Site-selective laser and Zeeman infrared spectroscopy of Dy³⁺ centers in SrF₂:Dy³⁺

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Site-selective laser spectroscopy, Zeeman infrared, and optical absorption have been employed to investigate trivalent dysprosium centers in rare-earth-doped alkaline-earth fluoride crystals. These studies have characterized the two dominant centers in $SrF_2:0.05\%$ Dy³⁺, which are determined to be the fluorine compensated C_{4v} and C_{3v} centers analogous to those observed in other $SrF_2:R^{3+}$ systems. The C_{3v} center is shown to correspond to the *J* center of $SrF_2:Er^{3+}$, rather than the *B* center reported for $SrF_2:Ho^{3+}$. The wave functions determined from crystal-field calculations have been tested through comparison of measured and calculated Zeeman infrared interactions. Zeeman interactions between close-lying Kramers doublets have enabled the experimental determination of the C_{3v} crystal-field coordinate basis, resolving an ambiguity that occurs in the crystal-field parametrization.

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I. INTRODUCTION

Rare-earth-doped alkaline-earth fluorides have been the subject of investigation for many years, with a considerable body of literature addressing the defect structure, optical properties, and crystal-field interactions across the lanthanide series. The single-ion-defect structures of $SrF_2: R^{3+}$ have been investigated with laser-selective excitation over the majority of the lanthanide series¹⁻⁹ with a change in the dominate site from a C_{4v} to C_{3v} symmetry structure occurring in the region of Ho in the lanthanide series. Despite the extensive literature on the rare-earth-doped fluorites, the spectroscopy of the $SrF_2:Dy^{3+}$ system has not been previously investigated in great detail and there are no laser-selective excitation studies reported in the literature. Of the early studies of Dy^{3+} centers in the fluorites, ^{10–13} Eremin, Luks, and Stolov¹⁴ have presented the most information to date on $SrF_2:Dy^{3+}$, identifying a total of 16 energy levels of the fluorine-compensated trigonal center. A crystal-field analysis based on a subset of 10 of these levels has also been presented by Eremin et al.

This work reports laser-selective excitation studies of $\operatorname{SrF}_2:0.05\% \operatorname{Dy}^{3+}$, for which two dominant sites have been characterized. The first of these is identified as a tetragonal C_{4v} center, with a charge compensating F^- ion in the $\langle 100 \rangle$ nearest-neighbor interstitial position, analogous to that observed for $\operatorname{SrF}_2: R^{3+}$ where the rare earth is from the early part of the lanthanide series. The second center is assigned as a trigonal $C_{3v} J$ center,⁷ corresponding to that present in $\operatorname{SrF}_2: \operatorname{Er}^{3+}$, where the trigonal distortion is due to a F^- charge compensating ion in the $\langle 111 \rangle$ next-nearest-neighbor interstitial position. This assignment of the trigonal center makes it distinct from the trigonal *B* center⁹ of $\operatorname{SrF}_2: \operatorname{Ho}^{3+}$, for which the structure has not been definitively determined.

The irreducible representation labels of the C_{4v} and C_{3v} levels have been determined through crystal-field (CF) calculations and where possible with reference to polarized fluorescence data. The crystal-field analysis allows correlation of the C_{3v} center with that observed in $SrF_2:Er^{3+}$, thereby confirming the trigonal center reported for $SrF_2:Ho^{3+}$ to be anomalous. Zeeman infrared measurements have enabled an independent check on the accuracy of the wave functions that are obtained from the crystal-field calculations. The Zeeman data support both the symmetry assignment of the centers and the wave functions that are determined from the crystal-field calculation.

An intrinsic ambiguity in the crystal-field parameters and in the corresponding wave functions is examined. This ambiguity stems from the use of a Hamiltonian which does not uniquely specify the orientation of the coordinate basis with respect to the crystal structure. The appropriate basis for the C_{3v} crystal-field parameters and wave functions has been experimentally determined through Zeeman infrared absorption measurements.

II. EXPERIMENT

Fluorescence resulting from site-selective laser excitation of the ${}^{4}F_{9/2}$ multiplet at $\approx 21\,000$ cm⁻¹ has been used to determine the energy levels of the lower-lying Dy³⁺ multiplets. Because 9 of the 12 lower multiplets are greater than 9000 cm⁻¹ from the emitting ${}^{4}F_{9/2}$ levels, it has been possible to obtain fluorescence data for a large number of levels with visible and near-infrared photomultiplier detection. Infrared absorption of several of the lower multiplets has also been measured.

For these experiments the crystals of $SrF_2:Dy^{3+}$ were grown in this institution by the Bridgeman-Stockbarger technique. A graphite crucible containing the weighed amounts of alkaline-earth fluoride and DyF_3 was heated under vacuum and lowered at a rate of 4 mm/h through the heating coil of an rf furnace. Oriented samples along $\langle 100 \rangle$ planes were obtained by cutting and polishing using $\langle 111 \rangle$ cleavage planes for alignment. $\langle 111 \rangle$ -oriented samples were oriented directly from the cleavage planes. The samples were mounted on the cold stage of a closed-cycle helium refrigerator for 15 K measurements or in a liquid helium immersion Dewar for 2 K measurements.

The electronic transitions of the $Dy^{3+} {}^{4}F_{9/2}$ multiplet were excited by a UV argon-laser-pumped Coumarin 460 dye laser. Fluorescence was collected at right angles to the

TABLE I. Free-ion multiplet energies and composition for Dy^{3+} , based on the free-ion parameters of Carnall *et al.* (Ref. 16) and the Slater and spin-orbit parameters of the $SrF_2:Dy^{3+} C_{4v}$ center. The superscript labels in the decomposition distinguishes the *LSJ* multiplets with different *LS* term parentage. The conventional Dieke alphabetic multiplet labeling is also given, in parentheses.

Multiplet	Multiplet c	omposition	Barycenter energy (cm ⁻¹)
$^{6}H_{15/2}(Z)$	$0.97 {}^{6}H_{15/2} \rangle$	$-0.21 ^{4}I_{15/2}\rangle$	0
${}^{6}H_{13/2}(Y)$	$-0.98 ^{6}H_{13/2}\rangle$	$+0.15 ^{4}I_{13/2}\rangle$	3460
${}^{6}H_{11/2}(X)$	$0.96 ^{6}H_{11/2}\rangle$	$+0.17 ^{6}F_{11/2}\rangle$	5790
${}^{6}H_{9/2}(W)$	$-0.97 ^{6}H_{9/2}\rangle$	$-0.17 ^4 G_{9/2}\rangle$	7645
${}^{6}F_{11/2}(W)$	$0.96 {}^{6}F_{11/2} \rangle$	$-0.19 ^{6}H_{11/2}\rangle$	7665
${}^{6}F_{9/2}(A)$	$-0.94 ^{6}F_{9/2}\rangle$	$-0.26 ^{4}F_{9/2}\rangle^{a}$	8985
${}^{6}H_{7/2}(A)$	$-0.96 ^{6}H_{7/2}\rangle$	$-0.20 ^4G_{7/2}\rangle$	9060
${}^{6}H_{15/2}(B)$	$-0.96 ^{6}H_{5/2}\rangle$	$-0.21 ^4G_{5/2}\rangle$	10113
${}^{6}F_{7/2}(C)$	$0.96 {}^{6}F_{7/2}\rangle$	$+0.21 ^{4}F_{7/2}\rangle$	10900
${}^{6}F_{5/2}(D)$	$0.96 {}^{6}F_{5/2}\rangle$	$+0.14 ^{4}F_{5/2}\rangle$	12305
${}^{6}F_{3/2}(E)$	$0.95 ^{6}F_{3/2}\rangle$	$-0.18 ^4 D_{3/2}\rangle$	13105
${}^{6}F_{1/2}(-)$	$0.96 {}^{6}F_{1/2}\rangle$	$-0.19 ^4 D_{1/2}$	13650
${}^{4}F_{9/2}(F)$	$0.67 ^4 F_{9/2}\rangle^a$	$-0.32 ^{4}F_{9/2}\rangle^{b}$	21040
${}^{6}I_{15/2}(G)$	$0.67 ^4 I_{15/2} \rangle$	$+0.34 ^{4}K_{15/2}\rangle$	21965

laser propagation direction and analyzed by a SPEX 1403 double monochromator. The monochromator was equipped with a polarization scrambler to equalize its response, and the signal was detected with an RCA C31034 photomultiplier and photon counting electronics. For fluorescence below 11 000 cm⁻¹ a Spex 1700 single monochromator was used, with a liquid-nitrogen-cooled RCA-7102 photomultiplier tube providing the infrared detection.

For the Zeeman infrared (IR) measurements, samples were mounted in a department-built magnet cryostat, which in turn was mounted in a shielded compartment of a Bio-Rad FTS-40 Fourier transform (FT) spectrometer. The magnet cryostat incorporated on Oxford Instruments 4-T superconducting magnet. The sample itself was not immersed in the helium, but housed, under vacuum, in a tube in the bore of the magnet. Sample cooling was provided by thermal contact between the sample holder and the helium reservoir, resulting in an estimated sample temperature of 10 K. The propagation direction of the infrared radiation is parallel to the applied magnetic field, and therefore π (or π') polarized transitions between Zeeman levels are not observed.

III. SPECTROSCOPY OF SrF₂:Dy³⁺

The calculated free-ion energies of the Dy^{3+} multiplets lying below 23 000 cm⁻¹ are shown in Table I, together with the dominant *LSJ* compositions of the free-ion wave functions. These energy levels and wave functions have been calculated from the free-ion parameters for LaCl₃:Dy³⁺ given by Carnall *et al.*¹⁶ and the Slater and spin-orbit parameters found from the C_{4v} SrF₂:Dy³⁺ crystal-field calculation of Sec. IV.



FIG. 1. 15 K broadband and narrow-band excitation spectra and transmission spectra of $\text{SrF}_2:0.05\% \text{ Dy}^{3+}$. The spectra are, from the top, transmission spectra; broadband excitation monitoring at 665 nm, corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions; narrow-band excitation spectrum of the $C_{4\nu}$ center, monitoring the $F_1 \rightarrow X_4$ transition at 15 058 cm⁻¹; narrow-band excitation spectrum of the $C_{3\nu}$ center, monitoring the $F_1 \rightarrow X_6$ transition at 14 898 cm⁻¹. The most intense transitions in the excitation spectra have been truncated to enable the minor features to be observed.

For the Kramers ion Dy^{3+} in sites of C_{4v} symmetry, all energy levels will transform as one of the point-group irreducible representations (irreps) Γ_6 or Γ_7 and similarly as one of Γ_4 or $\Gamma_{5,6}$ for sites of C_{3v} symmetry.¹⁷ For Kramers ions in these site symmetry environments there will be no point group forbidden transitions, although a polarization dependence may occur.¹⁵ Due to the multiple orientations of the Dy^{3+} sites that occur in the cubic fluorite structure, any polarization dependence will not be observable in absorption spectra, but may be present in fluorescence emission following polarized excitation.

The optical absorption of the ${}^{4}F_{9/2}$ multiplet of a 3-cmlong $SrF_2:0.1\%$ Dy³⁺ boule, at a sample temperature of 15 K, is presented in Fig. 1. The weak absorption of this multiplet necessitated the use of a higher-concentration sample for the absorption measurements than that used for the laserselective excitation measurements. Also shown in Fig. 1 is the broadband excitation spectrum obtained while monitoring fluorescence at 665 nm with a bandwidth of ≈ 10 nm, which corresponds to ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ fluorescence transitions. From considering the Dy³⁺ multiplet barycenters it is expected that centers involving more than a single Dy³⁺ ion will decay rapidly and nonradiatively by any of a number of available cross-relaxation pathways. Such cross relaxation quenching of excitation has been observed in the $CaF_2:Sm^{3+}$ by Wells and Reeves⁴ and by Jamison and Reeves¹⁸ in $CaF_2:Dy^{3+}$. As all the transitions seen in absorption are likewise seen in the broadband excitation spectrum, ruling out the presence of centers that undergo nonradiative decay, it is inferred that all the transitions observed in



FIG. 2. 15 K and 2 K fluorescence spectra from the ${}^{4}F_{9/2}$ multiplet for the C_{4y} center in $SrF_2:0.05\%$ Dy³⁺. Transitions are labeled by their emitting and terminating levels, respectively. For emission to the ${}^{6}H_{15/2}$ multiplet the respective spectra are (a) exciting $Z_1 \rightarrow F_1$ at 21 020 cm⁻¹, at a temperature of 15 K, (b) exciting $Z_1 \rightarrow F_2$ at 21 043 cm⁻¹, at a temperature of 15 K, and (c) exciting $Z_1 \rightarrow F_1$ at a temperature of 2 K with the spectrometer shutter closed as scanning over the laser frequency. The transitions labeled $A_4 - A_9$ are as indicated from crystal-field calculations.

the absorption and broadband excitation spectra of Fig. 1 belong to single Dy^{3+} ion centers.

Figure 1 presents the narrow-band excitation spectra of the ${}^{4}F_{9/2}$ multiplet, which separates the various excitation transitions into two dominant centers. The spectrum assigned to the C_{3v} center was obtained for detection of fluorescence at 14 898 cm⁻¹, corresponding to the $F_1 \rightarrow X_6$ emission, while that for the C_{4v} center was recorded while monitoring at 15 058 cm⁻¹, corresponding to $F_1 \rightarrow X_4$ emission.

The C_{3v} center excitation spectrum reveals a 2.5 cm⁻¹ splitting of the F_1 and F_2 energy levels, resolved in transitions from both the Z_1 and Z_2 states. A prominent feature in the broadband excitation spectra is the set of three transitions at approximately $21\,165 \text{ cm}^{-1}$, although comparison with the narrow-band excitation spectra of Fig. 1 reveals that this set of transitions is composed of four transitions, two from each of the C_{3v} and C_{4v} centers. The narrow-band spectra also highlight the specific association of the broad transitions at approximately 21 400 cm⁻¹ with the C_{3v} center, which are assigned as vibronic transitions, indicating that the C_{3y} center is more strongly coupled to lattice vibrations. Vibronic transitions of the C_{3y} center have previously been reported by Eremin et al.,¹⁴ and as will be discussed in a Sec. III B, the identification of vibronic transitions has been extended to include transitions associated with two distinct phonon frequencies, both of which are represented in the ${}^{4}F_{9/2}$ excitation spectrum.

The center assignments and energy levels associated with the excitation transitions to the ${}^{4}F_{9/2}$ multiplet are presented in Tables VI and VII below.

A. Laser-selective fluorescence: C_{4v} center

The C_{4v} site-selective fluorescence spectra originating from the ${}^{4}F_{9/2}$ multiplet are presented in Fig. 2. The spectra were obtained both at 15 K and 2 K to enable a confirmation of transitions originating from the F_1 - F_2 splitting of 23 cm⁻¹. Excitation of the C_{4v} center was via the $Z_1 \rightarrow F_1$ transition at 20 120 cm⁻¹. Emission to the ${}^{6}H_{15/2}$ multiplet is also shown for $Z_1 \rightarrow F_2$ excitation at 21 043 cm⁻¹.

For emission to the ${}^{6}H_{11/2}$ multiplet the two broad transitions at 14 995 cm⁻¹ and 14 987 cm⁻¹ are both present in the lower-temperature spectrum and are therefore attributed to F_1 emission. The broad features on the high-energy side of these transitions in the 15 K spectrum are attributed to F_2 emission. Fluorescence transitions with frequencies of 15 160 cm⁻¹, 15 063 cm⁻¹, and 15 058 cm⁻¹ are assigned to the $F_1 \rightarrow X_1, X_3, X_4$ transitions. In explaining the absence of an assigned $F_1 \rightarrow X_2$ transition it is noted that crystal-field calculations for the C_{4v} center predict the three energy levels X_2, X_3 , and X_4 to all lie in close proximity. The broadening in the high-energy tail of the $F_1 \rightarrow X_3$ transition is also indicative of another underlying transition, which is interpreted as the $F_1 \rightarrow X_2$ fluorescence. Reference to the infrared absorption is unable to clarify the accuracy of this assignment of the X_2 energy level. The levels here labeled X_3 and X_4 are indeed seen in absorption, but the presence of any level at the expected position of X_2 is masked by the relatively strong absorption to the X_1 state of the C_{3v} center at 5958 cm⁻¹. The assignment of X_2 must therefore be considered tentative and has not been included in the crystal-field calculations. The C_{4v} ⁶ $H_{11/2}$ levels are considered in more detail in the context of Zeeman infrared measurements, in Sec. V.

Fluorescence transitions for the remaining multiplets are assigned as indicated in Fig. 2, with the inferred energy levels tabulated in Table VI, below.

Fluorescence polarization

Polarized fluorescence spectra were recorded to confirm the C_{4v} assignment and where possible gain additional information on the irrep label of energy levels.

The chosen geometry has the laser beam incident along the X axis and the fluorescence monitored in the Z direction. The polarization of the laser is set to either the Y or Z direction, while the fluorescence polarization was measured in the X or Y direction. The standard notation for this configuration is X(AB)Z, where X indicates the laser propagation direction and Z the fluorescence propagation direction. The laser and fluorescence polarization are represented by A and B, respectively. As the propagation directions are fixed as stated above, the X and Z designations are dropped in subsequent labeling. For fluorescence polarization measurements on the C_{4v} center, the sample was oriented with the crystallographic $\langle 100 \rangle$ axes, and hence the principal axes of the centers, aligned along the XYZ axes.

For the majority of R^{3+} ions previously studied in CaF₂ and SrF₂, most transitions have been seen to occur via the electric-dipole transition moment, with meaningful polarization data obtained. However, for the CaF₂:Sm³⁺ C_{4v} centers, Wells and Reeves⁴ have reported that the electric and magnetic dipole moments appear to be of comparable magnitude, leading to degraded polarization information. Similarly, the presence of significant magnetic-dipole transition moments degrades the clarity of the polarization information in the SrF₂:Dy³⁺ C_{4v} center fluorescence. It has therefore been sought to further characterize the expected polarization behavior of the fluorescence transitions while allowing for the inclusion of both electric- and magnetic-dipole transition moments.

Strickland and Jones (Ref. 19, Table II) list the relative electric- and magnetic-dipole contributions to polarized emission for the C_{4v} center for the excitation-fluorescence geometry employed here. In general the fluorescence intensity in any particular polarization configuration will be a combination of magnetic- and electric-dipole contributions, for both absorption and emission transitions, with the resulting fluorescence polarization ratios dependent on the unknown relative magnitudes of the σ - and π -polarized electric-dipole and σ' - and π' -polarized magnetic-dipole transition moments. Despite the apparent arbitrariness in the fluorescence polarization introduced through the specific transition moments, it is shown below that definite constraints apply, even when both magnetic- and electric-dipole



FIG. 3. 15 K polarized fluorescence recorded for ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ with $Z_1 \rightarrow F_2$ excitation. All spectra are as obtained with the photoelastic modulator. The various spectra are, from the top, the dc signal recorded for Z-polarized excitation, the ac signal with Z-polarized excitation, the dc signal for Y-polarized excitation, and the ac signal for Y-polarized excitation.

moments contribute to the fluorescence.

Because all fluorescence polarization measurements will include any degradation present in the polarization properties of the excitation transition, it is important to clarify some aspects of the chosen excitation transition. From the various contributions to the polarized transition intensities¹⁹ it can be shown that for a purely electric-dipole absorption, all possible emission transition moments will give rise to unpolarized fluorescence if the laser is polarized in the Z direction. That is, the polarized fluorescence intensities will have the ratio ZX:ZY=1:1 for all fluorescence transitions if the absorption transition is purely electric dipole. This holds true even if the emission itself is magnetic dipole in nature and the absorption contains a contribution of both σ and π dipole moments. For an excitation transition with both magneticand electric-dipole contributions, the YX:YY and ZX:ZY intensity ratios will depend on the relative magnitudes of the σ -, π -, σ' -, and π' -polarized transition moments of the fluorescence transition.

Polarized fluorescence measurements were obtained with a photoelastic modulator (PEM) which acts as on oscillating 0λ to $\lambda/2$ waveplate. It was arranged in conjunction with a polarizer to provide detection of X- and Y-polarized emission at the extremes of the oscillation. The PEM enables recording of a dc signal proportional to the addition of the orthogonally polarized intensities and an ac signal proportional to the differences of the two intensities. The ac signal therefore gives a direct indication of any deviation from 1:1 intensity ratios. As it is this deviation, or lack of deviation, that is to be highlighted here, the raw signals are presented in Fig. 3 rather than the inferred polarized intensities.

The fluorescence spectra obtained with $Z_1 \rightarrow F_2$ excitation indicate intensity ratios of ZX:ZY=1:1 for all fluorescence transitions, whereas the YX:YY relative intensities are dependent on the particular transition. It is concluded that the $C_{4v}Z_1 \rightarrow F_2$ absorption transition moment is purely electric

TABLE II. Expected YX:YY:ZX polarized relative intensities for a purely electric-dipole σ -polarized absorption transition. The ratios are expressed in terms of the fluorescence transition moments.

Fluorescence transition	<i>YX</i> : <i>YY</i> : <i>ZX</i> relative intensities
$\Gamma_7 \rightarrow \Gamma_6,$	$\sigma(1:2:1) + \sigma'(2:1:1)$
$\Gamma_6 \rightarrow \Gamma_7$	
$\Gamma_7 \rightarrow \Gamma_7,$	$\pi(1:0:1) + \sigma(1:2:1)$
$\Gamma_6 \rightarrow \Gamma_6$	$+\pi'(0:1:1)+\sigma'(2:1:1)$

dipole. It is emphasized that this in itself implies nothing regarding the irreps involved in the transitions, as both π and σ electric-dipole absorptions (and any combination thereof) give rise to equal intensities for ZX and ZY spectra.

The expected polarized florescence intensities are considerably simplified by this confirmation of a purely electricdipole absorption transition. Further simplification is obtained through consideration of the particular irreps of the states involved in the absorption transition. For the $SrF_2:Dy^{3+}C_{4v}$ center, crystal-field calculations indicate that the Z_1 , Z_2 , and F_1 states transform as Γ_7 irreps and that F_2 transforms as the Γ_6 irrep. Hence, for an excitation transition of $Z_1(\Gamma_7) \rightarrow F_2(\Gamma_6)$ only the σ -polarized transition moment will be nonzero.

Table II presents the expected relative intensities for the YX:YY:ZX polarization configurations, following an electric-dipole σ -polarized absorption transition, such as the $Z_1(\Gamma_7) \rightarrow F_2(\Gamma_6)$ excitation transition. The irrep assignments of the levels involved in this absorption transition, initially based on a crystal-field calculation, are further justified by the self-consistency of the relative polarized intensities obtained with this excitation.

From Table II constraints on the relative intensities for different polarization configurations can be obtained. These constraints enable information on the irreps of the states involved in the fluorescence transitions to be determined from the fluorescence polarization data despite the dependence on the (unknown) σ, π, σ' , and π' transition moments. These constrained relative intensities are shown in Table III; it is also noted that these constraints are not independent. For example, observed ratios of YX:YY:ZX=1:1:1 would satisfy each of the three constraints for a $\Gamma_6 \rightarrow \Gamma_7$ transition. However, a YX:YY=1:1 ratio would in that case imply an equal contribution from the σ electric-dipole moment and

TABLE III. Constraints on YX:YY:ZX polarized relative intensities for a purely electric-dipole σ -polarized absorption transition. No assumptions are made regarding the electric- or magnetic-dipole nature of the fluorescence transitions.

$\Gamma_7 \rightarrow \Gamma_6, \ \Gamma_6 \rightarrow \Gamma_7$	$\frac{1}{2} \leq \frac{YX}{YY} \leq 2$	$1 \leq \frac{YX}{ZX} \leq 2$	$1 \leq \frac{YY}{ZX} \leq 2$
$\Gamma_7 \rightarrow \Gamma_7, \ \Gamma_6 \rightarrow \Gamma_6$	$0 \leq \frac{YX}{YY} \leq \infty$	$0 \leq \frac{YX}{ZX} \leq 2$	$0 \leq \frac{YY}{ZX} \leq 2$

TABLE IV. Observed polarized fluorescence data for the $SrF_2:Dy^{3+}$ C_{4y} center, for $Z_1 \rightarrow F_2\sigma$ -polarized excitation. Where possible the dominant electric- or magnetic-dipole process is noted for fluorescence transitions between states transforming as unlike irreps. The justification for assigning a transition as between like irreps is also shown.

Transition	Energy (cm ⁻¹)	irreps (CF fit)	YX	YY	ZX	ZY	Notes
$F_1 \rightarrow Z_1$	21020	$\Gamma_7 \rightarrow \Gamma_7$	3.2	1.0	3.9	3.4	а
$F_2 \rightarrow Z_2$	21005	$\Gamma_6 \rightarrow \Gamma_7$	1.0	1.3	1.0	1.3	indeterminate
$F_1 \rightarrow Z_2$	20982	$\Gamma_7 \rightarrow \Gamma_7$	1.9	1.0	2.7	2.6	с
$F_1 \rightarrow Z_3$	20967	$\Gamma_7 \rightarrow \Gamma_6$	1.0	1.8	1.2	1.1	(e.d. transition)
$F_1 \rightarrow Z_4$	20926	$\Gamma_7 \rightarrow \Gamma_7$	1.0	1.5	1.2	1.3	indeterminate
$F_1 \rightarrow Y_1$	17477	$\Gamma_7 \rightarrow \Gamma_7$	1.9	1.0	1.9	1.8	с
$F_2 \rightarrow Y_2$	17468	$\Gamma_6 \rightarrow \Gamma_6$	8.9	1.0	9.4	7.8	a, c
$F_2 \rightarrow Y_3$	17455	$\Gamma_6 \rightarrow \Gamma_7$	1.0	1.7	1.1	1.0	(e.d. transition)
$F_2 \rightarrow Y_4$	17448	$\Gamma_6 \rightarrow \Gamma_6$	1.0	1.2	1.1	1.0	d
$F_1 \rightarrow Y_2$	17445	$\Gamma_7 \rightarrow \Gamma_6$	1.2	1.6	1.2	1.0	(e.d. transition)
$F_1 \rightarrow Y_3$	17433	$\Gamma_7 \rightarrow \Gamma_7$	1.0	1.1	1.0	1.0	d
$F_1 \rightarrow Y_4$	17425	$\Gamma_7 \rightarrow \Gamma_6$	1.0	1.6	1.0	1.1	(e.d. transition)
$F_2 \rightarrow X_1$	15183	$\Gamma_6 \rightarrow \Gamma_7$	2.0	1.3	1.6	1.0	(m.d. transition)
$F_1 \rightarrow X_1$	15160	$\Gamma_7 \rightarrow \Gamma_7$	1.2	1.0	1.2	1.1	d
$F_1 \rightarrow X_3$	15063	$\Gamma_7 \rightarrow \Gamma_7$	1.0	2.7	3.0	2.7	b
$F_1 \rightarrow X_4$	15058	$\Gamma_7 \rightarrow \Gamma_6$	1.8	1.1	1.1	1.0	(m.d. transition)
$F_1 \rightarrow X_5$	14995	$\Gamma_7 \rightarrow \Gamma_7$	1.0	1.8	1.9	2.0	b
$F_2 \rightarrow W_1$	13416	$\Gamma_6 \rightarrow \Gamma_6$	1.0	2.0	2.6	2.2	b
$F_1 \rightarrow W_1$	13393	$\Gamma_7 \rightarrow \Gamma_6$	2.0	1.0	1.4	1.1	(m.d. transition)
$F_1 \rightarrow W_2$	13365	$\Gamma_7 \rightarrow \Gamma_7$	1.0	1.2	1.8	1.4	b
$F_1 \rightarrow W_3$	13288	$\Gamma_7 \rightarrow \Gamma_6$	2.4	1.0	1.6	1.1	(m.d. transition)
$F_1 \rightarrow W_4$	13254	$\Gamma_7 \rightarrow \Gamma_7$	1.0	2.8	4.3	3.0	b
$F_1 \rightarrow A_1$	12015	$\Gamma_7 \rightarrow \Gamma_7$	1.8	1.0	1.9	1.2	с
$F_1 \rightarrow A_2$	11982	$\Gamma_7 {\rightarrow} \Gamma_6$	2.0	1.8	1.2	1.0	

 $a\frac{1}{2} \leq \frac{YX}{YY} \leq 2$ not satisfied.

^b $1 \leq \frac{YX}{ZX} \leq 2$ not satisfied.

 $c_1 \leq \frac{YY}{ZX} \leq 2$ not satisfied.

 $^{d}a \rightarrow c$ satisfied, but conflict in ratios.

the σ' magnetic-dipole moment. This in turn implies a YX:YY:ZX=3:3:2 ratio. Therefore a 1:1:1 ratio is only consistent with a transition between like irreps.

Polarized fluorescence intensities of the $SrF_2:Dy^{3+}C_{4y}$ center were obtained by successive measurements of spectra in each of the four polarization configurations, while simultaneously normalizing with respect to the laser power, and are tabulated in Table IV. Some indication of the uncertainties in the polarization data is obtained by consideration of the variation of the ZX:ZY ratios from the expected (and experimentally observed with the photoelastic modulator) 1:1 ratios. In Table IV data is only presented for which the uncertainties of the measurement were not considered to be overwhelming.

A number of transitions are observed to proceed via a significant magnetic-dipole transition moment. To account for these transitions it is noted that an expansion of the freeion wave functions beyond that given in Table I shows the



FIG. 4. Narrow-band excitation of the ${}^{4}F_{9/2}$ multiplet for the C_{3v} center in SrF₂. The vibronic interval of 135 cm⁻¹ is indicated for several transitions, along with the TO phonon interval of 217 cm⁻¹.

emitting ${}^{4}F_{9/2}$ multiplet to contains an admixture of $\approx 9\%$ ${}^{6}F_{9/2}$. Therefore the fluorescence transitions to the *W* manifold ($\sim {}^{6}F_{11/2}$) and the A manifold ($\sim {}^{6}F_{9/2}$) will satisfy the ΔL , $\Delta S = 0$, $|\Delta J| = 0,1$ magnetic-dipole selection rules. The magnetic-dipole transitions to the ${}^{6}H_{11/2}$ multiplet are allowed through a small admixture of ${}^{6}F_{11/2}$ to the terminating multiplet.

The polarization data have facilitated the irrep labeling of 19 of the 33 experimentally determined energy levels. It is noted that this method of analysis of the polarized fluorescence in principle enables the relative magnitude of electric and magnetic transition moments to be determined. As the magnetic-dipole moments can be calculated directly from the wave functions, this would lead to a determination of the electric-dipole transition moments without the experimental difficulties involved in calibration of absolute intensities.

B. Laser-selective excitation: C_{3v} center

Apparent in the narrow-band excitation spectrum of the C_{3y} center in SrF₂:Dy³⁺ is the increased (relative to the C_{4y} center) intensity of the vibronic absorption transitions to the ${}^{4}F_{9/2}$ multiplet. The excitation spectrum of Fig. 4 and the fluorescence spectra to be discussed in the following section offer evidence for both 217 cm^{-1} and 135 cm^{-1} vibronics in $SrF_2:Dy^{3+}C_{3y}$ centers. The 217 cm⁻¹ electronic-vibronic separation of the transitions indicated in the lower part of the excitation spectrum is consistent with the frequency of the TO phonon in pure SrF2.²⁰ The physical origin of the 135 cm⁻¹ vibronic transitions indicated in Fig. 4 is not so apparent as there are no peaks in the SrF₂ phonon density of states in this region.²¹ Richman²² has reported similar vibronics of 140 cm in the $SrF_2:Sm^{2+}$ system, but without any assignment to the phonon involved in the transitions. Eremin, Luks, and Stolov¹⁴ observe a 134 cm⁻¹ repetition in the fluorescence spectrum to the ground multiplet of trigonal centers in $SrF_2:Dy^{3+}$, which was also attributed to vibronic transitions.

The chosen ${}^{4}F_{9/2}$ excitation transition for the C_{3v} center fluorescence studies was the $Z_1 \rightarrow F_2$ transition at 20 967 cm⁻¹. With the F_1 level placed only 2.5 cm⁻¹ below F_2 , the choice of excitation into the F_2 level was made because of the greater absorption strength to the F_2 level.

The fluorescence spectra to the nine lower multiplets are presented in Fig. 5. The upper-state F_1 - F_2 splitting is observed for many of the narrow-linewidth transitions, most notably those terminating on the ${}^6H_{11/2}$ multiplet. However, because of the broadening of the upper states of most terminating multiplets, this splitting is unresolved, with a consequent lack of resolution in the inferred energies of the terminating states.

For C_{3v} center fluorescence to the ground-state multiplet, the spectrometer shutter was closed when within 5 cm^{-1} of the laser frequency and transitions to the Z_1 level were therefore not directly observed as this eliminated both the F_1 and F_2 emission to that level. It is also apparent that the number of transitions to the ground multiplet by far exceeds that expected for the eight levels of ${}^{6}H_{15/2}$. These excess transitions are attributed to vibronic transitions, with many of these transitions consistent with a 135 cm⁻¹ vibronic interval. Of those vibronic transitions so indicated in Fig. 5, those associated with the $F_{1,2} \rightarrow Z_2, Z_3, Z_4$ electronic transitions were also identified by Eremin et al.¹⁴ Further inclusion of the 217 cm^{-1} TO phonon interval enables assignments to be made for many of the remaining transitions. In assigning the electronic transitions to the levels of ${}^{6}H_{15/2}$, the crystal-field calculation of Sec. IV B has been taken into account, which predicts the energy levels Z_6 and Z_7, Z_8 to lie at energies of $\approx 500 \text{ cm}^{-1}$ and $\approx 570 \text{ cm}^{-1}$, respectively. Crystal-field calculations also suggest a $\approx 5-10 \text{ cm}^{-1}$ separation of the Z_4 and Z_5 states, and therefore transitions to the Z_5 level may well be masked by the broad $F_{1,2} \rightarrow Z_4$ transition and nearby vibronic transitions. The emission spectra for transitions terminating on the ${}^{6}H_{13/2}$ multiplet reveal several transitions that are assigned as vibronic, with the same phonon offsets of 135 cm⁻¹ and 217 cm⁻¹ discussed above. The broad peak at $\approx 17200 \text{ cm}^{-1}$ is consistent with the possibility of several vibronic transitions of this frequency. However, it is noted that crystal-field calculations also place an electronic level (Y₅) at an energy such that the $F_{1,2} \rightarrow Y_5$ transitions would also be expected to be in the region of 17200 cm^{-1} . Of the three peaks between $17\,100 \text{ cm}^{-1}$ and $17\,150 \text{ cm}^{-1}$ only the two lower-frequency transitions are consistent with vibronics associated with the two phonon frequencies of 135 cm^{-1} and 217 cm^{-1} . The higher-frequency transition is assigned as electronic, partially guided by crystal-field calculations which place both the Y_6 and Y_7 levels at an energy such that the $F_{1,2} \rightarrow Y_6, Y_7$ transitions have a frequency within 5 cm^{-1} of this observed emission.

The fluorescence to the ${}^{6}H_{11/2}$ multiplet allows the determination of all six energy levels of this multiplet. The entire span of the energy levels is less than 150 cm⁻¹, and the transitions are sufficiently sharp for the F_1 - F_2 separation to be observed in the transitions to all six terminating energy levels. Transitions terminating on the X_2 level were not re-



FIG. 5. 15 K fluorescence spectra of the C_{3y} center in $SrF_2:Dy^{3+}$ for emission from the ${}^{4}F_{9/2}$ multiplet. For the ${}^{6}H_{15/2}$ spectrum the spectrometer shutter was closed in the region of the laser frequency, masking the $F_{1,2}$ $\rightarrow Z_1$ transitions. The vibronic interval of 134 cm⁻¹ is indicated for several transitions to the ${}^{6}H_{15/2}$ and ${}^{6}H_{13/2}$ multiplets, as are vibronic transitions associated with the 217 cm⁻¹ transverse optical phonon. Transitions are labeled by their emitting and terminating levels, respectively. The transitions labeled $A_4 - A_8$ and $W_6 - W_9$ are as indicated from crystal-field calculations.

solved from the X_3 transitions by Eremin, Luks, and Stolov.¹⁴ No vibronic transitions to this multiplet have been observed. The presence of strong vibronic transitions in only the fluorescence to the two lower multiplets (${}^{6}H_{15/2}$ and ${}^{6}H_{13/2}$) is also observed for the CaF₂:Dy³⁺ cubic center.¹⁸ While not explaining this occurrence of vibronic transitions, it is noted that from the C_{4v} -center-polarized fluorescence data that transitions to the two lower multiplets are distinct in that they are predominately electric-dipole processes, while transitions to the higher multiplets tend to proceed with a large magnetic-dipole contribution.

The transition frequencies for the $F_{1,2} \rightarrow W_6 - W_9$ expected on the basis of crystal-field calculations are also indicated in Fig. 5. The transitions to W_{10} and W_{11} are predicted to be a further $\approx 300 \text{ cm}^{-1}$ lower in frequency, but were not observed.

In the fluorescence spectrum to the A manifold, transition frequencies for $F_{1,2} \rightarrow A_4 - A_8$ predicted from the crystal-field calculations have also been indicated. Some of these transitions below 11 700 cm⁻¹ have been tentatively assigned, but to avoid a circular argument the energy levels of the A manifold inferred from these transitions were not included in the crystal-field least-squares calculation.

IV. CRYSTAL-FIELD ANALYSES

The energy level structures of the C_{4v} and C_{3v} centers have been analyzed through parametrized crystal-field calculations, enabling a comparison between the $SrF_2:Dy^{3+}$ and previously reported $SrF_2:R^{3+}$ sites. The wave functions determined from these calculations have also been used for analysis of the Zeeman infrared measurements discussed in Sec. V

The free-ion Hamiltonian used in the calculation is given by

$$H = \sum_{k} F^{k} f_{k} + \sum_{i} \zeta(r_{i}) \boldsymbol{l}_{i} \cdot \boldsymbol{s}_{i} + \alpha L(L+1) + \beta G(G_{2})$$
$$+ \Gamma G(R_{7}) + \sum_{k} M^{k} m_{k} + \sum_{k} P^{k} p_{k} + \sum_{k} T^{k} \boldsymbol{t}_{k} \qquad (1)$$

and includes relativistic and three-body corrections with fixed parameter values taken from Carnall, Crosswhite, and Crosswhite¹⁶ for Dy^{3+} in LaCl₃ (reproduced in Table V). The free-ion Slater and spin-orbit parameters and the average configuration energy were allowed to vary in the course of least-squares fitting to the experimental energy levels. The initial Slater and spin-orbit parameters were also taken from the LaCl₃: Dy^{3+} values reported by Carnall *et al.*¹⁶

The crystal-field Hamiltonians, Eqs. (2) and (3), have been expressed in terms of cubic and axial contributions, with each crystal-field parameter transforming as specific irreducible representations of a group chain,²⁸ in keeping with the common recent practice for investigation of the trivalent rare earths in fluorite-type crystals:^{9,4,6,19}

TABLE V. Minor free-ion parameters for Dy^{3+} used in the crystal-field calculations. Parameters are as taken from Carnall, Crosswhite, and Crosswhite (Ref. 16).

Parameter	Value (cm^{-1})	Parameter	Value (cm^{-1})
M _{Tot}	3.92	T_2	-423
P_{Tot}	771	T_3	-50
α	17.64	T_4	-117
eta	-608	T_{6}	334
Γ	1498	T_7	-432
		T_8	- 353

$$\begin{split} H_{C_{4v}} &= B_A^2 C_0^{(2)} + B_A^4 \bigg[C_0^{(4)} - \sqrt{\frac{7}{10}} (C_4^{(4)} + C_{-4}^{(4)}) \bigg] \\ &+ B_A^6 \bigg[C_0^{(6)} + \sqrt{\frac{1}{14}} (C_4^{(6)} + C_{-4}^{(6)}) \bigg] \\ &+ B_C^4 \bigg[C_0^{(4)} + \sqrt{\frac{5}{14}} (C_4^{(4)} + C_{-4}^{(4)}) \bigg] \\ &+ B_C^6 \bigg[C_0^{(6)} - \sqrt{\frac{7}{2}} (C_4^{(6)} + C_{-4}^{(6)}) \bigg], \end{split} \tag{2}$$

$$\begin{aligned} H_{C_{3v}} &= B_A^2 C_0^{(2)} + B_A^4 \bigg[C_0^{(4)} - \frac{1}{2} \sqrt{\frac{7}{10}} (C_3^{(4)} - C_{-3}^{(4)}) \bigg] \\ &+ B_A^6 \bigg[\sqrt{\frac{11}{42}} (C_3^{(6)} - C_{-3}^{(6)}) + \sqrt{\frac{5}{21}} (C_6^{(6)} + C_{-6}^{(6)}) \bigg] \\ &+ B_A^{6'} \bigg[C_0^{(6)} + \frac{4}{7} \sqrt{\frac{10}{21}} (C_3^{(6)} - C_{-3}^{(6)}) \\ &- \frac{4}{7} \sqrt{\frac{11}{21}} (C_6^{(6)} + C_{-6}^{(6)}) \bigg] \\ &+ B_C^4 \bigg[C_0^{(4)} + \sqrt{\frac{10}{7}} (C_3^{(4)} - C_{-3}^{(4)}) \bigg] \\ &+ B_C^6 \bigg[C_0^{(6)} - \sqrt{\frac{35}{96}} (C_3^{(6)} - C_{-3}^{(6)}) \\ &+ \frac{1}{8} \sqrt{\frac{77}{3}} (C_6^{(6)} + C_{-6}^{(6)}) \bigg]. \end{aligned}$$
(3)

1

The functional form of Hamiltonians of Eq. (2) and (3) effectively specifies the coordinate basis, with the exception of a remaining ambiguity that is discussed in the context of the Zeeman infrared measurements in Sec. V. The cubic parts of the C_{4v} and C_{3v} Hamiltonians differ from each other because of a change in the coordinate system, with the *z* axis taken along the fourfold and threefold rotation axes of the parent cubic basis, respectively. For the C_{3v} Hamiltonian, the *x* axis is further constrained to lying in one of the reflection planes of the C_{3v} center, with the *y* axis normal to this reflection plane.²³

The program "*f*-shell empirical" of M.F. Reid²⁴ was used to perform the least-squares fitting of the experimentally determined energy levels with those calculated with the Hamiltonians of Eqs. (1)-(3).

A. SrF₂:Dy³⁺ C_{4v}

For initial irrep and level assignments a preliminary calculation was carried out using the free-ion parameters of Carnall *et al.* and crystal-field parameters interpolated from the values reported for the C_{4v} centers of $\text{SrF}_2:\text{Tb}^{3+}$ (Ref. 6) and $\text{SrF}_2:\text{Ho}^{3+}$ (Refs. 4 and 9) The calculations provided irreps consistent with the polarization data for all levels included, with the minor exception of the X_2 and X_3 levels, where the level ordering was swapped. However, given that the calculation places these levels within 3 cm⁻¹ of each other, this was not considered to be a significant deviation outside of the general difference between calculated and experimental energy levels of $\leq 10 \text{ cm}^{-1}$.

A final standard deviation of 6.3 cm⁻¹ was obtained between the 33 experimental levels included in the leastsquares fitting and the calculated energy levels. The calculated and experimental energy levels are presented in Table VI along with the least-squares-determined crystal-field paramters. Figure 6 presents the crystal-field parameters that have been reported for $SrF_2: R^{3+} C_{4v}$ centers for seven lanthan ide ions and those for the Dy^{3+} calculation reported here. The magnitude of the B_C^4 parameter obtained from the Dy3+ crystal-field calculation does not fit with a smooth trend across the rare-earth series. Attempts to constrain the B_C^4 parameter to a magnitude in line with the value interpo-lated from the Tb³⁺ and Ho³⁺ parameters were unsuccessful; fixing the B_C^4 parameter to a value of -1100 cm^{-1} and allowing the remaining crystal-field parameters to vary in the least-squares calculation gives rise to significant changes in the calculated energy levels scheme, including changed level ordering that is inconsistent with the irrep assignments derived from the polarized fluorescence data.

The wave functions obtained from the best-fit procedure were used in the analysis of the Zeeman infrared measurements reported in Sec. V, and despite the apparent anomaly in the B_C^4 parameter the calculated and experimental Zeeman splitting patterns match sufficiently well to add to the confidence in the crystal-field calculation.

B. SrF₂:Dy³⁺ C_{3v}

For the C_{3v} center it was not possible to use polarized fluorescence data to provide information on irrep assignment. The reasons for this are two-fold: first, the expected C_{3v} center polarization ratios are intrinsically not well defined due to the nonorthogonal nature of the eight possible orientations of the C_{3v} principal axis,¹⁵ and second, what polarization behavior remains is, for many transitions, obscured by the overlapping and unresolved emission from both the F_1 and F_2 states. Therefore irrep assignment has been based solely on comparison between the calculated and experimentally determined energy levels. An initial calculation using the $SrF_2:Er^{3+}$ *J*-center crystal-field parameters⁷ TABLE VI. Experimental and calculated energy levels for the $SrF_2:Dy^{3+}C_{4v}$ center. Standard deviation data refers to fitted levels only. Experimental energies have been corrected to cm⁻¹ in vacuum.

			Energy	$y (cm^{-1})$				Energy	(cm^{-1})
Multiplet	Level	Irrep	Calc.	Expt.	Multiplet	Level	Irrep	Calc.	Expt.
${}^{6}H_{15/2}$	Z_1^{a}	Γ_7	2.2	0.0		A_3	Γ_6	9075	9080
10/2	Z_2^{a}	Γ_7	35	38		A_4	Γ_7	9207	9195 ^b
	Z_3^{a}	Γ_6	45	53		A_5	Γ_6	9258	9236 ^b
	Z_4^{a}	Γ_7	93	94		A_6	Γ_7	9272	9281 ^b
	Z_5	Γ_6	157			A_7	Γ_6	9287	9329 ^b
	Z_6	Γ_6	227			A_8	Γ_7	9343	9365 ^b
	Z_7	Γ_6	441			A_9	Γ_6	9560	9582 ^b
	Z_8	Γ_7	472		${}^{6}H_{5/2}$	B_1	Γ_7	10168	10172
${}^{6}H_{13/2}$	Y_1^{a}	Γ_7	3549	3543		B_2	Γ_6	10370	10360
	Y_2^{a}	Γ_6	3574	3575		B_3	Γ_7	10381	10390
	Y_3^{a}	Γ_7	3590	3587	${}^{6}F_{7/2}$	C_1	Γ_6	11048	11041
	Y_4^{a}	Γ_6	3595	3595		C_2	Γ_7	11141	11139
	Y_5	Γ_7	3669	3671		C_3	Γ_7	11205	11214
	Y_{6}	Γ_7	3762			C_4	Γ_6	11241	11247
	Y_7	Γ_6	3791		${}^{6}F_{5/2}$	D_1	Γ_7	12491	
${}^{6}H_{11/2}$	X_1^{a}	Γ_7	5859	5860		D_2	Γ_6	12523	
	X_2	Γ_6	5953			D_3	Γ_7	12602	
	X_3^{a}	Γ_7	5950	5957	${}^{6}F_{3/2}$	E_1	Γ_6	13337	
	X_4^{a}	Γ_6	5965	5962		E_2	Γ_7	13340	
	X_5^{a}	Γ_7	6033	6025	${}^{6}F_{1/2}$	_	Γ_6	13882	
	X_6	Γ_6	6038	6033	${}^{4}F_{9/2}$	F_1^{a}	Γ_7	21020	21020
${}^{6}H_{9/2}, {}^{6}F_{11/2}$	W_1^{a}	Γ_6	7627	7627		F_2^{a}	Γ_6	21038	21043
	W_2^{a}	Γ_7	7646	7655		F_3	Γ_7	21151	21162
	W_3^{a}	Γ_6	7739	7732		F_4	Γ_6	21187	21171
	W_4^{a}	Γ_7	7772	7766		F_5	Γ_6	21483	
	W_5	Γ_6	7797	7792					
	W_6	Γ_7	7844		Number of da	ta points			33
	W_7	Γ_6	7875		Number of fre	e parameters			10
	W_8	Γ_7	7892		Standard devia	ation			6.3 cm^{-1}
	W_{9}	Γ_6	7987						
	W_{10}	Γ_7	8124		Fi	tted crystal fiel	d and tree-ic	on parameters	F "
	W_{11}	Γ_6	8131		B_A^z B_A^+	B_A° B_C^{+}	$B_C^{\circ} = F_2$	F ₄	$F_6 \qquad \zeta$
${}^{6}H_{7/2}, {}^{6}F_{9/2}$	A_1^{a}	Γ_7	9006	9005	346 434	522 -1334	502 94448	67892 4	5273 1916
	A_2	Γ_6	9034	9038					

^aLevels with supporting polarization data for irrep assignment.

^bLevels not used in the least-squares calculation.

and the free-ion parameters of Carnall, Crosswhite, and Crosswhite¹⁶ was used to provide starting irrep assignments to the experimental energy levels. A total of 38 experimental energy levels were used in the parameter refinement. A number of additional levels, which were not included in the calculation due to uncertainty in their measurement or assignment, are found to agree closely with the calculated energies.

Table VII presents a listing of all the calculated energy levels below $\approx 22\,000 \text{ cm}^{-1}$ and the corresponding experimentally inferred energies. The standard deviation between the 38 experimental levels used in the least-squares procedure and the corresponding calculated levels is 6.6 cm⁻¹.

The parameters determined from the least-squares minimization are shown in Table VIII (see also Fig. 7) along with the parameters reported for the trigonal center⁹ in SrF₂:Ho³⁺ and the trigonal *J* center⁷ in SrF₂:Er³⁺. The similarity between the Dy³⁺ and Er³⁺ parameters is taken as an indication of the same structure of the two centers, while the disparity with the Ho³⁺ *B* center parameters indicates that the Ho³⁺ center reported in Ref. 9 is anomalous in the lanthanide series. For comparison the parameters given by Eremin, Luks, and Stolov¹⁴ for the SrF₂:Dy³⁺ C_{3v} center are also presented, based on an analysis of ten experimental energy levels. The comparison of parameters required a trans-



FIG. 6. Reported crystal-field parameters for the C_{4v} center in SrF₂: R^{3+} and those found here for SrF₂:Dy³⁺. The references for the parameters for rare earths other than Dy are Ce (Ref. 1), Pr (Ref. 2), Nd (Ref. 3), Sm (Ref. 4), Eu (Ref. 5), Tb (Ref. 6), and Ho (Ref. 9).

formation between the two different parametrization schemes used by Eremin et al. and that used in this work. Eremin *et al.* have employed a Hamiltonian of the form $\Sigma B_k^q V_k^q$ where the V_k^q polynomials are given by Al'tshuler and Kozyrev.²⁵ Eremin et al. also report only the absolute value of the B_4^3 and B_6^3 parameters, as the sign contains some ambiguity due to the possibility of different coordinate systems giving rise to different signs in these parameters²⁶ (although the relative signs are not arbitrary). To enable a comparison between parameters, the parameters of both Eremin et al. and those reported here were converted to the parametrization scheme of Wybourne $(\Sigma B_q^k C_q^k)$. The signs of the B_3^4 and B_3^6 parameters of Eremin *et al.* were then chosen to match those found here and then further transformed from the parametrization represented by Eqs. (2) and (3). It is these transformed parameters of Eremin et al. that are shown in Table VIII.

V. ZEEMAN INFRARED

The infrared absorption obtained for the ${}^{6}H_{13/2}$ and ${}^{6}H_{11/2}$ multiplets and the *W* manifold which consists of the mixed ${}^{6}H_{9/2}$ and ${}^{6}F_{11/2}$ multiplets is presented in Fig. 8. Absorption transitions have been assigned from correlation with the energy levels obtained from the laser selective fluorescence.

The Zeeman infrared absorption spectra of the C_{3v} and C_{4v} sites have been measured and compared to calculations based on the crystal-field analysis wave functions. In all cases the samples were oriented with the magnetic field along either the $\langle 111 \rangle$ or $\langle 100 \rangle$ crystal axis. Because of the multiple orientations of the C_{3v} and C_{4v} sites in the cubic fluorite crystal structure, the Zeeman splitting of centers aligned differently with respect to the magnetic field need to be considered, with it implicit that several magnetically inequivalent centers arise simultaneously in any given spectrum. As a matter of notation, angular brackets $\langle ijk \rangle$ refer to a general crystallographic direction, with [ijk] referring to the *z*-axis orientation of specific sites.

A. Crystal-field basis ambiguity

The crystal-field parameters and implied wave functions obtained in Sec. IV are only unique if accompanied by a specified coordinate basis, with both choices of the C_{4y} axes depicted in Fig. 9 possessing a Hamiltonian of the functional form in Eq. (2). Rotation of the coordinate basis by $\pi/4$ around the principal axis, while not a C_{4v} symmetry operation, will result in identical eigenvalues when accompanied by appropriate changes in parameter values. In the Wybourne parametrization this corresponds to a sign ambiguity in the B_4^k parameters, while transformation of wave functions between bases involves changes in the relative signs of the wave function $|JM\rangle$ components.²⁶ This ambiguity in crystal-field parameters and wave function decomposition does not influence the energy level structure, irrep symmetry, or the first-order Zeeman interactions. It can, however, have measurable influence on the higher-order Zeeman interactions involving mixing between states.²⁷ The reduction of the symmetry that is imposed by the application of a magnetic field at an oblique angle to the principal axis can enable the appropriate basis to be determined. This is accomplished by calculating the Zeeman splittings with the wave functions obtained from the crystal-field calculations and with the relevant magnetic field components for each of the two bases. The appropriate magnetic field components for both bases of Fig. 9 are calculated in Sec. V B with the calculated Zeeman splittings in each basis compared with that obtained experimentally. While the focus here is on an experimental determination of the C_{4v} basis, if the structure of the center is known, such a determination may also be obtained through appealing to ab initio calculations. Superposition model calculations for the C_{4v} center in $\mathrm{SrF}_2:R^{3+}$ and $\mathrm{CaF}_2:R^{3+}$ have been reported by Reid and Butler,²⁸ with these calculations indicating that for the crystal-field parameters reported here the appropriate x, y basis is that depicted in Fig. 9(A).

For the C_{3v} center, bases can be chosen that are rotated by 180° around the *z* axis relative to each other, as shown schematically in Fig. 10. Both bases have a crystal-field Hamiltonian of the form given in Eq. (3). This ambiguity in the C_{3v} basis is entirely analogous to that of the C_{4v} center, as can be seen from recognizing that the π rotation of the x, y axes is equivalent to a $\pi/3$ rotation when the C_{3v} symmetry operations are taken into account.

Calculations based on an effective charge model and the known strcture of the C_{3v} center have been reported for $SrF_2: R^{3+} C_{3y}$ centers by Lesniak and Richardson;²⁹ however, the basis used for these calculations was not reported. An indication of the appropriate basis was obtained here from a simple point-charge model calculation for both bases of Fig. 10. The predicted parameters are shown in Table IX along with the parameters obtained from the crystal-field calculation of Sec. IV B. The calculated crystal-field parameters of Lesniak and Richardson are also shown for comparison. While such a simple point-charge calculation should not be expected to produce particularly accurate parameters, the B_A^4/B_C^4 and $B_q^6/B_{q'}^6$ parameter ratios and the relative signs of the parameters will be more meaningful, due to an effective cancellation of the inaccuracies in the radial integrals. This point-charge calculation suggests that the appropriate basis for the C_{3v} crystal-field parameters obtained in Sec. IV B is

TABLE VII. Experimental and calculated energy levels for the $SrF_2:Dy^{3+}C_{3v}$ center. Experimental energies have been corrected to cm^{-1} in vacuum.

			Energy	(cm^{-1})				Energy (cm^{-1})
Multiplet	Level	Irrep	Calc.	Expt.	Multiplet	Level	Irrep	Calc.	Expt.
⁶ <i>H</i> _{15/2}	Z_1	$\Gamma_{5,6}$	-1.7	0.0	${}^{6}H_{7/2}, {}^{6}F_{9/2}$	A_1	Γ_4	9020	9019
	Z_2	Γ_4	35	39	112 / 912	A_2	Γ_{56}	9038	9041
	Z_3	Γ_4	69	73		A_3	Γ_4	9067	9071
	Z_4	$\Gamma_{5,6}$	122	123		A_4	Γ_4	9318	9319 ^a
	Z_5	Γ_4	128			A_5	$\Gamma_{5.6}$	9334.5	9329 ^a
	Z_6	Γ_4	499	491		A_6	Γ_4	9334.8	9339 ^a
	Z_7	$\Gamma_{5,6}$	563	564		A_7	$\Gamma_{5.6}$	9384	9354 ^a
	Z_8	Γ_4	567	571		A_8	Γ_4	9394	9394 ^a
⁶ H _{13/2}	Y_1	Γ_4	3558	3554		A_9	Γ_4	9722	
	Y_2	Γ_4	3620	3625	${}^{6}H_{5/2}$	B_1	Γ_4	10263	10272
	Y_3	$\Gamma_{5,6}$	3633	3638	0,2	B_2	Γ_4	10401	10399
	Y_4	Γ_4	3643	3643		$\bar{B_3}$	Γ_{56}	10410	10414
	Y_5	Γ_4	3777		${}^{6}F_{7/2}$	C_1	Γ_4	11088	11082
	Y_{6}	Γ_4	3837	3830 ^a		C_2	Γ_4	11288	11300
	Y_7	$\Gamma_{5,6}$	3840	3830 ^a		$\bar{C_3}$	Γ_4	11327	11326
${}^{6}H_{11/2}$	X_1	Γ_4	5968.5	5956.5		C_4	$\Gamma_{5.6}$	11336	11334
	X_2	$\Gamma_{5,6}$	5984.5	5990.0	${}^{6}F_{5/2}$	D_1	$\Gamma_{5.6}$	12553	
	X_3	Γ_4	5991.5	5995.0		D_2	Γ_4	12558	
	X_4	Γ_4	6029.5	6020.0		D_3	Γ_4	12721	
	X_5	$\Gamma_{5,6}$	6057.0	6048.5	${}^{6}F_{3/2}$	E_1	$\Gamma_{5.6}$	13408	
	X_6	Γ_4	6077.9	6067.0		E_2	Γ_4	13412	
${}^{6}H_{9/2}, {}^{6}F_{11/2}$	W_1	$\Gamma_{5,6}$	7644	7649	${}^{6}F_{1/2}$	_	Γ_4	13944	
	W_2	Γ_4	7650	7655	${}^{4}F_{9/2}$	F_1	$\Gamma_{5.6}$	20970.7	20964.7
	W_3	Γ_4	7759	7753		F_2	Γ_4	20971.8	20967.2
	W_4	$\Gamma_{5,6}$	7761	7761		$\overline{F_3}$	$\Gamma_{5.6}$	21152	21154
	W_5	Γ_4	7793	7787		F_4	Γ_4	21157	21162
	W_6	Γ_4	7954			F_5	Γ_4	21658	21660
	W_7	$\Gamma_{5,6}$	7957						
	W_8	Γ_4	7969		Number of data	points			38
	W_9	Γ_4	7982		Number of free	parameters			11
	W_{10}	Γ_4	8273		Standard deviat	ion			6.6 cm^{-1}
	W_{11}	$\Gamma_{5,6}$	8299						

^aLevels not used in parameter refinement.

that depicted in Fig. 10(A) and that the calculations of Lesniak and Richardson have been performed in the alternative basis of Fig. 10(B).

B. Magnetic field components for Zeeman calculations

To calculate the Zeeman splittings of the C_{4v} and C_{3v} center energy levels, the magnetic field components are required for the specific geometrical arrangement of the applied field with respect to the C_{4v} and C_{3v} bases. Because there are multiple orientations of a given center in the cubic host crystal, several magnetically inequivalent centers may be present in the sample for a given experimental arrangement. As an example of site- and basis-dependent magnetic field components the specific case of $B \| \langle 111 \rangle$ crystalographic axes is considered in detail for both the C_{4v} and C_{3v} centers.

The C_{4v} center will have charge compensating fluorine in any one of the six nearest-neighbor $\langle 100 \rangle$ interstitial positions, thus defining the orientation of the particular site. For this particular configuration of the magnetic field with a C_{4v} center, all six orientations of the center have the principal axis equally inclined to the magnetic field, at an angle of 54.7°. The x and y axes can be chosen to include an arbitrary rotation of 0°, 90°, 180°, or 270° about the z axis as the wave functions will be independent of such a rotation.

For the basis of Fig. 9(A), with the x and y axes along the crystallographic [100] and [010] directions, by explicitly considering all six centers it is found that the magnetic field components can be expressed as

$$B_x = \frac{1}{\sqrt{3}}B, \quad B_y = \frac{1}{\sqrt{3}} \quad B_z = \pm \frac{1}{\sqrt{3}}B.$$

TABLE VIII. The free-ion and crystal-field parameters found for the $\text{SrF}_2:\text{Dy}^{3+}$ C_{3v} center for refinement with 38 experimental energy levels. Parameters found by Eremin *et al.* and those reported for other $\text{SrF}_2:R^{3+}$ C_{3v} centers are given for comparison. The Slater parameters are not determined in the calculations of Refs. 14 and 7, and not reported for the calculations of Ref. 9. The spin-orbit parameter is not determined in the single multiplet calculations of Ref. 14. All parameters are in units of cm⁻¹.

Parameter	Dy C_{3v} This work	Dy (Ref. 14)	Eu (Ref. 5)	Ho (<i>B</i>) (Ref. 9)	Er (<i>J</i>) (Ref. 7)
F ₂	94325		83206		
F_4	67516		59076	_	_
F_{6}	45641		42435	_	_
ζ	1913		1327	2136	2578
B_A^2	184	206	217	52	189
B_A^4	99	- 49	106	-184	-142
B_A^6	-18	531	- 193	- 526	-222
B_A^6	85	-108	-47	-149	106
B_C^4	1423	1369	1227	-58	1097
$B_C^{\widetilde{6}}$	1168	972	1091	605	999

The sign on the B_z component indicates whether a particular site has the *z* component of the magnetic field parallel or antiparallel to the principal axis. The symmetry-allowed $m\pi/2$ rotations of the *x* and *y* axes around the *z* axis enable these axes to be chosen to have a positive magnetic field component.

For the alternative basis of Fig. 9(B), with the x and y axes along the [110] and [$\overline{1}$ 10] directions, the magnetic field components can be expressed as

$$B_x = 0, \quad B_y = \sqrt{\frac{2}{3}}B, \quad B_z = \pm \frac{1}{\sqrt{3}}B.$$

The allowed $m\pi/2$ rotations about the z axis enable the B_y component to always be chosen as positive.

For the C_{3v} center orientated with $B||\langle 111 \rangle$ there are two sets of magnetically inequivalent sites. Of the eight C_{3v} prin-



FIG. 7. Reported crystal-field parameters for the C_{3v} center in $\text{SrF}_2: R^{3+}$ and those found here for $\text{SrF}_2: \text{Dy}^{3+}$. References are given in Table VIII.

cipal axis orientations there will be two sites in which the principal axis is aligned parallel or antiparallel with the magnetic field. The remaining six sites will be arranged at an oblique angle to the field.

(a) The parallel sites [111], [111]. The magnetic field components are given by $B_x = B_y = 0$, $B_z = \pm B$. Because both B_x and B_y are zero, no ambiguity in the Zeeman splittings results from the two possible C_{3y} bases.

(b) The oblique sites $[\bar{1}11]$, $[11\bar{1}]$, $[11\bar{1}]$, [111], [111], $[\bar{1}1\bar{1}]$, [111]. These sites have the principal axis at an angle of 70.5° to the magnetic field. For the basis of Fig. 10(A) all six oblique sites can be taken to have their magnetic field components given by

$$B_x = \pm \frac{2\sqrt{2}}{3}B, \quad B_y = 0, \quad B_z = \pm \frac{1}{3}B,$$

where the signs of B_x and B_z are not independent. The allowed threefold rotation of the x and y axes about the z axis has been employed so that the B_y component can always be chosen to be zero. For the alternative C_{3v} basis, Fig. 10(B), the magnetic field components are given by

$$B_x = \pm \frac{2\sqrt{2}}{3}B, \quad B_y = 0, \quad B_z = \pm \frac{1}{3}B.$$

Similar geometric considerations apply to samples aligned with $B || \langle 100 \rangle$, with the results summarized in Tables X and XI.

C. Experimental results and analysis

Zeeman infrared absorption measurements were carried out on oriented SrF₂:Dy³⁺ samples using the 4 T axial magnet incorporated into the Bio-Rad FTIR spectrometer described in Sec. II. Calculated Zeeman splittings are based on the wave functions obtained from the crystal-field leastsquares analyses. The matrix elements take into account all the J_z components for the LSJ of that multiplet for which the normalized coefficients are greater than 0.1 (1%). For the W manifold, the states considered contained a significant admixture of both ${}^{6}H_{9/2}$ and ${}^{6}F_{11/2}$ multiplets. Likewise, states of the A manifold consisted of significant contributions from both ${}^{6}H_{7/2}$ and ${}^{6}F_{9/2}$ multiplets. For calculating the splitting of states of these manifolds both LSJ contributions were taken into account. The Z_1 and Z_2 Zeeman interactions were included for both C_{3v} and C_{4v} centers, although the effects of mixing between these levels was minor. To enable comparison with experiment, the zero-field transition frequencies for the calculations were set equal to those seen experimentally, rather than that obtained from the crystal-field calculation. Importantly, this sets the separation between energy levels to that obtained from experiment. It is this separation between levels that determines the magnitude of the interactions between levels when a magnetic field is applied, and the few cm^{-1} inaccuracies in the calculated energy level positions would then be expected to significantly alter the calculated Zeeman patterns.



1. C_{4v} center, $B || \langle 111 \rangle$

For the Zeeman interaction of the C_{4v} center in samples oriented with the crystal $\langle 111 \rangle$ axis parallel to the magnetic field, as noted earlier all six possible orientations of the center are magnetically equivalent. The splitting of a doublet in the $B \| \langle 111 \rangle$ configuration has been related to the perpendicular (\bot) and parallel ($\|$) splitting factors by the relationship

$$S_{\langle 111 \rangle} = \sqrt{\frac{S_{\parallel}^2 + 2S_{\perp}^2}{3}}.$$
 (4)

Table XII summarizes the experimental and calculated Zeeman splittings obtained for a number of levels of the C_{4v} site. For the A_1 level, the observation of all four transitions between the Z_1 - and A_1 -split Kramers doublets enabled the splitting factor of both the ground state and the A_1 level to be deduced. For the Zeeman splitting of the W_2 level all four transitions were also observed, permitting the determination of the splittings of the W_2 level and an independent measurement of the ground-state splitting factor. For the Zeeman splittings of the X_1 level only transitions between either the lower split levels or the upper levels of the Z_1 and X_1 doublets were observed. Therefore to enable the splitting of the X_1 state to be deduced, the Z_1 splitting was taken from the



FIG. 8. 15 K infrared transmission spectra of SrF₂: 0.05% Dy³⁺. From left to right, the spectra are of the ${}^{6}H_{13/2}$ multiplet ${}^{6}H_{11/2}$ multiplet, and ${}^{6}H_{9/2}$ and ${}^{6}F_{11/2}$ multiplets (the *W* manifold). The *W* manifold spectrum has a steeply declining detector response removed for clarity.

measurements discussed above. Likewise, for the interaction of the Y_1 state with the magnetic field the Z_1 splitting behavior found from the A_1 and W_2 transitions was employed in deducing the Y_1 splitting factors. Very good agreement between measured and calculated splitting factors has been obtained for all the above-mentioned C_{4y} states.

Because of the lack of influence of neighboring energy levels in the Zeeman interactions of the states given in Table XII, the calculated splitting patterns are independent of the choice of x, y basis. For the C_{4y} center an exception to this basis independence lies in the Zeeman splittings of the X_2 , X_3 , and X_4 levels at approximately 5960 cm⁻¹. As these three levels consist of the different irreps of $X_2(\Gamma_6)$, $X_3(\Gamma_7)$, and $X_4(\Gamma_6)$ and all three levels lie within $\approx 20 \text{ cm}^{-1}$, there exists the possibility of considerable mixing of the wave functions and basis-dependent repulsion of the energy levels as they split under the action of the magnetic field. Unfortunately the presence of three close-lying levels, rather than just a Γ_6, Γ_7 pair, leads to the complicated splitting pattern of Fig. 11. The zero-field energy of the X_2 level has also not been unambiguously identified, although there are indications from the laser selective fluorescence that it lies $\approx 1-2$ cm⁻¹ below X_3 . One further complication to the analysis is the presence of an overlapping absorption transition to the $C_{3v}X_1$ level at 5958 cm⁻¹. Therefore the $B||\langle 111 \rangle$ Zeeman spectra for the $C_{4y}X_2$, X_3 , and X_4 levels and the $C_{3v}X_1$ level have been analyzed concurrently. The Zeeman infrared absorption spectra for these states are



FIG. 9. The two possible bases of the C_{4v} symmetry center for the Hamiltonian used here. In the upper figure, the small spheres represent the fluorine ions surrounding the rare-earth ion (large sphere). The symmetry of the center is shown schematically as viewed looking down the *z* axis. The square represents the cross section of the fluorine cage enclosing the rare-earth ion.

FIG. 10. The two possible bases of the C_{3v} symmetry center for the Hamiltonian used here. In the upper figure, the small spheres represent the fluorine ions surrounding the rare-earth ion (large sphere). The symmetry of the center is shown schematically as viewed looking down the *z* axis.

TABLE IX. Comparison of $\text{SrF}_2:\text{Dy}^{3+}C_{3v}$ crystal-field parameters with those calculated from a point-charge calculation in the two bases of Fig. 10. All parameter values are given in units of cm⁻¹.

C _{3v}	Point-cha	arge calc.	CF calc.	Lesniak and Richardson
Parameter	Basis A	Basis B	(Table VII)	(Ref. 29)
B_A^2	215	215	184	191
B_C^4	315	-150	1423	-643
B_A^4	3	468	99	2013
B_C^6	88	38	1168	492
$B_A^{\tilde{6}}$	0	109	-18	1433
B_A^6 '	1	51	85	668

shown in Fig. 11, together with the experimental and calculated splitting diagrams for the two choices of C_{4v} basis. The X_2 - X_3 separation was taken as 1 cm⁻¹. In these calculations the isolation of the $C_{3v}X_1$ level from other states of this site precludes there being any difference between the C_{3v} basis choices.

As shown in Fig. 11 there are significant differences in the calculated splitting patterns for the two choices of C_{4v} basis, most notably in the differing separation of the pairs of transitions marked by * and †. In the comparison with experiment, the calculated transitions of basis B marked \dagger are not observed, while conversely not all the observed transitions are adequately described by the calculation of basis A. As both calculations show some discrepancy with the experimental results, the appropriate basis inferred from the superposition model calculations of Reid and Butler²⁸ [basis A, with the x, y axes along the $\langle 100 \rangle$ and $\langle 010 \rangle$ crystal axes] cannot be objectively confirmed from the available experimental data. However, it is considered that higher-field measurements of these transitions, particularly those marked * in Fig. 11, have the potential to provide an experimental confirmation of the C_{4v} coordinate basis.

Splitting factors for the X_2 , X_3 , and X_4 states cannot be unambiguously determined from experiment, and therefore no quantitative comparison between theory and experiment has been made for these states.

TABLE X. Magnetic field components for the C_{4v} symmetry center bases of Fig. 9.

Field orientation	Basis	Centers	$\mathbf{B}_x, \mathbf{B}_y, \mathbf{B}_z$
$\boldsymbol{B} \ \langle 111 \rangle$	A	All	$\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \pm \frac{1}{\sqrt{3}}.$
	В	All	$0, \sqrt{\frac{2}{3}}, \pm \frac{1}{\sqrt{3}}$
$\boldsymbol{B} \ \langle 100 \rangle$	А, В А	[100], [Ī00] [010], [0Ī0], [001], [00Ī]	0,0,±1 1,0,0
	В	[010], [010], [001], [001]]	$\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0.$

2. C_{3v} center, $B \| \langle 100 \rangle$

For the C_{3v} center only the transitions to the X_2 , X_3 , and Y_1 states were sufficiently intense and spectrally isolated to be amenable to Zeeman infrared measurements.

Figure 12 presents the Zeeman spectra of the $X_2(\Gamma_{5,6})$ and $X_3(\Gamma_4)$ levels of the $C_{3\nu}$ center, lying at energies of 5990 cm⁻¹ and 5995 cm⁻¹, respectively. Because of the small separation of these two levels, there is repulsion of the split energy levels as they move closer together with increasing field strength, leading to a *x*,*y*-basis dependence in the calculated Zeeman splittings.

For the C_{3v} centers in a geometry of **B** $||\langle 100 \rangle$ orientated sample, all eight C_{3v} site orientations are magnetically equivalent. In this Zeeman geometry each zero-field transition will give rise to four Zeeman transitions. A feature of the splittings of Fig. 12 is that what would be expected to be a single transition does in fact split into several resolvable transitions at high magnetic fields. This is attributed to a small sample misalignment, with the eight C_{3y} center orientations occurring in the cubic fluorite structure no longer equally inclined to the magnetic field direction. We note that the magnet used for these experiments is constructed in such a way that the sample orientation cannot be modified once the magnetic has been cooled, and it was therefore not possible to make adjustments to the sample alignment on the basis of high-field spectra. The Zeeman splittings of the C_{4y} center in a $\langle 100 \rangle$ -orientated sample, obtained at the same time as those of the C_{3v} center, are also consistent with sample misalignment. Similar anomalous Zeeman splittings have been observed in SrF_2 : Er^{3+} and BaF_2 : Er^{3+} by Wells, Dean, and Reeves³⁰ and were attributed to a non- C_{3v} distortion of the site. While this possibility cannot be entirely excluded, we note that the measurements of Wells et al. were made with the same magnetic used here. It is also likely that with their unusually large splitting factors Er^{3+} and Dy^{3+} ions in this center will be particularly sensitive to magnetic field misalignment.

Figure 12 shows the calculated Zeeman splittings for both C_{3y} bases, with the indicated transitions showing a significantly smaller energy level repulsion for the basis of Fig. 10(A). Sample misalignment is included in the calculations for both C_{3v} basis choices, with a misalignment of (θ, ϕ) $=(4^{\circ},1^{\circ})$. Variations is the misalignment angles produce only a small change in the calculated transition energies, and in all cases the transitions marked by braces (}) are in significantly better agreement for basis A. Quantitative discrimination between the calculations of Fig. 12 is provided from the standard deviation between measured and calculated transition energies, at a field strength of 3 T; for bases A and B the standard deviation is 0.48 cm^{-1} and 0.81 cm^{-1} , respectively. It is concluded that the appropriate basis for the C_{3y} center with crystal-field parameters of Sec. IV B is that depicted in Fig. 10(A). This is also the basis that is expected from the comparison of the C_{3y} center point-charge calculations and the crystal-field parameters derived from the laserselective fluorescence data.

The Zeeman infrared splittings of the $C_{3v} Y_1$ level have also been examined. Only two of the four transitions be-

Field orientation	Basis	Centers	B_x, B_y, B_z
$B \ \langle 111 \rangle$	A, B	[111],[111]	0,0,±1.
	Α	[Ī11], [1Ī1], [11Ī], [111], [Ī11], [Ī1Ī], [111]	$\pm \frac{2\sqrt{2}}{3}, 0, \pm \frac{1}{3}$
	В	[Ī11], [1Ī1], [11Ī], [111], [Ī1Ī], [Ī1Ī], [111]	$\pm \frac{2\sqrt{2}}{3}, 0, \pm \frac{1}{3}$
$\boldsymbol{B} \ \langle 100 \rangle$	Α	All	$\pm\sqrt{\frac{2}{3}},0,\pm\frac{1}{\sqrt{3}}$
	В	All	$\pm \sqrt{\frac{2}{3}}, 0, \pm \frac{1}{\sqrt{3}}$

TABLE XI. Magnetic field components for the C_{3v} symmetry center bases of Fig. 10.

tween the Zeeman sublevels are observed, and therefore the $\langle 100 \rangle$ splitting factors for both the Z_1 and Y_1 states cannot be directly determined. With the observed splittings due to the difference in the Zeeman splittings of the two states only the difference in the splitting factors $\Delta S_{\langle 100 \rangle} \equiv |S_{\langle 100 \rangle}(Z_1) - S_{\langle 100 \rangle}(Y_1)|$ can be inferred from experiment. The experimental and calculated differences in splitting factors at 2 T are $\Delta S_{\langle 100 \rangle 2T} = 1.07$ and 0.88, respectively. The calculation is based on individual level splitting factors of $S_{\langle 100 \rangle}(Z_1)_{2T} = 10.03$ and $S_{\langle 100 \rangle}(Y_1)_{2T} = 9.15$.

VI. CONCLUSION

Through laser site-selective spectroscopy the two dominant sites in $\text{SrF}_2:0.05\% \text{ Dy}^{3+}$ have been characterized. These sites have been found to be of C_{4v} and C_{3v} symmetry.

Polarized fluorescence of the C_{4v} center has enabled irrep assignment of many levels and has shown that magneticdipole transitions moments are significant in many transitions. Crystal-field analyses of the C_{4v} center produces crystal-field parameters consistent with trends throughout the rare-earth series.

The C_{3v} center has a stronger coupling to the SrF₂ lattice, as revealed by the large number of vibronic transitions with an increased relative intensity compared to the C_{4v} center. Vibronics associated with an unassigned phonon of energy 135 cm⁻¹ and the transverse optical phonon with an energy of 217 cm⁻¹ have been identified. The C_{3v} crystal-field parameters indicate a site with the same structure as the

TABLE XII. Experimental and calculated splitting factors for the $SrF_2:Dy^{3+} C_{4v}$ center.

C_{4v}	Field		Calculated		Expt.
Level	(Tesla)	S_{\parallel}	S_{\perp}	$S_{\langle 111 angle}$	$S_{\langle 111 angle}$
Z_1	1.5	16.79	0.65	9.72	9.7
Y_1	2.0	14.38	0.09	8.30	8.4
X_1	4.0	12.83	0.13	7.41	7.4
W_2	1.0	2.27	4.18	3.66	3.5
A_1	1.5	0.07	2.97	2.43	2.4



FIG. 11. (left) Zeeman infrared absorption spectra of $\operatorname{SrF}_2:\operatorname{Dy}^{3+}$ showing the C_{4v} and C_{3v} absorption spectra in the region of 5960 cm⁻¹ for magnetic field strength between 0 and 4 T, with $B \| \langle 111 \rangle$. Note that the zero-field position of X_2 of the C_{4v} center is not observed, but calculations put it in this region. (center, right) Calculated and measured splitting diagram for the X_2 , X_3 , and X_4 levels of the C_{4v} center and the X_1 level of the C_{3v} center. The calculation are for the C_{4v} basis choices A and B, respectively, of Fig. 9, and for the X_2 level lying 1 cm⁻¹ below X_3 . The solid line is the calculated transition energies of the the C_{4v} center, with the dashed lines showing the C_{3v} transitions.



FIG. 12. Zeeman infrared absorption spectra of $SrF_2:Dy^{3+}$, showing the $\langle 100 \rangle$ splittings of X_2 and X_3 of the C_{3v} center. The X_4 level was also included in the calculations. Transitions originating from levels greater than 10 cm⁻¹ above ground state are not shown in the calculations. The two calculations are for the *x*, *y* bases of Fig. 10.

 $SrF_2:Eu^{3+}$ and $SrF_2:Er^{3+}(J)$ trigonal centers. In contrast, the crystal-field parameters display considerable disparity with those reported for the C_{3v} center of $SrF_2:Ho^{3+}$, indicating that it is the Ho³⁺ trigonal center that is to be considered anomalous in the $SrF_2:R^{3+}$ series.

The accuracy of the wave functions determined from the crystal-field calculation, for both the C_{4v} and C_{3v} sites, has been tested through examination of the Zeeman infrared splitting of levels in the lower-lying multiplets. An ambiguity present in the C_{4v} and C_{3v} crystal-field parametrizations, due to the two possible choices of coordinate bases, has been examined through the nonlinear Zeeman interaction. The C_{3v}

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basis appropriate for the crystal-field parameters reported here has been experimentally determined from Zeeman infrared absorption measurements.

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