Coulombic antiferromagnet in spin-1/2 pyrochlores with dipole-octupole doublets

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Exotic state of matter could coexist with conventional orders such that the gauge fields and fractionalized excitations could prevail in a seemingly ordered state. We explore the Coulombic antiferromagnet in the spin-1/2 pyrochlores with dipole-octupole doublets. This fractionalized antiferromagnetic state carries both antiferromagnetic order and emergent quantum electrodynamics with the gapless gauge photon and fractionalized quasiparticles. We explain the characteristic physical properties including the thermodynamics and the dynamics of this exotic state. This includes for example the anomalously large $T^3$ specific heat and the broad spinon continuum in the inelastic neutron scattering. We discuss the experimental and material’s relevance and expect this work to inspire interests in the search of exotic physics among the ordered magnets.

Exotic quantum states of matter with long-range quantum entanglement such as fractional quantum Hall effects and quantum spin liquids are characterized by emergent gauge fields and fractionalized excitations. Due to the emergent non-local gauge structures, these states are usually robust against weak local perturbations. Moreover, the emergent gauge field and fractionalization could survive even in the presence of long-range orders. This happens, for example when the residual interactions between the fractionalized quasiparticles induce the condensation of composite objects without completely destroying the internal gauge structures. Such a scenario was theoretically proposed about twenty years ago for the superconducting cuprates where the hosting exotic state was suggested to be $\mathbb{Z}_2$ topological order. Over there, the bilinear of the fermionic spinons was condensed to generate the antiferromagnetic long-range order while the fractionalization and the $\mathbb{Z}_2$ gauge structure persist. To distinguish it from the conventional antiferromagnet, this fractionalized antiferromagnet was dubbed “AF* state”. Although its connection to the cuprates remains illusive, such an exotically ordered state points to the important possibility of emergent exotic physics in the seemingly ordered systems, i.e. the coexistence of long-range order with the long-range quantum entanglement.

Despite the possibility of exoticity in the long-range ordered systems, the popular search of exotic physics is to examine spin liquid candidates among disordered magnets with frustration such that the frustration enhances the quantum fluctuations and suppresses the magnetic orders down to zero temperature. In this Letter, we consider the possibility of fractionalized antiferromagnet in the spin-1/2 quantum pyrochlore antiferromagnet with dipole-octupole doublets where the emergent U(1) gauge field and the fractionalization coexist with the antiferromagnetic order. The pyrochlore magnets have been an active topic in the modern research of quantum magnetism and have attracted quite some attention in last two decades. The classical spin ice has been observed in the pyrochlore spin ice magnets and understood based on the interacting Ising spins. The quantum counterpart, referred as pyrochlore quantum spin ice or pyrochlore ice U(1) spin liquid, is less conclusive. There have been two kinds of relevant models. Due to the low energy scales of the emergent excitations such as the gauge photons and the fractionalized excitations, the experimental side is less conclusive compared to the classical case. So far, the existing candidates that remain disorder and promising are the Tb-based, Pr-based pyrochlores with the non-Kramers doublets, and more recently the Ce-based pyrochlores, Ce₂Sn₂O₇ and Ce₂Zr₂O₇, with the dipole-octupole (DO) doublets. No such fractionalized antiferromagnet was previously obtained for the conventional Kramers doublets like Yb³⁺ ions or the non-Kramers doublets like Pr³⁺, and thus we turn to the dipole-octupole doublets and explore its properties and the possible existence. We show the system could stabilize another exotic quantum state, namely, the Coulombic antiferromagnet, in addition to the pyrochlore AF* state for the cuprates except that the gauge sector is U(1) in 3D and all the fractionalized quasiparticles are gapped. Thus, we refer this exotic state as “pyrochlore AF* state”.

FIG. 1. (Color online.) Phase diagram for $H_a$ in Eq. (3) from the gauge mean-field theory. The phase boundary between the pyrochlore AF* state and the fragmented AFM is continuous via the spinon condensation. The remaining phase boundaries are all first order. U(1) QSL refers to the pyrochlore U(1) spin liquid. The AF* state is referred as the Coulombic antiferromagnet.
To begin with, we consider the generic symmetry-allowed spin model for the DO doubllets with

\[ H = \sum_{\langle ij \rangle} \left[ J_2 S^z_i S^z_j + J_z S^z_i S^z_j + J_{xz}(S^x_i S^y_j + S^x_j S^y_i) \right] - \sum_{\langle\langle ij \rangle\rangle} J_y S^z_i S^z_j + \cdots, \]

(1)

where the spin \( S_i \) is defined on the DO doublet and \( \langle ij \rangle \) (\( \langle\langle ij \rangle\rangle \)) refers to the nearest (second) neighbors. The terms inside \( "[[\]]\) are the symmetry-allowed interactions between the nearest neighbors, while \( \cdots \) refers to other interactions such as the dipole-dipole interaction between the \( S^z \)-component and the superexchange beyond the nearest neighbors. For the unfrustrated regime of the nearest-neighbor model, the ground state can be well-understood, and no fractionalized antiferromagnet (AF*) phase was found. Thus, extra interactions and/or the frustrated regime are required to support its existence, and we have included a second-neighbor \( S^z-S^z \) interaction in our study.

Microscopically, the \( S^z(S^z \text{ or } S^y) \) component for the DO doubllet carries the magnetic dipole (octupole) moment. One should keep the \( S^z-S^z \) coupling if the dipole-dipole interaction is considered. From the symmetry analysis, however, \( S^z \) and \( S^x(S^y) \) transform identically as a magnetic dipole (octupole) under the space group. This is the symmetry reason why there exists the \( S^z-S^z \) coupling in Eq. (1). If one restricts to the nearest-neighbor model, one can apply a rotation about the \( y \)-axis to eliminate the crossing term between \( S^z \) and \( S^z \). With the further-neighbor interactions, it becomes impossible because such a rotation immediately re-generates the crossing terms from the further neighbors. After the rotation, Eq. (1) takes a new form,

\[ H = \sum_{\langle ij \rangle} \left[ \tilde{J}_2 \tilde{S}^z_i \tilde{S}^z_j + \tilde{J}_z \tilde{S}^z_i \tilde{S}^z_j + J_y \tilde{S}^y_i \tilde{S}^y_j \right] - \sum_{\langle\langle ij \rangle\rangle} J_y \tilde{S}^z_i \tilde{S}^z_j + \cdots, \]

(2)

where \( \tilde{S}^z_i = \cos \theta S^z_i + \sin \theta S^y_i, \tilde{S}^x_i = \cos \theta S^z_i - \sin \theta S^y_i, \tilde{J}_2 \) and \( \tilde{J}_z \) are the rotated couplings and are related to the old ones, and the crossing term reappears. As we show below, the irremovable crossing term is responsible for the emergence of the pyrochlore AF* state from the U(1) spin liquid.

Since other interactions in “…” necessarily renormalize the \( J_2 \) interactions, to capture the qualitative physics, we here consider an alternative model with the renormalized couplings,

\[ H_a = \sum_{\langle ij \rangle} \left[ \tilde{J}_2 \tilde{S}^z_i \tilde{S}^z_j - \tilde{J}_z (\tilde{S}^z_i \tilde{S}^z_j + \tilde{S}^y_i \tilde{S}^y_j) \right] - \sum_{\langle\langle ij \rangle\rangle} J_{2xz} (\tilde{S}^z_i \tilde{S}^z_j + \tilde{S}^z_i \tilde{S}^z_j). \]

(3)

To avoid further complication, we have set \( \tilde{J}_2 = J_y = -\tilde{J}_z \). \( H_a \) is our minimal model to reveal the pyrochlore AF* state.

We start from the large antiferromagnetic \( J_x \) regime and consider the instability to the nearby phases. With the large antiferromagnetic \( J_z \), the system prefers the “two-plus two-minus” ice configuration for \( \tilde{S}^z \) and realizes a pyrochlore U(1) spin liquid with the perturbed quantum fluctuations. This is a reasonable starting point because both the pyrochlore U(1) spin liquid and the AF* state share the same gauge structure. In this limit, the system is characterized by the emergent U(1) gauge field and the fractionalized excitations. To reveal it, we implement the spinon-gauge construction and express the spin operators as

\[ \tilde{S}^x_{r,r+e_\mu} \equiv \tilde{S}^x_r + e_\mu, \quad \tilde{S}^y_{r,r+e_\mu} = \Phi^\dagger_r \tilde{S}^y_{r+e_\mu} \Phi^\dagger_r, \]

(4)

\[ \tilde{S}^z_{r,r+e_\mu} = \tilde{S}^z_r, \quad [\Phi^\dagger_r, \tilde{S}^z_r] = 0. \]

(5)

where the pyrochlore spin is now interpreted as sitting on the link connecting the centers \( r \) and \( r + e_\mu \) of the neighboring tetrahedra. The tetrahedra centers form a diamond lattice, and \( e_\mu \) refers to the four nearest-neighbor vectors that connect the I sublattice sites to the II sublattice sites. Here \( \tilde{S}_{r,r+e_\mu} \) is a spin-1/2 variable that corresponds to the emergent U(1) gauge field. The spinons carry the emergent gauge charge, and \( \Phi^\dagger_r \) (\( \Phi_r \)) creates (annihilates) a spinon at the diamond site \( r \) such that the spinon particle number \( Q_r \) satisfies

\[ [\Phi^\dagger_r, Q_r] = \Phi^\dagger_r \delta_{rr'}, \quad [\Phi^\dagger_r, Q_{rr'}] = -\Phi^\dagger_r \delta_{rr'}. \]

(6)

As the Hilbert space is enlarged by the spinon-gauge construction, the constraint \( Q_r = \eta_r \sum_{\mu} \tilde{S}^x_{r,r+e_\mu} \) is imposed. The spinon-gauge construction captures the nature of the pyrochlore U(1) spin liquid as a string-net condensed phase, where \( \tilde{S}^z_r \) corresponds to the shortest open string with the spinons at the two ends. The model \( H_a \) becomes

\[ H_a = \sum_r \frac{J_x}{2} \tilde{S}^x_r \tilde{S}^x_r - \sum_{r, \mu \neq \nu} \frac{J_y}{2} \tilde{S}^y_{r,r+e_\mu} \tilde{S}^y_{r,r+e_\nu} - \sum_{r \in \eta} \sum_{\mu} \sum_{j \in [r,r+e_\mu]} \frac{J_{2xz}}{2} \Phi^\dagger_r \tilde{S}^z_{r,r+e_\mu} \tilde{S}^z_{r,r+e_\mu} + h.c. \]

(7)

where \([r, r+e_\mu]_2\) refers to the set of the second neighbors from this site at \( r + e_\mu/2 \). To solve \( H_a \), we decouple it into the
behaves as such a transition is an Anderson-Higgs’ transition. The vis-
r(1) spin liquid and the pyrochlore AF
gram is depicted in Fig. 1. Two exotic phases, the pyrochlore
form throughout the system. The gauge mean-field phase dia-
36
r(1) states in Fig. 1 is first order. Both states have gapped
order. The fragmented AFM in Fig. 1 is a conventional anti-
spinon and gapless r(1) gauge photon excitations, while the
two states in Fig. 1 is first order. Both states have gapped
order is present. This is a bit different from the case without
inter-sublattice hopping τ2 ̸= 0 when the magnetic
order is present. This is a bit different from the case without
the sublattice mixing where the spinon number is separately
conserved on each diamond sublattice and the two spinon
bands are degenerate. In our case here the two spinon dis-
perations are not degenerate, and we have
\[ \omega_\pm(k) = \sqrt{2J_2} |\lambda - t_1 \sum_n \cos(k \cdot a_n) + t_2 \sum_\mu e^{i k \cdot e_\mu}|^{\frac{1}{2}}, \]
where \{a_n\} refers to the twelve second-neighbor vectors on
the diamond lattice, and \( \lambda \) is the Lagrangian multiplier used to
\[
H_{\text{spinon}} = \sum_r \frac{j_r}{2} Q_r^2 - \sum_{r \mu \neq \nu} \frac{1}{2} J_{x} \chi_1 \Phi_{r+\eta_\mu e_\mu} \Phi_{r+\eta_\nu e_\nu} - \sum_{r \in I} \sum_\mu 6J_{2xz} \chi_2 (\Phi_{r+\eta_\mu e_\mu} + \Phi_{r+\eta_\nu e_\nu} \Phi_{r}),
\]
\[
H_{\text{gauge}} = -\sum_{\langle ij \rangle} \tilde{J}_I (\hat{s}_i^x \hat{s}_j^x + \hat{s}_i^y \hat{s}_j^y) - \sum_{\langle \langle ij \rangle \rangle} J_{2xz} I_2 (\hat{s}_i^x \hat{s}_j^x + \hat{s}_i^y \hat{s}_j^y),
\]
where we have set
\[
\chi_1 = \langle \hat{s}_i^x \hat{s}_j^x \rangle, \quad \text{for } \langle ij \rangle,
\]
\[
\chi_2 = \langle \hat{s}_i^+ \hat{s}_j^y \rangle, \quad \text{for } \langle \langle ij \rangle \rangle,
\]
and
\[
I_1 = \langle \Phi_{r}^\dagger \Phi_{r^*} \rangle, \quad \text{for } \langle \langle ij \rangle \rangle,
\]
\[
I_2 = \langle \Phi_{r}^\dagger \Phi_{r^*} \rangle, \quad \text{for } \langle ij \rangle.
\]
These parameters are solved self-consistently. Due to the spatial uniformity of the model, these parameters are uniform throughout the system. The gauge mean-field phase diagram is depicted in Fig. 1. Two exotic phases, the pyrochlore U(1) spin liquid and the pyrochlore AF* state, occupy the regions with small \( J_{x} \) and \( J_{2xz} \). The transition between these two states in Fig. 1 is first order. Both states have gapped spinon and gapless U(1) gauge photon excitations, while the pyrochlore AF* state has an antiferromagnetic all-in-all-out order. The fragmented AFM in Fig. 1 is a conventional antiferromagnet with an all-in-all-out order, and can be obtained from the AF* state via the spinon condensation at the \( \Gamma \) point. Such a transition is an Anderson-Higgs’ transition. The visible part of the magnetic order is in the \( S^z \) component and behaves as
\[
\langle \hat{S}_r^z \rangle = \cos \theta \langle \hat{S}_r^x \rangle + \sin \theta \langle \hat{S}_r^y \rangle = \frac{1}{2} \cos \theta [\langle \Phi_{r}^\dagger \Phi_{r^*} \rangle \langle \hat{s}_r^x \rangle + \text{h.c.}] + \sin \theta \langle \hat{s}_r^x \rangle. 
\]
The “fragmented AFM” is used to capture this moment fragmenta-
tion where the ordered momentum is fragmented into
the gauge link piece and the spinon condensate piece. Al-
though the \( S^x \) moment also develops order, it is invisible or
hidden due to its magnetic multipolar nature. Moreover,
the \( S^z \) moment, despite being ordered, could simultaneously
function as a disordering operator to flip the \( S^x \) order and gen-
erate the magnetic excitations.
From Eq. (14), it is clear that the all-in all-out \( S^z \) order appears when there exists the spinon tunneling between two diamond sublattices and/or a non-vanishing emergent gauge field. Due to the generic coupling between \( S^x \) and \( S^z \) or between \( \hat{S}_x \) and \( \hat{S}_y \), these two conditions are actually con-
comitant. In the above, we have explicitly shown that the py-
rochlore AF* state appears from the irremovable coupling be-
tween \( \hat{S}_x \) and \( \hat{S}_y \) and supports both contributions in Eq. (14)
non-vanishing. It is also possible that, the spinon interaction
leads to the condensation in the spinon particle-hole channel
and results in an antiferromagnetic order. The key physical
properties of the pyrochlore AF* state, however, are indepen-
dent from the physical origin and are discussed below.

Despite the presence of the all-in all-out order, the quantum
fluctuations of the pyrochlore AF* state are still governed by
the fractionalized spinons and the emergent U(1) gauge fluctua-
tions. Thus, the gapless U(1) gauge photon is responsible for
the \( T^3 \) specific heat at low temperatures. Due to the low en-
ergy scale of the exchange coupling, the coefficient of the \( T^3 
state are still governed by
specific heat should be quite large and visible experimentally.
We further explore the spectroscopic consequences of the
pyrochlore AF* state. Due to the fractionalized nature of this
state, the excitation spectrum should be quite different from
the spin-wave excitation for the conventional ordered antifer-
romagnet. This can be analyzed from a more phenomenolog-
ical treatment that introduces the all-in all-out order on top of
the fractionalized spin liquid state. The resulting spinon
Hamiltonian will be of an identical structure as Eq. (8), and
we write it down here,
\[
H_{\text{AF*}} = \sum_r \frac{j_r}{2} Q_r^2 - \sum_{r \mu \neq \nu} \sum_\mu t_1 \Phi_{r+\eta_\mu e_\mu} \Phi_{r+\eta_\nu e_\nu} - \sum_{r \in I} \sum_\mu 6J_{2xz} \chi_2 (\Phi_{r+\eta_\mu e_\mu} + \Phi_{r+\eta_\nu e_\nu} \Phi_{r}), 
\]
where the inter-sublattice hopping \( t_2 \neq 0 \) when the magnetic
order is present. This is a bit different from the case without
the sublattice mixing where the spinon number is separately
conserved on each diamond sublattice and the two spinon
bands are degenerate. In our case here the two spinon dis-
perations are not degenerate, and we have

\[
\omega_\pm(k) = \sqrt{2J_2} |\lambda - t_1 \sum_n \cos(k \cdot a_n) + t_2 \sum_\mu e^{i k \cdot e_\mu}|^{\frac{1}{2}}, 
\]
where \{a_n\} refers to the twelve second-neighbor vectors on
the diamond lattice, and \( \lambda \) is the Lagrangian multiplier used to

| Phases          | \( \langle \Phi \rangle \) | \( \langle \hat{s}^x \rangle \) | \( \langle \hat{s}^\pm \rangle \) | \( \langle S^x \rangle \) | \( \langle S^z \rangle \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| U(1) QSL        | 0               | 0               | 0               | 0               | 0               |
| AF* state       | 0               | 0               | 0               | 0               | 0               |
| Fragmented AFM  | 0               | 0               | 0               | 0               | 0               |

| TABLE I. Description of each phase within gauge mean-field theory. |
and the other two are dispersive. The dispersion for the fragmented AFM in the Supplementary material for the pyrochlore AF\textsuperscript{∗} state. The magnetic transition\textsuperscript{39} in Nd\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7} was found to be continuous\textsuperscript{40}. It would be illuminating to examine the critical exponents at the transition.

Below the ordering transition, Nd\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7} shows an anomalously large $T^\gamma$ specific heat, and Ref. 40 expected a linearly dispersive mode with an excitation velocity $v_\text{ex} = 55\text{m/s}$. There are two reasons against the Goldstone magnon mode interpretation for this mode. First, the Nd\textsuperscript{3+} ground state doublet is a DO doublet\textsuperscript{19} and is well separated from the excited ones by a crystal field gap of 26meV\textsuperscript{40} such that the effective spin-$1/2$ moment from the ground states captures the magnetic properties below $\sim 20\text{K}$. The effective model does not have any continuous symmetry\textsuperscript{19} to support gapless Goldstone modes, nor have an accidental continuous degeneracy to support pseudo-Goldstone modes via quantum order by disorder\textsuperscript{41,42}. Second, how about a fine-tuned spin model that is close to the point with a continuous spin symmetry? To obtain the all-in all-out order, the model should be a ferromagnetic model with a continuous symmetry. Little frustration would be expected for the continuous ferromagnetic case, which is incompatible with the frustrated nature of the slow paramagnetic spin dynamics from the inelastic neutron and $\mu$SR measurements\textsuperscript{40,43}. Moreover, the ordered fraction of Nd\textsuperscript{3+} moments is not small\textsuperscript{40}, so it is unlikely to be proximate to a quantum transition with gapless critical modes. If the pyrochlore AF\textsuperscript{∗} state proposal for Nd\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7} is relevant, $v_\text{ex}$ would be interpreted as the speed of emergent gauge photon. To further examine the proposal, we suggest the inelastic neutron scattering measurement to directly detect the gauge photon as well as the continuum of the spinons and the electric monopoles.

In contrast to Nd\textsubscript{2}Sn\textsubscript{2}O\textsubscript{7}, Nd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and Nd\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7} are deep in the "fragmented AFM" state with an all-in all-out order in the $S^2$ component and the well-defined spin-wave modes\textsuperscript{44–48}. As the actual order involves the hidden $S^2$ component, the $S^2$ operator is then responsible for flipping the order in $S^2$ in addition to having the order within itself. This interesting moment fragmentation\textsuperscript{49} arises from the $J_{xx}$ crossing term\textsuperscript{19} in Eq. (1), and has been well-understood from the peculiar microscopic properties and the model for the DO doublet of the Nd\textsuperscript{3+} ions\textsuperscript{44,47,48}. Here we do not get into too much details. Another Nd-compound Nd\textsubscript{2}GaSbO\textsubscript{7} with the all-in all-out order was experimentally studied and the moment fragmentation physics was absent\textsuperscript{50}. The continuum-like feature in the ordered regime seems more compatible with the continuous excitations of the AF\textsuperscript{2} state. Due to the intrinsic disorder, however, more information needs to be collected and examined.

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![FIG. 2. Spinon continuum along the high symmetry momentum lines of the pyrochlore AF\textsuperscript{∗} state. Here $t_1 = 0.025$, $t_2 = 0.02$, and $J_z$ is set to unity.](image)
Here we list the conventions for the coordinates for the main text and this Supplementary material. The pyrochlore lattice has four sublattices, and the coordinates of the reference points from each sublattice are given as

0th sublattice: \( \mathbf{b}_0 = (0, 0, 0) \), \((A1)\)

1st sublattice: \( \mathbf{b}_1 = (0, \frac{1}{4}, \frac{1}{4}) \), \((A2)\)

2nd sublattice: \( \mathbf{b}_2 = (\frac{1}{4}, 0, \frac{1}{4}) \), \((A3)\)

3rd sublattice: \( \mathbf{b}_3 = (\frac{1}{4}, \frac{1}{4}, 0) \), \((A4)\)

For each site on the pyrochlore lattice, there are twelve second-neighbor sites, and the connecting vectors are different for different sublattices. This information is used in the calculation of the gauge sector of the mean-field theory and the Weiss mean-field theory in Sec. B.

The centers of the tetrahedra on the pyrochlore lattice form a diamond lattice. This is where the spinon resides. The reference points for the two diamond sublattices are

\[ \text{I sublattice: } (\pm \frac{1}{8}, \pm \frac{1}{8}, \pm \frac{1}{8}) \], \((A5)\)

\[ \text{II sublattice: } (-\frac{1}{8}, -\frac{1}{8}, -\frac{1}{8}) \], \((A6)\)

The four nearest-neighbor vectors on the diamond lattice are given as

\[ \mathbf{e}_0 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \], \((A7)\)

\[ \mathbf{e}_1 = (\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}) \], \((A8)\)

\[ \mathbf{e}_2 = (-\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}) \], \((A9)\)

\[ \mathbf{e}_3 = (-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}) \], \((A10)\)

where the subindices correspond to the sublattices of the pyrochlore lattice whose positions are the mid-points of the vectors.

**Appendix B: Weiss mean-field theory**

The main text is using the exotic spinon-gauge construction and treatment because we are dealing with exotic quantum phases of matter. In the phase diagram that we found there exist the conventional ordered phase like the fragmented antiferromagnet. The conventional ordered phases can be understood from the more conventional means. Thus, we here adopt the conventional Weiss type of mean-field approach to explore the ordered phases. Although the Weiss mean-field theory fails to capture the properties of the exotic states, it is helpful to ensure the ground for the fully ordered phases in the phase diagram. For this purpose, we replace the spin operator as the mean-field order and consider the spin as a classical vector. The classical mean-field ground state is obtained by optimizing the energy of the Hamiltonian in the classical limit,

\[ H = \sum_{k} \sum_{\mu \nu} \sum_{\alpha \beta} S_{k,\mu}^{\alpha} M_{\mu,\alpha,\beta}(k) S_{-k,\nu}^{\beta} \]. \((B1)\)

**Appendix A: Conventions for the coordinates**

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36 See the Supplemental Material for detailed information.
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where $M(k)$ is the $12 \times 12$ “exchange matrix” in the momentum space, and $S_k^\alpha$ is the Fourier component of the spin vector with

$$S_i^\alpha = \frac{1}{\sqrt{N}} \sum_k S_k^\alpha e^{i k \cdot R_i}.$$  \hspace{1cm} (B2)

Here $R_i$ is the coordinate of the site $i$, $i$ belongs to the $\mu$-th sublattice, $N$ is the total number of unit cell. The exchange matrix is given as

$$M(k) = \begin{bmatrix} T_{00}(k) & T_{01}(k) & T_{02}(k) & T_{03}(k) \\ T_{10}(k) & T_{11}(k) & T_{12}(k) & T_{13}(k) \\ T_{20}(k) & T_{21}(k) & T_{22}(k) & T_{23}(k) \\ T_{30}(k) & T_{31}(k) & T_{32}(k) & T_{33}(k) \end{bmatrix},$$  \hspace{1cm} (B3)

where $T_{\mu \nu}(k)$ is the $3 \times 3$ exchange matrix between the $\mu$-th and the $\nu$-th sublattices. As there does not exist the coupling from the same sublattice, the diagonal matrices are all 0 with

$$T_{\mu \nu}(k) = 0.$$  \hspace{1cm} (B4)

For the off-diagonal ones with $\mu \neq \nu$, the contribution from the nearest-neighbor interaction is simply given as

$$\cos[k \cdot b_{\mu} - k \cdot b_{\nu}] \begin{bmatrix} J_z & 0 & 0 \\ 0 & J_y & 0 \\ 0 & 0 & J_z \end{bmatrix}.$$  \hspace{1cm} (B5)

The contribution from the second neighbor interaction is more complex. There exist 12 second neighbors for each site and they belong to different sublattices. After a careful listing, one obtains for the interaction $\sum_{\langle ij \rangle} -J_{2xz} (S_i^z S_j^z + S_i^z S_j^z)$ that, the contribution to $T_{01}(k)$ is

$$2 \cos \frac{k_y}{2} \cos \left( \frac{k_x - k_z}{4} \right) \begin{bmatrix} 0 & 0 & -J_{2xz} \\ 0 & 0 & 0 \\ -J_{2xz} & 0 & 0 \end{bmatrix},$$  \hspace{1cm} (B6)

due to the crossing coupling $J_{2xz}$. The $S_z$ order works as an effective uniform Zeeman coupling to the $S_z$ moment through the crossing coupling $J_{2xz}$. Once $S_z$ develops an uniform order (for example from the $J_z$ coupling), it immediately polarizes $S_x$ and generates a $S^x$ order even when there exists a nearest-neighbor antiferromagnetic $S_x$-$S_x$ interaction.

**Appendix C: Calculation for gauge mean-field theory**

We sketch the calculation of the phase diagram and the spinon excitation within the gauge mean-field theory. We first...
consider the gauge field sector because it is much simpler than the spinon sector. The gauge field mean-field Hamiltonian is given as

$$H_{\text{gauge}} = -\sum_{\langle ij \rangle} \tilde{J}_i I_1 (\tilde{s}_i \tilde{s}_j + s_i s_j) - \sum_{\langle ij \rangle} J_{2xz} I_2 (\tilde{s}_i^x \tilde{s}_j^z + \tilde{s}_i^z \tilde{s}_j^x).$$  \hspace{1cm} (C1)

It is clear from the spinon mean-field Hamiltonian $H_{\text{spinon}}$, both $I_1$ and $I_2$ are positive. Thus, this ferromagnetic like interaction in Eq. (C1) is quite straightforward to solve with a simple classical treatment. We choose a mean-field ansatz with

$$\langle s_i^z \rangle = \frac{1}{2} \cos \phi,$$  \hspace{1cm} (C2)

$$\langle s_i^x \rangle = \frac{1}{2} \sin \phi,$$  \hspace{1cm} (C3)

where $\phi$ should be determined. The energy of $H_{\text{gauge}}$ is optimized by $\phi$ that satisfies

$$\tan(2\phi) = \frac{4I_2 J_{2xz}}{I_1 J_{\perp}}.$$  \hspace{1cm} (C4)

The gauge mean-field parameters, $\chi_1$ and $\chi_2$, are then obtained as

$$\chi_1 = \langle s_i^+ s_j^- \rangle = \langle s_i^+ \rangle \langle s_j^- \rangle = \frac{1}{4} \cos^2 \phi,$$  \hspace{1cm} (C5)

$$\chi_2 = \langle s_i^+ s_j^z \rangle = \langle s_i^+ \rangle \langle s_j^z \rangle = \frac{1}{4} \cos \phi \sin \phi.$$  \hspace{1cm} (C6)

Due to the ferromagnetic interaction in $H_{\text{gauge}}$, the mean-field parameters, $\chi_1$ and $\chi_2$, are uniform throughout the lattice. Equipped with the above results, one can proceed to solve for the spinon sector. The spinon sector Hamiltonian is given as

$$H_{\text{spinon}} = \sum_r \frac{\tilde{J}_r}{2} Q_r^2 - \sum_r \sum_{\mu \neq \nu} \frac{1}{2} \tilde{J}_r \chi_1 \Phi^\dagger_\nu \Phi_\nu e_\mu \Phi_{\nu \mu} e_\nu$$

$$- \sum_{\rho \in \rho_1} \sum_{\mu \neq \nu} 6J_{2xz} \chi_2 \langle \Phi^\dagger_\nu \Phi_\nu e_\mu + \Phi^\dagger_\mu \Phi_\mu e_\nu \rangle.$$  \hspace{1cm} (C7)

It was found to be more convenient to use a rotor representation for the spinon operator such that $\Phi_r = e^{-i\omega_r}$ and $|\Phi_r| = 1$. This approximation neglects the amplitude fluctuation of the spinon fields and should be reasonable in the regimes where the spinon matter drives the physics.

To implement the constraint, we introduce a Lagrangian multiplier $\lambda$ such that

$$H_{\text{spinon}} \rightarrow H_{\text{spinon}} + \sum_r \lambda_r (\Phi^\dagger_\nu \Phi_r - 1),$$  \hspace{1cm} (C8)

where $\lambda_r$ should be determined self-consistently from the modified spinon Hamiltonian and satisfy

$$\langle \Phi^\dagger_\nu \Phi_r \rangle = 1$$  \hspace{1cm} (C9)

on every site. It is now more convenient to use path integral formulation to solve the spinon sector. In a coherent state path integral, we integrate out the “momentum-like” field $Q_r$ and establish the partition function as

$$Z = \int D\Phi D\Phi e^{-S - \sum_r \int d\tau \lambda_r (\Phi^\dagger_\nu \Phi_r - 1)}.$$  \hspace{1cm} (C10)

Here the effective action $S$ has the form as

$$S = \int d\tau \sum_r \frac{\left| \tilde{J}_r \Phi_r \right|^2}{2J_x} - \sum_r \sum_{\mu \neq \nu} \frac{1}{2} J_r \chi_1 \Phi^\dagger_\nu \Phi_\nu e_\mu e_\nu$$

$$- \sum_{\rho \in \rho_1} \sum_{\mu \neq \nu} 6J_{2xz} \chi_2 (\Phi^\dagger_\nu \Phi_\nu e_\mu + \Phi^\dagger_\mu \Phi_\mu e_\nu).$$  \hspace{1cm} (C11)

In a saddle point approximation, we have $\lambda_r = \lambda$. This is also demanded by the uniform state requirement. The spinon dispersion can be immediately read off from Eq. (C11) and Eq. (C10), and are given as

$$\omega_+ (k) = \sqrt{2J_x} \left[ \lambda - \frac{J_x \chi_1}{2} \sum_{\{a_n\}} \cos (k \cdot a_n) + \frac{6J_{2xz} \chi_2}{\sum_{\{a_n\}}} \frac{1}{\omega_+ (k)} \right]^{1/2},$$  \hspace{1cm} (C12)

where $\{e_\mu\}$ ($\{a_n\}$) refers to the set of 4 first-neighbor (12 second-neighbor) vectors on the diamond lattice. In both the pyrochlore U(1) spin liquid and the pyrochlore AF state, the spinons are fully gapped. Once it becomes gapless, the spinons will be condensed and generate magnetism of some sorts.

The mean-field parameters, $I_1$ and $I_2$, as well as the spinon amplitude, are the spinon bilinears. It is quite convenient to evaluate from the path integral approach. We find that

$$\langle \Phi^\dagger_\nu \Phi_r \rangle = \frac{1}{2N_{\text{uc}}} \sum_k \frac{1}{\omega_+ (k)} + \frac{1}{\omega_+ (k)},$$  \hspace{1cm} (C13)

and this quantity should be equal to 1. Here $N_{\text{uc}}$ refers to the total number of unit cell. Moreover, for the second-neighbor sites $\langle \Phi^\dagger_\nu \Phi_r \rangle$, we have

$$I_1 = \langle \Phi^\dagger_\nu \Phi_r \rangle$$

$$= \frac{1}{2N_{\text{uc}}} \sum_k e^{ik \cdot a_n} \frac{1}{\omega_+ (k)} + \frac{1}{\omega_+ (k)}.$$  \hspace{1cm} (C14)
where \( a_n \) is the vector connecting \( r' \) and \( r \). Due to the spatial uniformity, \( I_1 \) is uniform and real. For the first-neighbor sites \( \langle rr' \rangle \), we have

\[
I_2 = \langle \Phi_r^\dagger \Phi_{r'} \rangle = \frac{1}{2N_{u.c.}} \sum_k e^{-i k \cdot e_u} \left\{ \sum_{\mu} \delta_n^\mu \left[ \sum_{\nu} e^{i k \cdot e_n} \frac{1}{\omega_+(k)} - \frac{1}{\omega_-(k)} \right] \right\},
\]

(C15)

where \( e_u \) is the vector connecting \( r' \) and \( r \). Here \( I_2 \) describes the inter-sublattice hopping/hybridization on the diamond lattice. It is zero in the absence of the magnetic order, and the two spinon bands are degenerate. We should emphasize that, in the calculation of \( I_1 \) and \( \langle \Phi_r^\dagger \Phi_{r'} \rangle \), we are working with the gapped spinons. The parameters \( I_1 \) and \( I_2 \) are then feed back to the gauge field sector. We solve the spinon sector and the gauge field sector together self-consistently. The self-consistent mean-field results are finally determined based on their variational energy \( \langle H_a \rangle \) where \( H_a \) is given in Eq. 7 of the main text. We evaluate \( \langle H_a \rangle \) with respect to the gauge mean-field states as

\[
\langle H_a \rangle = \sum_r \frac{\tilde{J}_x}{2} Q_r^2 - \sum_r \sum_{\mu \neq \nu} \frac{\tilde{J}_{\mu \nu}}{2} \langle \Phi_r^\dagger \Phi_{r'} \rangle \Phi_r^{\dagger \nu} \Phi_{r'}^{\nu} \Phi_r^{\mu} \Phi_{r'}^{\mu} + 2J_{xz} \chi^2 (r - r' + e_{\mu}) \chi^2 (r_{\mu} + e_{\mu}) \frac{1}{2} \left[ \omega_+(k) + \omega_-(k) \right] - 12 \tilde{J}_x \chi_1 N_{u.c.} - 48 J_{2xz} \tilde{I}_2 N_{u.c.},
\]

where in the evaluation of the first kinetic energy term, we have made use of the factor that, for each harmonic oscillator, the kinetic energy of the ground state is simply \( 1/2 \) of the total zero-point energy. As this is a complex field, we have an extra factor of 2 for the kinetic energy part. The remaining contributions are simply evaluated against their mean-field values in the real space.

**Appendix D: Spinons in U(1) spin liquid**

The spinons in both pyrochlore U(1) spin liquid and the pyrochlore AF* state are fully gapped. The difference is that, for the pyrochlore U(1) spin liquid under consideration in Fig. 1, the spinons are degenerate, while for the pyrochlore AF* state, the spinons are not degenerate due to the inter-sublattice hopping from the magnetic order. As a comparison, we plot the spinon continuum for the pyrochlore U(1) spin liquid in Fig. 4. The spinon dispersion is obtained from Eq. 11 of the main text by setting \( t_2 = 0 \). This spinon dispersion is equivalent to \( J'_z = 0.1 \tilde{J}_z \) in Fig. 1 of the main text. Although this is not a parallel comparison, the bandwidth of the spinon continuum is much reduced in the pyrochlore U(1) spin liquid.

**Appendix E: With dominant \( \tilde{S}_x \) interaction**

Throughout this paper, we have considered a predominant and frustrated \( \tilde{S}_x \) interaction and analyzed the resulting magnetic orders and phases. In fact, due to the identical symmetry property, it would be qualitatively equivalent to consider the case with a predominant and frustrated \( \tilde{S}_x \) interaction. One can still obtain the pyrochlore U(1) spin liquid, the pyrochlore AF* and the fragmented AFM states. The procedures are identical to the ones that have been used in this paper, and the phases have qualitatively the same physical properties. The reason to select the predominant \( \tilde{S}_x \) interaction is based on the Curie-Weiss temperature. For the nearest-neighbor XYZ model for the DO doublet, we have

\[
\Theta_{CW} = \frac{1}{2} J_z.
\]

(E1)

The Curie-Weiss temperature of Nd$_2$Sn$_2$O$_7$ between 5K and 15K is \(-0.32K\). Even though the further neighbor interactions would modify Eq. (E1), this still give a rough estimate that \( J_z \) is more likely to be ferromagnetic. Thus, we consider a predominant and frustrated \( \tilde{S}_x \) interaction in this paper. In the end, \( \tilde{S}_x \) and \( \tilde{S}_z \) are simply notations for calculation, only the physical \( \tilde{S}_x \) and \( \tilde{S}_z \) are meaningful.

**Appendix F: Spinon interactions**

In this paper, we have considered the mechanism of mutual induction between the gauge link and the gauge field as the mechanism for the pyrochlore AF* state. It is also possible that, the magnetic order is induced by the condensation of spinon bilinears in the particle-hole channel from the spinon interaction. The spinon interaction is universally present in the pyrochlore U(1) spin liquid. The more significant ones are the short-range interaction from the exchange interaction. In fact, in Ref. 19, the current authors and collaborators have shown that, the XYZ model already contains a significant spinon interaction. Over there, the spinon interaction was not found to generate an intermediate AF*–like state between the U(1) spin liquid and the ordered state. It is, however, still reasonable for us to vision that some other spin exchange may stabilize the pyrochlore AF* state purely from the spinon interactions.

Despite the possibility of other mechanisms, the pyrochlore AF* state, once it is realized, should have the expected physical properties. It is these exotic physical properties and the related phenomena that stand out and make the candidate system Nd$_2$Sn$_2$O$_7$ exciting.

**Appendix G: Possibility of the frustrated \( \pi \)-flux regime**

In this paper, we have chosen the 0-flux for the parent pyrochlore ice U(1) spin liquid. Although the sign of \( J_z \) is ferromagnetic, it is still possible that the rotated transverse coupling can be frustrated. In the case, one would encounter the frustrated \( \pi \) flux U(1) spin liquid. This seems to happen in
the Ce-based pyrochlore Ce₂Sn₂O₇ and Ce₂Zr₂O₇ where the candidate spin liquid was expected to U(1) spin liquid of the octupolar type.²⁷–³²

For the U(1) spin liquid, the spion realizes the lattice translation symmetry in a projective fashion and the proximate states that grow out of it would naturally break the lattice translation symmetry. For the all-in all-out magnetic order in the Nd-based pyrochlore, the magnetic unit cell is identical to the crystal unit cell, and thus the system preserves the lattice translation. Thus, we do not consider the possibility of the frustrated π-flux regime.

Appendix H: Spin-wave theory for “fragmented AFM”

It seems that the other Nd-based dipole-octupole pyrochlore magnets including Nd₂GaSbO₇, Nd₂Zr₂O₇ and Nd₂Hf₂O₇ all develop the all-in all-out magnetic order. Nd₂Zr₂O₇ and Nd₂Hf₂O₇ are well-interpreted from the picture of moment fragmentation.⁴⁴,⁴⁷–⁴⁹ While these two systems were shown to have the all-in all-out magnetic order, the inelastic neutron scattering pattern at low temperatures develops pinch-point-like structures that are reminiscent of the spin ice, indicating the presence of the spin-ice-like correlation in the spin fluctuations. The “fragmented AFM” in Fig. 1 of the main text and Fig. 3 turns to belong to the same phase as the ones that were discussed in Nd₂Zr₂O₇ and Nd₂Hf₂O₇. To capture the dynamical property of this phase, it is illuminating to compute the magnetic excitation for the fragmented AFM and compare with the spinon continuum for the U(1) spin liquid and the AF⁺ state.

As we have remarked, the fragmented AFM develops an experimentally visible order in the S⁺ component, and an invisible order in the S⁻ component. What is more, S⁺ could also function as a disordering operator to quantum mechanically flip the S⁻ order and generate the magnetic excitation. That is precisely the reason why one can observe the magnetic excitation with the inelastic neutron scattering measurement.

To compute the magnetic excitation, we stay on the horizontal axis of Fig. 1 of the main text and consider the model with

\[ H = \sum_{ij} J \tilde{S}_i \tilde{S}_j - J_\perp (\tilde{S}_i \tilde{S}_j + S^y_i S^y_j). \]  

This simplification avoids the complicated crossing coupling between S+x and S+z from the second neighbor, but still captures the fragmented nature of the ordering. This Hamiltonian in Eq. (H1) has an accidental U(1) symmetry that should be absent in the generic case. For a large J, the system develops magnetic order in the yz plane, and we choose the order to be on the S+z such that the order is smoothly connected to the generic case with a finite Jzz. We then perform the spin wave expansion and replace the spin operator with the Holstein-Primackob bosons,

\[ \tilde{S}^z_i = \frac{1}{2} - a_i^\dagger a_i, \]  
\[ \tilde{S}^x_i = \frac{1}{2} (a_i^\dagger + a_i), \]  
\[ S^y_i = \frac{1}{2i} (a_i - a_i^\dagger), \]

and the Hamiltonian in the linear spin wave theory becomes

\[ H = \sum_{\langle ij \rangle} (\tilde{J}_\perp a_i^\dagger a_j + \tilde{J}_x (a_i a_j + a_i^\dagger a_j^\dagger)) + (H6) \]

where the ‘const’ is related to the classical energy and does not influence the magnetic excitation. The magnetic excitations are depicted in Fig. 5. There exist two flat bands that arise from the frustrated interaction in the S+z component. The spin-ice-like correlation was also argued to be originated from the frustrated S+z interaction.⁴⁸ In Fig. 5, we have a gapless mode at Γ point. This is a Goldstone mode due to the U(1) symmetry breaking of the magnetic order for our model in Eq. (H1). In the generic case, we do not have such a continuous symmetry, and we should always expect a gapped spin-wave spectrum.

In the inelastic neutron scattering measurement, only the S+z−S+z correlation is directly visible. The S+z operator, under the spin wave expansion, is given as

\[ S^z_i = \cos \theta \tilde{S}^z_i + \sin \theta \tilde{S}^x_i = \cos \theta (\frac{1}{2} - a_i a_i^\dagger) + \frac{1}{2} \sin \theta (a_i^\dagger + a_i). \]  

where the ordered piece simply contributes to the magnetic Bragg peak, and the second term in Eq. (H6) generates the magnetic excitations with single magnons. Moreover, the a_i^\dagger a_i in Eq. (H6) would generate a two-magnon continuum that should appear at high energies that the ones in Fig. 5. This two-magnon continuum might have a very low intensity but seems unavoidable. So far, this two-magnon continuum has not been emphasized in the literature of the Nd-based pyrochlore magnets.