Anisotropic Exchange within Decoupled Tetrahedra in the Quantum Breathing Pyrochlore $Ba_3Yb_2Zn_5O_{11}$

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The low energy spin excitation spectrum of the breathing pyrochlore $Ba_3Yb_2Zn_5O_{11}$ has been investigated with inelastic neutron scattering. Several nearly resolution limited modes with no observable dispersion are observed at 250 mK while, at elevated temperatures, transitions between excited levels become visible. To gain deeper insight, a theoretical model of isolated Yb^{3+} tetrahedra parametrized by four anisotropic exchange constants is constructed. The model reproduces the inelastic neutron scattering data, specific heat, and magnetic susceptibility with high fidelity. The fitted exchange parameters reveal a Heisenberg antiferromagnet with a very large Dzyaloshinskii-Moriya interaction. Using this model, we predict the appearance of an unusual octupolar paramagnet at low temperatures and speculate on the development of intertetrahedron correlations.

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Frustrated or competing interactions have been repeatedly found to be at the root of many unusual phenomena in condensed matter physics [1–5]. By destabilizing conventional long-range order down to low temperature, frustration in magnetic systems can lead to many exotic phases, from unconventional multipolar [6,7] and valence bond solid orders [1,4] to disordered phases such as classical and quantum spin liquids [1,4]. Recently, magnets frustrated not by geometry but by competing interactions have become prominent for the novel behaviors that they host. Such competing interactions might be additional isotropic exchanges acting beyond nearest neighbors [8–10], biquadratic, or other multipolar interactions [11]. One possibility attracting increasing interest is that competing strongly *anisotropic* interactions may stabilize a wide range of unusual phenomena.

An exciting research direction in this context concerns itself with so-called quantum spin ice [12]. This quantum spin liquid can be stabilized by perturbing classical spin ice with additional anisotropic transverse exchange interactions that induce quantum fluctuations. Particularly interesting is the potential realization of such physics in the rare-earth pyrochlores $R_2M_2O_7$ [13–15], which can be described in terms of pseudo-spin-1/2 degrees of freedom interacting via anisotropic exchanges [12,15,16]. These materials display a wealth of interesting phenomena, from the possibility of quantum [17–19] order-by-disorder physics in $Er_2Ti_2O_7$ [20] and unconventional ordered states [21,22], as well as several candidates for quantum spin liquids [23,24]. In many of these compounds, the physics is delicate, showing strong sample to sample variations [25] or sensitivity to very small amounts of disorder [26,27]. Consequently, an accurate determination of the effective model is crucial in making definite progress in this area.

Given the critical importance played by the precise value of the anisotropic exchanges, a number of experiments have aimed at determining those couplings [15,17]. There is, unfortunately, significant difficulty in obtaining accurate values for these couplings stemming from two key

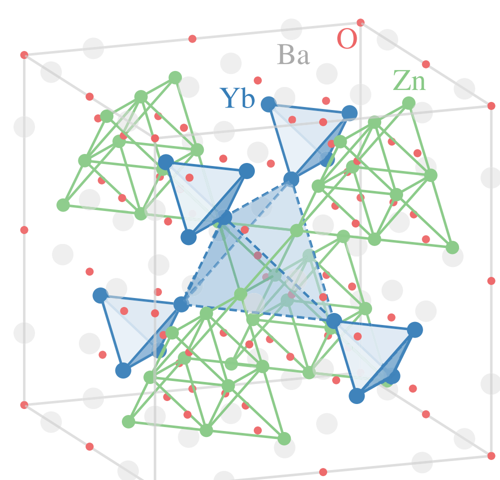

FIG. 1. Crystal structure of $Ba_3Yb_2Zn_5O_{11}$. Each Yb^{3+} ion is part of a large and small tetrahedron in the breathing pyrochlore lattice.

limitations. First, only approximate methods are available to relate the model to experiments, restricting comparisons to regimes where the theory becomes controlled, such as in a high magnetic field [15,17,28] or at high temperature [28–31]. Second, to avoid overfitting the experimental data, one must work with a reasonable number of fitting parameters—for example, restricting to a subset of the allowed interactions by ignoring interactions beyond nearest neighbors or possible multispin interactions [20]. Even in $Yb_2Ti_2O_7$, where the latter concern is largely absent, there currently remains no consensus on the values of the anisotropic exchange parameters [15,32]. At the present time, a reference rare-earth pyrochlorelike compound with solely bilinear anisotropic interactions and for which essentially exact methods can be employed to compare with experimental data is badly needed to cement the validity of the effective spin-1/2 description of such materials.

In this Letter, we study $Ba_3Yb_2Zn_5O_{11}$ (BYZO), a so-called breathing pyrochlore (BP) compound [33,34], which provides an ideal platform for understanding anisotropic exchange models. As shown in Fig. 1, BYZO consists of small tetrahedra with a short nearest-neighbor bond distance $r_< \sim 3$ Å connected by large tetrahedra with size $r_> \sim 6$ Å. Because of the large ratio $r_>/r_< \sim 2$, the intertetrahedron couplings are expected to be small compared to the intratetrahedron couplings, leading to effectively decoupled small tetrahedra. This can be compared to the Cr-based BP compounds, where the small and large tetrahedra differ in size by only ~5% [35–37]. To characterize BYZO spectroscopically, we have investigated its low energy spin excitations using inelastic neutron scattering (INS). This INS data, combined with the thermodynamic measurements of Ref. [33], allows for a complete and unambiguous determination of the effective model for BYZO. We find that a single tetrahedron pseudospin model can quantitatively account for all of the current experimental data on BYZO. In addition to the antiferromagnetic Heisenberg exchange postulated in Ref. [33], we find that a significant Dzyaloshinskii-Moriya (DM) exchange is needed to obtain the correct level structure determined from INS. The fitted exchange parameters are far from the spin ice limit recently considered in Ref. [38] or the purely Heisenberg limits studied in Ref. [39]. Instead, we find that the ground state of each tetrahedron is doubly degenerate, consistent with the residual entropy observed experimentally at $T \sim 300$ mK [33]. These E doublets are nearly nonmagnetic, carrying a scalar spin chirality as well as octupolar, all-in–all-out moments. The state of BYZO at currently studied base temperatures is thus an "octupolar paramagnet" without significant intertetrahedron correlations. Notwithstanding the broad agenda of accurately determining the anisotropic exchanges in rare-earth pyrochlore materials, the complete characterization of the single-tetrahedron model should provide a useful guide for further experimental studies of BYZO and other BPs. Specifically, we estimate that the intertetrahedron correlations could begin to set in below 500 mK, at the edge of currently explored temperatures, possibly leading to an interesting new physics [40–44] in this material.

Experimental results.—Polycrystalline samples of BYZO were synthesized by a solid-state reaction and characterized by specific heat, magnetization, and neutron powder diffraction measurements [45]. These measurements confirm the previously reported cubic structure [33,49,50] (space group $F\bar{4}3m$, no. 216) with lattice parameter $a = 13.47117(3)$ at 10 K and $a = 13.48997(3)$ at 300 K.

INS data were collected using the HYSPEC spectrometer [51] at the Spallation Neutron Source at Oak Ridge National Laboratory; measurements with the incident energy $E_\mathrm{i} = 3.8$ meV at 0.25 and 20 K are shown in Fig. 2. The data at 0.25 K [Figs. 2(a) and 2(b)] exhibit several well-defined modes with no observable dispersion. The $|\mathbf{Q}|$ dependence of the inelastic scattering intensity exhibits a broad peak centered near $|\mathbf{Q}| = 1.3$ Å^{-1} [see Fig. 2(b) and the Supplemental Material (SM) [45]]. The width in energy of the modes is close to the instrumental resolution [45]. At elevated temperatures [Figs. 2(b) and 2(d)], three new excitations become visible resulting from transitions between the excited states.

The origin of the observed low energy excitations appears to be modes originating from *decoupled* Yb tetrahedra. Several pieces of evidence support this assertion. Low-lying crystal field levels can be excluded, as the origin of these modes as three higher energy crystal field levels are experimentally observed (the maximum number for Yb^{3+}), with the lowest lying level at ~38 meV [34,45]. The magnetic susceptibility and specific heat data do not show any signs of long-range magnetic order down to 0.38 K [33,45] that would indicate correlations between the small tetrahedra. Examination of the elastic scattering at 0.25 K is consistent with this conclusion, revealing no indication of long-range magnetic order. Finally, the lack of dispersion suggests that these modes arise primarily from isolated tetrahedra and that the interactions connecting the tetrahedra are weak. There is a weak and broad feature at ~1 meV. We have been unable to identify the origin of this feature, but we note that it has a $|\mathbf{Q}|$ dependence [45] distinct from that of the other nearly resolution limited modes.

Theoretical model.—We now use these experimental observations, along with the thermodynamic data from Ref. [33], to construct a model of BYZO. Given the dispersionless modes seen in the INS, and the large ratio $r_>/r_< \sim 2$ between the large and small tetrahedron sizes, we expect isolated Yb_4 tetrahedra to provide a very good description of the low energy physics. Each of the four Yb^{3+} ions has a Hund's rule ground state of $^2F_{7/2}$, with the $J = 7/2$ manifold split by the C_{3v} $(3m)$ crystalline electric field environment. Since this energy scale, ~38 meV [34], is much larger than the intratetrahedron interactions, only the ground doublet is relevant at low temperatures. This

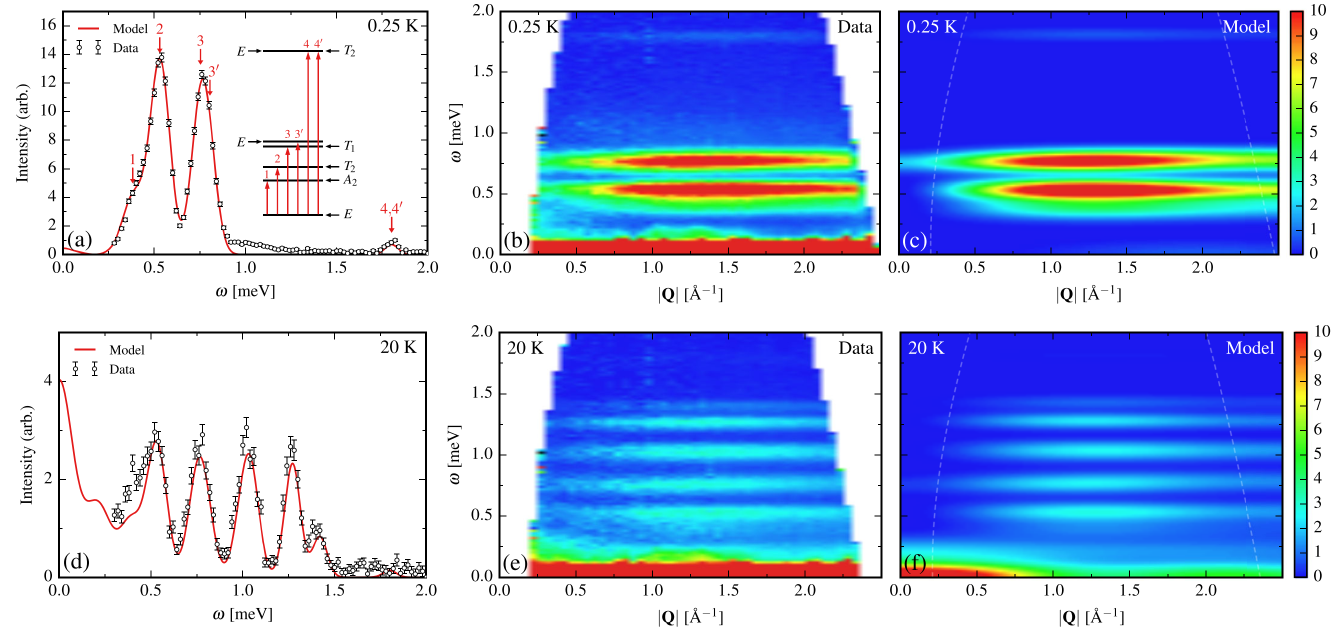

FIG. 2. INS data ($E_{\mathrm{i}} = 3.8$ meV) and comparison to our theoretical model at (a)–(c) 0.25 K and (d)–(f) 20 K. The overall theoretical intensity scale was fit using the constant wave vector cut (a) at 0.25 K. A Gaussian broadening with energy dependence following the experimental energy resolution function [45] was included in the theoretical calculation. (a),(d) Cut of the INS data averaged over the window 1.25 Å^{-1} $< |\mathbf{Q}| <$ 1.35 Å^{-1} at (a) 0.25 K and (d) 20 K. Results for a model of Eq. (2) with fitted parameters of Eq. (3) are also shown. (Inset) An illustration of the level structure of the single-tetrahedron model and the positions of the transitions from the ground doublet into the excited states. Intensity map of the powder averaged INS data at (b) 0.25 K and (e) 20 K. The excitations are nearly dispersion free over the full $|\mathbf{Q}|$ range. (c),(f) Model calculations for the parameters of Eq. (3) are shown at (c) 0.25 K and (f) 20 K. The Yb^{3+} form factor was evaluated in the dipole approximation [52].

doublet defines an effective pseudospin $\mathbf{S}_i$ at each of the four Yb^{3+} sites. This pseudospin is related to the magnetic moment $\boldsymbol{\mu}_i$ at each site through the g factors, g_z and $g_\pm$, present due to the local C_{3v} symmetry. Explicitly,

$$\boldsymbol{\mu}_i \equiv \mu_B[g_\pm(\hat{\mathbf{x}}_i S_i^x + \hat{\mathbf{y}}_i S_i^y) + g_z \hat{\mathbf{z}}_i S_i^z], \quad (1)$$

where $(\hat{\mathbf{x}}_i, \hat{\mathbf{y}}_i, \hat{\mathbf{z}}_i)$ are the local axes of tetrahedron site i [45]. Regardless of the detailed composition of the ground doublet, since $J = 7/2$, the interactions between the Yb^{3+}'s are expected to be anisotropic and, *a priori*, not necessarily near the Ising or the Heisenberg limit [53]. Symmetry constrains their form; each Yb^{3+}-Yb^{3+} bond has the symmetry C_{2v} ($2mm$) and each small Yb_4 tetrahedron has full tetrahedral symmetry T_d ($\bar{4}3m$) [33,50]. Assuming an effective spin-1/2 doublet [54], there are four allowed anisotropic exchange interactions [15,16],

$$\begin{aligned} H_{\mathrm{eff}} \equiv \sum_{i=1}^{4}\sum_{j<i}\{ & J_{zz}S_i^z S_j^z - J_\pm(S_i^+ S_j^- + S_i^- S_j^+) \\ & + J_{\pm\pm}(\gamma_{ij} S_i^+ S_j^+ + \mathrm{H.c.}) \\ & + J_{z\pm}[\zeta_{ij}(S_i^z S_j^+ + S_i^+ S_j^z) + \mathrm{H.c.}]\}, \end{aligned} \quad (2)$$

where the phases γ_{ij} and ζ_{ij} are defined in the SM [45]. This effective model includes all two-spin interactions, such as those from superexchange and any renormalizations from other microscopic interactions, such as magnetoelastic couplings. The spectrum is partly determined by symmetry. The four-pseudospin states break into the irreducible representations $A_2 \oplus 3E \oplus T_1 \oplus 2T_2$ under the action of the tetrahedral group [16]. This gives a singlet (A_2), three doublets (E), and three triplets (T_1 or T_2). From the observed residual entropy [33], it seems plausible that the ground state of the tetrahedron is an E doublet, which gives an entropy of $k_{\mathrm{B}} \ln(2)/4 \sim 0.1733 k_{\mathrm{B}}/Yb^{3+}$.

Best fit parameters.—The model of Eq. (2), supplemented with the definition of the moment in Eq. (1), is determined by the six parameters J_{zz}, $J_\pm$, $J_{\pm\pm}$, $J_{z\pm}$, g_z, and $g_\pm$. To fix these parameters, we perform a fit to the specific heat and susceptibility data of Ref. [33] and a cut of the INS data averaged over the range 1.25 Å^{-1} $< |\mathbf{Q}| <$ 1.35 Å^{-1} at 0.25 K [55]. Three additional fitting parameters were included: a constant shift of the susceptibility, χ_0, to account for the Van Vleck and diamagnetic core contributions of the Yb^{3+} ions, the intensity scale of the INS cut, and the overall scale of the Gaussian broadening used in the theoretical INS intensity. Further details of the fitting are given in the SM [45].

From this analysis, we find a unique best fit which provides excellent agreement with *all* of the known experimental data on BYZO. The best fit parameters are

$$J_{zz} = -0.037\ \text{meV}, \quad J_{\pm} = +0.141\ \text{meV},$$
$$J_{\pm\pm} = +0.158\ \text{meV}, \quad J_{z\pm} = +0.298\ \text{meV},$$
$$g_{\pm} = 2.36, \quad g_z = 3.07. \tag{3}$$

Comparison to the specific heat and susceptibility is shown in Fig. 3. Agreement is excellent; small differences can be seen in the specific heat at higher temperatures, likely due to some uncertainty in the subtraction of the lattice contribution. Comparison to a cut of the INS data at 0.25 K is shown in Fig. 2(a), along with an illustration of the level structure of the single-tetrahedron model with the parameters of Eq. (3). The level structure matches very well with the energies of the peaks in the INS cut at 0.25 K. Explicitly, one has

$$E_0 \equiv 0.000\ \text{meV}(E), \quad E_{3'} = 0.806\ \text{meV}(E),$$
$$E_1 = 0.382\ \text{meV}(A_2), \quad E_4 = 1.8020\ \text{meV}(T_2),$$
$$E_2 = 0.530\ \text{meV}(T_2), \quad E_{4'} = 1.8021\ \text{meV}(E),$$
$$E_3 = 0.754\ \text{meV}(T_1), \tag{4}$$

where the irreducible representation in T_d of each level is indicated. The model accurately reproduces the wave vector and temperature dependence of the INS data, as seen in Figs. 2(c), 2(d), and 2(f). Additional comparisons to magnetization and INS data can be found in the SM [45]. Some features of these energy levels are better understood by adopting global quantization axes and defining global pseudospin operators $\tilde{\mathbf{S}}_i$. The model in the global basis is parametrized by four anisotropic exchanges, J_1, J_2, J_3, and J_4 [56]. The best fit parameters of Eq. (3) correspond to [45]

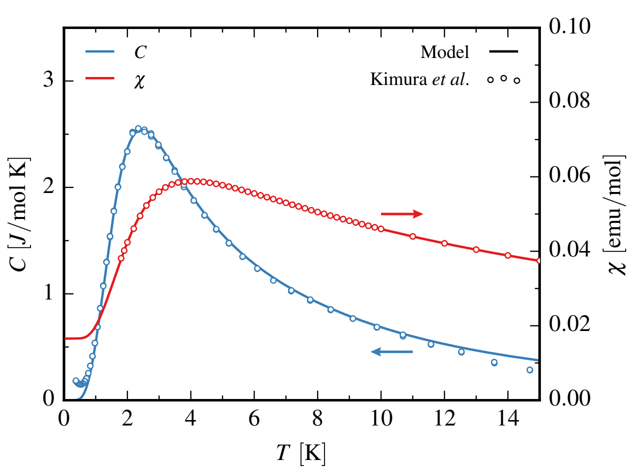

FIG. 3. Comparison of the (magnetic) specific heat, C, and the susceptibility, χ, of Kimura *et al.* [33] to the model of Eq. (2) with fitted parameters of Eq. (3). A constant shift, χ_0, was included in the fit of the susceptibility to account for the Van Vleck and diamagnetic core contributions of the Yb^{3+} ions.

$$J_1 = +0.587\ \text{meV}, \quad J_2 = +0.573\ \text{meV},$$
$$J_3 = -0.011\ \text{meV}, \quad J_4 = -0.117\ \text{meV}. \tag{5}$$

Since $J_1 \sim J_2 \equiv J$ and $J_3 \sim 0$, these fitted parameters describe a Heisenberg antiferromagnet with a large (indirect) DM interaction $D \equiv \sqrt{2}J_4 \sim -0.28J$ [45,57] and negligible symmetric anisotropies. We can thus understand the E doublet ground state as an extension of the pair of $S = 0$ singlets that form the ground state in the Heisenberg limit [33]. Similarly, the approximate quintet $E_4 \sim E_{4'}$ maps to the fivefold degenerate $S = 2$ states of the antiferromagnetic Heisenberg model. Indeed, when only Heisenberg and DM interactions are present, these remain exact eigenstates and degenerate, leaving only the small symmetric anisotropies to provide any splitting. While this mapping is appealing, there are key differences; for example, the three $S = 1$ triplets present in the Heisenberg model are strongly mixed by the DM interactions.

Discussion.—The physics at very low temperatures, $T \ll E_1$, should be controlled by the ground E doublet. The states of this E doublet, $|\pm\rangle$, are rather exotic. As in the Heisenberg limit, they are largely nonmagnetic, carrying a uniform (scalar) spin chirality $\langle\pm|\tilde{\mathbf{S}}_i \cdot (\tilde{\mathbf{S}}_j \times \tilde{\mathbf{S}}_k)|\pm\rangle \sim \pm 0.4$ on each triangle of the tetrahedron [33]. However, because of the large DM interaction, the states acquire all-in–all-out (AIAO) moments. This is expected, as the AIAO moments and the uniform spin chirality transform identically under tetrahedral symmetry [42,43]. Explicitly, the projection of a global pseudo-spin operator $\tilde{\mathbf{S}}_i$ into the E doublet takes the form $\langle\pm|\tilde{\mathbf{S}}_i|\pm\rangle = \pm\lambda\hat{\mathbf{z}}_i$ with $\lambda \sim 0.13$ for the parameters of Eq. (3) and $\langle\pm|\tilde{\mathbf{S}}_i|\mp\rangle = 0$. These AIAO moments are *octupolar* in character, with the net magnetic moment on each tetrahedron vanishing. We thus expect BYZO to be an octupolar paramagnet at temperatures much smaller than E_1. Direct signatures of this unusual paramagnetic state may appear in more indirect magnetic probes, such as nonlinear susceptibilities.

Going to lower temperatures, one can potentially see indications of collective behavior of the small tetrahedra. Depending on the structure of the intertetrahedron interactions, a variety of states could be stabilized, such as weak AIAO order or valence bond solid phases [42,43]. Tantalizing hints of the onset of such correlations may already be present in the experimental data. We note that the INS data is slightly broader than the calculated instrumental resolution (by ~0.01 meV), which may be suggestive of weak dispersion, while the specific heat data of Kimura *et al.* [33] shows a slight upturn below ~500 mK that is not explained by the single-tetrahedron model. We thus suspect that the current lowest temperatures explored in BYZO are at the threshold of observing such intertetrahedron correlations and possibly even ordering of these E doublets. Given the complete characterization of the intratetrahedron physics presented in this Letter, we feel the field is well poised to push the study of BYZO to even lower temperatures and explore such intertetrahedra physics.

From a broader perspective, our Letter suggests that there may be trends or structure to the exchange constants in rare-earth magnets that may have been overlooked in previous theoretical works. The surprisingly simple form of the exchanges, simply Heisenberg and DM interactions without strong symmetric anisotropy, would appear to be highly unusual for a system with such strong spin-orbit coupling. Further insights on how this comes about may contribute to our understanding of exchange in quantum pyrochlores such as $Yb_2Ti_2O_7$ or $Tb_2Ti_2O_7$ where the values of the exchange parameters are still under debate.

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J. G. R. and L. S. W. contributed equally to this Letter.

Note added.—Recently, Ref. [58] was published, reaching very similar conclusions on the exchange interactions in $Ba_3Yb_2Zn_5O_{11}$.

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