Abstract

In this review, we provide an introduction to the physics of a series of frustrated quantum rare-earth pyrochlores. We first give a background on the microscopic single- and two-ion physics of these materials, discussing the origins and properties of their exchange interactions and their minimal low-energy effective models before outlining what is known about their classical and quantum phases. We then make use of this understanding to discuss four important material examples, \( \text{Er}_2\text{Ti}_2\text{O}_7 \), \( \text{Yb}_2\text{Ti}_2\text{O}_7 \), \( \text{Tb}_2\text{Ti}_2\text{O}_7 \), and \( \text{Pr}_2\text{Zr}_2\text{O}_7 \), covering in some detail what is known experimentally and theoretically for each and then summarizing some key questions that remain open. Finally, we offer an outlook on some alternative material platforms for realizing similar physics and discuss what we see as prospects for future investigations on these quantum rare-earth pyrochlores.

Keywords

magnetism, frustration, topological, spin liquid, pyrochlore, anisotropic exchange, spin ice, order-by-disorder
1. INTRODUCTION

Condensed matter systems perhaps serve as the widest and most diverse playground for studying the physics of classical and quantum many-body phenomena. In many cases, the interactions between the microscopic constituents of the system cooperate, or only compete weakly, to drive the pertinent degrees of freedom into some ordered state. Examples include simple crystals and metals, liquid crystals, conventional superconductors, and many magnetically ordered systems such as ferro- and antiferromagnets.

Alternatively, instead of cooperating, interactions can strongly compete, with no clear choice of the ultimate ground state of the system. One generically refers to a system with multiple interactions that have mutually incompatible tendencies as being frustrated. Systems that are highly frustrated can have many degenerate or near-degenerate states at low energy, opening a route toward realizing unconventional phases as well as potentially leading to exotic low-energy excitations.

Many paradigmatic and well-studied examples of highly frustrated condensed matter systems have arisen in the field of magnetism, in the context of both classical and quantum spin systems. Much of this effort has focused on geometrically frustrated magnets (1, 2), in which the interactions between the spins are uniform and antiferromagnetic. Here, the frustration arises solely due to the spatial arrangement of the spins preventing the desired mutually antiparallel alignment with all neighboring spins. Examples are typically drawn from Heisenberg, Ising, and $XY$-like spin systems in which the spin lattice is built from triangular or tetrahedral units; these include triangular, kagome, and pyrochlore lattices (among many others) that are naturally geometrically frustrated.

If the frustration is sufficiently high, the magnetic ordering usually expected at low temperatures can be averted entirely. One key motivation for the study of such systems is that, in some cases, the ultimate ground state can be a quantum spin liquid (QSL) (3). These are intrinsically quantum states of matter, defined by a topological order (4) of sorts that characterizes the long-range entanglement present in the ground-state wave function. This topological order is also accompanied by fractionalized excitations that can have exotic mutual statistics as well as an unusual response to typical experimental probes. Even if a QSL is not ultimately stabilized, proximity to such a state may have strong effects on the low-energy properties of the system, controlling much of its behavior. Going further, even in frustrated systems that are not proximate to a QSL, interesting physics can be at play, for example, in the development of unconventional long-range orders.

Alternative types of nongeometric frustration have attracted increasing attention in recent years. The simplest examples can be constructed straightforwardly from unfrustrated systems. For example, starting with an antiferromagnet on a bipartite lattice with nearest-neighbor exchange, one can add further neighbor exchanges that disrupt the two-sublattice Néel ordering. A different kind of nongeometric frustration has been realized recently in highly anisotropic magnets, induced by large atomic spin-orbit coupling (5). In these systems the relative importance of different anisotropic exchange interactions generates the frustration, potentially realizing an entirely different kind of limit than what can be found in geometrically frustrated systems. Examples of magnets frustrated by anisotropy are drawn from heavy transition metal magnets as well as from magnets built from lanthanide (rare-earth) and actinide series ions. A prominent set of such materials are the so-called Kitaev magnets (6) realized in $\text{Na}_2\text{IrO}_3$, $(\alpha, \beta, \gamma)-\text{Li}_2\text{IrO}_3$, and $\alpha$-$\text{RuCl}_3$, whose low-energy physics is close to Kitaev’s celebrated honeycomb model (7).

In this review, we give an introduction to the physics of a family of frustrated highly anisotropic rare-earth magnets on the pyrochlore lattice (see Figure 1a). These are of the form $\text{R}_2\text{M}_2\text{O}_7$, where
where \( R \) is a trivalent rare-earth ion and \( M \) is a nonmagnetic tetravalent transition metal ion (8). The best known of these compounds are the dipolar spin ices (SIs) \( \text{Dy}_2\text{Ti}_2\text{O}_7 \) and \( \text{Ho}_2\text{Ti}_2\text{O}_7 \), which are almost entirely classical (9) highly frustrated magnets. Our focus here is not on these classical systems (10) but on the quantum rare-earth pyrochlores of this series. Due to the large spin-orbit coupling, along with the localized nature of the rare-earth ions, one naturally finds highly anisotropic exchange interactions that, in many cases, are strongly frustrated. After a review of the microscopic physics at play, we delve into the study of four specific compounds: \( \text{Er}_2\text{Ti}_2\text{O}_7 \), \( \text{Yb}_2\text{Ti}_2\text{O}_7 \), \( \text{Tb}_2\text{Ti}_2\text{O}_7 \), and \( \text{Pr}_2\text{Zr}_2\text{O}_7 \). Each of these represents an archetypal example from a group of related materials, covering a range of behaviors, from the weakly frustrated \( \text{Er}_2\text{Ti}_2\text{O}_7 \) to the highly frustrated \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) and \( \text{Tb}_2\text{Ti}_2\text{O}_7 \), to randomly disordered \( \text{Pr}_2\text{Zr}_2\text{O}_7 \). None of these systems conform strongly to the SI limit (10), or even the geometrically frustrated Heisenberg limit (11), but they nevertheless exhibit new and interesting behavior. Finally, for each compound, we provide an outlook to the future as well as discuss some alternative material platforms for realizing similar physics.

2. MICROSCOPIC BACKGROUND

2.1. Single-Ion Physics

In rare-earth magnets, the single-ion physics strongly dominates over the two-ion exchange interactions and, thus, must be dealt with first (see Reference 12 for details). This single-ion physics is tractable, displaying a reasonably clear hierarchy of energy scales, with Coulomb interactions dominating over spin-orbit coupling, which dominates over the effects of the crystalline environment. The free-ion ground state is found by first minimizing the Coulomb and spin-orbit energies, in accordance with Hund’s rules, yielding a ground-state manifold with definite total angular momentum \( J \). Next, the effect of the crystal field in solid removes most of this remaining
(2J + 1)-fold degeneracy (13), with the charged ions of the crystal imposing electric fields\(^1\) that break the rotational symmetry and splits the \(J\) manifold.

For the \(A_2B_2O_7\) pyrochlore systems we are most interested in, the \(D_{3d}\) site symmetry (8) includes a \(C_3\) rotation, three \(C_2\) rotations (in the plane perpendicular to the three-fold axis), and their combinations with inversion (see Figure 1b). In such an environment, the crystal field potential, \(V(J)\), can be written as

\[
V(J) = B_{20}O_{20}(J) + B_{40}O_{40}(J) + B_{43}O_{43}(J) + B_{60}O_{60}(J) + B_{63}O_{63}(J) + B_{66}O_{66}(J),
\]

where the operators \(O_{KQ}(J)\) are Stevens operator equivalents (14), polynomials of order \(K\) in the total angular momentum \(J\). The precise details of this Hamiltonian and the associated splittings vary from material to material and from ion to ion. Typically, these energy scales are typically large relative to the two-ion interactions, but small relative to the energy required to reach the other \(J\) manifolds. We can further restrict ourselves to the lowest-lying states of the free-ion ground-state \(J\) manifold as determined by the crystalline electric field interaction.

For materials of interest, these low-lying states take the form of a doublet. We denote the states of this doublet as \(|\pm\rangle\) and define pseudospin operators, \(S\), as

\[
S^z = \frac{|+\rangle\langle+| - |\rangle\langle-|}{2}, \quad S^\pm = |\pm\rangle\langle\mp|.
\]

For Kramers ions with an odd number of electrons (half-integer \(J\)), all of the crystal field levels are doubly degenerate due to Kramers’s theorem. For non-Kramers ions (integer \(J\)) that have an even number of \(4f\) electrons, any two-fold degeneracy must be enforced by the crystal symmetry.

Each of these crystal field doublets can be classified in terms of the irreducible representations of the site symmetry group \(D_{3d}\) and its double group (15). Altogether, there are three distinct types, two Kramers doublets and one non-Kramers doublet. The most familiar is the \(\Gamma_4\) doublet, which we refer to as an effective spin-1/2 as, in all aspects of symmetry, it behaves identically to an \(S = 1/2\) spin. The second type of doublet is built from the two one-dimensional irreducible representations \(\Gamma_3\) and \(\Gamma_6\). Because these two representations do not mix under the spatial symmetries except through time reversal, this doublet behaves very differently than an effective spin-1/2 (16). This \(\Gamma_3 \oplus \Gamma_6\) doublet has been dubbed a dipolar-octupolar doublet, as \(S^z\) corresponds to a component of the magnetic dipole moment, whereas the \(S^\pm\) components correspond to parts of a magnetic octupole moment, changing the angular momentum in units of three.\(^2\)

Finally, we have the non-Kramers doublet, which transforms in the \(E_g\) irreducible representation. This is similar in spirit to the dipolar-octupolar case: Though the \(S^z\) component transforms like a magnetic dipole, the \(S^\pm\) components transform like electric quadrupoles (17). This key feature, that \(S^\pm\) is time-reversal even, makes this doublet qualitatively distinct from the two Kramers cases. We stress that the \(D_{3d}\) site symmetry is necessary to preserve this degeneracy; without it, local electric field gradients can couple to the quadrupole moment (appearing as on-site terms like \(S^\pm\)) and split the doublet (see Section 7).

These symmetry properties have consequences for the components of the \(g\)-factor of the ion, which defines the magnetic moment \(\mu\), at site \(i\):

\[
\mu_i = -g_i\mu_B P_{ij}P = -\mu_B \left[ g_{ix} \hat{S}^i_x + g_{iy} \hat{S}^i_y + g_{iz} \hat{S}^i_z \right].
\]

\(^1\)A full accounting of all the sources of crystal field effects is complicated, with pure electrostatics being only one contribution. We refer the reader to the discussion in Reference 13 for a more complete discussion.

\(^2\)Note that for \(D_{3d}\) symmetry, the magnetic dipoles and octupoles are not necessarily distinct, with \(S^z\) and \(S^\pm\) transforming identically.
Table 1  Types of crystal field doublets in rare-earth pyrochlores

| Doublet          | Irreducible representation | \( g_\pm \) | \( g_\pm \) | Time reversal | \( C_3 \) | \( C_2 \) | States | Examples |
|------------------|---------------------------|------------|------------|--------------|--------|--------|--------|---------|
| Effective spin-1/2 | \( \Gamma_4 \)           | \( \neq 0 \) | \( \neq 0 \) | \( S \to -S \) | \( S^z \to +S^z \) | \( S^z \to -S^z \) | \( \pm 1 \), \( \pm \frac{3}{2} \), \ldots | \( \text{Er}_2\text{Ti}_2\text{O}_7 \), \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) |
| Dipolar-octupolar | \( \Gamma_5 \oplus \Gamma_6 \) | \( \neq 0 \) | 0          | \( S \to -S \) | \( S \to +S \) | \( S^z \to +S^z \) | \( \pm \frac{1}{2} \), \( \pm \frac{3}{2} \), \ldots | \( \text{Dy}_2\text{Ti}_2\text{O}_7 \) |
| Non-Kramers      | \( E_g \)                 | \( \neq 0 \) | 0          | \( S^z \to -S^z \) | \( S^z \to +S^z \) | \( S^z \to \pm S^z \) | \( \pm 1 \), \( \pm \frac{3}{2} \), \( \pm \frac{3}{2} \), \ldots | \( \text{Ho}_2\text{Ti}_2\text{O}_7 \), \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) |

\(^a\)We give the conventional name and notation for the irreducible representation of \( D_{2d} \) to which it belongs (15) as well as the action of the elements of \( D_{2d} \) and time reversal on the pseudospin operators, \( S \), of each doublet. In addition, we give examples of \( J \) manifold states that can be combined to create each doublet, as well as providing some material examples.

Here, \( g_J \) is the Landé \( g \)-factor, \( \mu_B \) the Bohr magneton, and \( P \) is a projector into the ground crystal field doublet. The vectors \( \hat{x}_i, \hat{y}_i, \) and \( \hat{z}_i \) define a local frame (18) for the rare-earth ion, with \( \hat{z}_i \) along the \( C_3 \) axis and \( \hat{y}_i \) along a \( C_2 \) axis (see Figure 1b). For the effective spin-1/2, one can have strong Ising moments with \( g_\pm \gg g_\parallel \), strongly \( XY \) moments with \( g_\parallel \gg g_\parallel \), or something in between \( g_\parallel \sim g_\parallel \) depending on the details of the crystal field. However, for the dipolar-octupolar and non-Kramers doublets, since the transverse components \( S^\pm \) transform as octupoles and quadrupoles (respectively), \( g_\pm = 0 \) exactly,\(^3\) and thus they carry strictly Ising-like magnetic moments. We summarize the properties of these three types of doublets in Table 1.

2.2. Two-Ion Physics

The interactions between rare-earth ions are considerably more complex than the single-ion physics discussed in the previous section (9, 19, 20). Given this complexity, we comment on these interactions in broad and somewhat phenomenological terms. In this regard, it is useful to move back up (in energy scale) from a description in terms of the crystal field ground doublets to a description in terms of the full free-ion \( J \) manifolds before descending back to the pseudospins discussed in Section 2.1. Although the description in terms of the \( J \) manifolds is quite involved, the final description in terms of the pseudospins is relatively compact and simple.

Generically, pairwise interactions between the angular momenta \( J_i \) can be written as

\[ \frac{1}{2} \sum_{ij} \sum_{KQ} \sum_{K'Q'} M_{ij}^{KQ,K'Q'} \mathcal{O}_{KQ}(J_i) \mathcal{O}_{K'Q'}(J_j) + \sum_i \mathcal{V}(J_i), \]

where the \( \mathcal{O}_{KQ}(J) \) are multipole operators, polynomials of order \( K \) in the \( J \) operator (with \( |Q| \leq K \)). The second piece is the on-site crystal field potential, \( \mathcal{V}(J) \), discussed in Section 2.1. Explicitly, one can choose a basis such that the matrix elements of these multipole operators are proportional to Clebsch–Gordan coefficients (see, e.g., Reference 21) with \( \langle J, M | \mathcal{O}_{KQ}(J) | J, M' \rangle \propto \langle J, M ; K, Q | J, M' \rangle \), though we do not need this level of detail here.

Simple bilinear exchanges such as \( J_i J_j \), used widely in the literature (22), are interactions between rank-1 multipoles with \( K = K' = 1 \). Generically, one does not expect the multipolar exchanges to take such a naive form; interactions between multipoles of rank greater than one are expected to be as significant as, if not more significant than, these rank-1 terms. This includes

\(^3\)Although this is plainly true for the non-Kramers case, we must note that for the dipolar-octupolar doublet, strictly, one can always find a basis for the doublet such that \( g_\parallel = 0 \).
interactions such as quadrupole–quadrupole (rank-2) and octupole–octupole (rank-3) as well as cross terms such as dipole–octupole (rank-1, rank-3) and so forth for higher ranks.\(^4\)

For an ion with angular momentum \(J\), these multipoles can have rank up to \(2J\), so there are in principle many, many interactions encoded in \(M^{KQ,K'Q'}_{ij}\) to consider per bond. However, there are some strong constraints arising from the microscopic mechanisms that generate these interactions. Examples include electro- and magnetostatic interactions, spin–phonon interactions, and direct and superexchange. For our purposes, the most important of these are the superexchange interactions and, in some cases, the magnetic dipole–dipole interactions (8). It is important to note that for essentially all the mechanisms discussed above, the interactions are strongly suppressed for ranks \(K > 7\). This is due to the nearly free-ion nature of the rare-earth ions limiting the maximal total angular momentum transferred by the \(4f\) electron involved in each step of the superexchange process to \(7/2\) (9, 20). To a good approximation, we can thus generally restrict \(K\) and \(K'\) to be \(\leq 7\) in Equation 4.

For some systems, this bound, when combined with the single-ion physics, can prove highly restrictive. For example, in \(\text{Dy}_2\text{Ti}_2\text{O}_7\) or \(\text{Ho}_2\text{Ti}_2\text{O}_7\), the crystal field ground doublet is primarily of the form \(\sim |J, \pm J\rangle\) with \(J = 15/2\) and \(J = 8\), respectively. The rank-15 and rank-16 operators needed to transition between the \(|J, \pm J\rangle\) states are thus strongly suppressed by any of the two-ion interaction mechanisms discussed above, and the exchange interactions are essentially rendered classical (9). In the opposite extreme, for example for \(\text{Yb}^{3+}\), one has \(J = 7/2\) where only rank \(\leq 7\) operators are needed to mix the states of crystal field ground doublets, regardless of the ground doublet composition. One can thus have cases in which the single- and two-ion anisotropy are intimately linked, whereas for other ions or crystal environments, they are essentially unrelated.

Admittedly, the complexity of these multipolar models is somewhat disheartening given the enormous number of free parameters encoded by the multipolar exchanges, even after accounting for the rank-7 bound and relevant lattice symmetries. However, all is not lost: For most cases of interest, the separation between the exchange and the crystal field energy scales allows some significant simplification. At the coarsest level, one may carry out first-order degenerate perturbation theory, taking the crystal field energy scale, \(\Lambda\), to be much larger than the multipolar exchange scale \(\mathcal{M}\), obtaining a model only in terms of the pseudospins (Equation 2). This amounts to simply projecting Equation 4 into the subspace of the ground doublets,

\[
\frac{1}{2} \sum_{ij} \sum_{KQ,K'Q'} M^{KQ,K'Q'}_{ij} \mathcal{O}_{KQ}(\mathbf{J}_i) \mathcal{O}_{K'Q'}(\mathbf{J}_j) + \sum_i V(\mathbf{J}_i) \xrightarrow{\text{P}(\mathbf{J}_i)^P} \frac{1}{2} \sum_{ij} \mathbf{J}_i \cdot \mathbf{J}_j + \text{constant}, \tag{5}
\]

where \(\mathbf{J}_ij\) is an exchange matrix between the pseudospins, \(\mathbf{S}_i\). Thankfully, the exchange matrices in this smaller subspace are more tightly constrained by symmetry than the full multipolar exchanges entering into Equation 4. The symmetries relevant for a nearest-neighbor bond of the pyrochlore lattice include a two-fold rotation and two reflections, as shown in Figure 1c. One can show that for both types of Kramers ground doublets, there are four symmetry-allowed nearest-neighbor exchanges (18), whereas for a non-Kramers doublet there are only three (17, 19). Without any constraints from the multipole ranks or the compositions of the crystal field doublets, and absent other information, one would anticipate generic behavior, with all of these exchanges of the same order of magnitude, and such is expected for all the compounds of interest in this review.

\(^4\)Note that, as for the single-ion physics, the spin-only moments of \(\text{Gd}^{3+}\) or \(\text{Eu}^{2+}\) are special cases (8) that do not readily conform to the expectations discussed here.
The symmetry-allowed nearest-neighbor model appropriate for the effective spin-1/2 doublet is the most complex, taking the form (18, 23)

\[
\sum_{\langle ij \rangle} \left\{ J_{zz} S^z_i S^z_j - J_{\pm}(S^+_i S^-_j + S^-_i S^+_j) + J_{\pm\pm}(\gamma_{ij} S^+_i S^+_j + \gamma^*_{ij} S^-_i S^-_j) \right. \\
\left. + J_{\pm\mp} \left[ \zeta_{ij}(S^+_i S^+_j + S^-_i S^-_j) + \zeta^*_{ij}(S^-_i S^-_j + S^+_i S^+_j) \right] \right\},
\]

where \( \langle ij \rangle \) denotes the nearest neighbors of the pyrochlore lattice. The allowed exchanges include an Ising coupling, \( J_{zz} \), and XY-like exchange, \( J_{\pm} \), as well as \( J_{\pm\pm} \) and \( J_{\pm\mp} \) couplings, which carry bond-dependent phase factors \( \zeta_{ij} = -\gamma_{ij}^* \) (18) and, thus, do not have as simple a geometric interpretation. In a global frame for the pseudospins, these four exchanges can be recast as a Heisenberg, Kitaev, pseudodipolar and Dzyaloshinskii–Moriya (DM) exchange (24, 25). We note that the sign of \( J_{\pm\pm} \) is somewhat arbitrary as it can be changed by a local \( \mathbb{C}_2 \) pseudospin rotation about the \( \hat{z} \) axis. Although simple in this local basis, when expressed in a global frame, one finds equivalences between superficially very different exchange parameters (25).

The model for ions with a non-Kramers doublet is identical to the effective spin-1/2 case, save for time-reversal symmetry forcing \( J_{\pm\mp} = 0 \); one thus has (17, 23)

\[
\sum_{\langle ij \rangle} \left\{ J_{zz} S^z_i S^z_j - J_{\pm}(S^+_i S^-_j + S^-_i S^+_j) + J_{\pm\pm}(\gamma_{ij} S^+_i S^+_j + \gamma^*_{ij} S^-_i S^-_j) \right\}.
\]

This affords the system an accidental symmetry; due to the decoupling of \( S^z \) and \( S^\pm \), a \( \mathbb{C}_2 \) pseudospin rotation about the \( \hat{z} \) is now a symmetry of the model, not merely a duality. We stress that this is an accidental symmetry, present only for two-spin interactions, which can be lifted by multi-spin interactions. We also note that the sign of \( J_{\pm\pm} \) can be flipped by a pseudospin rotation by \( \pi/2 \) about \( \hat{z} \), leaving the other couplings invariant, so one can take \( J_{\pm\pm} \geq 0 \) without loss of generality.

Last, we consider the dipolar–octupolar case. Due to the trivial action of the \( \mathbb{C}_1 \) rotation on these states, one finds the same basic form as the effective spin-1/2 case, except that the phase factors are absent, with \( \gamma_{ij} = \zeta_{ij} = 1 \). This can be recast as (16)

\[
\sum_{\langle ij \rangle} \left[ J_{xx} S^x_i S^x_j + J_{yy} S^y_i S^y_j + J_{zz} S^z_i S^z_j + J_{zz} (S^+_i S^-_j + S^-_i S^+_j) \right],
\]

where we have defined \( J_{xx} \equiv 2(J_{\pm\pm} - J_{\pm}) \), \( J_{yy} \equiv -2(J_{\pm\mp} + J_{\pm}) \), and \( J_{zz} \equiv 2J_{\pm\pm} \). Unlike the effective spin-1/2 and non-Kramers cases, there is no bond dependence in the exchange interactions. We note that the \( J_{zz} \) exchange can be removed by a redefinition of the pseudospin axes (16), though one must be mindful that this transformation must be also applied to the definition of the magnetic moment, Equation 3, and to any further neighbor exchanges.

2.3. Virtual Crystal Field Corrections

To close this section, we discuss another route to generating exchange interactions between the pseudospins, distinct from the microscopic mechanisms mentioned earlier, which involves corrections due to the finite crystal field energy scale. Recall that the projection of the multipolar interactions to the pseudospin model (Equation 5) results from first-order degenerate perturbation theory in the small parameter \( \mathcal{M}/\Lambda \), where \( \mathcal{M} \) is a typical multipolar exchange scale (Equation 4) and \( \Lambda \) is the gap to the first excited crystal field level. Going beyond first order introduces additional effective interactions between the pseudospins that depend on the details of
the multipolar exchanges, $M_{ij}$, and the crystal field potential, $V(J_i)$. We refer to these as virtual crystal field corrections (26, 27).

For all types of doublets, the second-order correction generates renormalization of the nearest-neighbor exchanges discussed above, as well as new second- and third-neighbor exchanges, with a scale set roughly by $\sim M^2/\Lambda$. In addition, the non-Kramers case also admits three-spin interaction terms, appearing at second order, for example, of the form (27)

$$\sum_{\langle ijk \rangle} (K_{ijk} S_i^z S_j^z S_k^z + \text{h.c.}),$$

where $\langle ij \rangle$ and $\langle jk \rangle$ are nearest-neighbor bonds and $i \neq k$. This is forbidden for both types of Kramers doublets as it breaks time-reversal symmetry. Note that this interaction explicitly breaks the accidental $C_2$ symmetry present in the non-Kramers model with only two-spin interactions (Equation 7). Additional three-spin terms that do not involve $S^z$ are also allowed by symmetry but are more difficult to generate at second order by virtual crystal field corrections. We note that these kinds of perturbative corrections also affect the observables of the system, which can also acquire corrections at order $M/\Lambda$ (27).

3. PHASES

The phase diagrams of the minimal, nearest-neighbor models for effective spin-1/2 (Equation 6), non-Kramers doublet (Equation 7) and dipolar–octupolar doublets (Equation 8) have been studied in a number of works. In this section, we survey what is known about the phases that appear in such models at zero temperature.

3.1. Classical Phases and Ordered States

A broad outline of the phases that occur can be exposed through an analysis of the classical ordered ground states, i.e., simple product states of the pseudospins. A rather comprehensive discussion for the effective spin-1/2 case can be found in Reference 24, from which one can infer many of the results for the non-Kramers case (17). The classical dipolar–octupolar phase diagram has been studied in Reference 16. In all cases, one generically finds the classical ordered phases do not enlarge the primitive unit cell (24) and, thus, can be classified by how they transform under the point group of the pyrochlore lattice (15). We refer to these ordered states as $Q=0$ states.

The classification of these phases for the effective spin-1/2 and non-Kramers cases is essentially identical, because they only differ under the action of time reversal. Altogether, we identify five distinct types of ordered states (24): $A_{2g}$, $E_g$, $T_{1g}$, $T'_{1g}$, and $T_{2g}$ (15), summarized in Table 2. For the effective spin-1/2 case, these are magnetic orders, whereas for the non-Kramers case, the $E_g$, $T_{1g}$, and $T_{2g}$ states correspond to quadrupolar orders that do not break time-reversal symmetry. Both the $T_{1g}$ and $T'_{1g}$ orders transform identically under spatial symmetries and, thus, can be mixed freely for the effective spin-1/2 case—we refer to any such state as a splayed ferromagnet (SFM). The mixing between the $T_{1g}$ and $T'_{1g}$ is typically characterized by the splay angle, $\theta_s$, which varies smoothly with the exchanges, and measures the angle of the pseudospins from the appropriate global [100] cubic axis (24). The classical phase diagram as a function of $J_{\pm}/|J_{zz}|$ and $J_{\pm\pm}/|J_{zz}|$ for both signs of $J_{zz}$ and several values of $J_{\pm}/|J_{zz}|$ is shown in Figure 2, accompanied by illustrations of each of the ordered states.

Because much of the classical phase diagram consists of robust ground states (with only symmetry-enforced degeneracies), the effects of quantum fluctuations would naively be expected to be mostly benign. However, there are exceptions, several of which are realized by the material
Table 2  Classical order parameters for each of the five types of \( Q = 0 \) phases for effective spin-1/2 or non-Kramers doublets on the pyrochlore lattice

| Name(s)                                          | Order parameter                                                                 | Examples                                      |
|-------------------------------------------------|---------------------------------------------------------------------------------|-----------------------------------------------|
| \( A_{2g} (\Gamma_3) \), all-in/all-out          | \( M_{A_{2g}} = S_1^x + S_2^x + S_3^x + S_4^x \)                              | None                                          |
| \( E_g (\Gamma_3) \)                             | \( M_{E_g} = \left( \frac{S_1^y + S_2^y + S_3^y + S_4^y}{S_1^y + S_2^y + S_3^y + S_4^y} \right) \) | \( \text{Er}_2\text{Ti}_2\text{O}_7, \text{Er}_2\text{Ge}_2\text{O}_7, \text{Yb}_2\text{Ge}_2\text{O}_7 \) |
| \( T_{2g} (\Gamma_7) \), Palmer–Chalker         | \( M_{T_{2g}} = \) \[ \begin{pmatrix} S_1^y + S_2^y + S_3^y - S_4^y \\ S_1^y + S_2^y + S_3^y - S_4^y \\ S_1^y + S_2^y + S_3^y - S_4^y \end{pmatrix} \] | \( \text{Er}_2\text{Sn}_2\text{O}_7, \text{Er}_2\text{Pt}_2\text{O}_7 \) |
| \( T_{1g} (\Gamma_9) \), ordered spin ice       | \( M_{T_{1g}} = \left( \begin{array}{c} S_1^y + S_2^y + S_3^y - S_4^y \\ S_1^y - S_2^y + S_3^y - S_4^y \\ S_1^y - S_2^y + S_3^y - S_4^y \end{array} \right) \) | \( \text{Tb}_2\text{Sn}_2\text{O}_7 \) |
| \( T'_{1g} (\Gamma_9) \), splayed ferromagnet    | \( M_{T'_{1g}} = \) \[ \begin{pmatrix} S_1^y + S_2^y + S_3^y - S_4^y \\ -\frac{\sqrt{3}}{2} S_1^y + \frac{\sqrt{3}}{2} S_2^y \\ -\frac{\sqrt{3}}{2} S_1^y + \frac{\sqrt{3}}{2} S_2^y \end{pmatrix} \] | \( \text{Yb}_2\text{Ti}_2\text{O}_7, \text{Yb}_2\text{Sn}_2\text{O}_7 \) |

* Some material examples are given. There are two different \( T_{1g} \) types of order that can mix freely for the effective spin-1/2 case, whereas for the non-Kramers case they differ under the action of time reversal. Pseudospin configurations for each ordering type are shown in Figure 2.
Figure 2

(a–f) Classical phase diagrams of the effective spin-1/2 and non-Kramers doublet models (Equations 6 and 7). We show phases for (a–c) $J_{zz} > 0$ and (d–f) $J_{zz} < 0$ with (a,d) $J_{zz} = 0$, (b,e) $J_{zz} = |J_{zz}|/4$, and (c,f) $J_{zz} = |J_{zz}|/2$. The phase diagrams for $J_{zz} < 0$ are related to these by a local $C_2$ rotation about $\hat{z}_i$. In the $E_g$ ($T_1^g$) phase, we show the state chosen semiclassically at order $O(1/S)$, which is always $\psi_2$ or $\psi_3$. The splay angle, $\theta_s$, in the SFM phase is indicated by a color gradient, interpolating between orange, which represents the $T_1^g$ state (ordered SI), and red, indicating the $T_1^g$ state where the pseudospins lie in the local $XY$ plane. Example configurations of pseudospins for each of these orders (see Table 2) are shown. Abbreviations: AIAO, all-in/all-out; PC, Palmer–Chalker; SFM, splayed ferromagnet; SI, spin ice.

examples we discuss later. One important example is the $E_g$ phase, the so-called $\Gamma_5$ manifold, in which there is an accidental $U(1)$ classical degeneracy (24, 28–30). Explicitly, one can rotate the pseudospins continuously in the local $XY$ plane about their local $\hat{z}_i = [111]$ axes without changing the classical energy. Two high-symmetry basis states of this manifold are the $\psi_2$ and $\psi_3$ states (illustrated in Figure 2). In the phase diagrams shown in Figure 2, we have indicated which of the $\Gamma_5$ states (always $\psi_2$ or $\psi_3$) is selected by the leading quantum corrections to the classical energy (see Section 4 for a more detailed discussion). Additional $U(1)$ degeneracies can be found at
various phase boundaries between the classical phases, such as between the \( E_g \) and \( T_{1g} \) or \( T_{2g} \) orders (see Reference 24 for a more complete discussion).

Another exception arises for the non-Kramers case (see Figure 2a,d): For \( |J_\pm| \ll J_{zz} \) and \( |J_{\pm\pm}| \ll J_{zz} \), the lowest energy \( Q = 0 \) state is \( T_{1g} \), a so-called ordered SI state (17), which is a specific case of the general SFM states. In fact, for this case, all SI states are classical ground states; we refer to all such states in this region in Figure 2a generically as SI. We discuss briefly how this degeneracy is lifted by quantum effects in Section 3.2. Note that this classical degeneracy does not survive in the effective spin-1/2 case, where generically \( J_{\pm\pm} \neq 0 \), with the ground state being a mix of \( T_{1g} \) and \( T_{1g}' \).

The classification of ordered states for the dipolar–octupolar doublet (16) is somewhat different, as shown in Table 3. Because both \( S^x \) and \( S^z \) transform in the same way as do magnetic dipoles, one has several versions of the all-in/all-out (AIAO) and ordered SI states found in the effective spin-1/2 and non-Kramers cases. However, since the \( S^y \) pseudospin operator is invariant under all spatial symmetries, there are two qualitatively new kinds of order: a kind of octupolar ordered SI as well as an octupolar variant of the AIAO order (\( A_{1g} \)), which has the intriguing property that it only breaks time-reversal symmetry. For a discussion of the classical phase diagram of the dipolar–octupolar model (Equation 8), we refer the reader to Reference 16.

### 3.2. Quantum Phases

Extensive classical degeneracies in the exchange models of Equations 6–8 are mostly confined to phase boundaries and special isolated points in the space of exchange parameters. The best known and studied of these is that of the SI manifold (10), which appears when \( J_{zz} > 0 \) and \( J_\pm = J_{\pm\pm} = J_{\pm\pm} = 0 \) (analogously for the dipolar–octupolar case). The classical thermal physics of this point displays several fascinating phenomena (10), from the emergence of a version of magnetostatics (a “Coulomb” phase) to the appearance of effective magnetic monopoles as elementary excitations. As discussed in Section 3.1, this also holds over a finite region of phase space for the non-Kramers case (see Figure 2a). When the effects of quantum fluctuations are included (\( J_{zz} \gg J_\pm, J_{\pm\pm} \gg J_{\pm\pm} \)), a QSL is known to be induced, the so-called quantum spin ice (QSI) phase, described by a \( U(1) \) gauge theory with an emergent photon excitation (see Reference 31 for a review). This phase is stable to all perturbations and thus occupies a finite region of phase space about the classical

| \( A_{1g} \) (\( \Gamma_1 \)), octupolar all-in/all-out | \( M_{A_{1g}} = S^1_1 + S^2_2 + S^3_3 + S^4_4 \) | None |
| \( A_{2g} \) (\( \Gamma_3 \)), all-in/all-out | \( M_{A_{1g}} = S^1_1 + S^2_2 + S^3_3 + S^4_4 \) | Nd\(_2\)Zr\(_2\)O\(_7\), Nd\(_2\)Hf\(_2\)O\(_7\) |
| \( T_{1g} \) (\( \Gamma_9 \)), ordered spin ice | \( M_{T_{1g}} = \begin{pmatrix} S^1_1 + S^2_2 - S^3_3 - S^4_4 \\ S^1_1 - S^2_2 + S^3_3 - S^4_4 \\ S^1_1 - S^2_2 - S^3_3 + S^4_4 \\ S^1_1 + S^2_2 + S^3_3 + S^4_4 \end{pmatrix} \) | None |
| \( T_{2g} \) (\( \Gamma_7 \)), ordered-octupolar spin ice | \( M_{T_{1g}} = \begin{pmatrix} S^1_1 + S^2_2 - S^3_3 - S^4_4 \\ S^1_1 - S^2_2 + S^3_3 - S^4_4 \\ S^1_1 - S^2_2 - S^3_3 + S^4_4 \\ S^1_1 + S^2_2 + S^3_3 + S^4_4 \end{pmatrix} \) | None |

*The two types of all-in/all-out order can mix freely, as can the two types of ordered spin ice states.*
SI point (32). Other exotic phases have been proposed to be near the classical SI point, such as the Coulomb ferromagnet of Reference 33, though clear evidence of such a phase in the nearest-neighbor models of Equations 6–8 has yet to be found (34).

Finally, we note that there exist other kinds of extensively degenerate manifolds in the classical phase diagram. The most prominent of these is that of the antiferromagnetic Heisenberg point (for example, near \( J_{zz} = -2J_\pm \) and \( J_{\pm\pm} = J_{\pm\pm} = 0 \)). Classically, this model is known to host a spin liquid (35) phase with Coulomb correlations, similar to that found in classical SI. Much of the physics of the Heisenberg model in the quantum limit is unknown, though a variety of exotic states have been proposed (11, 36, 37). A more unusual classical degenerate manifold, found in a highly anisotropic regime, was recently studied in Reference 38 and has a description in terms of a higher-rank gauge theory. How such a manifold responds to the inclusion of quantum fluctuations is unknown but is a topic of current interest.

4. ORDER-BY-DISORDER IN ERBIUM PYROCHLORES

With the above background in hand, we consider specific material examples from the \( A_2B_2O_7 \) family of pyrochlores that realize different aspects of this physics. The first of the quantum pyrochlores that we discuss is \( \text{Er}_2\text{Ti}_2\text{O}_7 \). This compound is the most conventional of this family of materials but still harbors many surprises and rich physics at low energy. We introduce the physics of this material somewhat ahistorically but will highlight the experimental and theoretical milestones that moved our understanding forward as we encounter them. Altogether, \( \text{Er}_2\text{Ti}_2\text{O}_7 \) represents a beautiful example of a frustrated anisotropic quantum magnet that can be, and has been, investigated in fine detail both experimentally and theoretically.

At the atomic level, \( \text{Er}^{3+} \) has a \( J = 15/2 \) free-ion ground-state manifold, with the crystal field selecting an effective spin-1/2 ground state. Because it is reasonably well separated (39) from the excited crystal field levels (\( \Lambda \sim 6 \) meV), the nearest-neighbor effective spin-1/2 model of Equation 6 should be a reasonable description. Based on \( XY \)-like moments (39, 40) and the negative Curie–Weiss temperature, early studies (39) assumed that the physics was that of a Heisenberg antiferromagnet (39) but with the moments pinned to the local \( XY \) plane. In the local basis, this maps to exchange parameters \( J_\pm > 0, J_{\pm\pm} = 2J_\pm, \) and \( J_{zz} = J_{z\pm} = 0 \). Classically, such a model includes the \( \Gamma_5 \) manifold as a ground state (see Section 3), though its full ground-state manifold is larger and more complicated (41, 42). More realistic values of the anisotropic exchange parameters have since been determined by fitting the spectra observed in inelastic neutron scattering at high fields. For example, Reference 28 finds good agreement with the parameters

\[
\begin{align*}
J_{zz} &= -2.5 \cdot 10^{-2} \text{ meV}, \\
J_\pm &= +6.5 \cdot 10^{-2} \text{ meV}, \\
J_{\pm\pm} &= +4.2 \cdot 10^{-2} \text{ meV}, \\
J_{z\pm} &= -0.88 \cdot 10^{-2} \text{ meV},
\end{align*}
\]

where the \( g \) factors were determined to be \( g_z = 2.45 \) and \( g_\pm = 5.97 \). Although qualitatively similar to the naïve expectations for an easy plane \( XY \) antiferromagnet, with \( J_\pm \) and \( J_{\pm\pm} > |J_{zz}| \) and \( |J_{z\pm}| \), there are some significant differences, with no clear separation of scales between the four exchanges. Other studies (43) have found similar values for the exchanges. In addition, the predictions of these parameters (Equation 10) for thermodynamic quantities at high temperature are consistent with experiments (44).

Experimentally, \( \text{Er}_2\text{Ti}_2\text{O}_7 \) orders antiferromagnetically at \( T_N \sim 1.2 \) K via a second-order phase transition (39). Early neutron diffraction measurements indicated that the ordered phase was drawn from the \( \Gamma_5 \) manifold, which is consistent with early expectations as well as the parameters
of Equation 10. Later experiments (45) identified the ground state as being $\psi_2$ (see Section 3.1), establishing that the degeneracy expected classically is indeed lifted below $T_N$. Exploring and explaining the mechanism of this degeneracy lifting have been the focus of much of the theoretical and experimental work on $\text{Er}_2\text{Ti}_2\text{O}_7$.

4.1. Order-by-Disorder and Ground-State Selection

Much of the interest in the physics of $\text{Er}_2\text{Ti}_2\text{O}_7$ stems from the accidental classical degeneracy (i.e., not due to a symmetry) of these $\Gamma_5$ states. How this is resolved in practice has been dubbed order-by-disorder (46–48). Interpreted broadly, this refers to the lifting of an accidental degeneracy that appears in some artificial limit (e.g., classical spins, zero temperature, no disorder) upon moving away from this limit.

One of the earliest and most commonly discussed flavors of order-by-disorder is order-by-thermal-disorder (46). In this case, one has a degeneracy in the classical energy at zero temperature but not in the free energy at any finite temperature. In other words, though the energies of the states are the same, the landscape of nearby excited states is different, and thus the entropies are different. We discuss other kinds of order-by-disorder, but they all share this same essential character. Several types relevant for $\text{Er}_2\text{Ti}_2\text{O}_7$ include the following:

1. Order-by-thermal-disorder (29, 41, 42, 44, 49, 50): degeneracy lifted through finite temperature. Two distinct types: near-zero temperature ($T \to 0^+$) and near criticality ($T \to T_N - 0^+$).
2. Order-by-quantum-disorder (28, 29, 42): degeneracy lifted through quantum zero-point spin fluctuations in the semiclassical limit ($1/S \to 0$).
3. Order-by-structural-disorder (51, 52): degeneracy lifted by the dilution of the magnetic $\text{Er}^{3+}$ ions or the introduction of random exchange disorder.
4. Order-by-virtual-crystal-field-fluctuations (21, 53): degeneracy lifted by higher-order multispin interactions generated by virtual crystal field corrections (see Section 2.3).

The selection of the ground state in $\text{Er}_2\text{Ti}_2\text{O}_7$ is a good starting point to study order-by-disorder because the accidental classical degeneracy is present for any symmetry-allowed two-spin interactions of arbitrary range (28). This implies that any selection must proceed through some fluctuation effect (e.g., quantum, thermal) or otherwise proceed energetically via multispin interactions. This can be seen straightforwardly in a Landau–Ginzburg description: Due to the high symmetry of the pyrochlore lattice, the effective free energy for the $\Gamma_5$ order parameter takes the form

$$F(\mathbf{m}) \sim A_2 m^2 + A_4 m^4 + A_6 m^6 - B_6 m^6 \cos(6\phi) + \cdots, \quad 11,$$

where $\mathbf{m} \equiv m(\cos \phi \hat{x} + \sin \phi \hat{y})$ describes the pseudospin configuration in the local basis. The vector $\mathbf{m}$ transforms in the $E_g$ representation of the point group of the pyrochlore lattice, with the angle $\phi$ tuning between the different states of the $\Gamma_5$ manifold (as shown in Figure 3a). This immediately implies that, at the classical level, multispin interactions are needed to break the degeneracy because the classical energy directly maps to something of the form of Equation 11 when evaluated for a $\Gamma_5$ state but only with the parts that are quadratic in $m$. Assuming the terms higher

---

5Allowing for a canting of the moments away from the local $XY$ plane endows the Landau–Ginzburg free energy with fourth-order terms (30, 50) such as $\sim m^3 m_z \cos(3\phi)$, where $m$ is magnitude of the $XY$ part, and $m_z$ the out-of-plane part. Such terms can be removed by solving for the equilibrium value of $m_z \propto m^3 \cos(3\phi)$, thus obtaining a free energy of the form given in Equation 11.
than sixth order are small, the selection effect is encoded in the sign of $B_6$, with $B_6 > 0$ selecting $\psi_2$ and $B_6 < 0$ selecting $\psi_3$, with an overall energy difference of $\delta E = 2B_6$.

This selection energy from order-by-quantum-disorder can be explicitly computed at $O(1/S)$ in the semiclassical $S \to \infty$ limit (28, 29). At leading order, one can describe the small fluctuations about the ordered state as a set of independent bosonic magnon modes. Each of these modes contributes to the ground-state energy through its zero-point motion, distinguishing the classically degenerate $\Gamma_5$ states. One finds that this zero-point energy selects $\psi_2$ at $O(1/S)$, as is found experimentally (45). The dependence of this zero-point energy on the $\Gamma_5$ angle, $\phi$, is illustrated in Figure 3a, where one finds a very small energy difference (per pseudospin) of $\delta E \sim 0.086 \mu$eV between the $\psi_2$ and $\psi_3$ states. In reality, several order-by-disorder effects should be operational in Er$_2$Ti$_2$O$_7$: Since the effects of quantum fluctuations or any direct multispin terms are not tunable in any reasonable way, all should be present (21, 53).

Determining the order-by-disorder mechanism is thus a quantitative question, and one may ultimately only be able to identify a mechanism as being dominant over all others. With these

---

**Figure 3**

(a) Quantum zero-point energy, $E(\phi)$, as a function of $\Gamma_5$ state (inset) indexed by the angle $\phi$, computed at $O(1/S)$ in spin-wave theory using the parameters of Reference 28. (b) Inelastic neutron scattering intensity at low energy near $Q \equiv [111]$ showing the pseudo-Goldstone mode with a small gap of $\Delta \sim 53 \mu$eV. Adapted from Reference 54 with permission. Copyrighted by the American Physical Society.
theoreticalexpectationsfororder-by-disorderinEr$_2$Ti$_2$O$_7$havingbeenoutlined,wenextconsider
some of the implications of order-by-disorder for experiments in this material.

4.2. Pseudo-Goldstone Mode

A key feature of order-by-disorder scenarios is the presence of a nearly gapless mode in the spec-
trum. This pseudo-Goldstone mode (39) is a remnant of the accidental classical degeneracy, with
the cost to produce long-wavelength deformations within this manifold being small, but made
nonzero due to order-by-disorder. The presence of such a mode in Er$_2$Ti$_2$O$_7$ is a necessary con-
sequence of order-by-disorder and, thus, provides a quantitative goalpost for benchmarking any
theory of the order-by-disorder mechanism.

More explicitly, one expects classically that at zero temperature the
$\Gamma_5$ ordered phase will
be characterized by a gapless magnon, $\sim v|q - Q|$, emanating from the magnetic Bragg peak at
Q $\sim |111|$. Including the effects of any type of order-by-disorder will induce a gap
and give a
spectrum of the form $\sim \sqrt{v^2|q - Q|^2 + \Delta^2}$, as illustrated in Figure 3b. One roughly expects this
gap to be related to the magnitude of the selection energy as $\Delta^2 \sim \delta E$, where $\delta E = 2B_6$ is the
energy difference between $\psi_2$ and $\psi_3$ states, and $J$ is a typical exchange scale (22). If the effects
of order-by-disorder are weak, in the sense that the appropriate classical limit is nearly reached,
the gapping of this pseudo-Goldstone mode, $\Delta$, may be much smaller than the dominant energy
scales of the problem. For example, if one estimates the gap using the selection energy, $\delta E$, found
at 1/S in spin-wave theory, then one finds $\Delta \sim 0.03$ meV (28), which is consistent with what is
found using interacting spin-wave theory (55). This is significantly smaller than the bandwidth of
the magnon excitations in Er$_2$Ti$_2$O$_7$, which span roughly $\sim 0.5$ meV (28, 56).

Evidence for such a pseudo-Goldstone mode in Er$_2$Ti$_2$O$_7$ was first detected experimentally
in the approximately $\sim T^3$ specific heat at low temperature (39, 40, 57, 58). More directly, early
inelastic neutron scattering experiments (56) observed an approximately linearly dispersing mode
near Q $\sim |111|$, but could not resolve the gap, bounding it to be $\Delta \lesssim 0.1$ meV. More recent
detailed inelastic neutron scattering studies (43, 54, 59) focusing on this mode have resolved the
gap and found it to be $\Delta \sim 0.04$–0.05 meV, which is an order of magnitude smaller than the
naïve energy scale (see Figure 3b). The presence of this mode in Er$_2$Ti$_2$O$_7$, with its strongly
suppressed energy scale, is a clear experimental signal that one or more of the aforementioned
order-by-disorder mechanisms is at work in Er$_2$Ti$_2$O$_7$.

4.3. Current and Future Directions

As we have seen in the previous sections, the presence of order-by-disorder has been reasonably
well established in Er$_2$Ti$_2$O$_7$ through a variety of direct experimental observations and theoretical
arguments. Much of the more recent interest in Er$_2$Ti$_2$O$_7$ has focused on the effects of pertur-
bations to the selection at low temperature, such as through the application of magnetic fields or
through the introduction of nonmagnetic ions, such as Y$^{3+}$, to dilute the magnetic Er$^{3+}$ sites.

The effect of a magnetic field on Er$_2$Ti$_2$O$_7$ has several interesting regimes, such as quan-
tum criticality in a [110] field (56), as well as rich physics at low fields where aspects of the
order-by-disorder come into play. This low-field behavior has been explored in detail in recent
theoretical (60) and experimental (59, 61) studies. Due to the small energy scales, the compe-
tition between the order-by-disorder selection and the selection by the applied field occurs at
small magnetic fields on the order of $\lesssim 0.5$ T. This selection is highly direction dependent, with
qualitatively different behavior for $\psi_2$ and $\psi_3$ ordering. Experimentally, most of these transitions
have been observed in Er$_2$Ti$_2$O$_7$ and are qualitatively consistent with theoretical expectations (60,
Given the inherent tunability of an applied field, coupled with the diverse set of behaviors predicted, the exploration of this low-field behavior serves as an instructive setting for addressing detailed quantitative questions about order-by-disorder in Er\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}.

The question of order-by-structural-disorder has also been studied in some detail recently. Early theoretical calculations predicted that site dilution or exchange disorder would favor the selection of a $\psi_3$ ground state (51, 52). At larger disorder strengths, recent studies (62) find a “cluster spin glass” phase, consisting of a frozen mix of $\psi_2$ and $\psi_3$ clusters, past a dilution of $\sim$35\% or so. When the competition with the selection effects in the clean limit is considered, one expects a transition between $\psi_2$ and $\psi_3$ at some critical dilution or disorder strength that can be estimated to be roughly 10–30\% for Er\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, based on the size of the measured pseudo-Goldstone gap. One then expects the clean $\psi_2$ phase to evolve into such a cluster glass phase, with the appearance of a $\psi_3$ phase at intermediate dilution depending on the precise value of the order-by-disorder selection energy scale in the clean limit. Experimentally, this has been realized by the synthesis of solid solutions of the form Er\textsubscript{2}$\times$Y\textsubscript{2}$\times$Ti\textsubscript{2}O\textsubscript{7} with $\delta=0,0.1,$ and $0.2$ (63, 64). Analysis of elastic and inelastic neutron scattering data has been interpreted as being consistent with the $\delta=0.1$ sample being in the $\psi_2$ phase (as in the clean limit) and the $\delta=0.2$ sample being in the cluster glass phase. Whether there is an intermediate $\psi_3$ phase between these two dilution strengths (62) remains an open question.

The physics discussed in this section has focused on Er\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, though there are several rare-earth pyrochlore materials that share much of the same physics. These include Er\textsubscript{2}Ge\textsubscript{2}O\textsubscript{7}, which has been suggested to exhibit a $\psi_3$ ground state (65) (rather than a $\psi_2$ state), and Yb\textsubscript{2}Ge\textsubscript{2}O\textsubscript{7} (66), which is also thought to host a $\psi_3$ ground state (as we discuss in Section 5). Further detailed investigations of Er\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, as well as Er\textsubscript{2}Ge\textsubscript{2}O\textsubscript{7} and Yb\textsubscript{2}Ge\textsubscript{2}O\textsubscript{7}, should prove valuable in improving our global understanding of order-by-disorder physics.

5. EXOTIC ORDER IN YTTERBIUM PYROCHLORES

We next consider the Yb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} pyrochlore, which has received significant attention as a potential candidate for realizing QSI (18). Despite these early expectations, Yb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} is, in some sense, more conventional than Er\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, appearing to order into a simple ferromagnet (67–72) without any residual classical degeneracy. However, this ferromagnetic state unexpectedly shows highly unusual dynamical behavior, yielding a puzzle as to what underpins the physics in this material.

The atomic physics of Yb\textsuperscript{3+} is simple, described by a single hole in the 4\textit{f} manifold, which has a $J=7/2$ free-ion ground-state manifold. Due to the large crystal field energy scale of $\sim$75 meV (73), we can consider solely the ground effective spin-1/2 doublet, and thus the model of Equation 6 should be a very good description. Attempts at determining the appropriate exchange parameters for Yb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} have yielded several different models (18, 74, 75), depending on exactly what data were analyzed and what sample was studied. The most systematic of these studies is the recent work of Reference 75, in which inelastic neutron scattering spectra in large [001] magnetic fields was analyzed, finding

\[
J_{zz} = +2.6 \times 10^{-2} \text{ meV}, \quad J_{\pm} = +7.4 \times 10^{-2} \text{ meV}, \\
J_{\pm\pm} = +4.8 \times 10^{-2} \text{ meV}, \quad J_{z\pm} = -15.9 \times 10^{-2} \text{ meV}.
\]

One sees that the $J_{z\pm}$ coupling is dominant, with these parameters far from the QSI regime put forth in early studies (18). The $g$ factors were also determined simultaneously, finding $g_z \sim 2.14$ and $g_{\pm} \sim 4.17$. A similar set of exchange parameters was also reported in Reference 74.
Figure 4

(a) Phase diagram of model Equation 6 in the (dual) global basis (see Section 5) showing the phase boundary between the SFM and the $\Gamma_5$ manifold relevant for $\text{Yb}_2\text{Ti}_2\text{O}_7$. Phases are identified using the same color scheme as is used in Figure 2. Hypothetical positions of the related $\text{Yb}_2\text{Sn}_2\text{O}_7$ (SFM) and $\text{Yb}_2\text{Ge}_2\text{O}_7$ ($\Gamma_5$) compounds are indicated. (b) Experimental excitation spectrum along a trajectory projected on the [100] direction for $\text{Yb}_2\text{Ti}_2\text{O}_7$ at 150 mK and zero field inside the SFM phase (75), showing a broad continuum of excitations. (c) Prediction of linear spin-wave theory using the parameters (75) of Equation 12 at zero field showing well-defined magnon modes and a clear gap at zero wavevector. Panels b and c adapted from Reference 75 with permission. Copyrighted by the American Physical Society. Abbreviations: LSWT, linear spin-wave theory; SFM, splayed ferromagnet.

Experimentally, though there is some sample dependence, the developing consensus appears to be that $\text{Yb}_2\text{Ti}_2\text{O}_7$ orders into an SFM state through a first-order transition at $T_c \approx 0.25$ K (67–72), with the magnetic moments roughly along the cubic [100] axes, with small splay angle.6 This is consistent with classical expectations (75) for the exchange parameters of Equation 12. The details of this transition, such as the height of the specific heat peak, the precise $T_c$, or the splay angle, appear to depend on the specific sample considered (67–72), suggesting a sensitivity to disorder or internal stress (71).

5.1. Spin Dynamics in the Ordered State

The key mystery in $\text{Yb}_2\text{Ti}_2\text{O}_7$, and more broadly in $\text{Yb}_2\text{Ge}_2\text{O}_7$ and $\text{Yb}_2\text{Sn}_2\text{O}_7$, lies in its zero-field spin dynamics. The naïve theoretical expectations for the dynamics in the SFM state are entirely unremarkable. Due to the large anisotropy in the exchange interactions, there should be no gapless or nearly gapless modes, and thus one should just expect a gapped magnon, perhaps with a minimum near $\mathbf{Q} = 0$, i.e., the ordering wavevector. Using the exchange parameters for $\text{Yb}_2\text{Ti}_2\text{O}_7$, one would predict a one-magnon gap to be roughly $\sim 0.2$ meV (75), as illustrated in Figure 4c.

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6Some aspects of this transition are contentious given that the magnetic Bragg peaks are difficult to resolve atop the structural Bragg peaks.
This is well within experimental bounds and does not require the significant experimental effort put forth to observe the small order-by-disorder gap in $\text{Er}_2\text{Ti}_2\text{O}_7$, as discussed in Section 4.2.

However, what is actually found in $\text{Yb}_2\text{Ti}_2\text{O}_7$, in both single crystals (74, 75) and powder samples (76), is in strong disagreement with these expectations. The observed spectrum is nearly gapless with no well-defined spin-wave modes. The spectrum has been described as a “ferromagnetic continuum” (70, 74–76), with a broad intensity distribution emanating from $\mathbf{Q} = 0$, as shown in Figure 4b. A similar continuum is observed in powder samples of $\text{Yb}_2\text{Sn}_2\text{O}_7$, which has the same SFM ground state (76).

Even more striking is how this excitation spectrum evolves as a function of magnetic field. In Reference 75, a field along [001] was considered to preserve the symmetries of the SFM ground state. It was observed that this continuum evolves smoothly from the sharp spin waves expected, and indeed found, at sufficiently large field, without any apparent phase transition. As one lowers the field, the one- and two-magnon excitations merge completely below $B \sim 1$ T (75, 77), signaling a strong departure from naïve semiclassical expectations. There are several exotic phases one could propose to explain the zero-field continuum; for example, the excitations could be a spinon particle–hole continuum of a gapless $U(1)$ spin liquid (78) (but modified to carry a small ferromagnetic moment—a kind of fractionalized SFM state). Such proposals are, however, superficially at odds with the zero-field state being smoothly connected to the trivial high-field state.

The mystery deepens when considering the sister material, $\text{Yb}_2\text{Ge}_2\text{O}_7$ (66, 79). This compound does not order in an SFM state but into the $\Gamma_5$ manifold (79) in which $\text{Er}_2\text{Ti}_2\text{O}_7$ orders. Given the exchange regime found in $\text{Yb}_2\text{Ti}_2\text{O}_7$, one might theoretically expect that order-by-quantum-disorder in $\text{Yb}_2\text{Ge}_2\text{O}_7$ selects a $\psi_3$ ground state, though a $\psi_2$ ground state is also a possibility (80). One then expects similar phenomenology to $\text{Er}_2\text{Ti}_2\text{O}_7$: novel order-by-disorder physics atop what is essentially a simple classical ordered state (80). However, the spin dynamics of $\text{Yb}_2\text{Ge}_2\text{O}_7$ show a ferromagnetic continuum similar to that seen in $\text{Yb}_2\text{Ti}_2\text{O}_7$, despite its antiferromagnetic $\Gamma_5$ ground state (76). This seems somewhat contradictory; from the field dependence in $\text{Yb}_2\text{Ti}_2\text{O}_7$, the continuum of excitations would seem to be a property of the SFM ground state, evolving smoothly into the trivial polarized paramagnet, yet it also appears in the antiferromagnetic ground state of $\text{Yb}_2\text{Ge}_2\text{O}_7$.

What is driving this physics has not yet been resolved; it is not clear if the explanation is (in some sense) conventional or if it necessitates structural disorder in some essential way or is truly exotic, such as involving proximity to a QSL of some kind. In the next section, we outline some more conventional ideas that may underlie some of this physics.

5.2. Splayed Ferromagnet and Multiphase Competition

To get a better understanding of the $\text{Yb}_2\text{M}_2\text{O}_7$ family (where $\text{M} = \text{Ti}, \text{Ge}, \text{or Sn}$), we focus on what is understood at the classical and semiclassical levels, though it can only present a partial picture of what is going on in $\text{Yb}_2\text{Ti}_2\text{O}_7$. One distinctive feature of the exchange parameters of Equation 12 is that they sit near a (classical) phase boundary between the SFM state and the $\Gamma_3$ manifold of states (74, 80). This feature is also shared with several of the earlier proposals for the exchange interactions in $\text{Yb}_2\text{Ti}_2\text{O}_7$ (18, 74, 81).

Some of the aspects of the classical phase boundary can be more clearly grasped by changing to a global frame for the exchanges. As mentioned in Section 3, the four ($J_{zz}, J_{\pm 1, \pm 1}$, and $J_{z \pm}$) exchanges of Equation 6 can be mapped (24) to four exchanges ($J, K, L$, and $D$, where $J$ is a Heisenberg exchange, $K$ and $L$ are Kitaev and pseudodipolar exchanges, and $D$ is a DM interaction). Before performing this mapping, one can first apply the duality discussed in Section 2.2,
rotating by π about \( \mathbf{\hat{z}} \), to flip the sign of \( J_{\pm} \) (25). For the parameters of Equation 12, after reversing the sign of \( J_{\pm} \), one finds that \( J \) and \( D \) are dominant, with \( J > 0 \) and \( D < 0 \) and \( K \) and \( \Gamma \ll J \) and \( |D| \). Classically, the model with \( K = \Gamma = 0 \) has been studied in References 82–84, and it describes the relevant phase boundary between the SFM and \( \Gamma_5 \) phases. As illustrated in Figure 4a, one finds that \( K + \Gamma > 0 \) favors an SFM state, whereas \( K + \Gamma < 0 \) favors the \( \Gamma_5 \) states. Just as in \( \text{Er}_2\text{Ti}_2\text{O}_7 \), several kinds of order-by-disorder (74, 80) are expected to play an important role in the physics of the SFM–\( \Gamma_5 \) phase boundary. First and foremost is the stabilization of a (primarily) \( \psi_3 \) state by order-by-quantum-disorder at zero temperature (80). This stabilization energy is not present on the SFM side, and thus we expect quantum fluctuations to enlarge the \( \Gamma_5 \) region at the expense of the SFM region (80).

The proximity of these compounds to this SFM–\( \Gamma_5 \) phase boundary may play an important role in explaining the sensitivity of these compounds to structural disorder or (possibly) to the origin of the unusual dynamics. For example, it may alter some of the naïve expectations for the excitation spectrum of the SFM phase that we outlined earlier. Other possibilities, within such a framework, may be more extrinsic and involve both the interplay between the SFM–\( \Gamma_5 \) competition and structural disorder. As we have seen in \( \text{Er}_2\text{Ti}_2\text{O}_7 \), disorder can lead to a rather rich phenomenology for such systems with strongly competing ground states.

5.3. Current and Future Directions

One key experimental question is the role of structural disorder in these compounds. Does it play a fundamental role in the unusual dynamics? Or would this physics remain in a perfect, clean sample? Some of these questions could be answered by experiments that look at the dynamics in (nominally) better quality samples, such as those that were reported in Reference 85. A complementary view is provided by experiments on \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) under applied pressure (71). These experiments find that the application of moderate hydrostatic pressure can stabilize the SFM state (71), removing some of the ambiguities that have plagued its detection in samples under ambient conditions. This could indicate that most of the \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) samples under study could have some distribution of residual strains that are affecting the low-energy physics. Although the application of pressure sharpens the appearance of the static order, it remains to be seen how the unusual dynamics is modified. An alternate interpretation is that pressure is pushing \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) away from the SFM–\( \Gamma_5 \) boundary (80), thus rendering its physics more classical and less frustrated. Measurements of the dynamics of \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) under pressure would be very useful to resolve these questions.

More phenomenologically, one may try to gain some understanding from the universality of the appearance of the continuum of excitations (76), given it appears in all three \( \text{Yb}_2\text{M}_2\text{O}_7 \) compounds, with both SFM and \( \Gamma_5 \) ground states. One might speculate that there is a parent state from which the dynamics is natural and originates, with the SFM and \( \Gamma_5 \) states regarded as secondary instabilities. Within such an interpretation, the broad peak in specific heat at higher temperatures, observed in all these compounds, could be viewed as signaling the entrance into a manifold of states representative of an (unknown) parent state, with the ordering transitions being secondary instabilities. Studies of the recently synthesized \( \text{Yb}_2\text{Pt}_2\text{O}_7 \) (86), which has not yet been as well characterized, would be useful in this regard, though the somewhat different ionic physics of \( \text{Pt}^{4+} \) could complicate a direct comparison.

We end this section with some of the key questions that remain to be answered for \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) and the related \( \text{Yb}_2\text{Ge}_2\text{O}_7 \) and \( \text{Yb}_2\text{Sn}_2\text{O}_7 \) materials:

1. Is there a parent state from which the unusual dynamics derives, and what is this parent state?
2. What role does the proximity to the SFM–Γ₃ boundary play?
3. To what extent do extrinsic effects, such as structural disorder, play an important role?

6. SPIN LIQUID IN TERBIUM PYROCHLORES

The compound Tb₂Ti₂O₇ has resisted attempts at understanding since its initial synthesis (40). Unlike Er₂Ti₂O₇ and Yb₂Ti₂O₇, Tb₂Ti₂O₇ does not magnetically order and, thus, has long been considered a QSL candidate. In this section, we offer a perspective on the current experimental status of Tb₂Ti₂O₇ and sketch the challenges that have plagued theoretical efforts in explaining its behavior. The plain fact that Tb₂Ti₂O₇ has resisted such attempts for so long is a testament to the depth and breadth of the physics exhibited by this compound. The numerous mysteries and puzzles to be addressed, only a few of which we touch on here, represent a definite opportunity, for both theory and experiment, to advance our understanding of systems with complex local degrees of freedom and many competing orders.

At the free-ion level, Tb³⁺ has a \( J = 6 \) free-ion ground-state manifold that is further split by the crystal field, yielding a non-Kramers doublet (87–90). Unlike the Er³⁺ and Yb³⁺ cases, the first excited state, another non-Kramers doublet, is only separated by the relatively small energy \( \Lambda \sim 1.4 \text{ meV} \). This renders the nature of the two-ion interactions more subtle. If the manifolds associated with the two low-lying levels do not cross [consistent with the experimental spectra (88, 91–93)], then a description in terms of the ground doublets should be possible. The question then falls to the size of the virtual crystal corrections discussed in Section 2.3. If significant, the physics of Equation 7 would then need to be augmented to include second- and third-neighbor (anisotropic) exchanges as well as three-spin terms in the vein of Equation 9 (26, 27).

Although the crystal field scale \( \Lambda \sim 1.4 \text{ meV} \) is small relative to the crystal field scale in other rare-earth magnets, it is still about an order of magnitude larger than typical exchange scales in rare earths, for example, as found in Er₂Ti₂O₇ or Yb₂Ti₂O₇. Taking \( \mathcal{M} \sim 0.2 \text{ meV} \), one might expect the first correction to be on the order of \( \mathcal{M}^2/\Lambda \sim 0.02 \text{ meV} \ll \mathcal{M} \), neglecting any matrix element effects. Although likely not the whole story, to move forward in our discussion of Tb₂Ti₂O₇, we adopt a somewhat pragmatic view, cautiously invoking the pseudospin model appropriate for a non-Kramers doublet (Equation 7) as a first description of Tb₂Ti₂O₇ and treating these virtual crystal field corrections as secondary effects.

Given the Ising-like magnetic moments, early efforts focused on scenarios based on a (argued) proximity to classical SI (26, 27, 87, 94, 95). Such an interpretation faces several challenges, such as the wrong sign of Curie–Weiss temperature and the presence of paramagnetic scattering at [002], which is forbidden for Ising-like moments (26, 94, 95). Some of these issues can be partially resolved by considering a simple model of (rank-1) Heisenberg exchange and dipolar interactions in the full \( J \) manifold, so as to include admixing with the higher crystal field states (26, 27) and effectively allowing for a finite transverse \( g \) factor (see Section 2.3). This led to a picture in which Tb₂Ti₂O₇ sits near the boundary with the AIAO states \( (J_{zz} = 0) \) due to virtual crystal corrections inducing a strong renormalization of \( J_{zz} \) (26).

Some recent works (92, 96, 97) have attempted to estimate the three \( (J_{zz}, J_\pm, \text{ and } J_{\pm\pm}) \) parameters from comparisons with experimental data, but the results are less conclusive than they are for Er₂Ti₂O₇ or even Yb₂Ti₂O₇. One representative example is provided by Reference 97, which proposes

\[
J_{zz} = 0.34 \text{ meV}, \quad J_\pm = 0 \text{ meV}, \quad J_{\pm\pm} = 0.146 \text{ meV}.
\]

These parameters put the system close to SI and two quadrupolar ordered phases, analogs of the \( \Gamma_3 \) manifold discussed for Er₂Ti₂O₇ and Yb₂Ti₂O₇, and of the \( T_{2g} \), Palmer–Chalker state (see
Figure 5

(a) Phase diagram of Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ as a function of the composition parameter $x$, showing the disordered and ordered phases appearing for $x \lesssim 0$ and $x \gtrsim 0$. Data taken from Reference 100. (b,c) Broad scattering at (b) [002] when ZFC and (c) sharper quasi-Bragg peaks wavevectors equivalent to $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ when FC in slightly off stoichiometric Tb$_{2+x}$Ti$_{2-x}$O$_{7+y}$ with $x \sim -0.001$ at $T = 100$ mK. Panel b adapted from Reference 101 with permission. Copyrighted by the American Physical Society. Abbreviations: FC, field cooled; QSL, quantum spin liquid; ZFC, zero-field cooled.

Figure 2 and Table 2). More controlled approaches to determining these parameters, such as the high-field studies undertaken for Er$_2$Ti$_2$O$_7$ and Yb$_2$Ti$_2$O$_7$, are complicated by the presence of the low-lying first excited crystal field doublet at $\Lambda \sim 1.4$ meV.

6.1. Spin Liquid and Correlations

The experimental study of Tb$_2$Ti$_2$O$_7$ has a long and complicated history. A key question to be answered is the nature of the paramagnetic state that persists to low temperatures. Early studies of the low-energy properties of Tb$_2$Ti$_2$O$_7$ focused on this lack of ordering (98, 99). This was principally inferred from the specific heat and the susceptibility, which show only broad features down to the lowest measured temperatures. This absence of ordering led to Tb$_2$Ti$_2$O$_7$ being put forth as a QSL candidate.

However, the lack of clear ordering does not necessarily imply a QSL ground state; more telling evidence can be found in the magnetic correlations. The development of a correlated paramagnet in Tb$_2$Ti$_2$O$_7$ can be seen as one goes below $\sim 20$ K (99). This most clearly manifests in (nominally) elastic neutron scattering measurements in which one observes an increase in diffuse elastic intensity around the wavevector [002] at low temperature (99), as shown in Figure 5b. More recent experiments (102, 103) have observed that this feature sharpens into quasi-Bragg peaks near wavevectors equivalent to $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$, as shown in Figure 5c. In addition to these peaks,
the surrounding diffuse intensity forms a distinctive “butterfly” shape (104). The appearance of these features is dependent on the experimental history: the \([\frac{1}{2} \frac{1}{2} \frac{1}{2}]\) peaks appear under field-cooled conditions (103) but not when zero-field cooled. This suggests some freezing at low temperatures, though not necessarily total, accompanied by nontrivial static magnetic correlations with characteristic wavevector \([\frac{1}{2} \frac{1}{2} \frac{1}{2}]\).

We now turn to dynamical probes. In addition to the presence of static correlations, it has been established through a variety of methods that there are dynamic magnetic correlations down to low temperatures (105, 106). This can be seen directly in the inelastic neutron scattering spectrum that shows broad low-energy excitations. More recent experiments (such as those of References 92, 97, 107, and 108) see a small gap of \(\sim 0.1\) meV with excitations extending in energy up to \(\sim 0.3\) meV or so. The presence of such dynamics has been corroborated by \(\mu\)SR measurements (106), as well as AC susceptibility measurements (106, 109). How the glassy behavior of the static \([\frac{1}{2} \frac{1}{2} \frac{1}{2}]\) feature fits into such a picture is unclear.

The lack of ordering, and the presence of both static and dynamic correlations at low temperatures, suggests that \(\text{Tb}_2\text{Ti}_2\text{O}_7\) realizes some kind of spin liquid state or possibly some kind of partially frozen glassy state. The nature of this state remains unclear, though new insights have been recently uncovered from the introduction of minute amounts of disorder into \(\text{Tb}_2\text{Ti}_2\text{O}_7\).

### 6.2. Stoichiometry and Quadrupolar Order

A relatively recent milestone (110) is the controlled synthesis of off-stoichiometric samples of \(\text{Tb}_2\text{Ti}_2\text{O}_7\), with formula \(\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}\). Such samples show an extreme sensitivity to the value of the composition parameter \(x\), even in a small window of 1–2% deviations from stoichiometry. It was found (110) that the lack of ordering observed previously only occurs for \(-0.02 \lesssim x \lesssim 0\), with the \(0 \lesssim x \lesssim 0.03\) samples showing an ordering transition in the specific heat at \(\sim 0.5\) K, as illustrated in Figure 5a. The ordered state for \(x \gtrsim 0\) samples appears to be nonmagnetic, suggesting a quadrupolar ordering, such as the quadrupolar \(E_g(\Gamma_3)\), \(T’_1\), or \(T_g\) (Palmer–Chalker) states discussed in Section 3 (97, 108). Such a quadrupolar phase has been argued to be qualitatively consistent with the behavior of the phase diagram as a function of magnetic field (97). The sensitivity to very small deviations in stoichiometry also provides a plausible explanation for some of the sample dependence reported in the literature for \(\text{Tb}_2\text{Ti}_2\text{O}_7\).

Much of the phenomenology established in the early studies has been revisited in light of this question of stoichiometry. The signatures of the (static) spin correlations seen in (nominally) stoichiometric samples are also present in off-stoichiometry samples (101), independent of the presence of the transition at \(\sim 0.5\) K (110). The dynamic correlations observed in inelastic neutron scattering have also been studied in the off-stoichiometric samples. As in the (nominally) stoichiometric samples, one finds an excitation gapped by \(\sim 0.1\) meV, but which sharpens significantly as one goes to larger values of \(x\) (111). This overall behavior has been interpreted as the proximity of \(\text{Tb}_2\text{Ti}_2\text{O}_7\) to the boundary of a QSI phase and a quadrupolar ordered phase (97), with these excitations interpreted as the pseudospin waves associated with the quadrupolar order (108). However, direct detection of this putative quadrupolar order is still lacking.

### 6.3. Discussion and Outlook

There are several major open questions concerning \(\text{Tb}_2\text{Ti}_2\text{O}_7\). Some are theoretical questions that we have broached earlier, such as the applicability of the pseudospin model. If the virtual
crystal field corrections are sufficiently large, this mapping may break down completely, suggesting it may be necessary to include both low-lying doublets on equal footing. How the presence of such a “pseudo-orbital” degree of freedom would affect the physics remains to be seen. There are also several open experimental questions, such as the nature of the ordered state seen for \( x \gtrsim 0 \) samples and of the disordered state seen for \( x \lesssim 0 \). Furthermore, there is the overall question of why Tb2Ti2O7 is so sensitive to deviations from stoichiometry, e.g., some manifestation of an extreme sensitivity to disorder. Studies of related compounds such as Tb2Sn2O7, which shows magnetic ordering into an ice state (112), or Tb2Hf2O7, which is thought to have strong structural disorder (113), may shed some light on these questions.

Another important line of inquiry to which we have not done justice is that of magnetoelastic excitations (93, 114, 115) in Tb2Ti2O7. This thread goes back to early experiments that studied its high-temperature magnetoelastic properties (116, 117). Although likely primarily a single-ion effect, their size and temperature dependence highlights the large electric quadrupole moment carried by the Tb\(^{3+}\) electronic states. Due to the non-Kramers structure of the ground and first-excited doublets, this large quadrupolar moment can carry over to the low-energy physics. Recent inelastic neutron scattering studies have found that these kinds of magnetoelastic effects persist in the low-energy spectrum. This can be directly seen in the hybridization of the phonon modes with low-lying crystal field levels at \( \Lambda \sim 1.4 \) meV. Like the static correlations, this hybridization appears independent of the precise stoichiometry (118). What role such magnetoelastic effects play in the low-energy physics of Tb2Ti2O7 remains an interesting topic for further study.

We also note that there are several other experimental features of Tb2Ti2O7 that we did not touch upon here. These include the rich behaviors observed under applied magnetic fields (97, 103, 119–121), as well as the highly unusual features that have been observed in the thermal conductivity (122). With many fundamental questions remaining to be answered, the Tb2M2O7 (M = Ti, Sn, and Ge) family, more broadly, still presents promising opportunities to expand our understanding of highly frustrated magnetic systems, especially those with significant magnetoelastic couplings and pseudo-orbital degrees of freedom.

7. DISORDER AND SPIN LIQUIDS IN PRASEODYMIUM PYROCHLORES

The final quantum pyrochlore we discuss is Pr2Zr2O7, which has recently attracted attention as a QSI candidate both theoretically (123, 124) and experimentally (125–127). The free-ion ground state of Pr\(^{3+}\) is a \( J = 4 \) manifold, with a non-Kramers doublet selected by the crystal field in Pr2Zr2O7 (125, 127). Due to the large crystal field energy scale, \( \sim 10 \) meV (125, 127), one can likely ignore virtual crystal field corrections, and thus the two-ion interactions take the form of Equation 7 with three independent couplings. Early work (19, 125) estimated that this compound was near the QSI limit, with \( J_{zz} > 0 \) and \( |J_\pm| \) and \( |J_{\pm\pm}| \ll J_{zz} \); more recent studies (126, 128) have suggested larger values of \( J_\pm \), with some uncertainty in \( J_{zz} \). This was experimentally inferred from the lack of ordering (125, 127), the broad hump in the specific heat (125, 127), and the SI-like pattern (125) in the (quasielastic) structure factor (see Figure 6a). Some theoretical calculations of the exchange interactions have also suggested that such a regime was not unreasonable for the Pr2M2O7 family (19).

7.1. Structural Disorder

The key feature missing from this description, which distinguishes Pr2Zr2O7 from the other pyrochlores we have discussed so far, is the presence of significant structural disorder even in
nominally stoichiometric samples. The presence of structural disorder in Pr₂Zr₂O₇ was first exposed in studies of its inelastic neutron scattering spectrum (129). At reasonably low temperatures, one finds a continuum of scattering that extends from low energies and out to several millielectronvolts, as shown in Figure 6b. Accounting for detailed balance, one finds that this continuum persists essentially unchanged to high temperatures (129). This strongly suggests that this represents a distribution of quenched structural disorder that strongly affects the magnetic physics of the Pr³⁺ ions.

Recall that the effect of structural disorder on non-Kramers doublets is more dramatic than it is for the effective spin-1/2 or dipolar–octupolar doublets. For Kramers ions, because the degeneracy of their doublet is protected by time-reversal symmetry, structural distortions can only directly introduce disorder in the two-ion interactions. In contrast, for non-Kramers doublets, if the $D_{3d}$ site symmetry is broken, for example, by disorder or strain, the $E_g$ doublet is no longer protected and splits. Within the manifold of pseudospin states, such a perturbation maps to a transverse field

$$
\sum_i \left( \Gamma_i S_i^+ + \Gamma_i^* S_i^- \right),
$$

where $\Gamma_i \equiv |\Gamma_i| e^{i\theta_i}$ depends on the microscopic details of the disorder. These local (transverse) “fields” must also appear in concert with any exchange disorder that is also inevitably induced by structural disorder; the relative importance of such bond disorder remains to be ascertained.

If we assume that this transverse-field disorder is dominant, then one can extract a probability distribution for $|\Gamma_i|$ from the continuum observed experimentally in inelastic neutron scattering. The analysis of Reference 129 finds a half-Lorentzian distribution

$$
\rho(\Gamma) = \frac{2}{\pi} \left( \frac{\Gamma_0}{\Gamma^2 + \Gamma_0^2} \right),
$$

where $\Gamma_0 = 0.27$ meV is the in-plane transverse field that can give rise to a finite on-site transverse field. Data from Reference 129. Panel a adapted from Reference 125 with permission.
with $\Gamma_0 \sim 0.27$ meV providing a good description (see Figure 6b). These random fields represent a significant perturbation to typical rare-earth exchange scales and thus should be critical in understanding the physics of Pr$_2$Zr$_2$O$_7$. This distribution of transverse fields is also consistent with the strong reduction and smearing of the hyperfine contribution to the specific heat observed in early studies (125); the large transverse fields pin the pseudospins in the local $XY$ (quadrupolar) directions that couple only weakly with the nuclear spins, reducing the hyperfine specific heat (128).

The spatial distribution and origin of this disorder are less clear, though there have been some tantalizing experimental hints. First, it was found in Reference 129 that the [200] Bragg peak, forbidden in a clean sample, is (weakly) visible in Pr$_2$Zr$_2$O$_7$. This forbidden peak also has an anomalously large width, suggesting a correlation length of $\xi \sim 23$ Å (two unit cells) for the structural disorder (129). Second, some allowed Bragg peaks, such as [220], remain resolution limited. A simple picture that is consistent with these features is that the structural disorder consists of an off-centering of the Pr$^{3+}$ ions, with the rare-earth ions displaced in the plane perpendicular to the local $\hat{z}_i$ axis, as illustrated in the inset of Figure 6b. Rough point-charge estimates of the transverse fields induced by such displacements give a length scale of $\sim 0.1$ Å to get splittings comparable with what is seen experimentally. Such small off-centering disorder is also consistent with the anisotropic uncertainties reported in refinements of the crystal structure of Pr$_2$Zr$_2$O$_7$ (130). Similar off-centering has also been studied in the related (nonmagnetic) pyrochlore compounds La$_2$Zr$_2$O$_7$ (131, 132) and Bi$_2$Ti$_2$O$_7$ (133). A more detailed analysis of the diffuse part of elastic neutron scattering is broadly consistent with this interpretation (128), finding evidence for a distribution of random strains in Pr$_2$Zr$_2$O$_7$.

A reasonable description of Pr$_2$Zr$_2$O$_7$ must then include these strong random transverse fields. What kind of ground state this leads to depends on the details of the exchanges as well as the relative importance of exchange disorder. Evidence of static spin correlations in the diffuse neutron scattering, as shown in Figure 6a, suggests that the exchanges may favor ice-like states (125–128), implying a purely single-ion picture is not sufficient to fully understand Pr$_2$Zr$_2$O$_7$. For strong exchange and weak exchange disorder, one might then expect a disordered variant of QSI (123, 124), though the visibility of such a phase could be limited to extremely low temperatures. For weak exchange, one would likely find a frozen quadrupolar glass, with the pseudospins pinned along the direction preferred by the local disorder configuration. Because the distribution, $\rho(\Gamma)$, appears to extend to small $\Gamma$, even in such a case there should be regions in which the disorder is weak and the exchange dominates. Most interesting perhaps is the intermediate regime, in which the exchange interactions and the disorder are on equal footing. How the competition between these two (naïvely) opposing tendencies is actually borne out in Pr$_2$Zr$_2$O$_7$ remains an interesting and open question.

7.2. Discussion and Outlook

There remain several questions to resolve for Pr$_2$Zr$_2$O$_7$, as well as new and intriguing experimental observations that demand explanation and understanding. Indeed, the study of Pr$_2$Zr$_2$O$_7$, with its intrinsic disorder, may provide some insight for understanding the sample dependence found in Yb$_2$Ti$_2$O$_7$ or the extreme sensitivity to off-stoichiometry found in Tb$_2$Ti$_2$O$_7$.

First, there is the very recent work of Reference 134, which finds an anomalous upturn in the thermal conductivity of Pr$_2$Zr$_2$O$_7$ at $\sim 0.5$ K. This increase is interpreted as a feature of a QSI ground state, signaling the onset of thermal transport by the emergent photon excitation (32). In light of the evidence for significant on-site disorder, this interpretation likely requires additional justification, for example, via a demonstration that disorder is less important in the samples in which the thermal conductivity was measured. However, the appearance of the peak is still
unusual in itself: Within a picture of strong transverse field disorder, how can this increase be explained? One possibility involves a renormalization of the phonon velocity due to interaction with the pseudospins; this could be significant since they carry quadrupolar moments and, thus, could have significant magnetoelastic couplings. The hyperfine interactions could also play a role, as they onset at a comparable temperature; though they cannot contribute directly to thermal transport, they could in principle affect the pseudospins and, thus, the phonons through spin-phonon interactions.

A more promising route toward a QSI state in these compounds may be through the sister compound Pr$_2$Hf$_2$O$_7$ (135, 136). In this compound, very similar phenomenology is observed: no ordering, a broad specific-heat peak, and an SI-like pattern in neutron scattering. However, there is no reported evidence of the same kind of structural disorder seen in Pr$_2$Zr$_2$O$_7$. An analysis in Reference 137 suggests that a modulation of the neutron scattering intensity is consistent with the expectations for QSI, though there are potentially alternate explanations for such a feature. However, there remains an absence of direct evidence for disorder as found in Pr$_2$Zr$_2$O$_7$ as well as the presence of a finite energy excitation that suggests nontrivial spin dynamics, suggesting the physics could be rather different from that of Pr$_2$Zr$_2$O$_7$. Although there are other kinds of disorder that could be invisible to the kind of analysis used for Pr$_2$Zr$_2$O$_7$ (e.g., perhaps random displacement of the Pr$^{3+}$ ions along ẑ), this compound represents a promising avenue for future studies.

8. OUTLOOK

Beyond the four specific material examples that we have focused on, we would like to close this review by commenting on some other systems, some similar, some quite different, that could realize some of the same physics, and potentially clarify the broader aspects of frustrated magnetism in such highly anisotropic compounds.

The first of these systems are another class of rare-earth magnets with a pyrochlore lattice, the spinels (138) of the form A$_2$RX$_4$ (where A = Mg or Cd and X = Se or S). These have been synthesized for several different rare earths such as Ho$^{3+}$, Er$^{3+}$, and Yb$^{3+}$ in powder form. Early studies have shown the same diversity seen in the R$_2$M$_2$O$_7$ pyrochlores, with examples of classical dipolar SI (139–141), as well as potential candidates for order-by-quantum-disorder as found in Er$_2$Ti$_2$O$_7$ (142, 143). More speculatively, it is possible that the Yb spinels (142, 143) may exhibit similar physics to Yb$_2$Ge$_2$O$_7$ and its cousins (25)—if so, they could shed new light on the underlying physics of the Yb$_2$M$_2$O$_7$ family. Synthesis of single crystals as well as detailed studies of the excitations of these rare-earth pyrochlore spinels are thus needed.

A family of materials more far afield consists of the recently synthesized transition metal fluoride pyrochlores (144–146). These transition metal magnets are expected to be more isotropic than their rare-earth counterparts, though there has been some evidence for XY'-like features in their excitation spectra (147, 148). One key feature of these compounds is the presence of structural (charge) disorder on the nonmagnetic pyrochlore sites of the crystal lattice. A recent study of one such compound (149) shows that, despite the disorder, it is a good realization of a classical pyrochlore Heisenberg antiferromagnet over a broad range of temperatures (150). Although the presence of the structural disorder complicates the low-energy physics, it also affords new opportunities for the study of frustrated disordered systems similar in spirit to Pr$_2$Zr$_2$O$_7$. Indeed, a natural possibility could be that the charge disorder is frustrated in itself, satisfying an “ice-rule,” as was originally discussed by Anderson (151).

More speculatively, one may ask whether any of this kind of physics is realizable in transition metal magnets with strong spin-orbit coupling (5, 152). Many of the experimental challenges in
studying rare-earth magnets stem from their intrinsically low energy scales, requiring experiments at low temperature and high resolution in spectroscopic probes. Many of these issues would be significantly alleviated in transition metal realizations, where the exchange scale could be orders of magnitude larger. Indeed, this could even open avenues to new kinds of experimental probes, such as resonant elastic and inelastic light scattering, that potentially also directly measure less conventional, nonmagnetic excitations (153). As it stands, the currently known heavy transition metal pyrochlores (such as the pyrochlore iridates) are not strongly insulating and do not show much diversity in their magnetic physics, with nearly all of them ordering in an AIAO state (152). Perhaps if the DM interaction found in these or related compounds could be driven negative (indirect) (82–84), some of the physics discussed in Section 5 could be realized.

In this review, we have covered the microscopic and theoretical background necessary for understanding quantum rare-earth pyrochlores, as well as discussed four important material examples in detail. Many of these materials raise foundational questions that remain unanswered, such as the nature of their ground state and its low-lying excitations. For \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) and \( \text{Tb}_2\text{Ti}_2\text{O}_7 \), in particular, the answers to these questions have been elusive for two decades. Our primary aim was to provide an overview of the rich physics that can be explored in these systems and outline the key questions and perspectives we feel will be useful in moving toward resolving these puzzles. Given the recent serious breakthroughs that have occurred for each of these compounds, we are hopeful that a more complete understanding is not far out of reach. Beyond this, we hope this review serves as an invitation to the study of these systems and look forward to seeing what other lessons can be learned from this growing family of materials.

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Errata
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