is restored by cutting off after the tenth neighbor seems untenable to us, and we do not observe it in our simulations even on extending the interaction to the 12th neighbor (which is halfway across our sample). Possibly the different results obtained in Ref. 6 is due to additional approximations involved, such as



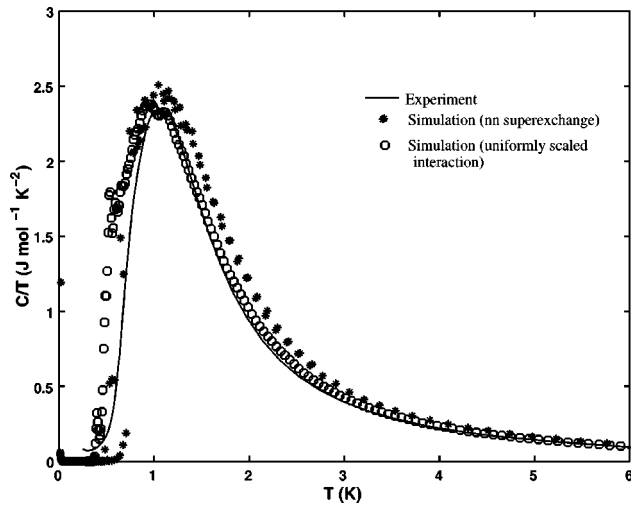


FIG. 7. A comparison with experimental data for dysprosium titanate of a simulation using nearest-neighbor superexchange and long-ranged dipole-dipole interactions, and a simulation using uniformly scaled down dipole-dipole interactions (as was done in Ref. 2).

Ewald sums, and a somewhat smaller sample size; our simulations use no approximations in calculating the energy except the cutoff, which as we have seen, is quite justifiable. Longer simulations on bigger systems may throw more light on this question, but we now turn to some other interesting aspects of the problem.

This true ground-state ordering is more easily visualised (though less easily analyzed) with the cubic unit cell rather than our parallelepiped; this is discussed in Sec. VI.

### III. DYSPROSIUM TITANATE

Dysprosium titanate, which we earlier reported as showing icelike behavior experimentally and in simulations, appears to have a much weaker superexchange between nearest neighbors. With a nearest-neighbor-only model of the superexchange, we find we need a superexchange of around  $+1.1$  K, that is, the nearest-neighbor interaction is around  $-1.25$  K compared to the bare dipole-dipole value of  $-2.35$  K. With these numbers, we get a reasonable agreement of the simulation with experiment (Fig. 7). However, we get even better agreement by uniformly scaling down the long-ranged dipole-dipole interaction by roughly the same factor of  $1.25/2.35$ . (This is what was reported in our earlier paper.) This suggests that the superexchange is not strictly nearest-neighbor but extends over to further neighbors.

We need to understand why  $\text{Ho}_2\text{Ti}_2\text{O}_7$ -like behavior is not observed in this case. With either of the two models above (small nearest-neighbor-only superexchange, or uniformly scaled-down dipole-dipole interaction) the ground state for the cluster of four tetrahedra remains the same as before, the difference in energy from the next-lowest state too remains roughly the same, and the above arguments should still go through.

The difference is that, because of the stronger nearest-neighbor interactions here, this system undergoes a crossover

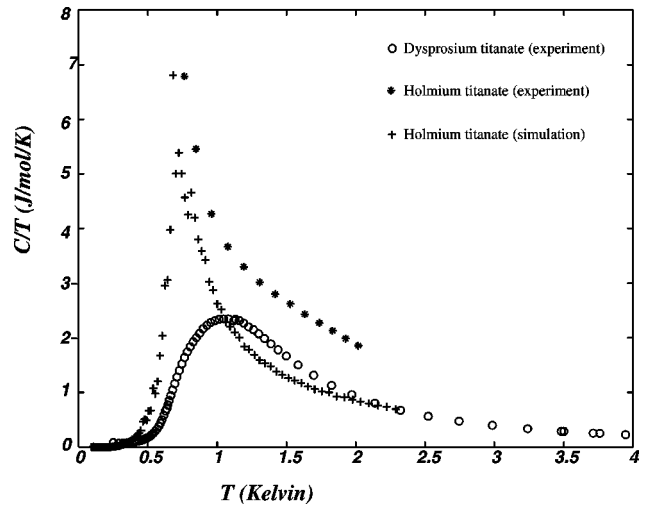


FIG. 8. Specific heat curves of dysprosium titanate (experimental, and simulations give excellent agreement) and holmium titanate (experimental, and a simulation retaining dipole-dipole interactions to 12 nearest-neighbor distances). By the time the ordering temperature is reached (which is expected to be the same for both systems) dysprosium titanate is already frozen into an icelike configuration from which it would find it hard to locate a lower-energy state.

from a paramagnetic phase to an ice-ruled phase at a considerably higher temperature (greater than 1 K); and by the time it cools down to the temperature ( $<0.7$  K) where we expect a transition of the sort described here, it is already stuck in a disordered icelike state and (because of the stronger nearest-neighbor interactions) cannot easily break out of this state to access other states. It appears that the temperature of the crossover to the icelike phase is dictated by the nearest-neighbor interactions. In dysprosium titanate these have an energy of around 1.3 K, and hence the ice rule is already in place by the time we go down to 0.7 K and the spins are almost frozen, thus the ordering transition no longer has a chance to occur. In holmium titanate, on the other hand, the nearest-neighbor interaction is around 0.4 K, thus at 0.7 K the system is in no sense frozen, plenty of spin flips take place and the ordering transition occurs (Fig. 8).

So while our arguments show that the true ground state here is ordered and only 12-fold degenerate, the system tends to get stuck in fairly generic icelike states. We have checked that the energy of the disordered low-temperature state of the system in our simulations is always slightly but significantly higher (by around 0.5–1%) than the energy of the fully ordered state if we include the full long-ranged interactions in calculating the energy.

The low-temperature states we see are governed mainly by the ice rule (though evidence of some local ordering of four-clusters can be seen) and are probably macroscopic in number. This is why we observe an anomaly in the integrated entropy which we earlier attributed to a possible ground-state entropy. This low-temperature “entropy” (as estimated from Fig. 9) is around 10% lower than  $1/2 \ln(3/2)$ , which is itself an underestimate by around 10%. Very much the same thing is likely to be true in the real system (dysprosium titanate) too: its true ground state is ordered but the

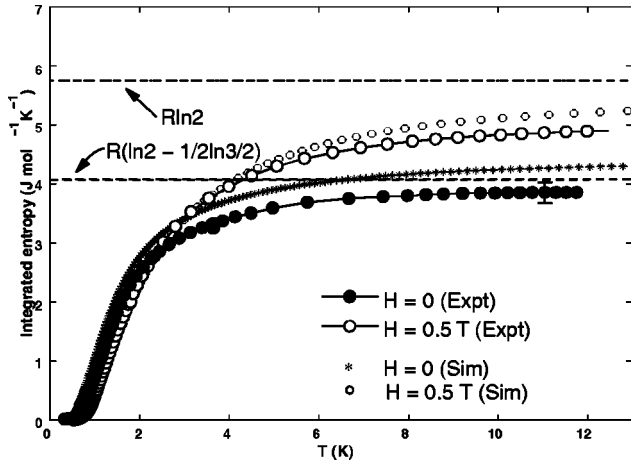


FIG. 9. The integrated specific heat per unit temperature in simulations without a magnetic field and with a half-tesla magnetic field. This shows the entropy gained over the ground-state entropy. The entropy is expected to be  $R \ln 2$  (dotted line) at high temperatures; the integrated value falls short of this, indicating a ground-state entropy, but the ground-state entropy is reduced in the presence of a magnetic field. Both the experimental data, taken from our earlier paper,<sup>2</sup> and the simulation results are plotted here for easy comparison. Based on simulations, we suggest that a magnetic field of around 3 T should recover all or nearly all the ground-state entropy.

system can almost never access this ground-state. The measured ground state entropy here is closer to  $1/2 \ln(3/2)$ , in fact a bit more; it is probably a bit less than the true ground-state entropy of nearest-neighbor spin ice, though.

In the presence of a magnetic field, some interesting things happen. As reported earlier,<sup>2</sup> some of the observed ground-state entropy is recovered experimentally; we see this also in simulations (Fig. 9). Since only the dipole moment couples to the field, the quantitative agreement in this curve is an additional confirmation of our model of co-existing dipole-dipole interactions and superexchange. The curves are similar in features and the amount of entropy recovered is also roughly the same. In stronger fields, sharp spikelike features start to show up in the experimental specific-heat curves at low temperatures. Here, too, we find reasonable qualitative and quantitative agreement between simulations and experiment. All this confirms that our calculation of the dipole moment of the  $f$  electrons and our supposition that the reduced energy scales are due to another interaction (superexchange) are correct, since the interaction with a magnetic field is purely magnetostatic. The experiments were done using powder samples, and the simulations show that the behavior is strongly dependent on the direction of the field (see Fig. 10). To compare with powder averaged experimental results, we would need a very large number of simulations in random directions, which we have not done to our satisfaction.

The nature of the ground state also depends on the field direction, and with a sufficiently strong field and a suitable field direction the ground state may not even satisfy the ice rule. For instance, with a field along the  $z$  axis in Fig. 3 (which corresponds to the  $[111]$  direction with the conven-

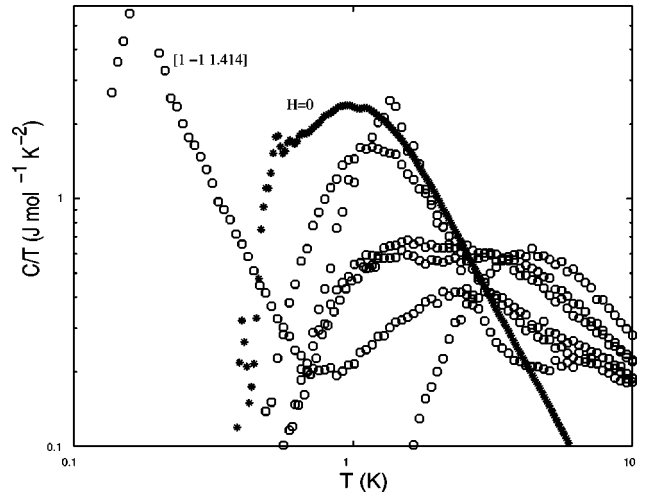


FIG. 10. Specific heat in the presence of a 2-T magnetic field, for various directions of the field.

tional unit cell) the ground state consists of three spins pointing into each upward tetrahedron and one pointing out of it.

It is interesting to ask how the transition to a different ground state occurs as one slowly turns on a magnetic field at low temperatures. Figure 11 shows the result of doing this in a simulation at 0.2 K, for a field in the  $[1\bar{1}\sqrt{2}]$  and  $[111]$  direction. The system seems to go through several magnetic transitions before reaching its fully polarized state.

All these features would be averaged over in the experiments on the powder samples, and single crystals of these materials could turn out to be worth studying in their own right.

#### IV. AN ANALOGOUS SIX-VERTEX MODEL

If we examine the nature of states just above the transition in simulations of our holmium titanate model, we find that a large fraction of the tetrahedra are already in the ice-ruled

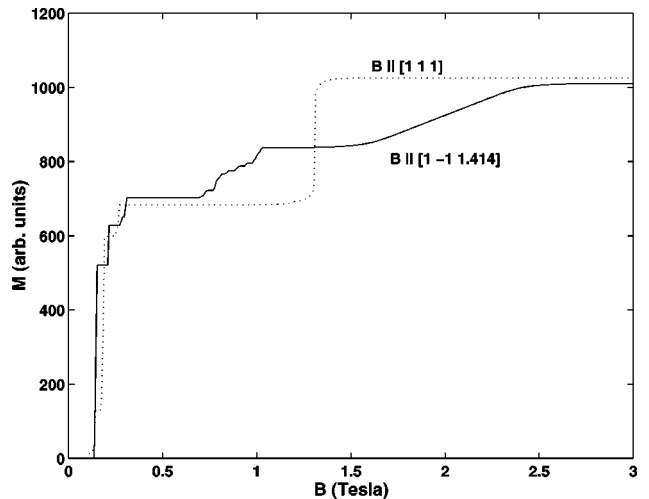


FIG. 11. The growth of magnetization in the simulation sample, for magnetic field in the  $[1\bar{1}\sqrt{2}]$  and  $[111]$  directions, at a temperature of 0.2 K.

state. This suggests that the sharp transition here is not the transition from paramagnetism to an icelike phase, but a phase transition from a disordered icelike state to an ordered or partially ordered state.

To check that this is the case, we can try putting the ice constraint in by hand, and check that the phase transition is still reproduced at the same temperature. The model we get then is a form of six-vertex model on the ‘‘diamond’’ lattice, whose sites are the centers of the tetrahedra in the pyrochlore lattice. The six-vertex model has been widely studied on the square lattice; the diamond lattice, like the square lattice, has a coordination number of four and can be divided in two sublattices, but is three dimensional. So we study a system where one assigns arrows to bonds on the diamond lattice, such that each site (or ‘‘vertex’’) has two arrows pointing in at it and two pointing away: so six kinds of vertices are possible. But unlike conventional six-vertex models, we do not assign different weights to these six vertices, since all of them are really equivalent here; instead, the thermodynamics comes from interactions between different vertices. In other words, we have a Hamiltonian of the sort

$$H = \sum_{i,j} \equiv \sum_{i,j} J(c(i), c(j), \mathbf{r}_i - \mathbf{r}_j), \quad (6)$$

where  $c_i$  is the configuration (a six-valued variable) of the  $i$ th vertex, and  $J$  is the interaction energy of vertices  $i$  and  $j$ , which depends not only on their configurations but on the vector joining them (thanks to the underlying direction-dependent dipole-dipole interaction). We have to calculate the pairwise  $J$ 's appropriately.

What we do is the following: we note that the sites on the diamond lattice fall into two sublattices, corresponding to up and down tetrahedra. First consider adjacent vertices (adjacent corner-sharing tetrahedra). The internal interactions between these spins can be separated into nearest-neighbor interactions, which we can assume has already been taken into account via the ice rule, and next-neighbor interactions, which we can equally include by considering only next-neighbor vertices (that is, nearest-neighbor tetrahedra of like orientation). We thus ignore interactions between nearest-neighbor vertices and consider interactions only between next-neighbor vertices, or nearest-neighbor vertices on a single sublattice. The interaction between two such vertices is the energy of interaction between the two corresponding tetrahedra, as given by the sum of interaction energies of all pairs of spins. We ignore all further-range interactions. But the interactions already included, if carried out over all vertices over both sublattices, will actually double count the pairwise spin-spin interactions: we therefore also insert a factor of half.

Formally, we can write

$$H = \sum_{\{i,j\}} E_{ij} \equiv \sum_{\{i,j\}} E(\mathbf{S}_i, \mathbf{S}_j, \mathbf{r}_i - \mathbf{r}_j) \quad (7)$$

and then break this sum up into nearest-neighbor terms, next-neighbor terms, and so on; throw out the nearest-neighbor terms because we have used them in enforcing the ice constraint; and group the next few terms into pairs where one

spin belongs to one ‘‘up’’ tetrahedron, the other spin belongs to an adjacent ‘‘up’’ tetrahedron;

$$H = \sum_{\{\alpha,\beta\}} \sum_{m=1}^4 \sum_{n=1}^4 E(\mathbf{S}_{\alpha m}, \mathbf{S}_{\beta n}, \mathbf{R}_\alpha - \mathbf{R}_\beta + \mathbf{x}_m - \mathbf{x}_n) + \text{other terms}, \quad (8)$$

where the sum is over neighboring ‘‘up’’ tetrahedra at sites  $\alpha$  and  $\beta$ , and we sum the interaction of each of the four spins at  $\alpha$  with each of the four spins at  $\beta$ .  $\mathbf{R}_\alpha$  is the position of spin 1 on tetrahedron  $\alpha$ , likewise  $\mathbf{R}_\beta$ , and  $x_m$  are as in Eq. (2). All the ‘‘other terms’’ involve spins separated by three times the nearest-neighbor distance or more, so we drop them. We can do precisely the same grouping of terms for the ‘‘down’’ tetrahedra; we do both, and insert a factor of half. Thus our Ising spin Hamiltonian is reduced to the vertex Hamiltonian (7) with appropriately chosen interaction energies  $J$ , extending only to the nearest neighbor on the same sublattice.

As before, we simulate this Hamiltonian. First, a word on how we do this. Flipping a single bond will not do: it will destroy the ice constraint on both adjoining vertices. We must find a closed loop, a set of bonds whose arrows lead from vertex to vertex and return to the starting vertex, and flip the whole loop at one go. Such ‘‘loop algorithms’’ have been discussed previously<sup>9</sup> and it has been pointed out that, in a six-vertex model, every line of arrows if followed must return to the starting vertex and every configuration is accessible via loop flips alone, so a random loop-flip algorithm is ergodic. The earlier algorithms have several improvements and optimizations; however, they are concerned with conventional vertex models where different vertices have different weights but do not interact, and cannot be completely translated to this situation. We found it sufficient to merely pick up random starting sites, form loops randomly, calculate the energy difference, and flip them according to the Metropolis algorithm.

The results are shown in Fig. 12. It exhibits a phase transition at exactly the point where both the real system, and our model for it, do. This is a distinctly first-order phase transition. Thus we have verified that the phenomenon driving this phase transition is not the formation of icelike tetrahedra, but the further ordering of tetrahedra that have already attained ice-rule configurations; and we have displayed a fairly simple vertex model which shows the same features as our Ising pyrochlore.

The ground state of this system would be expected to be fully ordered, but typically only partially ordered states are accessible. The argument is similar to that in the case of holmium titanate, and the simulations bear this out.

## V. A SQUARE LATTICE VERTEX MODEL

The sort of physics involved can perhaps be better seen in a square-lattice vertex model. Such models have been extensively studied,<sup>10</sup> but the thermodynamics has typically arisen from assigning different weights to different vertices; instead we give the same weight to all vertices, but consider interactions between diagonally opposite vertices (the gray lines

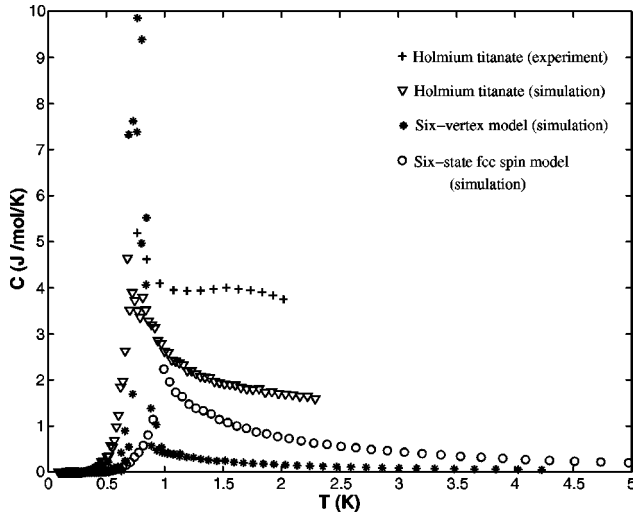


FIG. 12. Comparison of specific-heat curves for holmium titanate (the real system); our model of holmium titanate; the six-vertex model of Sec. IV; and the six-state spin model of Sec. VI

in Fig. 13). We ignore nearest-neighbor interactions for the same reason as earlier, i.e., that is taken care of by assigning an ice rule.

The possible interactions are shown in Fig. 14; for symmetry reasons, we need have only three interaction parameters, all other nonzero interactions can be obtained from these by rotation, reflection, or inversion of one or both vertices (inverting a single vertex will simply change the sign of the interaction energy). If we calculate the interaction parameters from an assumed dipole-dipole interaction between magnets aligned along the edges connecting the respective vertices, we obtain  $A = -8.6678$ ,  $B = 10.753$ , and  $C = -10.345$  (arbitrary units). The ground state then looks as shown on the left of Fig. 15; but a very slight alteration in the choice of  $A$ ,  $B$ , and  $C$  will give a ground state as shown on the right of Fig. 15, and the choice  $A - B = 2C$  may lead

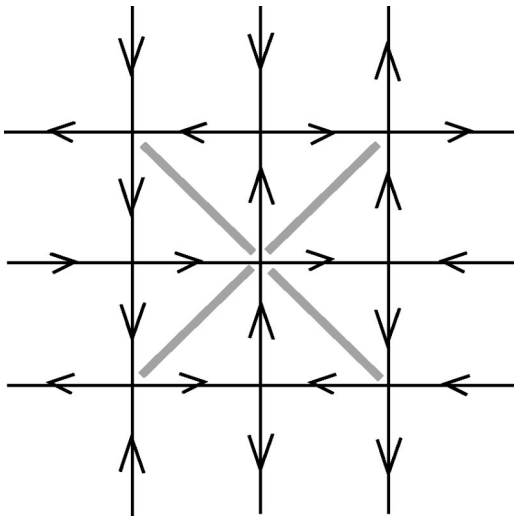


FIG. 13. An ice model on the square lattice, with similar properties to the earlier, diamond-lattice model. Interactions are between diagonally-opposite vertices (gray lines).

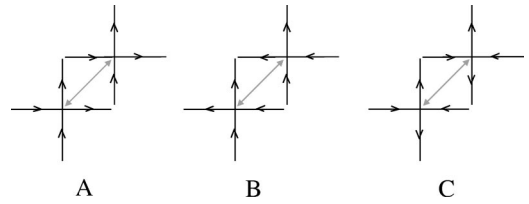


FIG. 14. The three possible interactions between neighboring vertices. All other possibilities are symmetry related, or zero. In particular, reversing all arrows on a single vertex will simply change the sign of the interaction.

to rather interesting results. The model is probably worth studying both in its own right and because of the long historical interest square-lattice vertex models have held; but since it is not really related to the rest of this paper, we postpone further discussion of it to a future work.

### VI. MULTISTATE SPIN MODEL ON AN FCC LATTICE

In our vertex model earlier, we had two sublattices, and interactions only within a single sublattice. Apart from the ice-rule constraint, the two sublattice could just as well be noninteracting. So the next logical step is to separate the two sublattices. We consider an fcc lattice, with a six-valued variable at each site. Only nearest-neighbor interactions are considered, and as before, the value of the interaction is determined from the underlying pyrochlore Ising variables. The major difference with the vertex model case is that we have now forgotten about the “down” tetrahedra: an arbitrary configuration of four neighboring “up” tetrahedra would not satisfy the ice rule for the enclosed “down” tetrahedron, but we are no longer worrying about that now.

It turns out that the dynamics of interaction between these “up” tetrahedra takes care of that for us. The system displays a phase transition at very nearly the same temperature as the vertex model and the Ising pyrochlore (Fig. 12), and at temperatures just above the transition the configuration is such that nearly all the “down” tetrahedra in the correspondingly configured pyrochlore would satisfy the ice rule; at zero temperature the system is partially ordered, in exactly the way we observed in holmium titanate, but the partially ordered states in this case really are the ground states.

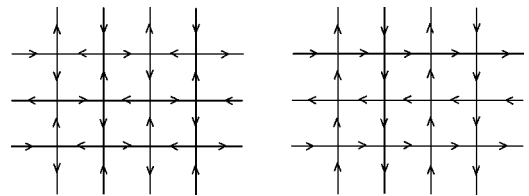


FIG. 15. With interaction energies  $A$ ,  $B$ , and  $C$  between vertices calculated from dipole-dipole interactions between spins aligned along their edges, we obtain a ground state as on the left. But a slightly different choice of weights will yield a ground state as on the right, and there is the possibility of a “level crossing” between the ground states for a choice  $A - B = 2C$ .



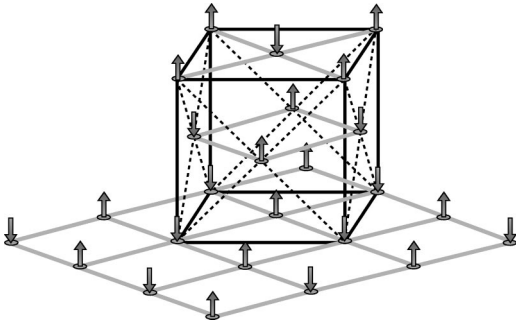


FIG. 16. Ising antiferromagnet on an fcc lattice, with nearest-neighbor interaction  $J$  (solid gray lines) in the plane and  $J' < J$  (dotted lines) between planes. Each plane orders antiferromagnetically but they stack up in a random manner. Surprisingly, this is also the ground state when  $J' = J$ .

The partial ordering is now more easily visualized with the conventional cubic unit cell rather than the parallelepiped which we used. Note first that each ice-ruled state of a tetrahedron has a dipole moment, perpendicular to the side connecting the two inward-pointing spins and to the side connecting the two outward-pointing spins. If one looks at the cubic unit cell, we can see that the six allowed values of this dipole moment are along the three edges of this cube: so what we have is a six-state magnetic model on an fcc lattice where each spin can point along one of the Cartesian axes. In the ground state, one of these axes is picked out, so that each spin points along the same line in one of two opposite directions; each plane perpendicular to this direction is antiferromagnetically ordered; and perpendicular to this plane, the ordering is random.

It is tempting to use the total dipole moments of the tetrahedra as the site variables, and for the interaction simply to use their mutual magnetic interactions, since we know that the dipole-dipole interaction favors antiferromagnetic ordering in planes perpendicular to the spins; but it turns out that this is not the ground state of such a system. Only by using the actual interaction energies of the tetrahedra do we obtain such a ground state. However, there is an obvious connection between this system and a well studied problem, which we turn to in the next section.

## VII. ISING MODEL ON THE FCC LATTICE

The nearest-neighbor antiferromagnetic Ising model on the fcc geometry has been studied by several authors, and its ground state is known to have exactly the sort of ordering we are considering.

The ordering is easy to understand if there is a bit of anisotropy in the system: consider Fig. 16, where we have an fcc crystal, and within the  $x$ - $y$  plane and planes parallel to it there is an antiferromagnetic interaction  $J$  between nearest neighbors, but out of the plane there is an interaction  $J' < J$ . Then the planes prefer to order antiferromagnetically, but adjacent planes have zero interaction energy regardless

of their relative ordering, so the ordering along the  $z$  axis is random. The interesting thing is that this remains true even when  $J' = J$ : the only change is a new factor of 3 in the degeneracy because of the new rotational symmetry of the system.

The order of the transition is also of interest. In the isotropic case, it is a first-order transition. With strong anisotropy (a weak interplane coupling), however, we would expect a second-order transition because the system effectively is like weakly interacting two-dimensional Ising systems, which have a second-order transition at the Onsager temperature. In fact, simulations suggest that for  $J'$  close to  $J$ , the transition is first order, but for  $J'$  somewhat less it is second order, and for  $J' = 0.6J$  the transition temperature is almost exactly the Onsager temperature. Since the planes have a zero interaction energy in the ground state and a very small interaction energy at low temperatures, they behave like almost uncoupled 2D Ising systems. Thus this system seems to exhibit either a first-order transition or a second-order transition with the same sort of ground state, depending on the parameters.

## VIII. CONCLUSION

We have clarified the true nature of the ground states of the Ising pyrochlores holmium titanate and dysprosium titanate. We have pointed out that the icelike behavior of dysprosium titanate seems to arise not from a macroscopic degeneracy of the true ground state, but from its inaccessibility in practice, and consequently the tendency of the system to fall into one of a large number of slightly excited icelike states. In holmium titanate, the ordering temperature is higher than the expected ice-formation temperature; here, too, the system gets stuck into excited states, but these are partially ordered states and the model system shows a clear phase transition. By rigidly enforcing the ice constraint, we show that this transition exists independently of the broad ice-state crossover in spin ice, and we exhibit several models, including the well-known fcc Ising model and a diamond lattice vertex model, which undergo a similar phase transition. Analogous to this vertex model we also exhibit a square lattice vertex model which has differently ordered ground states depending on what interaction parameters we choose, and which we hope to examine further sometime in the future.

In addition, we have looked at what happens to dysprosium titanate when a magnetic field is applied, and compared our conclusions to available experimental data; we have reproduced earlier experimental data for a weak field and see similarities in our simulations and the strong-field data, further confirming our underlying model. We see strongly anisotropic behavior in these systems and predict some interesting results for possible experiments on single-crystal samples.

This work appears as part of the Ph.D. thesis of R.S.<sup>11</sup>

*Note added.* After this manuscript was prepared, we learned that the ordering discussed by us has recently been observed in simulations by den Hertog *et al.*<sup>12</sup>

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