

# Defect Model of a Tetragonal $\text{Sm}^{3+}$ Center Found from EPR Measurements in $\text{CaF}_2$ and $\text{SrF}_2$ 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 ( $C_{4v}$ )  $\text{Sm}^{3+}$  center in  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals are calculated by considering the crystal-field J-mixing among the ground  $^6\text{H}_{5/2}$ , the first excited  $^6\text{H}_{7/2}$  and second excited  $^6\text{H}_{9/2}$  state multiplets. In the calculations the free-ion and crystal-field parameters of the tetragonal  $\text{Sm}^{3+}\text{-F}^-$  center obtained from polarized laser-selective excitation spectroscopy are used. The calculated results suggest that the tetragonal  $\text{Sm}^{3+}\text{-F}^-$  center is the  $\text{Sm}^{3+}$  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;  $\text{Sm}^{3+}$ ;  $\text{CaF}_2$ ;  $\text{SrF}_2$ .

## 1. Introduction

The doping of alkaline earth fluorides  $\text{CaF}_2$  and  $\text{SrF}_2$  with rare earth ions usually results in the replacement of divalent alkaline ions by trivalent rare earth ( $\text{Re}^{3+}$ ) 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  $\text{Re}^{3+}$ -doped  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals. For example, early EPR studies [1, 3] found a tetragonal ( $C_{4v}$ )  $\text{Sm}^{3+}$  center with  $g_{\parallel} \approx 0.907(10)$  and  $g_{\perp} \approx 0.544(10)$  in  $\text{CaF}_2\text{:Sm}^{3+}$ . Weber and Bierig [1] suggested that this center probably arises from an interstitial  $\text{F}^-$  charge compensator located at the center of one of the nearest empty cubes of the lattice (so we name it  $\text{Sm}^{3+}\text{-F}^-$  ( $C_{4v}$ ) center). On later studies [4–7] of EPR in  $\text{CaF}_2\text{:Sm}^{3+}$  and  $\text{SrF}_2\text{:Sm}^{3+}$  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  $\text{CaF}_2\text{:Sm}^{3+}$ ) and thus differed in the charge compensation configuration from the earlier studies. However, this  $\text{Sm}^{3+}$  ( $C_{4v}$ ) center was also suggested as  $\text{Sm}^{3+}\text{-F}^-$  ( $C_{4v}$ ) center [7, 8]. It

is interest to determine which EPR center is the  $\text{Sm}^{3+}\text{-F}^-$  ( $C_{4v}$ ) 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  $\text{Sm}^{3+}$ -doped  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals was recently performed by Wells and Reeves [10]. They [10] found that the dominant center present in both host crystals is the  $\text{Sm}^{3+}\text{-F}^-$  ( $C_{4v}$ ) 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  $\text{Sm}^{3+}$  ( $C_{4v}$ ) centers found by the EPR measurements, they did not suggest which EPR  $\text{Sm}^{3+}$  ( $C_{4v}$ ) center is the  $\text{Sm}^{3+}\text{-F}^-$  ( $C_{4v}$ ) center. Since the EPR parameters ( $\mathbf{g}$  factors and hyperfine structure constants  $A$ ) of a  $4f^n$  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  $\text{Sm}^{3+}$  center in  $\text{CaF}_2$  and  $\text{SrF}_2$  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  $\text{cm}^{-1}$ ) for the  $\text{Sm}^{3+}\text{-F}^-$  ( $\text{C}_{4v}$ ) centers in  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals [10].

Parameter	$\text{CaF}_2:\text{Sm}^{3+}$	$\text{SrF}_2:\text{Sm}^{3+}$
$F^2$	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  $\text{Sm}^{3+}$  ( $4f^5$ ) ion is  $^6\text{H}_{5/2}$ , 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  $\mathbf{g}$  factors calculated by considering the mixing in only the ground state multiplet  $^6\text{H}_{5/2}$  or, further, the crystal-field J-mixing of the first excited state multiplet  $^6\text{H}_{7/2}$  into the ground state multiplet  $^6\text{H}_{5/2}$  can not agree with the observed values [11], we consider the J-mixing among the ground  $^6\text{H}_{5/2}$ , the first excited  $^6\text{H}_{7/2}$  and second excited  $^6\text{H}_{9/2}$  state multiplets via crystal-field interaction here. Thus a  $24 \times 24$  energy matrix is established. Substituting the free-ion and crystal-field parameters obtained from the optical spectra for the  $\text{Sm}^{3+}\text{-F}^-$  ( $\text{C}_{4v}$ ) center in  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals (see Table 1) into the matrix and diagonalizing it, we can obtain that the wave function of the ground doublet of  $\text{CaF}_2:\text{Sm}^{3+}$  is

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

and that for  $\text{SrF}_2:\text{Sm}^{3+}$  it is

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

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

structure constant and  $N_J$  the diagonal matrix element for the  $^{2S+1}L_J$  state [12]), we have the perturbation formulas of the EPR parameters for  $4f^n$  ions as follows:

$$g_{\parallel} = 2g_J \langle \Gamma\gamma | \hat{J}_Z | \Gamma\gamma \rangle, \quad g_{\perp} = g_J \langle \Gamma\gamma | \hat{J}_{\pm} | \Gamma\gamma' \rangle,$$

$$A_{\parallel} = 2PN_J \langle \Gamma\gamma | \hat{N}_Z | \Gamma\gamma \rangle, \quad A_{\perp} = PN_J \langle \Gamma\gamma | \hat{N}_{\pm} | \Gamma\gamma' \rangle. \quad (3)$$

Considering the covalence of the  $\text{Sm}^{3+}\text{-F}^-$  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  $\text{CaF}_2$  is slightly stronger than that of the host crystal  $\text{SrF}_2$  [14]. (ii) The effect of pressure on the free-ion parameters (Coulomb repulsion  $F^K$  and spin-orbit coupling coefficient  $\zeta_{4f}$ ) of the  $\text{Re}^{3+}$  ions in crystal [15, 16] suggests that these parameters decrease with decreasing metal-ligand distance and hence with increasing covalence of the bond. For  $\text{CaF}_2:\text{Sm}^{3+}$ , the above free-ion parameters are slightly smaller than those of  $\text{SrF}_2:\text{Sm}^{3+}$  (see Table 1), and so its covalence is stronger. Thus we can reasonably assume for  $\text{CaF}_2:\text{Sm}^{3+}$ ,  $k \approx 0.976$  and for  $\text{SrF}_2:\text{Sm}^{3+}$ ,  $k \approx 0.980$ . Applying (1) and (2), the factors  $k$  and the free-ion values of  $P$  ( $^{147}\text{Sm}$ )  $\approx -51.7(6) \times 10^{-4} \text{cm}^{-1}$  and  $P$  ( $^{149}\text{Sm}$ )  $\approx -41.8(6) \times 10^{-4} \text{cm}^{-1}$  [12] to (3), the EPR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  for the tetragonal  $\text{Sm}^{3+}$  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  $\text{Sm}^{3+}\text{-F}^-$  ( $\text{C}_{4v}$ ) centers in  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals are consistent with the observed values given in [4–7]. So, the tetragonal EPR  $\text{Sm}^{3+}$  center in  $\text{CaF}_2$  and  $\text{SrF}_2$  found in [4–7] rather than that in [1, 3] is the  $\text{Sm}^{3+}\text{-F}^-$  ( $\text{C}_{4v}$ ) 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  $\mathbf{g}$  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

		$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}(^{147}\text{Sm})$	$A_{\perp}(^{147}\text{Sm})$	$A_{\parallel}(^{149}\text{Sm})$	$A_{\perp}(^{149}\text{Sm})$
$\text{CaF}_2:\text{Sm}^{3+}$	Cal.	0.023	0.822	7.2	$221 \pm 5$	6.1	$180 \pm 4$
	Expt. [4–7]	$0 \pm 0.06$	$0.823 \pm 0.003$	$0 \pm 10$	$230 \pm 5$	$0 \pm 10$	$190 \pm 5$
	Expt. [1, 3]	$0.907 \pm 0.010$	$0.544 \pm 0.010$				
$\text{SrF}_2:\text{Sm}^{3+}$	Cal.	0.027	0.824	7.3	$225 \pm 5$	6.2	$183 \pm 4$
	Expt. [4–7]	$< 0.1$	$0.823 \pm 0.003$	$0 \pm 10$	$230 \pm 4$	$0 \pm 10$	$190 \pm 4$

Table 2. The EPR  $\mathbf{g}$  factors and hyperfine structure constants  $A_i$  (in units of  $10^{-4}\text{cm}^{-1}$ ) for the tetragonal  $\text{Sm}^{3+}$  center in  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals.

and the  $\mathbf{g}$  factors  $g_{\parallel}$ ,  $g_{\perp}$  and hyperfine structure constants  $A_{\parallel}$ ,  $A_{\perp}$  (for isotopes  $^{147}\text{Sm}^{3+}$  and  $^{149}\text{Sm}^{3+}$ ) observed in [4–7] for  $\text{Sm}^{3+}$ -doped  $\text{CaF}_2$  and  $\text{SrF}_2$  can be

satisfactorily explained. The defect model of the tetragonal EPR  $\text{Sm}^{3+}$  center in  $\text{CaF}_2$  found in [1, 3] remains to be further studied.

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