Effective point-charge analysis of crystal electric fields – application to rare-earth pyrochlores and tripod kagome magnets $R_3Mg_2Sb_3O_{14}$

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(Dated: May 13, 2020)

An indispensable step to understand collective magnetic phenomena in rare-earth compounds is the determination of spatially-anisotropic single-ion properties resulting from spin-orbit coupling and crystal electric field (CEF). The CEF Hamiltonian has a discrete energy spectrum – accessible to spectroscopic probes such as neutron scattering – controlled by a number of independent parameters reflecting the point-symmetry of the magnetic sites. Determining these parameters in low-symmetry systems is often challenging. Here, we describe a general method to analyze CEF excitation spectra using adjustable effective point-charges. We benchmark our method to existing neutron-scattering measurements on pyrochlore rare-earth oxides and obtain a universal point-charge model that describes a large family of related materials. We adapt this model to the newly discovered tripod Kagome magnets ($R_3Mg_2Sb_3O_{14}$, $R =$ Tb, Ho, Er, Yb) for which we report broadband inelastic neutron-scattering spectra. Analysis of these data using adjustable point-charges yields the CEF wave-functions for each compound. From this, we calculate thermomagnetic properties that accurately reflect our measurements on powder samples, and predict the effective gyromagnetic tensor for pseudo-spin degrees of freedom – a crucial step to understand the exotic collective properties of these kagome magnets at low temperature. We present further applications of our method to other tripod kagome materials and triangular rare-earth compounds $RMgGaO_4$ ($R =$ Yb, Tm). Overall, this study establishes a widely applicable methodology to predict CEF and single-ion properties of rare-earth compounds based on interpretable and adjustable models of effective point-charges.

I. INTRODUCTION

In most magnetic insulators, electrons in the partially-filled atomic shells of transition-metal or rare-earth cations give rise to localized magnetic moments. In general, determining the individual properties of these magnetic moments is difficult because electrons’ spins are coupled to their orbital angular momentum and to the surrounding environment of diamagnetic anions by the spin-orbit and Coulomb interactions. Furthermore, magnetic moments can interact with each other through exchange interactions, often via an intermediary ligand, or directly via dipole-dipole interactions. Nonetheless, in the low-energy limit, it is often possible to describe the magnetic dipole moment of these complex multi-electron systems as an effective spin degree of freedom, with an anisotropic gyromagnetic tensor that stems from the spatial distribution of local magnetization, and an anisotropic bi-linear exchange Hamiltonian that describes the interactions between two nearby effective spins. Anisotropic dipole moments and bond-dependent exchange interactions play a central role in forefront problems in quantum magnetism such as the realization of quantum spin-ice in pyrochlore systems. Kitaev spin-liquids on the honeycomb lattice, or triangular-lattice rare-earth antiferromagnets such as YbMgGaO$_4$. The first step to understand the magnetism of these frustrated magnets is to accurately capture their spin-space anisotropy, i.e., properties of their gyromagnetic $g$-tensor and exchange tensors.

For an isolated rare-earth ion, the spin-orbit interaction couples the total spin $S$ and orbital $L$ angular momenta of the unpaired electrons’ manifold such that the total angular momentum $J = L + S$ is usually a good quantum number. When ions are embedded in a crystal, the $2J+1$ level degeneracy is split by the electrostatic field produced by surrounding ligands, e.g. the crystal electric-field (CEF). The theoretical framework of the CEF theory was developed in 1952 by Stevens who first expressed the electrostatic potential of rare-earth ions as a linear combination of angular momentum operators, the Stevens’ operators, from which the $g$-tensor can be directly obtained. In 1964, Hutchings demonstrated that CEF energy levels can in principle be calculated from a point-charge ionic model of the ligand environment. Later work showed that the number of CEF parameters solely depends on the point-group symmetry of the ionic site, from 2 for cubic, 6 or 8 for hexagonal, to a maximum number of 26 for lower symmetry environments. For rare-earth systems, the energy scale of the CEF generally varies between a few meV to hundreds of meV, depending on the nature of the ligands and their distance to the magnetic ions, which is at least one order of magnitude larger than exchange interactions. This separation of energy scale suggests that the collective multi-ion effects at low energies can be viewed as a perturbation to the high-energy single-ion physics; and all non-zero components of the exchange tensor can in principle be obtained from the CEF wave-functions using a perturbation theory after considering the combination effects of space group symmetry, time reversal symmetry associated with Kramers/non-Kramers ions, and dipolar/multipolar nature of effective moments. In this sense, understanding spin-space anisotropy depends profoundly on the determination of the CEF Hamiltonian and its parameters.

To date, ab-initio calculations of CEF effects for $f$-electron systems have not proven trustworthy. Therefore, the determination of the CEF Hamiltonian in a real material relies heavily on interpretation and fitting of experimental data. Inelas-
tic neutron scattering is one of the most advantageous experimental techniques to do so because it directly measures the CEF eigenvalues (excitation energies) as well as the dipolar matrix elements between CEF eigenfunctions (excitation intensities)\textsuperscript{21,22}. Typically, the analysis consists in searching a high-dimensional space for CEF parameters that best fit the experimental observables. In many cases, this process can be problematic: (i) the CEF parameters are not directly associated with any measurable physical quantities, one usually does not know where to start within the high-dimensional parameter space; (ii) not all CEF levels can be resolved experimentally due to low-intensity, mediocre resolution of neutron-scattering experiments at high energy-transfer or overlap with the phonon background; (iii) it is possible to encounter degenerate best-fit solutions yielding totally different CEF wavefunctions. The situation becomes especially challenging in low-symmetry materials where the number of experimental observables is considerably less than the number of CEF parameters. A widely adopted strategy to resolve this problem is to start with a point-charge (PC) calculation by which the parameters. Examples where such approach is to start with a point-charge (PC) calculation by which the parameters. A widely adopted strategy to resolve this problem is to start with a point-charge (PC) calculation by which the unknown positions of the surrounding ligands are used to estimate the CEF parameters. Examples where such approach has been used include the pyrochlore Yb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}\textsuperscript{23}, and Nd-based tripod kagome compounds\textsuperscript{24}. However, as pointed out by Hutchings himself and as we will further demonstrate below, PC calculations based on a purely crystallographic model – where point electric charges are placed at the crystal lattice sites – have weaknesses because they neglect the finite extent of charges on the ions, covalent bonding with the ligands, and the complex effects of “screening”\textsuperscript{\textregistered} of the magnetic electrons by the outer electron shells of the magnetic ions\textsuperscript{14}. Therefore, CEF calculations from the crystallographic PC model are usually not realistic.

In this manuscript, we adopt a new approach to solve this problem. Instead of fitting the CEF excitations using Steven’s operators, we employ a direct calculation and fitting algorithm based on an effective-PC model, which relies on point electric-charges located on the rare-earth-ion to ligand segment and carrying a reduced charge. This model overcomes the weakness of PC calculations in a semi-empirical way, and has recently been successfully used in the community of single-molecule magnets\textsuperscript{25,26}. The advantage of our approach is a physically meaningful parameterization and a constrained parameter space. This proves to be extremely valuable for low-symmetry systems, such as the tripod kagome magnets\textsuperscript{27–32} presented in this study [Fig. 1] for which the number of required parameters is reduced from 15 to 9.

The structure of the paper is as follows. First, in Sec. II, we describe the experimental methods as well as and the theoretical principles involved. Second, in Sec. III, we introduce the concept of effective-PC Model and provide a benchmark to the the existing inelastic neutron scattering measurements of pyrochlore rare-earth oxides. Then, in Sec. III, we proceed with the main experimental results of this work, the CEF excitations of the newly discovered tripod kagome magnets ($R_3Mg_2Sb_3O_{14}$, $R$ = Tb, Ho, Er, Yb)\textsuperscript{31}. We modify the effective-PC model and perform fit to the data, from which susceptibility, isothermal magnetization, $g$-tensor, and principal axes are obtained and compared to the experimental observations. Finally, we discuss some other applications of the effective-PC model, including understanding the pressure effects on the transverse field, as well as making predictions for other tripod kagome materials and triangular compounds $RMgGaO_4$ ($R$ = Yb, Tm). In short, although our work does not provide new physical insights into the CEF theory, it describes a general methodology to modify the PC model to more accurately analyze and predict CEF phenomena in real materials.

II. METHODS

A. Sample Synthesis

All the tripod kagome compounds $R_3Mg_2Sb_3O_{14}$ ($R$ = Tb, Ho, Er, Yb) were synthesized by a sol-gel technique using rare-earth oxides (Tb\textsubscript{2}O\textsubscript{3}, Er\textsubscript{2}O\textsubscript{3}, Ho\textsubscript{2}O\textsubscript{3}, Yb\textsubscript{2}O\textsubscript{3}, 99.9%), MgO (99.99%), Sb\textsubscript{2}O\textsubscript{3} (99.9%), nitric acid (ACS grade), tartaric acid (C\textsubscript{4}H\textsubscript{6}O\textsubscript{6}), and citric acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}) as starting materials. For each compound, stoichiometric ratios of $R(NO_3)_3$, Mg(NO\textsubscript{3})\textsubscript{3} (prepared by dissolving rare earth ox-
| No. | $R_2X_2O_7$ | $R_3Mg_2Sb_3O_{14}$ | $RMgGaO_4$ |
|-----|-------------|-----------------|------------|
|     | $r$ (Å)     | $\theta (^\circ)$ | $\phi (^\circ)$ | $q$ (e) | $r$ (Å) | $\theta (^\circ)$ | $\phi (^\circ)$ | $q$ (e) | $r$ (Å) | $\theta (^\circ)$ | $\phi (^\circ)$ | $q$ (e) |
| 1   | $r_1$     | 0     | 0     | $q_1$ | $r_1$ | 0     | 0     | $q_1$ | $r_1$ | $\theta_1$ | 0     | $q_1$ |
| 2   | $r_1$     | 180   | 0     | $q_1$ | $r_1$ | 1     | 0     | $q_1$ | $r_1$ | $\theta_1$ | 120   | $q_1$ |
| 3   | $r_2$     | $\theta_2$ | 60 | $q_2$ | $r_2$ | $\theta_2$ | $\phi_2$ | $q_2$ | $r_2$ | $\theta_1$ | 240   | $q_2$ |
| 4   | $r_2$     | 180-$\theta_2$ | 120 | $q_2$ | $r_2$ | 180-$\theta_2$ | 180-$\phi_2$ | $q_2$ | $r_2$ | 180-$\theta_1$ | 60    | $q_2$ |
| 5   | $r_2$     | $\theta_2$ | 300 | $q_2$ | $r_2$ | $\theta_2$ | 360-$\phi_2$ | $q_2$ | $r_2$ | 180-$\theta_1$ | 180   | $q_2$ |
| 6   | $r_2$     | 180-$\theta_2$ | 240 | $q_2$ | $r_2$ | 180-$\theta_2$ | 180+$\phi_2$ | $q_2$ | $r_2$ | 180-$\theta_1$ | 300   | $q_2$ |
| 7   | $r_2$     | $\theta_3$ | 180 | $q_3$ | $r_2$ | $\theta_3$ | 180 | $q_3$ | $r_2$ | 180-$\theta_3$ | 0     | $q_3$ |
| 8   | $r_2$     | 180-$\theta_3$ | 0 | $q_3$ | $r_1$, $\theta_1$, $\phi_1$ |

PC parameters: $r_1$, $r_2$, $\theta_1$, $\theta_2$, $\phi_1$, $\phi_2$, $q_1$, $q_2$, $q_3$.

CEF parameters: $A_{0}^{0}, A_{4}^{0}, A_{6}^{0}, A_{8}^{0}$, $A_{0}^{2}, A_{4}^{2}, A_{6}^{2}, A_{8}^{2}$, $A_{0}^{4}, A_{4}^{4}, A_{6}^{4}, A_{8}^{4}$, $A_{0}^{6}, A_{4}^{6}, A_{6}^{6}, A_{8}^{6}$.

Crystallographic PC model: $r_i = r_i^c$, $\theta_i = \theta_i^c$, $\phi_i = \phi_i^c$, $q_i = 2e$.

Effective PC model: $q_1 = 0.5e$, $q_2 = 0.333e$, $q_3 = 0.15e$.

TABLE I. Parametrization of Point-Charge (PC) models written in spherical coordinates for the point-group symmetry of rare-earth pyrochlores $R_2X_2O_7$ ($D_{2h}$), tripod kagome magnet $R_3Mg_2Sb_3O_{14}$ ($C_{2h}$), and triangular-lattice rare-earth antiferromagnets $RMgGaO_4$ ($D_{2h}$). The last case describes a rare-earth ion in the center of an octahedron with 3-fold symmetry which also applies to the site-disordered $R$ ions in $R_2X_2O_7$ and $R_3Mg_2Sb_3O_{14}$. The amount of charge is measured in the unit of electron charge (e). The variables $r_i^c$, $\theta_i^c$, and $\phi_i^c$ denote the crystallographic parameters associated with the rare-earth ion to oxygen-ligand parameters in real materials. For the effective PC model, $f$ denotes a reduction factor associated with the shortest $R$–$O$ bond distance, and we find $f \approx 0.72$ is a proper choice for most materials in this study.

ides and MgO in hot diluted nitric acid solution, and antimonyl tartarate (prepared by dissolving $Sb_2O_3$ in hot tartaric acid solution) were first mixed in a beaker. Citrate acid with a metal-to-citrate molar ratio of 1:2 was then added to the solution followed by a subsequent heating on a hot plate at 120°C overnight to remove excessive water. The obtained gel-like solution was slowly heated to 200°C in a box furnace to decompose the nitrate, and was pyrolyzed at 600°C for 12 hours in air. The obtained powder was ground up, pressed into a pellet and re-heated at 1300 to 1350°C until a well reacted crystallized powder was obtained. It is noteworthy that powder samples of tripod kagome compounds synthesized by the conventional solid state reactions are usually accompanied by 2-3% magnetic impurities (mainly a robust $R_3SbO_7$ phase), which had been a considerable complication for interpreting the thermodynamic properties of the system in previous studies. A big advantage of the sol-gel synthesis is its high efficiency in getting impurity-free samples. A comparison between measurements on two $Ho_3Mg_2Sb_3O_{14}$ samples synthesized by the two methods can be found in Ref. 32.

### B. Experimental Measurements

Inelastic neutron-scattering measurements were performed on the fine-resolution Fermi chopper spectrometer (SEQUOIA) at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL), USA. For each of the tripod kagome compounds, a powder sample with a typical mass $\approx 5g$ was loaded in an aluminum container (an aluminum annular cylinder was used for $Er_3Mg_2Sb_3O_{14}$ to minimize absorption), and was cooled down to 5 K using a closed-cycle refrigerator. Data were collected with incident neutron energies $E_i = 240, 120,$ and 30 meV (yielding an elastic energy-resolution of 5.5, 1.9, and 0.5 meV, respectively) at temperatures $T = 300$ K, 100 K, 50 K, and 5 K. The same measurements were repeated for an empty aluminum sample holder and used for background subtraction. Data reduction was performed using the Mantid to yield the neutron scattering intensity $I(Q, \omega)$ as a function of momentum-transfer $Q$ and energy-transfer $\omega$. Data were further processed with the DAVE program. The phonon contribution to the scattering intensity was subtracted in two different ways. For the $E_i = 30$ meV datasets, we take advantage of the absence of low-energy CEF excitations in $Yb_3Mg_2Sb_3O_{14}$ below $E \approx 50$ meV and use its spectra as phonon background for the other three compounds. For the higher $E_i$ datasets, phonon background was modeled and subsequently subtracted by assuming a $Q^2$ intensity dependence.

Magnetic susceptibility and isothermal magnetization were measured using a Quantum Design Physical Properties Measurement System (PPMS). Magnetic susceptibility, $\chi(T) = M(T)/H$, was measured while cooling the sample from $T = 400$ K to 1.8 K in an external field $\mu_0H = 0.1$ T. Isothermal magnetization, $M(H)$, were measured between $0 \leq \mu_0H \leq 14$ T at selected temperatures between $T = 1.8$ K and 40 K. The measured were was corrected for the diamagnetic background of the sample holder which is crucial for the values of $1/\chi(T)$ at high temperatures. Diamagnetic contribution from the sample is much smaller, therefore is not corrected in this study.

### C. Point-Charge Calculations

The electrostatic potential experienced by $f$-electrons can be expended in a series of polynomials of order sixth or lower,
such that the CEF Hamiltonian has the form,

$$\mathcal{H}_{CEF} = \sum_{n,m} [\gamma_n^m \theta_n^m] O_n^m = \sum_{n,m} B_n^m O_n^m,$$

(1)

where $O_n^m$ ($m \leq n$) are the Stevens’ operators, $A_n^m$ and $B_n^m$ are the CEF parameters. Here, $(\theta^n)$ represent numerical multiplication factors for the expectation values of the 4f-electron radial wave function which have been tabulated for each $\text{f}^{14+}$ ion.

Following the method outlined by Hutchings, the CEF levels can be calculated on the basis of a simple PC model where the electrostatic potential is approximated by a sum over the Coulomb potentials from N surrounding PCs at positions $\mathbf{R}_i$ with charges $q_i$, (in the unit of electron charge, e), i.e. $V(r, \theta, \phi) = \sum_i q_i / |\mathbf{R}_i - \mathbf{r}|$. When expressing the potential in tesseral harmonics $Z_{nm}$, the PC Hamiltonian becomes:

$$\mathcal{H}_{CEF} = -\sum_i q_i e \sum_{n,m} r^n Z_{nm}(r, \theta, \phi),$$

(2)

$$\gamma_i^{nm} = \frac{4\pi}{2n+1} Z_{nm}(\mathbf{R}_i) / R_i^{n+1}.$$

By connecting the expression of $Z_{nm}$ to $O_n^{14}$, the $A_n^m$ parameters are determined by the following expression:

$$A_n^m = -\sum_i C_n^m \gamma_i^{nm} q_i e,$$

(3)

where $C_n^m$ are the prefactors of the spherical harmonics, and $\gamma_i^{nm}$ are given by Eq. 2.

From here, it is clear that within the PC approximation, Eq. 2 and Eq. 3 allow one to construct the CEF Hamiltonian (Eq. 1) from the coordination and charge of surrounding ligands. In that context, the CEF parameters can be interpreted as a summation over the tesseral harmonics coefficients for the N surrounding PCs of the ligands. Because the number of CEF parameters required to describe $\mathcal{H}_{CEF}$ solely depends on the point-group symmetry of the rare-earth site, as tabulated by Walter, it is not directly related to the number of independent PC variables associated with the surrounding ligands. As a consequence, the PC model shows clear advantages over the conventional Stevens’ operators approach: (i) unlike the CEF parameters ($A_n^m$ or $B_n^m$), the PC variables ($\mathbf{R}_i, q_i$) are more physically meaningful; (ii) thus, the number of free parameters can be greatly reduced using explicit physical or chemical constraints; (iii) through PC calculations, one can easily track the changes of the CEF properties induced by modifications to the crystallographic structure. These advantages are particularly important in the case of low symmetry systems, such as the tripod kagome compounds discussed further below.

D. Point-charge Fit to CEF excitations

For a rare-earth ion with total angular momentum $J$, the eigenstates of Eq. 1 are $2J+1$ levels with eigenvalues $E_n$ and eigenvectors expressed in the total angular momentum basis as $|\Gamma_n\rangle = \sum_{j=\ldots J} C_{n,j} |J, J_z = j\rangle$.

Inelastic neutron-scattering probes the magnetic-dipole-active transitions between these levels. Within the dipole approximation, the powder averaged neutron-scattering intensity is:

$$I(Q, \omega) = CF^2(Q) \sum_{n,m} \frac{\sum_{x,y,z} |\langle \Gamma_n | J_x | \Gamma_m \rangle|^2 e^{-E_n/k_B T}}{\sum_j e^{-E_j/k_B T}} \times \delta(\hbar \omega + E_n - E_m),$$

(4)

where $C$ is a constant, $F^2(Q)$ is the squared magnetic form factor, $k_B$ is the Boltzmann constant, $E_n$ and $E_m$ are the eigenvalues of the CEF Hamiltonian, and $\hbar \omega$ is the neutron energy transfer. Each measurement was performed at fixed temperature $T$ and incident neutron energy $E_i$. The measured $I(Q, \omega)$ was integrated within a certain $Q$ range (see individual plots below) and subsequently normalized to its maximum intensity to obtain the $I(\omega)$ that we plot further below.

To analyze $I(\omega)$, we start from a set of PC parameters ($\mathbf{R}_i, q_i$), use Eqs. 2 and 3 to construct the CEF Hamiltonian, and diagonalize Eq. 1 to obtain the eigenvalues $E_n$ and eigenfunctions $|\Gamma_n\rangle$. Several available program packages are capable of doing such calculations, including SIMPRE, McPhase, and PyCrystalField. We then use Eq. 4 to calculate the neutron scattering intensity by replacing the Dirac $\delta$-function with a Lorentzian to account for the finite energy-resolution of our measurements which is energy-dependent for SEQUOIA. By varying the $\mathbf{R}_i$ and $q_i$ variables of our PC model, a least-squares fit is performed to minimize the difference between calculated and observed CEF spectra. The agreement is measured by a self-defined weighted profile factor:

$$R_{wp} = \frac{1}{N} \sum_{E_i,T} \left( \frac{\sum_i \left( I_{calc}^{i} - I_{obs}^{i} \right)^2}{\sigma_i^{obs} \sigma_i^{calc}} \right)^2,$$

(5)

where the first summation is a notation where all data-sets measured with different $E_i$ and $T$ are included, and $I_{calc}^{i}$, $I_{obs}^{i}$, $\sigma_i^{calc}$, $\sigma_i^{obs}$ represent calculated intensity, observed intensity, and measurement error, respectively, for the $N$ data points. Due to the high dimensionality of the parameter space, the NelderA$\ddot{A}$sMead method was adopted to search for local minimum in the parameter space whereas the choice of initial $\mathbf{R}_i$ and $q_i$ will be discussed below in Secs. III and IV.

E. Susceptibility & Magnetization

Static magnetic properties in an external magnetic field $\mathbf{H}$ can also be calculated from the single-ion CEF Hamiltonian,

$$\mathcal{H} = \mathcal{H}_{CEF} - \mu_B g_J \mathbf{J} \cdot \mathbf{H},$$

(6)

With the eigenstate ($E_n$) and eigenfunction ($|\Gamma_n\rangle$) of the CEF Hamiltonian available, the three components ($x = x, y, z$) of the magnetization $M_{CEF}(\mathbf{H}, T)$ in a Cartesian coordinate system are given by

$$M_{CEF}(\mathbf{H}, T) = g_J \sum_i e^{-\frac{E_i}{k_B T}} \langle n | J_x | n \rangle / \sum_n e^{-\frac{E_n}{k_B T}},$$

(7)
from which the DC magnetic susceptibility tensor can be calculated numerically following

$$\chi_{\alpha\beta} = \frac{\partial M_{\alpha}}{\partial H_{\beta}}. \tag{8}$$

Within a linear response regime, $\chi_{\alpha\beta}$ remains a constant for small $H$, such that the powder-averaged magnetic susceptibility in a suitable choice of $x, y, z$ axes is:

$$\chi_{\text{CEF}}^{\text{powder}} = \frac{1}{3} (\chi_{xx} + \chi_{yy} + \chi_{zz}). \tag{9}$$

Outside the linear response regime, the powder-averaged isothermal magnetization $M_{\text{powder}}(H, T)$ for a polycrystalline sample can be calculated numerically assuming randomly oriented structural domains,

$$M_{\text{powder}}^{\text{CEF}}(H, T) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi (\mathbf{M}^{\text{CEF}}(H, T) \cdot \mathbf{H}) \sin \theta d\theta d\phi. \tag{10}$$

The above susceptibility and magnetization calculations only contain CEF contributions and neglect exchange and dipolar interactions between magnetic ions. In the temperature regime for which two-ion interactions are non-negligible, the corrections to the susceptibility and magnetization can be largely accounted by a Weiss molecular field.$^{41}$ That is, we assume that each magnetic ion experiences a local field proportional to the magnetization in the paramagnetic region,

$$\mathbf{H}_{\text{Weiss}} = \lambda \mathbf{M}^{\text{CEF}}(\mathbf{H}_{\text{Weiss}} + \mathbf{H}, T), \tag{11}$$

where $\lambda$ is a constant that reflects the average magnetic couplings between ions. Given a value of $\lambda$, Eq. 11 can be solved self-consistently to find the local molecular field ($H_{\text{Weiss}}$) given the temperature ($T$) and the external field ($H$). By replacing $M^{\text{CEF}}(H, T)$ by the corrected magnetization $M^{\text{CEF}} + \lambda(H, T) = M^{\text{CEF}}(H_{\text{Weiss}} + H, T)$ in Eqs. 8-10, we obtain the corrected powder-averaged magnetic susceptibility $\chi_{\text{CEF}}^{\text{powder}} + \lambda$, and isothermal magnetization $M^{\text{CEF}} + \lambda(H, T)$. In the limit of high temperature and small field, the correction to the susceptibility takes a simple form of the Weiss law,

$$1/\chi_{\text{CEF}}^{\text{powder}} = 1/\chi^{\text{CEF}}_{\text{powder}} + \lambda. \tag{12}$$

F. principal axes & effective g-tensor

In rare-earth oxides, the CEF energy-scale is usually much larger than two-ion exchange and dipolar interactions. When the spectrum of the single-ion Hamiltonian yields a group of ground-state eigenstates that are well separated from excited levels, the interactions between magnetic moments expressed in the total angular-momentum basis can be projected into the ground-state subspace at low temperature because only these states are thermally populated. In this context, it is desirable to use the concept of “effective spin" $S$ (or sometimes referred as pseudo spin), which is a fictitious angular momentum such that $2S + 1$ is set equal to the degeneracy of the single-ion ground-state. In the case where the CEF ground-state is a doublet, we construct effective spin-$1/2$ operators from the CEF doublet wave-functions in the total angular momentum basis ($|\pm\rangle$), following

$$S^\alpha = \frac{1}{2} \left( \begin{array}{c} \langle + | J_\alpha | + \rangle \\ \langle - | J_\alpha | - \rangle \end{array} \right), \alpha = x, y, z. \tag{13}$$

FIG. 2. Comparison between the CEF levels measured by inelastic neutron-scattering$^{23,43,47,50}$ and the calculated/fitted CEF levels from different PC model for rare-earth pyrochlore titanates $R_2Ti_2O_7$ ($R = \text{Tb}, \text{Ho}, \text{Er}, \text{Yb}$). See Sec. III and Tab. I for the definitions of our PC models. Dashed and solid lines represent singlet and doublet CEF levels, respectively. The CEF levels that are not directly observed experimentally are marked by stars, and are not included in the PC fit.
The effective spin is thus connected to the the Pauli matrices \((\sigma_\alpha)\) by an anisotropic \(g\)-tensor,

\[
\begin{pmatrix}
S_x \\
S_y \\
S_z
\end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix}
g_{xx} & g_{xy} & g_{xz} \\
g_{yx} & g_{yy} & g_{yz} \\
g_{zx} & g_{zy} & g_{zz}
\end{pmatrix} \begin{pmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z
\end{pmatrix},
\]

from which we obtain the mapping of the Zeeman splitting under an external magnetic field \((\mathbf{H})\) from the total angular-momentum basis to the pseudo-spin basis

\[
\mathcal{H}_{Zeeman} = -\mu_B g_B \mathbf{H} \cdot \mathbf{J} \mapsto -\mu_B (\mathbf{H} \cdot g \cdot \mathbf{S}).
\]

In an arbitrarily chosen coordinate system, \(g\) is an \(3 \times 3\) tensor. Our aim is to find a principal coordinate system such that \(g\) is diagonal. In axial symmetry, we can choose the \(z\)-axis as the local symmetry axis so that all the off-diagonal terms vanish, and the \(g\)-tensor can be rewritten as \(g_{xx} = g_{yy} = g_{zz} = g_0\). This is exactly the case for the rare-earth pyrochlores and triangular-lattice compounds discussed in this study. If we choose the local 3-fold local axis (the \(R\)-O1 bond direction) as the \(z\)-axis, \(g\) is automatically diagonal despite the choices of \(xy\)-axes, meaning a continuous rotational symmetry is preserved for the single-ion magnetism [Fig. 1(a)]. In contrast, one expects \(g_{xx} \neq g_{yy} \neq g_{zz}\) in lower-symmetry systems for which it remains a technical challenge to determine \(g\) as well as its principal axes. In the tripod kagome structure, one principal axis is the local \(C_2\) rotation axis (labeled as \(y\) in Fig. 1). Unlike the pyrochlores, the other two principal axes, \(x\) and \(z\), are undetermined and can in principle lie anywhere within the plane perpendicular to \(y\) (illustrated as a grey plane in Fig. 1(b)). Presumably, the \(z\) axis is likely to be the shortest \(R\)-O1 bond direction due to its structural similarity to the pyrochlore structure. However, PC calculations show that the directions of principal axes strongly depends on the details of surrounding ligands. Generally, it requires a finite rotation along the \(C_2\) axis to make \(g\) diagonal, as illustrated in Fig. 1(b).

We show here that the principal axes and \(g\) can be determined by a two-step rotation. Starting from the CEF wavefunctions \(|\pm\rangle\), the first step is a pseudo-spin rotation of Eq. 14 with rotation matrix \(A\),

\[
S = \frac{\hbar}{2} (gA^{-1})(A\sigma) = \frac{\hbar}{2} g' \sigma'.
\]

This rotation has nothing to do with the rotation in real space which is rather a rotation of pseudo-spin to make \(g'\) symmetric. The second step is a co-rotation of real space and pseudo-spin space through a rotation matrix \(B\),

\[
BS = \frac{\hbar}{2} (Bg'B^{-1})(B\sigma').
\]

For the tripod kagome compounds, if we start with \(|\pm\rangle\) from the PC calculation using the \(xyz\) coordinate shown in Fig. 1, \(B\) will be the rotation along the \(C_2\) axis which ultimately determines the principal axes \(x' y' z'\) as well as the diagonalized effective \(g\)-tensor.

### III. Rare-Earth Pyrochlores: A Benchmark

Before applying our PC calculations and analysis to new material systems, it is desirable and necessary to validate our method on a well-studied family of compounds. The rare-earth pyrochlores serve as a perfect testing ground; first, because their structure is closely related to that of our target systems, the tripod kagome magnets; second, because their CEF Hamiltonian is relatively simple with only six Stevens’ operators due to the presence of a 3-fold symmetry axis; finally and most importantly, because their CEF excitations have been intensively investigated by neutron scattering over the last two decades, providing a complete and reliable set of data.

#### A. Crystallographic point-charge model

Rare-earth pyrochlore oxides possess a general chemical formula of \(R_2X_2O_7\) (\(X = Ti, Sn, Ge, Pt, Zr, etc.\)) with space group \(Fd3m\), and point group \(D_{3d}\) at the rare-earth ion site. Each \(R^{3+}\) is surrounded by eight oxygen atoms with two short \(R\)-O1 bonds lying along the local three-fold axis and six long \(R\)-O2 bonds forming a puckered ring [Fig. 1]. It requires three independent parameters to fully describe the coordination of the eight oxygens. In spherical coordinates where \(z\) is chosen as the 3-fold axis, these are \(r_1, r_2, \theta_2\), representing the crystallographic distance of the \(R\)-O1 bond, \(R\)-O2 bond, and the \(O1-\ O2\) angle, respectively. Modeling the oxygen ligands by eight PCs requires two additional variables, \(q_1\) and \(q_2\), that describe the amount of charge associated with \(O1\) and \(O2\). The minimal PC model thus contains five parameters for 8 PCs (see Tab. I for details).

The most intuitive choice of PC parameters is to adopt the crystallographic ligand-charge positions, \(i.e. r_1 = r_1^{1}, r_2 = r_2^{1}, \theta_2 = \theta_2^{1}\), and net charges of isolated \(O^{2-}\) ions, \(i.e. q_1 = q_2 = 2e\). This model is the electrostatic point-charge model first considered by Bethe in 1929\(^5\), which we call the Crystallographic PC model. In Fig. 2, we compare the CEF levels calculated from this model with the experimentally measured CEF levels for the rare-earth titanates \(R_2\)Ti\(_2\)O\(_7\). The crystallographic PC model generally underestimates the overall CEF energy scales for all systems; and more dramatically, it predicts a Ising-like \(g\)-tensor \((g_\parallel > g_\perp)\) for \(Er_2\)Ti\(_2\)O\(_7\) while the actual spin anisotropy in the real compound is known to be XY-like \((g_\parallel < g_\perp)\). We notice that the second-order CEF term predicted by the model is too large while the fourth and sixth order terms are considerably smaller in comparison to the experimental values. This is not a surprise given the known weaknesses of the PC model\(^5\) and calls for a modification to the crystallographic PC model.

#### B. Effective point-charge model

Many efforts have been undertaken over the years to correlate the CEF parameters derived from the PC model with experimental observations, including introducing a shielding parameter\(^5\), adding dipolar and quadrupolar electric potential
corrections\textsuperscript{55}, and taking into account the electro-negativity\textsuperscript{53} and wave-functions overlap\textsuperscript{56} of the metal and ligand ions. These improvements rely on the admittance of following effects: the finite extent of charges on the ions, the contribution from the rest of the crystalline net, and the covalency between the metal and ligand wave-functions. Interestingly, all these modified PC models make the following adjustments to the PC parameters: first, the effective charges carry a considerably reduced charge compared to bare ones; second, rather than being strictly localized at the crystallographic ligand centers, the effective PCs are placed somewhere in the middle of the metal-ligand bond. The difference between the various models is their attempts to relate the reduction in charge and distance to semi-empirical physical quantities, e.g. electronegativity\textsuperscript{53}, and wave-function overlap\textsuperscript{26,56}. However, we find that none of these semi-empirical approaches work well for the pyrochlore compounds discussed below. Thus, in this study, we adopt the general concept of effective PC model by which each ligand carries an effective PC with adjustable charge amount and distance to the metal ion.

We start from the local geometry of the pyrochlore structure to build up the effective PC model. As shown in Fig. 1(c), both O1 and O2 are in a tetrahedral environment, somewhat similar to the $sp^{3}$ hybridization environment in a CH\textsubscript{4} molecule. However, O1 is at the center of a regular tetrahedron formed by four $R^{3+}$ ions while O2 is inside an irregular tetrahedron formed by two $R^{3+}$ and two $X^{4+}$ ions. Since the covalency of $O^{2-}$ with $R^{3+}$ is different from that of $X^{4+}$, it becomes necessary to distinguish the effective PCs associated with O1 and O2. If the $2e$ charge amount of $O^{2-}$ is distributed on a tetrahedron based on the amount of positive charge on the surrounding ions, then on average O1 contributes $0.5e$ to each $R^{3+}$ while O2 contributes $0.333e$ to each $R^{3+}$ and $0.667e$ to each $X^{4+}$, i.e. $q_{1} = 0.5e$, $q_{2} = 0.333e$ [Tab. I]. This simple counting argument ensures that the total negative charges due to ligands is balanced with the positive charge of metallic ions.

Under these assumptions, we find that a single effective distance parameter is sufficient to describe the CEF excitations reasonably well. This yields a reduction factor $f$ associated with the shortest crystallographic metal-ligand distance used, i.e. $r_{1} = r_{2} = f \times r_{\text{O}}^{2}$. According to the electronegativity argument\textsuperscript{53}, $f = \epsilon_{R}/(\epsilon_{R} + \epsilon_{O}) \approx 0.75$, where $\epsilon_{R}$ and $\epsilon_{O}$ are the Pauling electronegativity of the rare-earth and oxygen ions, respectively. By fixing $q_{1} = 0.5e$, $q_{2} = 0.333e$ and varying $f$, we find that the best agreement with experiment observations is achieved for $f \approx 0.72$, for which the calculated CEF levels are in close agreement with the measured levels (green lines in Fig. 2). Perhaps more importantly, this effective PC model predicts the correct spin anisotropy of the CEF ground-state wave-functions for all four compounds (see Tab. II). Since the effective PC model is still defined by the local crystallography, the agreement with experiments is encouraging and shows that a universal and physically meaningful PC model can achieved for the series rare-earth pyrochlore titanate compounds.

C. Point-charge fit

Starting from the effective PC model discussed above, we embark on the investigation of the effects of ligand-metal distances ($r_{1}$, $r_{2}$) and angle ($\theta_{2}$) on the CEF levels. An example is presented in Fig. 3 for Yb$_{2}$Ti$_{2}$O$_{7}$, which shows that the overall CEF energy scale is determined by the ligand-
TABLE II. Calculated and fitted parameters and $g$-tensors from the effective PC model for rare-earth pyrochlores. For $R_2Ti_2O_7$ ($R = \text{Tb, Ho, Er, Yb}$), the Effective PC parameters are defined in Table I with $f = 0.72$, and the calculated CEF levels are plotted as green lines in Fig. 2. For each compound of the $Er_2X_2O_7$ ($X = \text{Ti, Ge, Sn, Pt}$) family, a fit to the re-convoluted experimental neutron scattering data was performed with the five PC parameters as variables, as shown in Fig. 4.

| Effective PC model | PC parameters | Ratio | CEF parameters (meV) | $g$-tensor |
|-------------------|---------------|-------|---------------------|------------|
|                   | $r_1(\AA)$   | $r_2(\AA)$ | $\theta_2(^\circ)$ | $q_1(e)$ | $q_2(e)$ | $A^3_2$ | $A^3_4$ | $A^3_6$ | $A^3_8$ | $g_{||}$ | $g_{\perp}$ | $g_{||}$ | $g_{\perp}$ |
| **Calc.**         | 1.638         | 1.638  | 79.5                | 0.5      | 0.333   | 1.5  | 19.8 | 39.5     | 318.6 | 5.9 | 910.0 | 98.7    | 11.4 | 0.0 | 10.7 | 0.0^\text{79} |
| Ho$_2$Ti$_2$O$_7$ | 1.594         | 1.594  | 79.4                | 0.5      | 0.333   | 1.5  | 19.2 | 38.6     | 313.0 | 5.6 | 87.5  | 94.5    | 19.5 | 0.0 | 19.6 | 0.0^\text{41} |
| Er$_2$Ti$_2$O$_7$ | 1.571         | 1.571  | 79.1                | 0.5      | 0.333   | 1.5  | 19.9 | 38.5     | 323.3 | 5.8 | 89.1  | 94.1    | 0.5  | 7.2 | 3.9  | 6.3^\text{50} |
| Yb$_2$Ti$_2$O$_7$ | 1.540         | 1.540  | 78.9                | 0.5      | 0.333   | 1.5  | 15.2 | 37.5     | 321.9 | 5.6 | 85.8  | 89.4    | 2.7  | 3.7 | 1.9  | 3.6^\text{23} |
| **Fit**           | 1.628         | 1.662  | 78.8                | 0.651    | 0.470   | 1.42 | 20.4 | 41.3     | 351.5 | 6.1 | 85.9  | 89.1    | 3.2  | 6.4 | 3.9  | 6.3^\text{50} |
| Er$_2$Ge$_2$O$_7$ | 1.569         | 1.546  | 81.2                | 0.566    | 0.351   | 1.5  | 20.0 | 46.4     | 304.6 | 5.4 | 91.2  | 115.2   | 2.5  | 6.7 | 2.1  | 7.0^\text{50} |
| Er$_2$Sn$_2$O$_7$ | 1.611         | 1.556  | 80.3                | 0.538    | 0.300   | 1.73 | 27.4 | 37.8     | 274.5 | 4.6 | 79.6  | 92.9    | 1.2  | 7.2 | 0.1  | 7.6^\text{50} |
| Er$_2$Pt$_2$O$_7$ | 1.576         | 1.498  | 80.5                | 0.506    | 0.268   | 1.89 | 27.5 | 40.2     | 290.1 | 4.8 | 91.1  | 108.2   | 0.2  | 7.6 | 0.3  | 7.7^\text{50} |

For all compounds, a good fit to experimental data requires $r_1/r_2 > 1$ except for $X = \text{Ti}$. Furthermore, the larger the $X$ atomic number, the larger the fitted $r_1/r_2$ ratio. A possible explanation is that the covalency between oxygen and $X$ is very different between $X^{4+}$ ions with empty $d$-orbitals (e.g. $\text{Ti}^{4+}$) and ions with filled $d$-orbitals (e.g. $\text{Ge}^{4+}$, $\text{Sn}^{4+}$, $\text{Pt}^{4+}$). It suggests that although the Coulomb potential of these non-magnetic ions is not explicitly contributing to the CEF in the PC model, it is nonetheless reflected in the parameters of our effective PC model and thus can tune the single-ion properties.

In short, by examining the existing experimental data for two families of rare-earth pyrochlore oxides, our results provide a solid benchmark of the effective PC model, showing that: (i) by combining the effects of local crystallography and covalency, it is possible to derive a physically meaningful and universal effective PC model that faithfully reproduces the CEF spectra for a series of compounds; (ii) because the effective PC model reduces the number of free parameters compared to the traditional approach, a least-squares fit to experimental data allows to faithfully predict the spatially-anisotropic single-ion properties of a given system.

IV. TRIPOD KAGOME MAGNETS

In this section, we turn to the tripod kagome magnets. We first consider the site symmetry as well as the local environment of the tripod kagome structure and arrive at a modified effective PC model. Next, we present the experimental results from the inelastic neutron scattering measurements on $R_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ ($R = \text{Tb, Ho, Er, Yb}$), and perform PC fits to their CEF excitation spectra. We check the validity of our PC fit by comparing calculated magnetic susceptibility and isothermal magnetization to experiments. Finally, we calculate the $g$-tensor of the CEF ground-state for each compound, and discuss the implications for the collective multi-ion physics.
A. From structure to effective PC model

The crystal structure of the tripod kagome compounds $R_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ can be viewed as a variant of the pyrochlore which contains kagome planes of magnetic rare-earth ions separated by nonmagnetic $\text{Mg}^{2+}$ triangular layers [Fig. 1(a)]. The space-group has changed from cubic $F\bar{3}m$ in the pyrochlores to trigonal group $R\bar{3}m$ in the tripod systems. Importantly, although each $R^{3+}$ ion is still surrounded by eight oxygen atoms, the site symmetry is reduced from $D_{3d}$ to $C_{2\bar{3}}$. This can be seen directly from the local structure, which instead of having one three-fold and three two-fold rotational axes, only preserves axial symmetry with a two-fold rotational $C_2$ axis that lies in the kagome plane [Fig. 1(b)]. As a consequence, whereas it requires only 6 Stevens’ operators to describe the CEF Hamiltonian of the pyrochlores, it calls for 15 CEF parameters for the tripod kagome magnets$^{16}$. If we choose the $y$-axis as the $C_2$ axis, these are $A_m^n$ (or $B_m^n$) with $a = 2, 4, 6$ and $m = 0, 1, \ldots, n$. For many of the compounds in the tripod-kagome family, determining the parameters of the CEF Hamiltonian directly from neutron-scattering spectra is impossible because the experimental observables are considerably fewer than the fitting parameters. For example, only three excitation levels and two intensity ratios can be extracted from the CEF excitations for $\text{Yb}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ which is vastly insufficient to determine the 15 CEF parameters.

Instead of fitting the CEF parameters directly, we employ an effective PC model similar to the one demonstrated for pyrochlores. Given the local two-fold symmetry, 9 independent parameters are required to fully describe the PC model for $R_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$. These are $r_1, r_2, r_3, \theta_2, \theta_3, \phi_3, q_1, q_2, q_3$, with the detailed coordination of the eight surrounding PCs listed in Tab. I. Compared to the 5 PC parameters for pyrochlores, the 4 additional parameters $(r_3, \theta_3, \phi_3, q_3)$ are associated with the O3 position that is split from O2 as a result of breaking the three-fold symmetry. Following the procedure established for pyrochlores, we build an effective PC model using the crystallographic $R$-$O$-$R$ bond angles with $\theta_2 \approx 78^\circ$, $\theta_3 \approx 76.5^\circ$, $\phi_3 \approx 59^\circ$31, and use the same reduction factor, $f \approx 0.72$, for the PC distances, i.e. $r_1 = r_2 = r_3 = f \times r_i^1$. 

![FIG. 5. Momentum- and energy-dependence of the inelastic neutron scattering intensity $I(Q, \omega)$ for $R_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ ($R = \text{Tb, Ho, Er, Yb}$) measured with different neutron incident energies at different temperatures. The top two rows show the $E_i = 30$ meV datasets at $T = 5$ K and 100 K, respectively. The bottom two rows shows the $E_i = 120$ meV datasets except for $\text{Yb}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ for which $E_i = 240$ meV was used. Distinct groups of excitations from the CEF ground-state are marked by blue arrows.](image-url)
We begin with $\text{Er}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ ($J = 15/2$) for which we expect seven CEF excitation levels from the ground-state Kramers doublet. Four of the seven excitations are clearly seen below 55 meV at 5 K at $h\nu = 6.4(2)$, 10.5(3), 21.6(4), and 50(1) meV, respectively [Fig. 5 and Fig. 6(a–b)]. Between 55 meV and 70 meV, a somewhat continuous spectra is observed which is likely originating from three CEF excitations in addition to some background. Within this energy range, two intensity maxima are observed at 65(1) and 67.5(9) meV. Instead of attempting to resolve the missing CEF level, we perform a global fit to all the spectra in Fig. 6 by vary the 9 PC parameters. The best fit to the data is achieved for $\theta_2 = 80.75^\circ$, $\theta_3 = 73.97^\circ$, $\phi = 59.28^\circ$, $q_1 = 0.504$, $q_2 = 0.301$, $q_3 = 0.181$, a solution that is not far from the initial model. The fitted value of PC distances shows a trend opposite to the crystallographic R-O distances, with distances decreasing from $r_1 = 1.734$ Å to $r_2 = 1.540$ Å, and $r_3 = 1.479$ Å. Given the large difference in atomic number between Mg$^{2+}$ and Sb$^{5+}$ as well as the empty versus filled d-orbitals, this is not a surprise in light of the results on $\text{Er}_2\text{X}_2\text{O}_7$ discussed above. The CEF parameters as well as the CEF wave-functions for $\text{Er}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ are listed in Tab. III. The curves fitted from the PC model agree well with all measured data-sets except for an intensity mismatch around 3.8 meV which shows up at both 5 K and 100 K (marked by stars).

We can rule out magnetic impurities as well as the transition between the 6.4(2) to 10.5(3) meV. A similar weak peak is observed in $\text{Ho}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ at $3$ meV [Fig. 7], but not in $\text{Yb}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ [Fig. 5(d)], ruling out the possibility of an unsubtracted phonon signal. A likely explanation is structural-site-disorder. Previous studies of the tripod kagome compounds generally indicate 3-5% $R^{3+}$ ions located at the Mg$^{2+}$ site, which is surrounded by 6 oxygen ligands what likely gives rise to different CEF excitations. A Lorentzian peak fit to the 5 K, $E_i = 30$ meV spectra indicates a 3.4(3)% peak intensity of the 3.4 meV feature compared to that of the strongest peak at 6.4(2) meV, consistent with the percentage of site-disorder. Furthermore, our effective PC model based on an octahedral ligand environment (Tab. I) predicts that the most intense CEF excitation is indeed around 5 meV for both site-disordered Er$^{3+}$ and Ho$^{3+}$ ions. This scenario is further supported by recent CEF measurements on spinel MgEr$_2$Se$_4$ where the strongest CEF excitations is observed at 4.16 meV for Er in a similar ligand environment$^{77}$.

Next, we look at $\text{Ho}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ ($J = 8$) for which the CEF spectra is expected to comprise 2$J+1=17$ singlet levels. However, instead of seeing 16 CEF levels, our measurements resolve 5 crystal-field excitations [Fig. 5(b), Fig. 7], whose energy scheme and relative intensities resemble those of $\text{Ho}_2\text{Ti}_2\text{O}_7$ except for an overall renormalization in energy. This is expected because as long as the deviation from trigonal symmetry is small, all the non-Kramers doublets in the pyrochlores should only split weakly in energy, what is generally beyond the resolution of our neutron measurements. In this sense, it is almost impossible to perform a conventional CEF fit based on the resolved CEF energies and intensity ratios. Thus, we perform a global fit to the four spectra in Fig. 7 to refine and effective PC model that best reflects the CEF.

**FIG. 6.** Energy dependence of the measured CEF excitations for $\text{Er}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ (open black circles) and our best PC fits to data (solid red lines). The experimental data are extracted from the contour maps of Fig. 5 with the phonon background subtracted. The star labels an unexpected mode which is likely associated with a small percentage of the site-disordered Er at the Mg site.

Compared to pyrochlores, the local environment for the oxygen atoms in the puckered-ring has changed dramatically. The O2 ion in a tripod-kagome structure is in the center of two $R^{3+}$, one Mg$^{2+}$, and one Sb$^{5+}$, whereas the O3 ion is in the center of one $R^{3+}$, one Mg$^{2+}$, and two Sb$^{5+}$. Since Sb$^{5+}$ captures a majority of the covalent electrons from O$^{2-}$, we expect a much smaller effective charge amount associated with O3 compared to O2. Thus, we choose $q_1 = 0.5e$, $q_2 = 0.3e$, $q_3 = 0.15e$ for the effective PC model of the tripod kagome structure.

**B. PC fit to inelastic neutron scattering**

We refine the effective PC model by fitting inelastic neutron scattering spectra. An overview of the inelastic neutron scattering spectra for $R_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ ($R = \text{Tb}, \text{Ho}, \text{Er}, \text{Yb}$) is shown in Fig. 5. Four datasets are plotted for each compound, showing the excitation spectra measured at low ($T = 5$ K) and high ($T = 100$ K or $300$ K) temperatures, and with several incident neutron energies. We clearly observe CEF excitations from the ground-state, which intensities decay with $Q$, and mark them with blue arrows. Phonon excitations are only observed for $\text{Yb}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$ below 60 meV [Fig. 5(d)] and subtracted according to Sec. II. Following this data analysis procedure, the energy-dependence of the signal is in Figs. 6–9 for each compound, respectively.
Excitations. The initial values of our PC parameters are chosen as the fitted values for \( \text{Er}_3 \text{Mg}_2 \text{Sb}_3 \text{O}_{14} \) and the best fit is shown as red lines in Fig. 7.

We continue with \( \text{Yb}_3 \text{Mg}_2 \text{Sb}_3 \text{O}_{14} \) for which \( \text{Yb}^{3+} \) has \( J = 7/2 \) for which we expect to see three CEF excitations from the ground-state Kramers doublet. Our measurements indeed resolve three modes at 69.3(5) meV, 89(1), and 113(1) meV, respectively [Fig. 5(d), Fig. 8]. We isolate the pure CEF signals by subtracting the low-\( Q \) intensities with a fraction of the high-\( Q \) intensities, and the normalized CEF spectra is shown as black dots in Fig. 8 (b). Since the Boltzmann factor at 300 K is not large enough to populate the higher CEF levels, only the 5 K data-set is used for the PC fit. In the current case, the number of experimental observable is considerably less than either the number of CEF parameters (15) or that of PC parameters (9), so we expect a lot of degenerate solutions which would give us identical fits to the spectra. As the effective PC model provides a physically meaningful starting point, we only seek for local minimum of \( R_{wp} \) around our starting parameters and impose that the fitted results be accepted only if \( r_1 > r_2 > r_3 \) and \( 0.5c \approx e_1 > e_2 > e_3 \). Starting from the PC parameters of \( \text{Er}_3 \text{Mg}_2 \text{Sb}_3 \text{O}_{14} \), the best fit to the experimental data is plotted as the red line in Fig. 8(b).

Finally, we turn to \( \text{Tb}_3 \text{Mg}_2 \text{Sb}_3 \text{O}_{14} \). The \( \text{Tb}^{3+} \) ion has \( J = 6 \), for which we expect to see 13 singlet CEF excitations at 5 K. However, we observe only 3 groups of excitations [Fig. 5(a)]. While the first excitation at 2.2(3) meV is relatively sharp, the latter two excitation modes are extremely broad and their main peak intensities are distributed between 10-20 meV and 30-40 meV, respectively. Similar to that of \( \text{Yb}_3 \text{Mg}_2 \text{Sb}_3 \text{O}_{14} \), we start from the PC parameters of \( \text{Er}_3 \text{Mg}_2 \text{Sb}_3 \text{O}_{14} \), and obtains a fit to data that fulfills the criteria \( r_1 > r_2 > r_3 \) and \( 0.5c \approx e_1 > e_2 > e_3 \). Note that for this compound, we need to manually set peak widths in order to reach a satisfactory fit. In addition, some over-fit to the background is noticeable above 40 meV [Fig. 9] where the excitation spectra is dominated by phonons [Fig. 5(a)].
C. Susceptibility/magnetization & g-tensor/principle-axes

Table III lists the fitted values of the PC parameters, the corresponding CEF parameters, and CEF wave-functions for \(R_3\text{Mg}_2\text{Sb}_2\text{O}_{14}\) \((R = \text{Tb}, \text{Ho}, \text{Er}, \text{Yb})\). Using these parameters, we calculate the power-averaged DC susceptibility \(\chi_{\text{powder}}\) and isothermal magnetization \(M_{\text{CEF+\lambda}}\) from the CEF levels of each of the compounds. As shown in Fig. 10 (a), the calculated \(1/\chi_{\text{powder}}\) and \(M_{\text{CEF+\lambda}}\) generally agrees with the measured curves for all temperatures and magnetic fields, what strongly validates our approach. When taking a closer look at the data for \(\text{Er}_3\text{Mg}_2\text{Sb}_2\text{O}_{14}\), \(1/\chi_{\text{CEF}}\) seems to underestimate the measured values by a constant amount [Fig. 10(a) inset], meanwhile, \(M_{\text{CEF+\lambda}}\) tends to overestimate the measured magnetization, which becomes more obvious at low temperatures [Fig. 10(b)]. Both disagreements can be explained by two-ion antiferromagnetic interactions. Once we account for this effect using a Weiss molecular field, the corrected susceptibility \(\chi_{\text{powder}}\) and magnetization \(M_{\text{CEF+\lambda}}\) with \(\lambda = 0.321\) K almost perfectly agrees with the experimental values. The same correction can be made for the other three compounds. We obtain the value of \(\lambda\) by fitting the susceptibility below 25 K which yields 0.012 K for \(\text{Ho}_3\text{Mg}_2\text{Sb}_2\text{O}_{14}\), 0.302 K for \(\text{Yb}_3\text{Mg}_2\text{Sb}_2\text{O}_{14}\), and 0.215 K for \(\text{Tb}_3\text{Mg}_2\text{Sb}_2\text{O}_{14}\). We notice that for the Tb compound, the corrected \(1/\chi_{\text{CEF+\lambda}}\) still clearly deviates from the experimental curve below 10 K. Meanwhile, although \(M_{\text{CEF+\lambda}}\) accounts for the magnetization at 40 K quite well, it obviously overestimates magnetization at high-field and low-temperature. Therefore, we conclude that while our PC fits successfully describes the CEF Hamiltonian for \(R_3\text{Mg}_2\text{Sb}_2\text{O}_{14}\) \((R = \text{Ho}, \text{Er}, \text{Yb})\), further investigations are necessary to determine unambiguously the CEF Hamiltonian for \(\text{Tb}_3\text{Mg}_2\text{Sb}_2\text{O}_{14}\).

The CEF scheme for the four compounds from our PC fit is summarized in Fig. 11. For Er and Yb compounds, the CEF ground state is a well isolated Kramers doublet (designated by \(|\pm\rangle\)). For Tb and Ho compounds, the CEF ground-state comprises two singlets (designated by \(|0\rangle\) and \(|1\rangle\)) that are weakly split in energy. Importantly, \(|0\rangle\) and \(|1\rangle\) can be approximately expressed in the symmetric and anti-symmetric form of a non-Kramers doublet,

\[
|0\rangle \approx \frac{1}{\sqrt{2}}(|+\rangle + |\text{−}\rangle), \quad |1\rangle \approx \frac{1}{\sqrt{2}}(|+\rangle - |\text{−}\rangle). \quad (18)
\]

Since symmetric and anti-symmetric wave-functions are the eigenstates of the \(\sigma^+\) Pauli matrix, an energy splitting between two crystal-field singlets can be exactly mapped into a transverse magnetic field acting on a corresponding doublet. Therefore, the mapping from the total angular momentum basis to the effective spin-1/2 basis is still valid as long as the...
The CEF two-singlet in Ho\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\) gives rise to an effective Ising moment with Ising axes pointing into the center of local tetrahedron [Fig. 10(c)]. The strong dipolar interactions in such an arrangement prefer one-in-two-out or two-in-one-out configurations in a triangle, which gives rise to emergent magnetic charges and classical spin-fragmentation physics at low temperatures\(^{30,59}\). Along with the effective transverse field generated from the splitting of 0.15 meV of the two-singlet CEF ground state, the systems maps into a canonical model for quantum magnetism: interacting Ising spins under a transverse field. As demonstrated in our separate study\(^\text{32}\), a transverse Ising model based on a dipolar kagome ice is promising to stabilize a high-entangled quantum state, and Ho\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\) provides an example on how quantum fluctuations can be generated from CEF effects alone.

Similarly, Tb\(^{3+}\) ions in Tb\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\) possess a two-singlet CEF ground state with a separation of 0.06 meV, according to our PC fits. Although this number might not be accurate, the anisotropy of pseudo-spins is expected to be the same Ising type as that of Ho\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\) if restricted to the lowest two singlets [Fig. 10(c)]. Interestingly, unlike Ho\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\), neither a magnetic order nor emergent magnetic charge order in observed experimentally in Tb\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\)\(^{51}\). The difference is likely coming from the two low-lying excited CEF singlets at 2.0 meV and 2.6 meV, which is absent in Ho\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\). These levels are comparable in energy to the spin-spin interactions, proper effective GCE Hamilton will necessarily include 4 singlet levels, akin the virtual CEF excitation theory proposed for Tb\(_2\)TiO\(_3\)\(^{60}\). We emphasize that determining the CEF Hamilton for Tb-related compounds has been proven to be a challenging task. Even within the pyrochlore family, the CEF Hamiltonian for Tb-pyrochlores has received the most attention and controversy over the last decade\(^{44,46,47}\). This is due, first, to weak CEF levels that are not easily determined by neutron experiments what complicates the CEF fits; second, the high energy CEF excitations are strongly contaminated by phonons where magneto-elastic coupling is likely to play a key role. Similar magneto-elastic coupling have been demonstrated to be related to the peak splitting of the strongest CEF excitations in Ho-pyrochlores\(^{51}\). For Tb\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\), we notice that the high-energy phonon signals are much more intense (in absolute scale) than that of the other three compounds, providing an anomalous background that prevents us determining any CEF levels above 70 meV [Fig. 5(a-d)].

A previous study has shown that Yb\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\) exhibits long ranged magnetic order at 1.67 K with a magnetic structure that has not been reported to date\(^{51}\). With \(g_{xx} > g_{yy} \gg g_{zz}\), the anisotropy ellipsoid of Yb\(^{3+}\) has an almond shape where none of the three components in \(g\)-tensor is negligible [Fig. 10 (c)]. Since the super-exchange can be obtained as a perturbation to the CEF Hamiltonian, we expect that the exchange interactions that couple to the \(xy\) components of spins will be stronger than others associated with the \(z\) component, with possible existence of off-diagonal couplings between \(xy\) and \(z\) components. Therefore, the magnetic structure is unlikely to be the all-in-all-out type as that observed in Nd\(_3\)Mg\(_2\)Sb\(_3\)O\(_{14}\)\(^{29}\), but rather likely to be a non-coplanar
Table III. Tabulated results of the PC parameters, diagonalized g-tensors, CEF parameters, CEF energies, and wave-functions of the CEF ground states for $R_3$Mg$_2$Sb$_2$O$_{14}$. The results for compounds with $R =$ Tb, Ho, Er, Yb are obtained from PC fits of Fig. 6 to 8. The numbers for Dy$_3$Mg$_2$Sb$_2$O$_{14}$ and Tm$_3$Mg$_2$Sb$_2$O$_{14}$ are predicted results from Effective PC models.

| Effective PC model | PC parameters | g-tensor |
|--------------------|---------------|----------|
| $Tb_3$Mg$_2$Sb$_2$O$_{14}$ PC Fit | $r_1$(Å) 1.771  $r_2$(Å) 1.624  $r_3$(Å) 1.387  $\theta_1(\degree)$ 83.2  $\theta_2(\degree)$ 79.6  $\theta_3(\degree)$ 56.6  $\varphi_1(\degree)$ 0.597  $\varphi_2(\degree)$ 0.288  $\varphi_3(\degree)$ 0.120  $g_{xx}$ 0  $g_{yy}$ 0  $g_{zz}$ 14.35  $\gamma(\degree)$ 3.2 |
| $Ho_3$Mg$_2$Sb$_2$O$_{14}$ PC Fit | $r_1$(Å) 1.639  $r_2$(Å) 1.572  $r_3$(Å) 1.395  $\theta_1(\degree)$ 81.1  $\theta_2(\degree)$ 79.6  $\theta_3(\degree)$ 54.7  $\varphi_1(\degree)$ 0.504  $\varphi_2(\degree)$ 0.302  $\varphi_3(\degree)$ 0.122  $g_{xx}$ 0  $g_{yy}$ 0  $g_{zz}$ 19.47  $\gamma(\degree)$ 0.3 |
| $Er_3$Mg$_2$Sb$_2$O$_{14}$ PC Fit | $r_1$(Å) 1.734  $r_2$(Å) 1.540  $r_3$(Å) 1.479  $\theta_1(\degree)$ 80.8  $\theta_2(\degree)$ 74.0  $\theta_3(\degree)$ 59.3  $\varphi_1(\degree)$ 0.504  $\varphi_2(\degree)$ 0.301  $\varphi_3(\degree)$ 0.181  $g_{xx}$ 13.88  $g_{yy}$ 0.53  $g_{zz}$ 0.74  $\gamma(\degree)$ 3.3 |
| $Yb_3$Mg$_2$Sb$_2$O$_{14}$ PC Fit | $r_1$(Å) 1.550  $r_2$(Å) 1.475  $r_3$(Å) 1.340  $\theta_1(\degree)$ 80.0  $\theta_2(\degree)$ 74.0  $\theta_3(\degree)$ 62.4  $\varphi_1(\degree)$ 0.482  $\varphi_2(\degree)$ 0.223  $\varphi_3(\degree)$ 0.121  $g_{xx}$ 5.33  $g_{yy}$ 3.23  $g_{zz}$ 1.63  $\gamma(\degree)$ 3.2 |
| $Dy_3$Mg$_2$Sb$_2$O$_{14}$ PC Calc. | $r_1$(Å) 1.65  $r_2$(Å) 1.60  $r_3$(Å) 1.42  $\theta_1(\degree)$ 78  $\theta_2(\degree)$ 76.5  $\theta_3(\degree)$ 59  $\varphi_1(\degree)$ 0.5  $\varphi_2(\degree)$ 0.3  $\varphi_3(\degree)$ 0.15  $g_{xx}$ 0  $g_{yy}$ 0  $g_{zz}$ 19.65  $\gamma(\degree)$ 3.2 |
| $Tm_3$Mg$_2$Sb$_2$O$_{14}$ PC Calc. | $r_1$(Å) 1.6  $r_2$(Å) 1.35  $r_3$(Å) 1.35  $\theta_1(\degree)$ 78  $\theta_2(\degree)$ 76.5  $\theta_3(\degree)$ 59  $\varphi_1(\degree)$ 0.5  $\varphi_2(\degree)$ 0.3  $\varphi_3(\degree)$ 0.15  $g_{xx}$ 0  $g_{yy}$ 0  $g_{zz}$ 10.34  $\gamma(\degree)$ 4.5 |

The most surprising result of our work is that the g-tensor of $Er_3$Mg$_2$Sb$_2$O$_{14}$ is very uniaxial. This contradicts our previous assumption of XY anisotropy which was based on a comparison to Er-pyrochlore analogues\(^{27}\). However, this Ising-like anisotropy has two fundamental differences compared to that of the Ho or Tb compounds: first, the easy axis is not pointing along the local z-direction, but rather x-direction that is about 65° canted away from the kamagate plane; second, the components of $g_{yy}$ and $g_{zz}$ are not zero which in principle allow for observable spin dynamics even in the absence of transverse fields. The two consequences are, first, the system is still highly frustrated even allowing for antiferromagnetic interaction between the moments along local x-direction; second, similar to that in the Yb and Er pyrochlores\(^{61,62}\), we expect off-diagonal couplings between x components and yz components. Since no magnetic ordering down to 50 mK has been observed experimentally\(^{27,31}\), $Er_3$Mg$_2$Sb$_2$O$_{14}$ is a quantum spin liquid candidate whose interpretation calls for a quantum Ising model with anisotropic exchanges.

V. DISCUSSION: OTHER APPLICATIONS

A. Tuning the transverse field in $Ho_3$Mg$_2$Sb$_2$O$_{14}$

Similar to the example established for Yb$_2$Ti$_2$O$_7$ in Fig. 3, the effective PC model can be used to study how the CEF reacts to the changes of PC parameters. This can sometimes be extremely useful. Taking $Ho_3$Mg$_2$Sb$_2$O$_{14}$ for example, our previous work has shown that the excitation associated with the splitting of the ground-state doublet in $Ho_3$Mg$_2$Sb$_2$O$_{14}$ appears highly overdamped due to interactions between sites, which precludes a direct measurement of that energy scale.
TABLE IV. Tabulated CEF parameters, CEF energies, and $g$-tensors from the Effective PC calculations for the average structure of YbMgGaO$_4$ and TmMgGaO$_4$.

| PC Calc.       | PC parameters | CEF parameters (meV) | CEF energies | $g$-tensor |
|---------------|---------------|----------------------|--------------|------------|
|               | $r_1$(Å)     | $\theta_1$(°)       | $q_1$(Å)     | $A_0^\parallel$ | $A_0^\perp$ | $E_0$ (meV) | $g_i$ | $g_\perp$ |
| YbMgGaO$_4$   | 1.607        | 61.7                 | 0.5          | -58.1       | -15.1       | 695.0      | 5.1       | -34.6 | 52.0 | 0.413 | 84.3 | 129.6 | 3.32 | 2.10 |
| TmMgGaO$_4$   | 1.613        | 61.7                 | 0.5          | -77.5       | -15.7       | 721.7      | 5.5       | -36.9 | 55.4 | 32.5 | 68.5 | 120.6 | 132.3 |

FIG. 12. CEF energy of Ho$_3$Mg$_2$Sb$_3$O$_{14}$ as a function of lattice change in a log-log scale. The lattice contraction/expansion is characterized by a ratio, $f$, where $f=1$ corresponds to the fitted PC model in Table. By performing a linear fit of the two-singlet splitting between $f=0.96$ and 1.04, we obtained an exponential dependence as $\Delta \sim f^{-14.0(1)}$.

With neutrons$^{32}$. To minimize the interaction effects between sites and to directly observe the two-singlet excitation, we synthesized a very dilute Ho tripod kagome compound (Ho$_{0.01}$La$_{0.99}$)$_3$Mg$_2$Sb$_3$O$_{14}$ whose single-ion excitation can be understood within a two singlet splitting of $\Delta=1.14$ K$^{32}$. As the lattice parameters the doped compound are approximately 2.9% larger than that of Ho$_3$Mg$_2$Sb$_3$O$_{14}$, a natural question that arises is how $\Delta$ responds to the change in lattice parameters. This can be easily investigated by our PC calculations. If we assume the PC parameters for distance ($r_1$) changes linearly with the lattice contraction/expansion, we can track the CEF energies as a function of a lattice change. By varying the lattice parameters nearby the fitted PC parameters for Ho$_3$Mg$_2$Sb$_3$O$_{14}$, denoted by a ratio, $f$, all the excited CEF levels have an exponential dependence of the lattice contraction/expansion, evidenced by the linear dependence of the CEF energies as a function of $f$ in a log-log plot [Fig. 12]. Notably, the two singlet splitting has a much more dramatic response to lattice changes compared to other excited CEF levels, i.e. $\Delta \sim f^{-14.0(1)}$ versus $E_i \sim f^{-4.0(1)}$. It means that if we extrapolate the value of $\Delta$ from (Ho$_{0.01}$La$_{0.99}$)$_3$Mg$_2$Sb$_3$O$_{14}$ to Ho$_3$Mg$_2$Sb$_3$O$_{14}$, the corresponding value of $\Delta$ will be $1.14 \times (1.029)^{14} = 1.72$ K. It also means that one can efficiently tune the transverse field in Ho$_3$Mg$_2$Sb$_3$O$_{14}$ by applying physical or chemical pressure: a 3% change in lattice will result in 50% change in $\Delta$. Recalling the $1/f^3$ dependence of the dipolar interaction, it means lattice contraction/expansion can effectively tune the ratio of transverse field over the dipolar interactions in Ho$_3$Mg$_2$Sb$_3$O$_{14}$. Importantly, this ratio is the essence of the transverse Ising model on a kagome dipole magnet which determines the boundary between several distinct quantum phases, as demonstrated by our previous simulations$^{32}$. This example shows how PC calculations can be used to investigate the effects of physical or chemical pressure on the quantum dynamics of transverse Ising model, which also provides insights into the search for quantum spin ices based on non-Kramers ions.

B. Scaling CEF to Dy$_3$Mg$_2$Sb$_3$O$_{14}$ and Tm$_3$Mg$_2$Sb$_3$O$_{14}$

In the spirit of the Effective PC model, we can make predictions of CEF for other tripod kagome compounds. This is similar to the scaling arguments proposed for the pyrochlores but within a more physically-meaningful framework$^{63}$. Starting from the Effective PC model for the tripod structure, we can choose $q_1 = 0.5e$, $q_2 = 0.3e$, $q_3 = 0.15e$, and $\theta_2 = 78^\circ$, $\theta_3 = 76.5^\circ$, $\phi_3 = 59^\circ$ which are the approximate numbers from the local crystallography. For the distance PC parameters, we extrapolate the fitted $r_1$ values from $R_3$Mg$_2$Sb$_3$O$_{14}$ ($R=Tb$, Ho, Er, Yb) since Dy and Tm are between Tb/Ho and Er/Yb in the periodic table, respectively. The numbers for the Effective PC model are listed in the Table III and the predicted CEF levels are plotted in Fig. 11. Consistent with earlier studies, the Dy$^{3+}$ ion exhibits a well isolated Kramers doublet ground state where the first excited CEF level is around 32 meV$^{30}$. On the other hand, Tm$_3$Mg$_2$Sb$_3$O$_{14}$ is expected to host a well isolated singlet ground state with an energy separation of 6 meV from the first excited singlet. This energy separation is expected to be at least one order of magnitude larger than the spin-spin interactions, making interesting many-body physics irrelevant at low temperature. Therefore, similar to that of Pr$_3$Mg$_2$Sb$_3$O$_{14}$, we expect only single-ion magnetism for Tm$_3$Mg$_2$Sb$_3$O$_{14}$. We comment that a tripod kagome variant, Tm$_2$Zn$_2$Sb$_3$O$_{14}$, whose low-temperature magnetism has been investigated recently$^{64}$, is likely to be associated with both a large two CEF singlets splitting and site-disorder effects which are enhanced for Zn-based tripod kagome compounds due to the large $R$ atomic number$^{31}$. 
C. Triangular magnets TmMgGaO₄ and YbMgGaO₄

Given the success of our effective PC model to treat the pyrochlore and tripod kagome compounds, it is natural to extend the model for other rare earth oxides, for example, YbMgGaO₄ and TmMgGaO₄. While it is known that there is some structure disorders associated with Mg/Ga occupying the same site¹⁰,¹²,⁶⁵, both compounds share the same average structure where the rare-earth ions sit in an octahedral environment with \( D_{3d} \) point group, and oxide ligands are in the center of a tetrahedron formed by three rare earth ion and one non-magnetic ion. Although it requires the same number of Stevens’ parameters to describe its CEF as for the pyrochlores, many fewer PC parameters are needed to describe the local ligand geometry (see Table I). Similar to the Effective PC model established in the previous sections, we chose the three PC parameters, \( r_1 = 0.72 \rightleftharpoons \), \( \theta_1 = 61.7^\circ \), and \( q_1 = 0.5 \rightleftharpoons \). The predicted CEF levels for YbMgGaO₄ and TmMgGaO₄ are tabulated in Table IV and plotted in Fig. 11. Interestingly, TmMgGaO₄ exhibits the same two-singlets ground state as Ho₂Mg₂Sb₂O₁₄ and Tb₃Mg₂Sb₂O₁₁₄, where the 0.4 meV splitting of the two-singlet can be mapped to a transverse field that is comparable to spin-spin interactions. The estimated splitting is close to the experimental number based on the heat capacity measurement of a diluted sample⁶⁶ and also agrees with the number from theoretical fits to the spin dynamics⁶⁷,⁶⁸, suggesting that the Effective PC model is doing a good job at capturing the CEF levels of the average structure. In contrast, the predicted CEF levels for YbMgGaO₄ shows three excited levels at 40.9, 83.6, and 128.5 meV, respectively. While the former two levels are close in energy to the 38 and 97 meV levels measured experimentally¹²,⁶⁵, the other CEF level (at 128.5 meV) is much higher in energy than that observed experimentally (at 61 meV). Interestingly, our previous measurements indeed observe an additional weak CEF signal at 134 meV¹², and this observation is also reported by Li et al. but interpreted as a possible neutron multiple scattering effect⁶⁵. The discrepancies between PC model and experiments indicate that the CEF Hamiltonian of YbMgGaO₄ needs to be revisited with a different approach.

VI. SUMMARY & OUTLOOK

In summary, this manuscript introduces the concept of effective PC model to understand the CEF excitations measured by inelastic neutron scattering in rare-earth based magnets. It provides a clear methodology that is benchmarked successfully to rare-earth pyrochlore oxides and subsequently applied to tripod kagome magnets. We predict that our approach will be useful in practice for systems with low point-group symmetry where a large number of CEF parameters are expected. Compared to the conventional Stevens’ operator approach widely used in the last few decades, the advantages of the PC approach includes a physically meaningful parameterization, a reduced parameter space, and a level of accuracy sufficient for CEF excitations to be utilized to determine the principal axes of the spin-space anisotropy tensor. Perhaps the most exciting message from our results is that a reasonable estimation of the CEF spectra and spin-space anisotropies can be made simply from the local crystallography provided PC parameters are adjusted. Our manuscript provides a methodology to achieve that adjustment. Given the current emphasis on magnetic quantum matter with anisotropic spins and exchange interactions, we expect our PC calculation method to be useful in searching for rare-earth materials with desired anisotropy properties.

ACKNOWLEDGMENTS

The authors thank J. A. M Paddison for many helpful discussions and Huibo Cao for critical reading of the manuscript. The work of Z.L.D., X.B. and M.M. at Georgia Tech was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Neutron Scattering Program under Award Number DE-SC0018660. The work of H.D.Z. at the University of Tennessee was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under award DE-SC-0020254. The research at Oak Ridge National Laboratory’s Spallation Neutron Source was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Scientific User Facilities Division.

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