Quantum spin ice under a [111] magnetic field: from pyrochlore to kagomé

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Quantum spin ice, modeled for magnetic rare-earth pyrochlores, has attracted great interest for hosting a U(1) quantum spin liquid, which involves spin-ice monopoles as gapped deconfined spinons, as well as gapless excitations analogous to photons. However, the global phase diagram under a [111] magnetic field remains open. Here we uncover by means of unbiased quantum Monte-Carlo simulations that a supersolid of monopoles, showing both a superfluidity and a partial ionization, intervenes the kagomé spin ice and a fully ionized monopole insulator, in contrast to classical spin ice where a direct discontinuous phase transition takes place. We also show that on cooling, kagomé spin ice evolves towards a valence bond solid similar to what appears in the associated kagomé lattice model [S. V. Isakov et al., Phys. Rev. Lett. 97, 147202 (2006)]. Possible relevance to experiments is discussed.

There exists a prototype of magnetic rare-earth pyrochlores [1] that involve a strong geometrical frustration of interactions among effective pseudospin-1/2 moments located at the vertices of a corner-sharing network of tetrahedra (Fig. 1a). For instance, many low-temperature magnetic and thermodynamic properties of Dy2Ti2O7 and Ho2Ti2O7 [2–5] are practically described by the nearest-neighbor antiferromagnetic Ising model, \[ H_{\text{Cl}} = J \sum_{\langle r, r' \rangle} S^z_r S^z_{r'}, \quad J > 0, \] where \( S_r = (S^x_r, S^y_r, S^z_r) \) represents a pseudospin-1/2 operator at a pyrochlore lattice site \( r \) in a C2-invariant set of local spin frames [6, 7] \( (e^0_\mu, e'^0_\mu, e^\pm_\mu) \) with the sublattice index \( \mu = 0, 1, 2, 3 \) (Fig. 1b). This interaction forces a 2-in, 2-out spin ice rule [2]: in each tetrahedron, the energy is minimized by two spins pointing inwards to the other two outwards from the center (Fig. 1d), in an analogy to proton displacements in hexagonal water ice [8]. This leaves a residual ice entropy associated with the macroscopic degeneracy of the spin-ice-rule vacuums. Creating 3-in, 1-out or 3-out local defects – monopoles – with which we assign a charge \( Q = +1 \) or \(-1 \) (Fig. 1e), costs half the spin-ice-rule interaction energy, \( J/2 \). These monopoles behave as static quasiparticles obeying an analogous Coulomb law and can only be excited thermally [4, 5]. The average low-temperature pseudospin and monopole charge configuration, as well as its excitation spectrum, is depicted in Fig. 2c.

On the other hand, Yb2Ti2O7 [7, 11], Tb2Ti2O7 [12], and Pr2Zr2O7 [13] have been understood as quantum spin ice [6, 14] where spin-flip exchange interactions, for instance,

\[ H_{\perp} = J_{\perp} \sum_{\langle r, r' \rangle} (S^x_r S^x_{r'} + S^y_r S^y_{r'}) , \]

become active in the background of the spin-ice-rule interaction \( H_{\text{Cl}} \). Spin flips are accompanied by a transfer of monopole charge (Fig. 1f), so that the monopoles exhibit quantum kinematics as bosonic spinons, leading to a broadening of charge-1 excitations (Fig. 2d). If the spin-ice rule interaction dominates over the kinetic energy, the monopoles remain incompressible with an energy gap in their excitations. Then, a “diamagnetic current” and the associated “flux” generated by successive
spin flips around closed paths (Fig. 1g) may be fixed. This deconfines the monopoles and leaves gapless spin excitations described by “photons” in a magnetic analogue of quantum electrodynamics [4, 15] (Fig. 2d with $B = 0$). The quantum spin ice is now in what is called a U(1) quantum spin liquid state [15] which can also be viewed as a quantum pyrochlore neutral monopole insulator. This has been evidenced by quantum Monte-Carlo simulations on the minimal $H_{\text{XXZ}} = H_{\perp} + H_{\perp}$ for $0 > J_{\perp} > J_{\perp}^{\text{sf}} = -0.104J$ [16, 17]. Conversely, if the kinetic energy dominates over the spin-ice-rule interaction, as is the case when $J_{\perp} < J_{\perp}^{\text{sf}}$, the monopoles are Bose-Einstein condensed and thus confined [18], resulting in a monopole superfluid (Fig. 2e). Note that the superfluid density of monopoles is proportional to a transverse spin stiffness $\rho$ [19]. Hence, a finite monopole superfluid density points to an XY ferromagnet of pseudospins.

Now, of our interest is the fate of quantum spin ice against a [111] magnetic field $B = Be_{0}$. The Hamilton-
with the magnetization $m_{R_+}$ of the “upward” oriented tetrahedron centered at $R_+$ and the sublattice vector $b_\mu$ measured from $R_+$. We have assumed that only $S_\perp^\mu$ couples to the magnetic field, as is the case for non-Kramers ions Pr$^{3+}$ and Tb$^{3+}$ [14, 20], e.g. in Pr$_2$Fe$_2$O$_7$ [21], Pr$_2$Zr$_2$O$_7$ [13], Pr$_2$Hf$_2$O$_7$ [22], and Tb$_2$Ir$_2$O$_7$ [12, 23], where $S_\perp^x$ and $S_\perp^y$ correspond to electric quadrupoles of monopoles and a long-range transverse spin order that lift the macroscopic degeneracy of the spin-ice manifold. This transition has been dubbed a monopole crystallization [26]–[29]. At $\delta Q = 1$ and $J_\perp > J_\parallel^f$, the supersolid is distinguished from the superfluid at zero field by having a finite monopole charge disproportionation. The spin stiffness is strongly anisotropic with $\rho_{(111)}$ being an order of magnitude larger than $\rho_{(111)}$, indicating that the transverse spin order is triggered by correlations within the kagomé layers.

A further increase in $B$ drives a phase transition at $B_3 \sim 4J$ to the fully ionized monopole insulator characterized by $\delta Q = 1$ and $\rho_{(111)} = \rho_{(111)} = 0$. Reflecting that the monopole supersolid emerges because of a kinetic energy gain of monopoles, this phase shrinks with decreasing $|J_\perp|$ and is absent in classical spin ice systems. The lowest-temperature results are schematically summarized in Fig. 2a, and the global phase diagram in Fig. 2b.

To understand the low-temperature properties in the kagomé spin ice plateau regime, we compute the spatial profiles of energy-integrated diffuse neutron-scattering cross-sections. Figure 4a shows the profile in the classical kagomé spin ice regime at $T = J/20$ and $B = 1.3J$. There appear short-range correlations associated with a broad peak at $q_A = \frac{2\pi}{a}(\frac{2}{3}, -\frac{2}{3}, 0)$ and symmetry-related points, in addition to a broadened pinch-point singularity at $q = \frac{2\pi}{a}(\frac{2}{3}, \frac{2}{3}, -\frac{4}{3})$ and symmetry-related points, with $a$ being the cubic lattice constant. The pattern clearly matches the experimental observation in Dy$_2$Ir$_2$O$_7$ [37]. On cooling down to $T = J/320$, short-range correlations apparently develop around the superlattice point $q_{sl}$ and symmetry-related points on the (111) plane (Fig. 4b). This correlation around $q_{sl}$ is found to be anisotropic. Along the cut $\frac{2\pi}{a}(h, -h, 0)$ within the (111) plane, the peak sharpens on cooling (Fig. 4c), while along an out-of-plane direction $\frac{2\pi}{a}(l + \frac{2}{3}, l - \frac{2}{3}, l)$, the intensity remains to be flat within errorbars (Fig. 4d). Besides, while the...
peak intensity at \(q_{sl}\) exhibits a logarithmic increase on cooling as in classical kagomé spin ice [25], it starts being saturated at \(T \sim J/30\), indicating that a lifting of the extensive degeneracy of the classical kagomé spin ice manifold is visible on this energy scale. Then, it restarts increasing more rapidly below \(T \sim 0.01J\) (Fig. 4e). It is likely that the ground state has a two-dimensional long-range order enlarging the unit cell by \(\sqrt{3} \times \sqrt{3}\) as in the single-layer quantum kagomé spin ice model [38] (Fig. 2f). At present, however, it is difficult to reliably collect lower temperature data on our pyrochlore model with quantum Monte-Carlo simulations. It remains open whether this valence bond solid forms a two-dimensional or three-dimensional pattern.

So far, there has been no concrete experimental evidence of the U(1) quantum spin liquid in candidate quantum spin ice materials at zero magnetic field. Nevertheless, praseodymium pyrochlores remain to be promising candidates, since diffuse neutron-scattering patterns in \(\text{Pr}_2\text{Zr}_2\text{O}_7\) at zero magnetic field [13] are consistent with the previous numerical simulation on the same model indicating the emergent photon modes [17]. Also, a step in the magnetization curve has already been observed in \(\text{Pr}_2\text{Ir}_2\text{O}_7\) [21] most likely as a precursor to the \(2/3\) magnetization plateau. A careful annealing under a [111] magnetic field might lead to the quantum kagomé valence bond solid. Then, it will also be possible to observe the monopole supersolid by increasing the field above the plateau and measuring the electric quadrupole moments with polarized neutron scattering experiments.

The monopole supersolid phase, if observed, is a manifestation of a quantumness in spin ice and of monopoles.

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represents the total spin current associated with \( S^\tau \). This is exactly half the total monopole current \( I^{\mu} \).
\[ I^{\mu} = \frac{i J}{2} \sum_{r,r'} (r-r') (S^+_r S^-_{r'} - S^-_r S^+_{r'}) \]
and therefore, the spin stiffness is nothing but the superfluid stiffness of monopoles. In the above equation, similarly to Ref. [18], we have introduced a canonical conjugate pair of directed diamond-lattice link variables of an analogous “electric field” \( E_{R,\nu} = -S_{R,\nu} + b^\dagger \) and “vector potential” \( A_{R,\nu} = i \delta_{R,\nu} \delta_{\mu,\nu} \) satisfying \( [E_{R,\nu} + b^\dagger, A_{R,\nu} + b^\dagger, E_{R,\nu} + b^\dagger] = \frac{\delta_{R,\nu}}{\delta_{\mu,\nu}} \) as well as spinon operators \( \Phi_R = e^{-i \nu R} \) and \( \Phi^\dagger_R = e^{i \nu R} \) decreasing and increasing monopole charge by 1, respectively, with \( \nu \) being a phase canonical conjugate to the monopole charge \( Q_{R} = \sum_{\mu} E_{R,\mu} + 2 \nu b^\dagger \).
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