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# Site-selective spectroscopy of the $Ho^{3+}$ dimer centers in $CaF_2$ and $SrF_2$ crystals

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Three distinct dimer centers are observed in $CaF_2$:0.1% $Ho^{3+}$ crystals while two similar centers are present in $SrF_2$:0.1% $Ho^{3+}$ crystals. The $Ho^{3+}$ dimer centers in $CaF_2$ are formed by preferential pair aggregation of $1|1_1$ ($C_{4v}$ symmetry) and $1|1_2$ ($C_{3v}$ symmetry) configuration monomers. The $1|1_1$ and $1|1_2$ centers comprise a single $Ho^{3+}$ ion and a charge-compensating $F^-$ ion which occupies the nearest-neighbor and next-nearest-neighbor interstitial position respectively, relative to the $Ho^{3+}$ ion. In $SrF_2$:$Ho^{3+}$, dimerization of $1|1_1$ rather than $1|1_2$ monomers appears to be favorable. In both $CaF_2$ and $SrF_2$ lattices, the type and population of $Ho^{3+}$ dimer centers that form at the intermediate $Ho^{3+}$ concentrations (~0.1%) are determined by the distribution of monomer centers at low concentrations ($\lesssim$0.01%). Crystal-field energy levels and some fluorescence lifetime data for the five dimer centers are presented. For each dimer center in $SrF_2$, the fluorescence lifetime of the *D* multiplet is about three times that of the corresponding center in $CaF_2$. [S0163-1829(99)12305-1]

## I. INTRODUCTION

Trivalent rare-earth ($R^{3+}$) ions are readily incorporated into fluorite-type lattices, where they substitute some of the divalent cations. Charge balance is achieved by additional fluorine anions ($F^-$) occupying some of the previously vacant interstitial sites. The various nonequivalent positions of the charge compensating $F^-$ ions relative to the $R^{3+}$ ions give rise to a variety of distinct substitutional trivalent rare-earth ion-interstitial fluorine ion ($R^{3+}$-$F^-$) centers. The occurrence of a particular center in a given host crystal is dependent on the dopant rare-earth ion, its concentration and on the thermal history of the sample.

Theoretical calculations show that two groups of $R^{3+}$-$F^-$ centers form in $CaF_2$, $SrF_2$, and $BaF_2$ crystals for doping levels of up to 1 mol %.[1–4] The division is based on whether there are one or more $R^{3+}$ ions per center. The first group comprises centers with a single $R^{3+}$ ion per center. These include the $1|1_1$ ($C_{4v}$ symmetry) and $1|1_2$ ($C_{3v}$ symmetry) monomer centres which correspond to the nearest-neighbor (NN) and next-nearest-neighbor (NNN) positions for the charge-compensating interstitial $F^-$ ion, respectively.[1,3] The $i|q_r$ notation adopted here gives the number of $R^{3+}$ ions at a particular center ($i$) as well as the number of interstitial $F^-$ ions associated with the center ($q$). The subscript ($r$) denotes the positions of the interstitial $F^-$ ions relative to the $R^{3+}$ ions of the center, with $r=1,2$ representing the NN and NNN positions, respectively.[1] In general, the calculations of Corish *et al.*[1] show the $1|1_1$ monomer center to be dominant in $CaF_2$, while the $1|1_2$ center is more stable in $BaF_2$ for all $R^{3+}$ ions. Both types of centers are shown to be favorable in the $SrF_2$ lattice. These conclusions are consistent with the EPR results of Brown *et al.*[5]

$R^{3+}$ dimers plus higher-order clusters constitute the second group of centers.[1,2,4] According to the calculations of Corish *et al.*,[1] the dominant cluster centers in rare-earth-doped $CaF_2$ and $BaF_2$ crystals are of the $2|2_1$ and $2|2_2$ rhombic configurations, respectively. These are derived from the corresponding monomer center favorable in the particular lattice. For $SrF_2$:$R^{3+}$ crystals, the calculations show both $2|2_1$- and $2|2_2$-type cluster centers to be favorable, with a slight bias towards the $2|2_2$ dimer. An important modification of the $2|2_1$ cluster results from the trapping of a free interstitial $F^-$ ion. This cluster center, labeled $2|3_1$, is predicted to be favorable in $CaF_2$ and less likely in $SrF_2$ and $BaF_2$ crystals.

The different $R^{3+}$-$F^-$ centers present in a given host can be analyzed and each center's crystal-field energy levels derived by the technique of selective laser excitation. This procedure allows optical transitions of each center to be excited separately from all other centers present, under appropriate conditions. For a given center, the symmetry of the $R^{3+}$ ion site and the symmetry properties of its crystal-field energy levels can be deduced from polarization studies of the observed transitions. The technique is also suitable for studies of the dependence of the type and population of $R^{3+}$-$F^-$ centers present in a given host crystal on the $R^{3+}$ ion dopant concentration. From experiments of this nature,[6–9] monomer centers are found to be dominant for rare-earth dopant concentrations of up to 0.05 mol %, the population increasing almost linearly with rare-earth concentration. Their population then decreases gradually as the dopant concentration is further increased beyond 0.05%. In contrast, the dimer and higher-order cluster centers are absent for $R^{3+}$ concentrations of less than 0.01% but appear above 0.01% and increase gradually in number to exceed the monomer center population at about 0.05% and become dominant above 0.2%.

Using the technique of selective laser excitation, Seelbinder and Wright[10] found only two $Ho^{3+}$ centers, labeled *A* and *B*, in $CaF_2$:0.01% $Ho^{3+}$ crystals. However, at the higher $Ho^{3+}$ concentration of 0.2% they identified a further three centers, which they labeled *C, D*, and *E*. They suggested that these latter centers result from clustering of $Ho^{3+}$ ions. Excitation and fluorescence transitions in the range 15 400–22 700 $cm^{-1}$ were published for each of the cluster centers, but energy-level schemes were not derived. Tang *et al.*[11] carried out laser selective excitation studies of $CaF_2$:$Ho^{3+}$ for $Ho^{3+}$ concentrations ranging from 0.01 to 10% and reported the wavelengths and lifetimes of fluorescence transitions occurring in the 550 and 700 nm regions, for the *A* and *B* centers. The cluster centers of Seelbinder and Wright[10] were not observed by Tang *et al.*[11] who attributed the absence of these centers to efficient quenching of fluorescence for centers with two or more $Ho^{3+}$ ions.

In a subsequent polarization study of the excitation and fluorescence transitions of the *A* and *B* centers in $CaF_2$:0.005% $Ho^{3+}$ crystals, Mujaji *et al.*[12] showed that the $Ho^{3+}$ ions are in tetragonal ($C_{4v}$) and trigonal ($C_{3v}$) symmetry sites, respectively. The *A* center necessarily has the $1|1_1$ configuration, while the *B* center is consistent with the $1|1_2$ model. For both centers, energy-level schemes were derived, crystal-field analyses done, and irrep labels assigned to the crystal-field energy levels. The crystal-field energy levels of Mujaji *et al.*[12] were confirmed by Zhang *et al.*[13] who also reported on a third center (labeled dimer by them) observed in their $CaF_2$:0.1% $Ho^{3+}$ sample. They make no comparison between their dimer center and the *C, D*, and *E* cluster centers reported by Seelbinder and Wright.[10]

A study of $SrF_2$:1% $Ho^{3+}$ using excitation by an argon-ion laser appears in the literature[14] with fluorescence transitions in the 18 000, 15 000, and 13 000 $cm^{-1}$ regions being listed. A later selective laser excitation and polarization study of $SrF_2$:0.01% $Ho^{3+}$ crystals[12] revealed a total of five centers. The center labeled *A* had much stronger excitation and fluorescence transitions than the *B* center. The spectral appearance and polarization behavior of both centers were as found for the corresponding *A* and *B* centers in $CaF_2$:$Ho^{3+}$ crystals. The configurations of the *A* and *B* centers in $SrF_2$ were deduced to be $1|1_1$ and $1|1_2$, respectively. Intensity of the fluorescence for the *B* center was estimated to be about 2% of that of the *A* center, while the change of site symmetry from tetragonal to trigonal for the principal $R^{3+}$ center in $SrF_2$ was found to occur between $Ho^{3+}$ and $Er^{3+}$. The dominance of the tetragonal symmetry $Ho^{3+}$ (*A*) center in optical studies contradicts results from EPR measurements[15] where only resonances associated with the trigonal symmetry center were observed at both 9.5 and 35 GHz. This discrepancy is explained through the 2.7 $cm^{-1}$ ground-state splitting observed in optical transitions of the *A* center, in zero field,[12] which precludes observation of the center by EPR. The other three centers found in the $SrF_2$:$Ho^{3+}$ crystals were from unintentional $Ca^{2+}$ or $Ba^{2+}$ impurities in the crystals. The configurations proposed for these centers are modifications of the $1|1_1$ cluster.

For $BaF_2$:$Ho^{3+}$, excitation and fluorescence transitions in the 440–470 nm and 530–770 nm regions, respectively, have been reported from a laser excitation study of a 0.1% $Ho^{3+}$ doped crystal.[16] From this work, it was concluded that a single dominant center and some other minor center(s) occur in $BaF_2$:$Ho^{3+}$ crystals. A subsequent site-selective excitation study of 0.01% and 0.1% $Ho^{3+}$-doped samples[17] showed the $1|1_2$ cluster to be dominant in $BaF_2$. A minor center, suspected to be of the $2|2_2$ configuration was also present in the 0.1%-doped crystal.

In the present paper, we present results from selective laser excitation studies of the dimer centers in $CaF_2$:0.1% $Ho^{3+}$ and $SrF_2$:0.1% $Ho^{3+}$ single crystal including some fluorescence lifetime data. For $CaF_2$:$Ho^{3+}$, the three dimer centers labeled *C, D*, and *E* by Seelbinder and Wright[10] are observed in this study in addition to the *A* and *B* centers. For each center, an energy-level scheme is derived from the observed excitation and fluorescence transitions. The $2|2_1$ and $2|2_2$ cluster configurations are proposed for the *C* and *D* centers respectively, while the *E* center is most likely to be a $2|3_1$ cluster. Only two cluster centers are observed in $SrF_2$:$Ho^{3+}$ in the current work. These centers are henceforth labeled *C* and *E* because of similarities to the corresponding centers in $CaF_2$. An energy-level scheme for the four multiplets accessible with the available excitation conditions is derived for both centers. The center configurations are as proposed for the corresponding *C* and *E* centers in $CaF_2$:$Ho^{3+}$. The absence of the *D* center and presence of the *E* center is in apparent contradiction to the calculations of Corish *et al.*[1] which predict the $2|2_2$ configuration to be slightly more favorable than the $2|2_1$, and the $2|3_1$ cluster to be unstable in $SrF_2$. However, since earlier polarization studies of the site-selective excitation and fluorescence transitions[12] revealed the *A* center ($1|1_1$ configuration) to be dominant over the *B* center ($1|1_2$ configuration), observation of the $2|2_1$ and $2|3_1$ clusters in the present work is consistent with the prevalence of $1|1_1$ monomers in $SrF_2$ crystals. Absence of the *D* center ($2|2_2$ cluster) is not too surprising given the weak intensity of the $1|1_2$ monomer transitions in crystals having low $Ho^{3+}$ concentrations.[12]

The clustering of $Ho^{3+}$ ions however appears to be markedly different from that of $Er^{3+}$ ions. Unlike $Ho^{3+}$, $Er^{3+}$ which is the next rare-earth ion along the series forms a multiplicity of cluster centers at the 0.2% doping level. In $CaF_2$:0.2% $Er^{3+}$,[18] 16 centers with at least two $Er^{3+}$ ions per center were observed while five cluster centers were present in $SrF_2$:0.2% $Er^{3+}$.[7] There is some correlation for only three pairs of the $Er^{3+}$ centers in $CaF_2$ and $SrF_2$ crystals. In contrast, only three cluster centers are found in 0.1% and 0.2% $Ho^{3+}$-doped $CaF_2$ crystals while only two such centers appear in similarly doped $SrF_2$ crystals. The two $Ho^{3+}$ cluster centers present in $SrF_2$ closely resemble two of the three centers in $CaF_2$.

## II. EXPERIMENTAL

The $CaF_2$:$Ho^{3+}$ and $SrF_2$:$Ho^{3+}$ crystals with $Ho^{3+}$ concentrations of 0.1% and 0.2% used for this work were provided by G. D. Jones, R. J. Reeves, and J. P. R. Wells of the University of Canterbury, New Zealand. The crystals were grown by the Bridgman-Stockbarger method in a 38 kW A. D. Little rf induction furnace from $CaF_2$ and $SrF_2$ off-cuts and 99.9% pure $HoF_3$ powder.

Samples for absorption measurements had path lengths of about 10 mm while those for laser selective excitation measurements were typically 7×7×2 mm. Optical-absorption spectra were recorded on samples at liquid-nitrogen temperature, using a Cary 17 spectrophotometer.

For laser selective excitation measurements, a Spectra-

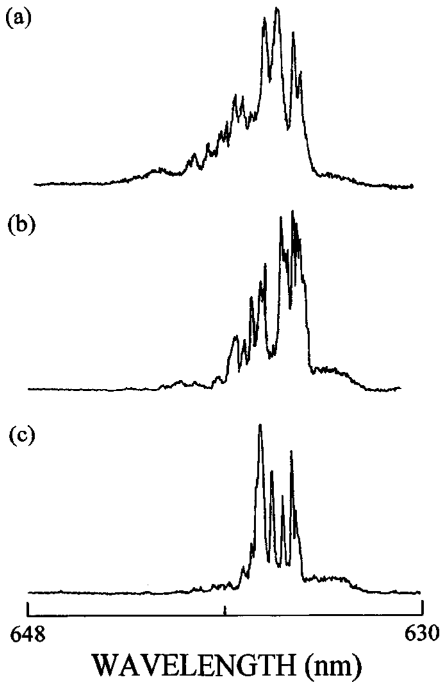

FIG. 1. Excitation spectra of the $D(^5F_5)$ multiplet for all centers present in $CaF_2$:0.1% $Ho^{3+}$ crystals obtained by monitoring all the $D\rightarrow Z$ transitions above 650 nm, as measured at (a) 77 K, (b) 30 K, and (c) 10 K.

Physics 171 argon-ion laser was used to pump a Spectra-Physics 375 dye laser. The Rhodamine 640 (perchlorate) dye used for this work emits laser radiation in the 615–670 nm range. Samples were cooled to below 12 K in an Oxford CF 1204 dynamic exchange gas cryostat with a continuous flow of liquid helium. The sample temperature was monitored by a resistance sensor and a thermocouple in conjunction with an Oxford ITC4 temperature controller. It was occasionally necessary to raise the sample temperature to between 20 and 77 K to verify excited-state transitions.

Fluorescence from the sample, collected using a 90° geometry, was focused onto the entrance slit of a Jarrell Ash 25-100 1 m double Czerny-Turner scanning monochromator. The monochromator is equipped with a thermoelectrically cooled Burle C31034-02 photomultiplier tube, an EG&G Princeton Applied Research model 1121 A preamplifier/discriminator and a model 1112 photon counter. The signal was collected in analogue form for broadband and site-selective excitation spectra and in digital form for fluorescence spectral measurements.

The wavelengths and energies reported in this work are in nm and $cm^{-1}$ in air, respectively. The fluorescence lifetimes were measured with the equipment used in earlier studies.[19]

## III. THE $Ho^{3+}$ CLUSTER CENTERS IN $CaF_2$ AND $SrF_2$ CRYSTALS

The range of laser emission of the Rhodamine 640 (perchlorate) dye covers the $D(^5F_5)$ multiplet of the $Ho^{3+}$ ion and is therefore suitable for exciting its $Z(^5I_8)\rightarrow D$ transitions. For the cluster centers described in this work, the $Ho^{3+}$ ions are in sites of either $C_2$ or $C_s$ symmetry and therefore none of the ion's crystal-field energy levels are degenerate. For such centers, the crystal-field energy levels can only transform as the $\gamma_1$ and $\gamma_2$ irreps of the $C_2$ or $C_s$ point groups.[20] Electric-dipole selection rules allow both $\gamma_i\rightarrow\gamma_i$, $i=1$ or 2, and $\gamma_1\leftrightarrow\gamma_2$-type transitions. As a result, more transitions (both site-selective excitation and fluorescence) are observed for the cluster centers than for the high symmetry $A$ and $B$ centers. The number of crystal-field energy levels for a given $LSJ$ multiplet is subject to a maximum of $2J+1$, for both $C_2$ and $C_s$ symmetry centers.

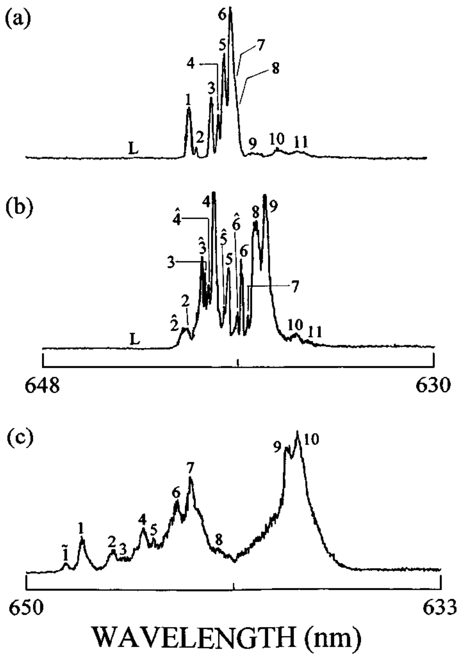

FIG. 2. Site-selective excitation spectra measured at 10 K of the $D(^5F_5)$ multiplet in $CaF_2$:0.1% $Ho^{3+}$ crystals for (a) the $C$ center, monitoring the $D_1\rightarrow Z_9$ transition at 15 516.3 $cm^{-1}$; (b) the $D$ center, monitoring the $D_3\rightarrow Z_8$ transition at 15 526.5 $cm^{-1}$; (c) the $E$ center, monitoring the $D_1\rightarrow Z_{13}$ transition at 15 056.6 $cm^{-1}$. Transitions originating from the ground state ($Z_1$) are identified by numerical labels for energy levels of the $D$ multiplet. Transitions from the higher energy $Z_2$ and $Z_3$ levels of the ground multiplet are shown by ˆ and ˜ respectively. The transition being monitored is shown by $L$, where possible.

### A. Spectroscopy of the $C$, $D$, and $E$ centers in $CaF_2$:0.1% $Ho^{3+}$

The 77 K absorption spectra of $CaF_2$:0.1% $Ho^{3+}$ and $CaF_2$:0.2% $Ho^{3+}$ crystals had the same features as the broadband excitation spectrum shown in Fig. 1(a), except for different intensity distributions. The broadband excitation spectrum was obtained by continuously scanning the dye laser wavelength over the 630–648 nm range while monitoring fluorescence transitions above 650 nm. There are fewer and sharper excitation transitions at the lower temperatures of 30 and 10 K [Figs. 1(b) and 1(c), respectively], as the higher-energy transitions are frozen out at these temperatures.

Using the technique of laser selective excitation, absorption transitions not associated with the already documented $A$ and $B$ centers could be assigned to one of three centers. The site-selective excitation spectra for these three centers, labeled $C$, $D$, and $E$, are shown in Figs. 2(a), 2(b), and 2(c), respectively.

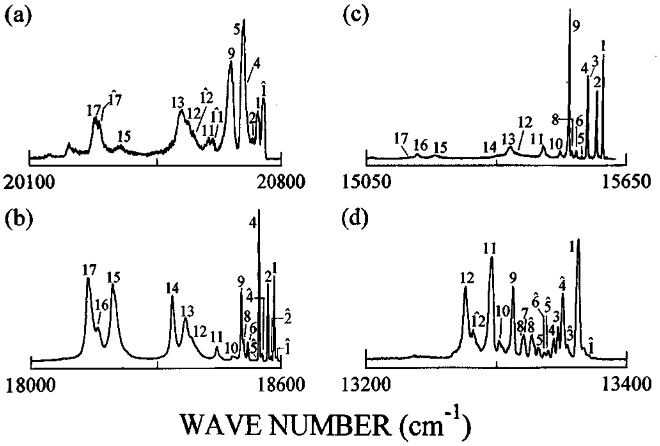

FIG. 3. Fluorescence spectra measured at 10 K for the $C$ center in $CaF_2$:0.1% $Ho^{3+}$ with excitation of the $Z_1 \rightarrow D_3$ transition at 15 629.9 cm$^{-1}$ (639.8 nm), showing the (a) $F \rightarrow Z$, (b) $E \rightarrow Z$, (c) $D \rightarrow Z$, and (d) $E \rightarrow Y$ transitions. The transitions are identified by numerical labels for energy levels of the terminating multiplet. Transitions originating from the higher energy $F_2$ and $E_2$ levels are shown by ˆ.

### 1. The $CaF_2$:$Ho^{3+}$ C center

The direct ($D \rightarrow Z$) and upconversion ($F \rightarrow Z$; $E \rightarrow Z,Y$) fluorescence spectra obtained for the $C$ center with excitation of the $Z_1 \rightarrow D_3$ transition at 15 629.9 cm$^{-1}$ (639.8 nm), are shown in Fig. 3. The direct fluorescence transitions in the 15 650–15 400 cm$^{-1}$ and the upconversion fluorescence transitions observed in this work are in agreement with the earlier results of Seelbinder and Wright[10] while the weaker $D \rightarrow Z$ transitions below 15 400 cm$^{-1}$ [Fig. 3(c)] were not reported by them. The upconversion fluorescence originating from the $F$ multiplet was much weaker than that from the $E$ multiplet.

TABLE I. Crystal-field energy levels for the $Z(^5I_8)$, $Y(^5I_7)$, $D(^5F_5)$, $E(^5S_2)$, and $F(^5F_3)$ multiplets of the $C$ center identified in $CaF_2$:0.1% $Ho^{3+}$ crystals. The energies are in cm$^{-1}$ in air.

| Level | $Z(^5I_8)$ | $Y(^5I_7)$ | $D(^5F_5)$ | $E(^5S_2)$ | $F(^5F_3)$ |
|---|---|---|---|---|---|
| 1 | 0.0 | 5220.0 | 15 594.6 | 18 583.2 | 20 733.0 |
| 2 | 13.9 | 5233.5 | 15 605.7 | 18 590.7 | 20 749.8 |
| 3 | 34.3 | 5235.7 | 15 629.9 | | |
| 4 | 35.2 | 5238.9 | 15 640.9 | | |
| 5 | 47.4 | 5251.0 | 15 647.0 | | |
| 6 | 59.5 | 5253.9 | 15 664.2 | | |
| 7 | 68.8 | 5262.5 | 15 674.0 | | |
| 8 | 70.5 | 5263.4 | 15 681.3 | | |
| 9 | 78.3 | 5270.6 | 15 703.5 | | |
| 10 | 97.5 | 5281.4 | 15 739.3 | | |
| 11 | 137.9 | 5287.5 | 15 760.4 | | |
| 12 | 197.6 | 5307.4 | | | |
| 13 | 213.9 | | | | |
| 14 | 243.6 | | | | |
| 15 | 388.6 | | | | |
| 16 | 429.1 | | | | |
| 17 | 446.4 | | | | |

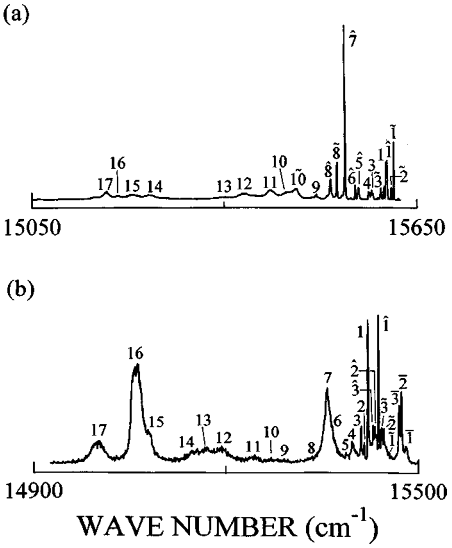

FIG. 4. Fluorescence spectra measured at 10 K for the $D \rightarrow Z$ transitions of the $D$ and $E$ centers in $CaF_2$:0.1% $Ho^{3+}$ (a) the $D$ center, with excitation of the $Z_1 \rightarrow D_4$ transition at 15 622.5 cm$^{-1}$ (640.1 nm); (b) the $E$ center, with excitation of the $Z_1 \rightarrow D_9$ transition at 15 648.3 cm$^{-1}$ (639.0 nm). Transitions from the $D_2$, $D_3$, and $D_4$ energy levels are shown by ˆ, ˜ and ¯ respectively.

All the 17 crystal-field energy levels for the $Z$ multiplet ($2J+1$ levels are expected for a centre of low symmetry) were deduced from the $F \rightarrow Z$, $E \rightarrow Z$, and $D \rightarrow Z$ spectra of Figs. 3(a), 3(b), and 3(c), respectively. The first excited state ($Z_2$) is 13.9 cm$^{-1}$ above the ground state, while the $Z_3$ and $Z_4$ energy levels have a rather small separation of only 0.9 cm$^{-1}$. For the $Y$ ($^5I_7$) multiplet, transitions from the $E_1$ and $E_2$ energy levels to only 12 of the possible 15 crystal-field energy levels were observed. The $E_1 \rightarrow Y_1$ transition shows some structure on the high-energy side [Fig. 3(d)] while the $E_1 \rightarrow Y_{4,11}$ transitions are broad and asymmetrical. It is likely that the three unobserved energy levels lie too close to the $Y_1$, $Y_4$, and $Y_{11}$ energy levels to be resolvable. All 11 energy levels of the $D$ ($^5F_5$) multiplet were derived from the center's excitation and direct fluorecence. Only two energy levels could be deduced for both the higher energy $E$ ($^5S_2$) and $F$ ($^5F_3$) multiplets. The crystal-field energy level scheme derived for the five multiplets is presented in Table I.

### 2. The $CaF_2$:$Ho^{3+}$ D center

The site-selective excitation ($Z \rightarrow D$) and direct fluorescence spectra for the $D$ center are shown in Figs. 2(b) and 4(a), respectively. Transitions for this center lie in the same energy range as for the $C$ center. Fluorescence transitions in the region 15 630–15 490 cm$^{-1}$ [Fig. 4(a)] confirm the results of Seelbinder and Wright[10] while transitions in the region 15 460–15 150 cm$^{-1}$ were not reported by them. The center does not exhibit any significant upconversion fluorescence.

The crystal-field energy levels derived for the $Z$ and $D$ multiplets of the $D$ center are included in Table II. Although the $Z_1 - Z_2$ separation of 4.6 cm$^{-1}$ is much smaller than for the $C$ center, the energy levels for the $Z$ and $D$ multiplets of both centers are spread over the same energy ranges.

TABLE II. Crystal-field energy levels for the $Z(^5I_8)$ and $D(^5F_5)$ multiplets of the $D$ and $E$ centers identified in $CaF_2$:0.1% $Ho^{3+}$ crystals. The energies are in $cm^{-1}$ in air.

| | *D* Center | | *E* Center | |
|---|---|---|---|---|
| Level | $Z(^5I_8)$ | $D(^5F_5)$ | $Z(^5I_8)$ | $D(^5F_5)$ |
| 1 | 0.0 | 15 602.3 | 0.0 | 15 421.7 |
| 2 | 4.6 | 15 603.6 | 6.0 | 15 438.2 |
| 3 | 21.9 | 15 614.1 | 9.5 | 15 453.0 |
| 4 | 27.4 | 15 622.5 | 24.5 | 15 479.8 |
| 5 | 43.9 | 15 644.5 | 32.9 | 15 484.7 |
| 6 | 49.2 | 15 662.9 | 63.1 | 15 501.3 |
| 7 | 65.0 | 15 671.5 | 176.2 | 15 515.2 |
| 8 | 87.6 | 15 688.7 | 226.4 | 15 550.0 |
| 9 | 107.8 | 15 697.3 | 250.6 | 15 648.3 |
| 10 | 150.8 | 15 731.9 | 275.2 | 15 660.8 |
| 11 | 179.4 | 15 745.5 | 342.2 | |
| 12 | 221.0 | | 359.0 | |
| 13 | 302.3 | | 365.1 | |
| 14 | 368.8 | | 372.8 | |
| 15 | 395.3 | | 421.7 | |
| 16 | 417.2 | | | |
| 17 | 436.2 | | | |

### 3. The $CaF_2$:$Ho^{3+}$ E center

The site-selective $Z \rightarrow D$ excitation spectrum for the $E$ center [Fig. 2(c)] is markedly different from corresponding spectra for the $C$ and $D$ centers in that most of its transitions are broader and occur at much longer wavelengths (lower energies). The fluorescence transitions [Fig. 4(b)] also occur at the lower energies of 15 500–14 900 $cm^{-1}$ compared to the $C$ and $D$ centers' transitions which lie in the range 15 650–15 050 $cm^{-1}$. The direct $D \rightarrow Z$ fluorescence spectrum is characterized by very sharp transitions superimposed on a broad background in the 15 500–15 400 $cm^{-1}$ region and comparably strong but broad transitions below 15 200 $cm^{-1}$. Fluorescence transitions in the range 15 360–14 950 $cm^{-1}$ [Fig. 4(b)] were not reported in the earlier work of Seelbinder and Wright.[10] Upconversion fluorescence is not observed for the $E$ center.

Transitions for the $E$ center are much weaker than those for the other two cluster centers. The relative intensities of the fluorescence transitions of the $E$ center for excitation of several of the $Z \rightarrow D$ transitions as documented in this work are consistent with a single cluster center. This is in contrast with the results of Seelbinder and Wright[10] where the transitions could be further subdivided into three centers $E$-1, $E$-2, and $E$-3. There is no justification for such further classification in the current work.

The crystal-field energy levels derived for the $Z$ and $D$ multiplets of the $E$ center are included in Table II.

### 4. Discussion of the C, D, and E centers in $CaF_2$:$Ho^{3+}$

Transitions of the $C$ center are the most intense while those for the $E$ center are weakest. Significant upconversion fluorescence was observed for the $C$ center while that for the $D$ center was too weak to measure. None was observed for the $E$ center. Transitions for all three centers are absent at the low $Ho^{3+}$ concentrations of 0.01% or less, but appear at 0.1% and have increased intensities at the 0.2% $Ho^{3+}$ concentration. These centers necessarily contain $Ho^{3+}$ dimers; trimer and higher-order clustering is only expected for $R^{3+}$ concentrations above 0.25%.[8]

The spectra and crystal-field energy levels derived for the $C$ and $D$ centers bear some resemblance to those for the $C_{4v}$ ($A$) and $C_{3v}$ ($B$) symmetry centers, respectively. The crystal-field energy levels of the $C$ center, however, occur at relatively lower energies and are more closely spaced than those of the $A$ center. The similarities between the $D$ and the $B$ centers can be appreciated by comparing the energy-level positions of the $D$ center's $Z_{1,2,3,4}$ levels (Table II) with the $B$ center's $Z_{1,2}$ levels. For the $B$ center, the ground and first excited states are degenerate and have a 27.0 $cm^{-1}$ separation.[12] For the $D$ center, small separations of 4.6 and 5.5 $cm^{-1}$ occur for the $Z_1 - Z_2$ and $Z_3 - Z_4$ energy-level pairs respectively while the mean of each pair of levels is close to the $C_{3v}$ symmetry energy level position. The $Z_{1,2}$ and $Z_{3,4}$ energy level pairs can therefore be attributed to the lifting of the degeneracy of the $B$ center's ground and first excited levels. This arises from the lower $Ho^{3+}$ site symmetry at the cluster. Thus it appears that the $C$ center results from pair aggregation of $C_{4v}$-symmetry monomers while the $D$ center is from aggregation of pairs of $C_{3v}$-symmetry monomers. The centers are tentatively assigned the $2|2_1$ and $2|2_2$ configuration models, respectively. Except for the much lower transition energies, the fluorescence spectrum for the $E$ center has the same general appearance as for the $A$ center. This $E$ center is assigned the $2|3_1$ cluster configuration. It is noted that the above suggested defect configurations are consistent with the calculations of Corish *et al.*[1] and the models suggested by them.

For the $2|2_1$ configuration proposed for the $C$ center, the $Ho^{3+}$ site symmetry is reduced to $C_s$ by relaxation of the two common lattice $F^-$ ions in $\langle 111 \rangle$ directions.[1] The $2J+1$ crystal-field energy levels deduced here for the $Z$, $Y$, and $D$ multiplets (Table I) are appropriate for a $C_s$ symmetry center. As the $Ho^{3+}$ ions in a $2|2_1$ cluster are nearer each other than in a $2|2_2$ configuration, the interaction between them is expected to be stronger and more favorable for energy exchange processes; hence the relatively strong upconversion fluorescence observed for this center. A possible sequence resulting in upconversion at a dimer is that both ions are excited to the $D$ multiplet ($\sim$15 500 $cm^{-1}$) and one ion subsequently transfers about 7000 $cm^{-1}$ of its energy to the other, resulting in a final state comprising the donor ion in the $A$ multiplet ($\sim$8500 $cm^{-1}$) and the acceptor ion in the close-lying $G;H;I$ multiplets ($\sim$21 500 $cm^{-1}$). Nonradiative decay processes to the $F$ ($\sim$20 000 $cm^{-1}$) and $E$ ($\sim$18 400 $cm^{-1}$) multiplets would yield upconversion fluorescence consistent with the current observations. This nonradiative quenching of the $G$, $H$, and $I$ multiplets by the $F$ and $E$ multiplets should be strong given the high cutoff phonon energy of 465 $cm^{-1}$ for $CaF_2$.[21] Similar upconversion mechanisms have been proposed for the $Er^{3+}$ clusters.[22]

The site symmetry for the $Ho^{3+}$ ion in a $2|2_2$ configuration center is $C_{2v}$ and therefore the ion's crystal-field energy levels ought to transform as the $\gamma_i$, $i=1$ to 4, of the $C_{2v}$ point group. For a $C_{2v}$-symmetry center, electric-dipole selection rules do not allow any transitions of the type $\gamma_i \leftrightarrow \gamma_j$, for $i,j=1,2,3$ and $i \neq j$, while the $\gamma_4$ irrep levels are degenerate.[20] The *D* center does not exhibit the above properties. None of the center's transitions appear to be forbidden and all the crystal-field energy levels deduced from this work (Table II) are nondegenerate. It appears that, for the *D* center the $Ho^{3+}$ site symmetry has been lowered from $C_{2v}$ to either $C_2$ or $C_s$ by some nonaxial distortion on the center or by relaxation of the lattice $F^-$ ions associated with the center. For a center of either of these lower symmetries, $\gamma_i \leftrightarrow \gamma_j$ $(i,j=1,2)$-type transitions are allowed and the resulting crystal-field energy levels are nondegenerate, as found here for the *D* center. The traces of upconversion fluorescence observed for the *D* center is consistent with a weaker interaction between the $Ho^{3+}$ ions of this dimer (in comparison with the *C* center), resulting from the larger separation between the $Ho^{3+}$ ions in the $2|2_2$ configuration cluster.

The distinctly different excitation and fluorescence spectra for the *E* center arise from the distortion caused by the captured $F^-$ ion on the two $Ho^{3+}$-$F^-$ dipoles of a previously symmetric rhombic configuration. The nondegeneracy of the crystal-field energy levels derived for the centers *Z* and *D* multiplets is consistent with a $C_s$ symmetry center. There appears to be no correlation between any of the *C, D,* and *E* centers and the dimer center of Zhang *et al.*[13]

### B. Spectroscopy of the *C* and *E* centers in $SrF_2$:0.1% $Ho^{3+}$

An absorption spectrum was recorded for $SrF_2$:0.2% $Ho^{3+}$ only as the absorption features in the 0.1% $Ho^{3+}$-doped sample were too weak. The absorption spectrum however shows the same transitions as the broadband excitation spectrum obtained in the 0.1% $Ho^{3+}$-doped sample with the monochromator set to monitor all fluorescence transitions above 656 nm [Fig. 5(a)]. The $SrF_2$:0.1% $Ho^{3+}$ sample was used for laser selective excitation measurements as the transitions were narrower and therefore less likely to overlap. The broadband excitation spectrum recorded at 10 K [Fig. 5(b)] contains the low-energy transitions, while the 77 K spectrum [Fig. 5(a)] is dominated by higher energy transitions. Although excitation transitions for the previously documented *A*, *SC*1, *SC*2, and *SB*1 centers (Ref. 12) are still present, some absorption transitions not associated with the above centers are also apparent. The transitions could be assigned to one of two centers, labeled *C* and *E* from comparison with the centers in $CaF_2$:$Ho^{3+}$. The site-selective excitation spectra for the two centers are shown in (c) and (d) of Fig. 5, respectively.

Both centers are $Ho^{3+}$ cluster centers as they also appear at the 0.1% $Ho^{3+}$ concentration and have stronger transitions in the 0.2% doped sample. Direct $D \rightarrow Z$ and upconversion $E \rightarrow Z,Y$ fluorescence is observed for both centers, as shown in Fig. 6. The $F \rightarrow Z$ upconversion fluorescence was too weak to measure for both centers. Energy-level schemes derived for the *Z, Y, D,* and *E* multiplets of the cluster centers are presented in Table III.

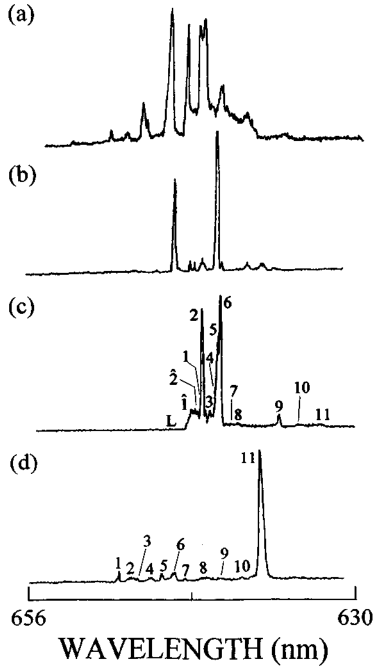

FIG. 5. Excitation spectra of the *D* multiplet in $SrF_2$:0.1% $Ho^{3+}$ crystals for (a) all centers present at 77 K, monitoring all $D \rightarrow Z$ transitions above 656 nm; (b) all centers present at 10 K, monitoring all $D \rightarrow Z$ transitions above 656 nm; (c) the *C* center, monitoring the $D_1 \rightarrow Z_4$ transition at 15 544.9 $cm^{-1}$; (d) the *E* center, monitoring the $D_1 \rightarrow Z_{16}$ transition at 15 074.1 $cm^{-1}$. Transitions are identified as in Fig. 2.

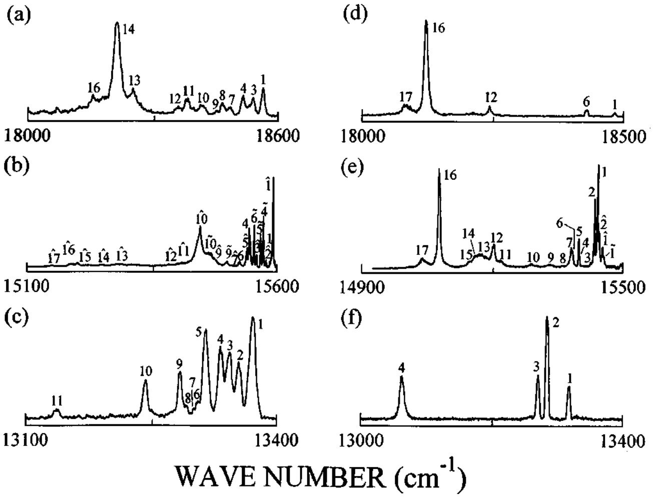

FIG. 6. Fluorescence spectra measured at 10 K for the *C* and *E* centers in $SrF_2$:0.1% $Ho^{3+}$ crystals for excitation of the $Z_1 \rightarrow D_6$ transition at 15 645.8 $cm^{-1}$ (639.1 nm) and the $Z_1 \rightarrow D_{11}$ transition at 15 715.8 $cm^{-1}$ (636.3 nm), respectively. (a) and (d) the $E \rightarrow Z$ transitions of the *C* and *E* centers, respectively; (b) and (e) the $D \rightarrow Z$ transitions of the *C* and *E* centers, respectively; (c) and (f) the $E \rightarrow Y$ transitions of the *C* and *E* centers, respectively. Transitions are identified as in Fig. 4.

#### 1. *The $SrF_2$:$Ho^{3+}$ C center*

The site-selective excitation spectrum of the *C* center [Fig. 5(c)] was obtained with the monochromator set to monitor the $D_1 \rightarrow Z_4$ transition at 15 544.9 $cm^{-1}$, while the fluorescence spectra shown in Fig. 6 are for excitation of the $Z_1 \rightarrow D_6$ transition at 15 645.8 $cm^{-1}$ (639.1 nm). Transitions for this center are more intense than for the *E* center. Although fluorescence transitions of the *C* center in $SrF_2$ (Fig. 6) occur in the same energy regions as for the *C* center of

TABLE III. Crystal-field energy levels for the $Z(^5I_8)$, $Y(^5I_7)$, $D(^5F_5)$, and $E(^5S_2)$ multiplets of the *C* and *E* centers identified in $SrF_2$:0.1% $Ho^{3+}$ crystals. The energies are in $cm^{-1}$ in air.

| | *C* Center | | | | *E* Center | | | |
|---|---|---|---|---|---|---|---|---|
| Level | $Z(^5I_8)$ | $Y(^5I_7)$ | $D(^5F_5)$ | $E(^5S_2)$ | $Z(^5I_8)$ | $Y(^5I_7)$ | $D(^5F_5)$ | $E(^5S_2)$ |
| 1 | 0.0 | 5191.5 | 15 590.2 | 18 563.6 | 0.0 | 5165.5 | 15 440.7 | 18 481.0 |
| 2 | 13.6 | 5208.7 | 15 591.7 | | 7.1 | 5201.1 | 15 452.8 | 18 483.2 |
| 3 | 32.2 | 5220.1 | 15 617.7 | | 15.0 | 5215.1 | 15 455.8 | 18 485.8 |
| 4 | 45.3 | 5230.9 | 15 628.9 | | 40.4 | 5422.3 | 15 484.7 | |
| 5 | 50.5 | 5249.1 | 15 637.2 | | 42.6 | | 15 499.1 | |
| 6 | 63.5 | 5258.3 | 15 645.8 | | 56.7 | | 15 511.1 | |
| 7 | 73.7 | 5263.1 | 15 664.9 | | 60.2 | | 15 536.4 | |
| 8 | 95.4 | 5272.2 | 15 682.1 | | 80.7 | | 15 593.3 | |
| 9 | 117.0 | 5279.7 | 15 725.7 | | 110.4 | | 15 622.5 | |
| 10 | 146.9 | 5321.9 | 15 775.3 | | 154.0 | | 15 666.6 | |
| 11 | 182.3 | 5426.8 | 15 805.3 | | 224.0 | | 15 715.8 | |
| 12 | 209.3 | | | | 239.6 | | | |
| 13 | 309.4 | | | | 269.8 | | | |
| 14 | 350.1 | | | | 281.9 | | | |
| 15 | 393.1 | | | | 296.1 | | | |
| 16 | 405.0 | | | | 366.6 | | | |
| 17 | 443.3 | | | | 404.2 | | | |

$CaF_2$, the crystal-field energy levels are more spread out in $SrF_2$. The lowest energy levels for the *Y*, *D*, and *E* multiplets occur at lower energies than in $CaF_2$ while the highest energy levels of the same excited multiplets are at higher energies. The $Z_1$-$Z_2$ energy-level separations of 13.6 $cm^{-1}$ in $SrF_2$ and 13.9 $cm^{-1}$ in $CaF_2$ are comparable.

### *2. The $SrF_2$:$Ho^{3+}$ E center*

There are much more striking similarities between the *E* centers in $SrF_2$ and $CaF_2$. As found for the *E* center in $CaF_2$, site-selective excitation transitions for the *E* center in $SrF_2$ are weak and broad while the fluorescence transitions occur at much lower energies than for the *C* center. The $D\rightarrow Z$ fluorescence spectrum [Fig. 6(e)] has sharp transitions superimposed on a broad background in the region 15 500–15 360 $cm^{-1}$ as well as some relatively intense transitions below 15 300 $cm^{-1}$, as highlighted for the corresponding center in $CaF_2$. The *E* center in $SrF_2$, however, exhibits some upconversion fluorescence from the *E* multiplet [Figs. 6(d) and 6(f)].

The $Z_1$ and $Z_2$ energy levels are separated by 7.1 $cm^{-1}$ in $SrF_2$ (Table III) and 6.0 $cm^{-1}$ in $CaF_2$ (Table II), while the $D_1$ energy level is at 15 440.7 $cm^{-1}$ in $SrF_2$ and 15 421.7 $cm^{-1}$ in $CaF_2$. The respective $D_2$ levels are 12.1 and 16.5 $cm^{-1}$ higher in energy.

### *3. Discussion of the C and E centers in $SrF_2$:$Ho^{3+}$*

As found for the *A* and *B* centers,[12] the *C* and *E* centers in $SrF_2$:$Ho^{3+}$ crystals bear strong spectral resemblance to the corresponding centers in $CaF_2$:$Ho^{3+}$ crystals. Because of these strong similarities, the *C* and *E* centers in $SrF_2$ are also assigned the $2|2_1$ and $2|3_1$ configuration models proposed for the *C* and *E* centers in $CaF_2$, respectively. The mechanism leading to upconversion fluorescence for both centers is as proposed for the *C* center in $CaF_2$. The cutoff phonon energy of 360 $cm^{-1}$ for $SrF_2$ (Ref. 23) is still favorable for nonradiative quenching of the *G*, *H*, and *I* multiplets.

A thorough search did not reveal any transitions that could be assigned to a possible *D* center. We advance two possible explanations for the absence of *D* center transitions in $SrF_2$:$Ho^{3+}$ crystals.

(i) Earlier studies of $SrF_2$:0.1% $Ho^{3+}$ crystals[12] revealed the $1|1_1$ cluster to be dominant at the low $Ho^{3+}$ concentrations, with transitions for the $1|1_2$ cluster having intensities of only 2% of those of the major center. If such fluorescence intensities are an acceptable measure of center population, then $SrF_2$:$Ho^{3+}$ crystals have a very low population of $1|1_2$ monomers while the $1|1_1$ monomer is much more prevalent. This scarcity of $1|1_2$ monomers is consistent with the absence of any fluorescence transitions that could be assigned to the *D* ($2|2_2$ configuration) center which emanates from aggregation of $1|1_2$-type centers.

(ii) Alternatively, the depressed transition intensities for the *B* center in $SrF_2$:$Ho^{3+}$ crystals might not be a true reflection of the center population. It is possible that for this *B* center, the $Ho^{3+}$ ion resides in a site of near-cubic rather than exact $C_{3v}$ symmetry. The resulting center would be expected to have low line strengths, hence much weaker optical transitions. Dimerization of such centers could yield a substantial $2|2_2$ center population but the optical transitions would still have depressed intensities.

In either case, the absence of any $2|2_2$ centers is not unreasonable given the preferential occurrence of $1|1_1$ monomer centers.

Dimerization in $SrF_2$ crystals appears to depend on the monomer center distribution at low ($\lesssim$0.01%) $Ho^{3+}$ concentrations, in the same way as in $CaF_2$ crystals. Specifically, excitation and fluorescence transitions of the $1|1_1(A)$ and $1|1_2(B)$ monomer centers in $CaF_2$:$Ho^{3+}$ crystals were of comparable intensities at the low $Ho^{3+}$ concentration

TABLE IV. Fluorescence lifetimes measured at 15 K for the *D* multiplet of the $Ho^{3+}$ dimer centers identified in 0.1% $Ho^{3+}$-doped $CaF_2$ and $SrF_2$ crystals, for direct $Z \rightarrow D$ excitation.

| | $\tau(\mu s)$ | |
|---|---|---|
| Center | $CaF_2$ | $SrF_2$ |
| *C* | 103 ±2 | 267 ±5 |
| *D* | 123 ±2 | |
| *E* | 17.1±0.4 | 58.4±0.6 |

regime[10,12] and both the $2|2_1$ and $2|2_2$ dimer centers occur at the raised $Ho^{3+}$ levels. Meanwhile, in $SrF_2$:$Ho^{3+}$ where intensities of the $1|1_1$ monomer center transitions are two orders of magnitude higher than for the $1|1_2$ center,[12] transitions for the $2|2_1$ rhombic center are present while none could be observed for the $2|2_2$ dimer.

The presence of the $2|3_1$ cluster (*E*) center in the $SrF_2$ lattice results from the prevalence of the $1|1_1$ monomers from which it is also derived. As for the *E* center in $CaF_2$, the markedly different spectra and energy-level scheme are attributable to the altered interstitial $F^-$ ion distribution at the dimer center necessitated by the trapped additional $F^-$ ion. Judging by the upconversion fluorescence, the *E* center population is higher in $SrF_2$ than in $CaF_2$ crystals, for the same $Ho^{3+}$ concentration.

## IV. FLUORESCENCE LIFETIMES

Fluorescence lifetimes measured for the *D* multiplets of the five centers are given in Table IV. The lifetimes of the *C*, *D*, and *E* centers in $CaF_2$:$Ho^{3+}$ reported in this work are in agreement with published results.[10] The fluorescence lifetimes for the *C* and *E* centers in $SrF_2$:$Ho^{3+}$ are $267 \pm 5$ $\mu$s and $58.4 \pm 0.6$ $\mu$s, respectively. These lifetimes are consistently larger, being 2.6 and 3.4 times the $CaF_2$ values of $103 \pm 2$ $\mu$s and $17.1 \pm 0.2$ $\mu$s, respectively. Similar trends associated with the $Ho^{3+}$ *D* multiplet in $CaF_2$ and $SrF_2$ crystals are apparent from the results in Table V of Mujaji *et al.*,[12] for the *A* center and its varieties. For each of the five $C_{4v}$-symmetry centers reported therein, the *D* multiplet fluorescence lifetime in $SrF_2$ is about three times the $CaF_2$ value.

## V. CONCLUSIONS

Crystal-field energy levels have been established and model configurations proposed for the five rhombic centers identified in $CaF_2$:0.1% $Ho^{3+}$ and $SrF_2$:0.1% $Ho^{3+}$ crystals. The occurrence of dimer centers in $CaF_2$:$Ho^{3+}$ crystals is found to be consistent with the predictions of Corish and co-workers.[1] For $SrF_2$:$Ho^{3+}$, the theoretical calculations predict the $2|2_2$ cluster to be slightly more favorable than the $2|2_1$ cluster while the $2|3_1$ configuration center is not to be expected at all. The experimental results presented in this work show that only the $2|2_1$ and $2|3_1$ configuration clusters are present in $SrF_2$:$Ho^{3+}$. These experimental results are supported by the dominance of the $1|1_1(A)$ over the $1|1_2(B)$ monomer centers in optical measurements in $SrF_2$:$Ho^{3+}$ crystals for low $Ho^{3+}$ concentrations. Dimerization of $1|1_1$ rather than $1|1_2$ configuration monomers is therefore much more favorable in $SrF_2$:$Ho^{3+}$ crystals. For each dimer center in $SrF_2$, the fluorescence lifetime for the *D* multiplet is approximately three times the lifetime for the corresponding center in $CaF_2$.

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