Defect Model of a Tetragonal Sm^{3+} Center Found from EPR Measurements in CaF_2 and SrF_2 Crystals

Wen-Chen Zheng^{a,b}, Hui-Ning Dong^{a,c}, Shao-Yi Wu^{b,d}, and Sheng Tang^a

^a Department of Material Science, Sichuan University, Chengdu 610064, P. R. China

^b International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

^c Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, China

^d Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

Reprint requests to W.-C. Z.; E-mail: zhengwenchen@netease.com

Z. Naturforsch. **58a**, 373 – 375 (2003); received February 14, 2003

The EPR parameters ($\mathbf{g}$ factors $g_{\parallel}$, $g_{\perp}$ and hyperfine structure constants $A_{\parallel}$, $A_{\perp}$) of a tetragonal (C_{4v}) Sm^{3+} center in CaF_2 and 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 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; Sm^{3+} ; CaF_2 ; SrF_2 .

1. Introduction

The doping of alkaline earth fluorides CaF_2 and SrF_2 with rare earth ions usually results in the replacement of divalent alkaline ions by trivalent rare earth (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 Re^{3+} -doped CaF_2 and SrF_2 crystals. For example, early EPR studies [1, 3] found a tetragonal (C_{4v}) 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 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 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 Sm^{3+} -doped CaF_2 and 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 Sm^{3+} (C_{4v}) centers found by the EPR measurements, they did not suggest which EPR 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 Sm^{3+} center in CaF_2 and 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 cm^{-1}) for the $\text{Sm}^{3+}\text{-F}^-$ (C_{4v}) centers in CaF_2 and 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
α	20.6	20.6
β	-724	-724
r	1700	1700
ζ_{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^{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 Γ_6 or Γ_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 24×24 energy matrix is established. Substituting the free-ion and crystal-field parameters obtained from the optical spectra for the $\text{Sm}^{3+}\text{-F}^-$ (C_{4v}) center in CaF_2 and 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 CaF_2 is slightly stronger than that of the host crystal SrF_2 [14]. (ii) The effect of pressure on the free-ion parameters (Coulomb repulsion F^K and spin-orbit coupling coefficient ζ_{4f}) of the 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}Sm) $\approx -51.7(6) \times 10^{-4} \text{cm}^{-1}$ and P (^{149}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 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 $\text{Sm}^{3+}\text{-F}^-$ (C_{4v}) centers in CaF_2 and SrF_2 crystals are consistent with the observed values given in [4–7]. So, the tetragonal EPR Sm^{3+} center in CaF_2 and SrF_2 found in [4–7] rather than that in [1, 3] is the $\text{Sm}^{3+}\text{-F}^-$ (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 ± 5	6.1	180 ± 4
	Expt. [4–7]	0 ± 0.06	0.823 ± 0.003	0 ± 10	230 ± 5	0 ± 10	190 ± 5
	Expt. [1, 3]	0.907 ± 0.010	0.544 ± 0.010				
$\text{SrF}_2:\text{Sm}^{3+}$	Cal.	0.027	0.824	7.3	225 ± 5	6.2	183 ± 4
	Expt. [4–7]	< 0.1	0.823 ± 0.003	0 ± 10	230 ± 4	0 ± 10	190 ± 4

Table 2. The EPR $\mathbf{g}$ factors and hyperfine structure constants A_i (in units of 10^{-4}cm^{-1}) for the tetragonal Sm^{3+} center in CaF_2 and 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 Sm^{3+} -doped CaF_2 and SrF_2 can be

satisfactorily explained. The defect model of the tetragonal EPR Sm^{3+} center in CaF_2 found in [1, 3] remains to be further studied.

- [1] M. J. Weber and R. W. Bierig, Phys. Rev. **134A**, 1492 (1964).
- [2] T. S. Chang and M. I. Cohen, J. Chem. Phys. **64**, 5255 (1976).
- [3] W. Low, Phys. Rev. **134A**, 1479 (1964).
- [4] A. A. Antinpin, I. N. Kurkin, L. D. Livanova, L. Z. Potvorova, and L. Ya. Shekun, Sov. Phys. Solid State **7**, 1271 (1965).
- [5] A. A. Antinpin, I. N. Kurkin, L. D. Livanova, L. Z. Potvorova, and L. Ya. Shekun, Sov. Phys. Tech. Phys. **11**, 821 (1966).
- [6] H. N. Evans and S. D. Mclaughlan, Phys. Lett. **23**, 638 (1966).
- [7] R. C. Newman and R. J. Woodward, J. Phys. C **7**, L433 (1974).
- [8] I. J. Ashburner, R. C. Newman, and S. D. Mclaughlan, Phys. Lett. **27A**, 212 (1968).
- [9] J. C. Wright and K. M. Cirillo-Penn, Radiat. Eff. Def. Solids, **119–121**, 231 (1991).
- [10] J.-P. R. Wells and R. J. Reeves, Phys. Rev. **B61**, 13593 (2000).
- [11] M. Yamaga, M. Honda, J.-P. R. Wells, T. P. J. Han, and H. G. Gallagher, J. Phys.:Condens. Matter **12**, 8727 (2000).
- [12] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition-Ions, Oxford University press, London 1970.
- [13] I. A. Sorin and M. V. Vlasova, Electron Spin Resonance of Paramagnetic Crystals (Translated from Russian by P. Gluck), Plenum Press, New York 1973.
- [14] B. F. Levine, J. Chem. Phys. **59**, 1463 (1973).
- [15] C. Bungenstock, Th. Troster, and W. B. Holzapfel, Phys. Rev. **B62**, 7945 (2000).
- [16] Y. R. Shen and W. B. Holzapfel, Phys. Rev. **B52**, 12618 (1995).