P H Y S I C A L   R E V I E W   L E T T E R S

# Dynamically Induced Frustration as a Route to a Quantum Spin Ice State in Tb$_2$Ti$_2$O$_7$ via Virtual Crystal Field Excitations and Quantum Many-Body Effects

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The Tb$_2$Ti$_2$O$_7$ pyrochlore magnetic material is attracting much attention for its *spin liquid* state, failing to develop long-range order down to 50 mK despite a Curie-Weiss temperature $\theta_{CW} \sim -14$ K. In this Letter we reinvestigate the theoretical description of this material by considering a quantum model of independent tetrahedra to describe its low-temperature properties. The naturally tuned proximity of this system near a Néel to spin ice phase boundary allows for a resurgence of quantum fluctuation effects that lead to an important renormalization of its effective low-energy spin Hamiltonian. As a result, Tb$_2$Ti$_2$O$_7$ is argued to be a *quantum spin ice*. We put forward an experimental test of this proposal using neutron scattering on a single crystal.

Magnetic frustration arises when the lattice geometry prevents a system from finding its classical ground state energy by minimizing the energy between pairs of interacting magnetic moments (spins), pair by pair. Particularly interesting are models of geometrically frustrated magnets where there exists a macroscopic number of classical ground states not related by any global symmetry [1]. A prominent class of such systems are the *spin ices* where Ising spins reside on a three-dimensional pyrochlore lattice of corner-sharing tetrahedra [2–4]. Because of their macroscopic number of quasidegenerate low-energy states, spin ice materials possess an extensive low-temperature magnetic entropy [5–7] similar to that found in the proton disordered phase of common water ice [8].

A current and exciting direction of research in frustrated magnetism is the study of low-energy effective Hamiltonians and gauge theories [9–11] to describe highly frustrated systems which, when ignoring quantum effects, display an extensive classical ground state degeneracy similarly to spin ices [4]. Despite the seemingly broad conceptual context of gauge theory approaches, there have so far been few real frustrated quantum magnetic materials identified as potential candidates for the exotic behaviors proposed by these theories [10]. In this Letter we argue that the paradoxical Tb$_2$Ti$_2$O$_7$ (TTO) pyrochlore [12–18] belongs to such a class of materials. Specifically, we use a simple model to illustrate that the starting point of the above theories, namely, a frustrated Ising spin ice Hamiltonian plus weak transverse terms, indeed constitutes the predominant part of the low-energy effective Hamiltonian, $H_{\text{eff}}$, of TTO. However, as we show below, the microscopic mechanism that leads to the "dynamically induced frustration" and the proposed spin ice assignment for TTO has heretofore escaped scrutiny. We find that frustration and the spin-ice-like structure of $H_{\text{eff}}$ dynamically emerge from virtual transitions to excited single-ion crystal field (CF) states and, most importantly, from quantum many-body effects. These transitions drastically modify the symmetries of the many-body wave functions in the low-energy sector, leading to a significant renormalization of the longitudinal (Ising) part of $H_{\text{eff}}$. This renormalization plays a crucial role for materials, such as TTO, that are naturally tuned near the boundary between a Néel ordered phase and the spin ice states. In particular, these transitions reposition TTO in the spin ice region of coupling parameter space. We are led to suggest that TTO is a novel quantum variant of the classical Ising spin ice materials studied so far [2–7,19–21].

The main reason for the interest devoted to TTO lies in its failure to develop long-range order down to at least 50 mK [12,16] despite an antiferromagnetic Curie-Weiss temperature, $\theta_{CW} \sim -14$ K [13]. Similarly to the Dy$_2$Ti$_2$O$_7$ (DTO) [5,20] and Ho$_2$Ti$_2$O$_7$ (HTO) [2,7,19] spin ices, magnetic Tb$^{3+}$ in TTO possesses a single-ion CF Ising ground state doublet with wave functions $|\Psi_0^\pm\rangle$, where $\langle\Psi_0^\pm|J^z|\Psi_0^\pm\rangle$ are the only nonvanishing matrix elements of the **J** angular momentum operator [13,21,22]. Monte Carlo simulations of a model with such classical Ising spins [6] that can only point "in" or "out" of an elementary tetrahedron [3,22] and interact via nearest-neighbor (NN) antiferromagnetic exchange [23,24] and long-range dipolar couplings predict, in dramatic contrast with the experimental findings [12–16], a transition to a four sublattice Néel order at $T_c \sim 1.2$ K [6]. A key difference between TTO and spin ices is that, in the latter, the excited CF states lie at an energy above the ground doublet several hundred times larger than the exchange and dipolar interactions and there is therefore little admixing between the excited CF states and the ground doublet induced by the spin interactions [13,21]. This is not necessarily the case for TTO where the first excited doublet lies at only $\Delta \sim$ 18.7 K above the ground Ising doublet [13]. It is therefore necessary to investigate how the $H_{\text{eff}}$ of TTO is affected by virtual quantum mechanical CF excitations.

PHYSICAL REVIEW LETTERS

The bare Hamiltonian of TTO is taken [23] as $H = H_{cf} + H_e + H_d$. $H_{cf}$ is the single-ion CF Hamiltonian [13], $H_e = \mathcal{J}\sum_{\langle i,j\rangle}\mathbf{J}_i \cdot \mathbf{J}_j$ is the NN exchange interaction and $H_d = \mathcal{D}R_{nn}^3 \sum_{(i>j)}[\mathbf{J}_i \cdot \mathbf{J}_j - 3(\mathbf{J}_i \cdot \hat{r}_{ij})(\mathbf{J}_j \cdot \hat{r}_{ij})]|\mathbf{R}_{ij}|^{-3}$ is the dipole-dipole interaction. $\mathbf{R}_{ij} \equiv \mathbf{R}_j - \mathbf{R}_i = |\mathbf{R}_{ij}|\hat{r}_{ij}$, where $\mathbf{R}_i$ is the position of atom $i$ with total angular momentum $\mathbf{J}_i$. $\mathcal{J}$ is the NN exchange coupling with the convention here that $\mathcal{J} > 0$ is antiferromagnetic. $\mathcal{D} = (\mu_0/4\pi)(g\mu_B)^2/R_{nn}^3$ is the dipolar coupling, and $g = 3/2$ is the Landé factor for $Tb^{3+}$. $R_{nn} = 3.59$ Å is the NN distance, giving $\mathcal{D} \approx 0.0315$ K [13]. To introduce the single-ion wave functions which become admixed by the spin interactions, $H_{int} = H_e + H_d$, we focus on the essential part of $H_{cf}$: its doublet ground states, $|\Psi_0^\pm\rangle$, and its lowest excited doublet states, $|\Psi_e^\pm\rangle$, at an energy $\Delta = 18.7$ K above $|\Psi_0^\pm\rangle$. The excited states above $\Delta$ do not lead to qualitatively different new physics. $Tb^{3+}$ has orbital angular momentum $\mathbf{L} = 3$, spin $\mathbf{S} = 3$, and total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ with $\mathbf{J} = 6$. We express $|\Psi_0^\pm\rangle$ and $|\Psi_e^\pm\rangle$ in terms of the eigenstates $|\mathbf{J} = 6, m_\mathbf{J}\rangle$ of $J_z$ within the fixed $\mathbf{J} = 6$ manifold. Exact diagonalization of $H_{cf}$ using the CF parameters taken from Ref. [21] for HTO, but rescaled for TTO, gives: $|\Psi_0^\pm\rangle = \alpha_4|\pm 4\rangle \pm \alpha_5|\mp 5\rangle + \alpha_2|\mp 2\rangle \pm \alpha_1|\pm 1\rangle$ and $|\Psi_e^\pm\rangle = \pm\beta_5|\pm 5\rangle + \beta_4|\mp 4\rangle + \beta_2|\pm 2\rangle \pm \beta_1|\mp 1\rangle$ [25].

*Single-tetrahedron model—exact diagonalization.—* Since the spin-spin correlations in TTO never exceed a length scale much beyond a single tetrahedron [15–17], we consider a simple model of noninteracting tetrahedra for TTO. Such approximation of independent tetrahedra explains some properties of the classical Heisenberg pyrochlore antiferromagnet model [26] and, by incorporating transverse spin fluctuations [24,27], captures rough features of the TTO neutron scattering pattern [15]. Our aim in using this approximation is to expose the generic effects of virtual CF excitations on $H_{eff}$ and the consequential physics at play near the Néel to spin ice boundary. We ignore the long-range nature of the dipole-dipole interactions in $H_d$ since it is the NN contribution of these interactions that predominantly controls the transition from the Néel phase to the spin ice state [28,29]. Henceforth, we set $\mathcal{D} = 0.0315$ K, work with fixed $\{\alpha_m, \beta_m\}$ [25], and treat $\mathcal{J}$ and $\Delta$ as independent tunable parameters.

Diagonalizing $H_{int}$ for a single tetrahedron within the space of the $4^4 = 256$ CF states, we obtain the zero temperature $\mathcal{J} - \Delta$ phase diagram shown in Fig. 1. For the classical Ising limit ($1/\Delta = 0$), we recover the transition between "Néel order" (all-in/all-out, twofold degenerate, $\mathcal{J} > 5\mathcal{D}$) and a spin ice manifold (two-in/two-out, sixfold degenerate, $\mathcal{J} < 5\mathcal{D}$). Such a classical Ising model [6,13] places TTO *above* the classical $\mathcal{J} = 5\mathcal{D}$ boundary [6,30] (horizontal dashed line), i.e., in the Néel state [13]. However, for $1/\Delta > 0$, quantum effects, due to the admixing of $|\Psi_0^\pm\rangle$ with $|\Psi_e^\pm\rangle$ via $H_{int}$, become increasingly important, as shown by the renormalized $\mathcal{J}_c(1/\Delta)$ boundary in Fig. 1 (filled circles). This boundary separates quan-
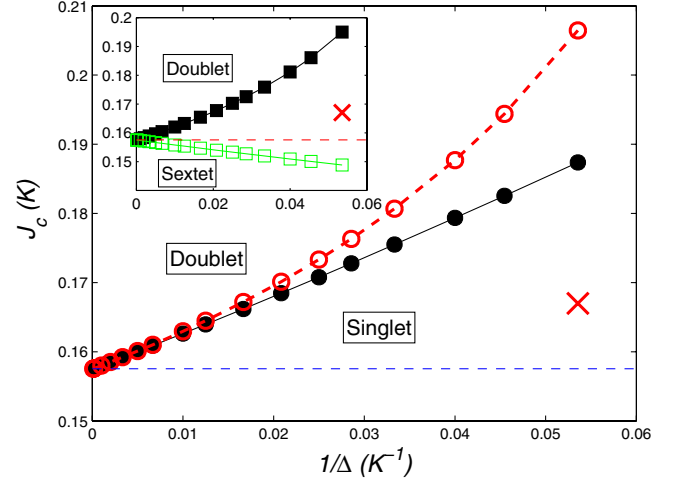


FIG. 1 (color online). $\mathcal{J} - \Delta$ phase diagram of a single tetrahedron. TTO has $\mathcal{J} = 0.167$ K and $\Delta = 18.7$ K (cross symbol). Main panel: The boundary $\mathcal{J}_c(1/\Delta)$ (filled circles) separates a ground state singlet ($\mathcal{J} < \mathcal{J}_c$) from a ground state doublet ($\mathcal{J} > \mathcal{J}_c$). The open circles show the same boundary, but as predicted by exact diagonalization of $H_{eff}$. Inset: neglecting transverse terms in $H_{eff}$ ($\lambda = 0$), the filled squares show the renormalized classical sextet-doublet boundary set by the condition $J_{ij}^{zz}(\mathcal{J}, 1/\Delta) = 0$. The open squares show the *incorrect* sextet-doublet boundary predicted when $J_{ij}^{zz}$ for pair $\langle i, j\rangle$ in $H_{eff}$ is obtained by ignoring contributions in *PHRHP* coming from (intermediate) excited states $|\Psi_e^\pm\rangle$ that belong to the two other $Tb^{3+}$ ions ($k$ and $l$) on the tetrahedron.

tum variants of the classical phases and TTO, with $\mathcal{J} = 0.167$ K and $\Delta = 18.7$ K, is now *deeply* repositioned in the singlet regime, i.e., is a *quantum spin ice*. The quantum spin ice state for $\mathcal{J} < \mathcal{J}_c$ is a singlet predominently built from the symmetrized 6 two-in/two-out otherwise degenerate classical spin ice states whose degeneracy is lifted by quantum effects. The ground state also contains a small (of order $1/\Delta$) spectral weight contribution from the excited CF $|\Psi_e^\pm\rangle$ states. The manifold of 15 lowest energy excited states consists of three triplets and three doublets spanning an energy band $\delta W \approx 0.5$ K above the ground state singlet. This energy band is further separated by a gap of 16 K to the higher energy excited states.

*Single-tetrahedron model—effective Hamiltonian.—*To shed light on the virtual CF excitation channels leading to $\mathcal{J}_c(1/\Delta)$, we construct an effective $S = \frac{1}{2}$ anisotropic Hamiltonian, $H_{eff}$. Using second order perturbation theory [31] in $1/\Delta$, we have $H_{eff} = PHP + PHRHP$, with $P = \sum_\alpha |\Phi_{0,\alpha}\rangle\langle\Phi_{0,\alpha}|$ and $R = \sum_\beta |\Phi_{e,\beta}\rangle(E_0 - E_\beta)^{-1}\langle\Phi_{e,\beta}|$, where $E_0 = \langle\Phi_{0,\alpha}|H_{cf}|\Phi_{0,\alpha}\rangle$ and $E_\beta = \langle\Phi_{e,\beta}|H_{cf}|\Phi_{e,\beta}\rangle$. Here $\{|\Phi_{0,\alpha}\rangle\}$ are the $2^4 = 16$ states constructed as direct products of the noninteracting single ion $|\Psi_0^\pm\rangle$ CF doublet ground states of $H_{cf}$. The $|\Phi_{e,\beta}\rangle$ are the remaining $4^4 - 16 = 240$ states. We recast $H_{eff}$ in the form of an effective anisotropic $S = \frac{1}{2}$ spin Hamiltonian in the individual local [111] spin $\sigma_i^z$ basis [22]: $H_{eff} = \sum_{\langle i,j\rangle;\mu,\nu} J_{ij}^{\mu\nu}\sigma_i^\mu \sigma_j^\nu$, where $\mu$, $\nu$, are spin component indices, $\sigma_i^\mu$ are Pauli matrices,

and $J_{ij}^{\mu\nu}$ are the effective anisotropic coupling constants. A constant energy term has been dropped from $H_{\text{eff}}$, while the one-site $J_i^{\mu}\sigma_i^{\mu}$ terms get eliminated by the symmetry of a tetrahedron. Figure 1 shows the singlet-doublet boundary predicted by $H_{\text{eff}}$ (open circles).

In order to expose the most important aspects of $H_{\text{eff}}$, we write it as $H_{\text{eff}} = \sum_{\langle i,j\rangle}J_{ij}^{zz}\sigma_i^z\sigma_j^z + \lambda\sum_{\langle i,j\rangle;\mu\nu}J_{ij}^{\mu\nu}(1 - \delta_{\mu z}\delta_{\nu z})\sigma_i^{\mu}\sigma_j^{\nu}$ with $J_{ij}^{\mu\nu} \equiv J_{ij}^{\mu\nu}(\mathcal{J}, 1/\Delta)$ and with $\lambda$ ultimately set to $\lambda = 1$. $H_{\text{eff}}$ contains transverse (non-Ising) $J_{ij}^{\mu\nu}(1 - \delta_{\mu z}\delta_{\nu z})\sigma_i^{\mu}\sigma_j^{\nu}$ terms where, for $\Delta = 18.7$ K, the largest transverse $J_{ij}^{\mu\nu}$ is approximately 50% of the Ising $J_{ij}^{zz}$ coupling. To generate these terms via the nonvanishing matrix elements of $J_i^z$ and $J_i^{\pm}$ between $|\Phi_{0,\alpha}\rangle$ and $|\Phi_{e,\beta}\rangle$ in *PHRHP*, it is important to retain more than the predominant $\alpha_4| \pm 4\rangle$ and $\beta_5| \pm 5\rangle$ components in $|\Psi_0^{\pm}\rangle$ and $|\Psi_e^{\pm}\rangle$. The term *PHP* corresponds to the classical [111] Ising model with NN exchange and dipolar interactions [6,13]. It is by *accident* that $\mathcal{J}/\mathcal{D}$ has a specific value such that *PHP* almost vanishes for TTO [6,13], hence allowing an opportunity for the resurgence of quantum effects via *PHRHP* in $H_{\text{eff}}$. Most importantly, the contribution of *PHRHP* to $J_{ij}^{zz}\sigma_i^z\sigma_j^z$ is *ferromagnetic*, and hence competes with the antiferromagnetic classical *PHP* Ising term and brings back frustration in TTO.

It is the key point of this Letter that the virtual excitation of a "third" ion $k$, with angular momentum $\mathbf{J}_k$ and $H = H_{ik} + H_{kj}$ in *PHRHP*, plays a crucial role in the renormalization of the classical Ising sector $J_{ij}^{zz}\sigma_i^z\sigma_j^z$ for pair $\langle i, j\rangle$ in $H_{\text{eff}}$. Failure to include these "third body" contributions to $H_{\text{eff}}$ results in an incorrect "classically renormalized" $J_{ij}^{zz}(\mathcal{J}, 1/\Delta) = 0$ boundary that is decreasing with increasing $1/\Delta$ (curve with open squares in inset of Fig. 1). Hence, it is the quantum many-body aspect of $H = H_{\text{cf}} + H_e + H_d$ that produces the interesting physics here, namely, the *correct* renormalization of the Ising part of its $H_{\text{eff}}$ from an unfrustrated system, when $1/\Delta = 0$, to that of a frustrated ferromagnetic NN spin ice model [3]. The aforementioned transverse (quantum) part of $H_{\text{eff}}$ ($\lambda \neq 0$) lifts the degeneracy of the (classical spin ice) sextet, giving a singlet ground state for an independent tetrahedron and 15 excited states within $\delta W \approx 0.5$ K above the ground state.

*Diffuse neutron scattering.*—The result that $H_{\text{eff}}$ for TTO is a NN *ferromagnetic* Ising spin ice model plus transverse terms may come as a surprise and be perceived as incompatible with neutron scattering measurements [14–16]. Indeed, the neutron scattering pattern of TTO [14–16] is qualitatively very different from that of the HTO [19] and DTO [20] spin ices. In TTO, there is an intensity maximum at 002 in the (hhl) scattering plane and a second broad maximum at 220 [15]. In spin ices, there are broad maxima at 003 and $\frac{3}{2}\frac{3}{2}1$ [4,19,20]. Therefore, the question is whether the above single-tetrahedron model characterized by a ferromagnetic Ising sector in its $H_{\text{eff}}$ gives a diffuse neutron scattering pattern compatible with experiment [14–16]. To address this question we compute

the diffuse neutron scattering intensity, $I(q)$, using standard formulas [32]: $I(\boldsymbol{q}) \propto |F(\boldsymbol{q})|^2\sum_{a,b;\alpha,\beta}[\delta_{\alpha\beta} - q_{\alpha}q_{\beta}|\boldsymbol{q}|^{-2}]\times S_{\text{diff}}^{(a,\alpha;b,\beta)}$ where $a$, $b$ are the sites on the tetrahedron, $\alpha$, $\beta$ are spin components and $F(\boldsymbol{q})$ is the $Tb^{3+}$ form factor. $S_{\text{diff}}^{(a,\alpha;b,\beta)} = \sum_{n,n'}\langle n|J^{\alpha}{}_a|n'\rangle\langle n'|J^{\beta}{}_b|n\rangle e^{i\boldsymbol{q}\cdot(r_b - r_a)}e^{-E_n/k_BT}$, where the states $\{n, n'\}$ are those whose energy $E_n$ falls within the experimental energy/frequency resolution window of $\sim 4.3$ K over which the neutron scattering intensity is energy integrated [15]. These are, incidently, the same low-energy states that span an energy $\delta W \approx 0.5$ K above the ground state. Numerical results for $I(\boldsymbol{q})/|F(\boldsymbol{q})|^2$ at $T = 9$ K are shown in Fig. 2. One finds a good match in the symmetry of the theoretical pattern in Fig. 2 with the experimental one in Fig. 6 of Ref. [15]. These results show that, despite a predominant ferromagnetic NN Ising component, $H_{\text{eff}}$ possesses sufficient low-energy transverse response (fluctuations) to account for the symmetry of the diffuse neutron scattering. These give, in particular, the intensity maximum at 002 that arise from spin fluctuations transverse to the local [111] Ising directions [15,24,27]. We propose that a scan of $I(\boldsymbol{q})/|F(\boldsymbol{q})|^2$ along the (hh2) direction may be used to ascertain whether TTO is indeed in a quantum spin ice state at low temperatures. Figure 3 shows that $I(\boldsymbol{q})/|F(\boldsymbol{q})|^2$ along (hh2) has a broad maximum at $h = 0$ in the singlet/spin ice regime, $\mathcal{J} < 0.187$ K for $1/\Delta = 0.053$ K$^{-1}$ (see main panel, Fig. 1), while it has maxima at $h = \pm\delta(\mathcal{J})$ in the doublet regime for $\mathcal{J} > 0.187$ K. The split hh2 intensity line scan as a characterization of the underlying (antiferromagnet vs spin ice) ground state is sharper the lower the temperature.

In conclusion, we have used a simple model of noninteracting tetrahedra to describe the low-temperature properties of the $Tb_2Ti_2O_7$ magnetic pyrochlore material. The present work identifies a new mechanism for dynamically induced frustration in a physical system which proceeds via CF excitations and quantum many-body effects. More specifically, we uncovered that interaction-induced fluctuations among otherwise noninteracting single-ion CF states lead to a renormalization of the low-energy effective
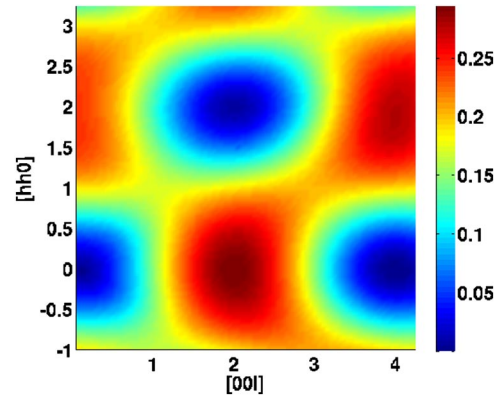


FIG. 2 (color online). Theoretical diffuse neutron scattering intensity $I(\boldsymbol{q})/|F(\boldsymbol{q})|^2$ for a single tetrahedron with four CF states per $Tb^{3+}$ in (hhl) plane at 9 K.
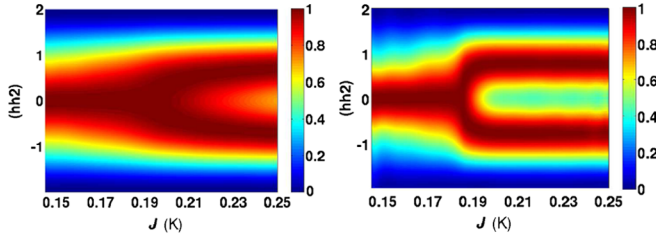
FIG. 3 (color online). Theoretical diffuse neutron scattering intensity $I(\boldsymbol{q})/|F(\boldsymbol{q})|^2$ along $\boldsymbol{q} = $ (hh2)] at 400 mK (left panel) and 40 mK (right panel) as a function of the nearest-neighbor antiferromagnetic exchange $\mathcal{J}$ for a single tetrahedron with four CF states per $Tb^{3+}$.

theory of $Tb_2Ti_2O_7$ from that of an *unfrustrated* [111] pyrochlore Ising antiferromagnet [3,6] to a frustrated nearest-neighbor spin ice model [3,4]. The remaining transverse fluctuations lift the classical icelike degeneracy and, at the single-tetrahedron level, the system is in a quantum mechanically fluctuating spin ice state, or *resonating spin ice*. The effects discussed here are likely responsible for some of the subtleties underlying the failure of this material to order at a temperature scale of 1 K [6,13,18,24]. Whether the true quantum mechanical ground state of the full lattice model of $Tb_2Ti_2O_7$ is a semiclassical long-range ordered state with finite quantum spin fluctuations [33], or a more exotic quantum ground state [9–11], is a challenging but very exciting problem for future studies. Finally, from a broader perspective, it is interesting to ask whether some of the effects discussed in this Letter may also be at work in inducing quantum fluctuations in other perplexing rare-earth materials such as $LiHo_xY_{1-x}F_4$ [34], the $Gd_3Ga_5O_{12}$ garnet [35] and the $Gd_2Ti_2O_7$ [35] and $Tb_2Sn_2O_7$ [36] pyrochlores, or the very recently discovered distorted kagome antiferromagnet $Nd_3Ga_5SiO_{14}$ [37].

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