Synthesis and characterization of the novel breathing pyrochlore compound Ba₃Tm₂Zn₅O₁₁

Lalit Yadav^{0,1} Rabindranath Bag^{0,1} Ramesh Dhakal^{0,2} Stephen M. Winter,² Jeffrey G. Rau^{0,3} Sachith E. Dissanayake,¹

Alexander I. Kolesnikov⁰,⁴ Andrey A. Podlesnyak⁰,⁴ Craig M. Brown⁰,⁵ Nicholas P. Butch,⁵ David Graf⁰,⁶ Michel J. P. Gingras⁰,⁷ and Sara Haravifard⁰,⁸,*

¹Department of Physics, Duke University, Durham, North Carolina, USA

²Department of Physics and Center for Functional Materials, Wake Forest University, Winston-Salem, North Carolina 27109, USA

³Department of Physics, University of Windsor, 401 Sunset Avenue, Windsor, Ontario N9B 3P4, Canada

⁴Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

⁵Center for Neutron Research, National Institute of Standards and Technology, MS 6100 Gaithersburg, Maryland 20899, USA

⁶National High Magnetic Field Laboratory and Department of Physics, Florida State University, Tallahassee, Florida 32310, USA

⁷Department of Physics and Astronomy, University of Waterloo, Ontario N2L 3G1, Canada

⁸Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, USA

(Received 28 June 2024; accepted 29 October 2024; published 6 December 2024)

In this study, a novel material from the rare-earth based breathing pyrochlore family, $Ba_3Tm_2Zn_5O_{11}$, was successfully synthesized. Powder x-ray diffraction and high-resolution powder neutron diffraction confirmed phase purity and the $F\bar{4}3m$ breathing pyrochlore crystal structure, while thermogravimetric analysis revealed incongruent melting behavior compared to its counterpart, $Ba_3Yb_2Zn_5O_{11}$. High-quality single crystals of $Ba_3Tm_2Zn_5O_{11}$ were grown using the traveling solvent floating zone technique and assessed using Laue x-ray diffraction and single crystal x-ray diffraction. Thermodynamic characterization indicated paramagnetic behavior down to 0.05 K, and inelastic neutron scattering measurements identified distinct dispersionless crystal electric field energy bands, with the fitted crystal electric field model predicting a single-ion singlet ground state and an energy gap of ~9 meV separating it from the first excited (singlet) state. Additional low-energy excitation studies on single crystals revealed dispersionless bands at 0.8 and 1 meV. Computed phonon dispersions from first-principles calculations ruled out phonons as the origin of these modes, further illustrating the puzzling and unique properties of $Ba_3Tm_2Zn_5O_{11}$.

DOI: 10.1103/PhysRevMaterials.8.123401

I. INTRODUCTION

Frustrated quantum magnets have over the past thirty years become a fruitful playground for the exploration of exotic magnetic ground states with suppressed tendency towards conventional long-range order and displaying unconventional excitations [1–3]. The competing interactions in these systems can originate from a frustrated lattice geometry, spin-spin interactions beyond nearest neighbors, or anisotropic spin-spin interactions. Geometrically frustrated lattices are commonly achieved using spins residing on either elementary triangular or tetrahedral units and forming regular two- and threedimensional lattices. In three dimensions, the pyrochlore lattice of corner-sharing tetrahedra has become the paradigmatic example of high magnetic frustration [1,3].

The pyrochlore architecture is prominently featured in the $A_2B_2O_7$ magnetic pyrochlores [4–6]. In these materials, the trivalent A^{3+} and tetravalent B^{4+} ions, respectively, span two independent interpenetrating pyrochlore lattices, with either or both sites capable of hosting a magnetic moment depending on the cation. Magnetic materials with nonmagnetic A^{3+} (e.g., Y^{3+} or Lu³⁺) and magnetic transition metal B^{4+} ions

have been studied [4] (e.g., Y₂Mn₂O₇ [7], Y₂Mo₂O₇ [8–10], $Lu_2Mo_2O_7$ [11], $Lu_2Mo_2O_5N_2$ [11] and $Lu_2V_2O_7$ [12]), and found to display a range of interesting thermodynamic, magnetic, as well as thermal transport [12] properties. However, a wider variety of materials displaying a gamut of magnetic behaviors has been afforded by the rare-insulating rare-earth compounds in which A is a magnetic trivalent 4f lanthanide rare-earth element (e.g., A = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb) and B is a nonmagnetic transition metal element (e.g., B = Ti, Sn, Ge, Zr, Hf) [4–6,13–15]. In these systems, the strong single-ion crystal field anisotropy typically results in a magnetic crystal field ground-state doublet described by an effective spin-1/2 degree of freedom. The interactions (e.g., magnetic, quadrupolar, etc) between the ions are then expressed in terms of anisotropic bilinear "exchange-like" couplings between those pseudospins 1/2 [6,16–18].

In addition to the $A_2B_2O_7$ pyrochlore oxides, the spinels AB_2X_4 (e.g., A = Zn, Mg; B = Cr, Fe, X = O, S), in which the magnetic transition metal B^{3+} ions reside on a pyrochlore lattice, have also been extensively studied [19]. The latter have provided great opportunities to study the physics of magnetic frustration on the pyrochlore lattice with transition metal ions (Cr^{3+} , Fe³⁺) beyond that explored with the $A_2B_2O_7$ compounds with nonmagnetic A^{3+} and magnetic B^{4+} transition metal ions [7–12]. About ten years ago [20], a new variety

^{*}Contact author: sara.haravifard@duke.edu



FIG. 1. (a) Powder x-ray diffraction pattern of $Ba_3Tm_2Zn_5O_{11}$ at room temperature is shown as black circle. The red, blue, and green lines represent the calculated intensity, the difference between observed and calculated intensity, and the expected Bragg's positions, respectively. The additional nonmagnetic ZnO and BaCO₃ impurity peaks are identified as *, specifically at the strongest peaks of these phases. (b) Crystal structure of $Ba_3Tm_2Zn_5O_{11}$, highlighting only the Tm^{3+} ions, is shown with the breathing ratio (d/d') and the alternating large and small corner sharing tetrahedra.

of magnetic spinels, $AA'B_4X_8$ (e.g., A = Li, Cu; A' = Ga, In; B = Cr; X = O, S, Se), with nonmagnetic cations on the A and A' sites being crystallographically ordered, began attracting attention [20–22]. In these materials, the magnetic Cr^{3+} ions reside on a so-called *breathing pyrochlore* (BP) lattice. This architecture consists of an alternating arrangement of expanded (large) and contracted (small) corner-shared tetrahedra, with the nearest-neighbor bond distances d and d' for the large and small tetrahedra, respectively [see Fig. 1(b) for an example of a breathing pyrochlore lattice with *breathing ratio* d/d' = 1.85].

The availability of BPs offers opportunities to explore interesting and enhanced frustration-driven phenomena. For example, theoretical studies have predicted that the parameter phase space of BP systems, which comprises different exchange couplings (J_A and J_B) and Dzyaloshinskii-Moriya (DM) interactions (D_A and D_B) between large (A) and small (B) tetrahedra may contribute to stabilize exotic ground states such as quantum spin ice [23], spin liquid [24], magnetic hedgehog lattice [25] and Weyl magnons [26]. In terms of experimental realizations, Cr-based BP systems such as Li(Ga, In)Cr₄(O, S)₈ [20,27], CuInCr₄S₈ [28] and CuAlCr₄S₈ [22] have been synthesized and investigated experimentally, as well as modelled theoretically [21]. To a large extent, these Cr-based BP systems have a similar structure compared to a regular (i.e., nonbreathing) pyrochlore since the breathing ratio is nearly unity ($d/d' \approx 1.05 \pm 0.02$). Moreover, the Cr³⁺ ion has effective S = 3/2 spin for which quantum fluctuations are suppressed and are expected to behave nearly classically [21].

A potential route to explore a different regime outside the $d/d \approx 1$ breathing ratio limit and the large S value characterizing the Li(Ga, In)Cr₄(O, S, Se)₈ materials is the rare-earth (RE) breathing pyrochlore (BP) family, known as Ba₃RE₂Zn₅O₁₁ [29]. So far, only one member has been systematically explored: the effective spin-1/2 system (Ba₃Yb₂Zn₅O₁₁). Unlike other breathing pyrochlores, the breathing ratio (d/d') of the Ba₃Yb₂Zn₅O₁₁ BP system is approximately 1.8 and thus much larger than the ratio for Cr-based BPs. At the very least, in this limit, one may hope that studying these materials will yield a better understanding of the microscopic aspects of magnetism associated to frustration as well as the nature of the effective spin-1/2 interactions in rare-earth systems [30,31] without the need to address the complexity of collective behavior. In further contrast to the Cr-based BPs, Ba₃Yb₂Zn₅O₁₁ exhibits no signs of long-range ordering down to 100 mK [29,32]. The limit of nearly isolated tetrahedra describes the physics of this compound quite well [29,32–37], implying that the exchange interactions between the tetrahedra in $Ba_3Yb_2Zn_5O_{11}$ are small [29]. On the other hand, Ba₃Yb₂Zn₅O₁₁ has been suggested as a candidate for rank-2 U(1) QSL because of the strong DM interaction [24] and has been found to exhibit low-temperature properties that hint at the significance of interactions between tetrahedra [32,38].

Theoretical calculations aimed at assessing the stability of breathing pyrochlore compounds conclude that the size of small and large tetrahedra could be either slightly different $(d/d' \approx 1)$ or significantly different $(d/d' \approx 2)$ [39]. In the first case, materials such as $Li(Ga, In)Cr_4(O, S, Se)_8$ and Pb₂Ir₂O_{7- δ}($\delta \approx 1$) [39] are closer to a standard d/d' = 1pyrochlore lattice with strongly coupled tetrahedra, while in the second case, the rare-earth BP compounds Ba₃RE₂Zn₅O₁₁ behave, to a large extent [32,34,38], as a system of quasiisolated tetrahedra. Nonetheless, in the second case, where a significant distance between small tetrahedra hinders intertetrahedron interactions, application of external pressure or the substitution with a magnetic ion possessing a larger magnetic moment may enhance the intertetrahedron interactions. Moreover, the ability of these intertetrahedron interactions to alter the single-tetrahedron physics is highly dependent on the specific single-ion crystal field manifold of states which varies between different RE ions. Additionally, the intratetrahedron interactions, which can, in principle and generally speaking, be strongly influenced by the choice of RE ion, may also play a significant role. To explore the role of inter- and intratetrahedra interactions in providing a clearer picture of magnetism in BPs, it is thus important to search for new materials in the $Ba_3RE_2Zn_5O_{11}$ family that may harbor stronger intertetrahedra interactions or display interesting physics qualitatively distinct from the one found in $Ba_3Yb_2Zn_5O_{11}$.

Building upon our previous synthesis and single-crystal growth achievements [37] and drawing from our accumulated expertise, we report in the present paper a groundbreaking synthesis, single crystal growth, and comprehensive characterization of the novel rare-earth BP compound $Ba_3Tm_2Zn_5O_{11}$. Neutron diffraction data confirms the phase purity and structure of Ba₃Tm₂Zn₅O₁₁ down to a temperature of 4 K. Unlike the relatively straightforward growth of single crystals of Ba₃Yb₂Zn₅O₁₁ [37], growing single crystals of this new Ba₃Tm₂Zn₅O₁₁ compound proved challenging because of the compound's incongruent melting behavior. To overcome this difficulty, we employed the traveling-solventfloating zone (TSFZ) technique, utilizing a solvent disk composed of BaZnO₂, which ultimately yielded large highquality single crystals of Ba₃Tm₂Zn₅O₁₁. Magnetic and heat capacity studies on these single crystals conclusively indicate the absence of any long-range magnetic ordering down to 0.1 K. Additionally, neutron scattering was employed to investigate the crystal electric field (CEF) levels and low-energy excitations of this material.

II. EXPERIMENTAL METHODS

Polycrystalline Ba₃Tm₂Zn₅O₁₁ powder was prepared by a solid-state reaction route using the starting precursors of Tm₂O₃ (99.9%, Alfa Aesar) with ZnO (99.99%, Alfa Aesar) and BaCO₃ (99.99%, Alfa Aesar). The starting precursors were weighed in the (1:5.05:3) molar ratio, respectively, and the well-ground mixture was sintered at 800 °C for 8 hours, 1000 °C for 12 hours, and 1110 °C for 48 hours with intermediate grinding. For the nonmagnetic analog, Ba₃Lu₂Zn₅O₁₁ was synthesized from the precursors Lu₂O₃ (99.9%, Alfa Aesar) with ZnO (99.99%, Alfa Aesar) and BaCO₃ (99.99%, Alfa Aesar) weighed in the (1:5:3) molar ratio, respectively, and sintered at 1100 °C for 48 hours. Additionally, attempts to synthesize Ba₃Er₂Zn₅O₁₁ revealed that it is highly unstable and likely not synthesizable. The phase purity of our samples and crystal structure were examined using a powder x-ray diffraction (PXRD) technique with a MiniFlex diffractometer from RIGAKU equipped with Cu K- α radiation source at room temperature. The temperature-dependent structural stability and long-range ordering were assessed through high-resolution powder neutron diffraction using the BT-1 spectrometer at NIST, Gaithersburg on a \approx 7 g Ba₃Tm₂Zn₅O₁₁ powder sample. The powder sample was packed in a vanadium can filled with helium-4 exchange gas so that the sample could be cooled down to the base temperature. Measurements were systematically performed at 4 K, 45 K, and 100 K using a helium-4 type closed-cycle refrigerator (CCR). The Cu (311) monochromator was used to produce incident neutron of wavelength 1.54 Å along with a 15' collimator installed upstream of the sample. The diffraction pattern was analyzed using the FullProf suite [40].

Once the phase purity of the powder sample was confirmed, a thermogravimetric analysis (TGA/DSC 3+, MET-TLER TOLEDO) was used to understand the intricacies of the melting behavior of this compound. Subsequently, single crystals of Ba₃Tm₂Zn₅O₁₁ were grown using a four semi-ellipsoidal mirrors optical floating zone furnace (Model: FZ-T-12000-X-VII-VPO-PC, Crystal System Corporation, Japan) equipped with xenon lamps with a maximum power of 12 kW. These mirrors focus the radiation from the xenon lamps to achieve a large vertical temperature gradient. Additionally, alumina shutters control the feed rod's exposure to the optical rays, adjusting the temperature gradient and aiding in tuning the liquid zone size. The quality of the grown crystals was examined using a Laue diffractometer (MUL-TIWIRE LABS MWL120). Single crystal x-ray diffraction of Ba₃Tm₂Zn₅O₁₁ was performed at the UNC Chapel Hill Department of Chemistry using a Bruker KAPPA Apex II diffractometer and measured at 230 K. The structure was solved using Superflip3 [41] and refined using full-matrix least squares with the Crystals software from the University of Oxford [42]. Magnetic characterization on the grown crystal was done using a vibrating sample magnetometer (VSM) and heat capacity data was collected using helium-4 (1.8 K \leq $T \leq 300 \,\mathrm{K}$) and dilution refrigeration (0.06 $\mathrm{K} \leq T \leq 2 \,\mathrm{K}$) set-up attached to the Physical Properties Measurement Systems, Quantum Design (PPMS Dynacool, QD, USA). To investigate the magnetic properties of Ba₃Tm₂Zn₅O₁₁ down to 0.02 K and in high magnetic fields, we performed tunnel diode oscillator (TDO) measurements at the DC Field Facility of the National High Magnetic Field Laboratory in Tallahassee. A bar-shaped single-crystal sample, with a length of approximately 2 mm, a width of 1 mm, and a thickness of 0.5 mm, was wound inside a detection coil, aligning the [111] Ba₃Tm₂Zn₅O₁₁ crystallographic direction along the coil axis.

The sample and coil together constituted the inductive component of an LC circuit connected to a tunnel diode operating in a negative resistance region, which was fine-tuned to achieve resonance within a frequency range of 10 to 50 MHz. The shift in the resonance frequency f, which relates to the change in the sample magnetization $M (df/dH \propto d^2M/dH^2)$ [43,44], was recorded as the field was swept to 18 T using superconducting magnets.

Inelastic neutron scattering (INS) measurements were conducted using the SEQUOIA spectrometer [45] at the spallation neutron source (SNS), Oak Ridge National Laboratory. Approximately 6 grams each of pure Ba₃Tm₂Zn₅O₁₁ and Ba₃Lu₂Zn₅O₁₁ (for the determination of the phonon contributions) powder samples were loaded into aluminium cans and sealed under helium-4 atmosphere. Measurements were collected at incident neutron energy $(E_i) E_i = 150 \text{ meV}$ and 100 meV in high-flux mode and at $E_i = 50 \text{ meV}$ and 25 meV in high-resolution mode over the temperature range $5 \text{ K} \leq$ $T \leq 150$ K. The data were analyzed using the DAVE MSlice [46] while the PyCrystalField [47] and MCphase [48] packages were utilized to determine the parameters of the crystal electric field (CEF) Hamiltonian for Tm^{3+} in $Ba_3Tm_2Zn_5O_{11}$. The low-energy inelastic scattering experiments were performed at the Cold Neutron Chopper Spectrometer (CNCS) [49] at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory on six pieces of coaligned high-quality single crystal samples of Ba₃Tm₂Zn₅O₁₁ with a total mass of ≈ 0.9 g. The crystals were mounted on a copper holder using superglue (see Fig. 4 below), aligning them in such a way that their [h + k, -h + k, -2k] scattering plane is perpendicular to the [111] crystallographic direction, with the magnetic field **H** along the [111] direction. The measurements were conducted in a dilution refrigerator with a base temperature of 0.1 K as well as an 8 T magnet insert, using $E_i = 3.32$ meV.

III. RESULTS

A. Crystal structure and phase purity

Ba₃Tm₂Zn₅O₁₁ is isostructural to Ba₃Yb₂Zn₅O₁₁ and crystallizes into the cubic structure with a space group of $F\overline{4}3m$ (no. 216). We show in Fig. 1, the powder x-ray diffraction pattern collected on Ba₃Tm₂Zn₅O₁₁ powder sample and the crystal structure obtained from the refined diffraction pattern. Figure 1(a) shows the experimental powder x-ray diffraction data and the calculated data obtained using Rietveld refinement along with the expected Bragg positions. The phase analysis confirms the phase purity of the synthesized Ba₃Tm₂Zn₅O₁₁ powder sample. More than 99% of the sample mass is in the BP phase with space group $F\overline{4}3m$. A negligible percentage of nonmagnetic impurity (BaCO₃ and ZnO) are identified with the associated peaks and are marked with * symbols in Fig. 1(a). The crystal structure of $Ba_3Tm_2Zn_5O_{11}$ thus corresponds to a breathing pyrochlore network where the Tm³⁺ magnetic ions form large and small tetrahedra, as shown in Fig. 1(b).

To examine the structural stability of the breathing pyrochlore structure, high-resolution powder neutron diffraction was carried out on Ba₃Tm₂Zn₅O₁₁ powder sample at the selected temperatures T = 4 K, 45 K, and 100 K. The measured diffraction data was structurally refined using the FullProf software, with no structural transition being observed down to 4 K. Apart from the expected lattice contraction with decreasing temperature, no significant changes in the structure were detected. In Fig. 2, one representative powder neutron diffraction data collected at 4 K is shown along with the calculated intensity. It is found that all the observed Bragg peaks can be indexed based on the space group $F\overline{43m}$ at 4 K. The small value of Chi-square (1.59) and Bragg R-factor (4.5) obtained from Rietveld refinement confirm a good agreement with the BP structure.

B. PDF analysis

To investigate the local structure of Ba₃Tm₂Zn₅O₁₁, total neutron scattering measurements were conducted on a powder sample using the Nanoscale-Ordered Materials Diffractometer (NOMAD) [50] at Oak Ridge National Laboratory. The data were collected across selected temperatures ranging from 2 K to 300 K. After normalization, the NOMAD data were Fourier transformed to obtain the pair distribution function (PDF) G(r), a real-space representation of atomic correlations that quantifies the likelihood of finding a pair of atoms separated by a distance r, averaged over time,

$$G(r) = A \times \left[\int_{Q_{\min}}^{Q_{\max}} Q(S(Q) - 1) \sin(Qr) dQ \right].$$
(1)



FIG. 2. Neutron powder diffraction data of $Ba_3Tm_2Zn_5O_{11}$ collected at 4 K using incident neutron of wavelength 1.54 Å. The black circles, red, and blue lines represent the observed intensity, calculated intensity, and difference between observed and calculated intensity, respectively. The short vertical-green lines show the expected locations of Bragg peaks associated with the breathing pyrochlore structure, as well as the peaks associated with the second harmonic of the neutron energy used for this experiment.

Here, Q_{max} was set to 30 Å⁻¹ and A is an arbitrary scale parameter determined from the analysis. The momentum transfer Q is defined as $Q = 4\pi \sin(\theta)/\lambda$, where λ is the neutron wavelength and θ is the scattering angle. The PDF data G(r) for the selected temperature range, displayed in Fig. 3



FIG. 3. The pair distribution function G(r) of the local structure of Ba₃Tm₂Zn₅O₁₁ collected at selected temperatures between 2 K and 100 K (scatter markers), compared with the average model (solid-red lines) refined using PDFGUI software with the assumed space group $F\bar{4}3m$. The data has been shifted vertically for clarity. The inset shows the thermal displacement factor U_{11} for different atoms. As can be seen, no anomalous temperature dependence or anomalously large value of any thermal factor is observed.

from 1.8 Å to 10 Å, have been shifted vertically for clarity. Small-box refinements of the PDF data were performed using the PDFgui [51] software. The average structure, modeled by the space group $F\bar{4}3m$, fits the data well with no peak splitting or significant mismatches observable. The inset of Fig. 3 shows the anisotropic atomic displacement parameter U_{11} for various atoms as a function of temperature, derived from the PDF fits. U_{11} decreases with temperature, which is expected as thermal fluctuations decrease. All U_{11} values are on the order of 10^{-3} , indicating no disorder or atomic tunneling between local atomic configurations [52].

C. Single crystal growth

In order to grow single crystals of $Ba_3Tm_2Zn_5O_{11}$, the melting behavior of $Ba_3Tm_2Zn_5O_{11}$ was studied by thermogravimetric analysis, as detailed in Appendix A. Upon heating, $Ba_3Tm_2Zn_5O_{11}$ was found to melt incongruently, decomposing into products according to the reaction (A1). Among the decomposed products, $BaZnO_2$ is the only component in the liquid phase that can be used as a flux solvent for subsequent crystal growth. Consequently, a traveling-solvent-floating-zone (TSFZ) technique was employed to grow large and high-quality single crystals of the $Ba_3Tm_2Zn_5O_{11}$ compound using $BaZnO_2$ as flux. The preparation details of the feed rod and flux are elaborated upon in Appendix B.

About 250-300 mg of BaZnO₂ solvent disk is used depending on the Ba₃Tm₂Zn₅O₁₁ feed rods' dimensions. The growth process is performed in two steps: Firstly, the feed rod is placed at the seed rod holder (lower shaft of the FZ furnace), and the solvent disk is melted partially and is stuck to the top end of the feed rod and exposed under a 0.1% of the maximum lamp power. Secondly, the feed rod with the attached BaZnO₂ solvent disk was suspended from the upper shaft of the furnace, and the growth process was started. The crystal growth is performed while bringing down the feed rod into the heating zone under 0.1-1.0% of the maximum lamp power and shutter length \approx 70–65 mm. The melted BaZnO₂ flux is partially absorbed by the feed rod and thereafter dissolves the $Ba_3Tm_2Zn_5O_{11}$. This eventually percolates down and forms a liquid blob with solid particles at the end of the feed rod. At this stage, the liquid blob contains mostly the BaZnO₂ liquid from the supplied external flux and other phases Ba₅Tm₈Zn₄O₂₁ (S), Ba₂Tm₂Zn₈O₁₃ (S), ZnO (S), and $BaZnO_2$ (L) from the decomposition of $Ba_3Tm_2Zn_5O_{11}$ feed rod. Once the amount of the BaZnO₂ liquid appeared to be sufficient on the surface of the feed rod, a liquid zone was formed, and both feed and seed rods were moved downwards with a growth speed of 1-3 mm/h. The lamp power was gradually reduced to its lowest value of 0.1% of maximum power. The feed and seed were made to rotate (8-20 rpm) in opposite directions to achieve a homogeneous mixture in the liquid zone. During the growth process, the $Ba_3Tm_2Zn_5O_{11}$ decomposes at the liquid zone's upper region, while at the lower region, the decomposed phases recombine, crystallizing into the breathing pyrochlore phase we seek.

To obtain centimeter-scale $Ba_3Tm_2Zn_5O_{11}$ single crystals, the best growth conditions were identified as follows: The oxygen pressure was set to a maximum of 0.95 MPa to minimize bubbling. A "two-scanning" method was used, where



FIG. 4. $Ba_3Tm_2Zn_5O_{11}$ single crystals extracted from different growths mutually coaligned along the [111] direction and mounted on the sample holder for the neutron experiments. Representative Laue patterns from different regions of single crystals are shown. The brightest (black) spot just below the central white disk corresponds to the $\langle 111 \rangle$ reflections.

the feed rod was initially passed through the heating zone at a high speed ($V_s > 1 \text{ mm/hr}$) to premelt the crystal. This premelted grown crystal was then used as the feed rod for the slow growth process ($V_s = 0.4 \text{ mm/hr}$), which improved molten zone stability by preventing liquid penetration into the highly dense premelted crystal feed rod. The optimized growth parameters are tabulated in Table IV in Appendix B and representative grown single crystals are shown in Fig. 4.

D. Single crystal characterization

Several high-quality single crystals of a few millimeters in size were extracted from the different growths and oriented using a Laue diffractometer. The crystals were oriented along the crystallographic [111] direction, and the magnetic and thermal characterizations were carried out on these oriented crystals. Figure 4 shows the coaligned $Ba_3Tm_2Zn_5O_{11}$ single crystals (each around 1 g) mounted on a copper-based sample holder for neutron study with some representative images of collected Laue patterns also shown. Each crystal specimen was aligned along the [111] direction and placed on the sample holder with Cu wire and super-glue as shown in Fig. 4. The similar Laue patterns obtained from the different mounted crystal specimens confirm the orientation of all $Ba_3Tm_2Zn_5O_{11}$ crystals to be along the crystallographic [111] direction.

Single crystal x-ray diffraction (XRD) was conducted on the Ba₃Tm₂Zn₅O₁₁ crystal to confirm the crystal structures, with refined atomic positions given in Table I. The Tm³⁺-Tm³⁺ and Tm–O bond distances, bond angles, and the breathing ratio (d/d') obtained from these positions are separately tabulated in Table II. The breathing ratio (d/d')determined for Ba₃Tm₂Zn₅O₁₁ is 1.8822(9), larger than the 1.82(2) value found for Ba₃Yb₂Zn₅O₁₁ [37].

TABLE I. Single crystal x-ray diffraction refinement results at 230 K using the space group $F\overline{4}3m$. Fractional atomic coordinates and equivalent isotropic displacement parameters $U_{\rm iso}$ (Å²) for Ba₃Tm₂Zn₅O₁₁. $U_{\rm iso}$ is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor. Values in parentheses indicate $\pm 1 \sigma$.

T = 230 K $a = a$	b = c = 13.4	$wR_2 = 0.0629$		
Atom (Wyckoff site)	x	у	z	$U_{\rm iso}$
Tm1 (16e)	0.6633(1)	0.6633(1)	0.6633(1)	0.014(1)
Ba1 (24f)	0.5000	0.5000	0.7950(1)	0.018(1)
Zn1 (16e)	0.4167(1)	0.5833(1)	0.5833(1)	0.015(1)
Zn2 (24g)	0.4167(2)	0.7500	0.7500	0.016(1)
O1 (4a)	0.5000	0.5000	1.0000	0.014(3)
O2 (4b)	0.5000	0.5000	0.5000	0.019(4)
O3 (16e)	0.3448(7)	0.6552(7)	0.8448(7)	0.009(2)
O4 (16e)	0.8314(9)	0.6686(9)	0.6686(9)	0.022(2)
O5 (48h)	0.4985(9)	0.6668(5)	0.6668(5)	0.017(2)

E. Magnetic and thermodynamic characterization

Magnetic measurements were carried out on an oriented Ba₃Tm₂Zn₅O₁₁ single crystal specimen. Magnetic susceptibility was measured in the presence of an external magnetic field of H = 1 T along **H** || [111]. The measurement was performed from 300 K to 2 K under ZFC (zero-field cooling) and FC (field cooling) conditions. Figure 5(a) shows the temperature-dependent magnetic susceptibility χ with **H** [111] under ZFC protocol. No splitting was observed between the ZFC and FC data, and the results are consistent with measurements on the powder sample, indicating no directional anisotropy. Low magnetic field (e.g., 0.01 T) χ measurements were also carried out. Although these measurements showed small fluctuations in the general trend of $\chi(T)$ on the order of less than 1%, no FC-ZFC splitting was observed. The inverse magnetic susceptibility was fitted using the Curie-Weiss (CW) law: $1/\chi = (T - \theta_{\rm CW})/C$; where C is the Curie constant and $\theta_{\rm CW}$ is the Curie-Weiss temperature. The effective moment $\mu_{\rm eff}$ can be calculated from the Curie constant by $\mu_{\rm eff} =$ $\sqrt{3k_{\rm B}C/N_A}$, where N_A is Avogadro's number. The Landé g factor can be determined from $C = ng^2 \mu_B^2 J (J+1)/3k_B$, where n is the number of free spins per formula unit. The CW fit was performed in the high-temperature range (90-300 K) regime where $1/\chi$ follows a linear temperature dependence and yielded C = 6.96 emu K mol⁻¹Oe⁻¹ and $\theta_{CW} = -26.3$ K.

This (negative) θ_{CW} parameter should not be viewed as a sole measure of "antiferromagnetic" interactions in this

TABLE II. Selected bond distances (Å) and bond angles (°) of $Ba_3Tm_2Zn_5O_{11}$ obtained from the refined single crystal x-ray diffraction data collected at 230 K. Values in parentheses indicate $\pm 1 \sigma$.

Tm-Tm (small tetrahedron)	3.3113(14)
Tm-Tm (large tetrahedron)	6.2325(15)
Breathing ratio d/d'	1.8822(9)
Tm-O4 bond length	2.272(13)
Tm-O5 bond length	2.225(13)
O5-Tm-O5 bond angles	92.3(3)
O5-Tm-O4 bond angles	86.3(5)

compound since the $1/\chi = 0$ temperature intercept reflects some combination of the crystal electric field (CEF) levels and the Tm³⁺-Tm³⁺ exchange and magnetic dipolar interactions [53]. The calculated effective moment $\mu_{\rm eff}$ of 7.46 $\mu_{\rm B}$ and g =1.151 agrees well with the theoretical value of $\mu_{eff} = 7.55 \,\mu_B$ and $g = \frac{7}{6}$ for free Tm³⁺ (L = 5, S = 1, J = 6) ion at ambient temperature. As the temperature decreases, the higher energy CEF energy levels depopulate, reducing the effective moment and hence changing the slope of $1/\chi$. Near $T \approx 45$ K, a shoulder-like feature emerges in $\chi(T)$ as the Tm³⁺ ion enters its CEF ground state. As we will see below from the inelastic neutron scattering analysis, the CEF ground state is a singlet and this plateauing of the susceptibility at low-temperature is the van Vleck component of χ . However, a slight upturn in χ at temperatures below 20 K cannot be explained by the van Vleck component, and its origin is unknown. We have investigated whether this up-turn could be caused by parasitic paramagnetic phases or dilute impurities, but we found no evidence that would confirm such a scenario. Finally, the lack of a sharp feature in the susceptibility data of Ba₃Tm₂Zn₅O₁₁ indicates an absence of long-range ordering down to 2 K while the indistinguishable FC and ZFC susceptibility further suggests a lack of spin glass freezing, also above 2 K.

The isothermal magnetization M(H) measurements were performed at selected temperatures (T = 2 K, 5 K, and 50 K) as shown in Fig. 5(b). The magnetic field was ramped up and down to 14 Tesla with no hysteresis observed in the field sweeps. At both low and high fields, M(H) shows a linear trend, consistent with the van Vleck paramagnetism of a CEF ground state singlet. This linear trend steepens up going from 50 K to 5 K and 2 K, indicating a paramagnetic behavior.

The right axis of Fig. 5(b) shows the integrated frequency response of TDO measured at 0.02 K up to 18 Tesla. The integrated frequency response is proportional to the magnetization and shows a linear behavior, similar to the 2 K magnetization data, suggesting no anomalous behavior or phase transition down to 0.02 K.

Figure 5(c) shows the temperature dependence of the total heat capacity of Ba₃Tm₂Zn₅O₁₁ single crystal in a magnetic field $\mathbf{H} \perp$ [111]. The heat capacity shows no sharp anomalies down to 100 mK, again indicating the absence of any phase transition. Upon applying a field up to 8 T, minimal changes are observed in the heat capacity as function of temperature [see inset of Fig. 5(c), which focuses on the low temperature regime]. Additionally, no differences were observed between the powder and single crystal measurements. Interestingly, the low-temperature heat capacity does not follow the expected Debye like phonon contribution $\propto T^3$ as fits to such a form proved unsuccessful with no temperature windows yielding a good fit (see Appendix E for details). On the other hand, the low-temperature heat capacity of Ba3Lu2Zn5O11 can be modeled well by a Debye like form, suggesting the presence of other additional nonphonon contributions to the heat capacity of $Ba_3Tm_2Zn_5O_{11}$.

F. Inelastic neutron scattering

Inelastic neutron scattering (INS) was used to probe the crystal electric field (CEF) levels of Ba₃Tm₂Zn₅O₁₁. The CEF levels originate from the splitting of Hund's ground state



FIG. 5. (a) Temperature dependence of susceptibility $\chi(T)$ and inverse susceptibility $1/\chi(T)$, measured at 1 T, revealing no significant difference between ZFC and FC down to 2 K. The dashed-red line is the Curie-Weiss fit. Note that $1 \text{ emu}/(\text{mol Oe}) = 4\pi \times 10^{-6} \text{ m}^3/\text{mol}$. (b) Isothermal magnetization M(H) curves at 2 K, 5 K, and 50 K. The inset illustrates the zoomed-in low-field magnetization, exhibiting no hysteresis during field ramping. The black linear guidelines are included to highlight the linear response. The right axis shows the TDO measurement (solid red curve overlapping the 2 K and 5 K magnetization data) taken at 0.02 K, where Δf is integrated with respect to the field. This integrated curve is proportional to the magnetization and has been scaled to match the M(H) data collected at 2 K. The similarity in trends between the TDO measurement and the M(H) data at 2 K indicates no anomalous behavior or phase transitions down to 0.02 K. (c) Temperature-dependent total heat capacity of Ba₃Tm₂Zn₅O₁₁ single crystal with applied magnetic field **H** perpendicular to [111] direction, down to 100 mK. Minimal alterations are observed in the heat capacity trace at 8 T, and the inset focuses on intermediate fields in the low-temperature regimes. The lack of any sharp anomaly in heat capacity indicates the absence of phase transitions.

due to the crystal environment around the magnetic ion. The Tm^{3+} ion in Ba₃Tm₂Zn₅O₁₁ reside at a site with C_{3v} point group symmetry whose local crystal environment splits the Tm^{3+} ion's ${}^{3}H_{6}$ 13 degenerate states into five singlets and four doublets. The effect of this crystalline electric field can be modelled by the single-ion CEF Hamiltonian H_{CEF} acting within the ${}^{3}H_{6}$ manifold

$$H_{\text{CEF}} = B_{20}O_{20} + B_{40}O_{40} + B_{43}O_{43} + B_{60}O_{60} + B_{63}O_{63} + B_{66}O_{66}, \qquad (2)$$

where the O_{lm} are the Stevens operators [47,54,55] and the B_{lm} are parameters characterizing the crystal field potential within the set of J = 6 states.

In Fig. 6, the top three panels show a representative INS spectrum sets collected using an incident neutron energy of $E_i = 50 \text{ meV}$ at temperatures of 6 K, 50 K, and 150 K. As shown in the bottom panels, we observed two distinct transitions at 9.4 meV and 15.4 meV, as well as low-intensity transitions centered at 25 meV and 31.4 meV [see inset of lower panel of Fig. 6(a)], whose intensities are less than 1% of



FIG. 6. Inelastic neutron scattering measurements and CEF model fits for polycrystalline Ba₃Tm₂Zn₅O₁₁. [(a)–(c), top] ΔE vs |*Q*| slices at temperatures of 6 K, 50 K, and 150 K, respectively, with incident energy $E_i = 50$ meV. The spectrum from Ba₃Lu₂Zn₅O₁₁ has been subtracted to remove the nonmagnetic background. Two prominent CEF bands located at 9.47 and 15.45 meV, alongside lower-intensity bands centered at 25 and 31.4 meV are visible. [(a)–(c), bottom) Constant-*Q* cuts with an integration window of 3–4 Å⁻¹ with overlayed CEF fits derived from the most optimal solution discussed in the main text. The insets in the bottom panels of (a) and (b) show the zoomed-in line cuts at higher energy, while the inset in the bottom panel of (c) shows the fit to the isothermal powder magnetization at 10 K.

TABLE III. Energy levels and their associated eigenvectors for the single-ion CEF Hamiltonian, obtained by fitting the Ba₃Tm₂Zn₅O₁₁ INS data. The wavefunctions are represented in the $|m_J\rangle$ basis. The energies are labeled as singlets (S) or doublets (D) in brackets next to the corresponding energy level.

E (meV)	$ -6\rangle$	-5>	$ -4\rangle$	-3>	$ -2\rangle$	$ -1\rangle$	$ 0\rangle$	$ 1\rangle$	2>	3>	4>	5>	6>
0.000 (S)	-0.4726	0.0	0.0	-0.526	0.0	0.0	0.0	0.0	0.0	-0.526	0.0	0.0	0.4726
9.467 (S)	0.6472	0.0	0.0	0.2399	0.0	0.0	0.2169	0.0	0.0	-0.2399	0.0	0.0	0.6472
15.450 (D)	0.0	0.0	0.5661	0.0	0.0	-0.1319	0.0	0.0	0.7455	0.0	0.0	-0.3262	0.0
15.450 (D)	0.0	-0.3262	0.0	0.0	-0.7455	0.0	0.0	-0.1319	0.0	0.0	-0.5661	0.0	0.0
25.052 (D)	0.0	0.5168	0.0	0.0	-0.2014	0.0	0.0	0.8026	0.0	0.0	-0.2196	0.0	0.0
25.052 (D)	0.0	0.0	0.2196	0.0	0.0	0.8026	0.0	0.0	0.2014	0.0	0.0	0.5168	0.0
31.012 (S)	0.0336	0.0	0.0	0.314	0.0	0.0	-0.8947	0.0	0.0	-0.314	0.0	0.0	0.0336
31.037 (S)	-0.526	0.0	0.0	0.4726	0.0	0.0	0.0	0.0	0.0	0.4726	0.0	0.0	0.526
42.643 (D)	0.0	0.5213	0.0	0.0	0.3437	0.0	0.0	-0.4281	0.0	0.0	-0.6532	0.0	0.0
42.643 (D)	0.0	0.0	0.6532	0.0	0.0	-0.4281	0.0	0.0	-0.3437	0.0	0.0	0.5213	0.0
53.874 (D)	0.0	0.0	-0.4523	0.0	0.0	-0.3939	0.0	0.0	0.5344	0.0	0.0	0.5956	0.0
53.874 (D)	0.0	-0.5956	0.0	0.0	0.5344	0.0	0.0	0.3939	0.0	0.0	-0.4523	0.0	0.0
57.365 (S)	0.2828	0.0	0.0	-0.5864	0.0	0.0	-0.3903	0.0	0.0	0.5864	0.0	0.0	0.2828

the most intense transition. While Ba₃Lu₂Zn₅O₁₁ was used to subtract the nonmagnetic background, discerning very weak CEF levels atop the large contributions of nearby phonon excitations proved challenging because of limited momentum coverage. Therefore, experimentally, we can only reliably observe four (at 9.4, 15.4, 25, and 31.4, all in meV) of the eight possible CEF transitions out of the CEF ground state. To fit the six CEF parameters in Eq. (2) using this data, we employed the PyCrystalField software [47]. As an additional constraint, we included isothermal magnetization data in the fitting procedure, as elaborated in further detail in Appendix C. The best fit parameters were ultimately determined to be (in meV) $B_{20} = -7.83 \times 10^{-2}$, $B_{40} = -1.01 \times 10^{-3}$, $B_{43} = 1.84 \times 10^{-2}$, $B_{60} = -1.59 \times 10^{-5}$, $B_{63} = 5.24 \times 10^{-4}$, and $B_{66} = -5.42 \times 10^{-4}$. Table III lists the energy levels and the corresponding eigenvectors determined from the fit. The bottom three panels in Fig. 6 show the calculated constant-Qcuts overlaid on the experimental data. The fit reproduces reasonably well the positions and relative intensities of the four observed transitions. It also predicts additional transitions at 42.6 meV, 53.8 meV, and 57.3 meV with intensity less than 1% of the 9.4 meV transition, consistent with our inability to discern the higher energy transitions against the experimental background. The ground eigenstate of H_{CEF} is identified as a singlet, with no other CEF level (of either low or high intensity) until the first excited state at 9.4 meV. The proposed CEF scheme also fits the isothermal magnetization data very well as shown in the inset of Fig. 6(c). Furthermore, the fitted CEF parameters reproduce the weak magnetic field dependence of the 9.4 meV and 15.4 meV transitions, as shown in Fig. 11 below. Given the singlet ground state and the substantial $\approx 10 \text{ meV}$ gap to the first excited state, we should expect to observe no significant features in the INS spectrum below 10 meV. Moreover, estimating the typical scale of the $Tm^{3+}-Tm^{3+}$ interactions, H_{Tm-Tm} , to be in the range 0.01-1 meV, which is typical for insulating rare-earth oxides, we would not expect the development of long-range order since the first excited crystal field level (at 9.4 meV) is at least more than a factor 10 compared to H_{Tm-Tm} , and thus causing only a small admixing between the ground singlet and the lowest excited crystal field states. This is similar to what is seen in the $Tm_2Ti_2O_7$ pyrochlore compound [56].

With the CEF scheme established, we conducted INS experiments on high-quality coaligned single crystals of Ba₃Tm₂Zn₅O₁₁ to probe the low-energy excitations in the compound with applied magnetic field $\mathbf{H} \parallel [111]$. We show in Fig. 7 the scattering intensity as a function of energy transfer, with a path taken through the high symmetry points of $\Gamma_0 - X_1 - \Gamma_1 - X_2 - \Gamma_2 - X_3 - \Gamma_0$ for selected fields, revealing dispersionless bands at $\approx 0.8 \text{ meV}$ and $\approx 1 \text{ meV}$ at 0 T. Applying a magnetic field leads to a systematic shift in the band intensities and centers. The band intensity gradually decreases as the field is increased from 0 T to 8 T, but remains visible even at 8 T. Within the resolution of the present data, no significant field-dependent shifts in the band energies were observed; however, the intensity of this excitation band clearly changes as a function of the applied field, as shown in the line-cuts of Figs. 7(g). The origin of this INS signal is rather mysterious and we have not been able to find a compelling explanation for it.

IV. DISCUSSION

From the experimental results presented in Sec. III, the following picture of $Ba_3Tm_2Zn_5O_{11}$ emerges: The Tm^{3+} ion in Ba₃Tm₂Zn₅O₁₁ has a singlet ground state with a gap of 9.4 meV to the lowest crystal field level. This gap is significantly larger than the expected intratetrahedron exchange interactions (e.g., in Ba₃Yb₂Zn₅O₁₁ they are roughly $J \approx$ 1 meV or so [34]) and thus also the intertetrahedron exchange interactions. The singlet ground state should thus lead to a "trivial" quantum paramagnetic ground state in Ba₃Tm₂Zn₅O₁₁, a product of CEF singlets on each Tm site, with the first excitation-a kind of CEF "exciton" appearing at ≈ 10 meV. This picture, similar to what is found in the Tm₂Ti₂O₇ pyrochlore [56], appears consistent with the thermodynamic data, susceptibility and magnetization data, which do not show any evidence of low-lying excitations below the CEF gap (e.g., via a significant entropy release).



FIG. 7. Scattering intensity as a function of energy transfer for Ba₃Tm₂Zn₅O₁₁. Panels (a)–(d) display data from INS experiments conducted on high-quality, coaligned single crystals with an applied field $\mathbf{H} \parallel [111]$, measured at 100 mK, and traversing through the high-symmetry points $\Gamma_0 - X_1 - \Gamma_1 - X_2 - \Gamma_2 - X_3 - \Gamma_0$, as illustrated in cartoon (e). Notably, two dispersionless excitations identified at 0.8 meV and 1.1 meV in a 0T field exhibit decreased intensities upon application of the field. (f) The band centers for the upper and lower bands at $\mathbf{k} = \Gamma_1$ show no significant energy shifts with the applied field. (g) However, constant-*Q* cuts, after applying powder averaging, reveal significant field-induced changes in the intensities of these excitation bands, suggesting a magnetic origin. Error bars indicate $\pm 1 \sigma$.

This description of $Ba_3Tm_2Zn_5O_{11}$, however, presents an interesting puzzle: What is the excitation observed in inelastic neutron scattering data at ≈ 1 meV in Fig. 7? From the above discussion, there should be nothing magnetic from the Tm^{3+} ions near 1 meV, as it lies well below the CEF gap. The CEF analysis rules out a low-lying CEF mode, as detailed in Appendix C. This additional mode likely points to other interactions or physical phenomena that manifest not only in the INS data but also in the heat capacity, that we discussed above in Sec. III E. We briefly mention here a number of possible natural origins for this excitation:

(1) Low-lying phonon excitation. While optical phonons typically lie higher in energy than 1 meV, one might ask whether the proximity to a structural instability could result in an anomalously low-energy phonon excitation. Indeed, we have experimentally found that the BP family becomes unstable for lanthanides lighter than Tm, suggesting that $Ba_3Tm_2Zn_5O_{11}$ may sit close to an instability.

(2) *Magnetic disorder.* One possibility is that the low energy excitations at $E \approx 1 \text{ meV}$ are caused by a small fraction of Tm^{3+} sites that have a different local environment than the bulk and thus harbor a low-lying crystal field excitation in the $\approx 1 \text{ meV}$ range. Alternatively, oxygen vacancies, if present, can create a charge imbalance around the Tm^{3+} ion, potentially reducing its oxidation state to Tm^{2+} and thereby creating low-lying crystal field excitations.

(3) Atomic tunnelling. If the crystal structure of $Ba_3Tm_2Zn_5O_{11}$ has two nearby local minima in the location of one of the atoms, quantum tunneling could result in a superposition of states and an associated tunnel splitting [57–60]. This excitation would be beyond the phonon picture

of lattice dynamics and could potentially be observable in inelastic neutron scattering [52].

(4) Spin-lattice coupling. Significant coupling of the Tm^{3+} CEF excitations to a lattice vibration could result in a change of character of those excitations and lead to new (and potentially low-lying) excitations.

We now briefly discuss each of these possibilities in order.

Low-lying phonon excitation. In order to rule out phonons as the identity of the low-energy modes in the range 0.8-1 meV, we computed the expected phonon dispersion from first principles calculations. Full details of these calculations are presented in Appendix F. In Fig. 8, we show the computed phonon dispersions. We find that the $F\bar{4}3m$ structure is energetically stable and that there are no anomalous low-energy phonons that could explain the nearly dispersionless modes appearing in the inelastic neutron scattering data. We estimate that the lowest optical phonon at the Γ points occurs at 2.5 meV, but that it is sufficiently dispersive to reach 5.7 meV at the X points. Similarly, the lowest acoustic branch reaches the same energy of 5.7 meV at the X points. Considering these calculations, we conclude that the dispersionless excitations detected in the 0.8 meV to 1 meV range are unlikely to be of phononic origin.

Magnetic disorder. To rule out any magnetic disorder, such as potential site mixing where Tm^{3+} might occupy a different atomic site or oxygen vacancies that could change the oxidation state to Tm^{2+} and thus experience a different crystal field around it, which could result in a 1 meV band, we further analyzed the powder neutron diffraction data shown in Fig. 2. We specifically investigated scenarios where the Tm^{3+} ion could be situated at other sites. We found that substituting



FIG. 8. Computed phonon dispersions for $Ba_3Tm_2Zn_5O_{11}$, showing absence of low-energy dispersionless modes (kpath as suggested in SeeK-path [66,67]). (Inset) Phonon dispersion along the *k*-path plotted in Fig. 7.

the Tm³⁺ ion at another site results in an occupancy close to 0% with no improvement in fitting quality. Additionally, we did not find any evidence of oxygen vacancy as the refined occupancy stayed close to 1. It therefore seems unlikely that the 1 meV band originates from a fraction of Tm³⁺ ions occupying a different local CEF environment or from the presence of Tm^{2+} ions. Another possibility could be the presence of a magnetic impurity phase in the single crystal sample that produces these excitations. However, in a powder inelastic scattering experiment conducted at the SEQUOIA spectrometer on a different powder sample (see Appendix D), we observed the same $\sim 1 \text{ meV}$ excitation band. We found through powder diffraction data analysis the powder sample to contain less than 1% magnetic impurity phase. Such a small amount would make it essentially impossible to detect such a small quantity in our INS measurements. Thus, this magnetic disorder scenario also appears unlikely.

Atomic tunnelling. In scenarios typically associated with atomic tunneling, atoms exhibit transitions between two nearby position configurations [57–60], which can manifest as anomalously large atomic displacement parameters [52]. In our study of Ba₃Tm₂Zn₅O₁₁, such anomalies were not observed. Specifically, single-crystal x-ray diffraction data collected at 230 K indicates that the isotropic displacement parameters (U_{iso}) for all atoms are of the order of 10^{-2} Å², as documented in Table I. This smallness in the displacement parameters suggests no significant deviations from the expected atomic positions.

To further investigate the possibility of atomic tunneling, we utilized neutron pair distribution function (PDF) analysis on powder samples, as detailed in Sec. III B. Neutron scattering is particularly sensitive to oxygen, thus providing complementary insights to the x-ray analysis. The PDF analysis, conducted across temperatures from 100 K to 2 K, affirmed that the average structure, corresponding to the space group $F\bar{4}3m$, accurately reflects the experimental data (see Fig. 3). This agreement between the local and average structures indicates that atomic tunneling is unlikely. Details concerning the behavior of atomic displacement parameters across the temperature range are further discussed in Sec. III B. The parameters we determined align with typical thermal behaviors, showing no evidence for the disorder or anomalies typically indicative of tunneling phenomena.

Spin-lattice coupling. Although phonons and crystal electric field (CEF) excitations are often considered decoupled [61], strong magnetoelastic coupling between the lattice and the orbital degrees of freedom can in principle bridge these excitations [62-65]. Two primary conditions facilitate this coupling [63,64]: (1) The presence of a phonon mode in the proximity of a CEF excitation, and (2) coupling between the phonon and CEF modes being allowed by symmetry. If these conditions are satisfied, magnetoelastic interactions can result in the mixing of phonon and CEF modes, leading to the formation of a new type of excitation known as a vibronic mode. In the case of $Ba_3Tm_2Zn_5O_{11}$, the lowest CEF excited state is located at approximately 10 meV. Given that the observed low-energy mode is around 1 meV (see Fig. 7), a very large magnetoelastic coupling would be required to reduce the gap by 9 meV and bring either excitation within the observed 1 meV range. Therefore, the possibility of such significant magnetoelastic coupling in Ba3Tm2Zn5O11 appears rather unlikely.

V. CONCLUSIONS

In conclusion, we have successfully synthesized Ba₃Tm₂Zn₅O₁₁, a novel magnetic material within the rare-earth-based breathing pyrochlore family, and grown high-quality single crystals of this compound using the traveling-solvent-floating-zone technique. Investigation into its magnetic and heat capacity properties revealed the absence of long-range magnetic ordering down to 0.05 K. Neutron scattering techniques were employed to characterize the crystal electric field levels, unveiling two additional magnetic bands at 0.8 and 1 meV despite the presence of singlet CEF ground state and 9.4 meV gap to the first excited CEF state. The absence of low-energy dispersionless modes in computed phonon dispersions excludes phonons as the identity of the observed excitations. These findings provide valuable insights into the structural, magnetic, and vibrational properties of Ba₃Tm₂Zn₅O₁₁, contributing to understanding its puzzling behavior at the atomic and electronic levels and paving the way for further studies.

ACKNOWLEDGMENTS

Work performed at Duke University is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award No. DE-SC0023405. R.B. acknowledges the support provided by Fritz London Endowed Post-doctoral Research Fellowship. The research at the University of Windsor (J.G.R) and the University of Waterloo (M.J.P.G.) was funded by the NSERC of Canada (M.J.P.G, J.G.R) and the Canada Research Chair Program (M.J.P.G, Tier I). A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-2128556 and the State of Florida. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work. The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.

APPENDIX A: MELTING BEHAVIOR

To understand the melting behavior of the $Ba_3Tm_2Zn_5O_{11}$ compound, simultaneous differential scanning calorimetry and thermogravimetric analysis were performed on a $Ba_3Tm_2Zn_5O_{11}$ powder sample. The sample was contained in an alumina crucible, and another alumina crucible was used as the reference while N₂ gas was used as the method gas. The samples were heated up to 1380 °C with a heating rate 10 °C/min. In Fig. 9, the percentage heat flow change and the change of $Ba_3Tm_2Zn_5O_{11}$ sample weight are shown in a comparison with the $Ba_3Yb_2Zn_5O_{11}$ sample. Note that



FIG. 9. The percentage of heat flow and weight loss of $Ba_3Yb_2Zn_5O_{11}$ (blue) and $Ba_3Tm_2Zn_5O_{11}$ (red) with respect to temperature while heating the sample up to 1380 °C in TGA. The sharp endothermic dip around 1210 °C is the region where melting event occurs. Melting in $Ba_3Yb_2Zn_5O_{11}$ is not accompanied by significant weight loss whereas in $Ba_3Tm_2Zn_5O_{11}$, weight reduces drastically suggesting $Ba_3Tm_2Zn_5O_{11}$ melts incongruently.

the synthesis of the Ba₃Yb₂Zn₅O₁₁ sample has been previously reported in Ref. [37]. It is found that Ba₃Yb₂Zn₅O₁₁ shows a sharp endothermic dip in heat flow at $T \approx 1220$ °C with no significant weight loss, which is a sign of melting as the phase transition from solid to liquid happens over a narrow temperature range. In contrast, Ba₃Tm₂Zn₅O₁₁ shows a broader endothermic dip in heat flow at $T \approx 1200$ °C with significant weight loss, indicating decomposition over a wider temperature range. Thus the behavior of heat flow and weight loss suggests that the melting behavior of Ba₃Tm₂Zn₅O₁₁ is different (i.e., incongruent in nature) compared to that of Ba₃Yb₂Zn₅O₁₁, which melts congruently.

To further validate our conclusion, PXRD data were collected on both $Ba_3Yb_2Zn_5O_{11}$ and $Ba_3Tm_2Zn_5O_{11}$ melted samples left after the TGA/DSC experiment. The PXRD analysis confirms that the $Ba_3Yb_2Zn_5O_{11}$ is chemically stable after melting and this agrees with our previous crystal growth report [37]. In contrast, the $Ba_3Tm_2Zn_5O_{11}$ decomposes into three different solid (S) and one liquid (L) phases,

$$13 Ba_{3}Tm_{2}Zn_{5}O_{11}(S)
\longrightarrow 3 Ba_{5}Tm_{8}Zn_{4}O_{21}(S) + Ba_{2}Tm_{2}Zn_{8}O_{13}(S)
+ 22 BaZnO_{2}(L) + 23 ZnO(S).$$
(A1)

This incongruent melting behavior of $Ba_3Tm_2Zn_5O_{11}$ poses a significant hurdle in growing single crystals as it cannot be achieved by using the simple floating-zone (FZ) technique similar that used to grow single crystals of the $Ba_3Yb_2Zn_5O_{11}$ compound [37]. To tackle this difficulty, a traveling-solvent-floating-zone (TSFZ) technique was used to grow large and high-quality single crystals of the $Ba_3Tm_2Zn_5O_{11}$ compound, with the detailed growth process discussed in Sec. II of the main text.

APPENDIX B: GROWTH PREPARATION

As described in Eq. (A1), BaZnO₂ is one of the products of the decomposition, and it is the only liquid in the decomposition above 1200 °C, which is used as a solvent/flux in the TSFZ growth process of Ba₃Tm₂Zn₅O₁₁. The BaZnO₂ powder was separately synthesized via a solid-state reaction route using BaCO₃ and ZnO as starting precursors. The wellground mixture was first sintered at 970 °C for 16 hours under an Ar atmosphere with the ground mixture then resintered at 1000 °C for 48 hours under N₂ flow. It was found that BaZnO₂ is not stable below a temperature of 525 °C as it decomposes into BaO2 and ZnO. To avoid decomposition, the sintered pellet of the BaZnO₂ sample was rapidly cooled down to room temperature from 1000 °C, resulting in a pure phase of BaZnO₂. In order to prepare a ceramic rod of Ba₃Tm₂Zn₅O₁₁ for single crystal growth, the pure Ba₃Tm₂Zn₅O₁₁ powder was compressed into cylindrical-shaped feed and seed rods using a hydrostatic pressure of approximately 700 bar. These cylindrical feed rods typically weighed between 9 to 12 grams and measured about 8 to 11 cm in length. These rods were sintered at 1130 °C for 24 hours under an oxygen environment in a vertical tube furnace (Crystal System Corporation) to achieve higher density. The details of the crystal growth parameters are tabulated in Table IV. The initial attempt (Growth No. 1), conducted without a solvent disk, resulted

Growth no.	O ₂ Pressure (MPa)	Rotation speed (rpm)	Feed speed (mm/h)	Growth speed (mm/h)	Shutter length (mm)	Solvent	Lamp power	Results
1	0.3-0.6	9-10	1-2.5	1.2 - 2	65-70	No flux	2-5%	Decomposed products
2	0.3-0.6	9-10	5-15	5-15	65 - 70	BaZnO ₂	2-5%	$Ba_3Tm_2Zn_5O_{11}$ in the crystal's shell
3	0.6	9-10	1 - 2.5	1.2 - 2	65 - 70	BaZnO ₂	0.10%	Ba ₃ Tm ₂ Zn ₅ O ₁₁ prominent but no crystal
4	0.6	9-10	1.8 - 1.9	1.0	70	$BaZnO_2$	0.10%	Largest grain size: 0.13 gm
5	0.95	14-15	1.15-2.19	1.15	70	$BaZnO_2$	0.10%	Largest grain size: 0.2 gm
6 a	0.95	20	4.5-3.3	1.5	70	$BaZnO_2$	0.10%	Crystallized feed rod for 6 b
6 b	0.95	15-18	0.55 - 0.75	0.4	70	$BaZnO_2$	0.10%	Largest grain size: 0.33 gm

TABLE IV. Experimental details of $Ba_3Tm_2Zn_5O_{11}$ crystal growth using optical floating zone technique.

in a crystal with impurity phases from the decomposition of Ba₃Tm₂Zn₅O₁₁, although traces of the Ba₃Tm₂Zn₅O₁₁ BP phase were detected on the crystal's surface. Furthermore, without using any solvent disk to sustain the liquid zone, the lamp power had to be increased to 5-6% of its maximum power, which likely contributed to decomposition. We attempted to use $BaCO_3$ or a combination of $(BaCO_3 + ZnO)$ as a flux, but the resulting grown crystal was found to exhibit the presence of the impurity phases identified in Eq. (A1). However, subsequent incorporation of a BaZnO₂ solvent disk and optimizing the shutter length to approximately 70 mm not only mitigated this issue, but also allowed for the lamp power to be substantially reduced to 0.1% of its maximum operating power. The crystal growth process was hampered by a number of challenges, such as maintaining a stable liquid zone, with growth speeds above 5 mm/hr leading to incomplete BP phase formation and speeds below 1 mm/hr causing a liquid zone instability. Furthermore, the release of trapped oxygen disrupted the growth, resulting in multiple crystalline grains instead of single crystals. To overcome these difficulties, the growth parameters were iteratively optimized in each growth, progressively enhancing crystal quality. The oxygen pressure was increased to a maximum of 0.95 MPa value in order to minimize bubbling. Ultimately, centimeterscale Ba₃Tm₂Zn₅O₁₁ single crystals were obtained using the "two-scanning" method discussed in Sec. II C of in the main text.

APPENDIX C: CEF ANALYSIS

In our study, we used the PyCrystalField [47] package to analyze the inelastic neutron scattering data at zero field (0 T) and determine the crystal electric field (CEF) B_{lm} parameters of Eq. (2). For simulating the field dependence of the CEF levels, we employed the MCPhase [48] package. We designed a custom cost function to account for the challenges in fitting the experimental data, including the presence of weak bands and the uncertainty caused by the unobserved bands. Our cost function included multiple contributions, such as the two-dimensional Q- and δE -dependent spectrum, background penalties for any excitation with intensity more than the background in areas where we did not see any energy band, integrated peak intensities to account for multiple energy levels within the observed peak width, powder magnetization and eigenvalue penalties to ensure the presence of eigenvalues at the positions of clearly observed bands.

Considering the multiple contributions to the cost function, we used adaptive weighing of the cost contributions to ensure that all sources of cost receive appropriate weight. The CEF fitting is heavily influenced by the choices of initial parameters and tends to get trapped in local minima. To solve this issue, we used various methods for the initial parameter estimation. For example, we used a point charge model to obtain the initiatial values for the B_{lm} parameters. We also tried rescaling the published CEF parameters from the sister compound Ba₃Yb₂Zn₅O₁₁ [29] using

$$B_{lm} = \frac{\theta^{(l)} \langle r^l \rangle}{\theta_0^{(l)} \langle r^l \rangle_0} \left(\frac{a}{a_0}\right)^{-l+1} B_{lm}^0 \tag{C1}$$

as discussed for other systems [30,68]. In addition, we also used logarithmic random sampling to sample values for initial parameters as the B_{lm} parameters can span a wide range of magnitudes. This strategy helped us explore a wide range of parameter space and reduced the risk of being trapped in local minima during the optimization process. In all, we explored about 100,000 random starting parameters using a computer cluster to run the program in parallel.

We present in Fig. 10 all the converged solutions obtained through various strategies. The y axis displays the error χ^2 on a logarithmic scale, while the x axis shows the values of the B_{lm} parameters. The optimal solution is highlighted by a red star while other converged solutions are shown as circular markers. We observed that solutions predicting low-lying energy levels between 0 and 8 meV exhibited significantly higher experimental disagreement, as indicated by the large χ^2 error, which is represented by the gray circular markers. Thus, our CEF analysis indicates that the crystal field ground state is a singlet with no intermediate CEF level between the ground state and the first excited state at 9.47 meV. The complete list of the 13 CEF energy levels calculated using the best fit B_{lm} parameters (all in meV) are as follows: 9.47, 15.45, 15.45, 25.05, 25.05, 31.01, 31.04, 42.64, 42.64, 53.87, 53.87, 57.36. Finally, we present the field dependence of the CEF excitations measured at the disk chopper spectrometer (DCS, NIST). Figure 11 shows the evolution of the 9.47 meV and 15.45 meV band as the field is applied up to 9 T. The CEF model fit is shown by the solid colored lines and agrees with the observed trend.



FIG. 10. The fitted crystal field parameters vs χ^2 error obtained through various strategies are depicted. The red star data point represents the best parameter, while all other circular markers denote other converged solutions. Note that solutions predicting an intermediate CEF level between 0 and 8 meV, shown by gray color, exhibited significantly larger χ^2 errors.



FIG. 11. The magnetic field dependence of CEF levels at 0.1 K. Constant-Q cuts have been derived from ΔE vs |Q| slices by integrating within the window of 1.8–4 Å⁻¹. The scatter points represent the experimental data, and the solid line represents the fit. The curves have been shifted along the y axis for better clarity. Error bars indicate $\pm 1 \sigma$.

APPENDIX D: LOW-ENERGY POWDER INS DATA

In the main results sections, we reported an anomalous energy mode at approximately 1 meV, observed in the single crystal INS experiment conducted at the CNCS spectrometer. This mode is also present in the powder INS data collected at the SEQUOIA spectrometer during our investigation of the CEF levels. In addition to the incident neutron energy, E_i , mentioned in the Methods section, we used a lower E_i of 8 meV, which provided sufficient resolution to resolve the 1 meV band. As shown in Fig. 12, the 1-meV mode is clearly visible in the powder data as well. This consistency rules out the possibility that the band observed in the single-crystal INS data arises from scattering caused by superglue, magnets, or other nonsamplerelated sources.

APPENDIX E: HEAT CAPACITY PHONONIC CONTRIBUTION

We attempted to extract the phononic contribution in the total heat capacity C_p of Ba₃Tm₂Zn₅O₁₁ by subtracting the heat capacity of the nonmagnetic analog Ba₃Lu₂Zn₅O₁₁. However,



FIG. 12. Powder INS data collected at the SEQUOIA spectrometer with $E_i = 8 \text{ meV}$ at 6 K, highlighting the anomalous 1 meV energy mode.

because of the larger heat capacity of Ba₃Lu₂Zn₅O₁₁ below \approx 18 K, the subtraction was unsuccessful. As a result, we fitted the low-temperature heat capacity data using the βT^3 term, where β is a proportionality constant. We explored various fitting windows between 2 K to 15 K, as illustrated in Fig. 13. However, we could not find any temperature window between 2 K to 15 K where the fit does not overestimate the total heat capacity at the lower temperature. Additionally, incorporating a linear αT term did not improve the fit. In contrast, nonmagnetic Ba₃Lu₂Zn₅O₁₁ total heat capacity can easily be fitted by the βT^3 term for the full temperature range between 2 K to 15 K. The inability to fit a βT^3 term to Ba₃Tm₂Zn₅O₁₁ suggests that there are additional contributions to its heat capacity, possibly from magnetic excitations, which are not present in Ba₃Lu₂Zn₅O₁₁. Further, the C_p of Ba₃Tm₂Zn₅O₁₁ lacks a Schottky anomaly peak centered at 4 K that would correspond to the 1 meV excitation observed in the INS spectra.

APPENDIX F: AB INITIO PHONON CALCULATIONS

In order to rule out phonons as the origin of the lowenergy modes in the inelastic neutron scattering (INS) data in Fig. 7, we performed *ab initio* calculations using the plane wave pseudopotential density functional theory method as implemented in the Vienna *Ab Initio* Simulation Package (VASP) [69–71]. For the purpose of this calculation, we used the projector augmented wave (PAW) pseudopotential [72,73] for all the elements. The exchange-correlation potential employed was the modified Perdew-Burke-Ernzerhof generalized gradient approximation for solids (PBEsol GGA) [74]. In order to perform phonon calculations, we started with the experimental coordinates obtained for the $F\bar{4}3m$ structure and relaxed the structure without imposing a final target symmetry. We also performed relaxations starting



FIG. 13. Comparison of the total heat capacity and phononic term fitting for Ba₃Tm₂Zn₅O₁₁ and nonmagnetic Ba₃Lu₂Zn₅O₁₁ compounds. Black scatter points represent the measured heat capacity, while the lines indicate the phononic term βT^3 fitting across various temperature windows. (a) For Ba₃Tm₂Zn₅O₁₁, all such fits fail to fit the total heat capacity at the lower temperature end, irrespective of the temperature window chosen. (b) In contrast, the heat capacity of Ba₃Lu₂Zn₅O₁₁ agrees well an βT^3 term across the entire range of 2 K to 15 K.

from lower-symmetry (perturbed) structures, but found that the $F\bar{4}3m$ symmetry was restored under relaxation, confirming the stability of the $F\bar{4}3m$ structure. The energy cutoff for the plane-wave basis set and energy convergence threshold for electronic self-consistent cycle was set to 600 eV and 10^{-8} eV, respectively. The Blocked-Davidson iteration scheme was used for the electronic minimization algorithm. We used a *k*-point grid of $8 \times 8 \times 8$ for structure relaxation. For the phonon calculations, we employed the finite displacement method [75,76] in conjunction with Phonopy [77,78], with a displacement magnitude of 0.01 Å. We used a realspace supercell of $2 \times 2 \times 2$ of the primitive unit cell, and a *k*-point grid of $2 \times 2 \times 2$.

- L. Balents, Spin liquids in frustrated magnets, Nature (London) 464, 199 (2010).
- [2] J. Knolle and R. Moessner, A field guide to spin liquids, Annu. Rev. Condens. Matter Phys. 10, 451 (2019).

- [3] C. Lacroix, P. Mendels, and F. Mila, *Introduction to Frustrated Magnetism* (Springer, New York, 2011).
- [4] J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, Magnetic pyrochlore oxides, Rev. Mod. Phys. 82, 53 (2010).
- [5] A. M. Hallas, J. Gaudet, and B. D. Gaulin, Experimental insights into ground-state selection of quantum XY pyrochlores, Annu. Rev. Condens. Matter Phys. 9, 105 (2018).
- [6] J. G. Rau and M. J. P. Gingras, Frustrated quantum rare-earth pyrochlores, Annu. Rev. Condens. Matter Phys. 10, 357 (2019).
- [7] J. E. Greedan, N. P. Raju, A. Maignan, C. Simon, J. S. Pedersen, A. M. Niraimathi, E. Gmelin, and M. A. Subramanian, Frustrated pyrochlore oxides, Y₂Mn₂O₇, Ho₂Mn₂O₇ and Yb₂Mn₂O₇: Bulk magnetism and magnetic microstructure, Phys. Rev. B 54, 7189 (1996).
- [8] M. J. P. Gingras, C. V. Stager, N. P. Raju, B. D. Gaulin, and J. E. Greedan, Static critical behavior of the spin-freezing transition in the geometrically frustrated pyrochlore antiferromagnet Y₂Mo₂O₇, Phys. Rev. Lett. **78**, 947 (1997).
- [9] J. S. Gardner, B. D. Gaulin, S.-H. Lee, C. Broholm, N. P. Raju, and J. E. Greedan, Glassy statics and dynamics in the chemically ordered pyrochlore antiferromagnet Y₂Mo₂O₇, Phys. Rev. Lett. 83, 211 (1999).
- [10] H. J. Silverstein, K. Fritsch, F. Flicker, A. M. Hallas, J. S. Gardner, Y. Qiu, G. Ehlers, A. T. Savici, Z. Yamani, K. A. Ross, B. D. Gaulin, M. J. P. Gingras, J. A. M. Paddison, K. Foyevtsova, R. Valenti, F. Hawthorne, C. R. Wiebe, and H. D. Zhou, Liquidlike correlations in single-crystalline Y₂Mo₂O₇: An unconventional spin glass, Phys. Rev. B **89**, 054433 (2014).
- [11] L. Clark, G. J. Nilsen, E. Kermarrec, G. Ehlers, K. S. Knight, A. Harrison, J. P. Attfield, and B. D. Gaulin, From spin glass to quantum spin liquid ground states in molybdate pyrochlores, Phys. Rev. Lett. **113**, 117201 (2014).
- [12] Y. Onose, T. Ideue, H. Katsura, Y. Shiomi, N. Nagaosa, and Y. Tokura, Observation of the magnon Hall effect, Science 329, 297 (2010).
- [13] C. Mauws, A. M. Hallas, G. Sala, A. A. Aczel, P. M. Sarte, J. Gaudet, D. Ziat, J. A. Quilliam, J. A. Lussier, M. Bieringer, H. D. Zhou, A. Wildes, M. B. Stone, D. Abernathy, G. M. Luke, B. D. Gaulin, and C. R. Wiebe, Dipolar-octupolar Ising antiferromagnetism in Sm₂Ti₂O₇: A moment fragmentation candidate, Phys. Rev. B **98**, 100401(R) (2018).
- [14] J. Xu, V. K. Anand, A. K. Bera, M. Frontzek, D. L. Abernathy, N. Casati, K. Siemensmeyer, and B. Lake, Magnetic structure and crystal-field states of the pyrochlore antiferromagnet Nd₂Zr₂O₇, Phys. Rev. B **92**, 224430 (2015).
- [15] P. Bonville, J. A. Hodges, M. Ocio, J. P. Sanchez, P. Vulliet, S. Sosin, and D. Braithwaite, Low temperature magnetic properties of geometrically frustrated Gd₂Sn₂O₇ and Gd₂Ti₂O₇, J. Phys.: Condens. Matter 15, 7777 (2003).
- [16] K. A. Ross, L. Savary, B. D. Gaulin, and L. Balents, Quantum excitations in quantum spin ice, Phys. Rev. X 1, 021002 (2011).
- [17] S. B. Lee, S. Onoda, and L. Balents, Generic quantum spin ice, Phys. Rev. B 86, 104412 (2012).
- [18] Y.-P. Huang, G. Chen, and M. Hermele, Quantum spin ices and topological phases from dipolar-octupolar doublets on the pyrochlore lattice, Phys. Rev. Lett. **112**, 167203 (2014).
- [19] V. Tsurkan, H.-A. Krug von Nidda, J. Deisenhofer, P. Lunkenheimer, and A. Loidl, On the complexity of spinels: Magnetic, electronic, and polar ground states, Phys. Rep. 926, 1 (2021).

- [20] Y. Okamoto, G. J. Nilsen, J. P. Attfield, and Z. Hiroi, Breathing pyrochlore lattice realized in A-site ordered spinel oxides $LiGaCr_4O_8$ and $LiInCr_4O_8$, Phys. Rev. Lett. **110**, 097203 (2013).
- [21] P. Ghosh, Y. Iqbal, T. Müller, R. T. Ponnaganti, R. Thomale, R. Narayanan, J. Reuther, M. J. P. Gingras, and H. O. Jeschke, Breathing chromium spinels: A showcase for a variety of pyrochlore Heisenberg Hamiltonians, npj Quantum Mater. 4, 63 (2019).
- [22] S. Sharma, M. Pocrnic, B. N. Richtik, C. R. Wiebe, J. Beare, J. Gautreau, J. P. Clancy, J. P. C. Ruff, M. Pula, Q. Chen, S. Yoon, Y. Cai, and G. M. Luke, Synthesis and physical and magnetic properties of CuAlCr₄S₈: A Cr-based breathing pyrochlore, Phys. Rev. B **106**, 024407 (2022).
- [23] L. Savary, X. Wang, H.-Y. Kee, Y. B. Kim, Y. Yu, and G. Chen, Quantum spin ice on the breathing pyrochlore lattice, Phys. Rev. B 94, 075146 (2016).
- [24] H. Yan, O. Benton, L. D. C. Jaubert, and N. Shannon, Rank–2 U(1) spin liquid on the breathing pyrochlore lattice, Phys. Rev. Lett. 124, 127203 (2020).
- [25] K. Aoyama and H. Kawamura, Zero-field miniature skyrmion crystal and chiral domain state in breathing-kagome antiferromagnets, J. Phys. Soc. Jpn. 92, 033701 (2023).
- [26] F.-Y. Li, Y.-D. Li, Y. B. Kim, L. Balents, Y. Yu, and G. Chen, Weyl magnons in breathing pyrochlore antiferromagnets, Nat. Commun. 7, 12691 (2016).
- [27] G. Pokharel, H. S. Arachchige, T. J. Williams, A. F. May, R. S. Fishman, G. Sala, S. Calder, G. Ehlers, D. S. Parker, T. Hong, A. Wildes, D. Mandrus, J. A. Paddison, and A. D. Christianson, Cluster frustration in the breathing pyrochlore magnet LiGaCr₄S₈, Phys. Rev. Lett. **125**, 167201 (2020).
- [28] M. Gen, Y. Okamoto, M. Mori, K. Takenaka, and Y. Kohama, Magnetization process of the breathing pyrochlore magnet $CuInCr_4S_8$ in ultra-high magnetic fields up to 150 T, Phys. Rev. B **101**, 054434 (2020).
- [29] T. Haku, M. Soda, M. Sera, K. Kimura, S. Itoh, T. Yokoo, and T. Masuda, Crystal field excitations in the breathing pyrochlore antiferromagnet Ba₃Yb₂Zn₅O₁₁, J. Phys. Soc. Jpn. 85, 034721 (2016).
- [30] J. G. Rau and M. J. P. Gingras, Frustration and anisotropic exchange in ytterbium magnets with edge-shared octahedra, Phys. Rev. B 98, 054408 (2018).
- [31] N. Iwahara, Z. Huang, I. Neefjes, and L. F. Chibotaru, Multipolar exchange interaction and complex order in insulating lanthanides, Phys. Rev. B 105, 144401 (2022).
- [32] J. G. Rau, L. S. Wu, A. F. May, A. E. Taylor, I. L. Liu, J. Higgins, N. P. Butch, K. A. Ross, H. S. Nair, M. D. Lumsden, M. J. Gingras, and A. D. Christianson, Behavior of the breathing pyrochlore lattice Ba₃Yb₂Zn₅O₁₁ in applied magnetic field, J. Phys.: Condens. Matter **30**, 455801 (2018).
- [33] K. Kimura, S. Nakatsuji, and T. Kimura, Experimental realization of a quantum breathing pyrochlore antiferromagnet, Phys. Rev. B 90, 060414(R) (2014).
- [34] J. G. Rau, L. S. Wu, A. F. May, L. Poudel, B. Winn, V. O. Garlea, A. Huq, P. Whitfield, A. E. Taylor, M. D. Lumsden, M. J. P. Gingras, and A. D. Christianson, Anisotropic exchange within decoupled tetrahedra in the quantum breathing pyrochlore Ba₃Yb₂Zn₅O₁₁, Phys. Rev. Lett. **116**, 257204 (2016).
- [35] T. Haku, K. Kimura, Y. Matsumoto, M. Soda, M. Sera, D. Yu, R. Mole, T. Takeuchi, S. Nakatsuji, Y. Kono *et al.*, Low-energy

excitations and ground-state selection in the quantum breathing pyrochlore antiferromagnet $Ba_3Yb_2Zn_5O_{11}$, Phys. Rev. B **93**, 220407(R) (2016).

- [36] T. Haku, M. Soda, M. Sera, K. Kimura, J. Taylor, S. Itoh, T. Yokoo, Y. Matsumoto, D. Yu, R. A. Mole, T. Takeuchi, S. Nakatsuji, Y. Kono, T. Sakakibara, L.-J. Chang, and T. Masuda, Neutron scattering study in breathing pyrochlore antiferromagnet Ba₃Yb₂Zn₅O₁₁, J. Phys.: Conf. Ser. 828, 012018 (2017).
- [37] S. Dissanayake, Z. Shi, J. G. Rau, R. Bag, W. Steinhardt, N. P. Butch, M. Frontzek, A. Podlesnyak, D. Graf, C. Marjerrison *et al.*, Towards understanding the magnetic properties of the breathing pyrochlore compound Ba₃Yb₂Zn₅O₁₁ through single-crystal studies, npj Quantum Mater. 7, 77 (2022).
- [38] R. Bag, S. E. Dissanayake, H. Yan, Z. Shi, D. Graf, E. S. Choi, C. Marjerrison, F. Lang, T. Lancaster, Y. Qiu *et al.*, Beyond single tetrahedron physics of the breathing pyrochlore compound Ba₃Yb₂Zn₅O₁₁, Phys. Rev. B **107**, L140408 (2023).
- [39] M. V. Talanov and V. M. Talanov, Formation of breathing pyrochlore lattices: Structural, thermodynamic and crystal chemical aspects, CrystEngComm 22, 1176 (2020).
- [40] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Phys. B: Condens. Matter 192, 55 (1993).
- [41] L. Palatinus and G. Chapuis, *SUPERFLIP* a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, J. Appl. Crystallogr. 40, 786 (2007).
- [42] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, and D. J. Watkin, *CRYSTALS* version 12: Software for guided crystal structure analysis, J. Appl. Crystallogr. 36, 1487 (2003).
- [43] R. B. Clover and W. P. Wolf, Magnetic susceptibility measurements with a tunnel diode oscillator, Rev. Sci. Instrum. 41, 617 (1970).
- [44] Z. Shi, W. Steinhardt, D. Graf, P. Corboz, F. Weickert, N. Harrison, M. Jaime, C. Marjerrison, H. A. Dabkowska, F. Mila, and S. Haravifard, Emergent bound states and impurity pairs in chemically doped Shastry-Sutherland system, Nat. Commun. 10, 2439 (2019).
- [45] G. E. Granroth, A. I. Kolesnikov, T. E. Sherline, J. P. Clancy, K. A. Ross, J. P. C. Ruff, B. D. Gaulin, and S. E. Nagler, SE-QUOIA: A newly operating chopper spectrometer at the SNS, J. Phys.: Conf. Ser. 251, 012058 (2010).
- [46] R. T. Azuah, L. R. Kneller, Y. Qiu, P. L. Tregenna-Piggott, C. M. Brown, J. R. Copley, and R. M. Dimeo, Dave: A comprehensive software suite for the reduction, visualization, and analysis of low energy neutron spectroscopic data, J. Res. Natl. Inst. Stand. Technol. 114, 341 (2009).
- [47] A. Scheie, PyCrystalField: Software for calculation, analysis and fitting of crystal electric field Hamiltonians, J. Appl. Crystallogr. 54, 356 (2021).
- [48] M. Rotter, Using McPhase to calculate magnetic phase diagrams of rare earth compounds, J. Magn. Magn. Mater. 272–276, E481 (2004).
- [49] G. Ehlers, A. A. Podlesnyak, J. L. Niedziela, E. B. Iverson, and P. E. Sokol, The new cold neutron chopper spectrometer at the Spallation Neutron Source: Design and performance, Rev. Sci. Instrum. 82, 085108 (2011).
- [50] J. Neuefeind, M. Feygenson, J. Carruth, R. Hoffmann, and K. K. Chipley, The nanoscale ordered materials diffractometer NOMAD at the Spallation Neutron Source SNS, Nucl. Instrum. Methods Phys. Res., Sect. B 287, 68 (2012).

- [51] C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Božin, J. Bloch, T. Proffen, and S. J. L. Billinge, PDFfit2 and PDFgui: Computer programs for studying nanostructure in crystals, J. Phys.: Condens. Matter 19, 335219 (2007).
- [52] B. Sun, S. Niu, R. P. Hermann, J. Moon, N. Shulumba, K. Page, B. Zhao, A. S. Thind, K. Mahalingam, J. Milam-Guerrero, R. Haiges, M. Mecklenburg, B. C. Melot, Y.-D. Jho, B. M. Howe, R. Mishra, A. Alatas, B. Winn, M. E. Manley, J. Ravichandran, and A. J. Minnich, High frequency atomic tunneling yields ultralow and glass-like thermal conductivity in chalcogenide single crystals, Nat. Commun. 11, 6039 (2020).
- [53] M. J. P. Gingras, B. C. den Hertog, M. Faucher, J. S. Gardner, S. R. Dunsiger, L. J. Chang, B. D. Gaulin, N. P. Raju, and J. E. Greedan, Thermodynamic and single-ion properties of Tb³⁺ within the collective paramagnetic-spin liquid state of the frustrated pyrochlore antiferromagnet Tb₂Ti₂O₇, Phys. Rev. B 62, 6496 (2000).
- [54] M. T. Hutchings, Point-charge calculations of energy levels of magnetic ions in crystalline electric fields, Solid State Phys. 16, 227 (1964).
- [55] K. Stevens, Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions, Proc. Phys. Soc. London, Sect. A 65, 209 (1952).
- [56] M. P. Zinkin, M. J. Harris, Z. Tun, R. A. Cowley, and B. M. Wanklyn, Lifting of the ground-state degeneracy by crystal-field interactions in the pyrochlore Tm₂Ti₂O₇, J. Phys.: Condens. Matter 8, 193 (1996).
- [57] V. Narayanamurti and R. O. Pohl, Tunneling states of defects in solids, Rev. Mod. Phys. 42, 201 (1970).
- [58] T. Goto, Y. Nemoto, T. Yamaguchi, M. Akatsu, T. Yanagisawa, O. Suzuki, and H. Kitazawa, Tunneling and rattling in clathrate crystal, Phys. Rev. B 70, 184126 (2004).
- [59] W. Gou, Y. Li, J. Chi, J. H. Ross, M. Beekman, and G. S. Nolas, NMR study of slow atomic motion in Sr₈Ga₁₆Ge₃₀ clathrate, Phys. Rev. B **71**, 174307 (2005).
- [60] R. P. Hermann, V. Keppens, P. Bonville, G. S. Nolas, F. Grandjean, G. J. Long, H. M. Christen, B. C. Chakoumakos, B. C. Sales, and D. Mandrus, Direct experimental evidence for atomic tunneling of europium in crystalline Eu₈Ga₁₆Ge₃₀, Phys. Rev. Lett. **97**, 017401 (2006).
- [61] D. T. Adroja, A. del Moral, C. de la Fuente, A. Fraile, E. A. Goremychkin, J. W. Taylor, A. D. Hillier, and F. Fernandez-Alonso, Vibron Quasibound State in the noncentrosymmetric tetragonal heavy-fermion compound CeCuAl₃, Phys. Rev. Lett. 108, 216402 (2012).
- [62] M. Loewenhaupt, B. D. Rainford, and F. Steglich, Dynamic Jahn-Teller effect in a rare-earth compound: CeAl₂, Phys. Rev. Lett. 42, 1709 (1979).
- [63] P. Thalmeier and P. Fulde, Bound state between a crystal-field excitation and a phonon in CeAl₂, Phys. Rev. Lett. 49, 1588 (1982).
- [64] P. Thalmeier, Theory of the bound state between phonons and a CEF excitation in CeAl₂, J. Phys. C **17**, 4153 (1984).
- [65] C.-K. Loong, M. Loewenhaupt, J. C. Nipko, M. Braden, and L. A. Boatner, Dynamic coupling of crystal-field and phonon states in YbPO₄, Phys. Rev. B 60, R12549(R) (1999).
- [66] Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, and I. Tanaka, Band structure diagram paths based on crystallography, Comput. Mater. Sci. 128, 140 (2017).

- [67] A. Togo, K. Shinohara, and I. Tanaka, Spglib: A software library for crystal symmetry search, Sci. Technol. Adv. Mater. Methods 4, 2384822 (2024).
- [68] A. Bertin, Y. Chapuis, P. D. De Réotier, and A. Yaouanc, Crystal electric field in the R₂Ti₂O₇ pyrochlore compounds, J. Phys.: Condens. Matter 24, 256003 (2012).
- [69] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, Phys. Rev. B 54, 11169 (1996).
- [70] G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6, 15 (1996).
- [71] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for liquid metals, *Phys. Rev. B* 47, 558 (1993).
- [72] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59, 1758 (1999).

- [73] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50, 17953 (1994).
- [74] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, Phys. Rev. Lett. **100**, 136406 (2008).
- [75] G. Kresse, J. Furthmüller, and J. Hafner, *Ab initio* force constant approach to phonon dispersion relations of diamond and graphite, Europhys. Lett. **32**, 729 (1995).
- [76] K. Parlinski, Z. Q. Li, and Y. Kawazoe, First-principles determination of the soft mode in cubic ZrO₂, Phys. Rev. Lett. 78, 4063 (1997).
- [77] A. Togo, L. Chaput, T. Tadano, and I. Tanaka, Implementation strategies in Phonopy and Phono3py, J. Phys.: Condens. Matter 35, 353001 (2023).
- [78] A. Togo, First-principles phonon calculations with Phonopy and Phono3py, J. Phys. Soc. Jpn. 92, 012001 (2023).