What is the quantum ground state of dipolar spin ice?

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Recent experiments on the spin ice Dy2Ti2O7, suggest that the Pauling “ice entropy”, characteristic of its Coulombic spin-liquid state, may be lost at low temperatures [D. Pomaranski et al., Nature Phys. 9, 353 (2013)]. However, despite nearly two decades of intensive study, the nature of the equilibrium ground state of spin-ice remains uncertain. Here we explore how long-range dipolar interactions D, short-range exchange interactions and quantum fluctuations combine to determine the ground state of dipolar spin ice. We find that ordered ground states are selected from a set of “chain states” in which dipolar interactions are exponentially screened. Using both quantum and classical Monte Carlo simulation, we establish phase diagrams as a function of quantum tunneling g, and temperature T, and find that only a very small g \( g \ll D \) is needed to stabilize a quantum spin-liquid ground state. We discuss the implications of these results for Dy2Ti2O7, and for the “quantum spin ice” materials Yb2Ti2O7, Tb2Ti2O7 and Pr2Zr2O7.

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The search for materials which realize a spin-liquid state, in which magnetic moments interact strongly, and yet fail to order, has become something of a cause célèbre [1, 2]. A rare three-dimensional example of a spin liquid is provided by “spin-ice”, a family of rare-earth pyrochlore oxides exemplified by Ho2Ti2O7 and Dy2Ti2O7, which exhibit a “Coulombic” phase—a classical spin liquid, described by U(1) a lattice gauge theory, whose excitations famously take the form of magnetic monopoles [3, 4]. The fate of this spin liquid at low temperatures is an important question, touching on the limits of our understanding of phase transitions [5], and the tantalising possibility of finding a quantum spin-liquid in three dimensions. None the less, after nearly two decades of intensive study, the nature of the quantum ground state of spin-ice materials remains a mystery.

This question gains fresh urgency from recent experiments on the spin-ice Dy2Ti2O7 [6], which suggest that the Pauling ice entropy, associated with an extensive number of states obeying the “two-in, two-out” ice rules [7, 8], may be lost at the lowest temperatures. Such a loss of entropy could herald the onset of a long-range ordered state, in which magnetic monopoles would be confined. Alternatively, it could signal the emergence of a three-dimensional quantum spin-liquid, in which monopoles would remain deconfined. The theoretical possibility of such a spin-liquid is now well-established [12, 12, 17, 20], and has generated considerable excitement in the context of recent experiments on “quantum spin-ice” systems such as Yb2Ti2O7 [10, 18, 20], Tb2Ti2O7 [21, 22], and Pr2Zr2O7 [23]. However these ideas have yet to be tested in a realistic model of spin-ice. And even unravelling the nature of classical, ordered ground states in a spin ice with both short-range exchange [6] and long-range dipolar interactions [11, 5], remains a significant challenge.

In this article we address the simple question: “What is the equilibrium ground state of dipolar spin ice, once quantum effects are taken into account?”, using Dy2Ti2O7 as a concrete example. Starting from a realistic model which treats both short-range exchange and long-range dipolar interactions, we use quantum Monte Carlo simulation to show that even a small amount of tunneling between different spin-ice configurations can stabilize a three-dimensional quantum spin-liquid (QSL) ground state. Where the model does order, we find that ground states are composed of chains of alternating “in” and “out” spins. Determining the hierarchy of competing ordered states then reduces to solving an Ising model on a two-dimensional, anisotropic triangular lattice, with only weak, short-range interactions. We use this mapping to identify the possible ordered ground states for parameters appropriate to Dy2Ti2O7 [6]. We also provide estimates of the quantum tunneling needed to stabilize a quantum spin liquid in Dy2Ti2O7, and a range of other materials. Our central results are summarized in the phase diagrams Fig. 1 and Fig. 3, with illustrations of possible ordered ground states given in Fig. 2. Additional details of calculations are provided in the supplemental materials.

After almost twenty years of study, it is generally accepted that the finite-temperature properties of spin ice materials are well-described by an effective Ising model with both short-range exchange and long-range dipolar interactions—the so-called “dipolar spin ice” (DSI)
FIG. 1: (Color online). Quantum and classical phase diagrams for a spin ice with long-range dipolar interactions $D$, as a function of second-neighbor exchange $J_2$. Quantum tunneling $g$, and temperature $T$, drive quantum (QSL) and classical (CSL) spin-liquid phases. These compete with four ordered phases, illustrated in Fig. 2. Results are taken from quantum and classical Monte Carlo simulations of $H_{QDSI}$ [Eq. (1)], for a cubic cluster of 128 spins. Inset: Illustration of quantum tunneling $H_{tunneling}$ [Eq. (4)] between different spin-ice configurations.

FIG. 2: (Color online). Ordered ground states of $H_{QDSI}$ [Eq. (1)]: a cubic antiferromagnet (CAF), tetragonal double-Q state (TDQ), ferromagnet (FM) and an orthorhombic “zig-zag” (OZZ) state. All states obey the ice rules, and are composed of alternating chains of “in” and “out” spins.

model [1–6]. Here we consider a natural quantum generalization of the DSI model, in which the virtual excitation of magnetic monopoles generates tunneling from one spin-ice configuration to another [12–15]:

$$H_{QDSI} = H_{dipolar} + H_{exchange} + H_{tunneling}$$  \(1\)

where

$$H_{dipolar} = 4D \sum_{i<j} \left( \frac{r_1}{r_{ij}} \right)^3 [\hat{z}_i \cdot \hat{z}_j - 3 (\hat{z}_i \cdot \hat{r}_{ij}) (\hat{z}_j \cdot \hat{r}_{ij})] S_i^z S_j^z$$  \(2\)

$$H_{exchange} = \sum_k 4J_k \sum_{\langle ij \rangle_k} (\hat{z}_i \cdot \hat{z}_j) S_i^z S_j^z$$  \(3\)

$$H_{tunneling} = -g \sum_{\square} |\bigcirc \bigcirc \rangle \langle \bigcirc \bigcirc | + |\bigcirc \bigcirc \rangle \langle \bigcirc \bigcirc |$$  \(4\)

Here, $S_i^z = \pm 1/2$; $\hat{z}_i$ is a unit vector parallel to the local easy axis on site $i$; $r_1$ is the distance between neighboring magnetic ions; $k$ counts equivalent pairs of sites, and $\square$ denotes the hexagonal plaquettes where $H_{tunneling}$ [Eq. (4)] acts, as illustrated in the inset to Fig. 1. The definitions of dipolar interactions $D$ and exchange interactions $J_k$ follow the conventions of [3–6], with parameters chosen so as to favor a low-temperature spin-ice state. For the purpose of quantum simulations, $H_{QDSI}$ [Eq. (1)] is taken to act on the space of all possible spin-ice ground states.

The tendency of $H_{QDSI}$ [Eq. (1)] to support ordered, classical ground states can be explored using mean field theory, setting quantum tunneling $g = 0$. For a general choice of parameters, we find one of three competing states, illustrated in Fig. 2:

(i) CAF — a cubic antiferromagnetic phase, identified in [2, 5], as the ground state of $H_{dipolar}$ [Eq (2)]. This state is 12-fold degenerate, with the ordering vector $\mathbf{q} = (0, 0, 2\pi)$.

(ii) TDQ — a tetragonal, double-q state. This state is 48-fold degenerate, with the ordering vectors $\mathbf{q} = (0, \pi, \pi)$ and $\mathbf{q} = (0, -\pi, \pi)$.

(iii) FM — the spin-ice state with the maximum possible magnetization, directed along a [100] crystal axis. This state is 6-fold degenerate, with the ordering vector $\mathbf{q} = (0, 0, 0)$.

All three of these states show a common organizing principle — they are built of chains of alternating “in”
and “out” spins, running parallel to [110] and [1\(\overline{1}0\)] crystal axes, and marked with green and yellow lines in Fig. 2. It was noted by Anderson [24] that alternating chains of positive and negative charge are an effective route to minimizing Coulomb interactions on the pyrochlore lattice. The parameters estimated in [24] place \(\text{Dy}_2\text{Ti}_2\text{O}_7\) in the CAF phase. The range of parameters used for classical and quantum Monte Carlo simulations is shown as a blue line.

Each alternating chain can be regarded as an Ising degree of freedom \(\sigma = \pm 1\), with \(\sigma \rightarrow -\sigma\) corresponding to reversing the direction of all “in” and “out” spins along the chain. The interactions between parallel chains can therefore be mapped onto an extended Ising model

\[
\mathcal{H}_{\text{Ising}}^{2\text{D}} = \frac{1}{2} \sum_{\mathbf{r}, \delta} K_{\delta} \sigma_{\mathbf{r}} \sigma_{\mathbf{r} + \mathbf{\delta}}
\]

where \(\delta\) connect the sites of an anisotropic triangular lattice. The leading interchain couplings \(K_{\delta}\) are

\[
\begin{align*}
K_{(1,\sqrt{3})} &= -0.0227D - J_2/3 - J_{3c} - J_{3d} \\
K_{(2,0)} &= 0.0022D + J_{3d} \\
K_{(0,2\sqrt{3})} &= -0.0008D
\end{align*}
\]

where \(J_2\) denotes 2\(^{nd}\)-neighbour exchange, and \(J_{3c}\) and \(J_{3d}\) inequivalent 3\(^{rd}\)-neighbour interactions, as described in the supplemental materials. Solving for the ground state of \(\mathcal{H}_{\text{Ising}}^{2\text{D}}\) [Eq. (5)], we find the same three ordered states as in mean-field theory, separated by the lines \(K_{(2,0)} = K_{(1,\sqrt{3})}\), where many different states become degenerate [35]. The resulting phase diagram is shown in Fig. 3.

At finite temperature, the system can gain an extensive “ice entropy” by fluctuating between different spin-ice configurations [21, 29], and the ordered ground states will give way to a classical spin liquid (CSL). We have performed classical Monte Carlo simulations of \(\mathcal{H}_{\text{QDSI}}\) [Eq. (1)], for quantum tunneling \(g = 0\), and a range of values of \(J_2/D\) spanning the CAF, TDQ and FM phases (see Fig. 3), setting all other \(J_k = 0\) [45]. For pure dipolar interactions (\(J_2 = 0\)) we reproduce the results of Melko et al. [3], finding CAF order with \(T_c \approx 0.1D\). The introduction of ferromagnetic second-neighbor interactions \(J_2 < 0\) suppresses the leading interaction between chains of spins, stabilising the TDQ, and driving the transition temperature down to just a few percent of \(D\). Stronger ferromagnetic \(J_2\) stabilizes the FM state, where \(T_c\) rises sharply. Above the ordering temperature, \(T > T_c\), simulations confirm the existence of a classical spin-liquid (CSL) state, with pinch-points in \(S(q)\) [Fig. 4(a)] characteristic of the the dipolar, 1/\(r^3\), spin correlations observed in spin ice [26]. All transitions from the CSL into ordered ground states were found to be first-order.

Just as thermal fluctuations stabilize a CSL, so quantum tunneling between different spin-ice configurations might be expected to stabilize a QSL, of the type previously studied in [12, 12, 17, 20]. We have carried out extensive quantum Monte Carlo simulations of \(\mathcal{H}_{\text{QDSI}}\) for finite \(g\), using the zero-temperature Green’s function

![Phase diagram of the extended Ising model](image)

FIG. 3. Phase diagram of the extended Ising model \(\mathcal{H}_{\text{Ising}}^{2\text{D}}\) [Eq. (5)], as a function of the leading interchain interactions \(K_{(1,\sqrt{3})}\) and \(K_{(2,0)}\). In this model, each Ising spin \(\sigma\) corresponds to a chain of alternating “in” and “out” spins in the original pyrochlore lattice. The parameters estimated in [24] place \(\text{Dy}_2\text{Ti}_2\text{O}_7\) in the CAF phase. The range of parameters used for classical and quantum Monte Carlo simulations is shown as a blue line.
Monte Carlo method described in [14, 15, 29, 30]. Results, for the same range of $J_2/D$ as used in classical Monte Carlo simulations, are shown in Fig. 4. The quantum phase diagram is dominated by a QSL phase, with the critical value of quantum tunneling $g_c$ needed to stabilize a QSL at $T = 0$ closely tracking the transition temperature $T_c$ for $g = 0$. Crucially, $g_c$ is always very small, being of order $g_c \sim 0.1D$ for $J_2/D = 0$, and decreasing to a few percent of $D$ for $J_2/D \sim -0.07$. Spin correlations in the quantum spin-liquid decay as $1/r^4$ [12], eliminating the characteristic pinch-points in $S(q)$ [14, 15]; cf. Fig. 4(b). Once again, simulations point toward first-order transitions from the QSL into ordered ground states.

As well as yielding a robust quantum spin liquid, quantum tunneling $g$ stabilizes a new ordered phase, not found in classical Monte Carlo simulations. This orthorhombic “zig-zag” (OZZ) phase, illustrated in Fig. 2(d), is one of the many degenerate ground states found at the border between the CAF and TDQ phases (see Fig. 3). Unlike the CAF phase, the OZZ state contains “flippable” hexagonal plaquettes where quantum tunneling can act (see inset to Fig. 1), which allow it to gain energy, relative to the CAF. As a result, a small wedge of OZZ order opens from the highly degenerate point $J_2/D = -0.0621$. It is interesting to speculate that further ordered phases might occur in the thermodynamic limit, perhaps in the form of the “fans” found in classical anisotropic next-nearest neighbor Ising (ANNNI) models [27, 28].

The strength of exchange and dipolar interactions in Dy$_2$Ti$_2$O$_7$ has been estimated by Yavors’kii et al. [6], who find $D = 1.32$ K, $J_1 = 3.41$ K, $J_2 = -0.14$ K, $J_3 = 0.03$ K, having set $J_{3c} = J_{3d} = J_3$. An obvious question, in the light of the experiments of Pomaranski et al. [6], is: “Given these parameters, what kind of ground state should we expect?” The simplest possibility is a classical ordered ground state, and for the parameters given in [6] we find that this should be a CAF (cf. Fig. 3). However, because of the exponential screening of dipolar interactions within chain states (cf. Eq. 6), this determination is extremely sensitive to the precise values of exchange parameters: an error as small as $\delta J \sim 7$ mK could be enough to convert the CAF into a TDQ ground state, while $\delta J \sim 50$ mK could stabilize a FM.

Since the parameterization of Yavors’kii et al. [6] was based on a “best fit” to a range of thermodynamic and scattering data, within certain simplifying assumptions, it seems safest to wait for further input from experiment before attempting to diagnose any specific order. None the less, the mapping onto an extended Ising model $\mathcal{H}_{\text{Ising}}$ [Eq. (5)] does make precise predictions for the classical ordered ground state for any given set of exchange interactions [Fig. 3, Eq. (6), and so can be used as a guide to interpreting experiment. And it seems entirely plausible that changes in $J_k$ of the scale $\delta J \sim 50$ mK could be achieved through the application hydrostatic pressure, or by chemical substitution [42], allowing a spin ice to be tuned from one ground state to another.

Including quantum effects through $\mathcal{H}_{\text{tunneling}}$ [4] raises the intriguing possibility that the ground state Dy$_2$Ti$_2$O$_7$ could be an OZZ state, or even a QSL. At the present time, no reliable estimate of the strength of quantum tunneling $g$ in Dy$_2$Ti$_2$O$_7$ is available. However based on what we know about $J_c$, we estimate that the value of $g$ needed to stabilize a QSL may be as little as $g_{\text{Dy}_2\text{Ti}_2\text{O}_7} \approx 70$ mK. While other effects come into play in the quantum spin ices Yb$_2$Ti$_2$O$_7$, Tb$_2$Ti$_2$O$_7$ and Pr$_2$Zr$_2$O$_7$, we can make a primitive estimate of the $g_c$ for these systems by assuming spin-ice correlations, and comparing $g_c$ with the known values of $D$. Doing so, we find encouragingly small numbers: $g_{\text{Yb}_2\text{Ti}_2\text{O}_7} \approx 3$ mK, $g_{\text{Tb}_2\text{Ti}_2\text{O}_7} \approx 30$ mK, and $g_{\text{Pr}_2\text{Zr}_2\text{O}_7} \approx 9$ mK.

In conclusion, determining the zero-temperature, quantum, ground state of a realistic model of a spin ice is an important challenge, motivated by recent experiments on Dy$_2$Ti$_2$O$_7$ [6] and ongoing studies of quantum spin ice materials [10, 18, 20, 29]. In this article, we have established that only a modest amount of quantum tunneling $g_c$ is needed to stabilize a quantum spin liquid (QSL), with deconfined fractional excitations [9, 12, 16, 20], in a spin ice with both short-range exchange and long-range dipolar interactions $\mathcal{H}_{\text{QDSI}}$ [Eq. (1)]. We have further shown that the ground states of this model (in which monopoles are confined), are built of chains of alternating “in” and “out” spins. These “chain states” can be described by an extended Ising model on an anisotropic triangular lattice, $\mathcal{H}_{\text{Ising}}$ [Eq. (5)]. Using Monte Carlo simulation, we have determined both the quantum and classical phase diagrams of $\mathcal{H}_{\text{QDSI}}$ [Eq. (1)], as a function of quantum tunneling $g_c$ and temperature $T$. These results are summarized in Fig. 1. Based on published estimates of exchange parameters [6], we find that an ordered ground state in Dy$_2$Ti$_2$O$_7$ would be a cubic antiferromagnet (CAF). However this state lies tantalisingly close in parameter space to other, competing ordered phases, and only a very small amount of quantum tunneling would be needed to convert it into a quantum spin liquid.

While we have chosen to emphasize Dy$_2$Ti$_2$O$_7$, there are a great many rare-earth pyrochlore oxides [43], in which to search for quantum spin ice, and other unusual forms of magnetism [12, 20, 44]. In many of these materials, dipolar interactions will also play a role, and the small values of $g_c$ found in our simulations offer hope that quantum spin-liquids may be found in other materials at low temperature.

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DEFINITION OF MODEL

Spin ice with long-range dipolar interactions and competing exchange

In this Letter we start from a minimal model for a spin ice material where magnetic ions have a doublet ground state with Ising character, interacting through both dipolar and exchange interactions \[ H_{\text{DSI}} = H_{\text{dipolar}} + H_{\text{exchange}}, \] (S1)
with \( H_{\text{dipolar}} \) and \( H_{\text{exchange}} \) defined below. We refer to this as the “Dipolar Spin Ice” (DSI) model [4].

The magnetic ions in spin ice occupy the sites of a pyrochlore lattice, built of corner-sharing tetrahedra. The associated magnetic moments can be described in terms of the Ising variable \( S_i^z = \pm 1/2 \) as

\[ M_i = 2 \mu_{\text{eff}} S_i^z \hat{z}, \] (S2)

where the easy axis \( \hat{z} \) on site \( i \) is parallel to the local [111] axis \( \langle \hat{z}_i \rangle = 1 \), and the effective moment is

\[ \mu_{\text{eff}} = g_e \hbar B \langle J^z \rangle. \] (S3)

Dipolar interactions between these magnetic moments are long-ranged, and have the form

\[ H_{\text{dipolar}} = 4D \sum_{i<j} \left( \frac{r_{ij}}{r_{ij}} \right)^3 \langle \hat{z}_i \cdot \hat{z}_j \rangle -3 \langle \hat{z}_i \cdot \hat{r}_{ij} \rangle \langle \hat{z}_j \cdot \hat{r}_{ij} \rangle S_i^z S_j^z, \] (S4)
where \( r_{ij} \) is the vector connecting sites \( i \) and \( j \) (with \( r_{ij} = |r_{ij}| \) and \( \mathbf{r}_{ij} = \mathbf{r}_{ij}/r_{ij} \));

\[
r_1 = \frac{a}{2\sqrt{2}} \tag{S5}
\]

is the distance between neighboring magnetic ions within a cubic unit cell of linear dimension \( a \); and

\[
D = \frac{\mu_0 \mu_0^2}{16\pi r_1^3} \tag{S6}
\]

is the strength of dipolar interactions at distance \( r_1 \). To keep the definition of \( D \) consistent with (S4), where \( S_i^z = \pm 1 \), an overall factor of 4 has been introduced in \( \mathcal{H}_{\text{dipolar}} \) [Eq. (S4)].

We also consider competing exchange interactions

\[
\mathcal{H}_{\text{exchange}} = \sum_k 4J_k \sum_{\langle ij \rangle_k} (\mathbf{\hat{z}}_i \cdot \mathbf{\hat{z}}_j) S_i^z S_j^z, \tag{S7}
\]

where \( k \) counts equivalent pairs of sites on the pyrochlore lattice, and an overall factor of 4 has been introduced in \( \mathcal{H}_{\text{exchange}} \) to keep the definition of \( J_k \) consistent with (S10).

Each site in the pyrochlore lattice has six first-neighbor bonds, of length \( r_1 \), and six second-neighbour bonds, of length \( \sqrt{3}r_1 \). These have interactions \( J_1 \) and \( J_2 \), respectively. There are two, inequivalent, types of third-neighbor bonds, with equal length \( 2r_1 \), but different symmetry. We denote the first of these, which is collinear with the nearest-neighbor bond, \( J_{3c} \), and the second, which connects spins across hexagonal plaquettes, \( J_{3d} \).

For the purposes of this study, we work with parameters \( D \) and \( J_k \) chosen such that the net effect of the interactions in \( \mathcal{H}_{\text{DSI}} \) [Eq. (S1)] is to enforce the “ice rules” constraint, in which two spins point “in”, and two spins “out”, of each of the tetrahedra within the pyrochlore lattice. Even where the ice rules hold, the presence of long-range interactions ensures that different spin-ice configurations have different energies, giving rise to the possibility of ordered ground states. However the differences in energy are smaller than might be expected, since dipolar interactions are “self-screened” (7,9) within spin-ice configurations, decaying as \( 1/r^5 \). As discussed below, there exist a subset of spin-ice configurations, the “chain states”, in which dipolar interactions are even better screened, decaying exponentially with distance.

The finite-temperature properties of the spin ice \( \text{Dy}_2\text{Ti}_2\text{O}_7 \) are well-described by the DSI model, and the corresponding parameters of \( \mathcal{H}_{\text{DSI}} \) [Eq. (S1)] have been estimated by Yavors’kii et al. (6). In \( \text{Dy}_2\text{Ti}_2\text{O}_7 \), \( a = 10.124 \) \( \AA \), and the Dy\(^{3+} \) ions have a Landé factor \( g_L = 4/3 \) associated with an Ising moment \( \langle J^z \rangle = 7.40 \).

It follows from Eq. (S6) that

\[
D = 1.3224 \text{ K.} \quad [\text{Dy}_2\text{Ti}_2\text{O}_7]
\]

Yavors’kii et al. also estimate the parameters for exchange interactions \( J_k \), on the basis of fits of classical Monte Carlo simulation to the structure factor \( S(q) \) measured in (diffuse) neutron scattering. They find

\[
J_1 = 3.41 \text{ K,} \quad J_2 = -0.14 \text{ K,} \quad [\text{Dy}_2\text{Ti}_2\text{O}_7] \quad J_3 = 0.03 \text{ K,} \quad
\]

working within the assumption that \( J_{3c} = J_{3d} = J_3 \).

**Quantum tunnelling between spin-ice states**

In addition to the minimal classical model \( \mathcal{H}_{\text{DSI}} \) [Eq. (S1)], we consider the leading effect of quantum fluctuations on a classical spin ice, namely quantum tunnelling between different spin configurations obeying the ice rules, i.e.

\[
\mathcal{H}_{\text{QDSI}} = \mathcal{H}_{\text{dipolar}} + \mathcal{H}_{\text{exchange}} + \mathcal{H}_{\text{tunnelling}}. \tag{S8}
\]

Spin ice configurations can be connected by reversing closed loops of spins. The shortest closed loop occurs on the hexagonal plaquettes of the pyrochlore lattice, as illustrated in the inset of Fig. 1 of the main text, and the associated Hamiltonian is

\[
\mathcal{H}_{\text{tunnelling}} = -g \sum_O |\uparrow\rangle \langle \uparrow| + |\downarrow\rangle \langle \downarrow|. \tag{S9}
\]

This tunneling process can be thought of as the spontaneous creation of a (virtual) pair of magnetic monopoles, which annihilate after one has traversed the hexagon.

Quantitative estimates of the tunneling matrix element \( g \) require a concrete model for the process by which monopoles are generated, and hop from site to site. The simplest example is given by exchange interactions of “XY” type,

\[
\mathcal{H}_{\text{socx}} = J_{zz} \sum_{\langle ij \rangle} S_i^z S_j^z - J_{\pm} \sum_{\langle ij \rangle} (S_i^+ S_j^- + S_i^- S_j^+), \tag{S10}
\]

with \( S_i^\pm \) promoted to a (pseudo) spin-1/2 operator such that \( [S_i^+, S_j^-] = 2S_i^z \delta_{ij} \). In this case \( \mathcal{H}_{\text{tunnelling}} \) [Eq. (S9)] can be derived in degenerate perturbation theory about classical states obeying the ice rules, and

\[
g = \frac{12J_+^2}{J_{zz}^2}.
\]

Quantum tunneling between spin-ice configurations of this form has been shown to stabilize a quantum spin liquid described by a quantum \( U(1) \) lattice gauge theory with photon excitations (12,15).

A more general starting point for describing a quantum spin ice is the anisotropic nearest-neighbor exchange interactions.
\[ H_{S=1/2} = \sum_{\langle ij \rangle} \left\{ J_{ij} S_i^+ S_j^- - J_\pm (S_i^z S_j^z + S_i^- S_j^+) \right\} \\
+ J_{\pm \pm} \left[ \gamma_{ij} S_i^+ S_j^+ + \gamma_{ij} S_i^- S_j^- \right] \\
+ J_{\pm \mp} \left[ S_i^z (\zeta_{ij} S_j^+ + \zeta_{ij} S_j^-) + i \leftrightarrow j \right] \] (S11)

where the sum \( \langle ij \rangle \) runs over the nearest-neighbor bonds of the pyrochlore lattice; and \( \gamma_{ij} \) and \( \zeta_{ij} \) are \( 4 \times 4 \) complex unimodular matrices encoding the rotations between the local axes \( \hat{z}_i \) and the cubic axes of crystal [16]. This (pseudo) spin-1/2 model has been shown to give a quantitative description of spin excitations in both the “quantum spin ice” Yb\(_2\)Ti\(_2\)O\(_7\) [16] and quantum order-by-disorder system Er\(_3\)Ti\(_2\)O\(_7\) [17]. The parameterization of \( H_{S=1/2} \) [Eq. (S11)], and its mean-field phase diagram have been explored in [18–20].

**Ewald summation of long-range dipolar interactions**

The Ewald summation provides an efficient and systematic means of computing long-range interactions in clusters with periodic boundary conditions where the sum over images is conditionally convergent as is the case for the dipolar interaction. This is accomplished by splitting the conditionally convergent sum over periodic images into two absolutely convergent sums - one in real space and the other in reciprocal space - through the introduction of a splitting parameter \( \alpha \) which determines the rate of convergence of the two sums. The summands both have an exponential factor and, in practice, the sums may converge rapidly for a careful choice of \( \alpha \). The dipole moments live within a cubic cell of edge length \( L \). The Ewald summation is given by [21]

\[ U = U^{(R)} + U^{(G)} + U^{(SE)} + U^{(MF)} , \] (S12)

where the real space sum is

\[ U^{(R)} = \frac{1}{2} \sum_{i,j=1}^{N} \sum_{n'} \left[ (\mathbf{S}_i \cdot \mathbf{R}_{ij} + \mathbf{n}) F_1 (|\mathbf{R}_{ij} + \mathbf{n}|) - (\mathbf{S}_i \cdot (\mathbf{R}_{ij} + \mathbf{n})) (\mathbf{S}_j \cdot (\mathbf{R}_{ij} + \mathbf{n})) F_2 (|\mathbf{R}_{ij} + \mathbf{n}|) \right] , \]

where \( \mathbf{n} \equiv (n_x, n_y, n_z)L \) with \( n_a \in \mathbb{Z} \) and the prime indicates that the divergent term is omitted from the sum. The reciprocal space sum is

\[ U^{(G)} = \frac{1}{2L^4} \sum_{G \neq 0} \frac{4\pi}{G^2} \exp \left[ - \left( \frac{\pi G}{\alpha L} \right)^2 \right] \times \sum_{i,j=1}^{N} (\mathbf{S}_i \cdot \mathbf{G}) (\mathbf{S}_j \cdot \mathbf{G}) \exp \left( \frac{2\pi i}{L} \mathbf{G} \cdot \mathbf{R}_{ij} \right) \]

and \( \mathbf{G} \equiv (G_x, G_y, G_z)L \) with \( G_a \in \mathbb{Z} \). The self-energy is

\[ U^{(SE)} = -\frac{2\alpha^3}{3\sqrt{\pi}} \sum_{i=1}^{N} S_i^2 . \]

There is also a macroscopic field term

\[ U^{(MF)} = \frac{2\pi}{(2\epsilon + 1)L^3} \sum_{i=1}^{N} \sum_{j=1}^{N} S_i \cdot S_j . \]

In the real space sum, the following functions appear:

\[ F_1 (x) = \frac{1}{x^3} \left( \text{erfc} (\alpha x) + \frac{2\alpha x}{\sqrt{\pi}} e^{-\alpha^2 x^2} \right) , \]

\[ F_2 (x) = \frac{1}{x^5} \left( 3 \text{erfc} (\alpha x) + \frac{2\alpha x}{\sqrt{\pi}} (3 + 2\alpha^2 x^2) e^{-\alpha^2 x^2} \right) , \]

where \( \text{erfc}(z) \) is the complementary error function.

Long-range interactions tend to be sensitive to the macroscopic boundary conditions. In particular, each periodic cell may have a net dipole moment. After a sum over images, the resulting supercell of periodic cells has a macroscopic moment which acts back on the microscopic moments in a way that depends on the shape of the sample and on the medium within which the sample is embedded. This physics is contained within the last term which is proportional to the net dipolar moment in the periodic cell and which also depends on parameter \( \epsilon \) - the relative permittivity of the surrounding medium. This term is the relic of the fact that the original sum over long-range dipolar interactions is conditionally convergent. To be concrete, we choose “metallic boundary conditions” in our work which amounts to setting the macroscopic field term to zero or \( \epsilon \to \infty \). Physically this amounts to cladding the supercell of periodic cells with a perfect “conductor” that polarizes and exactly cancels off the macroscopic field.

Since the different ground states of the dipolar spin ice model have different net dipole moments, the precise location of the phase boundaries within this model will depend on the macroscopic boundary conditions including the shape of the sample. In real materials, phases with a net moment, such as the ferromagnetic (FM) phase discussed in the main text, will form domains to screen the macroscopic moments in a way that depends on the shape of the sample and on the medium within which the sample is embedded. This physics is contained within the last term which is proportional to the net dipolar moment in the periodic cell and which also depends on parameter \( \epsilon \) - the relative permittivity of the surrounding medium.

**CLASSICAL MEAN-FIELD PHASE DIAGRAM**

**AT \( T = 0 \)**

“Soft-spin” approximation

Given a spin model \( H = \frac{1}{2} \sum_{ij} J_{ij} S_i S_j \) of classical Ising spins \( S_i \), we can learn a great deal about its ordering instabilities out of the paramagnetic phase from the Fourier transform of \( J_{ij} \) which we denote \( \tilde{J}_{ij} \). In
particular, if we compute the spectrum of $J_{ab}^{ab}$ where $a$ and $b$ label the lattice basis, the eigenvalues being $\lambda_i^a$ and associated eigenvectors $\mathbf{E}_i^{\mu}$, the mean field ordering wavevector upon lowering the temperature lies at the wavevector at which the lowest eigenvalue takes its lowest value, $\mathbf{Q}$. The eigenvector corresponding to this point, or eigenvectors if there is a degeneracy, provide information about the ground state of the spin model provided some linear combination of the eigenvectors can be found such that the components have equal magnitude.

The essential idea behind this mean-field theory \[8\, 22\], also known as the “self-consistent Gaussian approximation”, is to lift the hard constraint on the spin lengths which is reimposed as a soft spin constraint through a Lagrange multiplier. The spin model is reduced to a Gaussian theory in “soft spin” variables $m_i$ which can be solved exactly. The free energy to quadratic order is just

$$F = \frac{1}{2} \sum_{\mathbf{q}, \alpha, \mu} (T + \lambda_i^{\alpha}) |\phi_i^{\mu}|^2,$$

(S13)

where $\phi_i^{\mu}$ is obtained from $m_i$ by a diagonalizing transformation on $J_{ab}^{ab}$. This part of the free energy, $F$, changes sign when the temperature equals the global minimum among the eigenvalues as stated above.

We now consider the application of this technique to the dipolar spin ice model with second nearest neighbor exchange. The Fourier transform is taken with respect to the fcc primitive lattice vectors and $a$ is the edge length of the smallest cubic unit cell. When $J_2 = 0$ so that the sole coupling is the long-range dipolar interaction this mean field theory has been studied with $J_{ab}^{ab}$ computed through an Ewald summation \[8\]. In this case, the spectrum of $J_{ab}^{ab}$ which is a $4 \times 4$ matrix indexed by the tetrahedral basis, has two higher energy dispersive bands and two lower energy almost flat bands. The near-flatness is a consequence of the geometrical frustration of the nearest neighbor interactions and the phenomenon of projective equivalence: loosely, the correlations within the highly degenerate set of ice states and those induced by the long-range dipolar interaction almost match leaving a weak, short-range residual contribution from the dipolar coupling to break the degeneracy \[10\]. The absolute minimum of the nearly flat bands lies at $(2\pi/a) (0, 0, 1)$ and wavevectors related by the cubic symmetry of the pyrochlore lattice. This wavevector matches that of the ground state of the dipolar spin ice model found in Ref. \[3\] which we refer to as the CAF state in the main text.

When $J_2 < 0$, for small $J_2$ the second neighbor part of the dipolar interaction is partially cancelled by the exchange and the bandwidth of the two nearly flat bands decreases. This is illustrated in Fig. S1. For $J_2 < -0.068$, the magnitude of the second neighbor coupling starts to increase and the bandwidth of the lower pair of bands increases.

![](fig_s1.png)

**FIG. S1**: Band-width of spin-ice states in the presence of long-range dipolar interactions, as a function of competing 2nd-neighbor exchange $J_2/D$. Results are taken from the classical “soft-spin” approximation to $H_{DSI}$ \[Eq. (S1)\].

**Mean field phase diagram**

Turning to the long-range ordered phases, we find that the CAF state is stable for $|J_2/D| < 0.057(1)$. The bracket indicates the uncertainty in the last digit. For $|J_2/D| > 0.080(1)$, the ordering wavevector is $(0, 0, 0)$ which can only correspond to a state with all independent tetrahedra polarized in the same direction while satisfying the Ising constraint. For $0.057 < |J_2/D| < 0.080$ the ordering wave vector changes smoothly as shown in the Figures. S2a and S2b along the path $(Q, Q, 0)$ and $(Q, -Q, 0)$. In general there are twelve such wavevectors. In the middle of this set of couplings $J_2/D$, the ordering wave vector passes through $(2\pi/a)(1/2, 1/2, 0)$ at one point. The phase diagram is summarized in Fig. S2a.

If a magnetic structure is to be a ground state of a classical spin model, it should have moments that saturate the spin length at zero temperature. Since the Gaussian approximation we have considered so far does not impose a hard constraint on the spin length, we attempt to impose the constraint on the eigenvectors of $J_{ab}$ at the minimum in the spectrum. The soft spin mean field theory together with the imposition of the hard spin constraint is the well-known Luttinger-Tisza method \[24\].

The Luttinger-Tisza method has been applied to the dipolar spin ice model with $J_2 = 0$, and finds an ordering wave vector $(2\pi, 0, 0)$ \[3\]. Here the minimum eigenvalue is two-fold degenerate state. It is straightforward to see from these eigenvectors that there are linear combinations of the form $\mathbf{E}^{1\nu} = (1/2)(1, -1, 1, -1)$ and $\mathbf{E}^{2\nu} = (1/2)(-1, 1, 1, -1)$ for a given wavevector - here $(2\pi/a)(1, 0, 0)$. The result is that the ground state of this model is the twelve-fold degenerate cubic antiferromagnet (CAF), discussed in the main text. The twelve-fold degeneracy arises as follows: a factor two from the degeneracy of the eigenvectors, three from the associated cubic directions, and a further factor of two from time reversal.
FIG. S2: (a) Schematic mean-field phase diagram of spin-ice with long-range dipolar interactions $D$, as a function of competing 2nd-neighbor exchange $J_2$, as calculated within a classical “soft-spin” theory of $\mathcal{H}_{DS}$. The points show the ordering wavevector for the soft spin mean field theory taken from the minimum eigenvalue of $J_\mathbf{q}$. The ordering wavevector drifts from $[0,0,1] \equiv [1,1,0]$ ordering to $[0,0,0]$ ordering. The vertical dashed line illustrates the value of $J_2/D$ for which the hard spin constraint can be satisfied within the interval denoted by the red background. At this point, the ordered state is the TDQ state. In this figure, the ordering wavevector is $\mathbf{Q} = (2\pi/\alpha)(Q_{min}, Q_{min}, 0)$. (b) Section through lowest band in the $[H,H,0]$ direction for $J_\mathbf{q}$ of spin-ice with long-range dipolar interactions $D$, as a function of competing 3rd-neighbor exchange $J_2$. The minimum shifts from $(2\pi/\alpha)(1,1,0)$ to $(0,0,0)$ as $J_2/D$ becomes more negative (indicated by the arrow). For intermediate values of $J_2/D$, the ordering wave vector varies smoothly between these two values. In the middle of this (typically) incommensurate region, the wave vector is $(2\pi/\alpha)(1/2, 1/2, 0)$. At this point, the hard constraint on the spin length is compatible with an order parameter constructed from eigenvectors at the minima in the spectrum of $J_\mathbf{q}$.

For the state found at large negative $J_2$, with ordering vector $(0,0,0)$ (the FM), we get a three-fold degenerate lowest eigenvalue. We can normalize each spin component and we end up with unique solutions of the form $(1/2)(1,1,-1,-1)$, $(1/2)(1,-1,1,-1)$, $(1/2)(-1,1,1,-1)$. Together with time reversal we end up with the complete set of magnetic structures with net moment along the cubic edge directions.

Finally, we turn to the regime of intermediate couplings. The absolute minimum of $J_\mathbf{q}$ is singly degenerate and of the form $(1,-1,0,0)$. In order to satisfy the hard spin constraint, one must take linear combinations of eigenvectors belonging to different ordering wavevectors from the set of minima in the spectrum. In short, any ordered structure must be an multi-Q structure. In order to find potential ground states, we take a large finite cluster and carry out a numerical least squares minimization on the function

$$F[\Psi] = \sum_{i,a} (|\Psi_{i,a}|^2 - 1)^2,$$  

where the order parameters is built from available ordering wavevectors and their associated eigenvectors - the complete set of twelve $E_{\mathbf{Q}_{\mu}} \exp(i\mathbf{Q} \cdot \mathbf{r})$ with undetermined complex coefficients. We find that the hard spin constraint can be satisfied only at a single point over the range $-0.080 < J_2/D < -0.057$ at $J_2/D = -0.06807(1)$.

The form of the order parameter for the single multiple-Q structure allowed by the set of eigenvectors and ordering wavevectors obtained in the mean field theory is

$$\Psi_{i,a} = \sum_{\mu} (z_{a,\mu} \exp(i\mathbf{Q}_\mu \cdot \mathbf{R}_i) + z_{a,\mu}^* \exp(-i\mathbf{Q}_\mu \cdot \mathbf{R}_i)),$$  

where, for arbitrary order allowed by the mean field theory in the intermediate region, the sum $\mu$ runs over the six distinct ordering wavevectors given in the rows of Table S1 and $i$ runs over all fcc sites. The $z_{a,\mu}$ are proportional to the eigenvectors $E_{\mathbf{Q}_{\mu}}$.

The particular types of order which satisfy the hard-spin constraint are the tetragonal double-Q structures (TDQ) discussed in the main text. To obtain these states we choose wavevectors in pairs - the A, B or C pairs in the table. Each ordering wavevector within the pair controls the state on two of the four magnetically distinct sites on the pyrochlore lattice. The complex weights for the pair take the form $\sqrt{2}(\pm 1 \pm i)$. The degeneracy of the allowed states - which are all ice states - is $48 = 3 \times 4 \times 4$. This comes from the three choices of pair A, B or C. Then there are four choices of sign ($\pm(1+i)$, $\pm(1-i)$) for each of the two complex weights. Time reversal pairs are included within this set of states.

In the foregoing discussion, we have omitted any mention of the third-nearest-neighbor couplings and also we have concentrated on $J_2 < 0$ without discussing $J_2 > 0$. In fact, we have studied the full $J_2$, $J_{3c}$, $J_{3d}$ mean field phase diagram in the presence of the long-range dipolar interaction where the latter is the dominant coupling. Within this set of couplings, the soft spin mean field theory exhibits four classes of ordered structure:

1. The cubic antiferromagnet (CAF) state with $(2\pi/\alpha)(0,0,1)$ ordering wavevector.
TABLE SI: Table of eigenvectors for ordering wavevector $Q = \pi$. These states are built from the first, second or third pairs of states in the order listed here.

| Label | Ordering Wave Vectors | Eigenvectors |
|-------|-----------------------|--------------|
| A1    | $\pm (0, Q, Q)$       | $(1/\sqrt{2})(0, 1, -1, 0)$ |
| A2    | $\pm (0, Q, -Q)$      | $(1/\sqrt{2})(-1, 0, 0, 1)$ |
| B1    | $\pm (Q, 0, Q)$       | $(1/\sqrt{2})(0, 1, 0, -1)$ |
| B2    | $\pm (Q, 0, -Q)$      | $(1/\sqrt{2})(1, 0, -1, 0)$ |
| C1    | $\pm (Q, Q, 0)$       | $(1/\sqrt{2})(0, 0, 1, -1)$ |
| C2    | $\pm (Q, -Q, 0)$      | $(1/\sqrt{2})(-1, 1, 0, 0)$ |

2. The ferromagnet (FM) with $Q = 0$.

3. The $(Q, Q, 0)$ incommensurate region, from which the tetragonal double-Q (TDQ) state arises after imposing the hard spin constraint.

4. A second class of $(Q, Q, 0)$ states differing from those above in the nature of the lowest eigenvector. We have explored this fourth phase finding that the hard spin constraint cannot be imposed and that, therefore soft spin mean field theory does not generate any new candidate Ising ground states in this region of the phase diagram.

In conclusion, the phase diagram of the full $J_2$, $J_{3c}$, $J_{3d}$, $D$ model appears to have three ground states CAF, TDQ and FM, satisfying the spin-ice constraint, at least when $D$ is the dominant coupling. All three ground states appear within the $J_2$-$D$ model which has been the main focus of this paper. We note that all the ground states that we have identified have the property that the moments point head to tail along $[110]$ chains in the pyrochlore lattice. This observation leads to a dramatic simplification of the problem as we discuss in the next section.

MAPPING TO AN EFFECTIVE TRIANGULAR LATTICE ISING MODEL

All the different ordered phases we have found can be decomposed into two sets of infinitely long linear chains made of alternating “in” and “out” spins, so that the spin components along the chains are uniform and the components perpendicular to the chains are alternating. The chains belonging to the same set are parallel to each other and orthogonal to the chains in the other set. These sets are uniquely defined for the CAF, TDQ and OZZ state, while for the FM we have four sets of parallel chains which allows us to choose two equivalent orthogonal sets.

A similar problem was encountered by Anderson when he considered the charge ice problem with long range Coulomb repulsions as a minimal model to understand the charge order and its energy scale in magnetite [24]. Inspired by Madelung’s summation, he argued that the ground states are built from infinitely long linear chains with alternating charges. Each of these chains is charge neutral and therefore only weakly interacting with other chains. Since the total energy does not depend on the choice of these neutral objects (i.e. chains), we can select the objects such as to minimize the interaction energy among each other, in this case to change the power law decay to exponential decay. In the spin-ice problem, the alternating charges are replaced by alternating “in” and “out” spins.

In this section we derive the interactions between the Ising variables of the chains and present the mapping to an effective anisotropic Ising model on triangular lattice and its phase diagram, which serves to interpret the different ordered phases of spin ice.

Madelung summation of long-range dipolar interactions

As an example, let us consider the two sets of chains parallel to the $[1, 1, 0]$ and $[1, -1, 0]$ directions. The coordinates of the spins on the chains parallel to the $[1, 1, 0]$ are given by $(n + l, -n + l, m)$, while of those parallel to $[1, -1, 0]$ by $(n + 1 + l, n - l, m + 1)$, where the integer $l = -\infty, \cdots, 0, 1, \cdots, \infty$ is a running index to label the spins along a chain and the integers $n$ and $m$ (such that $m$ and $n + m/2$ are even) label the chains and also denote the position of the chains. Actually, for $l = 0$ the
(n, −n, m), if regarded as site coordinates, constitute an
anisotropic triangular lattice in the plane orthogonal to
the chains, as shown in Fig. S3b. In this plane, the local
coordinates of the sites on the chains parallel to the
chains, as shown in Fig. S3b. In this plane, the local
direction in as a function of distance
d/δ2 = 4√2 between the chains. The blue squares and
red diamonds show the K(0,δ2) and K(δ1,0) series, respectively,
while the dashed lines of the same color are the corresponding
asymptotic expressions Eqs. (S19) and (S20). The green circle
show exchanges for general (δ1, δ2). Except for the empty
symbols, the exchanges are all negative.

The coordinates of the sites on the chains parallel to the
[1, 1, 0] are given by (n + l, −n + l, m) = (δ1 + l, δ1 −
l, √2δ2). The factor r12 = √2 is included as the distance
between the spins is √2 in the present lattice. The alternation
in l comes from the alternating spin components perpendicular
to the chain, while the uniform term in the sum comes from the spin components parallel to the
chain.

The sum can be converted into an integral by introduc-
ing the Fourier representation for the Dirac delta func-
tions:

\[ K_δ = \frac{\sqrt{2}}{2} D \sum_{l=-\infty}^{\infty} \left[ (-1)^l \frac{2}{3} \frac{(δ_1^2 - 2δ_2^2 + l^2)}{(δ_1^2 + δ_2^2 + l^2)^{5/2}} + (-1)^l \right] \frac{2}{3} \frac{2 \sin(2pπl)}{\sin(πl)} \frac{(δ_1^2 + δ_2^2 - l^2)}{(δ_1^2 + δ_2^2 + l^2)^{5/2}} \]  

where \( K_1 \) and \( K_2 \) are the modified Bessel functions of
the second kind and \( δ = \sqrt{δ_1^2 + δ_2^2} \). The neglected in-
tegrals decay as \( e^{-πδ} \) faster with the distance (more
precisely, \( \sin(2pπl)/\sin(πl) = \sum_{q=1}^{p} \cos((2q + 1)πl) \), and
the integral with \( \cos(qπl) \) decays as \( e^{-qπδ} \). We show the
decay of the exchange energy in the two main direc-
tions, (0, δ2) and (δ1, 0), in Fig. S4. The dashed lines
show the asymptotic behavior at large distances:

\[ K_{(0,δ2)} / D \approx -\frac{π^2}{3} 2^{3/2} δ_2^{-1/2} e^{-πδ_2} \]  

and

\[ K_{(δ1,0)} / D \approx \frac{π}{3} 2^{3/2} δ_1^{-3/2} e^{-πδ_1} \]  

The effective interactions decay exponentially with dis-
tance from the chains, with the leading term at long
distances coming from the alternating spin components per-
pendicular to the chain:

\[ K_δ / D \approx \frac{2}{3} \int_{-\infty}^{\infty} dl \cos(πl) \frac{δ_1}{δ_1^2 + δ_2^2 + l^2}^{5/2} \right] \frac{2}{3} \frac{2 \sin(2pπl)}{\sin(πl)} \frac{(δ_1^2 + δ_2^2 - l^2)}{(δ_1^2 + δ_2^2 + l^2)^{5/2}} \]  

\[ \approx -\frac{2\sqrt{2}}{3} \left[ π^2 \left( \frac{δ_2}{δ} \right)^2 δ^{-1/2} - πδ^{-3/2} + \ldots \right] e^{-πδ} \]  

FIG. S4: The plot of the dipolar contributions to the
K(δ1, δ2) for different values of δ1 and δ2 as a function of the distance
d/δ1 = δ2/δ1 + δ2/δ2 between the chains. The blue squares and
red diamonds show the K(0, δ2) and K(δ1, 0) series, respectively,
while the dashed lines of the same color are the corresponding
asymptotic expressions Eqs. (S19) and (S20). The green circle
show exchanges for general (δ1, δ2). Except for the empty
symbols, the exchanges are all negative.

The coordinates of the sites on the chains parallel to the
[1, 1, 0] are given by (n + l, −n + l, m) = (δ1 + l, δ1 −
l, √2δ2). The factor r12 = √2 is included as the distance
between the spins is √2 in the present lattice. The alternation
in l comes from the alternating spin components perpendicular
to the chain, while the uniform term in the sum comes from the spin components parallel to the
chain.

The effective interactions decay exponentially with dis-
tance from the chains, with the leading term at long
distances coming from the alternating spin components per-
pendicular to the chain:

\[ K_δ / D \approx \frac{2}{3} \int_{-\infty}^{\infty} dl \cos(πl) \frac{δ_1}{δ_1^2 + δ_2^2 + l^2}^{5/2} \right] \frac{2}{3} \frac{2 \sin(2pπl)}{\sin(πl)} \frac{(δ_1^2 + δ_2^2 - l^2)}{(δ_1^2 + δ_2^2 + l^2)^{5/2}} \]  

\[ \approx -\frac{2\sqrt{2}}{3} \left[ π^2 \left( \frac{δ_2}{δ} \right)^2 δ^{-1/2} - πδ^{-3/2} + \ldots \right] e^{-πδ} \]  

\[ \approx -\frac{2\sqrt{2}}{3} \left[ π^2 \left( \frac{δ_2}{δ} \right)^2 δ^{-1/2} - πδ^{-3/2} + \ldots \right] e^{-πδ} \]  

TABLE SII: Parameters Kδ of the extended Ising model
H_{\text{Ising}} [Eq. (S21)], written in terms of the microscopic
parameters of H_{\text{Dipolar}} [Eq. (S8)]. The contribution of the long-range
dipolar interactions H_{\text{Dipolar}} [Eq. (S3)] shows exponential
decay as a function of distance |δ|.

| δ | K_{(1,\sqrt{2})} | K_{(2,0)} | K_{(0,2\sqrt{2})} | K_{(3,\sqrt{2})} | K_{(2,-2\sqrt{3})} | K_{(1,3\sqrt{2})} | K_{(4,0)} |
|---|---|---|---|---|---|---|---|
| | \sqrt{3} | -0.0227426D | -J_2/3 - J_{3c} - J_{3d} | 0.0021957D | -0.0008443D | -0.0000178D | 0.0000649D | -0.0000051D | 0.0000013D |
Description of chain states in terms of an extended Ising model

The interactions between chains of alternating “in” and “out” spins vanish for perpendicular chains, and decay exponentially with the distance between parallel chains [Fig. S4, Table SII]. This means that low-energy spin configurations split one set of chains parallel to [110], and a second set parallel to [110]. Since reversing the sense of all the spins belonging to one chain maps it to another valid chain configuration, each chain can be viewed as an Ising variable $\sigma = \pm 1$, and the interactions between parallel chains can be described using an extended Ising model on a two-dimensional, anisotropic, triangular lattice

$$H_{\text{Ising}}^{2D} = \frac{1}{2} \sum_{r, \delta} K_{\delta} \sigma_r \sigma_{r+\delta}, \quad (S21)$$

where $r$ and $\delta$ are defined on a triangular lattice with primitive vectors $a = (2, 0)$ and $b = (1, \sqrt{2})$, with distances measured in units of $r_1$ [Eq. (S3)]. The physics of this model, which has much in common with the anisotropic next-nearest neighbour Ising (ANNNI) model [27, 28], is dominated by the two leading interchain interactions, $K_{(1,\sqrt{3})}$ and $K_{(2,0)}$, whose values can be tuned using the exchange interactions $J_2$, $J_{3c}$ and $J_{3d}$ [cf. Table SII].

The ground state of the antiferromagnetic Ising model on the isotropic triangular lattice is known to be macroscopically degenerate [25]. This degeneracy is lifted by the introduction of the anisotropy, $K_{(1,\sqrt{3})} \neq K_{(2,0)}$, and by the longer range $K_{(0,2\sqrt{3})}$: by comparing the energies of the elementary triangles (shown in yellow), we end up with three different phases with energies $2K_{(1,\sqrt{3})} + K_{(2,0)}$ (CAF), $-K_{(2,0)}$ (TDQ), and $-2K_{(1,\sqrt{3})} + K_{(2,0)}$ (FM). The phase boundary between CAF and TDQ is given by $K_{(2,0)} = -K_{(1,\sqrt{3})} > 0$ and between TDQ and FM by $K_{(2,0)} = K_{(1,\sqrt{3})} > 0$. The phases are uniquely constructed from the configurations in the elementary triangles, except for the TDQ state, where the ferromagnetic $K_{(0,2\sqrt{3})}$ selects identical Ising spins along the (0, 1) direction.

If exchanges $J_3$ are set to zero, comparing $K_{(1,\sqrt{3})}$ and $K_{(2,0)}$ from Table SII the phase transition points are

$$J_2 = -0.0616D \quad (S22)$$

and

$$J_2 = -0.0748D \quad (S23)$$

between CAF and TDQ, and between TDQ and FM, respectively, in the thermodynamic limit. Taking into account the longer range $K_{\delta}$’s, the corresponding $J_2$ values are modified to

$$J_2 = -0.0621D \quad (S24)$$

These agree nicely with the numerical values from Monte Carlo simulations.

Precisely at the phase transition point the energies of different elementary triangles become equal. In the absence of the long range $K_{\delta}$ with $|\delta| \leq \sqrt{11}$ there would be a degeneracy at the phase transition point, since the degenerate triangular coverings do not lead to a unique state. However, in our case, this degeneracy is just the trivial twofold degeneracy of the level crossing. As a consequence, the TDQ, OZZ and CAF states have exactly the same classical energy at $T = 0$ at the phase boundary.

Let us for completeness also give the values of these interactions for the parameters calculated by Yavors'kii et al. for the Dy$_2$Ti$_2$O$_7$: The $D = 1.41K$, $J_2 = -0.14K$, and $J_3 = 0.025K$ (note $J_3 = J_{3c} = J_{3d}$) corresponds to

$$K_{(1,\sqrt{3})} = -0.035K, \quad J_2 = -0.025K, \quad (S26)$$

$$K_{(2,0)} = 0.028K, \quad (S27)$$

$$K_{(0,2\sqrt{3})} = 0.0012K, \quad (S28)$$

or $K_{(1,\sqrt{3})}/D = -0.025$ and $K_{(2,0)}/D = 0.020$. These set of parameters places Dy$_2$Ti$_2$O$_7$ in the CAF phase, close to the boundary to the TDQ (cf. Fig. 3 of the main text).

CLASSICAL MONTE CARLO SIMULATION

Details of simulations

Our classical Monte Carlo was carried out using cubic cells with periodic boundary conditions with $16 \times L^3$ Ising spins with $L = 2, 3, 4, 5$. The long-ranged dipolar interaction was handled using a pre-tabulated Ewald summation. We also included second neighbor exchange interactions. First neighbor exchange was not included since it does not lift the degeneracy of the ice states and our principal interest was in determining the nature of the ground states and the transition temperature. We were also interested in the nature of the correlations within the Coulomb regime but without concentrating on any particular spin ice material.

As is now standard for spin ice simulations, the Monte Carlo allowed for single spin flips and worm updates [5]. The worm updates allow for efficient sampling of spin ice states with a short autocorrelation time compared to simulation time scales. We simulated up to 128 temperatures simultaneously on the hydra cluster based in Garching with parallel tempering moves to assist equilibration. The highest temperature was taken below the heat capacity peak into the ice states.

We have carried out simulations to obtain the magnetic structures below the ordering temperatures and the heat capacity.
We have also looked at the spin flip component of the static structure factor $S(q)_{SF}$ which contains pinch point signatures of dipolar correlations (for details see Ref. [26]). Figure S5 shows $S(q)_{SF}$ at identical temperatures within the Coulomb phase for three different values of $J_2/D$ - one with couplings chosen within the CAF phase (in fact with $J_2 = 0$) (Fig. S5a), one in the middle of the TDQ region (Fig. S5b) and one in the FM regime (Fig. S5c). These structure factors are in qualitative agreement with those obtained from the soft-spin mean field theory, described above.

The simulations for $L = 4$ at low temperature were somewhat hampered by slow equilibration despite the presence of loop moves and parallel tempering. Whereas $L = 2$ simulations were found to be independent of the starting configuration, this ceased to be the case for $L = 4$. We therefore conducted simulations by starting from each of the three known ordered states and also from states that are degenerate at the phase boundaries - for example the zigzag state.

**Finite-temperature phase diagram**

The finite temperature phase diagram for the $J_2 < 0$ model has been studied using classical Monte Carlo for system sizes with $128$ ($L = 2$) and $1024$ ($L = 4$) which are commensurate with all three ordered phases. We computed the heat capacity and order parameter susceptibilities for all phases and identified the transition temperature from the peak in the latter quantity which tends to differ slightly from the temperature at which there is a peak in the heat capacity. The resulting phase diagram showing transition temperature extracted for both system sizes is given in Fig. S6. The size of the points indicates the difference between different simulated temperatures. There is a small difference between the results for the two system sizes - notably the phase boundary between two different phases is almost vertical for the smaller system size while fluctuations cause the regime of stability of the TDQ state to fan out at higher temperatures for $L = 4$.

We note that, despite the presence of degenerate ice states at the phase boundaries, no new phases were observed to arise in these classical simulations at finite temperature in addition to the three that are ground states.

FIG. S6: Finite-temperature phase diagram of spin-ice with long-range dipolar interactions, as a function of competing 2nd-neighbor exchange $J_2/D$. Results are taken from competing Monte Carlo simulation of $\mathcal{H}_{DSI}$ [Eq. (SI)] for cubic clusters of 128 (filled symbols) and 1024 spins (open symbols).
over a finite range of couplings. We have explored the possibility that boundary states fan into finite temperature phases using self-consistent mean field theory in real space for \( L = 2 \). Such a conventional real space mean field theory successfully captures the finite temperature phases of the original 3D ANNNI model [28]. We find that the mean field theory confirms the picture obtained from Monte Carlo simulations.

**QUANTUM MONTE CARLO SIMULATION**

We have performed Green’s function Monte Carlo (GFMC) simulations of \( H_{\text{QDSI}} \) [S8], using methods previously developed to study the quantum dimer model on a diamond lattice [29, 30], and quantum spin-ice in the absence of long-range dipolar interactions [13, 15]. The GFMC simulations use the guiding function optimized by variational Monte Carlo (VMC) for the number of flippable hexagons, an order parameter and the hexagon-hexagon correlations [30]. We used up to 1000 walkers in GFMC. We have performed calculations for the 128, 1024, and 2000 site clusters with the full cubic symmetry of the pyrochlore lattice, and for an 80-site cluster with reduced symmetry. To test the accuracy of the method, we compared it with exact diagonalization calculations for the 80-site cluster.

Among the ordered states, the FM and CAF configurations are both isolated if the tunnelling term is restricted to hexagonal plaquettes, so their energy is just given by the diagonal terms that can be easily evaluated for all the clusters we looked at.

The quantum spin-liquid state, being disordered, was also not too difficult to simulate, allowing us to compare its energy with the diagonal energy of the FM and CAF states to obtain the phase boundary using 128 and 1024 site clusters. The data points are shown in Fig. S7. The transition from either FM or CAF states into the spin liquid does not move significantly with increasing cluster size in the \( J_2 \) range where we were able to perform the simulations. The \( S(q) \) for the quantum spin liquid, shown in Fig. 4b of the main text, was obtained from GFMC simulations on the 2000 site cluster.

However, the most challenging part of the simulations was the region where the bandwidth shown in Fig. S1 is minimal, as there are many competing configurations. The classical energies show that for \( g = 0 \) there is a range of \( J_2 \) values between the FM state and the CAF state where the TDQ is the ground state. Since this state has 32 flippable hexagons in the 128 site cluster, we can expect that increasing \( g \) should introduce fluctuations and eventually a phase transition to the spin liquid. We draw the phase boundary by observing where the order parameter for the TDQ state, given by Eq. (S15), jumps as a function of the \( g \).

At the degeneracy point \( J_2 \approx -0.0622D \) we find another configuration with the same number of flippable hexagons – the OZZ state. This phase has a lower diagonal energy for \( J_2 \) beyond the degeneracy point, and we observe a small range on the quantum phase diagram where the zigzag state is the ground state. Simulating the ordering to the TDQ or the OZZ state using GFMC method was much more demanding, therefore so far we have got the results for the smaller (128 site) cluster, (see Fig. S7).

**2nd ORDER PERTURBATION THEORY**

We can use perturbation theory to calculate the effect of the quantum fluctuations due to \( g \). The ground state energy in the second order in \( g \) is given as

\[
E^{(2)} = E^{(0)} - N_{\text{flip}} \frac{g^2}{\Delta_0},
\]

where \( E^{(0)} \) is the classical ground state energy and \( \Delta_0 \) is the energy gap between the ground state and the excited state obtained by flipping the spins on a hexagon (where \( N_{\text{flip}} \) is the number of such hexagons). These numbers are presented for the 128 an 1024 site cluster in Table SIII.

Comparing these energies close to the classical phase boundary where the TDQ, the OZZ, and the CAF are degenerate, we get that OZZ state has the lowest energy and is stabilized between the TDQ and CAF phases. The phase transition lines between the TDQ and OZZ phases
are

\[ J_2/D = -0.0621 + 0.015(g/D)^2 \] (128 sites), \hspace{1cm} (S30)

\[ J_2/D = -0.0622 - 0.003(g/D)^2 \] (1024 sites). \hspace{1cm} (S31)

Similarly, the phase boundaries between the CAF and OZZ are given by

\[ J_2/D = -0.0621 + 6.01(g/D)^2 \] (128 sites), \hspace{1cm} (S32)

\[ J_2/D = -0.0622 + 5.95(g/D)^2 \] (1024 sites). \hspace{1cm} (S33)

These phase boundaries are shown in Fig. S7. The finite size effects are small, and they are also consistent with the QMC results.

**COMMENTS ON SPIN ICE-LIKE MAGNETS**

In this section, we discuss the results of the paper in the light of specific spin ice materials and their relatives. Our discussion will make reference to Table SIV which summarizes a number of parameters for a set of these materials. In all known cases, spin ice physics arises in rare-earth magnets. This is largely because the spin-orbit coupling is large compared to the crystal field and magnetic interactions and naturally leads to strong low energy magnetic anisotropies including Ising magnetism. The anisotropy gap \( \Delta E_{CF} \) is given in the table together with \( \theta_{CW} \) which is a guide to the magnitude of the magnetic interactions. The table divides non-Kramers magnets (upper part) from Kramers magnets. The former may have magnetic single ion doublets which are guaranteed to have an Ising anisotropy whereas their Kramers counterparts have doublets protected by time reversal symmetry which need not be Ising-like. indeed, the majority of spin-ice like materials are non-Kramers, the exceptions being Dy$_2$Ti$_2$O$_7$ which has a very large magnetic moment 15/2 which facilitates the appearance of Ising magnetism and, arguably, Yb$_2$Ti$_2$O$_7$ which has large transverse exchange couplings albeit a larger Ising exchange which has led it to be dubbed a “quantum spin ice” \[10\].

The table reports the dipole moment in the ground state doublet and the resulting effective dipolar coupling. Supposing the absence of other exchange (besides nearest neighbor antiferromagnetic Ising exchange), we can use the finite temperature phase diagram (Fig. S8) and quantum phase diagram (Fig. S7) to give, respectively, estimates of the transition temperature \( T_c \) out of the ordered phase into the Coulomb phase and the critical tunneling \( g_c \) out of the ordered phase into the U(1) liquid. The dipolar coupling which depends on the squared moment varies considerably over the series so that, for example, for the Pr$_{3+}$ materials, the critical tunneling need only be of the order of 10 mK to enter the spin liquid phase.

In reality, despite the nature of the single ion doublet of the non-Kramers materials, anisotropic exchange is likely an important ingredient in determining their low temperature properties. However, the spin ices Ho$_2$Ti$_2$O$_7$, Ho$_2$Sn$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ are dominated by the Ising exchange and Dy$_2$Ti$_2$O$_7$ in particular, is very well characterized. Although these are large moment magnets and the expected \( g_c \) is comparatively large, there is evidence in Dy$_2$Ti$_2$O$_7$ of a second nearest neighbor exchange with a negative sign which reduces the bandwidth of the spin ice states and decreases \( g_c \) as discussed in the main text.

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TABLE SIV: Table of data for different materials. The dipolar coupling (column three) is computed using the moment in the ground state doublet (column four). The critical values of the $g$ coupling required to enter into the $U(1)$ liquid phase is given as is the critical temperature from the ordered dipole-induced phase into the Coulomb phase. The ninth column gives the approximate gap to the first crystal-field excitation.

| Compound          | $J$ $^a$ | $D$ (K) $^b$ | Moment ($\mu_B$) $^c$ | $J_2$ (K) | $g_c$ [mK] $^d$ | $T_c$ [mK] $^e$ | $\theta_{CW}$ (K) | $\Delta E_{CF}$ (K) |
|-------------------|---------|--------------|------------------------|----------|----------------|----------------|------------------|------------------|
| Ho$_2$Ti$_2$O$_7$ | 31      | 8            | 1.4                    | $\sim$ 10 | –              | 180            | 200              | $\sim$ 1         | 200              |
| Ho$_2$Sn$_2$O$_7$ | 33      | 8            | 1.4                    | $\sim$ 10 | –              | 180            | 200              | 1.8              | 250              |
| Pr$_2$Sn$_2$O$_7$ | 34      | 4            | 0.078                  | 2.6       | –              | 10             | 11               | 0.3              | 200              |
| Pr$_2$Zr$_2$O$_7$ | 36      | 4            | 0.07                    | 2.47 $^f$ | –              | 9              | 10               | $\sim$ 1.4       | 111              |
| Pr$_2$Ir$_2$O$_7$| 38      | 4            | 0.12                    | 3.06      | –              | 16             | 17               | –20              | 160              |
| Tb$_2$Ti$_2$O$_7$ | 39      | 6            | 0.22                    | 4 $^{[10]}$| –              | 30             | 31               | $\sim$ 19 $^f$   | 14               |
| Dy$_2$Ti$_2$O$_7$ | 42      | 15/2         | 1.4                     | $\sim$ 10 | $-0.14$ $^{[13]}$ | 180            | 200              | $\sim$ 1         | 400              |
| Yb$_2$Ti$_2$O$_7$ | 44      | 7/2          | 0.02                    | 1.15      | –              | 3              | 3                | 0.5              | 750              |

$^a$Total angular momentum of the relevant magnetic multiplet  
$^b$Dipolar coupling within the ground state crystal field doublet  
$^c$Effective moment in the CF ground state doublet  
$^d$No further neighbor exchange  
$^e$No further neighbor exchange  

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