Finite Temperature Transitions in Large Magnetic Field in Dipolar Spin Ice

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We use Monte Carlo simulations to identify the mechanism that allows for phase transitions in dipolar spin ice to occur and survive for 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 \( q = X \) 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 Dy2Ti2O7 spin ice material for \( H \) above 1 Tesla.

In 1997, Harris et al. found the surprising experimental result that, despite overall ferromagnetic interactions of approximately 2 K in strength, the Ho2Ti2O7 magnetic pyrochlore material fails to order down to a temperature of 50 mK \(^1\). In Ho2Ti2O7 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 (111) cubic directions frustrates the ferromagnetic interactions \(^2\). 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 \(^4\). Specific heat measurements on Dy2Ti2O7 \(^5\), another Ising pyrochlore material, and Ho2Ti2O7 \(^5\) \(^6\) \(^7\) 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. \(^9\), and Ramirez et al. \(^10\) first explored this question by investigating the behavior of Ho2Ti2O7 \(^11\) and Dy2Ti2O7 \(^12\) under applied magnetic fields. In particular, specific heat measurements on powder samples of Dy2Ti2O7 revealed three prominent features \(^13\). 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 \( H \gtrsim 3 \) 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 Dy2Ti2O7 \(^14\).

Building on the work of Harris et al. on the effect of a [110] field (see Fig.\(^1\) on Ho2Ti2O7 \(^11\), Ramirez et al. suggested that some of these features might be due to phase transitions arising in crystallites that 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 \(^15\). A similar proposal had been made earlier for the case of garnet systems \(^16\). Experimental evidence \(^17\) 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 \(^18\). However, to date, there is no consensus as to whether or not the specific heat features at 0.35 K and 1.2 K are caused by the magnetic field directed on crystallites of particular orientation \(^19\). In this paper 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. We find a generic scenario for field-induced phase transitions which 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$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ 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. The magnetic moment, $\mu_{\text{eff}}$, of Ho$^{3+}$ and Dy$^{3+}$ in the above materials is $\mu_{\text{eff}} \sim 10\mu_B$, giving a dipolar coupling constant, $D$, at nearest-neighbor distance of approximately 1.4 K.

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:

$$H = -\mu_{\text{eff}} \sum_{i,a} S_i^a \cdot H - \sum_{\langle i,a \rangle, \langle j,b \rangle} J_{i,a,j,b} S_i^a \cdot S_j^b$$

$$+ D r_{ij}^3 \sum_{i \neq j} \frac{S_i^a \cdot S_j^b}{|R_{ij}^a|^3} \left(3(S_i^a \cdot R_{ij}^a)(S_j^b \cdot R_{ij}^b) - \frac{1}{|R_{ij}^a|^3} \frac{1}{|R_{ij}^b|^3}\right).$$

The first term is the Zeeman interaction between the spins and the magnetic field $H$. The second and third terms are the exchange and long-range dipolar interactions, respectively. The spin vector $S_i^a = \sigma_i^a \hat{z}$ at $R_i^a = R_i + r^a$ labels the Ising moment of magnitude $|S_i^a| = 1$ at FCC unit cell coordinate site $R_i$ and tetrahedral sub-lattice site coordinate $r^a$ ($a = 1, 2, 3, 4$), where the local $< 111 >$ Ising axis is denoted by $\hat{z}$ and the Ising variable is $\sigma_i^a = \pm 1$. The vector $R_{ij}^a = R_i - R_j$ connects spins $S_i^a$ and $S_j^b$. 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).

Previous comparison between Monte Carlo simulations of $H$ with experimental specific heat data has found that $J_1 \approx -3.72$ K for Dy$_2$Ti$_2$O$_7$ and $J_1 \approx -1.65$ K for Ho$_2$Ti$_2$O$_7$, 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$_2$Ti$_2$O$_7$.

Consider first the problem of spins in the dipolar spin ice model, subject to an external magnetic field $H$, from the perspective of symmetry. For $H \neq 0$, 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 $H$. In other words, the field is perpendicular to the Ising quantization direction $\hat{z}$ such that $H \cdot \hat{z} = 0$.

With the condition $H \cdot \hat{z} = 0$, there exists one completely free rotational degree of freedom in the orientation of the crystal with respect to $H$, 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. [5]. Measurements on a single crystal of Dy$_2$Ti$_2$O$_7$ with $H$ aligned along the $[112]$ direction revealed two broad specific heat peaks and no sign of a phase transition.

For $H$ larger than 0.5 T or so, an anomaly develops at $T_{\text{oni}} \sim 1.7$ K, independent of field strength, while a higher temperature anomaly occurs at $T_{\text{oni}} \sim 7$ K, independent of field strength. We now explain the results in Ref. [5]. 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 $H$ 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, $H_{\text{mic}}^{[111]}$, that enforces the two-in–two-out “spin ice rule” acting on the spins at sublattice $a$, hence forcing them to point “in”. A simple estimate gives the (internal) Zeeman energy scale to be $H_{\text{mic}}^{[111]} = 2(5D + J_1)/3 \approx 2.22$ 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 \( z^a = [111] \) spins, while experiencing zero applied external field \( H \), are subject to an inward internal microscopic field of magnitude \( H_{111}^{\text{mic}} = (1.71 \text{ K})/(7.09 \text{ KT}^{-1}) = 0.24 \text{ T} \) parallel to [111].

Such a large \( H_{111}^{\text{mic}} \sim 1.7 \text{ K} \) precludes a phase transition at \( T \ll H_{111}^{\text{mic}} \). However, a scenario for a low temperature phase transition can be reintroduced. Take the external applied field \( H \) cantled away from perfect alignment perpendicular to \( z^a = [111] \) (see Fig. 1, \( H \) arrow), towards the inside of the tetrahedron (i.e. towards the [110] direction), at an angle \( \theta \) such that \( \theta(H) \approx H_{111}^{\text{mic}}/|H| \) in the limit of large applied field strength. For this orientation of \( H \), the net local (internal + external) field acting on the \( a \) sublattice geometrically vanishes, so that the spins on \( a \) become (free) paramagnetic species. Spins on this \( a \) FCC sublattice are actually third nearest-neighbors on the pyrochlore structure (see Fig. 1), and therefore predominantly interact among themselves via long-range dipolar interactions (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, \( z^a = [111] \), we expect a phase transition to a ferromagnetic ground state, with the bulk magnetization along \( \pm [111] \). 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 T to 1.5 T and misaligned from [112] with an angle \( \theta(H) \), so as to give the geometric cancellation above. There is no discernable difference between the results above 1.5 T and the results obtained when considering only the \( \bar{a} \) sublattice (labelled “Inf.”), confirming the simple geometric arguments above.

The transition we observe is at \( \sim 0.65 \text{ K} \), not 0.35 K as found in powder specific heat measurements \[5\]. However, adding a very small antiferromagnetic third nearest-neighbor exchange \( J_3 = -0.022 \text{ K} \) 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 \((-0.03 \text{ K} < J_3 < -0.01 \text{ K})\) appears able to explain the paramagnetic zone boundary scattering observed in neutron scattering of Dy\(_2\)Ti\(_2\)O\(_7\) \[17\]. A more antiferromagnetic (negative) \( J_3 \) changes the ordered state to a Néel state with ordering wavevector \( q = (1/2, 1/2, 0) \). 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 \[10\], 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 \( H_{111}^{\text{mic}} \) assumed static spins on the three \( a \neq \bar{a} \) sublattices, and neglected thermal fluctuations. Conversely, the applied “compensating” field parallel to [111] from the canted \( H(\theta) \) is static. Hence, for any finite large [112] external field plus weak [111] compensating field of approximately 0.24 T, there is at nonzero temperature a net “overcompensating” outward field along [111] due to the thermal fluctuation (spin flips) of spins on the three \( a \neq \bar{a} \) sublattices. The global (111) Ising symmetry is therefore always explicitly broken. The \( \theta - H \) relationship above is akin to the first order \( H = 0, T < T_c \) transition line in a conventional Ising ferromagnet. By correcting the angle \( \theta(H) \), evaluated above for \( T = 0 \), to the one that would cancel the average \( H_{111}^{\text{mic}} \) 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 \( H \) 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 \( z^a \) directions. This occurs for \( H \) along the [110] and related crystallographic directions \[1, 5, 12, 13, 14, 22\]. As illustrated in Fig. 1, the [110] field direction couples to the Ising spins on two FCC sublattices (forming the \( \alpha \) chains), but leaves spins on the two FCC sublattices...
forming the $\beta$ 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 $\alpha$ chains vanishes on lattice sites that belong to $\beta$ chains. Although the spins on the $\beta$ chains are then in principle free to undergo an ordering transition via some long range exchange or dipolar interaction, experimental \cite{5, 13, 22} and numerical \cite{12, 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 $q = X$ state \cite{1} for $H$ parallel to [110], where ferromagnetic one-dimensional (1D) $\beta$ chains along [110] orient antiferromagnetically with respect to their four nearest neighbour chains (see Fig. \ref{fig:multi}). This is found by studying both the $q = X$ order parameter \cite{12} and relative zero-temperature energies of the various competing spin ice ground states \cite{12, 14}. A transition to $q = X$ occurs for all fields greater than $\sim 0.02$ T, although for weak fields ($H < 0.10$ T) non-local loop spin flips are needed in the model to find the ground state. \cite{22}. For fields weaker than 0.02 T, the transition is to the $q = (0, 0, 1)$ long-range-ordered state found by Melko et al. \cite{12, 22}. The critical temperature $T_c^{110}(|H_{110}|)$ for the $q = X$ ordering is strongly field dependent for field strengths between 0.02 T and 0.2 T \cite{12, 14}, but saturates at a critical temperature of $T_c^{110}(\infty) \sim 1.2$ K for $H > 0.2$ T, as also recently found in Ref. \cite{14}, but contrary to what was obtained in Ref. \cite{13}. For large $H$ along [110] the transition to $q = X$ proceeds via a 1D to 3D crossover with a correlation length $\xi_{1D}$ of approximately 20 nearest-neighbor lattice spacing at the crossover temperature. This crossover at such a large $\xi_{1D}$ 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 \cite{12} of $H$ along the [110] direction might be at play in preventing the development of perfect $q = X$ long range order in experiments \cite{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 \cite{12, 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 paper suggest that there might be important competition between $J_1$, $J_2$ and $J_3$ exchange in Dy$_2$Ti$_2$O$_7$, and that the original description of Dy$_2$Ti$_2$O$_7$ using only a nearest-neighbor exchange $J_1 = −3.72$ K \cite{13, 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$_2$Ti$_2$O$_7$, we suggest that the transition at $T_c^{[112]} \approx 0.35$ K can arise from crystallites for which the field is accidentally quasi-perpendicular to one of the $\{111\}$ directions, but slightly tilted towards the corresponding $\{111\}$ 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 $q = X$ 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$_2$Ti$_2$O$_7$. As an interesting by-product of this work, we have identified a novel realization of an Ising FCC dipolar ferromagnet.

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