

Spectroscopic investigations of multiple environments in Er:CaWO₄ through charge imbalance

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We present a detailed spectroscopic study of the $^4I_{13/2}$ and $^4I_{15/2}$ Er³⁺ multiplets of Er:CaWO₄ grown without a co-dopant. Using photoluminescence and photoluminescence excitation measurements, we find multiple environments into which erbium ions are incorporated in the crystal. For the four most prevalent environments, we provide a complete assignment of the $^4I_{13/2}$ and $^4I_{15/2}$ sublevel energies. Polarization-dependent absorption and emission spectroscopy allow us to identify the irreducible representations of the states and determine the dipole nature of transitions. In addition, we compare the different relaxation paths within $^4I_{13/2}$ and $^4I_{15/2}$ multiplets via line broadening and lifetime measurements. Finally, spectral, lifetime, and polarization measurements indicate similarities between the studied environments.

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I. INTRODUCTION

Quantum networks are a cornerstone technology for advancing quantum communication and distributed quantum computing [1,2]. Central to the success of these networks are quantum repeaters, which overcome the exponential decay of entanglement transmission over long distances using quantum memories [3–5], and microwave to optical transducers transferring microwave qubits to the optical regime [2,6]. Recent studies highlighted the pivotal role of atomlike defect centers in solid-state platforms with long coherence times for such quantum applications [7,8]. Ferrenti *et al.* (2020) [9] summarized the requirements for solid-state hosts of quantum defects to be intrinsically diamagnetic, have a large band gap, be free of paramagnetic impurities or unwanted defects, existence of a known method of epitaxial growth, absence of host nuclei with nonzero magnetic moments, and, finally, no crystalized phases in polar space groups. Under these considerations, the crystal CaWO₄ was identified as one of the most suitable candidates for hosting quantum defects [8,9]. In particular, the potential of the rare-earth ion erbium (Er³⁺) to maintain long spin coherence times in low nuclear spin environments while maintaining its uniquely suited emission into the low loss window of optical fibers at 1.5 μm [10] underscores its suitability for quantum applications. These properties are essential for minimizing decoherence and ensuring reliable quantum state transfer [11,12]. Er:CaWO₄ has attracted increasing attention due to its beneficial spin material system [13–17], leading to a measured spin coherence time of 23 ms [13]. Moreover, key milestones for quantum applications such as indistinguishable

single photon generation [14] and spin-photon entanglement [15] were recently demonstrated. In this matrix, Er³⁺ is replacing Ca²⁺, leading to a charge imbalance which causes additional transitions to appear [18–20]. In previous strategies for laser applications, alkali metals were co-doped to minimize additional lines. This co-doping adds another source of spin noise due to the nonzero nuclear spin and potentially reduces spin coherence. To further understand and use this charge-imbalanced system, detailed spectroscopic studies are essential yet up to now missing.

In this paper, we investigate the charge imbalanced Er:CaWO₄ and provide the full $^4I_{13/2}$ and $^4I_{15/2}$ energy structure of the four most visible environments. Furthermore, we present the orientations of their absorption and emission dipoles and, from these, assign their irreducible representations and transition selection rules assuming an S₄ symmetry. Additionally, we highlight differences in relaxation and depopulation paths.

II. CaWO₄, HOST

The uniaxial CaWO₄ matrix consists of three species. Based on the natural abundance of each element, the only potentially isotopes present with nonzero magnetic moments are ⁴³Ca (0.135%) and W¹⁸³ (14.31%) [21]. Figure 1(a) shows the tetragonal crystal structure of CaWO₄ with the incorporated Er³⁺ on a Ca²⁺ site with S₄ [22] point group symmetry [23,24]. The size of the unit cell is based on the literature values given in Ref. [25]. To visualize the size of the individual atoms, the covalent atomic radius is used [26]. Figure 1(b) highlights the crystalline environment of each species. Ca²⁺ or the incorporated Er³⁺ is bound in a deltahedron to eight O^{2−} ions with four bond lengths of 2.44 Å and four of 2.47 Å. Tungsten is bound in a tetrahedron to its four surrounding oxygen ions with a bond length of 1.80 Å. Oxygen is bound in a distorted geometry to two equally distant Ca²⁺ and one

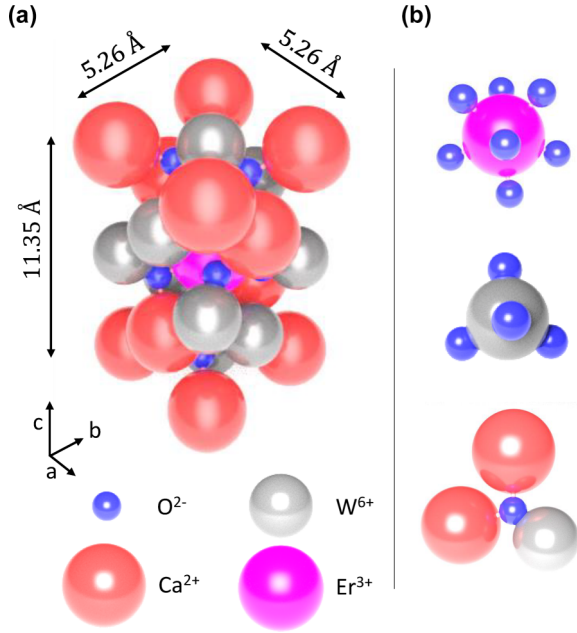


FIG. 1. Crystalline CaWO_4 host structure with incorporated Er^{3+} . (a) Schematic representation of the tetragonal $I4_1/a$ group. The visualization of covalent atomic radii and distances is to scale (data taken from Refs. [21,25]). (b) Crystal geometries surrounding the different species.

tungsten ion. Moreover, CaWO_4 is a crystal with $c = 11.35 \text{ \AA}$ and $a = b = 5.26 \text{ \AA}$, a refractive index of $n(o) = 1.88$ and $n(e) = 1.90$ at 1550 nm [27] and a band gap of 4.34 eV [25]. Er^{3+} is known to replace Ca^{2+} in two paramagnetic sites. Both differ by inversion of the environment through the S_4 symmetry site and are energetically indistinguishable without an applied electric field [23]. In addition, Kiel and Mims (1970) [24] found good agreement for the g tensor symmetry for Yb^{3+} between experiment and calculation by assuming an incorporation at the normal Ca^{2+} site without nearby charge compensation. Furthermore, Nassau and (1963) [19] studied the incorporation of rare-earth ions and charge compensation in CaWO_4 using Nd^{3+} and Ce^{3+} . They related additional peaks to vacancy formation that minimizes when Na^+ was co-doped. Additional interstitial incorporation of the lanthanoids seemed unlikely, as CaWO_4 (scheelite) is very compact. Replacement of a W^{6+} -ion for charge compensation was expected to be insignificant. However, co-dopants of the alkali metal family (monovalent ions) would add magnetic noise due to their nonzero nuclear spin and potentially reduce spin coherence. Thus, they are not favorable for quantum platforms [9]. Furthermore, paramagnetic resonance studies of not charge compensated rare-earth ions in CaWO_4 identified one to three sets of four lines, where the four lines transform to one another under a rotation of 90° about the c axis [28–30]. They suggest a Ca^{2+} vacancy at the nearest-neighbor [29] or next-nearest-neighbor site [31] to be the origin of these lines. Their point symmetries are treated as rhombic [31] or as a perturbation of the axial S_4 crystal fields [29].

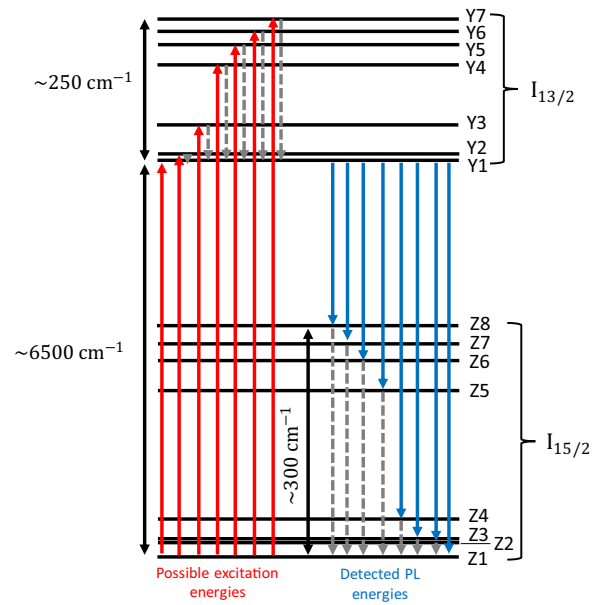


FIG. 2. Level scheme with potential optical excitation (red), photon emission (blue), and phonon emission (dashed-grey) paths. Intramultiplet-energies are to scale, the data is taken from environment I (see Table I).

III. SITE-SELECTIVE PHOTOLUMINESCENCE

In this section, we present a photoluminescence excitation (PLE) and photoluminescence (PL) study revealing at least four distinct environments experienced by Er^{3+} . For each of the four environments, we identify the energies of all seven $^4I_{13/2}$ and eight $^4I_{15/2}$ sublevels, which are split by crystal field. Figure 2 shows a schematic of erbium $^4I_{13/2}$ and $^4I_{15/2}$ multiplets in CaWO_4 with potential excitation and relaxation paths. As we measured at a temperature of 4.3 K , only the Z1 levels should be populated, and spontaneous phonon emission remains as a relaxation mechanism from higher to lower levels within a multiplet [32]. These phonon relaxation processes are typically in the order of $\leq 100 \text{ ps}$. As the radiative lifetime from the $^4I_{13/2}$ multiplet to the $^4I_{15/2}$ multiplet is on the order of milliseconds, optical relaxation from the $^4I_{13/2}$ multiplet is expected to predominantly occur from the Y1 sublevel [33]. Details of the experimental setup and sample can be found in Sec. VII A. Figures 3(a) and 3(b) show the PLE intensity in logarithmic scale as a function of the excitation wavelength and detection wavelength, while Figs. 3(c)–3(j) highlight specific PLE and PL spectra of four distinct environments. For Fig. 3(a), the spectrometer grating was centered at wavelength of 1550 nm , while the excitation was swept between 1460 nm to 1525 nm in steps of 25 pm . The integration time was 5 s with three averages and an excitation power of 0.26 mW . The excitation was left-circularly polarized. For Fig. 3(b), the excitation laser was swept from 1525 nm to 1533 nm in step sizes of 1 pm , while the detection window was centered around 1560 nm . For this measurement, we used a cross-polarized excitation-detection scheme to reduce laser scattering. The integration time was 5 s with ten averages and an excitation power of 0.5 mW . Both maps show a multiplicity of excited emissions with different widths, intensities, and patterns.

TABLE I. Summary of assigned $^4I_{13/2}$ and $^4I_{15/2}$ energy levels of different identified environments.

Sublevel	Environment 1 in cm^{-1}	Environment 2 in cm^{-1}	Environment 3 in cm^{-1}	Environment 4 in cm^{-1}
Y7	6717.93(6)	6823.63(6)	6820.86(6)	6795.56(44)
Y6	6701.16(6)	6738.23(6)	6749.43(6)	6753.82(7)
Y5	6683.38(6)	6713.40(6)	6702.75(6)	6700.05(6)
Y4	6654.96(6)	6687.32(6)	6665.32(6)	6679.26(6)
Y3	6573.30(5)	6614.09(5)	6603.81(5)	6652.33(6)
Y2	6533.033(4)	6566.81(5)	6563.70(5)	6577.77(5)
Y1	6524.715(4)	6541.433(4)	6536.933(4)	6527.935(4)
Z8	318.3(19)	437.1(19)	445.2(19)	362.5(19)
Z7	293.8(19)	336.3(19)	360.8(19)	294.8(19)
Z6	269.5(19)	315.8(19)	294.3(19)	268.0(19)
Z5	227.7(19)	262.8(19)	241.2(19)	224.1(19)
Z4	51.62(11)	104.69(11)	90.34(11)	65.32(11)
Z3	25.84(11)	72.52(11)	58.32(11)	31.92(11)
Z2	20.13(11)	39.17(11)	34.04(11)	20.01(11)
Z1	0.00	0.00	0.00	0.00

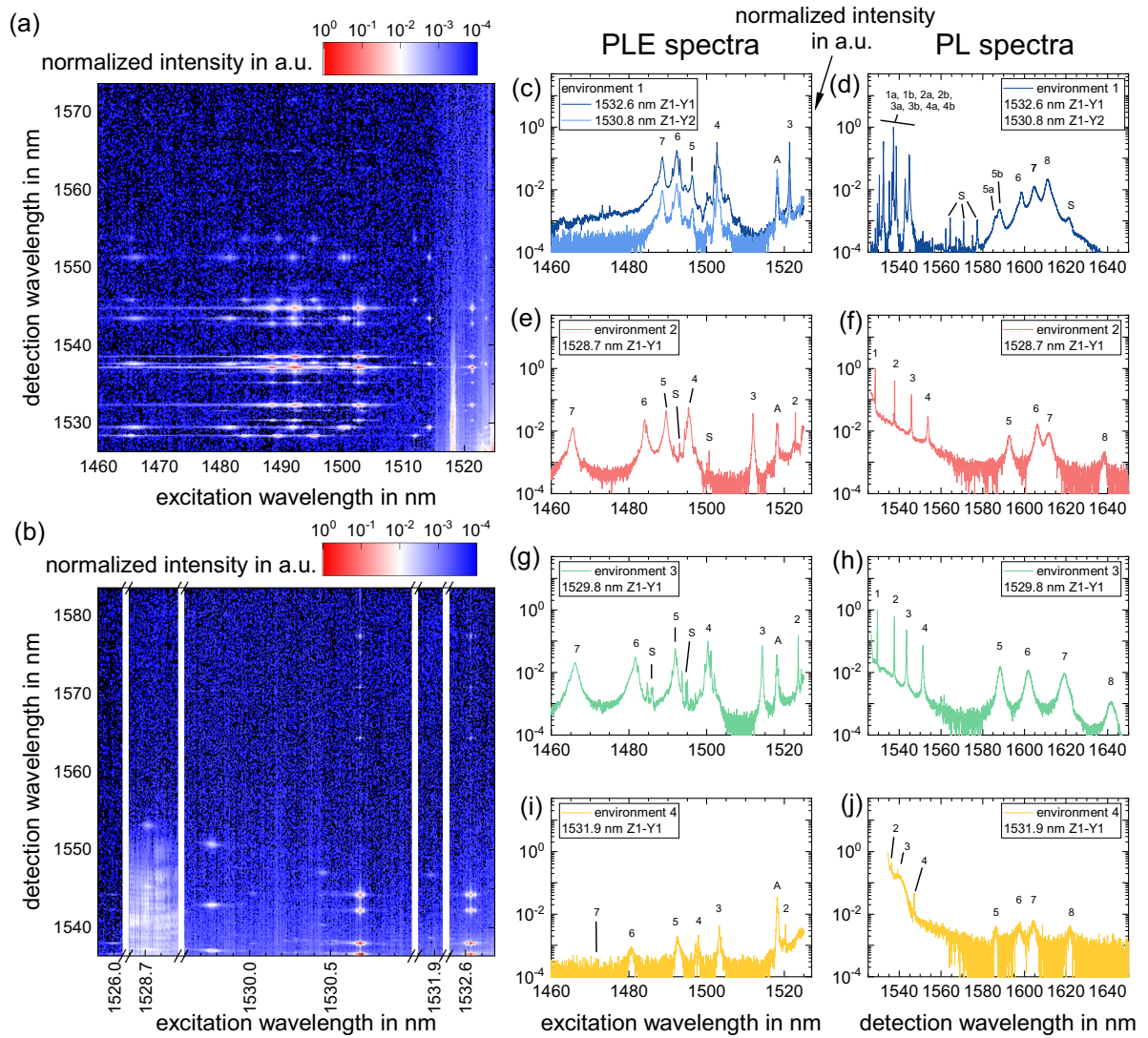


FIG. 3. Site-selective (PLE) and (PL) measurements. (a), (b) Logarithmic-scaled (PLE) maps. (c), (e), (g), (i) Logarithmic (PLE) spectra [cuts from (a)] of four assigned environments. (d), (f), (h), (j) Logarithmic (PL) spectra of four assigned environments. The numbers labeling the peaks correspond to (PLE) spectra to Y-level assignments and for (PL) spectra to Z-level assignments. The letters S and A are used to indicate that a peak corresponds to a satellite peak and scattered laser light in the spectrometer, respectively.

Compared to the only site known for Er:CaWO₄ [20] with charge compensation species, not only satellite peaks from this site but rather distinct other environments are present.

In Figs. 3(c), 3(e), 3(g), and 3(i), we highlight four cuts along the excitation wavelength (PLE spectra) of Fig. 3(a). These four cuts correspond to four different environments, for each of which we could fully assign all Y and Z energy levels. The indicated numbering of the peaks denotes the assigned Y levels. The summary of the assignment is in Table I. Environment 1 shows the highest peak intensity and its energy level aligns with the literature values of Er:CaWO₄ with charge compensation [20,34]. Figures 3(d), 3(f), 3(h), and 3(j) show the corresponding PL spectra of the different environments. For environment 3, the excitation was to the Y3 level and for environment 4 to the Y1 level. At these excitation wavelengths, only the specific environment is excited. The numbering of the peaks denotes the assigned Z levels. Although environment 1 is the reported literature environment [20] and shows the highest intensity, it has the most features and satellites within PLE and PL spectra. Although there is overlap in the excitation energy when exciting environment 1 and the other satellite environments, the actual PL in Figs. 3(d), 3(f), 3(h), and 3(j) suggest these satellites have a smaller energy displacement relative to environment 1 than is seen by environments 2–4. Thus, environment 1 and neighboring satellites seem to experience rather the assumed long-range charge compensation [16,24], whereas environments 2–4 may experience a rather nearby charge compensation, as suggested by paramagnetic resonance studies [28,29,31]. Furthermore, only Y1 to Z multiplet transitions are visible for environment 2–4, as discussed for Fig. 2. However, environment 1 shows additional emissions from Y2 to the Z levels. With a Y1Y2 spacing of approximately 250 GHz the Y2 population could still originate from an occupied phonon mode. As this feature was also seen in implanted Er:CaWO₄ [14], we can exclude a growth-related phenomenon. Finally, the transitions involving higher Y and Z levels are broadened through the spontaneous phonon emission. This is discussed in more detail in Sec. V.

IV. DIPOLE ORIENTATION AND SELECTION RULES

In this section, we present the measured emission and absorption polarization patterns of ⁴I_{13/2} to ⁴I_{15/2} transitions and assign, based on applied crystal field theory, the irreducible representation of involved energy levels. With the assigned states, we can specify if a transition is electric dipole (ED) or magnetic dipole (MD) allowed under a certain polarization.

As derived in Sec. VII B, the ⁴I_{13/2} crystal field levels have an S₄ point group symmetry and can be represented by a combination of 4(Γ₅ + Γ₆) and 3(Γ₇ + Γ₈), and ⁴I_{15/2} can be represented by 4(Γ₅ + Γ₆) and 4(Γ₇ + Γ₈). Additionally, the polarization selection rules can be worked out as described in Sec. VII C using Eq. (1) and are summarized in Tables II and III. The light polarization orientations with respect to the CaWO₄ crystal axis are summarized in Fig. 4:

$$\Gamma_i \otimes \Gamma_f^* = \sum_j \Pi_j. \quad (1)$$

Figure 5 shows measured PL intensity of environment 1 as a function of the emission and absorption polarization in polar

TABLE II. ED selection rules for S₄ point group symmetry.

S ₄	Γ ₅	Γ ₆	Γ ₇	Γ ₈
Γ ₅		σ + α	π	σ + α
Γ ₆	σ + α		σ + α	π
Γ ₇	π	σ + α		σ + α
Γ ₈	σ + α	π	σ + α	

coordinates and relates the derived selection rules to the different transitions. Error bars are in most cases smaller than the data points. In Fig. 5(a), the top row of polarization plots shows the dependence on polarization for emission from Y1 to the lower multiplet and the lower row presents the polarization dependence of the excitation from Z1 to the upper multiplet. The colored background indicates the resulting polarization selection rules discussed in Figs. 5(c) and 5(d). In the upper row, the main polarization axis for Y1Z2, Y1Z4, Y1Z5, and Y1Z6 is the *b* axis, and for Y1Z3, Y1Z7, and Y1Z8 the *c* axis. All these measurements show a bow-tie shape, indicating a reasonable signal suppression in the minor polarized axis. Y1Z1 shows a slight polarization along the *c* axis, with less suppression along the *b* axis. This 2 times 4 pattern satisfies the derived 4(Γ₅ + Γ₆) and 4(Γ₇ + Γ₈) splitting. The excitation plots Z1Y2, Z1Y3, Z1Y5, and Z1Y7 are mainly polarized in the *b* axis and Z1Y4 and Z1Y6 mainly in the *c* axis. Z1Y1 shows a slight polarization along the *b* axis. Thus, the excitation polarization does not satisfy the 4(Γ₅ + Γ₆) and 3(Γ₇ + Γ₈) splitting. To evaluate this further, we present the detection polarization of the first four transitions from the Y2 level in Fig. 5(b). All four show an inverted polarization compared with the detection polarizations Y1Z1, Y1Z2, Y1Z3, and Y1Z4 with suppression of the minor axis. This indicates Y2 as a different irreducible representation as state Y1. The table in Fig. 5(c) reduces the derived ED and MD selection rules for S₄ point group symmetry to a pair of different transitions. When there is a transition between states of the same irreducible representation, only the ED transition is allowed perpendicular to the *c* axis, while the MD transition is allowed in all orientations. On the other hand, if there is a transition between states of different irreducible representations, then the ED transition is allowed in all orientations but the MD transition is only allowed parallel to the *c* axis. We assume, that the combination of both dipoles is stronger than a single allowed dipole. Thus, transitions with an emission polarization axis strongest along the *c* axis should correspond to a change of irreducible representations of the initial and final level, whereas an axis of strongest polarization perpendicular to the *c* axis corresponds to no change in irreducible representation. For a given Y2-Z level transition, the Y1-Z level

TABLE III. MD selection rules for S₄ point group symmetry.

S ₄	Γ ₅	Γ ₆	Γ ₇	Γ ₈
Γ ₅	σ	π + α		π + α
Γ ₆	π + α	σ	π + α	
Γ ₇		π + α	σ	π + α
Γ ₈	π + α		π + α	σ

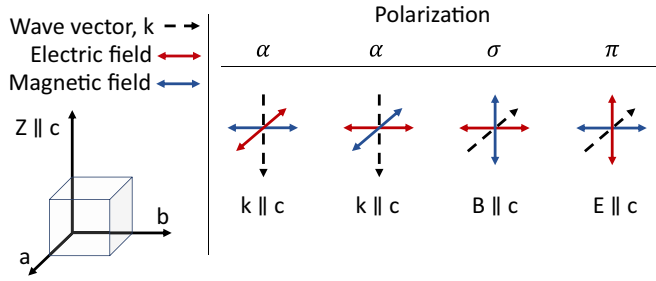


FIG. 4. Light polarization relative to the CaWO_4 crystal axes, with E and B being the electric and magnetic field components.

transition follows the alternative selection rule. This indicates that the irreducible representation of the Y1 level is not the same as for Y2. Hence, Y1Z1 must be of the opposite main polarization of Y2Z1, which is along the c axis. Z1Y2 and Y2Z1 are equal in orientation perpendicular to the c axis. This proves the requirement that the initial and final states are equal no matter if the transition is directly excited or if we look at the emission of that transition. This also shows that the dipole of Y1Z1 and Z1Y1 must be similarly oriented and opposite to the Y2 level. Thus, this transition needs to be mainly polarized along the c axis due to crystal field theory. In Ref. [34], they indicated a similar polarization behavior of the Y1Z1 absorption for charge compensated $\text{Er}^{3+}:\text{CaWO}_4$. However, it is unclear why the involved Y1 energy level is causing this rather unpolarized spectra.

With this, we can assign all transitions with a grey background from Fig. 5(a) to transitions between states of different irreducible representations and the remaining transitions to transitions between states with the same irreducible representation. Figure 5(d) shows a level scheme of the studied energy levels with assigned irreducible representation and three examples of the two types of allowed dipole transitions. As the $^4\text{I}_{13/2}$ multiplet consists of $4(\Gamma_5 + \Gamma_6)$ and $3(\Gamma_7 + \Gamma_8)$, Z1Y2, Z1Y3, Z1Y5, and Z1Y7 are of the nature $(\Gamma_5 + \Gamma_6) \leftrightarrow (\Gamma_5 + \Gamma_6)$, which means all five included energy levels can be represented by $(\Gamma_5 + \Gamma_6)$. Then Y1, Y4, and Y6 can be represented by $(\Gamma_7 + \Gamma_8)$. As we now know the nature of Y1, we can assign Z2, Z4, Z5, and Z6 to $(\Gamma_7 + \Gamma_8)$ and Z3, Z7, and Z8 to $(\Gamma_5 + \Gamma_6)$. Our final assignments agree with results from Refs. [34,35]. Additionally, they are perfectly inverse to the assignments of Ref. [20]. The reason for this seems to be that they mistakenly used the assignments of an even function, however, the $4f$ transitions are an odd function and both own the inverse numbers of $\Gamma_5 + \Gamma_6$ and $\Gamma_7 + \Gamma_8$ irreducible representations [36]. Figure 6 shows the emission and excitation polarization dependencies of environments 2–4 relative to the crystal orientation. All transitions in each environment show, in general, less dominant polarizations, with the exception of transitions Y1Z1, which seems to be better polarized compared to environment 1 [see Fig. 5(a)]. As the origin of these sites might be a nearest-neighbor, next-nearest neighbor, or further apart located Ca^{2+} vacancy [29], the polarization might be a fusion of four inequivalent sites. As these sites transform under a 90° rotation around the c -axis into each other, they would contribute equally to the polarization along the c axis. However, along any other polarization

orientation they might contribute differently depending on the symmetry, which could lead to the observable, less-defined polarizations. For rare-earth ions in CaWO_4 , the literature is not entirely consistent about point group symmetry of these charge-compensated sites. For instance, Ranon and Volterra [31] reported a rhombic symmetry and, in contrast, Mims and Gillen [29] treated the compensation as a perturbation of the S_4 crystal fields pointing out that any plausible compensation mechanism would otherwise lead to C_1 symmetry. Given these inconsistencies and potential off-axis alignments of dipoles of the four inequivalent sites, an assignment of irreducible representations is at this point inaccurate and studies to identify the symmetries unambiguously are needed first.

V. RELAXATION OF EXCITED STATES

In this section, we discuss the line broadening for each transition, compare it to the optical lifetime, and discuss the depopulation paths.

Figures 7(a)–7(d) highlight the absorption spectra of the Z1-Y1 transitions for environments 1–4 together with PLE maps of the Y1Z2 transitions. For environment 1, the figure shows a central linewidth of $\Delta_{1,\text{inh.}} = 524(9)\text{ MHz}$ with hyperfine features, while for environment 2–4 the peaks are broadened without a similar feature to $\Delta_{2,\text{inh.}} = 4.35(4)\text{ GHz}$, $\Delta_{3,\text{inh.}} = 4.44(4)\text{ GHz}$, and $\Delta_{4,\text{inh.}} = 3.94(24)\text{ GHz}$. The hyperfine feature represents the splitting of the 22.869 % natural abundant ^{167}Er [14,16,21,35,37]. The increased inhomogeneous broadening of environments 2–4 indicates a larger local disorder through, for instance, strain or defects. In addition, they emit for different excitation wavelengths. In particular, environment 3's emission wavelengths decrease with increasing excitation wavelengths. This can also be related to an effect of higher local disorder [38].

Figure 7(e) shows the full width at half maximum (FWHM) of Lorentzian fits as a function of the energy of the Z1-Y transitions used for excitation for all environments. We used Lorentzian fits, as they decently reproduce the line shapes while providing less complexity compared to the Voigt function. With increasing Y level number, the linewidth broadens from below 10 GHz to above 100 GHz. This results from the increasing influence of the spontaneous phonon emission compared to the mainly inhomogeneously broadened Y1Z1 transitions [32]. As spontaneous phonon emission is a homogeneous broadening mechanism, we can relate the radiative lifetime to it. As a consequence of the energy-time uncertainty principle, homogeneously broadened lines must satisfy $\Delta\omega \gtrsim 1/\tau_r$ [39]. The lifetime calculated from this is plotted to the right y axis and the resulting homogeneous broadening represents radiative lifetimes of upper Y levels. They decrease from smaller than 16 ps to faster than 1.6 ps and align with the literature [33]. The relation of energy broadening and acoustic phonon emission for low temperatures is [32]

$$\Delta E_{\text{sp}}(\text{in cm}^{-1}) = \sum_{f < i} \frac{1}{c} \frac{(\omega_0)^3 D^2}{2\pi\hbar} \left(\frac{1}{v_l^5} + \frac{2}{v_t^5} \right) |\langle f | V_l | i \rangle|^2, \quad (2)$$

where D is the deformation potential constant, ρ the mass density, v_l the longitudinal, and v_t transverse acoustic phonon

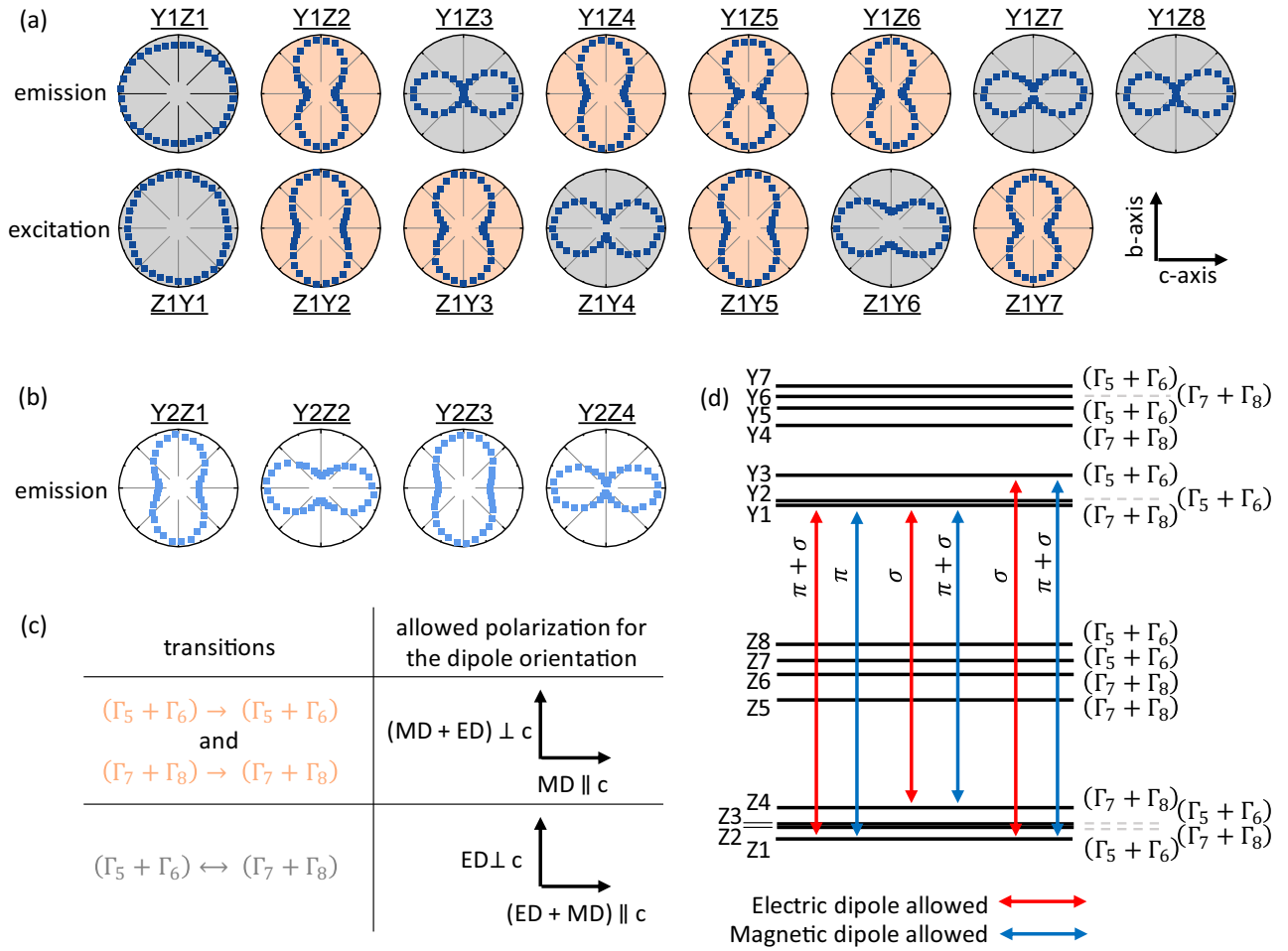


FIG. 5. Polarization-dependent analysis of environment 1. (a) Emission and excitation polarization relative to crystal orientation and $^4I_{15/2}$ and $^4I_{13/2}$ multiplet energy levels. (b) Detection polarization of Y2 emissions. (c) Resulting dipole selection rules from crystal field theory. (d) Identified irreducible representation of energy levels with indication of the three existing selection rules. The error bars are smaller than the data points.

velocity. All these parameters are independent of the energy level, leaving a relation of the sum over involved final f and initial i state with its energy gap ω_0^3 and first-order electron-phonon interaction potential term $|\langle f|V_1|i\rangle|^2$. We know ω_0 from Sec. III, however, further work would be needed to identify the unknown parameters to derive a value for the interaction potential. Phonon energies in CaWO_4 have been observed to be as high as 912 cm^{-1} [40]. As the energy difference between the lowest sublevel and the highest sublevel of the $^4I_{13/2}$ multiplet is approximately 250 cm^{-1} , a transition between any multiplet sublevel can occur to a lower sublevel with the emission of one or a couple of phonons. The equation predicts a nonlinear increasing dependency with the involved number of energy levels, which aligns with our observation.

Figure 7(f) depicts the same relation between linewidth/lifetime and energy for emission into different Z levels. The most narrow lines are close to our spectrometer resolution limit of 90 pm . Besides these transitions, the linewidth has a similar dependence on the energy which can also be attributed to spontaneous phonon emission.

Figure 7(g) shows the depopulation lifetime of the Y1 state measured using pulsed excitation and time-resolved detection. The measurement is taken by exciting to higher Y levels to avoid any potential radiation trapping [6,32,41–44]. Additionally, we used a frequency filter with a resolution of 0.15 nm in the detection to spectrally filter only on the specific Y1Z1 transition. This is especially important for excitations of higher Y levels, as more than one environment is excited simultaneously [see Fig. 3(a)]. The inset shows example decays of all environments where we fitted a single exponential curve with offset. The resulting depopulation times for environments 2 and 3 are quite similar for higher Y-level excitation and separate for lower values of Y2 excitation of $\tau_{2,Y2} = 6.12(1) \text{ ms}$ and $\tau_{3,Y2} = 6.01(1) \text{ ms}$. The depopulation time of environments 1 and 4 are also close with $\tau_{1,Y2} = 5.81(1) \text{ ms}$ and $\tau_{4,Y2} = 5.80(2) \text{ ms}$. In implanted and annealed Er:CaWO_4 , a lifetime of 6.3 ms was measured [14]. Causes for this discrepancy could be the potential lower temperature of this measurement of 0.47 K or the excitation of the Y1 line. For a crystal grown by a Czochralski technique with RF heating and Na^+ co-doping of 1:1 with $0.3\% \text{ Er}^{3+}$

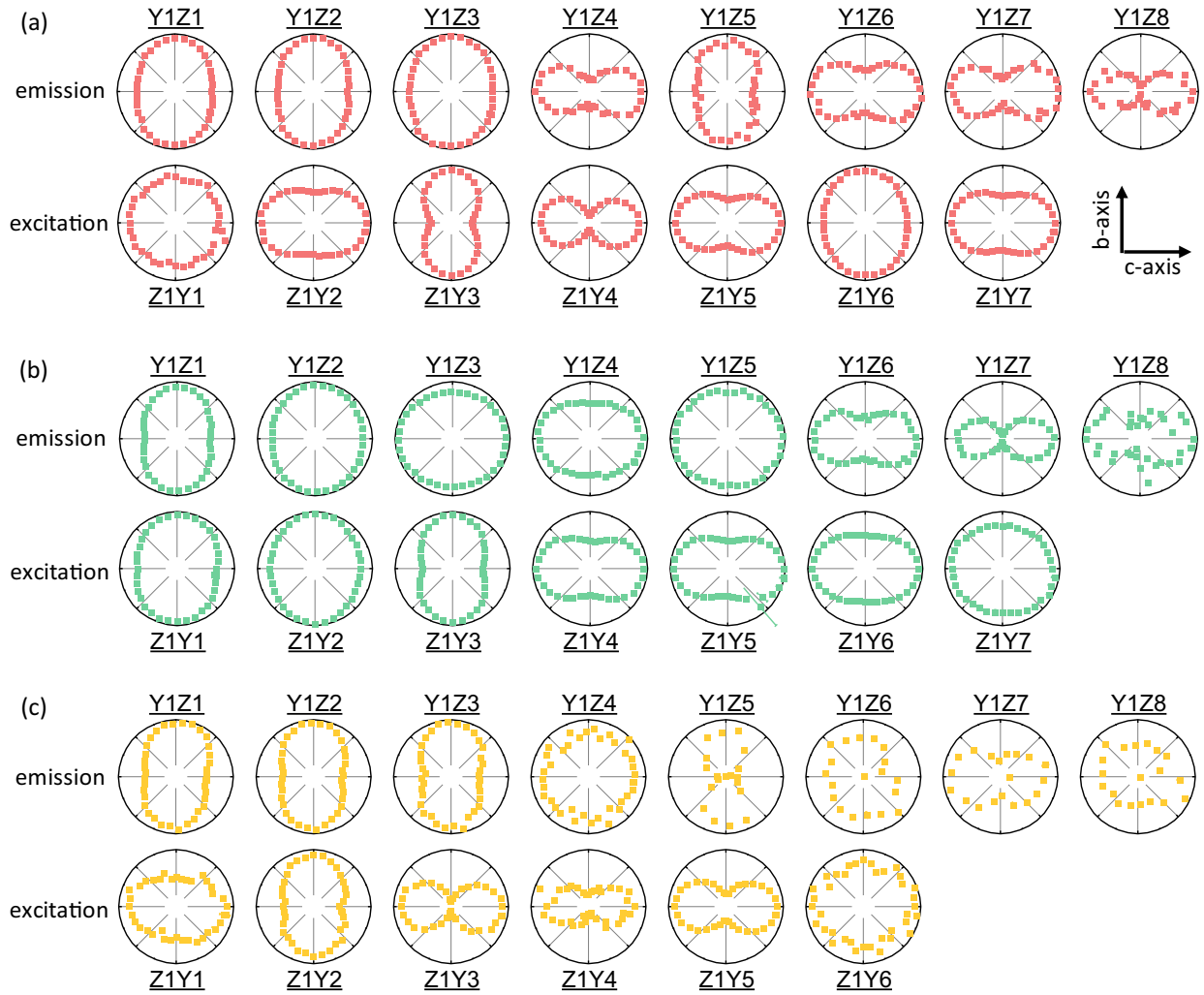


FIG. 6. Emission and excitation polarization of environments 2–4 with respect to the crystal orientation. (a) Environment 2, (b) environment 3, and (c) environment 4. The error bars are smaller than the data points. Z1Y7 of environment 4 could not be fitted due to a too-low signal-to-noise ratio.

doping, the lifetime at 10 K was measured to be 6.62 ms [18]. As no photon trapping was considered, this difference can either stem from the potentially less disordered environment or photon trapping due to the higher doping concentration.

In summary, all our studied environments show a depopulation lifetime of approximately 6.0 ± 0.2 ms. As interstitial incorporation of Er^{3+} is unlikely (see Sec. II) and would additionally have a different local environment, particularly with a lower coordination number [45], we believe that the similarities in lifetime, polarization, and spectra of the different environments indicate substitutional incorporation with local distortions through vacancies.

Figure 7(h) shows the Y1 to Z level branching ratio. For this, PL is taken in σ and π detection polarization while the excitation was constantly aligned to the most absorbing axis of the Z1Y3 lines. Additionally, the setup efficiency was recorded using a white light source and applied to the PL data. On the corrected data we fitted Lorentzian curves. Then, we sum the areas of these fits up according to the branching ratio

of uniaxial crystals [see Eqs. (8) and (15) in Sec. VIID) and present the difference.

Environments 2 and 3 show a U-shaped pattern, with their Y1Z1 transition with a relative intensity of 21.9(8)% and 19.7(6)%. Environment 1 shows a zigzag pattern with the Y1Z1 transition of 8.2(1)% and the highest value of the Y1Z8 transitions of 34.7(2)%. For quantum platforms, mainly the Y1Z1 transition is the transition of interest. Thus, the fraction of light emitted into this transition needs to be improved for applications. This can be done via the Purcell-enhancement of ions in a cavity. Taking the alignment of the cavity and Er^{3+} dipole in the uniaxial CaWO_4 into account, the branching ratio changes can be described by Eqs. (3) and (4):

$$A_P(J_1 \rightarrow J'_1) = F_P^{(\pi)} \frac{1}{3} A^{(\pi)}(J_1 \rightarrow J'_1) + F_P^{(a)} \frac{1}{3} A^{(a)}(J_1 \rightarrow J'_1) + F_P^{(b)} \frac{1}{3} A^{(b)}(J_1 \rightarrow J'_1), \quad (3)$$

$$\beta_{11} = \frac{A_P(J_1 \rightarrow J'_1)}{A_P(J_1 \rightarrow J'_1) + \sum_{j>1} A(J_1 \rightarrow J'_j)}. \quad (4)$$

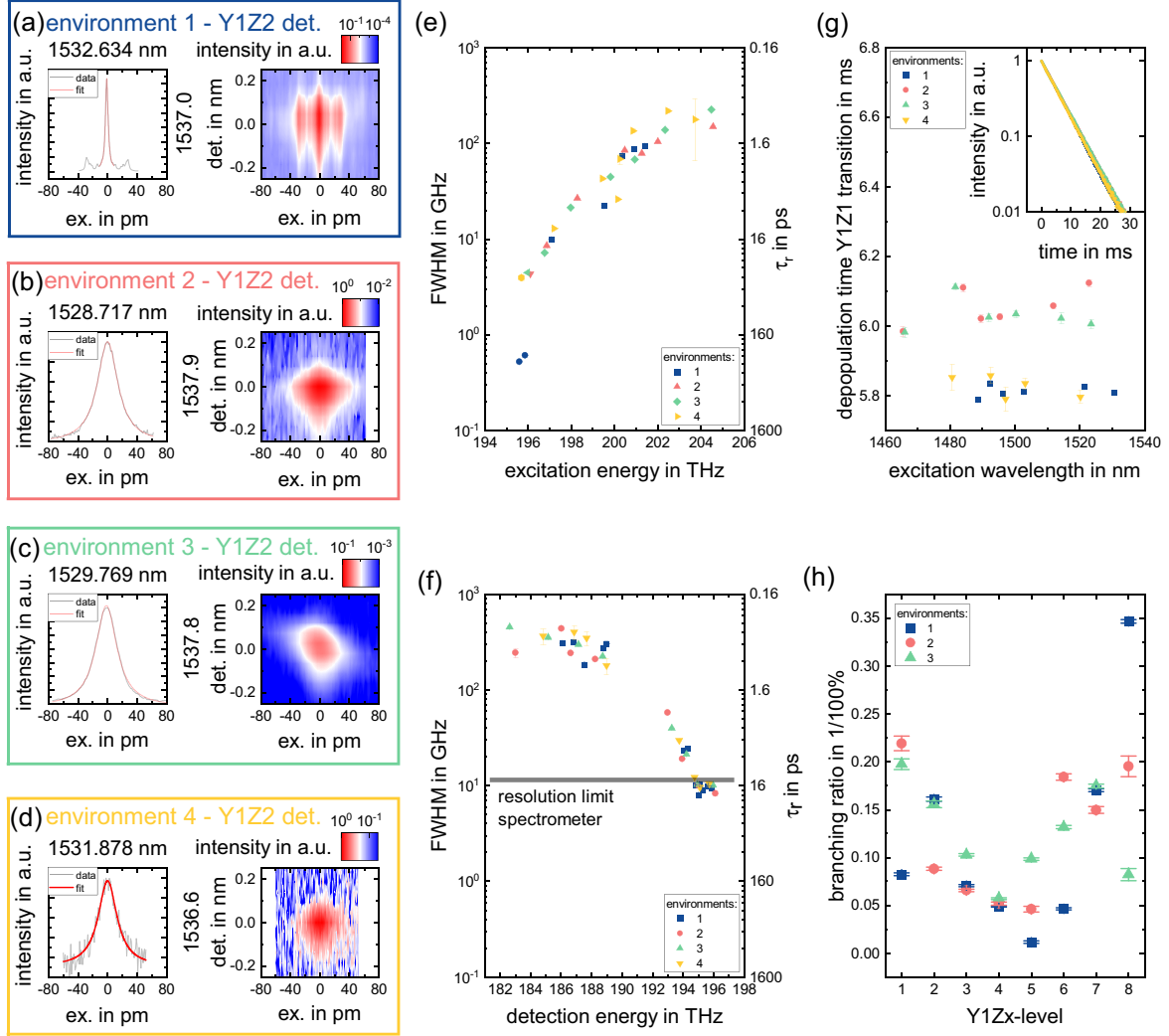


FIG. 7. Broadening through different decay paths. (a)–(d) Absorption spectra of environments Z1Y1 transition line width detection of the Y1Z2 emission [excitation (ex.) and detection (det.)]. (e), (f) Lorentzian fit FWHM evolution along higher Y and Z levels. The spectrometer resolution limit for a central wavelength of 1550 nm is shown. (g) Y1Z1-level depopulation time dependence of different Y level excitation. (h) Branching ratio of depopulation paths.

The Purcell enhancement is a function of $F_P \propto \frac{Q}{V}$ [39]. Hence, for single ion interactions where high quality factors and low volumes are feasible, the Y1Z1 transition probability $A_{11} \rightarrow 1$. For instance, if $A_P(J_1 \rightarrow J'_1)$ of environments 1 is enhanced by 100 or 1000 its branching ratio would increase to approximately 90% or 99%. However, this is not given for schemes coupling to an ensemble of ions and could limit the overall efficiency.

VI. SUMMARY

To summarize, for not charged-balanced Er:CaWO₄, we identified several environments and assigned all energy levels of $^4I_{15/2}$ and $^4I_{13/2}$ for four environments, where environment 1 matches the literature values. Further, we derived the polarization selection rules using crystal field theory, identified the irreducible representations of environment 1 for a S₄ point group symmetry, and showed similarities between environments 2 and 3. To reveal the nature of environments

2 and 3 point group symmetry, the symmetry-dependent g tensors of these environments could be measured. Finally, we investigated the linewidths and relaxation paths, where for all environments phonon-emission broadening of the lines was comparable. Environments 2 and 3 were especially similar in terms of depopulation time and branching ratio. Overall, we want to draw attention to the additional environments and give a detailed picture for further studies and applications.

VII. METHODS

A. General setup

The samples under investigation were Er:CaWO₄ crystals from SurfaceNet with a 10 ppm natural abundant erbium doping, of a size of 3 mm $\times$ 4.5 mm $\times$ 5.5 mm ($a \times b \times c$ axis) and polished on all sides. The doping was added during the hybrid Flow-Zone-Czochralski growth. The measurements were taken at 4.3 K in Attodry800XS and Attodry2100 closed cycle cryostats. For excitation, a CTL1500 from Toptica locked

TABLE IV. Symmetry elements of a S_4 point group symmetry and their descriptions [36,46].

Symmetry element	Description
E	The identity operator. In the context of double groups, this operator is equivalent to a 0 or 4π rotation around any given axis
$\bar{E}$	A rotation by 2π around any given axis
C_2	A rotation by π about the optical axis
$\bar{C}_2$	A rotation by 3π about the optical axis
S_4	An improper rotation consisting of a rotation of $\pi/2$ about the optical axis and a reflection through the plane perpendicular to the optical axis
$\bar{S}_4$	An improper rotation consisting of a rotation of $2\pi + \pi/2$ about the optical axis and a reflection through the plane perpendicular to the optical axis
S_4^{-1}	An improper rotation consisting of a rotation of $-\pi/2$ about the optical axis and a reflection through the plane perpendicular to the optical axis
$\bar{S}_4^{-1}$	An improper rotation consisting of a rotation of $2\pi - \pi/2$ about the optical axis and a reflection through the plane perpendicular to the optical axis

with a WS7-IR wave meter was used. Additionally, the power in the current excitation polarization at the setup was stabilized using a home-build PID control and a V1550PA fiber attenuator from Thorlabs. This stabilization was essential for the polarization-dependent analysis in Secs. IV and V. The fluorescent signal was detected by a Shamrock 750 spectrograph from Andor using a 6001/mm ruled, 1200 nm blaze grating and a Du491A 1.7 InGaAs detector. An SHB05T shutter from Thorlabs is used in the setup before entering the cryostat for background subtraction, which is applied for any data recorded. A 70:30 beam splitter divided excitation and detection paths.

B. Calculation of the $^4I_{13/2}$ and $^4I_{15/2}$, representation

When an ion such as Er^{3+} is placed in a crystal, the symmetry of the crystal field Hamiltonian is reduced from R3 to the point group symmetry of the location of the ion in the crystal. This point group symmetry of a site provides information on all the symmetry elements of the site. For the S_4 symmetry of Er^{3+} in CaWO_4 , these symmetry elements are E , C_2 , S_4 , and S_4^{-1} . The meaning of these elements are described in Table IV [36,46].

The electronic states have their own symmetry and this symmetry can be given a representation. It is convenient to write the representations of the state in terms of the irreducible representations of the point group symmetry. The irreducible representations are the simplest possible representations of a group from which all other representations can be expressed

and characterizes the behavior of the state under the symmetry elements of the point group. For an ion with total angular momentum J , the irreducible representation of the operator representing full rotational symmetry, R3, has dimensionality $(2J + 1)$. When placed into a crystal, the previously reducible representation can now be reduced to the irreducible representation of the subgroup associated with the point group symmetry of the site [46–48].

To decompose the reducible representations into the irreducible representations, the characters of the states in the reducible representation need to be rewritten as the sum of the characters from the irreducible representations of the point group. The character of a state with total angular momentum, J , in R3 point group symmetry for a rotational operation of angle ϕ around an arbitrary axis is given by [46]

$$\chi(\phi) = \frac{\sin((2J + 1)\phi/2)}{\sin(\phi/2)}, \quad (5)$$

$$\lim_{\phi \rightarrow 0} \chi(\phi) \approx \frac{2(J + 1)\phi/2}{\phi/2} = 2(J + 1). \quad (6)$$

In Eq. (5), J is the total angular momentum and ϕ is the rotation angle associated with the group element. For example, a C_2 group element corresponds to a π rotation, therefore $\phi = \pi$. For Er^{3+} , J has a noninteger value, meaning for every ϕ an additional 2π rotation will result in a different character value, $\chi(\phi + 2\pi) = -\chi(\phi)$. To account for the problem of every character being double-valued, a whole rotation around an arbitrary axis is redefined to be 4π rather than 2π . In doing

TABLE V. Character table for S_4 group (adapted from Refs. [32,36]).

	E	$\bar{E}$	S_4^{-1}	$\bar{S}_4^{-1}$	C_2	$\bar{C}_2$	S_4	$\bar{S}_4$	Bases
Γ_1	1	1	1	1	1	1	1	1	R_z
Γ_2	1	1	-1	-1	1	1	-1	-1	z, xy
Γ_3	1	1	i	i	-1	-1	$-i$	$-i$	x, y, R_x, R_y
Γ_4	1	1	$-i$	$-i$	-1	-1	i	i	x, y, R_x, R_y
Γ_5	1	-1	$e^{i\pi/4}$	$-e^{i\pi/4}$	i	$-i$	$-e^{i3\pi/4}$	$e^{i\pi/4}$	
Γ_6	1	-1	$-e^{i3\pi/4}$	$e^{i3\pi/4}$	$-i$	i	$e^{i\pi/4}$	$-e^{i3\pi/4}$	
Γ_7	1	-1	$-e^{i\pi/4}$	$e^{i\pi/4}$	i	$-i$	$e^{i3\pi/4}$	$-e^{i\pi/4}$	
Γ_8	1	-1	$e^{i3\pi/4}$	$-e^{i3\pi/4}$	$-i$	i	$-e^{i\pi/4}$	$e^{i3\pi/4}$	

TABLE VI. Multiplication table for S_4 Group. Taken from Ref. [32].

Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8	S_4
Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8	Γ_1
	Γ_1	Γ_4	Γ_3	Γ_7	Γ_8	Γ_5	Γ_6	Γ_2
		Γ_2	Γ_1	Γ_8	Γ_5	Γ_6	Γ_7	Γ_3
			Γ_2	Γ_6	Γ_7	Γ_8	Γ_5	Γ_4
				Γ_3	Γ_1	Γ_4	Γ_2	Γ_5
					Γ_4	Γ_2	Γ_3	Γ_6
						Γ_3	Γ_1	Γ_7
							Γ_4	Γ_8

so, a crystal double group is introduced where every element in the single-valued group now includes an equivalent element with an additional 2π rotation applied [46]. Furthermore, because J is a half-integer, whenever a symmetry element corresponds to a π rotation, the character element will be equal to zero. For symmetry elements containing a reflection, the inversion symmetry of the state also needs to be considered. A reflection can be decomposed into an inversion and rotation. Equation (5) gives the rotation component and the inversion symmetry is given by the parity of the orbitals (f orbitals have odd parity). To use Eq. (5) to find the character for a reflection symmetry element, ϕ is given a value of π and this results in a character value of zero. For the rotation-reflection element S_4 , ϕ is given a value of $\pi/2$ and the negative of the resultant character is used to account for the inversion symmetry component [32].

For the S_4 point group symmetry of our sample, the relevant characters are given in Tables IV and V [36]. Using these tables and Eq. (5), the irreducible representation for the lowest 2 terms of Er^{3+} can be calculated as a linear combination and are summarized in Table VII. $^4I_{13/2}$ and $^4I_{15/2}$ have a total angular momentum of $J = 13/2$ and $15/2$. For the S_4 point group symmetry, the irreducible representations Γ_5 and Γ_6 (Γ_7 and Γ_8) are each one dimensional and are the complex conjugates of each other. Due to Kramer's degeneracy, these irreducible representations will appear as a degenerate pair unless a magnetic field or exchange interaction is present to lift the degeneracy [48]. Just as a reminder, the character of the irreducible representation under the identity symmetry element, E , returns the dimensionality of the representation.

C. Derivation of dipole selection rules

To determine the symmetry specific selection rules, the irreducible representation of the ED and MD operators also needs to be reduced from R3 to the new lower site symmetry irreducible representation. Electric quadrupole transition selection rules are not considered as calculations have shown these transitions have a rate on the order of 0.01 s^{-1} . This is approximately three orders of magnitude smaller than the calculated magnetic and electric dipole rate of the $^4I_{13/2}$ to $^4I_{15/2}$ transition [49]. A dipole transition can only occur if the product of the initial state's irreducible representation and complex conjugate of the final state's irreducible representation includes the irreducible representation of the dipole moment operator [32]:

$$\Gamma_i \otimes \Gamma_f^* = \sum_j \Pi_j. \quad (7)$$

In Eq. (7), Γ_i and Γ_f are the irreducible representation of the initial state and final state, respectively, and $\sum_j \Pi_j$ is the irreducible representation of the dipole operator. The irreducible representation of the dipole operator can be broken down into the irreducible representations, which correspond to either the z or x - y component. This introduces polarization-dependent selection rules between the irreducible representations of the final and initial states in the crystal field splittings. As the electric dipole operator is a polar vector with odd parity and the magnetic dipole operator is an axial vector with even parity, the two dipole operators have different irreducible representations. The irreducible representations of the z and x - y components are summarized in Table VIII [32]. Figure 4 provides a summary and definition of the three types of polarizations which are used. These definitions are required to define which polarization-dependent transitions are allowed or forbidden. These polarizations, α , σ , π are all defined relative to the crystal axes. These polarizations are used in Tables II and III, where σ polarization refers to $E \perp c$ and $B \parallel c$, π polarization refers to $E \parallel k \parallel c$ and $B \perp c$, and α polarization refers to $E \perp c$ and $B \perp c$, where $\hat{Z}$ is defined along the c crystal axis (the optical axes in the uniaxial crystal CaWO_4).

Table VI is the multiplication table for the irreducible representations for the S_4 group. The allowed polarizations for electric and magnetic dipole transitions between two states with an irreducible representation ($\Gamma_7 + \Gamma_8$) can be calculated by comparing the result of $(\Gamma_7 + \Gamma_8) \otimes (\Gamma_7 + \Gamma_8)^* =$

TABLE VII. Character table with irreducible representations.

J	E	$\bar{E}$	S_4	$\bar{S}_4$	C_2	$\bar{C}_2$	S_4^{-1}	$\bar{S}_4^{-1}$	Irreducible representation	Number of levels
$\frac{1}{2}$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	$-\sqrt{2}$	$\sqrt{2}$	$(\Gamma_7 + \Gamma_8)$	1
$\frac{3}{2}$	4	-4	0	0	0	0	0	0	$(\Gamma_5 + \Gamma_6) + (\Gamma_7 + \Gamma_8)$	2
$\frac{5}{2}$	6	-6	$\sqrt{2}$	$-\sqrt{2}$	0	0	$\sqrt{2}$	$-\sqrt{2}$	$2(\Gamma_5 + \Gamma_6) + (\Gamma_7 + \Gamma_8)$	3
$\frac{7}{2}$	8	-8	0	0	0	0	0	0	$2(\Gamma_5 + \Gamma_6) + 2(\Gamma_7 + \Gamma_8)$	4
$\frac{9}{2}$	10	-10	$-\sqrt{2}$	$\sqrt{2}$	0	0	$-\sqrt{2}$	$\sqrt{2}$	$2(\Gamma_5 + \Gamma_6) + 3(\Gamma_7 + \Gamma_8)$	5
$\frac{11}{2}$	12	-12	0	0	0	0	0	0	$3(\Gamma_5 + \Gamma_6) + 3(\Gamma_7 + \Gamma_8)$	6
$\frac{13}{2}$	14	-14	$\sqrt{2}$	$-\sqrt{2}$	0	0	$\sqrt{2}$	$-\sqrt{2}$	$4(\Gamma_5 + \Gamma_6) + 3(\Gamma_7 + \Gamma_8)$	7
$\frac{15}{2}$	16	-16	0	0	0	0	0	0	$4(\Gamma_5 + \Gamma_6) + 4(\Gamma_7 + \Gamma_8)$	8

TABLE VIII. Selection rules for the S_4 point group symmetry.

Point group symmetry	Electric dipole (z)	Electric dipole (x, y)	Magnetic dipole (R_z)	Magnetic dipole (R_x, R_y)
S_4	Γ_2	$\Gamma_3 + \Gamma_4$	Γ_1	$\Gamma_3 + \Gamma_4$

$\Gamma_7 \otimes \Gamma_7^* + \Gamma_8 \otimes \Gamma_7^* + \Gamma_8 \otimes \Gamma_8^* = (\Gamma_3 + \Gamma_1 + \Gamma_4)$ to the irreducible representations of the dipole operators (found in Table VIII). The final result of $(\Gamma_7 + \Gamma_8) \otimes (\Gamma_7 + \Gamma_8)^*$ contains the irreducible representation of: (i) the component of the electric dipole operator in the plane perpendicular to the z direction (c axis of the crystal); (ii) the component of the magnetic dipole operator parallel to the z direction; and (iii) the component of the magnetic dipole operator in the plane perpendicular to the z direction. Transitions where the electric or magnetic dipole operators match these orientations are allowed transitions. We then compare in this example the orientations of the dipole operators required for a transition to be allowed to the polarizations defined in Fig. 4. It is shown that an electric dipole transition is allowed when there is α or σ polarization (when the electric field is in the x - y plane, perpendicular to the crystal c axis) while, for a magnetic dipole transition, all polarizations are allowed. The electric dipole selection rules for the relevant irreducible representations for S_4 site symmetry are given in Table II and the magnetic dipole selection rules are given in Table III [32].

D. Branching ratio

For uniaxial crystals as CaWO_4 , the transition probabilities between multiplets can be calculated as in Eq. (8) [32]:

$$A(J_i \rightarrow J_j) = \frac{1}{3}A^{(\pi)}(J_i \rightarrow J'_j) + \frac{2}{3}A^{(\sigma)}(J_i \rightarrow J'_j). \quad (8)$$

The radiative lifetime τ_r and the fluorescent branching ratio β_{ij} can be expressed as

$$\tau_r(j_i) = \frac{1}{\sum_{J'_j} A(J_i \rightarrow J'_j)}, \quad (9)$$

$$\beta_{ij} = \frac{A(J_i \rightarrow J'_j)}{\sum_{J'_j} A(J_i \rightarrow J'_j)}. \quad (10)$$

Moreover, in the derivation of the Fuchtbauer-Ladenburg equation the relation between fluorescent spectra and Einstein coefficient is noted [32]:

$$\frac{1}{hc} \int_{\text{spectrum}_{2 \rightarrow 1}} \lambda I^q(\lambda) d\lambda = GN_u A_{21}^q, \quad (11)$$

where I^q denotes the detected fluorescence intensity in polarization q , G the efficiency of the fluorescence detective system, and N_u the ion number of the high multiplet. We can now rewrite this, using the center of gravity

$$\frac{1}{hc} \bar{\lambda} \int_{\text{spectrum}_{2 \rightarrow 1}} I^q(\lambda) d\lambda = GN_u A_{21}^q. \quad (12)$$

Now the integral is the area of the detected peak in polarization q and $\bar{\lambda}$ the average wavelength of this peak. The detection efficiency is already applied to our spectra, leaving the ion number as the only unknown for calculating A_{21}^q . However, as we are in a linear region, where a change in power linearly increases or decreases the intensity, N_u is only a proportional factor. Moreover, for environments 2 and 3 only emission of Y1Z1 is detected and for environment 1 the main detection emission is also Y1Z1. Thus, N_u is assumed to be equal for all detected lines. Hence, N_u would cancel out in Eq. (10). As we took all included spectra with the same power with power stabilization, we can argue that

$$\frac{1}{hc} \cdot \bar{\lambda} \int_{\text{spectrum}_{2 \rightarrow 1}} \frac{I^q}{G}(\lambda) d\lambda \propto A_{21}^q. \quad (13)$$

Inserting this into Eq. (10) and considering Eq. (8) gives us

$$\beta_{1j} = \frac{[\bar{\lambda}(\frac{2}{3} \int_{\text{spectrum}_{2 \rightarrow 1}} \frac{I^\sigma}{G}(\lambda) d\lambda + \frac{1}{3} \int_{\text{spectrum}_{2 \rightarrow 1}} \frac{I^\pi}{G}(\lambda) d\lambda)](J_1 \rightarrow J'_j)}{\sum_{J'_j} [\bar{\lambda}(\frac{2}{3} \int_{\text{spectrum}_{2 \rightarrow 1}} \frac{I^\sigma}{G}(\lambda) d\lambda + \frac{1}{3} \int_{\text{spectrum}_{2 \rightarrow 1}} \frac{I^\pi}{G}(\lambda) d\lambda)](J_1 \rightarrow J'_j)}, \quad (14)$$

$$\beta_{1j} = \frac{[\bar{\lambda}(\frac{2}{3} \text{Ar}_{\text{cor}}^\sigma + \frac{1}{3} \text{Ar}_{\text{cor}}^\pi)](J_1 \rightarrow J'_j)}{\sum_{J'_j} [\bar{\lambda}(\frac{2}{3} \text{Ar}_{\text{cor}}^\sigma + \frac{1}{3} \text{Ar}_{\text{cor}}^\pi)](J_1 \rightarrow J'_j)}, \quad (15)$$

where $\text{Ar}_{\text{cor}}^\sigma$ is the area of σ polarization of the efficiency corrected spectra.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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