The Quantum Spin Liquid (QSL) is a state of matter hosting exotic fractionalized excitations and long range entanglement between spins with potential applications for quantum computing. Since QSL physics relies on quantum fluctuations that are enhanced by low spin and low dimensionality, spin-1/2 systems on two-dimensional lattices provide a natural experimental platform for realizing a QSL phase. It has also been shown that an effective spin-1/2 system can be generated even in compounds with high-angular-momentum ions like Yb$^{3+}$ and Er$^{3+}$, where the combination of crystal-field effects and strong spin-orbit coupling lead to highly anisotropic interactions between effective spin-1/2 degrees of freedom.

Magnetic frustration plays a central role in stabilizing QSL phases. While QSLs were traditionally associated with geometrically frustrated systems (e.g., triangular and kagome lattices), it has recently become well appreciated that exchange frustration due to highly anisotropic spin interactions can also stabilize QSL phases, even on bipartite lattices. Most famously, bond-dependent spin interactions on the honeycomb lattice give rise to the Kitaev model, an exactly solvable model with a gap.

![Diagram of YbCl$_3$ structure](Image)

FIG. 1: Monoclinic crystal structure of YbCl$_3$ with $a = 6.7291(3)$Å, $b = 11.6141(9)$Å, $c = 6.3129(3)$Å and $\beta = 110.5997(7)$ obtained at 10 K. Refined structure parameters are further described in SI. (a) YbCl$_3$ structure consisting of alternating planes of Yb$^{3+}$ cations (red spheres) forming a honeycomb lattice in the $ab$ plane, with Cl$^-$ anions (green spheres) separating the layers. (b) The crystal field environment surrounding the rare earth ions consists of 6 Cl ions arranged in a distorted octahedron with $C_2$ point group symmetry. (c) Single layer of Yb ions showing the honeycomb lattice arrangement in the monoclinic $ab$ plane with Yb-Yb distances at 10 K.

YbCl$_3$ crystallizes in the monoclinic space group $C12/m1$ ($\#12$). The crystal structure is composed of layers of Yb$^{3+}$ ions coordinated by slightly distorted Cl octahedra.
as illustrated in Fig. 1. Despite being formally monoclinic at 10 K, the Yb-Yb distances of 3.864 Å and 3.886 Å and the Cl-Yb-Cl bond angles of 96.12° and 96.73° are nearly identical. The result of this atomic arrangement are well-separated, nearly-perfect honeycomb layers of Yb$^{3+}$ ions in the ab-plane as shown in Fig. 1(a,c). The environment surrounding the Yb$^{3+}$ cations depicted in Fig. 1(b) consists of 6 Cl$^{-}$ anions arranged in distorted octahedra where the b-axis is the unique C$_2$ axis. Xing, et al. have reported that YbCl$_3$ undergoes short range magnetic ordering at 1.2 K. A small peak in the heat capacity at 0.6 K may indicate a transition to long range magnetic order. Moreover, the field dependence of the inferred ordering temperature suggests that the interactions in YbCl$_3$ are 2-dimensional. On the other hand, Yb-based quantum magnets have been the subject of several recent investigations and, surprisingly, in many cases these materials have been found to possess strong effective Heisenberg exchange interactions. Thus, key open questions for YbCl$_3$ are the nature of the spin Hamiltonian and the role of potential Kitaev terms. It is likewise important to determine the single-ion ground state out of which the collective physics grows and additionally if the ground state doublet is well isolated and can be considered to be in the effective quantum spin-1/2 limit. In this paper we address these issues using inelastic neutron scattering and thermodynamic measurements to study the crystal field and low energy excitation spectrum in polycrystalline samples of YbCl$_3$.

Anhydrous beads of YbCl$_3$ and LuCl$_3$ were purchased from Alfa Aesar and utilized in the experimental work presented here. Additional information and results of sample characterization are provided in the SI. Refinement of neutron powder diffraction data did not reveal any significant chlorine deficiency or secondary phases.

The crystal field excitations were measured with inelastic neutron scattering performed with the SEQUOIA spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory (ORNL). Approximately 4.2 g of polycrystalline YbCl$_3$ and 2.5 g of its nonmagnetic equivalent LuCl$_3$ were loaded into cylindrical Al cans and sealed under helium exchange gas. The use of the LuCl$_3$ measurement as a background subtraction is described in the SI. The samples and an equivalent empty can for Al background subtraction were measured at $T = 5$ K, 95 K and 185 K, with incident energies, $E_i = 6$ meV, 45 meV and 60 meV with the high resolution chopper. Unless otherwise noted, all inelastic data presented here have had the measured backgrounds subtracted with the data reduced using the software packages Dave and MANTID.

Figures 2(a) and (b) show the inelastic neutron scattering spectra as a function of wave-vector transfer, Q, and energy transfer, $\hbar\omega$, measured at $T = 5$ K and 95 K respectively. Figure 2(c) is the wave-vector integrated scattering intensity from the $E_i = 60$ meV measurements for $Q < 3$ Å$^{-1}$. The prominent higher energy modes are identified as crystal field excitations both from their $Q$-dependence and from comparison with the nonmagnetic analog LuCl$_3$. At $T = 5$ K they are centered at energy transfers of $\hbar\omega = 20.9$, 31.7, and 39.5 meV. The 20.9 meV mode is noticeably broadened toward higher energy transfers. Increasing temperature reduces intensity but does not appreciably shift or broaden these transitions, consistent with the behavior expected for crystal field excitations. Note, that there are some lower energy acoustic phonon modes in the data that are not well subtracted.
imaginary (and are parameters was achieved by rotating the environment by 10 K (inset of Fig. 3). The imaginary part of the eigenfunction is not shown because it was determined to be smaller than the real part. The calculated scattering function, \( S(|Q|, \hbar \omega) \), can be written as

\[
S(|Q|, \hbar \omega) = \sum_{i,i'} \frac{(\sum_{\alpha} |(i| J_\alpha |i')^2| e^{-\beta E_i}}{\sum_{\alpha} e^{-\beta E_i}} L(\Delta E + \hbar \omega, \Gamma_{i,i'})
\]

where \( \beta = 1/k_B T \), \( \alpha = x, y, z \), \( \Delta E = E_i - E_{i'} \), and \( L(\Delta E + \hbar \omega, \Gamma_{i,i'}) \) is a Lorentzian function \(^{21}\) with halfwidth \( \Gamma_{i,i'} \) that parameterizes the lineshape of the transitions between CEF levels (eigenfunctions of Eq. (1)) \( i \rightarrow i' \). We calculate the scattering function using this formalism, compare these values with the experimental data, and then vary the crystal field parameters to minimize the \( \chi^2 \) difference between the model and the data shown in Figs. 2(c) and Fig. 3.

The refinement of the Hamiltonian (Eq. (1)) in the scattering function described in Eq. (2) yields the crystal field parameters presented in Tab. I and the set of eigenfunctions written in Tab. II of the SI. The ground state eigenfunction is found to be

\[
0.695 \left| \frac{7}{2} \right> - 0.318 \left| \frac{5}{2} \right> + 0.546 \left| \frac{3}{2} \right> - 0.343 \left| \frac{1}{2} \right>
\]

(3)

The imaginary part of the eigenfunction is not shown because it was determined to be \( \approx 2 \) orders of magnitude smaller than the real part. The calculated \( S(|Q|, \hbar \omega) \) is plotted at both temperatures and is shown in Fig. 2(c) as solid lines. The integrated intensity of the three crystal field excitations is reproduced as is the magnetic susceptibility (Fig. 3) and the field dependent magnetization at 10 K (inset of Fig. 3).

The CEF model demonstrates that the Yb\(^{3+} \) ions have a planar anisotropy and a calculated magnetic moment of 2.24(5)\( \mu_B / \text{ion} \) is obtained for this ground state. The calculated components of the \( g \)-tensor for the ground state doublet, using the convention described above, for YbCl\(_3\) are \( g_z = 4.2(2) \), \( g_x = 3.8(2) \), and \( g_y = 2.2(2) \), which shows somewhat more anisotropy than Ref. 36. Additionally, using the crystal field model derived here as a starting point, we calculated a magnetic torque diagram at 2.1 K for an applied field of 5 T (Fig. 3 inset). The result reproduces the data in Ref. 29 (note the difference in coordinate conventions), demonstrating that the crystal field ground state is anisotropic independent of any additional exchange anisotropy.
FIG. 4: Low energy magnetic spectrum of YbCl₃. All data have had the T = 100 K YbCl₃ measurement subtracted as a background. (a) Scattering intensity as a function of Q (top axis) and hω. (b) Scattering intensity as a function of Q (top axis) integrated over hω = [0.1, 1.2] meV. The solid line is the RMC calculation described in the text. (c) Scattering intensity as a function of hω (bottom axis) integrated over Q = [0.2] Å⁻¹.

Despite the overall quality of the fits, one aspect of the crystal field excitation spectrum remains puzzling. The lineshape of the crystal field excitation centered at 21 meV extends toward higher energies. A similar broadening is not observed for the other crystal field excitations at 32 and 40 meV. Thus the broadening is a characteristic of the level at 21 meV and not of the ground state. To fully account for the spectral weight, we have modeled the lineshape for this excitation as two constrained Lorentzians with the widths fixed to be the same and the positions offset by a fixed amount. The lack of observable impurity peaks in the neutron diffraction data suggests that this effect is not due to an impurity phase. Deviations from ideal Cl stoichiometry are similarly hard to detect. Another possibility is that stacking faults result in a variation of the crystal field potential along the c-axis, though this was not evident in the diffraction data. The level at 21 meV would be more strongly affected by such stacking faults given the strong charge density out of the plane for this eigenfunction (see SI for plots of the charge density for each eigenfunction). Additionally, first principles calculations of the phonon density of states suggest that this feature is not the result of hybridization of the crystal field level with a phonon. Careful studies of single crystals are required to further understand the origin of this broadening. Finally, we note that using a single Lorentzian in the CEF modeling does not significantly change the refined CEF parameters as the additional spectral weight is relatively small.

To probe for low-energy magnetic correlations, we performed inelastic neutron scattering measurements using the HYSPEC instrument at ORNL. For these measurements, the same sample used in the SEQUOIA measurements was cooled to T = 1.6, 5, and 10 K and measured with E₀ = 3.8 meV at two different positions of the detector bank to cover a large range of Q. A T = 100 K measurement of the YbCl₃ sample was used as the background to isolate the magnetic scattering. Figure 4(a) shows the energy and wave-vector dependent magnetic spectrum in YbCl₃. A broad dispersive mode with additional scattering is evident. The additional scattering may be due to a quantum continuum however, other explanations such as broadened excitations from a short ranged ordered state, magnon decay, etc, cannot be excluded with the data at hand. The Q integrated scattering intensity in Fig. 4(c) shows a single peak at approximately 0.5 meV with no indication of a spin gap or additional scattering intensity above approximately 1.3 meV energy transfer. Given that long range magnetic order occurs at a maximum temperature of 0.6 K, the energy scale of the spin excitations suggests low dimensional and/or frustrated spin interactions in YbCl₃. The hω integrated intensity in Fig. 4(b) is a broad function which peaks at approximately Q = 1.1 Å⁻¹ likely corresponding to the reciprocal lattice points (1 1 0) and (0 2 0), which is consistent with spin correlations within the basal plane. The data in Fig. 4(c) were collected at T =1.6 K, which is at lower T than the maximum in the specific heat capacity. Thus, the low temperature spin excitations may be responsible for a portion of the loss of entropy despite the lack of apparent long range order. Additional measurements using single crystals are required to fully understand the nature of the magnetic ground state and the spin excitation spectrum.

To investigate the spin-spin correlations in YbCl₃, we performed Reverse Monte Carlo (RMC) calculations as implemented in Spinvert (see SI for more details). Within this approximation, we fit the integrated intensity of the low energy excitation spectrum as a function of Q. Ising, XY, and Heisenberg types of spin correlations were all tried as initial starting points for the simulations (See the SI for further detail). The result of the RMC modeling is shown as a solid line in Fig. 4(b). The radial spin-spin correlation function was calculated for each final spin configuration as a means to investigate the orientation of the spins with respect to each other. Assuming a purely hexagonal geometry, nearest neighbor spins are antiferromagnetically correlated, second neighbor spins have weak ferromagnetic correlations, while there is a
rapid decay of spin correlations at larger distances. This result is independent of the type of starting correlation used for the modeling.

We analyzed the spectroscopic properties of the interesting quantum magnet YbCl$_3$. Our studies show that YbCl$_3$ has crystal field excitations at $\hbar \omega = 20.9$, 31.7, and 39.5 meV. The ground state is a well separated effective spin-1/2 doublet with easy plane anisotropy and an average magnetic moment of 2.24(5)$\mu_B$/ion. At $T=1.6$ K, where long range order is not believed to exist, the low energy dynamics of the YbCl$_3$ are consistent with a low dimensional interacting spin system with antiferromagnetic nearest neighbor correlations.

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Supplemental Information

I. SAMPLE PREPARATION

Anhydrous beads of YbCl$_3$ (Alfa Aesar stock 40653) were utilized and care was taken to avoid exposure to air. The material was received in an argon-filled glass ampoule, which was opened inside a helium-filled glovebox. The material was stored in the glovebox prior to loading aluminum canisters for neutron scattering measurements. An indium seal was tightened inside the helium glovebox and checked with a helium leak detector. A powder sample of anhydrous LuCl$_3$ (Alfa Aesar stock 35802) was handled in the same way so that a non-magnetic analogue could be examined.

II. HEAT CAPACITY

Specific heat measurements down to 0.4 K were performed in a Quantum Design Physical Property Measurement System equipped with a $^3$He insert. The low-temperature specific heat $C_p(T)$ (left axis) and $C_p(T)/T$ (right axis) of YbCl$_3$ are shown in Fig. S1. Our $C_p(T)$ measurement shows a broad feature centered around 1.9 K, which corresponds to a maximum near 1.2 K in $C_p(T)/T$. Upon close inspection, a very weak feature can also be inferred near 0.6 K. These results are consistent with those reported by Xing et. al.[36]. As demonstrated by Xing et. al., the majority of the magnetic entropy is lost above 0.6 K.

III. POWGEN REFINEMENT RESULTS

Neutron powder diffraction measurements were performed using the POWGEN time-of-flight diffractometer at the Spallation Neutron Source.[39] Powder samples were measured in vanadium sample cans at $T = 100$ K.

\[ \text{FIG. S1: Specific heat data for polycrystalline samples of YbCl}_3. \text{ The scale is the same for } C_p \text{ and } C_p/T. \text{ These results are consistent with the single crystals results of Ref. [36].} \]

\[ \text{FIG. S2: Neutron diffraction data and Rietveld refinement of the C12/m1 structural model for YbCl}_3. \text{ The multiplying factors are used to provide additional detail. The bottom panel shows the difference between our refinement and the data.} \]
and \( T = 10 \, \text{K} \). The data were corrected for neutron absorption. The structural model was refined using the GSAS-II package. Data and refinement at 10 K are shown in Fig. [S2]. The refinement confirmed that our sample crystallizes into the monoclinic space group with \( a = 6.7291(3) \, \text{Å}, b = 11.6141(1) \, \text{Å}, c = 6.3121(3) \, \text{Å} \) and \( \beta = 110.5997(7) ^\circ \). Alternatively, as shown in the next section, neglecting the small monoclinic distortion, the in plane lattice parameters can be written in hexagonal notation as \( a = b = 6.720 \, \text{Å} \) with \( \gamma = 120 ^\circ \). Table [S2] shows a summary of our refinement parameters at 100 K and 10 K.

### IV. TRANSFORMATION EQUATIONS FROM MONOCLINIC TO HEXAGONAL NOTATION

When the structure is weakly monoclinic it can be useful to transform the crystallographic parameters from monoclinic symmetry to hexagonal symmetry. Here we consider the transformation of a single layer from monoclinic symmetry to hexagonal symmetry. Here we keep the \( a \) constant for the two systems, then the relations connecting the two symmetries are:

\[
\begin{align*}
\bar{a}_{\text{mon}} &= \bar{a}_{\text{hex}} \\
\bar{b}_{\text{mon}} &= \bar{a}_{\text{hex}} + 2\bar{b}_{\text{hex}}
\end{align*}
\]  

or equivalently:

\[
\begin{align*}
\bar{a}_{\text{hex}} &= \bar{a}_{\text{mon}} \\
\bar{b}_{\text{hex}} &= (\bar{b}_{\text{mon}} - \bar{a}_{\text{hex}})/2
\end{align*}
\]  

where the subscripts “\( \text{mon} \)” and “\( \text{hex} \)” denote monoclinic and hexagonal notation respectively. From these vectors the reciprocal lattice vectors can be calculated using the standard formulas \[S6\].

Therefore, in analogy, a monoclinic reflection \( q = (h, k) \) can be transformed into its hexagonal equivalent as follows:

\[
\begin{pmatrix}
h \\
k
\end{pmatrix}_{\text{mon}} = \begin{pmatrix}
1 & 0 \\
1 & 2
\end{pmatrix}
\begin{pmatrix}
h \\
k
\end{pmatrix}_{\text{hex}}
\]  

#### V. SEQUOIA CRYSTAL FIELD BACKGROUND ANALYSIS

In order to study the crystalline electric field (CEF) of YbCl\(_3\) we first investigated the background of our compound in the proximity of the three crystal field excitations. In principle, a good background subtraction to eliminate the phonon contamination can be done by measuring a non-magnetic equivalent of the main sample under the same experimental conditions. LuCl\(_3\) was used for this purpose.

We present in Fig. [S3] a-d) a comparison of the data set collected with SEQUOIA for YbCl\(_3\) and LuCl\(_3\) with \( E_i = 60 \, \text{meV} \) at 5 K and 95 K. An empty can data set at the same temperature has been subtracted to eliminate the contribution due to the sample holder. The last column of Fig. [S3] e-f) shows cuts in the momentum transfer range \( Q = [0,3] \, \text{Å}^{-1} \) at both temperatures in analogy with our analysis in the main text, to compare the phonon density of states and the crystal field spectrum.

The energy transfer range below 15 meV is dominated by the phonons of Yb(Lu), in particular the acoustic phonon at \( Q = 4 \, \text{Å}^{-1} \) and the optical phonon at 9.8 meV have been used to normalize the intensities of the two data sets. Cuts were taken through the acoustic phonon away from the nuclear Bragg peak for both samples, and the integrated intensities were compared to find the proper normalizing factor. Then this quantity was cross-checked by taking cuts along the optic phonon at \( Q \geq 4 \, \text{Å}^{-1} \), where the magnetic form factor of Yb\(^{3+}\) is small. With the data sets normalized in this manner, the LuCl\(_3\) data set was then subtracted from the YbCl\(_3\) data set. The resulting data sets were used in the refinements of the crystal field model.

The wave functions of the refined crystal field model of YbCl\(_3\) are presented in Tab. [S3]. The complex parts are omitted because they are approximately two orders of magnitude smaller than the real ones. One of the possible ways to visualize the eigenfunctions is to calculate and
plot the electronic charge density \( \rho_e(\vec{r}) = \langle \psi^\dagger | \psi \rangle \) of each of the crystal field levels. In general, under the influence of an external electric field, the crystal field states \( |\psi_i\rangle \) can be written as:

\[
|\psi_i\rangle = \sum_m a_{im} |J,\mu + mp\rangle
\]

where \( \mu \) denotes the CEF quantum number, \( m \) is an integer and \( J \) is the total angular momentum value. Here we choose, the axis quantization, \( \hat{z} \), to be parallel to the \( b \)-axis, then following the procedure described in Ref.\(^{53}\), \( \rho_e \) can be expressed in terms of spherical harmonics as:

\[
\rho_e(\vec{r}) = \sum_{k=0}^{\min(2l,2J)} \sum_{q=-k}^{+k} \rho_{kq}(\vec{r}) Y^q_k(\Omega)
\]

where \( l = 3 \) for rare earth ions, \( Y^q_k(\omega) \) is a spherical harmonic, and \( k \) is limited to even numbers due to the time reversal invariance of the charge density.

Now, an eigenfunction can always be partitioned into a radial part \( R_{nl}(\vec{r}) \) which depends only on the quantum number \( n \) and \( l \), and an angular part that is a linear combination of spherical harmonics:

\[
\rho_e(\vec{r}) = R^2_{nl}(\vec{r}) \sum_{k=0}^{\min(2l,2J)} \sum_{q=-k}^{+k} c_{kq} Y^q_k(\Omega)
\]

or alternatively using the tesseral harmonics \( Z_{kq} \) as\(^{55}\):

\[
\rho_e(\vec{r}) = R^2_{nl}(\vec{r}) \sum_{k=0}^{\min(2l,2J)} \sum_{q=0}^{+k} \zeta_{kq} Z^q_k(\Omega).
\]

Note that if a 2-fold axis perpendicular to the \( p \)-fold axis exists, then all the terms in the expansion are real.

The coefficients \( \zeta_{kq} \) in Eq. \( S11 \) can be calculated using Steven’s operators as:

\[
\zeta_{kq} = \sqrt{\frac{2k+1}{4\pi}} \theta_k b_{kq} \langle \psi^\dagger | O^q_k | \psi \rangle
\]

where \( \theta_k \) and \( b_{kq} \) values can be found in Refs.\(^{56,61}\) respectively, and \( O^q_k \) are the Steven’s operators. It can also be verified that:

\[
\langle \psi^\dagger | O^q_k | \psi \rangle = 0 \tag{S13}
\]

for \( q \) not multiple of \( p \) and:

\[
\langle \psi^\dagger | O^q_k | \psi \rangle = \sum_m a^2_m \langle J,\mu + mp | O_k | J,\mu + mp \rangle \tag{S14}
\]

for \( q \) multiple of \( p \) and with \( m \) integer.
FIG. S4: Real space representation of the angular part of the charge density $\rho_e(\vec{r})$ generated by the four crystal field levels. (a)-(d) correspond to the ground state (a) and then to progressively higher lying levels (b)-(d). $R_{nl}(\vec{r}) = 1$ was used for ease of visualization.

TABLE S3: Tabulated wave functions of the crystal field states in YbCl$_3$ obtained within the LS-coupling approximation. The crystal-field energies (in meV) are tabulated horizontally, the $m_J$-values of the ground-state multiplet vertically. Only coefficients of the wave functions $> 10^{-3}$ are shown. The imaginary parts of the eigenvectors are omitted because they are $\approx 2$ order of magnitude smaller than the real ones.

| $m_J$ | 0.0 | 0.0 | 21.08 | 21.08 | 32.03 | 32.03 | 39.28 | 39.28 |
|-------|-----|-----|--------|--------|--------|--------|--------|--------|
| $-7/2$ | -0.695 | -0.196 | 0.689 | -0.062 |
| $-5/2$ | -0.318 | 0.169 | 0.899 |
| $-3/2$ | -0.546 | -0.428 | -0.691 | -0.205 |
| $-1/2$ | -0.343 | -0.846 | -0.139 | -0.383 |
| 1/2 | 0.343 | -0.846 | 0.139 | 0.383 |
| 3/2 | 0.546 | -0.428 | 0.691 | 0.205 |
| 5/2 | 0.318 | -0.249 | 0.169 | -0.899 |
| 7/2 | 0.695 | -0.196 | -0.689 | 0.062 |

Finally, we can express the charge density using Eqs. S11-S14 as:

$$\rho_e(\vec{r}) = R_{nl}^2(\vec{r}) \sum_{k=0}^{\min(2l,2J)} \sqrt{\frac{2K + 1}{4\pi}} \theta_k$$

$$\sum_k b_{kq} \langle \psi^\dagger | O_k^q | \psi \rangle Z_{kq}(\Omega) (S15)$$

for even $k$. The calculated angular part of the charge density for the 4 crystal levels is presented in Fig. S4. Note that we assumed $R_{nl}(\vec{r}) = 1$ for ease of visualization.

A. DFT Phonon Calculation on LuCl$_3$

To confirm our understanding of the phonon density of states (DOS) and its relationship to the crystal field excitation spectrum, the phonon DOS of LuCl$_3$ was calculated using Density Functional Theory (DFT). The calculations were performed using the Vienna Ab initio Simulation Package (VASP). The calculation used Projector Augmented Wave (PAW) method to describe the effects of core electrons, and Perdew-Burke-Ernzerhof (PBE) implementation of the Generalized Gradient Approximation (GGA) for the exchange-correlation functional. The energy cutoff was 600 eV for the plane-wave basis of the valence electrons. The lattice parameters and atomic coordinates determined by neutron diffraction at 10 K (see Tab. S2) were used as the initial structure. The electronic structure was calculated on a $6 \times 3 \times 6$ Γ-centered mesh for the unit cell, and a $3 \times 3 \times 3$ Γ-centered mesh for the $2 \times 1 \times 2$ supercell. The total energy tolerance for electronic energy minimization was $10^{-8}$ eV, and for structure optimization it was $10^{-7}$ eV. The maximum inter-atomic force after relaxation was below 0.001 eV/Å, and the pressure after relaxation was below 2 MPa. The relaxed lattice parameters are $a = 6.620$ Å, $b = 11.437$ Å, $c = 6.319$ Å, $\alpha = 90^\circ$, $\beta = 110.395^\circ$, $\gamma = 90^\circ$. A Hubbard U term of 6.0 eV was applied on Lu for the localized 4f electrons. The optB86b-vdW functional for dispersion corrections was used to describe the van der Waals interactions between layers. Force constants
FIG. S5: (a-b) DFT calculation of the phonon DOS for LuCl$_3$ as measured at the SEQUOIA spectrometer with $E_i = 60$ meV. The calculations are in very good agreement with the data displayed in Fig. S3(c); the three dashed lines are guide to eyes that show the position of the CEF transitions of YbCl$_3$. (c) DFT Calculated phonon dispersion across the highly symmetric directions of the Brillouin zones for LuCl$_3$.

![DFT calculation of the phonon DOS for LuCl$_3$](image)

FIG. S6: (a) The distribution of the $\theta$ angles within the range $[0, \pi]$ calculated from the $\hat{z}$ axis (located at zero degree), shows that the spins are mainly laying in the $ab$ plane, as suggested by the anisotropy of the CF ground state. (b) Comparison of the calculated radial spin-spin correlation function for the three models used in the RMC simulation. The histogram shows that the there are antiferromagnetic nearest neighbor correlations. The presence of more than one marker at the same distance is due to slightly different bond-lengths of the spins in the lattice.

![Distribution of the $\theta$ angles](image)

The DFT calculations are in very good agreement with the data displayed in Fig. S3(c) for LuCl$_3$; in particular we can see that the first and third excited states (repre-
VI. REVERSE MONTE CARLO ANALYSIS

In order to extract information about the spin correlations in YbCl$_3$ from the powder data set we collected at HYSPEC, we performed a Reverse Monte Carlo (RMC) calculation following the approach described in Ref. [58]. The program SpinVert was used to fit the temperature subtracted data set (as explained in the main text), integrated in the energy range $\bar{h}\omega=[0.1,1.2]$ meV to avoid contamination from the elastic line.

A simulation super-cell of $6 \times 6 \times 6$ containing a total of $6^3 = 1296$ spins with periodic boundary conditions (PBCs) has been used to fit the spin excitation spectrum. For simplicity, the first attempt assumed all spins in the super-cell have Ising-like nature and are completely uncorrelated. The RMC has been done with a statistical average of 100000 configurations. The only fitting parameter in the code was a scaling factor to match the intensity of our calculation with the data set. The final spin configurations generated by the RMC were then averaged and the best fit with the HYSPEC data gave $R_{wp} = 7.1$, and a $\chi^2 = 11.1$.

In order to verify our model we performed a campaign of RMC simulations changing the anisotropy of the spins to XY-like and/or Heisenberg, increasing the size of the simulation super-cell to study possible size effects, and repeating the same type of calculations in monoclinic coordinates to check differences in the diffuse scattering pattern. We found that increasing the size of the super-cell above $6 \times 6 \times 6$ does not affect the quality of the fit, nor the calculated diffuse scattering; the calculation simply takes longer due to the higher number of spins in the super-cell. In the same way, performing the calculation in hexagonal or monoclinic notation does not affect the final result.

The lack of a spin Hamiltonian that describes the exchange interactions prevents us from fully understanding the dynamics in YbCl$_3$ at this time. However, the analysis of the angular distribution of the spins in the Heisenberg model (see Fig. S6) indicates that the spins are preferentially laying in the $ab$ plane as suggested by the local anisotropy of the crystal field ground state. Finally, from the generated spin configurations, we can calculate and compare the radial spin-spin correlation function for all three models (i.e., the Ising-like, XY-like, and Heisenberg models), to analyze the spin-spin correlations. Figure S6(b) shows that there is an antiferromagnetic nearest neighbor spin correlation. The second and third neighbors are ferromagnetically correlated. Furthermore, this behavior is qualitatively the same for all three models explored here.

The RMC calculations also provide a prediction of the diffuse scattering pattern which can be used to further constrain the type of spin-spin correlation when compared to single crystal neutron diffraction experiments. The calculated diffuse scattering patterns are shown in
Fig. S7(b-c).

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As explained in greater detail below, a constrained two component Lorentzian has been used for the crystal field level at 21 meV.