THEORETICAL INVESTIGATION OF ISOLATED DEFECT CENTERS  
IN Er₃⁺ DOPED CaF₂ CRYSTAL

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Abstract
Crystal-field analysis of two single erbium defect centers found in Er^{3+} doped CaF₂ crystal, called in the literature A and B centers, was performed. Assuming a tetragonal and trigonal site symmetry for A and B defect centers respectively, the parameterized crystal-field Hamiltonians were simplified and diagonalized in the intermediate coupling scheme. A least-squares fitting of the experimentally observed Stark energy sublevels of several Er^{3+} J-multiplets was carried out for each impurity center. Our crystal-field analysis confirms the expected $C_{4v}$ site symmetry for the A center. For the B center, however, the site symmetry is neither $C_{3v}$ nor $C_3$, in opposite to what is believed. Moreover, our analysis shows that the immediate cubic environment of the dopant is greatly affected by the interstitial-fluorine ion for the B center only.

Keywords : CaF₂; Erbium; Crystal-field theory; Site symmetry.

1. Introduction
Recently, more and more interest is devoted to trivalent rare-earth (RE^{3+}) doped CaF₂ crystals, due to their potential device applications as optoelectronic compounds. Many optical and electron paramagnetic resonance studies have been reported [1-8]. The interpretation of the corresponding spectra is complicated by the simultaneous presence of RE^{3+} impurity centers with different site symmetries. Indeed, the RE^{3+} ion enters substitutionally at the Ca^{2+} site. The extra positive charge of the dopant relative to the ion it replaces makes some type of charge-compensation mechanism necessary, either remote or local. In Er^{3+} (4f¹¹) doped CaF₂ crystals, interstitial fluorine ions (F⁻) are shown to be the major compensating mechanisms [1-4]. At very low erbium concentration, electron paramagnetic resonance studies show that the predominant site symmetries are cubic, tetragonal (called A center) and trigonal (called B center). Intuitive structural models have been therefore proposed [9].

The optical spectra of Er^{3+} doped CaF₂ crystals have been studied by several investigators. Using the site selective spectroscopy technique, reliable electronic energy-level diagrams were established for A and B centers [3-8]. The crystal-field analysis of these energy-level diagrams is a powerful technique for examining the exact site symmetry of these defect centers. For the A center, a detailed crystal-field analysis has been reported by Freeth et al [6], in which they confirmed the predicted $C_{4v}$ site symmetry of this center. A less detailed crystal-field analysis for the B center has been reported previously [5, 10]. Nevertheless, only one site symmetry has been examined ($C_{3v}$) using only two Er^{3+} J-multiplets.

In this paper we present a more complete crystal-field analysis of the electronic structure of Er^{3+} ion doped in CaF₂ crystal. Using the same procedure, the two principal single erbium defect centers labeled A and B were examined.

2. Theoretical details
The Hamiltonian model that was used to investigate the electronic structure of Er^{3+} ions doped in CaF₂ crystal is written as follows

$$
H = H_0 + V_c,
$$

where $H_0$ is the free-ion hamiltonian, which regroups the electrostatic and spin-orbit interactions, and $V_c$ is the crystal-field potential.

The latter term can be represented quite simply as follows [11]

$$
V_c = \sum_{k=0q=0}^{D} \sum_{A} A_{kq} Z_{kq}^A,
$$

where $A_{kq}$ are lattice sums which represent the effect of the static charges of neighboring ions, and $Z_{kq}^A$ are operators defined in a similar way to the tesseral harmonics [12] as follows

$$
Z_{kq}^A = C_{iq},
$$

where $C_{iq}$ are coefficients representing the site symmetry of the defect center.
where $B'$ and $B''$ are the Racah tensor operators. In order to calculate the spectra, only a finite number of terms in the expansion of $V_c$ needs to be considered. In octahedral site symmetry, $V_c$ becomes
\begin{equation}
V_c'(O) = B'\langle \vec{Z}_n + \sqrt{3}\vec{Z}_z \rangle + B'\langle \vec{Z}_n - \sqrt{3}\vec{Z}_z \rangle,
\end{equation}
where the $z$-axis of the coordinate system coincident with the fourfold symmetry axis of the cube, $B^4 = \sqrt{3}A_{14}$ and $B^6 = -\sqrt{3}A_{14}$. An alternative expression can be derived by taking the $z$-axis to be along the threefold symmetry axis of the cube, viz.
\begin{equation}
V_c'(O) = B'\langle \vec{Z}_n + \sqrt{3}\vec{Z}_z \rangle + B'\langle \vec{Z}_n - \sqrt{3}\vec{Z}_z \rangle + \epsilon\langle \vec{Z}_z \rangle
\end{equation}
where $B' = \sqrt{3}A_{14}$ and $B'' = \sqrt{3}A_{14}$. For trigonal impurity center, the hamiltonian $V_c$ takes the following form
\begin{equation}
V_c'(C_n) = V_c'(O) + B_n\vec{Z}_n + B_n\vec{Z}_n + B_n\vec{Z}_n
\end{equation}
with $B_n = A_n$, $B_n = [A_n - \sqrt{3}A_n]$ and $B_n = [A_n + \sqrt{3}A_n]$. For trigonal impurity centers the development in Eq. (2) is reduced to
\begin{equation}
V_c'(C_n) = V_c'(O) + B_n\vec{Z}_n + B_n\vec{Z}_n + B_n\vec{Z}_n + B_n\vec{Z}_n
\end{equation}
and
\begin{equation}
V_c'(C_n) = V_c'(O) + B_n\vec{Z}_n + B_n\vec{Z}_n + B_n\vec{Z}_n + B_n\vec{Z}_n
\end{equation}
with $B_n = A_n$, $B_n = [A_n - \sqrt{3}A_n]$, $B_n = [A_n + \sqrt{3}A_n]$.

The matrix elements of $\vec{Z}_z$ tensor operators are calculated numerically by the methods developed by Racah (see Ref. [13] and references therein), whereas the crystal-field parameters $B_{kl}$ are regarded as empirical parameters. For this purpose, a least-squares fitting program based on the Nelder and Mead’s [14] iterative routines was developed. The quality of the fits was determined by the root mean square (rms) deviation $\sigma$ (in cm$^{-1}$) defined as [10]
\begin{equation}
\sigma = \left[ \frac{1}{N-P} \sum_{i} \left( \frac{E_{i}^{\text{obs}} - E_{i}^{\text{calc}}}{E_{i}^{\text{obs}}} \right)^2 \right]^{1/2}
\end{equation}
where $E_i^{\text{obs}}$ and $E_i^{\text{calc}}$ are the experimentally observed and calculated energies for level $i$, respectively, $N$ denotes the number of levels fitted and $P$ is the number of parameters.

3. Results and discussions

The experimental support of our theoretical analyses, will be the measured crystalline-field splitting of the multiplets $^1I_{5/2}$, $^1I_{3/2}$, $^1I_{1/2}$, $^3S_{1/2}$, $^1F_{7/2}$, $^3H_{21/2}$, $^1F_{15/2}$, $^3F_{17/2}$, $^3F_{11/2}$ of Er$^{3+}$ ion diluted in CaF$_2$ host crystal, as derived from published results by Tallant and Wright [3] and Freeth et al [6]. Our calculations are performed by using the intermediate coupling wavefunctions given by Rajnak [15] for erbium in lanthanum trichloride crystal as “free-ion” basis functions for evaluating crystal-field matrix elements. The results of our theoretical analyses will be presented and discussed in the following, starting with the A center.

3.1. the A center

Using the hamiltonian model given in Eq. (7), the total hamiltonian of the Er$^{3+}$ ion was diagonalized on the basis of “free-ion” eigenstates by spanning $^1I_{5/2}$, $^1I_{3/2}$, $^1I_{1/2}$, $^3S_{1/2}$, $^1F_{7/2}$, $^3H_{21/2}$, $^1F_{15/2}$, $^3F_{17/2}$, $^3F_{11/2}$ multiplets. Since the energy difference between the five latter multiplets is small, of the same order of magnitude as the crystal-field splitting, the coupling between these multiplets via the crystal-field hamiltonian has been taken into account. Fitting the experimental Stark energy levels, by allowing the centroid of each multiplet along with the crystal-field parameters $B_{kl}$ to vary freely, a good agreement between twenty five calculated and observed energies was reached with an rms deviation of 2.7 cm$^{-1}$. The values of the fitted crystal-field parameters are listed in Table 1. The calculated energies compared to the experimental ones, and the symmetry properties of the corresponding wavefunctions were summarized in Table 2.

As shown in this table, the observed Stark energy levels are well accounted for. Compared to previous theoretical analyses, our crystal-field parameters as well as the energy level symmetry labels are in good agreement with those reported by Freeth et al [6] and Edgar et al [7]. For comparison the set of crystal-field parameters obtained by Freeth et al. are reported in Table 1.
This work from ref. [6] Site $C_{3v}$ Site $C_{3}$

<table>
<thead>
<tr>
<th></th>
<th>A center</th>
<th>B center</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_2'$</td>
<td>-1756.27</td>
<td>217.950</td>
</tr>
<tr>
<td>$B_4'$</td>
<td>454.01</td>
<td>603.305</td>
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<td>$B_{60}$</td>
<td>443.53</td>
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<td>$B_{80}$</td>
<td>408.83</td>
<td>-618.153</td>
</tr>
<tr>
<td>$B_{10}$</td>
<td>640.08</td>
<td>250.944</td>
</tr>
</tbody>
</table>

Table 1 : Fitted crystal-field parameters, in cm$^{-1}$, for Er$^{3+}$ ions doped in CaF$_2$ crystal at centers A and B.

The slight difference between the two sets of crystal-field parameters is due to the fact that more Stark levels, mainly those emerging from the excited multiplets, $S_{4g}$, $I_{21}(21)_{2g}$, $F_{2g}$, $F_{4g}$, and $F_{6g}$, have been involved in our calculation. As shown in this table, the contribution of the cubic hamiltonian (the first term in Eq.(6)) is important compared to that of the remaining tetragonal distortion terms, consistent with the intuitively simple structural model of an Er$^{3+}$ ion having a substantially unchanged immediate cubic environment of eight $F^-$ ions.

3.2. The B center

Assuming a trigonal site symmetry for this impurity center, the crystal-field hamiltonian models of Eqs. (7) and (8) were employed. Following the same procedure described in the preceding case, a fitting of the experimental Stark energy levels was carried out separately for $C_{3v}$ and $C_{3}$ site symmetries. A well defined minimum in the fits was obtained with an $rms$ deviation of 7.4 cm$^{-1}$ and 6.5 cm$^{-1}$, respectively. The resulting crystal-field parameters are listed in Table 1, while the calculated energies are compared to the experimental ones in Table 2.

As mentioned above, a crystal-field analysis of the B center with $C_{3v}$ symmetry, has been carried out recently by Maalej et al. [10], where only the $I_{2g}$ and $S_{4g}$ multiplets have been considered. A noticeable deviation between the experimental and calculated Stark energies of these two multiplets has been shown. Our present calculation shows that, in fact, this deviation is not restricted to $I_{2g}$ and $S_{4g}$ multiplets but concerns all the $J$-multiplets of Er$^{3+}$ ion. The deviation of the crystal-field splitting of the $S_{4g}$ multiplet is found here to be the half of that reported in Ref. [10]. This is due to the fact that more $J$-multiplets have been involved in our fitting procedure. The reanalysis of the B center using even lower site symmetry such as $C_{3}$, shows a slight improvement of the quality of the fit, but remains unsatisfactory in comparison to that obtained for the A center. These facts strongly suggest that the B center does not, in fact, have exact trigonal symmetry.

A direct comparison of the cubic parameters ($B_2'$ and $B_4'$) with those found for the A center, can be made using the $\{100\}$ to $\{111\}$ axes of quantization ratios [12] of $\nu_7$ and $\nu_8$ for the fourth and sixth degree crystal-field parameters, respectively. The resulting equivalent parameter values for the A center are $B_4'' = 32.332$ cm$^{-1}$ and $B_6'' = 807.31$ cm$^{-1}$. Compared to these values, the cubic parameters for the B center are significantly different (see Table 1). These cubic parameters reflect the influence of the site symmetry. Moreover, they become of the same order of magnitude as the trigonal distortion parameters. This indicates that there is not an eighthold $F^-$ ion coordination around the Er$^{3+}$ ion, but that $F^-$ vacancies occur in this shell. This conclusion is supported by a structural model for the B center proposed by Welsh [16], formed by three interstitial $F^{-}$ ions located at $(100)$, $(010)$ and $(001)$, and one vacancy at $(\nu, \nu, \nu)$ positions from the Er$^{3+}$ ion.

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Table 2: Experimental and calculated Stark energy levels, in cm$^{-1}$, for Er$^{3+}$ ions doped in CaF$_2$ crystal at centers A and B. $\Delta$ is the difference between the calculated and observed energies. $\gamma_i$ and $\gamma_i'$ are the irreducible representations of the double-groups $C_{4v}$ and $C_{3v}$, respectively.

<table>
<thead>
<tr>
<th>Crystal-field Level</th>
<th>A center</th>
<th>B center</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{exp}}$</td>
<td>$E_{\text{calc}}$</td>
<td>$\Delta$</td>
</tr>
<tr>
<td>$H_3$</td>
<td>22436.6</td>
<td>22438.0</td>
</tr>
<tr>
<td>$2^H_{11/2}$</td>
<td>19480.5</td>
<td>19451.6</td>
</tr>
<tr>
<td>$4^I_{13/2}$</td>
<td>15519.1</td>
<td>15539.1</td>
</tr>
<tr>
<td>$4^I_{15/2}$</td>
<td>6815.0</td>
<td>6813.3</td>
</tr>
<tr>
<td>$E_{\text{calc}}$</td>
<td>$\Delta$</td>
<td>$\gamma_i'$</td>
</tr>
<tr>
<td>$\gamma_6$</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>$\gamma_6'$</td>
<td>4.9</td>
<td></td>
</tr>
</tbody>
</table>

$PCN$
Nevertheless, on the one hand, the trigonal site symmetry of this unit is not consistent with our findings, and on the other hand, a single vacancy cannot account for the noticeable distortion of the immediate cubic environment of the impurity ion. So, we suggest a structural relaxation around the impurity center which might bring down more the B center site symmetry, leading to more vacant sites.

4. Conclusion

Using the crystal-field theory, the site symmetry of two single erbium defect centers found in CaF$_2$:Er$^{3+}$ crystal was reanalyzed carefully. Our theoretical analysis confirms the predicted $C_4v$ site symmetry for the A center. For the B center, however, a significant departure from the exact $C_1$ and $C_3$ site symmetries is evidenced, in opposite to what is believed.

References