

# Defect Model of a Tetragonal Sm<sup>3+</sup> Center Found from EPR Measurements in CaF<sub>2</sub> and SrF<sub>2</sub> Crystals

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The EPR parameters ( $\mathbf{g}$  factors  $g_{\parallel}, g_{\perp}$  and hyperfine structure constants  $A_{\parallel}, A_{\perp}$ ) of a tetragonal ( $C_{4v}$ ) Sm<sup>3+</sup> center in CaF<sub>2</sub> and SrF<sub>2</sub> crystals are calculated by considering the crystal-field J-mixing among the ground  $^6H_{5/2}$ , the first excited  $^6H_{7/2}$  and second excited  $^6H_{9/2}$  state multiplets. In the calculations the free-ion and crystal-field parameters of the tetragonal Sm<sup>3+</sup>-F<sup>−</sup> center obtained from polarized laser-selective excitation spectroscopy are used. The calculated results suggest that the tetragonal Sm<sup>3+</sup>-F<sup>−</sup> center is the Sm<sup>3+</sup> center found by later EPR measurements. The  $\mathbf{g}$  factors  $g_{\parallel}, g_{\perp}$  and hyperfine structure constants  $A_{\parallel}, A_{\perp}$  of this EPR center are satisfactorily explained.

**Key words:** Defect Model; Electron Paramagnetic Resonance; Crystal-field Theory; Sm<sup>3+</sup>; CaF<sub>2</sub>; SrF<sub>2</sub>.

## 1. Introduction

The doping of alkaline earth fluorides CaF<sub>2</sub> and SrF<sub>2</sub> with rare earth ions usually results in the replacement of divalent alkaline ions by trivalent rare earth (Re<sup>3+</sup>) ions. The required charge compensation can occur in many ways, leading to sites with cubic, trigonal, tetragonal or rhombic symmetry [1, 2]. There may be different impurity centers with even a consistent axial ( $C_{4v}$  or  $C_{3v}$ ) symmetry in Re<sup>3+</sup>-doped CaF<sub>2</sub> and SrF<sub>2</sub> crystals. For example, early EPR studies [1, 3] found a tetragonal ( $C_{4v}$ ) Sm<sup>3+</sup> center with  $g_{\parallel} \approx 0.907(10)$  and  $g_{\perp} \approx 0.544(10)$  in CaF<sub>2</sub>: Sm<sup>3+</sup>. Weber and Bierig [1] suggested that this center probably arises from an interstitial F<sup>−</sup> charge compensator located at the center of one of the nearest empty cubes of the lattice (so we name it Sm<sup>3+</sup>-F<sup>−</sup> ( $C_{4v}$ ) center). On later studies [4–7] of EPR in CaF<sub>2</sub>: Sm<sup>3+</sup> and SrF<sub>2</sub>: Sm<sup>3+</sup> a consistent  $C_{4v}$  symmetry center was found that was spectroscopically distinct (e.g.,  $g_{\parallel} \approx 0 \pm 0.06$ ,  $g_{\perp} \approx 0.823 \pm 0.003$  in CaF<sub>2</sub>: Sm<sup>3+</sup>) and thus differed in the charge compensation configuration from the earlier studies. However, this Sm<sup>3+</sup> ( $C_{4v}$ ) center was also suggested as Sm<sup>3+</sup>-F<sup>−</sup> ( $C_{4v}$ ) center [7, 8]. It

is interest to determine which EPR center is the Sm<sup>3+</sup>-F<sup>−</sup> ( $C_{4v}$ ) center. Polarized laser-selective excitation is a well-established method for identifying lines of multicenter spectra [9]. Polarized laser-selective excitation and fluorescence spectroscopy of Sm<sup>3+</sup>-doped CaF<sub>2</sub> and SrF<sub>2</sub> crystals was recently performed by Wells and Reeves [10]. They [10] found that the dominant center present in both host crystals is the Sm<sup>3+</sup>-F<sup>−</sup> ( $C_{4v}$ ) center and the optical spectral parameters (i.e., the free-ion and crystal-field parameters) of this center in both crystals were obtained (see Table 1). Although they pointed out that there are two different Sm<sup>3+</sup> ( $C_{4v}$ ) centers found by the EPR measurements, they did not suggest which EPR Sm<sup>3+</sup> ( $C_{4v}$ ) center is the Sm<sup>3+</sup>-F<sup>−</sup> ( $C_{4v}$ ) center. Since the EPR parameters ( $\mathbf{g}$  factors and hyperfine structure constants  $A$ ) of a 4f<sup>n</sup> ion in low symmetry are sensitive to the optical spectral parameters, in this paper we have calculated the EPR  $\mathbf{g}$  factors  $g_{\parallel}, g_{\perp}$  and hyperfine structure constants  $A_{\parallel}, A_{\perp}$  for a tetragonal Sm<sup>3+</sup> center in CaF<sub>2</sub> and SrF<sub>2</sub> crystals by using the above optical spectral parameters. The results (which are related to the assignment of the EPR  $C_{4v}$  center) are discussed.

Table 1. Free-ion and crystal-field parameters (in cm<sup>-1</sup>) for the Sm<sup>3+</sup>-F<sup>-</sup> (C<sub>4v</sub>) centers in CaF<sub>2</sub> and SrF<sub>2</sub> crystals [10].

Parameter	CaF <sub>2</sub> :Sm <sup>3+</sup>	SrF <sub>2</sub> :Sm <sup>3+</sup>
$F^2$	78824	79062
$F^4$	56842	56870
$F^6$	39972	40077
$\alpha$	20.6	20.6
$\beta$	-724	-724
$r$	1700	1700
$\zeta_{4f}$	1166	1168
$B_A^2$	746	472
$B_A^4$	590	545
$B_A^6$	617	489
$B_C^2$	-1227	-1204
$B_C^4$	670	562

## 2. Calculations

The ground state of a free Sm<sup>3+</sup> (4f<sup>5</sup>) ion is <sup>6</sup>H<sub>5/2</sub>, which is split into three Kramers doublets in a tetragonal crystal field. The lowest (or ground) doublet  $\Gamma\gamma$  may be  $\Gamma_6$  or  $\Gamma_7$  depending upon the crystal field parameters. Since the g factors calculated by considering the mixing in only the ground state multiplet <sup>6</sup>H<sub>5/2</sub> or, further, the crystal-field J-mixing of the first excited state multiplet <sup>6</sup>H<sub>7/2</sub> into the ground state multiplet <sup>6</sup>H<sub>5/2</sub> can not agree with the observed values [11], we consider the J-mixing among the ground <sup>6</sup>H<sub>5/2</sub>, the first excited <sup>6</sup>H<sub>7/2</sub> and second excited <sup>6</sup>H<sub>9/2</sub> state multiplets via crystal-field interaction here. Thus a 24 × 24 energy matrix is established. Substituting the free-ion and crystal-field parameters obtained from the optical spectra for the Sm<sup>3+</sup>-F<sup>-</sup> (C<sub>4v</sub>) center in CaF<sub>2</sub> and SrF<sub>2</sub> crystals (see Table 1) into the matrix and diagonalizing it, we can obtain that the wave function of the ground doublet of CaF<sub>2</sub>:Sm<sup>3+</sup> is

$$\begin{aligned} |\Gamma_6\rangle \approx & \pm 0.9865|5/2, \pm 1/2\rangle - 0.0413|7/2, \pm 1/2\rangle \\ & - 0.0867|7/2, \mp 7/2\rangle \pm 0.0037|9/2, \pm 1/2\rangle \quad (1) \\ & \pm 0.1251|9/2, \mp 7/2\rangle \pm 0.0052|9/2, \pm 9/2\rangle, \end{aligned}$$

and that for SrF<sub>2</sub>:Sm<sup>3+</sup> it is

$$\begin{aligned} |\Gamma_6\rangle \approx & \pm 0.9890|5/2, \pm 1/2\rangle - 0.0326|7/2, \pm 1/2\rangle \\ & - 0.0890|7/2, \mp 7/2\rangle \pm 0.0022|9/2, \pm 1/2\rangle \quad (2) \\ & \pm 0.1130|9/2, \mp 7/2\rangle \pm 0.0103|9/2, \pm 9/2\rangle. \end{aligned}$$

From the Zeeman interaction  $H_z$  ( $= g_J \mu_B \mathbf{H} \cdot \mathbf{J}$ , with the original meanings [12, 13]) and hyperfine interaction  $H_{hf}$  ( $= PN_J \hat{N}$ , where  $P$  is the dipolar hyperfine

structure constant and  $N_J$  the diagonal matrix element for the <sup>2S+1</sup>L<sub>J</sub> state [12]), we have the perturbation formulas of the EPR parameters for 4f<sup>n</sup> ions as follows:

$$\begin{aligned} g_{\parallel} &= 2g_J\langle\Gamma\gamma|\hat{J}_Z|\Gamma\gamma\rangle, g_{\perp} = g_J\langle\Gamma\gamma|\hat{J}_{\perp}|\Gamma\gamma\rangle, \\ A_{\parallel} &= 2PN_J\langle\Gamma\gamma|\hat{N}_Z|\Gamma\gamma\rangle, A_{\perp} = PN_J\langle\Gamma\gamma|\hat{N}_{\perp}|\Gamma\gamma\rangle. \quad (3) \end{aligned}$$

Considering the covalence of the Sm<sup>3+</sup>-F<sup>-</sup> bond in both crystals, the orbital angular momentum  $\hat{L}$  in the above formulas should be multiplied by an orbit reduction factor  $k$ . This factor, which is slightly smaller than 1, depends on the covalence of the metal-ligand bond. The shorter the metal-ligand distance  $R$ , the stronger the covalence of this bond and so the smaller the factor  $k$ . This point can be confirmed by the following facts: (i) The covalence of the host crystal CaF<sub>2</sub> is slightly stronger than that of the host crystal SrF<sub>2</sub> [14]. (ii) The effect of pressure on the free-ion parameters (Coulomb repulsion  $F^K$  and spin-orbit coupling coefficient  $\zeta_{4f}$ ) of the Re<sup>3+</sup> ions in crystal [15, 16] suggests that these parameters decrease with decreasing metal-ligand distance and hence with increasing covalence of the bond. For CaF<sub>2</sub>:Sm<sup>3+</sup>, the above free-ion parameters are slightly smaller than those of SrF<sub>2</sub>:Sm<sup>3+</sup> (see Table 1), and so its covalence is stronger. Thus we can reasonably assume for CaF<sub>2</sub>:Sm<sup>3+</sup>,  $k \approx 0.976$  and for SrF<sub>2</sub>:Sm<sup>3+</sup>,  $k \approx 0.980$ . Applying (1) and (2), the factors  $k$  and the free-ion values of  $P$  (<sup>147</sup>Sm)  $\approx -51.7(6) \times 10^{-4}$  cm<sup>-1</sup> and  $P$  (<sup>149</sup>Sm)  $\approx -41.8(6) \times 10^{-4}$  cm<sup>-1</sup> [12] to (3), the EPR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  for the tetragonal Sm<sup>3+</sup> centers in both crystals are calculated. The results are compared with the observed values in Table 2.

## 3. Conclusion and Discussion

From Table 2, it can be seen that the calculated EPR parameters using the free-ion and crystal-field parameters obtained from the optical spectra of Sm<sup>3+</sup>-F<sup>-</sup> (C<sub>4v</sub>) centers in CaF<sub>2</sub> and SrF<sub>2</sub> crystals are consistent with the observed values given in [4–7]. So, the tetragonal EPR Sm<sup>3+</sup> center in CaF<sub>2</sub> and SrF<sub>2</sub> found in [4–7] rather than that in [1, 3] is the Sm<sup>3+</sup>-F<sup>-</sup> (C<sub>4v</sub>) center. The assignment can not be transformed by changing the orbit reduction factor  $k$  because the factor  $k$  affects slightly the calculated average value of  $\bar{g} [= (g_{\parallel} + 2g_{\perp})/3]$  and  $\bar{A} [= (A_{\parallel} + 2A_{\perp})/3]$ , but it can not alter the sign of the anisotropy of the g factor and constant A (characterized by  $\Delta g = g_{\parallel} - g_{\perp}$  and  $\Delta A = A_{\parallel} - A_{\perp}$ ). So, the above assignment is reasonable

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{(147\text{Sm})}$	$A_{\perp}^{(147\text{Sm})}$	$A_{\parallel}^{(149\text{Sm})}$	$A_{\perp}^{(149\text{Sm})}$
CaF <sub>2</sub> :Sm <sup>3+</sup>	Cal.	0.023	0.822	7.2	221 ± 5	6.1
	Expt. [4–7]	0 ± 0.06	0.823 ± 0.003	0 ± 10	230 ± 5	0 ± 10
	Expt. [1, 3]	0.907 ± 0.010	0.544 ± 0.010			190 ± 5
SrF <sub>2</sub> :Sm <sup>3+</sup>	Cal.	0.027	0.824	7.3	225 ± 5	6.2
	Expt. [4–7]	< 0.1	0.823 ± 0.003	0 ± 10	230 ± 4	0 ± 10
						190 ± 4

and the **g** factors  $g_{\parallel}$ ,  $g_{\perp}$  and hyperfine structure constants  $A_{\parallel}$ ,  $A_{\perp}$  (for isotopes <sup>147</sup>Sm<sup>3+</sup> and <sup>149</sup>Sm<sup>3+</sup>) observed in [4–7] for Sm<sup>3+</sup>-doped CaF<sub>2</sub> and SrF<sub>2</sub> can be

satisfactorily explained. The defect model of the tetragonal EPR Sm<sup>3+</sup> center in CaF<sub>2</sub> found in [1, 3] remains to be further studied.

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Table 2. The EPR **g** factors and hyperfine structure constants  $A_i$  (in units of  $10^{-4}\text{cm}^{-1}$ ) for the tetragonal Sm<sup>3+</sup> center in CaF<sub>2</sub> and SrF<sub>2</sub> crystals.