

A comprehensive understanding of ground and optically-excited hyperfine structure of $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$

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Using high-performance computing techniques and targeted experimental investigation we have developed a predictive crystal-field model of the complex hyperfine structure of $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$. We simultaneously match site-selective spectroscopic data up to $20,000\text{ cm}^{-1}$, rotational Zeeman data, and ground- and excited-state hyperfine structure determined from high-resolution Raman-heterodyne spectroscopy on the $1.5\text{ }\mu\text{m}$ telecom transition. We achieve agreement of better than 50 MHz for assigned hyperfine transitions. The successful analysis of the complex hyperfine patterns opens the possibility of systematically searching this whole class of materials for the ZEFOZ transitions that have proved so useful in quantum information applications.

Over the last decade, substantial progress has been made towards realizing practical quantum information processing hardware using solid-state rare-earth ion based materials. Key areas of advancement have been optical quantum memories [1–6], quantum-gate implementations [7, 8], single photon sources [9], and microwave-to-optical photon modulators [10, 11]. To date, the host material of choice for all of these applications has been yttrium orthosilicate (Y_2SiO_5). The reason for this is twofold: for one, yttrium has a very small nuclear magnetic moment, while isotopes of Si and O with non-zero nuclear spin have very low natural abundances. At cryogenic temperatures, nuclear spin flips are the primary source of decoherence in rare-earth ion doped materials, resulting in Y_2SiO_5 based systems having outstanding coherence properties. The second reason is that the rare-earth substitutional site in Y_2SiO_5 has a C_1 point-group symmetry; this leads to highly admixed wavefunctions enabling efficient and diverse optical pumping schemes [7, 12, 13].

Accurate modeling of hyperfine structure is essential to development of quantum-information applications of these materials. For example, the availability of the spin Hamiltonian for $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ allowed for a computational search for magnetic field orientations exhibiting a near-zero gradient with respect to hyperfine energy levels. This is the basis of the Zero-First-Order-Zeeman (ZEFOZ) technique, which enabled an experimental demonstration of a coherence time of six hours in $^{151}\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ [2].

In this work we focus on $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ since, despite extensive past characterization, an accurate model of the excited ($^4\text{I}_{13/2}\text{Y}_1$) state remained an outstanding problem. In addition, $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ has many attractive properties for quantum information applications. This includes optical transitions in the $1.5\text{ }\mu\text{m}$ telecommunications band, an optical homogeneous linewidth of 50 Hz

[14], the narrowest observed in rare-earth doped materials to date, as well as a coherence time of more than one second [4].

Determining spin Hamiltonians for Kramers-ion systems such as $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ is much more challenging than for $^{151}\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$, where there is no electronic degeneracy. A nuclear spin of $7/2$ combined with a Kramers doublet gives 16 states for each electronic level. Spin Hamiltonian parameters are specific to particular electronic states of a single ion, so the ground-state spin Hamiltonian determined in Ref. [15] is not transferable to excited states. We avoid this limitation by using a crystal-field Hamiltonian for the entire $4f^{11}$ configuration, therefore allowing fits to the ground state data to inform the splittings of the excited states (and vice versa). This not only greatly enhances the predictive power of the model, but also enables fitting to a much wider range of experimental data. Crystal-field models also have considerable predictive power beyond an individual ion: for a fixed host material, there exist well established trends for crystal-field parameters across the rare-earth series. Consequently, once parameters are determined for a subset of rare-earth dopants, they can be extrapolated to previously unstudied rare-earth dopants in the same host [16]. Moreover, since the Hamiltonian automatically handles mixing of adjacent crystal-field levels, such models can be used to extend the ZEFOZ method to large magnetic fields where the traditional spin Hamiltonian approach breaks down. This is particularly relevant given the demonstration of a coherence time exceeding one second in $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ using a 7 Tesla magnetic field by Rančić *et al.* [4].

Determination of the eigenvalues and eigenvectors for low-symmetry systems is non-trivial. Data from Zeeman splitting is essential to give orientation information and to determine a unique set of parameters [17]. Previous work on C_1 symmetry sites has been based on *ab initio*

calculations [18, 19], or the use of a higher-symmetry approximation to reduce the number of parameters [20, 21]. These approaches are not accurate enough to model the complex hyperfine structure that we consider in this work.

In this Letter, we report a full phenomenological crystal-field fit for one of the C_1 point-group symmetry sites. The fit uses a large amount of optical and electron-paramagnetic resonance experimental data from the literature [15, 18, 22], combined with targeted Raman-heterodyne measurements to obtain high-precision hyperfine splittings of the ${}^4I_{13/2}Y_1$ excited state. The excited-state splittings were initially assigned by employing a preliminary model, which was refined as data was added.

Y_2SiO_5 is a monoclinic crystal with C_{2h}^6 space group symmetry. The yttrium ions occupy two crystallographically distinct sites, each with C_1 point-group symmetry, referred to as site 1 and site 2 [23]. For the low temperature phase of Y_2SiO_5 , these correspond to oxygen coordination numbers of six and seven, respectively. Due to the wavelength tuning range of our laser this work is focused on site 1. Y_2SiO_5 has three perpendicular optical-extinction axes: the crystallographic b axis, and two mutually perpendicular axes labeled D_1 and D_2 . We follow the convention of identifying these as the z , x , and y axes respectively [22].

The complete Hamiltonian appropriate for modelling the $4f^n$ configuration reads

$$H = H_{FI} + H_{CF} + H_Z + H_{HF} + H_Q. \quad (1)$$

The terms in the above equation represent the following interactions: the free-ion contribution, the crystal-field interaction, the Zeeman term, the nuclear magnetic dipole hyperfine interaction, and the nuclear quadrupole interaction. We use the usual free-ion Hamiltonian with the following parameters: E_0 accounting for a constant configurational shift, F^k , the Slater parameters characterizing aspherical electrostatic repulsion, and ζ , the spin-orbit coupling constant. Furthermore, we also include terms that parameterize two- and three- body interactions, as well as higher-order spin-dependent effects; for a more detailed description, the reader is referred to the review by Liu [24]. The most general crystal-field Hamiltonian has the form

$$H_{CF} = \sum_{k,q} B_q^k C_q^{(k)}, \quad (2)$$

for $k = 2, 4, 6$ and $q = -k \dots k$. The B_q^k parameters are the crystal-field expansion coefficients and $C_q^{(k)}$ are spherical tensor operators using Wybourne's normalization [25]. We note that all non-axial ($q \neq 0$) B_q^k parameters are complex, leading to a total of 27 parameters in Eq. (2). For the remaining terms in Eq. (1) we note that H_{HF} and H_Q , respectively, contain coupling constants A

and Q that must be determined from experiment, while H_Z has no free parameters. For a detailed description of these terms, as well as a discussion on the evaluation of their matrix elements, the reader is referred to McLeod and Reid [20, 26].

High precision magnetic and hyperfine interactions are generally expressed using the spin Hamiltonian formalism [27]. For a Kramers ion with non-zero nuclear spin this Hamiltonian has the form

$$\mathcal{H} = \beta_e \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I} - \beta_n g_n \mathbf{B} \cdot \mathbf{I}. \quad (3)$$

Here β_e is the Bohr magneton, \mathbf{B} is an external field vector, \mathbf{g} is the g -tensor, \mathbf{A} is the hyperfine tensor, and \mathbf{Q} is the electric-quadrupole tensor. Further, \mathbf{S} and \mathbf{I} are vectors of electronic and nuclear spin operators, respectively. β_n and g_n are the nuclear magneton and nuclear g -factors, respectively, which we neglect throughout this work.

For the initial phase of our fitting, we use a projection from the crystal-field Hamiltonian to the spin Hamiltonian, so that we can fit to spin-Hamiltonian parameters. This projection has the form

$$A_{sh} = V^\dagger A V, \quad (4)$$

for operator A and spin Hamiltonian effective operator A_{sh} . Here V are the eigenvectors one obtains by diagonalizing $H_{FI} + H_{CF}$, which can be interpreted as the zero order contribution to the spin Hamiltonian.

For C_1 symmetry this projection has some subtleties; specifically, there is a phase freedom in the matrix elements of \mathbf{S} in Eq. (3), corresponding to an arbitrary $SU(2)$ rotation. While the value of this phase does not affect the eigenvalue spectrum of the spin Hamiltonian, a specific orientation is required in order for the corresponding parameter matrices \mathbf{g} and \mathbf{A} to be symmetric. This issue is not encountered when one determines spin Hamiltonian parameter matrices from experimental data, for by choosing symmetric parameter matrices during the fitting, one implicitly fixes the phase to an appropriate value. We use a singular value-decomposition of the matrices to achieve a consistent phase after the projections (4). Details are given in the supplementary information.

We now outline the method employed to fit the crystal-field parameters to the data sets. There were two phases, an initial coarse fitting which excluded high-resolution Raman-heterodyne data, and a second polishing phase where hyperfine transition data was iteratively added as subsequent fits allowed for the unique assignment of more transitions. The initial coarse fitting employed site-selective excitation and fluorescence data from Doualan *et al.* [18], while simultaneously including the g -tensor of the ${}^4I_{13/2}Y_1$ level reported by Sun *et al.* [22], as well as the complete ground-state spin Hamiltonian reported by Chen *et al.* [15]. The site-selective data was, as usual in crystal-field calculations, directly fit to the eigenvalues of Eq. (1). In order to simultaneously fit to spin

Hamiltonian data, the projection (4) was utilized to obtain a theoretical set of parameter matrices which could be fitted to their experimental counterparts.

This procedure yielded a set of parameters of sufficient accuracy to identify several $^4I_{13/2}$ hyperfine transitions in our Raman-heterodyne data and thus complete the coarse step of the fitting. In order to perform the polishing stage, the projection (4) was abandoned and instead the Hamiltonian (1) was evaluated for a range of magnetic field values to directly obtain eigenvalues describing both the hyperfine structure as well as the site-selective data. This has the advantage that Raman-heterodyne data could be added step-by-step as transitions were identified. In order to ease the computational burden the calculations of hyperfine states were performed using a truncated basis using the intermediate-coupling method described by Carnall *et al.* [16]. All software used to perform these calculations is available from [28].

Raman-heterodyne spectroscopy was performed for two separate frequency regions. Between 0-100 MHz we used an RF coil, and between 600-1200 MHz a tunable aluminium single-loop single-gap resonator was used. Samples were cooled using a homebuilt cryostat (containing a Cryomech PT405 pulsetube cooler) with an HTS-100 Ltd superconducting vector magnet to provide an arbitrarily-oriented magnetic field. The light source was a Koheras AdjustiK E15 fiber laser, operating at 1536.48 nm on resonance with the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition of site 1. The sample was an isotopically purified $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ crystal (Scientific Materials Inc.) with $^{167}\text{Er}^{3+}$ substituted for Y^{3+} ions at a 50 ppm level. For a more detailed description of Raman-heterodyne spectroscopy, as well as the experimental setup and methods, the reader is referred to Ref. [29].

Figure 1 shows the hyperfine transitions of both the ground and the excited state with resonances in the 600-1200 MHz region, with respect to a small change in magnetic field along the D_2 axis. These measurements are for site 1 of $^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$. Most transitions were studied in further detail using higher resolution scans over restricted sub frequencies to provide detailed curvatures for comparison with our model. Furthermore, low frequency data at 85 MHz included curvatures with respect to an external field along the D_1 , D_2 , and b axes. The maximum deviation of any Raman-heterodyne transition that we directly fit to was 15 MHz. For a few transitions the assignments remained ambiguous due to the closely spaced spectral lines. The maximum difference between an observed transition and its theoretical prediction was 50 MHz, approximately 1% of the span of the hyperfine levels.

In Fig. 2 we represent the spread of electronic data for energies up to $20,000\text{ cm}^{-1}$. Figure 2 also includes detailed magnetic rotation data of the transition between the lowest $^4I_{13/2}$ level and the ground state, with splittings on the order of 200 GHz [22]. It should be noted

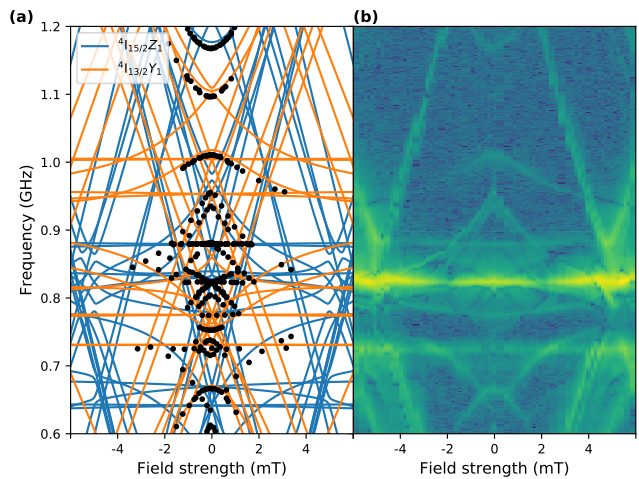


Figure 1. (a) Raman-heterodyne data (black markers) showing hyperfine transitions of the first levels of both the $^4I_{15/2}$ and $^4I_{13/2}$ multiplets of site 1 in $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$, superimposed with predictions from our crystal-field model. The magnetic field was varied in the direction of the D_2 axis. (b) A Raman-heterodyne scan of this region, detailing the hyperfine structure at these frequencies. The colormap uses a linear scale of arbitrary intensity with yellow/green indicating a resonance condition for a microwave transition in either the ground or the excited state.

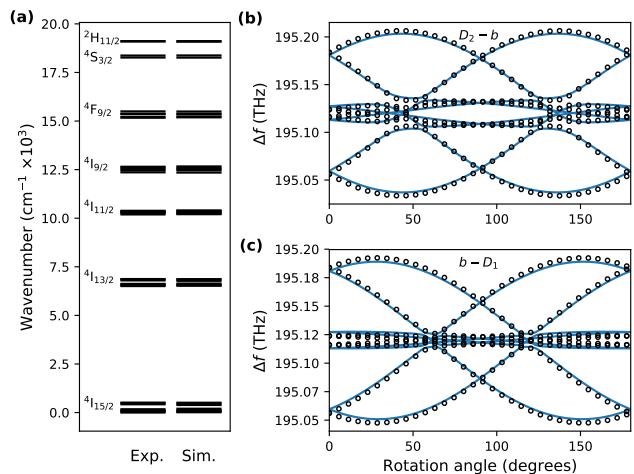


Figure 2. (a) Experimental and simulated crystal-field level splittings up to $^2H_{11/2}$ for site 1 of $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$; experimental values are from Doualan *et al.* [18]. (b) and (c) Rotation patterns for optical transitions between $^4I_{15/2}Z_1$ and $^4I_{13/2}Y_1$. Circles denote the predictions using g -tensor data from Sun *et al.* [22], while the solid lines correspond to our crystal-field model. The magnetic field magnitude used was 0.484 T (matching the experimental values used by Sun *et al.*), and the labels $D_2 - b$ and $b - D_1$ indicate the rotation planes using the standard orthogonal axes notation for Y_2SiO_5 .

that our model does not predict the absolute energies of crystal-field levels with an accuracy comparable to individual hyperfine splittings. In Table I we present the

Table I. Fitted values for the free-ion and crystal-field parameters for site 1 of $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$. The Judd and Tree's parameters, which are not included here, were fixed to the values obtained for $\text{Er}^{3+}:\text{LaF}_3$ by Carnall *et al.* [16].

Parameter	Fitted value (cm^{-1})	Uncertainty (cm^{-1})
E_0	35503.5	19.8
ζ	2362.9	1.8
F^2	96029.6	183.7
F^4	67670.6	223.2
F^6	53167.1	263.7
B_0^2	-149.8	5.4
B_1^2	420.6+396.0i	3.1+1.3i
B_2^2	-228.5+27.6i	1.8+3.4i
B_0^4	1131.2	30.4
B_1^4	985.7+34.2i	7.0+6.7i
B_2^4	296.8+145.0i	9.0+4.1i
B_3^4	-402.3-381.7i	9.7+8.9i
B_4^4	-282.3+1114.3i	13.4+12.0i
B_0^6	-263.2	3.1
B_1^6	111.9+222.9i	1.5+3.9i
B_2^6	124.7+195.9i	2.1+3.8i
B_3^6	-97.9+139.7i	5.1+9.7i
B_4^6	-93.7-145.0i	4.1+3.0i
B_5^6	13.9+109.5i	2.0+6.1i
B_6^6	3.0-108.6i	8.6+2.4i
A	0.005466	0.000003
Q	0.0716	0.0003

complete set of parameters determined from our calculation. Several additional parameters of Eq. (1) are not shown in Tab. I because they were held fixed at the values published for $\text{Er}^{3+}:\text{LaF}_3$ by Carnall *et al.* [16].

The parameter uncertainties shown in Tab. I were estimated using the Markov Chain Monte-Carlo technique from a run that included 290 000 accepted samples of the posterior probability distribution [30]. In the supplementary information we provide a more detailed description of the fitting procedure. We also include all predicted crystal-field level energies up to ${}^2\text{H}_{11/2}$ for a direct comparison with experimental values from Ref. [18]. Furthermore, the Raman-heterodyne data for the 0 – 120 MHz frequency window is presented and plotted together with the corresponding theoretical transition energies.

We may use our crystal-field fit to calculate the spin Hamiltonian parameters for any of the electronic levels. In Tab. II we present the parameters for the ground state along with the ${}^4\text{I}_{13/2}\text{Y}_1$ excited state. Alongside to our calculated values, we include parameters from the literature wherever they are available.

In the crystal-field analysis, 35 parameters (five free-ion parameters, 27 crystal-field parameters, and two hyperfine parameters) are fitted to 95 data points (35 electronic energies and 60 magnetic-hyperfine data points for

Table II. ${}^4\text{I}_{15/2}\text{Z}_1$ ground and ${}^4\text{I}_{13/2}\text{Y}_1$ excited state spin Hamiltonian parameters determined from our crystal-field Hamiltonian for site 1 of $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ (denoted by the prefix CF). All A and Q values are in MHz.

State	g_{xx}	g_{yy}	g_{zz}	g_{xy}	g_{xz}	g_{yz}
CF ground	2.10	8.37	5.49	-3.43	-3.21	5.16
[15] ground	2.90	8.90	5.12	-2.95	-3.56	5.57
CF excited	2.04	4.44	7.94	-2.24	-3.40	5.15
[22] excited	1.95	4.23	7.89	-2.21	-3.58	4.99
	A_{xx}	A_{yy}	A_{zz}	A_{xy}	A_{xz}	A_{yz}
CF ground	200.80	911.27	586.95	-344.23	-362.61	586.95
[15] ground	274.29	827.50	706.15	-202.52	-350.82	635.15
CF excited	271.96	583.12	1058.43	-293.37	-447.76	684.97
	Q_{xx}	Q_{yy}	Q_{zz}	Q_{xy}	Q_{xz}	Q_{yz}
CF ground	9.32	-6.37	-2.95	1.92	2.26	-9.55
[15] ground	10.40	-5.95	-4.44	-9.12	-9.96	-14.32
CF excited	6.84	0.30	-7.13	3.62	5.54	-7.13

Z_1 and Y_1 , enumerated in the supplementary information). By comparison, two *separate* spin Hamiltonians, requiring 34 parameters, would be required for a conventional analysis of the two states. The advantage of our approach is that the fit to the ground state hyperfine data enable the *prediction* of the excited state hyperfine structure.

In conclusion, the calculation presented here allows us to accurately characterize the hyperfine structure of the ground state and all excited state levels of ${}^{167}\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$, allowing modeling of optical pumping schemes via the 1.5 μm (or other) transitions, as well as high-field ZEFOZ applications. With suitable scaling, the crystal-field parameters are also applicable to other ions in Y_2SiO_5 , opening the possibility of identifying promising transitions prior to extensive experimental investigation.

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Supplementary information for:
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SINGULAR-VALUE DECOMPOSITION TO OBTAIN SYMMETRIC PARAMETER TENSORS

In the projection from the crystal-field Hamiltonian to the spin Hamiltonian (Eq. 4 of the main paper) there is a phase freedom in the \mathbf{S} matrix elements. This can lead to an asymmetric parameter matrix, which prevents one from using the projection to fit to spin Hamiltonian parameters tensors from experiment. Here we show how a singular-value decomposition was employed to transform the spin Hamiltonian tensors to a symmetric basis. For example, for the Zeeman interaction term, the singular-value decomposition of \mathbf{g} takes the form

$$\mathbf{g} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^\dagger, \quad (1)$$

where \mathbf{U} and \mathbf{V} are unitary, and $\mathbf{\Sigma}$ is diagonal. Since $\mathbf{U}^\dagger\mathbf{g}\mathbf{V}$ is diagonal, a similarity transformation with the unitary matrix \mathbf{U} leads to

$$\mathbf{U}\mathbf{U}^\dagger\mathbf{g}\mathbf{V}\mathbf{V}^\dagger = \mathbf{g}\mathbf{V}\mathbf{V}^\dagger. \quad (2)$$

Thus, we can define an SU(2)-rotated set of electronic spin operators $\mathbf{S}' = \mathbf{R}\mathbf{S}$ with $\mathbf{R} = \mathbf{V}\mathbf{U}^\dagger$ and a rotated spin Hamiltonian term of the form $\mathbf{B} \cdot \mathbf{g}' \cdot \mathbf{S}'$, with $\mathbf{g}' = \mathbf{g}\mathbf{V}\mathbf{V}^\dagger$ symmetric. An analogous procedure can be applied to the nuclear dipole interaction term $\mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}$. This method allows us to transform to a unique basis with symmetric spin-Hamiltonian tensors.

MAGNETICALLY INEQUIVALENT SITES

For each crystallographic site of Y_2SiO_5 (site 1 and site 2) there are two subclasses of ions which have different transition energies in an external field. These magnetically inequivalent sites are related by the C_{2h}^6 space-group symmetry. In the main text, we provided g -tensors for both the $^4\text{I}_{15/2}\text{Z}_1$ and the $^4\text{I}_{13/2}\text{Y}_1$ electronic levels for a single magnetically inequivalent site. The g -tensors for the second site can be obtained from the presented parameters using the rotation

$$\mathbf{R} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (3)$$

LOW FREQUENCY RAMAN-HETERODYNE DATA

As noted in the main text, Raman-heterodyne spectroscopy was performed in two frequency bands: between 0-120 MHz and 0.6-1.2 GHz. Here the low-frequency Raman-heterodyne data is presented for magnetic field sweeps along nine different directions. The data is shown in two almost identical figures: Fig. 1 shows a colormap of transition intensity with the theoretical predictions plotted on top; and Fig. 2 showing only the raw data, such that transitions which are partially obscured by our model are clearly visible. The theoretical lines correspond to the lowest energy transitions that the crystal-field Hamiltonian predicts for the $^4\text{I}_{13/2}\text{Y}_1$ hyperfine manifold. The colormap indicates the linear strength of the Raman-heterodyne signal, with yellow/light blue corresponding to a resonance condition. We note that the large yellow signal at low frequency is likely due to RF pickup, and is saturating the maximum colormap intensity. As a consequence, the transitions at 85 MHz have a somewhat lower intensity. As is evident from the figures, the 85 MHz transitions of both magnetically inequivalent sites agree with the data to within ~ 2 MHz for magnetic field sweeps in three dimensions.

During these experiments, some difficulty was experienced in achieving an optimal alignment of the sample inside the RF coil with respect to the magnetic field axes. Therefore, the exact orientation of the sample with respect to the magnet was later deduced by calculating the rotation required for the magnetically inequivalent sites to become degenerate. The transformation to go from the crystallographic D_1 , D_2 , and b axes to the X , Y , and Z coordinate system in the Figs. 1 and 2 has the form

$$\mathbf{R}(\theta) = \begin{bmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad (4)$$

with $\theta = 174^\circ$.

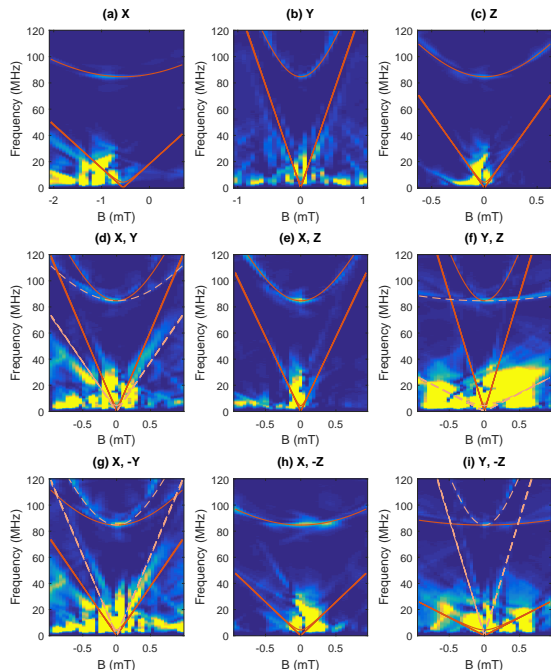


Figure 1. Raman-heterodyne data for nine distinct magnetic field sweeps, plotted with theoretical predictions. Field directions are indicated in subfigure titles; however, axes X , Y , and Z do not map directly to the crystallographic axes. See the text for details. In the colormaps yellow/light blue indicates a resonance condition, that is, the energy of a hyperfine transition. The red lines are our prediction for the lowest energy transitions of the ${}^4I_{13/2}Y_1$ excited state. For directions out of the D_1 - D_2 plane and not along the b axis, there are two magnetically inequivalent sites. For applicable field sweeps, both magnetically inequivalent sites are plotted, and distinguished by solid and dashed lines.

FITTING DETAILS

In order to perform the coarse part of the fitting procedure, we employed our own implementation of the basin-hopping algorithm [1] in conjunction with the Sblpx local minimization routine [2, 3]. The polishing fit, which included Raman-heterodyne data, instead used simulated annealing followed by a single Sblpx local optimization to obtain the final parameters. For the hyperfine portion of the calculation we used an intermediate coupled effective Hamiltonian [4] in a basis spanning only the ${}^4I_{15/2}$ and ${}^4I_{13/2}$ states. This lowered the dimension of the hyperfine Hamiltonian from 2912 to 224. Since a separate Hamiltonian had to be diagonalized for each magnetic field orientation, this reduction was essential to making the optimization computationally feasible.

In all fitting calculations, a number of higher order free-ion parameters were held fixed to the values determined by [4] for $\text{Er}^{3+}:\text{LaCl}_3$; for completeness, these values are

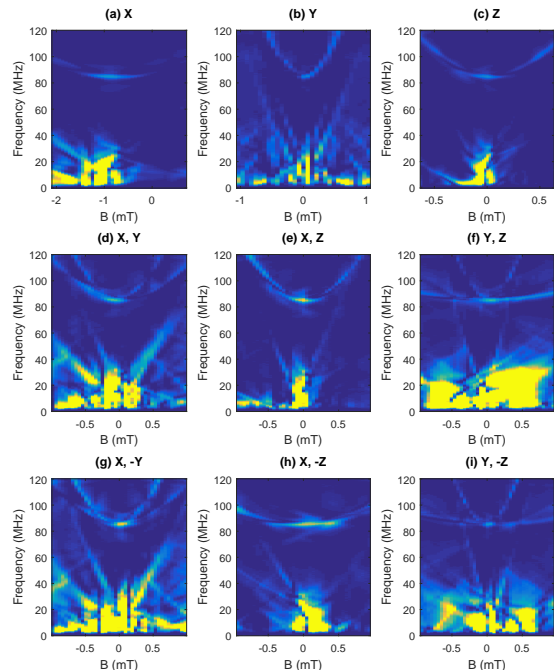


Figure 2. The same Raman-heterodyne data as for Fig. 1 but without the theoretical lines. These plots are included to more clearly show the resonances at 85 MHz which were obscured by the theory curves in the above figure. Again, field directions are indicated in subfigure titles, with the indicated field directions X , Y , and Z not coincident with the crystallographic axes. See the text for details.

Table I. Parameters for two electron Coulomb (α , β , γ), three electron Coulomb (T^2 , T^3 , T^4 , T^6 , T^7 , T^8), as well as higher order spin-dependent (M^{tot} , P^{tot}) interactions, held fixed throughout all calculations at values reported by Ref. [4].

Parameter	Value (cm^{-1})
α	17.79
β	-582.1
γ	1800
T^2	400
T^3	43
T^4	73
T^6	-271
T^7	308
T^8	299
M^{tot}	3.86
P^{tot}	594

provided in Tab. I.

To perform the polishing fit, the ground and excited state spin Hamiltonians were evaluated at a variety of magnetic field directions. These were sampled from the

parametric spiral

$$\mathbf{B} = B_0 \begin{bmatrix} \sqrt{1-t^2} \cos(6\pi t) \\ \sqrt{1-t^2} \sin(6\pi t) \\ t \end{bmatrix}, \quad t \in [-1, 1], \quad (5)$$

with B_0 the overall magnitude of the field vector. The fit then included the following 95 data points:

- 35 electronic levels up to ${}^2\text{H}_{11/2}F_1$.
- 12 data points for the hyperfine splittings of the ${}^4\text{I}_{15/2}Z_1$ level, sampled at equally spaced intervals according to Eq. (5), with $B_0 = 0.05$ Tesla.
- 12 data points for the Zeeman splittings of the ${}^4\text{I}_{13/2}Y_1$ level, also according to Eq. (5), with $B_0 = 0.05$ Tesla.
- 4 data points from low-frequency Raman-heterodyne measurements - here we had sufficient experimental data to calculate a three dimensional curvature tensor of transition energy with respect to a magnetic field. The four data points were added to the crystal-field fit at field vectors of $[0 \ 0 \ 0]$, $[0.5 \ 0.0 \ 0.0]$, $[0.0 \ 0.5 \ 0.0]$, and $[0.0 \ 0.0 \ 0.5]$ (with axes $[D_1 \ D_2 \ b]$ and values in mT). This data is discussed in Sec. .
- 32 data points from high-frequency Raman-heterodyne data - this dataset consisted of magnetic field sweeps along the crystallographic D_2 axis. Therefore, we fit second order polynomials to the transition energy curvature with respect to magnetic field along the D_2 direction. For the crystal-field fit, these polynomials were sampled at field values of 0.0, 0.3, and 0.5 mT. A total of 10 transitions were fit using this method. Two additional transitions had curvatures that were not well approximated by a second order polynomial as they had a very steep gradient around zero field. For these, the crystal-field fit was only performed at a single magnetic field strength of 0.5 mT. Fig. 1 (a) of the main text shows all of these transitions, with a subset of the transitions also visible in the wide-frequency scan shown in Fig. 1 (b).

In Tab. II we summarize the energies of the crystal-field levels up to the ${}^2\text{H}_{11/2}F_1$ level. These are shown with respect to the experimental energies determined by Doualan *et al.* [5] using site-selective excitation and fluorescence spectroscopy. We see that the maximum deviation is 36 cm^{-1} (${}^4\text{I}_{15/2}Z_6$), although Doualan *et al.* indicated that the assignment of this transition was uncertain. Ignoring levels with uncertain assignments, we obtain a standard deviation of 13.8 cm^{-1} for the differences between our model and the reported experimental values.

Table II. Theoretical energy levels up to the ${}^2\text{H}_{11/2}$ multiplet of $\text{Er}^{3+}:\text{Y}_2\text{SiO}_5$ site 1 calculated from our crystal-field model. For comparison, the experimentally determined values of energy levels reported by Doualan *et al.* [5] have been included. All quoted values are in cm^{-1} . Question marks denote uncertain assignments as indicated by the authors of Ref. [5].

Multiplet	State	Theory	Experiment	Difference
${}^4\text{I}_{15/2}$	Z ₁	15	0	-15
	Z ₂	47	42	-5
	Z ₃	75	86	11
	Z ₄	130	104	-26
	Z ₅	199	172	-27
	Z ₆	388	424?	36
	Z ₇	462	481	19
	Z ₈	508	513	5
${}^4\text{I}_{13/2}$	Y ₁	6522	6507	-15
	Y ₂	6560	6547	-13
	Y ₃	6583	6596	13
	Y ₄	6640	6623	-17
	Y ₅	6777	6798	21
	Y ₆	6833	6852	19
	Y ₇	6867	6871	4
${}^4\text{I}_{11/2}$	A ₁	10206	10193	-13
	A ₂	10236	10271?	35
	A ₃	10267	10292?	25
	A ₄	10339	10308?	-31
	A ₅	10381	10369	-12
	A ₆	10398	10383?	-15
${}^4\text{I}_{9/2}$	B ₁	12348	12360	11
	B ₂	12463	12460?	-4
	B ₃	12532	12528?	-5
	B ₄	12600	12612	12
	B ₅	12666	12650	-16
${}^4\text{H}_{9/2}$	D ₁	15190	15169	-21
	D ₂	15228	15220	-7
	D ₃	15342	15360?	19
	D ₄	15384	15382	-2
	D ₅	15492	15498	6
${}^4\text{S}_{3/2}$	E ₁	18264	18267	3
	E ₂	18377	18372	-5
	E ₃	19082	19091	9
${}^2\text{H}_{11/2}$	F ₁	19116	19116	0

Table III shows the hyperfine splittings of the ground state at zero field as predicted by our crystal-field model in conjunction with the splittings predicted using the spin Hamiltonian parameters from Ref. [6]. We note that the fitting did not directly include the values shown here, since magnetic field vectors were chosen using Eq. (5) which always had $B_0 = 0.05$ Tesla. This avoided any potential uncertainty in the spin Hamiltonian parameters at

Table IV. Transition energies measured using Raman-heterodyne spectroscopy compared with the energies predicted from crystal-field theory. This includes both the 85 MHz data as well as the transitions between 0.6 – 1.2 GHz. All but two transition energies are presented for zero external magnetic field; the two exceptions are denoted by a † for which an external field of 0.5 mT was used to calculate the energies. This was done since these transitions exhibit a very steep gradient around zero field, prohibiting an approximation of their curvature using a polynomial model; see text for further details. The transition column indicates which levels were assigned to these energies; level 1 is the ground state, while the lowest hyperfine level of the $^4I_{13/2}Y_1$ electronic state corresponds to 129.

Transition	Crystal-field model (MHz)	Raman Heterodyne (MHz)	Difference (MHz)
1 – 3†	873.8	880.0	–6.1
2 – 4†	873.4	880.4	–7.0
6 – 8	967.3	953.5	13.9
7 – 9	774.6	775.0	–0.4
7 – 10	1169.6	1169.0	0.6
8 – 10	834.1	824.7	9.4
9 – 11	932.3	931.5	0.7
135 – 137	1011.6	1011.3	0.2
135 – 138	1098.3	1097.7	0.7
136 – 137	666.8	667.7	–1.0
136 – 138	753.5	753.4	0.2
137 – 138	86.7	85.2	1.6
142 – 144	726.5	726.9	–0.4

Table III. The ground state hyperfine level energies at zero field as predicted by the crystal-field model. These are compared with the transition energies predicted by the spin Hamiltonian from Ref. [6]

Level	Crystal-field model (GHz)	Spin Hamiltonian (GHz)	Difference (MHz)
1	0.0000	0.0000	0.0
2	0.0000	0.0000	0.0
3	0.8736	0.8643	9.3
4	0.8737	0.8645	9.2
5	1.6942	1.6455	48.7
6	1.7037	1.6672	36.5
7	2.3355	2.1919	143.7
8	2.6710	2.7385	–67.5
9	3.1102	3.0662	44.0
10	3.5052	3.5237	–18.5
11	4.0424	4.0143	28.1
12	4.0482	4.0437	4.5
13	4.7107	4.7145	–3.8
14	4.7107	4.7154	–4.6
15	5.3482	5.4199	–71.7
16	5.3482	5.4199	–71.7

zero field (which were obtained by electron-paramagnetic resonance and therefore necessarily only from measure-

Finally, in Tab. IV we show the differences between the crystal-field model and the transition energies measured using Raman-heterodyne spectroscopy. For the transi-

In order to estimate the uncertainties of our fitted parameters we used the Markov Chain Monte-Carlo technique to sample the posterior probability distribution [7].

ments with a non-zero external magnetic field). The standard deviation for the differences between the two models was 51.2 MHz.

tions included here, at the magnetic field values indicated in the table, the standard deviation amounted to 5.3 MHz.

We completed a total of 3×10^6 trials with 2917230 accepted steps. From these we discarded the first 5×10^4 elements to allow the algorithm to “burn in”. From all

subsequent points, we used every 1000th element to ensure that consecutive samples were not correlated. The step size of individual iterations was tuned to achieve an acceptance rate of $\sim 10\%$, within the range generally recommended for this procedure [7].

We note that the primary limitation of this method for evaluating parameter uncertainties is that it assumes that we correctly weight the χ^2 contributions in accordance with the experimental uncertainties of each data element. Consequently if a substantially different weighting were selected, say to preferentially fit to electronic levels over hyperfine splittings, the resulting crystal-field parameters would deviate more than the indicated uncertainties. This would accordingly be reflected in the standard deviations given for Tabs. II, III, and IV.

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