Finite-Temperature Transitions in Dipolar Spin Ice in a Large Magnetic Field

Jacob P. C. Ruff,[1] Roger G. Melko,[2] and Michel J. P. Gingras[3]
[1]*Department of Physics, University of Waterloo, Ontario, Canada N2L 3G1*
[2]*Department of Physics, University of California, Santa Barbara, California 93106, USA*
[3]*Canadian Institute for Advanced Research, 180 Dundas Street West, Toronto, Ontario, Canada M5G 1Z8*
(Received 7 October 2004; published 23 August 2005)

We use Monte Carlo simulations to identify the mechanism that allows for phase transitions in dipolar spin ice to occur and survive for an applied magnetic field **H** much larger in strength than that of the spin-spin interactions. In the most generic and highest symmetry case, the spins on one out of four sublattices of the pyrochlore decouple from the total local exchange + dipolar + applied field. In the special case where **H** is aligned perfectly along the [110] crystallographic direction, spin chains perpendicular to **H** show a transition to $\mathbf{q} = X$ long-range order, which proceeds via a one- to three-dimensional crossover. We propose that these transitions are relevant to the origin of specific heat features observed in powder samples of the $Dy_2Ti_2O_7$ spin ice material for **H** above 1 Tesla.

DOI: 10.1103/PhysRevLett.95.097202 PACS numbers: 75.10.Hk, 05.50.+q, 75.30.Kz, 75.40.Mg

In 1997, Harris *et al.* found the surprising experimental result that, despite overall ferromagnetic interactions of approximately 2 K in strength, the $Ho_2Ti_2O_7$ magnetic pyrochlore material fails to order down to a temperature of 50 mK [1]. In $Ho_2Ti_2O_7$ the Ho^{3+} magnetic moments reside on a lattice of corner-shared tetrahedra (Fig. 1). It was argued that the strong local Ising anisotropy forcing the Ho^{3+} moments to point along the local $\langle 111 \rangle$ cubic directions frustrates the ferromagnetic interactions [1,2]. The number of ground states in this frustrated Ising system is macroscopic, giving a residual zero-temperature entropy close to that estimated by Pauling for the proton disordered state in common hexagonal water ice I_h [3]; hence the name *spin ice* [1,4]. Specific heat measurements on $Dy_2Ti_2O_7$ [5], another Ising pyrochlore material, and $Ho_2Ti_2O_7$ [6,7] have provided strong evidence that the low temperature state of these systems indeed possess an entropy close to that found by Pauling for water ice.

For water I_h, applied hydrostatic pressure introduces constraints that lift the proton degeneracy, giving a rich pressure-temperature phase diagram and a multitude of crystalline ice phases [8]. This leads naturally to the question of how to introduce constraints in magnetic spin ice and to search for analogous ordering behavior. Harris *et al.* [1], and Ramirez *et al.* [5] first explored this question by investigating the behavior of $Ho_2Ti_2O_7$ [1] and $Dy_2Ti_2O_7$ [5] under applied magnetic fields. In particular, specific heat measurements on powder samples of $Dy_2Ti_2O_7$ revealed three prominent features [5]. For a field **H** larger than 1 Tesla (T), a sharp peak suggesting a phase transition occurs at a field-independent temperature of 0.35 K, surviving up to the largest field considered (6 T). Another rounded peak at 1.2 K first appears at 0.75 T and also remains observable up to 6 T, although it is less sharp than the 0.35 K feature. Finally, a third peak at 0.5 K first appears at 1 T, where it is quite sharp, but disappears for $\mathbf{H} \gtrsim 3$ T. Over the past six years, much theoretical effort has been devoted to the search for a microscopic explanation of the field-induced spin correlations responsible for these specific heat features in powder samples of $Dy_2Ti_2O_7$ [5].

Building on the work of Harris *et al.* on the effect of a [110] field (see Fig. 1) on $Ho_2Ti_2O_7$ [1], Ramirez *et al.* suggested that some of these features might be due to phase transitions arising in crystallites that accidentally happen to be oriented such that some of the Ising spins in the unit cell are perpendicular to **H**. These "field-decoupled" spins would then be free to interact among themselves, giving transitions at temperatures that are field independent up to a very large field [5]. A similar proposal had been made earlier for the case of garnet systems [9]. Experimental evidence [10] suggests that the 0.5 K feature in powder samples arises due to a multicritical point at a temperature of 0.5 K and field of 1 T along the [111] crystallographic direction, which is related to the interesting phenomenology of kagomé ice [11]. However, to date, there is no

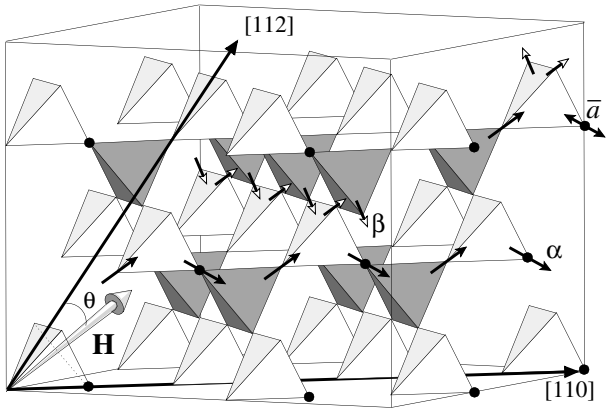

FIG. 1. Portion of the pyrochlore lattice, with the [110] and [112] cubic crystallographic axes. The double headed arrow shows a $[\bar{1}\,\bar{1}\,1]$ spin on a site of the $\bar{a}$ sublattice that is decoupled from the shown **H** (solid arrow). Sites on the $\bar{a}$ fcc sublattice (solid black circles) are shown.

consensus as to whether or not the specific heat features at 0.35 and 1.2 K are caused by the magnetic field directed on crystallites of particular orientation [12–14]. In this Letter we address this question by using the *dipolar spin ice model,* where Ising spins on the pyrochlore lattice interact via nearest-neighbor exchange and long-range magnetic dipole-dipole interactions [15]. We find a generic scenario for field-induced phase transitions that survive even when the field is much larger than the combined exchange and dipolar interactions.

It is now well established that the nearest-neighbor exchange in $Ho_2Ti_2O_7$ [6] and $Dy_2Ti_2O_7$ [15–17] is antiferromagnetic and that the spin ice phenomenon originates from long-range magnetic dipole-dipole interactions rather than from nearest-neighbor ferromagnetic exchange as originally proposed [1,2]. The magnetic moment, $\mu_{\rm eff}$, of Ho^{3+} and Dy^{3+} in the above materials is $\mu_{\rm eff} \sim 10\mu_B$, giving a dipolar coupling constant, D, at a nearest-neighbor distance of approximately 1.4 K [6,15]. The pyrochlore lattice is a non-Bravais lattice with four atoms per unit cell (e.g., a white tetrahedron in Fig. 1) with each sublattice making a regular fcc lattice. The dipolar spin ice model Hamiltonian is [15]

$$\mathcal{H} = -\mu_{\rm eff}\sum_{i,a}\mathbf{S}_i^a\cdot\mathbf{H} - \sum_{\langle(i,a),(j,b)\rangle} J_{i,a;j,b}\mathbf{S}_i^a\cdot\mathbf{S}_j^b + Dr_{\rm nn}^3\sum_{\substack{i>j\\a,b}}\frac{\mathbf{S}_i^a\cdot\mathbf{S}_j^b}{|\mathbf{R}_{ij}^{ab}|^3} - \frac{3(\mathbf{S}_i^a\cdot\mathbf{R}_{ij}^{ab})(\mathbf{S}_j^b\cdot\mathbf{R}_{ij}^{ab})}{|\mathbf{R}_{ij}^{ab}|^5}. \quad (1)$$

The first term is the Zeeman interaction between the spins and the magnetic field $\mathbf{H}$. The second and third terms are the exchange and long-range dipolar interactions, respectively. The spin vector $\mathbf{S}_i^a = \sigma_i^a\hat{z}^a$ at $\mathbf{R}_i^a = \mathbf{R}_i + \mathbf{r}^a$ labels the Ising moment of magnitude $|\mathbf{S}_i^a| = 1$ at fcc unit cell coordinate site $\mathbf{R}_i$ and tetrahedral sublattice site coordinate $\mathbf{r}^a$ $(a = 1, 2, 3, 4)$, where the local $\langle 111\rangle$ Ising axis is denoted by $\hat{z}^a$ and the Ising variable is $\sigma_i^a = \pm 1$. The vector $\mathbf{R}_{ij}^{ab} = \mathbf{R}_i^b - \mathbf{R}_i^a$ connects spins $\mathbf{S}_i^a$ and $\mathbf{S}_j^b$. If one restricts exchange coupling to nearest-neighbor spins, $J_{i,a;j,b} \equiv J_1$ represents the exchange energy and D the dipolar energy scale. $J_{i,a;j,b} > 0$ is ferromagnetic, $J_{i,a;j,b} < 0$ is antiferromagnetic ($J_1 > 0$ and $D = 0$ in the nearest-neighbor spin ice model [1,2]). Previous comparison between Monte Carlo (MC) simulations of $\mathcal{H}$ with experimental specific heat data found $J_1 \approx -3.72$ K for $Dy_2Ti_2O_7$ [15] and $J_1 \approx -1.65$ K for $Ho_2Ti_2O_7$ [6], with $D \approx 1.41$ K for both materials. In addition, we assume strictly classical spins and neglect quantum fluctuations induced by the applied transverse field, which admix the excited crystal field states with the ground state doublet. This is a reasonable approximation for fields smaller than 10 T, since the energy gap to the lowest excited states is $\sim$300 K in $Dy_2Ti_2O_7$ [18].

Consider first the problem of spins in the dipolar spin ice model, subject to an external magnetic field $\mathbf{H}$, from the perspective of symmetry. For $\mathbf{H} \neq 0$, the simplest scenario for a phase transition arises when one of the four fcc sublattices, call it $\bar{a}$ (see Fig. 1), is decoupled from $\mathbf{H}$. In other words, the field is perpendicular to the Ising quantization direction $\hat{z}^{\bar{a}}$ such that $\mathbf{H}\cdot\hat{z}^{\bar{a}} = 0$. With the condition $\mathbf{H}\cdot\hat{z}^{\bar{a}} = 0$, there exists one completely free rotational degree of freedom in the orientation of the crystal with respect to $\mathbf{H}$, which allows all spins belonging to the $\bar{a}$ sublattice to interact among themselves and participate in a phase transition. One obvious field orientation that satisfies this condition is the [112] direction, first investigated in Ref. [19]. Measurements on a single crystal of $Dy_2Ti_2O_7$ with $\mathbf{H}$ aligned along the [112] direction revealed two broad specific heat peaks and no sign of a phase transition [19]. For $\mathbf{H}$ larger than 0.5 T or so, an anomaly develops at $T_{112}^{\rm low} \sim 1.7$ K, independent of field strength, while a higher temperature anomaly occurs at $T_{112}^{\rm high} \propto |\mathbf{H}|$. We confirmed the results of Higashinaka *et al.* via Monte Carlo simulations on the spin ice model for $Dy_2Ti_2O_7$. In particular, using the above J_1 and D values for $Dy_2Ti_2O_7$, we find that for an infinite [112] field a broad Schottky-like specific heat anomaly occurs at $\sim$1.7 K, with no sign of a sharp phase transition.

We now explain the results in Ref. [19]. In the limit of strong [112] field, the spins on the three $a \neq \bar{a}$ sublattices that have a spin component parallel to the field are pinned by $\mathbf{H}$ at low temperatures in a ''one-in'' and ''two-out'' spin configuration (see top right tetrahedron in Fig. 1). Because of the dipolar and exchange interactions, the spins on the $a \neq \bar{a}$ sublattices produce an *internal* local microscopic field, $\mathbf{H}_{\bar{1}\,\bar{1}\,1}^{\rm mic}$, that enforces the two-in-two-out ''spin ice rule'' [4] acting on the spins at sublattice $\bar{a}$, hence forcing them to point ''in.'' A simple estimate gives the (internal) Zeeman energy scale to be $\mathrm{H}_{\bar{1}\,\bar{1}\,1}^{\rm mic} = 2(5D + J_1)/3 \sim 2.22$ K at nearest-neighbor distance, modified to 1.71 K using the Ewald method to sum dipolar contributions [12]. In other words, the candidate would-be field-decoupled $\hat{z}^{\bar{a}} = [\bar{1}\,\bar{1}\,1]$ spins, while experiencing zero applied external field $\mathbf{H}$, are subject to an inward internal microscopic field of magnitude $\mathrm{H}_{\bar{1}\,\bar{1}\,1}^{\rm mic} = (1.71\ \mathrm{K})/(7.09\ \mathrm{KT}^{-1}) = 0.24$ T parallel to $[\bar{1}\,\bar{1}\,1]$.

Such a large $\mathrm{H}_{\bar{1}\,\bar{1}\,1}^{\rm mic} \sim 1.7$ K precludes a phase transition at $T \ll \mathrm{H}_{\bar{1}\,\bar{1}\,1}^{\rm mic}$. However, a scenario for a low temperature phase transition can be reintroduced. Take the *external* applied field $\mathbf{H}$ canted away from perfect alignment perpendicular to $\hat{z}^{\bar{a}} = [\bar{1}\,\bar{1}\,1]$ (see Fig. 1, $\mathbf{H}$ arrow), towards the inside of the tetrahedron (i.e., towards the [110] direction), at an angle θ such that $\theta(|\mathbf{H}|) \approx \mathrm{H}_{\bar{1}\,\bar{1}\,1}^{\rm mic}/|\mathbf{H}|$ in the limit of large applied field strength. For this orientation of $\mathbf{H}$, the net local (internal + external) field acting on the $\bar{a}$ sublattice geometrically vanishes, so that the spins on $\bar{a}$ become (free) paramagnetic species. Spins on this $\bar{a}$ fcc sublattice are actually third nearest neighbors on the pyrochlore structure (see Fig. 1), and therefore predominantly interact among themselves via long-range dipolar interac-

tions (assuming momentarily zero third nearest-neighbor exchange J_3). Interestingly, this field-decoupling scheme freezes out (decimates) spins on the three $a \neq \bar{a}$ sublattices at large field, and consequently generates a very rare physical realization of an fcc Ising (dipolar) magnet [20].

We now determine the ground state for the spins on the $\bar{a}$ sublattice. First, recall that dipolar-coupled three-component (Heisenberg) spins have a ferromagnetic ground state on the fcc lattice, with an energy that is independent of the magnetization direction (as for all cubic lattices) [21]. Consequently, with the field-decoupled $\bar{a}$ spins above residing on an fcc sublattice with Ising direction, $\hat{z}^{\bar{a}} = [\bar{1}\,\bar{1}\,1]$, we expect a phase transition to a ferromagnetic ground state, with the bulk magnetization along $\pm[\bar{1}\,\bar{1}\,1]$. Results from Monte Carlo simulations considering only spins on the $\bar{a}$ fcc sublattice, shown in Fig. 2, confirm that the ordered state is, indeed, ferromagnetic below 0.65 K. The inset of Fig. 2 shows the results of simulations on the full pyrochlore lattice, with external fields ranging from 0.5 to 1.5 T and misaligned from [112] with an angle $\theta(|\mathbf{H}|)$, so as to give the geometrical cancellation above. There is no discernible difference between the results above 1.5 T and the results obtained when considering only the $\bar{a}$ sublattice (labeled "Inf."), confirming the simple geometric arguments above.

The transition we observe is at $\sim$0.65 K, not 0.35 K as found in powder specific heat measurements [5]. However, adding a very small antiferromagnetic third nearest-neighbor exchange $J_3 = -0.022$ K gives a transition to a ferromagnetic ground state at a temperature close to the experimental value of 0.35 K. Interestingly, an antiferromagnetic J_3 of this magnitude ($-0.03 < J_3 < -0.01$ K) appears able to explain the paramagnetic zone boundary

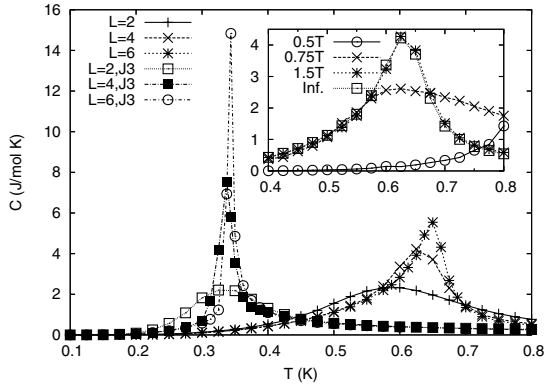

FIG. 2. Specific heat from MC simulations with only the ($\bar{a}$) fcc sublattice occupied by spins. The values $J = -3.72$ K and $D = 1.41$ K appropriate for $Dy_2Ti_2O_7$ yield a transition at 0.65 K. Adding a small $J_3 = -0.022$ K shifts this transition to a temperature that agrees with experiments (see text). L is the linear size of the system, the total number of spins in a pyrochlore lattice is $N = 16L^3$. Inset: Simulations of the full pyrochlore lattice with $\mathbf{H}(\theta)$ (see text). The system behaves like the $\bar{a}$ fcc lattice in the limit of large (Inf.) field.

scattering observed in neutron scattering of $Dy_2Ti_2O_7$ [17]. A more antiferromagnetic (negative) J_3 changes the ordered state to a Néel state with ordering wave vector $\mathbf{q} = (1/2, 1/2, 0)$. The present discussion suggests that measurements on a well oriented single crystal could allow for a precise determination of a very small J_3 value. A subsequent analysis of either dc susceptibility [16], specific heat [15], or elastic neutron scattering [17] could then help determine the full set of exchange parameters $J_1 - J_2 - J_3$ in spin ice materials.

The above calculation of $H^{\text{mic}}_{\bar{1}\,\bar{1}\,1}$ assumed static spins on the three $a \neq \bar{a}$ sublattices, and neglected thermal fluctuations. Conversely, the applied "compensating" field parallel to $[11\bar{1}]$ from the canted $H(\theta)$ is static. Hence, for any finite large [112] external field plus weak $[11\bar{1}]$ compensating field of approximately 0.24 T, there is at nonzero temperature a net "overcompensating" outward field along $[11\bar{1}]$ due to the thermal fluctuation (spin flips) of spins on the three $a \neq \bar{a}$ sublattices. The global $\langle 111 \rangle$ Ising symmetry is therefore always explicitly broken. The $\theta - \mathbf{H}$ relationship above is akin to the first order ($\mathbf{H} = 0, T < T_c$) transition line in a conventional Ising ferromagnet. By correcting the angle $\theta(|\mathbf{H}|)$, evaluated above for $T = 0$, to the one that would cancel the average $H^{\text{mic}}_{\bar{1}\,\bar{1}\,1}$ at $T = T_c$, a true spontaneous symmetry breaking can then occur at T_c. For $J_3 < -0.03$, the overcompensating field is not conjugate to the Néel order parameter and the transition is thermodynamically sharp for large applied $\mathbf{H}$ perpendicular to [111].

We now turn to the special case in which a second sublattice becomes accidentally field decoupled as the field is rotated in the plane perpendicular to one of the four $\hat{z}^{\bar{a}}$ directions. This occurs for $\mathbf{H}$ along the [110] and related crystallographic directions [1,5,12–14,22]. As illustrated in Fig. 1, the [110] field direction couples to the Ising spins on two fcc sublattices (forming the α chains), but leaves spins on the two fcc sublattices forming the β chains fully decoupled. Unlike the generic case above with only one ($\bar{a}$) decoupled sublattice, the net local internal field from static spins on the α chains vanishes on lattice sites that belong to β chains. Although the spins on the β chains are then in principle free to undergo an ordering transition via some long-range exchange or dipolar interaction, experimental [1,13,22] and numerical [13,14] evidence for this transition has so far been elusive. Our Monte Carlo simulation results on the dipolar spin ice model show strong evidence for a transition to the so-called $\mathbf{q} = X$ state [1] for $\mathbf{H}$ parallel to [110], where ferromagnetic one-dimensional (1D) β chains along [110] orient antiferromagnetically with respect to their four nearest-neighbor chains (see Fig. 3). This is found by studying both the $\mathbf{q} = X$ order parameter [12] and relative zero-temperature energies of the various competing spin ice ground states [12,14]. A transition to $\mathbf{q} = X$ occurs for all fields greater than $\sim$0.02 T, although for weak fields ($\mathbf{H} < 0.10$ T) nonlocal loop spin flips are

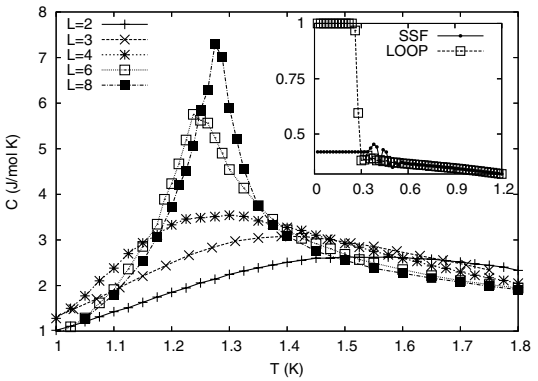

FIG. 3. Specific heat from MC simulations of β chains, equivalent to the limit large of [110] $\mathbf{H}$ applied to a single crystal of $Dy_2Ti_2O_7$. The inset shows the $\mathbf{q} = X$ order parameter obtained via loop Monte Carlo simulations ("LOOP," open squares) [12,23] for a [110] field of 0.05 T and compared with conventional Monte Carlo results using single spin flip (SSF, filled circle).

needed in the simulation to find the ground state [12,23]. For fields weaker than 0.02 T, the transition is to the $\mathbf{q} = (0, 0, 1)$ long-range ordered state found by Melko *et al.* [12,23]. The critical temperature $T_c^{110}(|\mathbf{H}_{110}|)$ for the $\mathbf{q} = X$ ordering is strongly field dependent for field strengths between 0.02 and 0.2 T [12,14], but saturates at a critical temperature of $T_c^{110}(\infty) \sim 1.2$ K for $\mathbf{H} > 0.2$ T, as also recently found in Ref. [14], but contrary to what was obtained in Ref. [13]. For large $\mathbf{H}$ along [110] the transition to $\mathbf{q} = X$ proceeds via a 1D to 3D crossover with a correlation length ξ_{1D} of approximately 20 nearest-neighbor lattice spacing at the crossover temperature. This crossover at such a large ξ_{1D} makes the study of finite-size scaling and 3D critical behavior very demanding at this transition. The presence of dilute defects or impurities or the lack of perfect alignment [12] of $\mathbf{H}$ along the [110] direction might be at play in preventing the development of perfect $\mathbf{q} = X$ long-range order in experiments [1,13,22]. Finally, we note that introducing $J_3 = -0.022$ K in Eq. (1) results in a shift of $T_c^{110}(\infty)$ to $T_c^{110}(\infty) \sim 1.6$ K, in disagreement with the position of the specific heat feature at 1.2 K [5,13]. Such a large shift of T_c^{110} is consistent with the T_c^{110} calculated using a 1D chain mean-field theory. Overall, the results presented in this Letter suggest that there might be important competition between J_1, J_2, and J_3 exchange in $Dy_2Ti_2O_7$, and that the original description of $Dy_2Ti_2O_7$ using only a nearest-neighbor exchange $J_1 = -3.72$ K [15,17] should be revisited.

In conclusion, we have identified a mechanism that causes field-independent phase transitions in the dipolar spin ice model when subject to a large external applied field. For polycrystalline $Dy_2Ti_2O_7$, we suggest that the transition at $T_c^{[112]} \approx 0.35$ K can arise from crystallites for which the field is accidentally quasiperpendicular to one of the $\langle 111 \rangle$ directions, but slightly canted towards the corresponding $\langle 11\bar{1} \rangle$ direction to cancel internal exchange plus dipolar local field. This proposed mechanism could be verified in a single crystal experiment. We also postulate a small third neighbor antiferromagnetic exchange to account for the precise $T_c^{[112]}$. In addition, we found unequivocal support for the existence of a transition to a long-range ordered $\mathbf{q} = X$ state for dipolar spin ice in a magnetic field along [110] in excess of 0.02 T, which is postulated to account for the $T_c^{[110]} \approx 1.2$ K transition in polycrystalline $Dy_2Ti_2O_7$. As an interesting by-product of this work, we have identified a novel realization of an Ising fcc dipolar ferromagnet.

We thank S. Bramwell, J. Chalker, M. Enjalran, T. Fennell, Y. Maeno, R. Higashinaka, and T. Yavorsk'ii for useful discussions. R. M. acknowledges financial support from the National Science Foundation, Grant No. DMR02-11166. M. G. acknowledges support from the NSERC of Canada, the Canada Research Chair Program, Research Corporation, and the Province of Ontario.

[1] M. J. Harris *et al.*, Phys. Rev. Lett. **79**, 2554 (1997).
[2] S. T. Bramwell and M. J. Harris, J. Phys. Condens. Matter **10**, L215 (1998).
[3] L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).
[4] S. T. Bramwell and M. J. P. Gingras, Science **294**, 1495 (2001).
[5] A. P. Ramirez *et al.*, Nature (London) **399**, 333 (1999).
[6] S. T. Bramwell *et al.*, Phys. Rev. Lett. **87**, 047205 (2001).
[7] A. L. Cornelius and J. S. Gardner, Phys. Rev. B **64**, 060406 (2001).
[8] R. F. Whitworth and V. F. Petrenko, *Physics of Ice* (Oxford University Press, New York, 1999).
[9] D. P. Landau and B. E. Keen, Phys. Rev. B **19**, 4805 (1979).
[10] R. Higashinaka *et al.*, J. Phys. Soc. Jpn. **73**, 2845 (2004).
[11] S. V. Isakov *et al.*, Phys. Rev. B **70**, 104418 (2004).
[12] R. G. Melko and M. J. P. Gingras, J. Phys. Condens. Matter **16**, R1277 (2004).
[13] Z. Hiroi *et al.*, J. Phys. Soc. Jpn. **72**, 3045 (2003).
[14] S.-I. Yoshida *et al.*, J. Phys. Soc. Jpn. **73**, 1619 (2004).
[15] B. C. den Hertog and M. J. P. Gingras, Phys. Rev. Lett. **84**, 3430 (2000).
[16] H. Fukazawa *et al.*, Phys. Rev. B **65**, 054410 (2002).
[17] T. Fennell *et al.*, Phys. Rev. B **70**, 134408 (2004).
[18] S. Rosenkranz *et al.*, J. Appl. Phys. **87**, 5914 (2000).
[19] R. Higashinaka *et al.*, Phys. Rev. B **68**, 014415 (2003).
[20] For another example of an fcc Ising dipolar magnet, see M. R. Roser and L. R. Corruccini, Phys. Rev. Lett. **65**, 1064 (1990).
[21] R. Becker, Z. Phys. **62**, 253 (1930); J. R. Tessman, Phys. Rev. **96**, 1192 (1954).
[22] T. Fennell *et al.*, cond-mat/0503160.
[23] R. G. Melko *et al.*, Phys. Rev. Lett. **87**, 067203 (2001).