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Effect of Chemical Pressure on the Crystal Electric Field States of Erbium Pyrochlore Magnets

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We have carried out a systematic study of the crystal electric field excitations in the family of cubic pyrochlores $\text{Er}_2\text{B}_2\text{O}_7$, with $B = \text{Ge, Ti, Pt, and Sn}$, using neutron spectroscopy. All members of this family are magnetic insulators based on $4f^{11} \text{Er}^{3+}$ and non-magnetic B^{4+} . At sufficiently low temperatures, long-range antiferromagnetic order is observed in each of these $\text{Er}_2\text{B}_2\text{O}_7$ pyrochlores. The different ionic sizes associated with different non-magnetic B^{4+} cations correspond to positive or negative chemical pressure, depending on the relative contraction or expansion of the crystal lattice, which gives rise to different local environments at the Er^{3+} site. Our results show that the g -tensor components are XY-like for all four members of the $\text{Er}_2\text{B}_2\text{O}_7$ series. However, the XY anisotropy is much stronger for $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ ($g_{\perp}/g_z > 25$), than for $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ ($g_{\perp}/g_z < 4$). The variation in the nature of the XY-anisotropy in these systems correlates strongly with their ground states, as $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ order into Γ_5 magnetic structures, while $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ order in the Γ_7 Palmer-Chalker structure.

INTRODUCTION

The cubic pyrochlore lattice is adopted by many magnetic materials with chemical composition $A_2\text{B}_2\text{O}_7$. This lattice is prone to magnetic frustration due to its architecture that consists of two inter-penetrating networks of corner-sharing tetrahedra on which both the A^{3+} and B^{4+} ions independently reside [1]. A peculiar attribute of the pyrochlore lattice is that the Ising axis and XY plane are both explicitly defined in a local, rather than global, coordinate frame. Ising spins on the pyrochlore lattice are constrained to point along the axis that connects the vertex of the tetrahedra to its center, termed the local $\langle 111 \rangle$ direction. Correspondingly, spins with XY anisotropy are constrained to lie in the plane perpendicular to the local $\langle 111 \rangle$ direction. Amongst the rare earth pyrochlores, XY anisotropy is obtained when the A sublattice is occupied by either Er^{3+} or Yb^{3+} .

XY pyrochlores have the potential to exhibit a range of exotic magnetic phenomena [2]. Theoretical studies have shown that XY pyrochlores can stabilize various spin liquid states including the much sought-after quantum spin ice state. The quantum spin ice state is a $U(1)$ quantum spin liquid with magnetic excitations that can be mapped onto diffusive magnetic monopoles such as in a classical spin ice, but with emergent electric monopoles and photon excitations [3]. It has been proposed that quantum spin ice physics may lie at the origin of the continuum of low energy spin excitations observed in $\text{Yb}_2\text{Ti}_2\text{O}_7$ [4]. Another interesting aspect of XY pyrochlore magnetism is the observation that order-by-disorder can affect their ground-

state selection. Order-by-disorder is the phenomenology whereby a particular magnetic structure is selected due to its propensity to fluctuate, an entropic selection rather than a conventional energetic selection [5, 6]. Order-by-disorder is known to favor the magnetic ground state observed in $\text{Er}_2\text{Ti}_2\text{O}_7$ [7–11], but appears to act in conjunction with an energetic selection mechanism that originates from virtual crystal field processes [12–14]. The effect of quenched disorder on the magnetism of XY pyrochlores has also been of significant interest, and in many cases is found to have a profound impact on the low temperature magnetism [15–21].

Underpinning the remarkable physics of the XY pyrochlores is the highly anisotropic nature of their exchange interactions. Classical calculations using an anisotropic exchange Hamiltonian have shown that several different ordered magnetic ground states exist within a narrow subspace of exchange parameters that are relevant to known XY pyrochlore magnets. This has led to theoretical proposals that competition between phases could account for many of their observed magnetic properties [22, 23]. Experimentally, evidence for phase competition is indeed found within the $\text{Er}_2\text{B}_2\text{O}_7$ family of XY pyrochlores. Both $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Ge}_2\text{O}_7$ order into the $k = 0 \Gamma_5$ manifold at $T_N = 1.2$ and 1.4 K, respectively [7, 24], but in a pure ψ_2 state for the former [25] and likely a pure ψ_3 state for the latter [24]. Meanwhile, both $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ order into the $k = 0 \Gamma_7$ manifold with significantly lower ordering temperatures, at $T_N = 0.3$ and 0.1 K, respectively [26, 27]. This state, the so-called Palmer-Chalker state, is stabilized for XY dipolar magnets with weak and isotropic exchange [28]. The experimentally determined anisotropic exchange couplings for these two Γ_7 magnets place them in close proximity to the classical

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phase boundary with Γ_5 [26, 27, 29]. The magnetic structures observed within the family of erbium pyrochlores, where only the non-magnetic B -site ion is varied, are all ones that exist in the computed anisotropic exchange phase diagram [23]. It is therefore interesting to uncover the microscopic origin of the changing magnetic ground states across this family that results from changing the non-magnetic B -site cation. To carry out such a detailed study, a key starting point is the precise determination of the spin anisotropy that originates from single-ion physics.

In this paper, we study the single ion properties of the four erbium pyrochlores within this family, $\text{Er}_2\text{Ge}_2\text{O}_7$, $\text{Er}_2\text{Ti}_2\text{O}_7$, $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$. We measure their crystal electric field excitations using neutron spectroscopic techniques. The analysis of these measurements allows us to determine the full CEF Hamiltonian for each member of this family. We find that the Er^{3+} moments in all four members possess XY-like anisotropy, but the strength of this anisotropy varies significantly across the family. We then show that the degree of XY anisotropy of the Er^{3+} moments correlates strongly with the precise magnetic ground state that is selected.

CRYSTAL-FIELD CALCULATION

The magnetism in the $\text{Er}_2\text{B}_2\text{O}_7$ pyrochlores originates from the Er^{3+} ions that possess a $[\text{Xe}]4f^{11}$ electronic configuration. Using Hund's rules, the total angular momentum of the spin-orbit ground state is $J = \frac{15}{2}$ with $L = 6$ and $S = \frac{3}{2}$. This spin-orbit ground state is $2J + 1 = 16$ -fold degenerate in the absence of the crystal electric field. The neighboring ions, primarily the O^{2-} that surround the Er^{3+} ions, generate the CEF, which acts on an energy scale of approximately 100 meV. Note that for Er^{3+} the first excited spin-orbit manifold is separated from the spin-orbit ground state by $\lambda J \approx 2.5$ eV [30]. Thus, for the Er^{3+} pyrochlores, we need not consider the higher J -multiplets in our CEF analysis. This is in contrast to systems with Ce^{3+} or Pr^{3+} , where λJ is an order of magnitude smaller and the inclusion of higher order multiplets is necessary to obtaining an accurate description of their CEF schemes [31].

The form of the CEF Hamiltonian depends on the point group symmetry at the Er^{3+} site, which has two-fold and three-fold rotation axes as well as an inversion symmetry with respect to the local $\langle 111 \rangle$ axis. These symmetry operations result in a D_{3d} point-group symmetry. Using the Steven's operator formalism, the CEF Hamiltonian for the D_{3d} point-group symmetry can be written as follows [32–35]:

$$\begin{aligned} \mathcal{H}_{\text{CEF}} = & A_2^0 \alpha_J \langle r^2 \rangle \hat{O}_2^0 + A_4^0 \beta_J \langle r^4 \rangle \hat{O}_4^0 + \\ & A_4^3 \beta_J \langle r^4 \rangle \hat{O}_4^3 + A_6^0 \gamma_J \langle r^6 \rangle \hat{O}_6^0 + \\ & A_6^3 \gamma_J \langle r^6 \rangle \hat{O}_6^3 + A_6^6 \gamma_J \langle r^6 \rangle \hat{O}_6^6. \end{aligned} \quad (1)$$

The \hat{O}_n^m are Steven's operators that are written in terms of J_+ , J_- , and J_z operators [36]. The α_J , β_J and γ_J are reduced matrix elements that have been previously calculated in Ref. [36]. The values for $\langle r^n \rangle$ are listed in Ref. [37] and consist of the expected value of the n th power of distance between a nucleus and the $4f$ electron shell. The 16 states of the spin-orbit ground state are split by the CEF into 8 doublets, and these are protected from further degeneracy-breaking by Kramer's theorem. The CEF energy eigenvalues and eigenfunctions associated with these 8 doublets are controlled by the crystal field parameters A_n^m , and these can be directly probed with inelastic neutron spectroscopy. The partial differential cross-section for magnetic neutron scattering can be written as follows [38]:

$$\frac{d^2\sigma}{d\Omega dE'} = C \frac{k_f}{k_i} F^2(|Q|) S(|Q|, \hbar\omega), \quad (2)$$

where Ω is the scattered solid angle, E' is the final neutron energy, $\frac{k_f}{k_i}$ is the ratio of the scattered and incident momentum of the neutron, C is a constant, and $F(|Q|)$ is the magnetic form factor. The scattering function $S(|Q|, \hbar\omega)$ for a CEF transition is given by:

$$S(|Q|, \hbar\omega) = \sum_{i,i'} \frac{\sum_{\alpha} |\langle i | J_{\alpha} | i' \rangle|^2 e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} L(\Delta E + \hbar\omega) \quad (3)$$

where $\alpha = x, y, z$ and $L(\Delta E + \hbar\omega) = L(E_i - E_{i'} + \hbar\omega)$ is a Lorentzian function that ensures energy conservation as the neutron induces transitions between the CEF levels $i \rightarrow i'$, which possess a finite energy width or lifetime.

In order to determine the CEF parameters, A_n^m , we start with a particular set of A_n^m and diagonalize the CEF Hamiltonian to obtain a set of initial energy eigenvalues and eigenfunctions. In this work, we used the A_n^m obtained for $\text{Er}_2\text{Ti}_2\text{O}_7$ from Ref. [39] as our starting CEF parameters. A least squares refinement of the A_n^m values is then performed to minimize the difference between the calculated and observed CEF spectra. This refinement considers both the energies of the transitions as well as their relative intensities.

EXPERIMENTAL DETAILS

The four erbium pyrochlore magnets were all studied in powder form. Large 10 g samples of both $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ were prepared via conventional solid state synthesis [40]. $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Pt}_2\text{O}_7$ were prepared using a belt-type high pressure apparatus, yielding 2.8 g and 1.1 g samples, respectively. The details of the high pressure synthetic method employed are given in Ref. [41] for $\text{Er}_2\text{Ge}_2\text{O}_7$ and in Ref. [42] for $\text{Er}_2\text{Pt}_2\text{O}_7$.

TABLE I. Summary of fitted structural parameters for the erbium pyrochlore magnets, as determined by Rietveld refinement of their powder neutron diffraction patterns measured at 10 K. The variance in the cubic lattice parameter, a , is largely controlled by the radius of the B -site cation. The only adjustable atomic coordinate within the pyrochlore ($Fd\bar{3}m$) structure is the x position of the apical oxygens (O1). The four entries of the final columns give the goodness-of-fit parameters for the Rietveld refinements, which are shown in Figure 1.

| | B (Å) | a (Å) | O1 x | Er-O1 (Å) | Er-O2 (Å) | $\frac{\text{Er-O2}}{\text{Er-O1}}$ | R_p | R_{wp} | R_{exp} | χ^2 |
|------------------------------------|---------|----------|--------|-----------|-----------|-------------------------------------|-------|----------|-----------|----------|
| $\text{Er}_2\text{Ge}_2\text{O}_7$ | 0.67 | 9.87(5) | 0.327 | 2.442 | 2.136 | 0.875 | 5.4% | 4.0% | 1.6% | 6.5 |
| $\text{Er}_2\text{Ti}_2\text{O}_7$ | 0.745 | 10.05(3) | 0.330 | 2.463 | 2.176 | 0.883 | 7.7% | 6.8% | 1.7% | 15.8 |
| $\text{Er}_2\text{Pt}_2\text{O}_7$ | 0.765 | 10.13(2) | 0.340 | 2.416 | 2.193 | 0.908 | 4.6% | 2.8% | 1.6% | 3.0 |
| $\text{Er}_2\text{Sn}_2\text{O}_7$ | 0.83 | 10.30(1) | 0.338 | 2.470 | 2.230 | 0.903 | 8.0% | 7.2% | 1.9% | 14.6 |

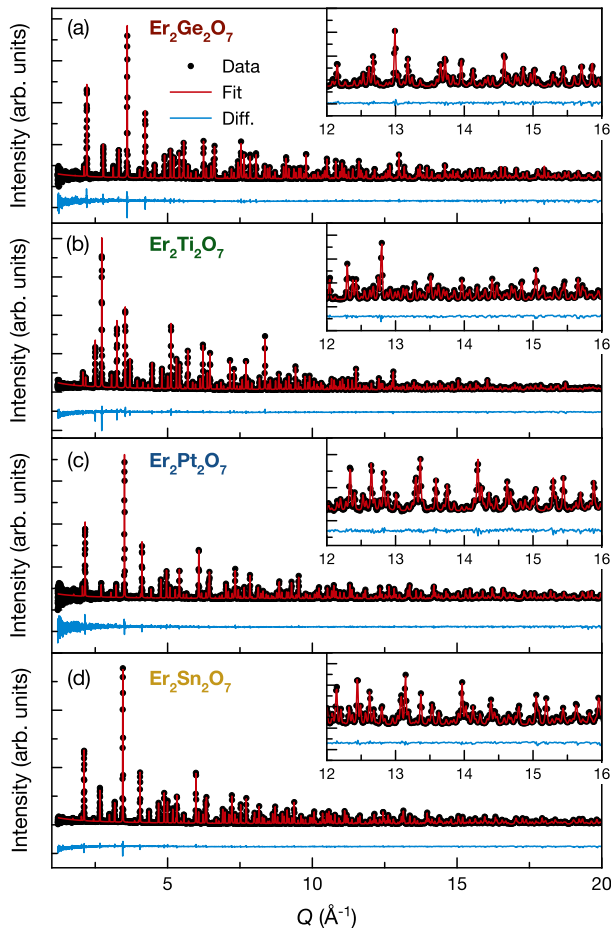


FIG. 1. Rietveld refinements of the time-of-flight neutron powder diffraction patterns for each of the erbium pyrochlore magnets, Er_2B_2O_7 , B = (a) Ge (b) Ti (c) Pt and (d) Sn. The data sets were collected at 10 K using Bank 2 of the POWGEN diffractometer ($\lambda_{\text{center}} = 1.066$ Å). The data were refined against the $Fd\bar{3}m$ space group, and the goodness-of-fit parameters for each sample are given in Table I. The insets show an expanded view of a high Q region, from 12 to 16 Å⁻¹.

Powder neutron diffraction was carried out on each of the four samples using the time-of-flight diffractometer POWGEN at the Spallation Neutron Source at Oak Ridge National Laboratory [43]. The samples were sealed in vanadium cans in the presence of a helium atmosphere

and were each measured for one hour at 10 K. These measurements were performed with a median wavelength of $\lambda = 1.066$ Å. This configuration allows for momentum transfers between $1.2 \text{ Å}^{-1} < Q < 22.8 \text{ Å}^{-1}$. Rietveld refinements of the data were carried out using the FullProf [44] software suite.

The inelastic neutron scattering measurements were performed using the direct geometry, time-of-flight chopper spectrometer, SEQUOIA, at the Spallation Neutron Source [45]. Each sample was measured at two temperatures (5 K and 100 K) and three incident neutron energies (25 meV, 90 meV and 150 meV). For all incident neutron energies, the fine Fermi chopper was used to achieve the maximum energy resolution, corresponding to 1 – 2% of the neutron’s initial energy, E_i . The resultant energy resolution at the elastic line was $\Delta E = 0.45$ meV for $E_i = 25$ meV, $\Delta E = 1.5$ meV for $E_i = 90$ meV, and $\Delta E = 2.8$ meV for $E_i = 150$ meV. The energy resolution improves as a function of energy transfer and at 80% E_i reaches a value that is approximately one third of the elastic resolution. The samples were packed in aluminum cans in annular geometry and sealed with indium in the presence of a helium atmosphere. An identical empty can was also measured and this served as a background, where all the data presented have had the empty can data set subtracted from them. The inelastic neutron scattering data were reduced using Mantid [46] and were analyzed using DAVE [47].

RESULTS AND ANALYSIS

Structural refinement by powder neutron diffraction

In order to characterize the structural properties of each of the four erbium pyrochlore magnets, we performed time-of-flight powder neutron diffraction. The data were analyzed by Rietveld refinement using the $Fd\bar{3}m$ space group, as shown in Figure 1. The fitted parameters resulting from these refinements are summarized in Table I. The largest structural differences going across this series arise from the substitution of the

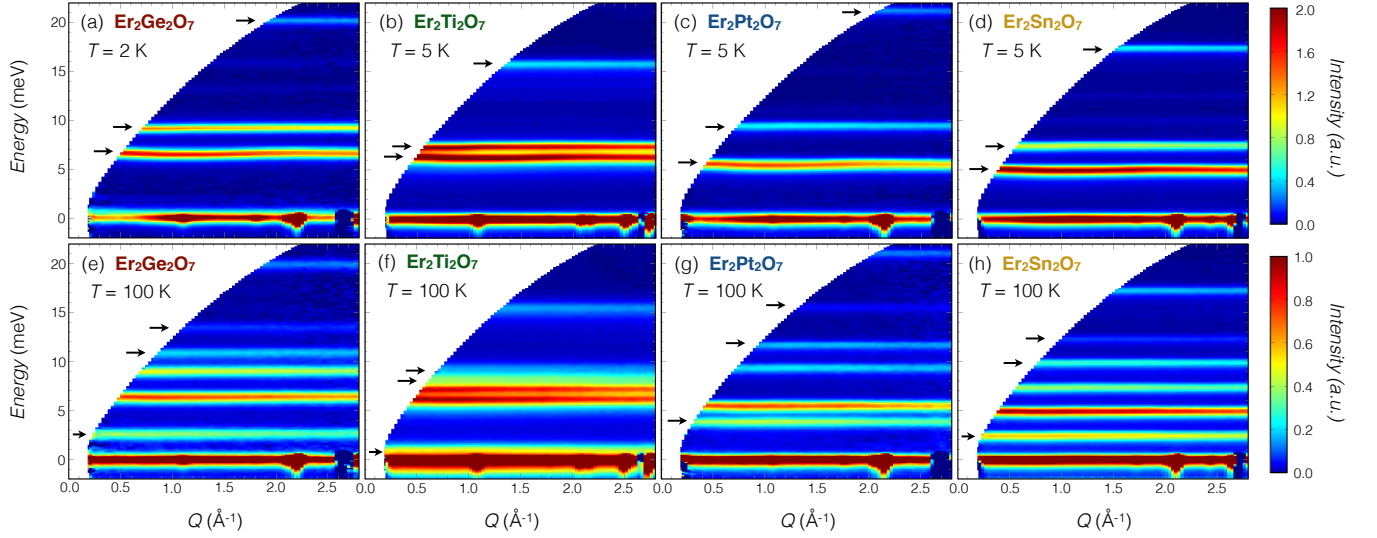


FIG. 2. Inelastic neutron scattering measurements with an incident energy of $E_i = 25$ meV for the $\text{Er}_2\text{B}_2\text{O}_7$ pyrochlores, $B =$ (a,e) Ge, (b,f) Ti, (c,g) Pt, and (d,h) Sn. The top row shows the spectra at base temperature (2 K or 5 K) for each sample. In each case, three ground state crystal electric field excitations are identified at the positions indicated by the arrows. The bottom row show the spectra at 100 K, which is high enough to thermally populate transitions from the first and second excited state levels. The excited state transitions at 100 K are indicated by the arrows. An empty can measurement has been subtracted from all data sets.

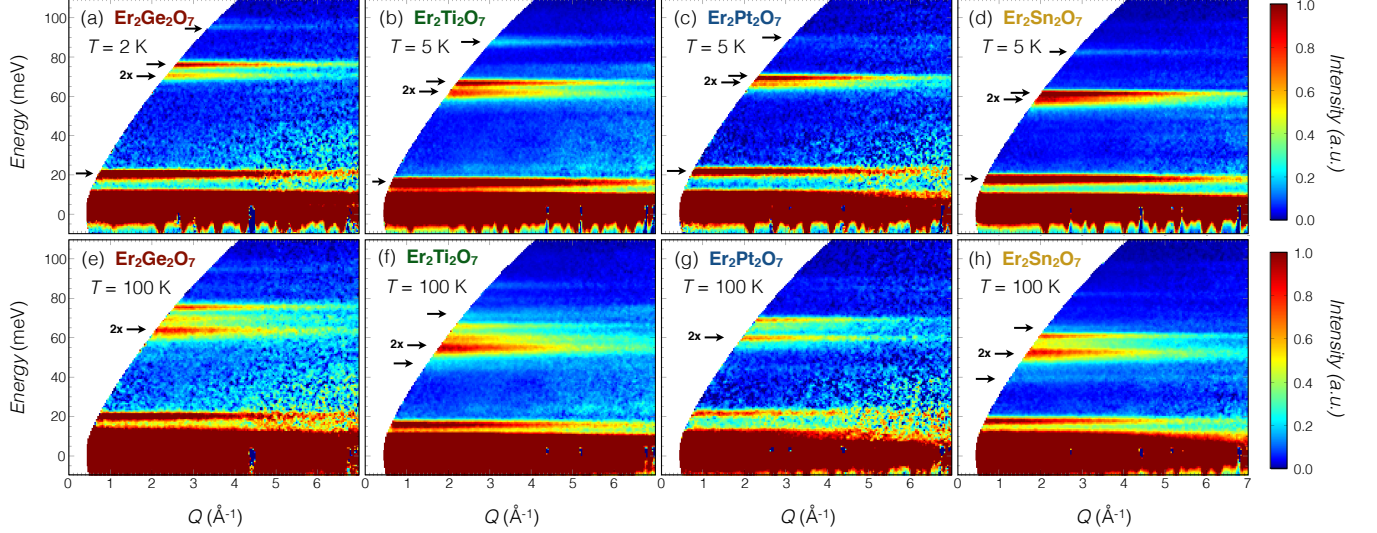


FIG. 3. Inelastic neutron scattering measurements with an incident energy of $E_i = 150$ meV for the $\text{Er}_2\text{B}_2\text{O}_7$ pyrochlores, $B =$ (a,e) Ge, (b,f) Ti, (c,g) Pt, and (d,h) Sn. The top row shows the spectra at base temperature (2 K or 5 K) for each sample. In each case, four higher energy ground state crystal electric field excitations are identified at the positions indicated by the arrows, in addition to the transition at ~ 20 meV, which was also seen in the $E_i = 25$ meV data set. The bottom row show the spectra at 100 K, which is high enough to thermally populate transitions from the first and second excited state levels. The excited state transitions at 100 K are indicated by the arrows. An empty can measurement has been subtracted from all data sets.

non-magnetic B -site. Indeed the cubic lattice parameter, a , is observed to vary linearly with the ionic radius of the B -site cation. Thus, $\text{Er}_2\text{Ge}_2\text{O}_7$, which has the smallest B -site cation, has a lattice parameter of $a = 9.87(5)$ Å, while $\text{Er}_2\text{Sn}_2\text{O}_7$ with the largest B -site, has a lattice parameter of $a = 10.30$ Å. Across the whole series, the

lattice parameter varies by 4%. It is interesting to note that the two middle members, $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Pt}_2\text{O}_7$, have the most similar B -site radii and correspondingly, the most similar lattice parameters, varying by only 0.7%. $\text{Er}_2\text{Pt}_2\text{O}_7$, however, is a unique member of this family due to the fact that platinum, unlike the

other non-magnetic B -site ions, does not have a closed electron shell configuration. Platinum in its 4+ oxidation state has an $[\text{Xe}]5d^6$ electron configuration, which is non-magnetic due to the filled t_{2g} levels and sizable gap to the empty e_g levels.

In the cubic pyrochlore structure, erbium sits at the $16d$ Wyckoff position and is surrounded by a distorted cube of oxygen anions. This distortion acts along the local $\langle 111 \rangle$ direction, compressing the cube along the body diagonal. Thus, there are two equivalent Er-O1 bonds and six equivalent Er-O2 bonds. The degree of this distortion is characterized by the oxygen (O1) x coordinate, which is the only adjustable parameter in the pyrochlore structure. An oxygen environment taking up a perfect cube would have $x = 0.375$, and the distortion grows with the deviation from this value. The distortion from an ideal cubic environment can alternatively be parameterized by the ratio of the Er-O1 and Er-O2 bond lengths, as tabulated in Table I. The most distorted erbium oxygen environment occurs in $\text{Er}_2\text{Ge}_2\text{O}_7$ and the least distorted environment occurs in $\text{Er}_2\text{Pt}_2\text{O}_7$. Aside from $\text{Er}_2\text{Pt}_2\text{O}_7$, this distortion scales linearly with lattice parameter. Lastly, it is worth mentioning that the erbium-oxygen bond distances are generally the shortest in $\text{Er}_2\text{Ge}_2\text{O}_7$ ($\langle \text{Er} - \text{O} \rangle = 2.21 \text{ \AA}$) and largest in $\text{Er}_2\text{Sn}_2\text{O}_7$ ($\langle \text{Er} - \text{O} \rangle = 2.29 \text{ \AA}$).

Determination of the crystal field Hamiltonian with inelastic neutron scattering

The crystal electric field (CEF) spectra of the four erbium pyrochlore magnets were measured with inelastic neutron scattering. Data sets employing incident energies of 25 meV and 150 meV were collected at $T = 2$ or 5 K for all samples, and are shown in the upper panels of Fig. 2 and Fig. 3. As CEF excitations are single ion properties, they largely lack dispersion and decrease in intensity as a function of momentum transfer ($|\vec{Q}|$) following the magnetic form factor of Er^{3+} . From these criteria, it is clear that the $E_i = 25$ meV data sets at base temperature in Fig. 2(a-d) each show three CEF excitations, as indicated by the black arrows. For example, $\text{Er}_2\text{Ti}_2\text{O}_7$ has CEF excitations at 6.3, 7.3 and 15.7 meV. An example of the $|\vec{Q}|$ dependence of the CEF scattering is shown in Fig. 4(a) for the 15.7 meV excitation in $\text{Er}_2\text{Ti}_2\text{O}_7$, where the solid line corresponds to the magnetic form factor of Er^{3+} . All other CEF transitions observed in this work follow a similar $|\vec{Q}|$ dependence. As will be discussed later, it is interesting to note that the lack of dispersion of the low energy CEF excitations is not complete. Weak dispersion in the lowest energy levels develops at low temperatures as a consequence of exchange coupling between the Er^{3+}

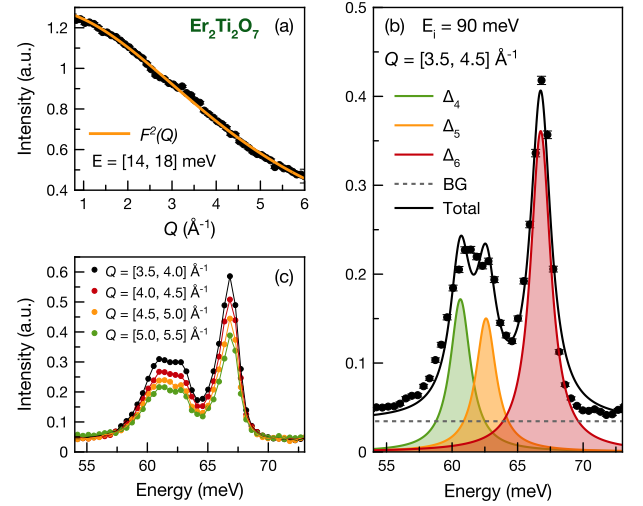


FIG. 4. (a) The $|\vec{Q}|$ dependence of the 15.7 meV CEF excitation of $\text{Er}_2\text{Ti}_2\text{O}_7$ is well captured by the single ion magnetic form factor of Er^{3+} . The same $|\vec{Q}|$ dependence is observed for all the CEF excitations resolved in this work. (b) The neutron scattering intensity as a function of energy transfer for $\text{Er}_2\text{Ti}_2\text{O}_7$, revealing the presence of three CEF excitations over the energy range shown. An example of a fit to the CEF spectra is shown. The fit captures the integrated intensity for all three CEF excitations and was used to optimize the CEF Hamiltonian. (c) The $|\vec{Q}|$ dependence associated with the Er^{3+} magnetic form factor can also be seen by performing energy cuts of the data with integrations over different $|\vec{Q}|$ ranges.

moments.

For each of the erbium pyrochlores studied in this work, the energy of the first CEF excitation is ~ 6 meV above the ground state. As these measurements were performed at $T = 2$ or 5 K, this first excited state cannot be significantly thermally populated and thus all observed CEF excitations necessarily originate from the CEF ground state. As previously discussed, the lowest energy manifold for Er^{3+} with $J = 15/2$ is composed of 8 doublets, one of which is the ground state. Thus, to resolve the full CEF manifold requires the identification of a total of seven transitions. Turning our attention to the base temperature $E_i = 150$ meV data sets shown in Fig. 3(a-d), three additional CEF transitions are clearly observed for all samples, as indicated by the black arrows. For example, $\text{Er}_2\text{Ti}_2\text{O}_7$ has CEF transitions at 61.0, 66.3 and 87.2 meV. From our analysis thus far, we can account for three CEF levels below 20 meV and three additional CEF levels between 50 meV and 100 meV.

As seven transitions are required to fully determine the energy scheme of the CEF manifold, there is a final CEF excitation that is not immediately resolved in the $E_i = 25$ meV and $E_i = 150$ meV data sets. However, inelastic neutron scattering spectra collected

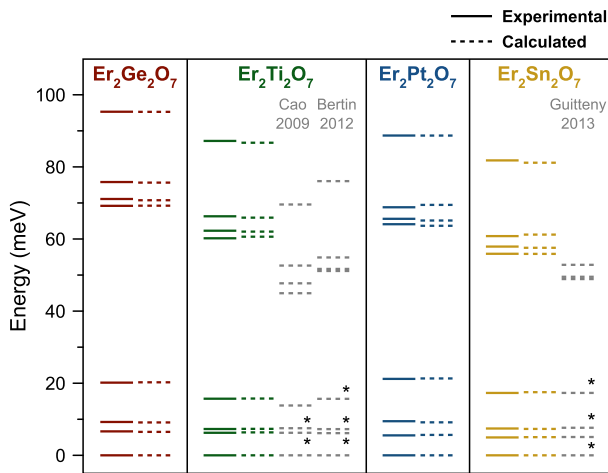


FIG. 5. Comparison between the experimentally resolved CEF energy schemes of the four erbium pyrochlore magnets and those calculated using the CEF Hamiltonians given in Table II. The calculated CEF spectra for $\text{Er}_2\text{Ti}_2\text{O}_7$ [39, 48] and $\text{Er}_2\text{Sn}_2\text{O}_7$ [29] derived from previous studies are also compared to our experimental data and are given by the gray dashed lines, where asterisks mark the levels that were fit.

with an incident energy of 90 meV allow us to resolve the missing CEF level. For $\text{Er}_2\text{Ti}_2\text{O}_7$, the level centered near 61.0 meV, as shown in Fig. 4(b), is in fact, two closely spaced CEF transitions that were unresolvable using higher incident energy with corresponding lower energy resolution. Fig. 4(c) shows the decreasing intensity of these two peaks as a function of momentum transfer, confirming that both features are magnetic in origin and thus, CEF excitations. The corresponding CEF level in each of the Er pyrochlore magnets is split by a similar amount. With this final CEF transition now accounted for, the entire CEF manifold is known and is presented in Fig. 5 for the four samples probed in this work.

Our experimentally deduced CEF scheme can be compared to the CEF Hamiltonians previously derived for $\text{Er}_2\text{Ti}_2\text{O}_7$ [39, 48] and $\text{Er}_2\text{Sn}_2\text{O}_7$ [29]. Using the parametrization from these previous works we have computed the CEF energy schemes, which are also presented by the dashed gray lines in Fig. 5. By comparing with our new results, it is clear that the previous CEF Hamiltonians do not reproduce well the high energy CEF levels. Thus, a new refinement of the CEF Hamiltonians was performed for $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ as well as for $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Pt}_2\text{O}_7$, for which no previous CEF Hamiltonian has been derived. In this work, it is now possible to rigorously constrain the CEF Hamiltonian because the full spin-orbit ground state manifold has been experimentally determined. This is in contrast to previous works that only considered the low energy excited states. To execute the fitting procedure, integrations of the scattered intensity as a

TABLE II. The refined CEF parameters A_n^m obtained for all four erbium pyrochlore magnets studied in this work.

| (all in meV) | A_2^0 | A_4^0 | A_4^3 | A_6^0 | A_6^3 | A_6^6 |
|------------------------------------|---------|---------|---------|---------|---------|---------|
| $\text{Er}_2\text{Ge}_2\text{O}_7$ | 39.3 | 36.2 | 275 | 1.23 | -19.10 | 26.6 |
| $\text{Er}_2\text{Ti}_2\text{O}_7$ | 37.5 | 33.5 | 282 | 1.25 | -17.15 | 21.6 |
| $\text{Er}_2\text{Pt}_2\text{O}_7$ | 49.0 | 31.2 | 262 | 1.10 | -19.15 | 24.6 |
| $\text{Er}_2\text{Sn}_2\text{O}_7$ | 50.8 | 28.4 | 266 | 1.10 | -17.15 | 20.9 |

function of energy transfer between $Q = 2.3$ to 2.8 \AA^{-1} for the $E_i = 25$ meV data set and $Q = 3.6$ to 4.6 \AA^{-1} for the $E_i = 150$ meV data set have been extracted from the base temperature contour maps of Fig. 2 and Fig. 3. The energy of each CEF level was determined by fitting the transition with a Lorentzian function for which the area represents the relative scattered intensity of the particular CEF transition. The relative intensities of the CEF transitions measured with the 25 meV, 90 meV and 150 meV were normalized to each other using the third-excited CEF state which appeared in all data sets (for example, the CEF at 20.2 meV for $\text{Er}_2\text{Ge}_2\text{O}_7$). In this manner, the CEF Hamiltonian was constrained using the energies of all transitions and their relative scattered intensities, giving a total of 13 constraints, for each of the four erbium pyrochlore magnets studied.

Using the extracted experimental constraints, the CEF Hamiltonian was first diagonalized using the CEF parameters of Bertin *et al.* derived for $\text{Er}_2\text{Ti}_2\text{O}_7$ [39]. A broad scan of the CEF parameters around this particular solution was performed to minimize the χ^2 value between the calculated and experimental CEF schemes, which considers both the energies of the transitions as well as their relative intensities. Very good agreement was obtained for all samples using the appropriate CEF parameters presented in Table II. The results of this optimization procedure are presented in Table IV of the Appendix, where the computed energies and intensities are compared to the experimental values. The resulting χ^2 of our calculation is equal to 1.3, 2.6, 2.3 and 3.2 for $\text{Er}_2\text{Ge}_2\text{O}_7$, $\text{Er}_2\text{Ti}_2\text{O}_7$, $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ respectively. To better appreciate the results of the fitting procedure, the entire neutron scattering spectra were computed between 0 and 120 meV using the CEF parameters of Table II with the addition of a sloping background to account for the phonon contribution. The resulting theoretical calculation is compared to the data in Fig. 6 for the four erbium pyrochlore samples. Excellent agreement between the calculated and measured scattering spectra is observed with no significant differences, validating the goodness of the fits.

To further scrutinize the quality of our CEF Hamiltonian parameters, inelastic neutron scattering spectra were collected at a temperature of 100 K, using both

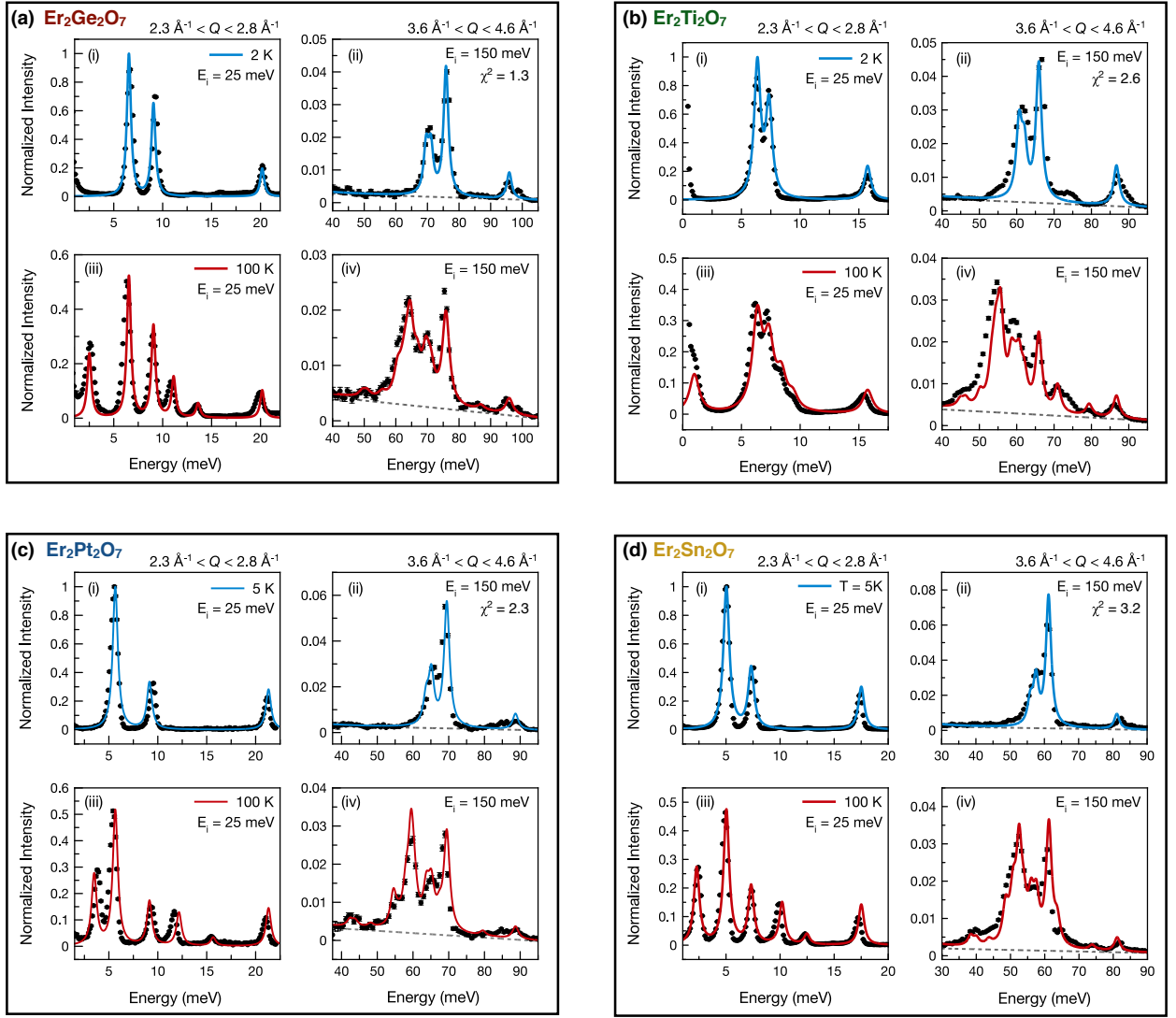


FIG. 6. Inelastic neutron spectra for (a) $\text{Er}_2\text{Ge}_2\text{O}_7$, (b) $\text{Er}_2\text{Ti}_2\text{O}_7$, (c) $\text{Er}_2\text{Pt}_2\text{O}_7$ and (d) $\text{Er}_2\text{Sn}_2\text{O}_7$ showing the scattering intensity as a function of energy transfer at base temperature ((i) $E_i = 25$ meV and (ii) $E_i = 150$ meV) and 100 K ((iii) $E_i = 25$ meV and (iv) $E_i = 150$ meV). These data sets are extrated from the contour maps of Fig. 2 and Fig. 3 with the indicated integration in momentum transfer, $|\vec{Q}|$. The calculated CEF spectra, using the CEF Hamiltonian parameters shown in Table II, are plotted by the blue ($T = 2$ and 5 K) and red ($T = 100$ K) lines.

$E_i = 25$ meV and $E_i = 150$ meV, which is shown in the bottom panels of Fig. 2 and Fig. 3. The increase of temperature from 5 K to 100 K produces new CEF excitations that originate from the increasing thermal population of the first and second excited CEF states. The new (relative to low temperature) low energy CEF excitations are indicated by the black arrows in the bottom panels of Fig. 2. For example, new transitions are observed at 1.1, 8.4 and 9.5 meV in $\text{Er}_2\text{Ti}_2\text{O}_7$ at 100 K. These originate from transitions between the 1st and 2nd excited CEF states, the 1st and 3rd excited CEF states, and the 2nd and 3rd excited CEF states. For the 100 K high energy spectra shown in Fig. 3, multiple new CEF excitations are observed between 40 and 100 meV. These

also correspond to transitions from the first and second excited CEF states to higher energy CEF states. The prominent new CEF transitions are indicated by black arrows in the bottom panels of Fig. 3.

Using Equation 2, we can compute the predicted inelastic scattering spectra at 100 K using the CEF parameters derived from our base temperature fits, given in Table II. The resulting calculations can be compared with the experimental data by performing cuts in energy integrated over the same range in $|\vec{Q}|$ as previously performed on the base temperature data sets. A sloping background has been added to the calculation to account for the increased phonon contribution. The

TABLE III. The composition of the CEF ground state doublet for the four erbium pyrochlore magnets studied in this work. The calculated components of the g -tensor perpendicular (g_{\perp}) and parallel (g_z) to the local $\langle 111 \rangle$ axis are also shown along with their ratio g_{\perp}/g_z and the calculated moment (μ_{cef}). The experimentally determined magnetic ground state (G.S) and its associated magnetic moment (μ_{ord}) obtained via powder neutron diffraction are also given for each erbium pyrochlore.

| | $ \pm 13/2\rangle$ | $ \pm 7/2\rangle$ | $ \pm 1/2\rangle$ | $ \mp 5/2\rangle$ | $ \mp 11/2\rangle$ | g_{\perp} | g_z | g_{\perp}/g_z | μ_{cef} (μ_B) | μ_{ord} (μ_B) | T_N (K) | G.S |
|------------------------------------|--------------------|-------------------|-------------------|-------------------|--------------------|-------------|---------|-----------------|-------------------------|-------------------------|-----------|-----------------|
| $\text{Er}_2\text{Ge}_2\text{O}_7$ | 0.395 | 0.338 | -0.521 | -0.176 | 0.653 | 7.0(6) | 2.1(4) | 3.3 | 3.6 | 3.23(6) | 1.4 | Γ_5 [24] |
| $\text{Er}_2\text{Ti}_2\text{O}_7$ | 0.389 | 0.257 | -0.491 | -0.082 | 0.732 | 6.3(5) | 3.9(5) | 1.6 | 3.7 | 3.25(9) | 1.2 | Γ_5 [25] |
| $\text{Er}_2\text{Pt}_2\text{O}_7$ | 0.381 | 0.439 | -0.563 | -0.280 | 0.516 | 7.7(6) | 0.30(7) | 28 | 3.9 | 3.4(2) | 0.3 | Γ_7 [26] |
| $\text{Er}_2\text{Sn}_2\text{O}_7$ | 0.541 | 0.244 | -0.578 | -0.413 | 0.379 | 7.6(7) | 0.14(5) | 54 | 3.8 | 3.1 | 0.1 | Γ_7 [27] |

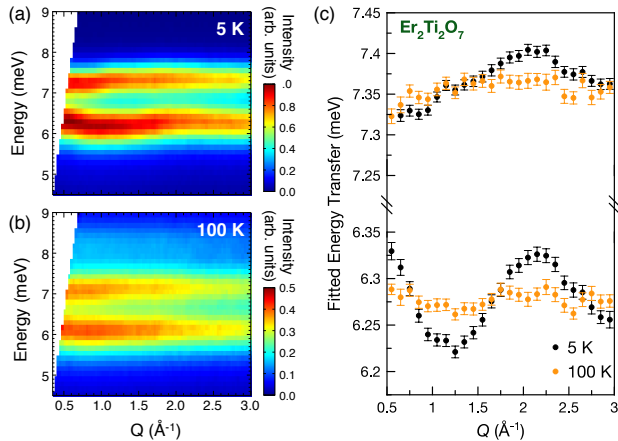


FIG. 7. An enhanced view of the lowest energy crystal electric field levels in $\text{Er}_2\text{Ti}_2\text{O}_7$ at (a) 5 K and (b) 100 K, revealing weak dispersion. (c) The maximum fitted intensity of these two CEF excitations as a function of $|\vec{Q}|$ at both 5 K and 100 K.

comparison between the theoretical curves and the experimental data at 100 K are shown in Fig. 6 for all four samples. The computed spectra is entirely consistent with the experimental data, demonstrating that our CEF Hamiltonian fits are well constrained and further validating the quality of the fit. Note that by comparing the 2 K and 100 K experimental spectra, slight negative energy shifts of the CEF transitions originating from the CEF ground state are observed upon raising the temperature. Such softening of the CEF excitations has also been observed in other rare-earth pyrochlore systems [49], and this is due to lattice expansion that occurs on raising the temperature, which in turn reduces the strength of the electric field at the Er^{3+} position.

As briefly alluded to earlier, our neutron scattering results reveal that the lowest energy CEF excitations in the erbium pyrochlores do not have a perfectly flat dispersion. To illustrate this effect, an enhanced view on the lowest energy CEF excitations of $\text{Er}_2\text{Ti}_2\text{O}_7$ measured with $E_i = 25$ meV is shown in Fig. 7(a). This reveals weak dispersion for the CEF excitation at 6.25 meV and possibly also for the CEF excitation at 7.3 meV. When the temperature is increased to $T = 100$ K, this dispersion

disappears, as shown in Fig. 7(b). To quantify the dispersion, we performed integrations along different $|\vec{Q}|$ values with a width of 0.1 \AA^{-1} . For every integration, we determined the positions of the low energy CEF excitations by fitting their line-shapes to a Gaussian function. The fitted centers of the Gaussian are plotted as a function of $|\vec{Q}|$ in Fig. 7(c) for both 5 K and 100 K. At 5 K, the 6.25 meV CEF excitation has a minimum in energy at $|\vec{Q}| \sim 1.1 \text{ \AA}^{-1}$, which corresponds to the range of $|\vec{Q}|$ where the $\langle 111 \rangle$ magnetic Bragg peak develops below $T_N = 1.2$ K in $\text{Er}_2\text{Ti}_2\text{O}_7$. The bandwidth of the dispersion of the 6.25 meV CEF excitation is $0.10(5)$ meV at 5 K, and perhaps slightly less for the CEF excitation near 7.3 meV. Weak dispersion is also observed for the first and second excited CEF levels of the three other erbium pyrochlores probed in this work. The shape of the dispersion, as well as its suppression at high temperature, are similar throughout the family. The origin of this weak dispersion is likely exchange interactions that lead to enhanced intersite correlations at low temperatures. Similar effects are observed in terbium pyrochlores, for which the lowest lying CEF excitations, located near 1 meV, display intense dispersion relative to their mean energy [50, 51].

DISCUSSION

With their CEF Hamiltonians in hand, it is interesting to analyze the evolution of the single-ion properties going across the erbium pyrochlore series. The composition of the CEF ground state doublet and the associated g -tensor components for each of the $\text{Er}_2\text{B}_2\text{O}_7$ materials are shown in Table III. Across the family, the compositions of the ground state doublets are qualitatively similar and consist of a mixture of $J_z = |\pm \frac{13}{2}\rangle, |\pm \frac{7}{2}\rangle, |\pm \frac{1}{2}\rangle, |\mp \frac{5}{2}\rangle, |\mp \frac{11}{2}\rangle$. In each case, the ground state doublet has local XY-like anisotropy because the g -tensor perpendicular to the local $\langle 111 \rangle$ (g_{\perp}) is larger than the parallel (g_z) component. However, the strength of the local XY anisotropy is an order of magnitude smaller for $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ than it is for $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$. This result suggests that the change in the g -tensor anisotropy going across the family could underly the stabilization of different magnetically ordered states. Indeed, both $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ order into the $k = 0 \Gamma_5$ manifold [24, 25]

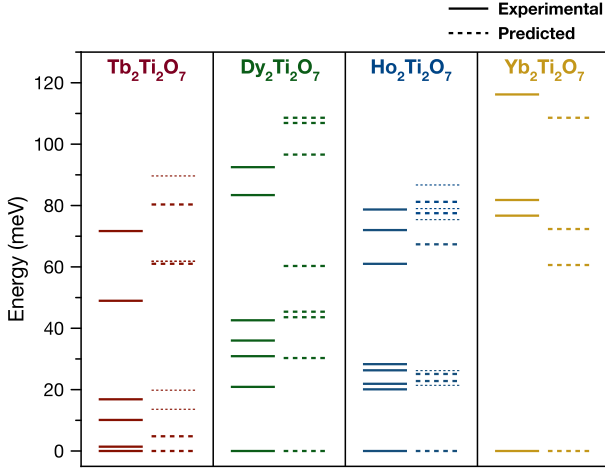


FIG. 8. Calculated CEF schemes for the rare earth titanates, $A_2\text{Ti}_2\text{O}_7$ ($A = \text{Tb}, \text{Dy}, \text{Ho}, \text{and Yb}$) obtained using scaling arguments from our fitted parameters for $\text{Er}_2\text{Ti}_2\text{O}_7$. The calculated levels are indicated by the dashed lines where, for $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, the singlet levels are denoted by a lighter dashed line. The experimentally determined CEF energies, reproduced from Refs. [49, 53, 54], are given by the solid lines.

and possess relatively weak XY anisotropy. In contrast, both $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ order into the $k = 0$ Γ_7 manifold [26, 27] and possess strong XY anisotropy.

To examine such a hypothesis, we can refer to the anisotropic exchange phase diagram of Ref. [52], where the four exchange couplings are labeled J_{zz} , J_{\pm} , $J_{\pm\pm}$, and $J_{z\pm}$. The classical phase boundary between the Γ_5 and Γ_7 states occurs at a critical ratio of $\frac{J_{\pm\pm}}{J_{\pm}} = 2$. Above this value, the predicted ground state is Γ_7 and below this value, the predicted ground state is Γ_5 [52]. Interestingly, both $J_{\pm\pm}$ and J_{\pm} are proportional to g_{\perp}^2 [29], and thus, the ratio of $\frac{J_{\pm\pm}}{J_{\pm}}$ should not, strictly speaking, depend on the g -tensor anisotropy. This would then suggest that the transition in magnetic ground state across the erbium pyrochlore family is driven by changes in the details of the orbital overlap and not the single-ion properties. Related to this point, it is interesting to note that the oxygen environment derived from our powder neutron analysis reveals a more cubic environment for $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ as compared to $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$. This may indicate a more isotropic exchange interaction for the two former materials, consistent with recent estimates of their exchange parameters [26, 27, 29]. Nonetheless, the two members of the erbium pyrochlore family that order into the Palmer-Chalker state also show extreme XY anisotropy, very small g_z , suppressed T_N , and a more cubic local environment around the Er^{3+} site as compared with the two members that order into Γ_5 states.

This new study of the erbium pyrochlores has resolved all possible CEF excitations within the lowest energy J multiplet, an analysis that has not been achieved for any other titanate pyrochlore besides $\text{Yb}_2\text{Ti}_2\text{O}_7$ [49], which has only three excited levels. Furthermore, as Er^{3+} is a Kramers ion, the assignment of each CEF level as a doublet is unambiguous, in contrast to non-Kramers $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$. It is therefore informative to use a scaling argument to approximate the CEF schemes for other pyrochlore magnets based on our new comprehensive results. As the titanates are the best studied family of insulating rare earth pyrochlores, we have focused on approximating the CEF schemes for $A_2\text{Ti}_2\text{O}_7$ ($A = \text{Tb}, \text{Dy}, \text{Ho}, \text{and Yb}$) starting from the parameters obtained for $\text{Er}_2\text{Ti}_2\text{O}_7$. The scaling argument that connects the CEF parameters, $A_n^m(R)$, between different rare earth-based pyrochlores is given by the following [32]:

$$A_n^m(R') = \frac{a^{n+1}(R)}{a^{n+1}(R')} A_n^m(R), \quad (4)$$

where the cubic lattice parameters, $a(R)$, have been taken from Ref. [55]. The resulting CEF Hamiltonian approximation is given in Fig. 8 where it is compared with the measured schemes from Refs. [49, 53, 54]. The CEF schemes obtained from this procedure have good qualitative agreement with the experimental data, but are quantitatively inaccurate, which should not be surprising for several reasons. First, this analysis assumes that the oxygen environment surrounding each rare earth ion has the same O1 x parameter and that the oxygen cage simply scales with the lattice parameter. However, it is known that the distortion of the oxygen cage depends on the A -site ion [56], which directly impacts the CEF energy scheme. Second, the shielding factor, which influences the overall scale of the CEF splitting, also depends on the A -site ion. This second point explains most of the discrepancy between our calculation and the experimental data. The correct form of the CEF scheme is observed for all the calculated spectra, but the overall energy range is either too high (for $A = \text{Tb}, \text{Dy}, \text{and Ho}$) or too low (for $A = \text{Yb}$). In the cases where the scaling is too large, the cation in question lies to the left of erbium on the periodic table and the opposite is true when the scaling is too small. The best agreement is obtained for $\text{Ho}_2\text{Ti}_2\text{O}_7$, where Er and Ho are next-door neighbors in the periodic table. These observations suggest that the shielding factor decreases on going from smaller (heavier) to bigger (lighter) rare earth ions.

Even if a quantitative discrepancy exists between the real and calculated CEF schemes, the scaling procedure can still be useful in terms of providing a starting point for analyzing the CEF scheme of any pyrochlore oxide. For example, it has been observed that the low energy CEF scheme for $\text{Tb}_2\text{Ti}_2\text{O}_7$ consists of four distinct magnetic excitations at approximately 1, 10, 14 and

16 meV [54, 57, 58]. However, no CEF Hamiltonian has been able to capture such a CEF energy scheme while remaining consistent with the high energy levels. Rather, one excited CEF doublet at 1 meV and two excited CEF singlets at 10 and 16 meV have been refined [54, 58]. To resolve this issue, it has been proposed that spin-phonon coupling is the origin of the extra inelastic feature observed at 14 meV [54]. Our CEF approximation for $\text{Tb}_2\text{Ti}_2\text{O}_7$, based on the scaling arguments above, also reveals only one excited CEF doublet at 4 meV and two excited CEF singlets at 12 and 20 meV. Thus, our scaling calculation further validates the spin-phonon origin of the enigmatic fourth excitation observed below 20 meV in $\text{Tb}_2\text{Ti}_2\text{O}_7$.

CONCLUSION

To conclude, we have carried out inelastic neutron scattering measurements on four members of the erbium pyrochlore family: $\text{Er}_2\text{B}_2\text{O}_7$ ($B = \text{Ge}, \text{Ti}, \text{Pt}, \text{and Sn}$). These measurements allow us to identify the entire set of CEF excitations belonging to the lowest energy J -multiplet for all four compounds. On the basis of these measurements, a CEF Hamiltonian was refined. These results give local XY-like anisotropy for the g -tensors of all four erbium pyrochlore magnets. However, large differences in the degree of XY anisotropy were observed, with $\text{Er}_2\text{Ge}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ displaying relatively more isotropic g -tensors as compared to $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$, which display extreme XY anisotropy with very low values of g_z . This variation in the relative XY anisotropy correlates strongly with magnetic ground state selection, as $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Ge}_2\text{O}_7$ order into the Γ_5 antiferromagnetic structures, while $\text{Er}_2\text{Pt}_2\text{O}_7$ and $\text{Er}_2\text{Sn}_2\text{O}_7$ order into the Γ_7 Palmer-Chalker structures. Finally, our study represents the most detailed analysis of the single-ion properties of these erbium pyrochlores to date, a key ingredient for a detailed characterization of their spin Hamiltonians, and crucial for a clear understanding of the exotic magnetism observed in the XY pyrochlore magnets.

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TABLE IV. Tables giving the experimental and calculated values of the seven CEF excited state energies as well as the relative scattered intensities. The relative scattered intensity has been normalized by the intensity of the transition between the CEF ground state and the first excited state.

| Er ₂ Ge ₂ O ₇ | | | | | Er ₂ Ti ₂ O ₇ | | | | |
|--|-----------------|------------------|------------------|-------------------|--|-----------------|------------------|------------------|-------------------|
| | E_{exp} (meV) | E_{calc} (meV) | I_{exp} (a.u.) | I_{calc} (a.u.) | | E_{exp} (meV) | E_{calc} (meV) | I_{exp} (a.u.) | I_{calc} (a.u.) |
| 1 | 6.6(1) | 6.5 | 1 | 1 | 1 | 6.3(1) | 6.4 | 1 | 1 |
| 2 | 9.3(1) | 9.1 | 0.65(5) | 0.57 | 2 | 7.3(1) | 7.3 | 0.75(5) | 0.88 |
| 3 | 20.2(1) | 20.3 | 0.20(3) | 0.24 | 3 | 15.7(1) | 15.7 | 0.20(5) | 0.3 |
| 4 | 69.2(3) | 69.2 | 0.04(3) | 0.04 | 4 | 60.2(3) | 60.6 | 0.04(2) | 0.07 |
| 5 | 71.1(3) | 70.8 | 0.04(3) | 0.04 | 5 | 62.3(3) | 62.0 | 0.04(2) | 0.05 |
| 6 | 75.8(3) | 75.6 | 0.10(2) | 0.14 | 6 | 66.3(3) | 65.9 | 0.09(2) | 0.13 |
| 7 | 95.3(4) | 95.3 | 0.015(5) | 0.03 | 7 | 87.2(4) | 86.7 | 0.01(1) | 0.04 |

| Er ₂ Pt ₂ O ₇ | | | | | Er ₂ Sn ₂ O ₇ | | | | |
|--|-----------------|------------------|------------------|-------------------|--|-----------------|------------------|------------------|-------------------|
| | E_{exp} (meV) | E_{calc} (meV) | I_{exp} (a.u.) | I_{calc} (a.u.) | | E_{exp} (meV) | E_{calc} (meV) | I_{exp} (a.u.) | I_{calc} (a.u.) |
| 1 | 5.5(1) | 5.7 | 1 | 1 | 1 | 5.0 | 5.0 | 1 | 1 |
| 2 | 9.5(1) | 9.1 | 0.29(5) | 0.33 | 2 | 7.4(1) | 7.3 | 0.36(5) | 0.43 |
| 3 | 21.2(1) | 21.3 | 0.21(5) | 0.28 | 3 | 17.3(1) | 17.5 | 0.24(5) | 0.3 |
| 4 | 64.1(3) | 63.7 | 0.04(2) | 0.03 | 4 | 55.9(3) | 55.8 | 0.04(2) | 0.04 |
| 5 | 65.6(3) | 65.1 | 0.06(2) | 0.06 | 5 | 57.9(3) | 57.5 | 0.06(2) | 0.07 |
| 6 | 68.8(3) | 69.5 | 0.12(2) | 0.16 | 6 | 66.8(3) | 61.2 | 0.10(2) | 0.2 |
| 7 | 88.7(4) | 88.7 | 0.01(1) | 0.02 | 7 | 81.8(4) | 81.1 | 0.02(1) | 0.02 |