Theoretical Studies of the EPR *g* Factors and Optical Spectra for Tetragonal Ce^{3+} Centers in CaF_2 and SrF_2 Crystals

Hui-Ning Dong[a,b], Shao-Yi Wu[b,c], and Wen-Chen Zheng[b,c]

[a] Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, China
[b] Department of Material Science, Sichuan University, Chengdu 610064, P. R. China
[c] International Centre for Materials Physics, Chinese Academy of Sciences,
Shenyang 110016, P. R. China

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

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By using the irreducible tensor operator technique, the complete energy matrix including the admixture between $J = 7/2$ and $J = 5/2$ manifolds and the covalency reduction effect for 4f ion in tetragonal symmetry is established. Based on this, the electron paramagnetic resonance (EPR) g factors for the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 crystals are reasonably explained and some levels of the $J = 5/2$ manifold for these centres are estimated. The results are discussed.

Key words: Crystal- and Ligand-field Theory; Electron Paramagnetic Resonance (EPR); Optical Spectra; Ce^{3+}; CaF_2; SrF_2.

1. Introduction

Many studies involving various experimental techniques have been done in an attempt to understand the behavior of trivalent cerium in CaF_2 and SrF_2 crystals [1 - 9]. This system is an attractive one for study because Ce^{3+} possesses a single optically active electron, whose 4f orbital, like those of other rare-earth ions, is acted on only weakly by external fields. In pure CaF_2 (or SrF_2) crystals, the Ca^{2+} (or Sr^{2+}) ion is under O_h symmetry with eight nearest-neighbor fluoride ions. When a Ce^{3+} ion substitutes for the central Ca^{2+} (or Sr^{2+}) ion, the original O_h symmetry of the host Ca^{2+} site would change to a lower symmetry (C_{4v} or C_{3v}) because of the charge compensation. For the tetragonal Ce^{3+} centers, the charge compensation is performed by an interstitial F^- ion approximately at the center of one of the nearest empty cubes of lattice F^- ions [2, 10]. The EPR g factors $g_\parallel$ and $g_\perp$ for the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 were measured by Kiel and Mims [3]. In order to explain these g-values, they applied the simple mixing eigenfunction of the ground state by a linear combination within the $J = 5/2$ manifold [3], i. e.,

$$\Gamma_7(\pm) = \sin\theta|5/2, \pm 5/2\rangle \pm \cos\theta|5/2, \mp 3/2\rangle, \quad (1)$$

where $\Gamma_7(\pm)$ denotes the two components of Γ_7 irreducible representation. $\cos\theta$ (or $\sin\theta$) is an adjustable parameter. The best fit of the $g_\parallel$ and $g_\perp$ values is obtained by setting $\cos\theta = 0.912$ and 0.900 for the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 crystals, respectively [3]. The calculated results of $g_\parallel$ and $g_\perp$ for both crystals are larger than the observed values (see Table 1). The differences in the observed and calculated g-values can be removed by further mixing $|7/2, \mp 5/2\rangle$ and $|7/2, \pm 3/2\rangle$ of the first excited state $^2F_{7/2}$. Thus, the ground doublet wave functions can be rewritten as [11, 12]:

$$\Gamma_7(\pm) = p|5/2, \mp 5/2\rangle + q|5/2, \pm 3/2\rangle \pm r|7/2, \mp 5/2\rangle \pm t|7/2, \pm 3/2\rangle \quad (2)$$

with the normalization relationship

$$p^2 + q^2 + r^2 + t^2 = 1, \quad (3)$$

where the mixing coefficients p, q, r, and t are often regarded as adjustable parameters. It is difficult to determine the four adjustable parameters from the two observed g-values ($g_\parallel$, $g_\perp$) and the normalization relationship [11] because of the uncertainty. So, for the tetragonal Ce^{3+} center in other crystal, some

Table 1. EPR parameters $g_{\|}$ and $g_{\perp}$ of the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 crystals.

			$g_{\|}$	$g_{\perp}$
CaF_2	Calc.	[3]	3.13	1.43
	Calc.	this work	3.036	1.394
	Expt.	[3]	3.038(3)	1.396(2)
SrF_2	Calc.	[3]	2.98	1.50
	Calc.	this work	2.921	1.466
	Expt.	[3]	2.922(3)	1.465(3)

Table 2. Energy levels for the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 crystals (in cm^{-1}).

Energy	— CaF_2 —			— SrF_2 —		
levels	Calc. ^{A}	Calc. ^{B}	Expt. ^{C}	Calc. ^{A}	Calc. ^{B}	Expt. ^{D}
$\Gamma_7(F_{7/2}, \Gamma_7)$	3395	3689	3559	3196	3458	3380
$\Gamma_6(F_{7/2}, \Gamma_8)$	3258	2476	2438	3090	2585	2393 ^{F}
$\Gamma_7(F_{7/2}, \Gamma_8)$	2770	2287	2304	2655	2406	2280
$\Gamma_6(F_{7/2}, \Gamma_6)$	2182	2186	2189	2190	2177	2215
$\Gamma_7(F_{5/2}, \Gamma_7)$	759	403	576	821	780	1085±250 ^{G}
$\Gamma_6(F_{5/2}, \Gamma_8)$	984	207	110 ^{E}	632	231	39±2 ^{G}
$\Gamma_7(F_{5/2}, \Gamma_8)$	0	0	0	0	0	0

^{A} [4]. ^{B} This work. ^{C} [2]. ^{D} [5]. ^{E} Estimated value. ^{F} Estimated by comparing with that of CaF_2:Ce^{3+} in [5]. ^{G} Estimated from the magnetic-susceptibility measurements in [5].

assumptions were made to determine the four parameters [11]. Even so, such studies have not been made for the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 crystals.

The optical spectra of the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 were also measured [2, 5]. Since the differences between some energy levels in the $J = 5/2$ manifold [i. e., the second- or/and third-lowest 4f levels $\Gamma_6(F_{5/2}, \Gamma_8)$ and $\Gamma_7(F_{5/2}, \Gamma_7)$] and the ground $\Gamma_7(F_{5/2}, \Gamma_8)$ are small, it is difficult to obtain these levels from optical measurements. In [2], Manthey predicted the energy level $\Gamma_6(F_{5/2}, \Gamma_8) \approx 110$ cm^{-1} for CaF_2:Ce^{3+} from the crystal-field parameters B_k^q given by him and the additional information of the measured g values [13]. However no details were reported, and the value of the level $\Gamma_6(F_{5/2}, \Gamma_8)$ calculated using these B_k^q is about 200 cm^{-1}. For SrF_2:Ce^{3+}, Walker and Mires [5] estimated the energy levels $\Gamma_7(F_{5/2}, \Gamma_8) = 1085 \pm 250$ cm^{-1} and $\Gamma_7(F_{5/2}, \Gamma_7) = 39 \pm 2$ cm^{-1} by studying the observed magnetic susceptibility. In their studies, the g factors were calculated by neglecting the admixture between the $J = 5/2$ and $J = 7/2$ manifolds. So, they thought that the magnetic-susceptibility measurements may not be the best way to locate the levels. In addition, Starostin et al. [4] made a crystal-field energy level studies from Hartree-Fock calculations for these optical spectra. The agreement between calculation and experiment is not satisfactory, particularly, the relative magnitude between levels $\Gamma_6(F_{5/2}, \Gamma_8)$ and $\Gamma_7(F_{5/2}, \Gamma_8)$ calculated in [4] is opposite to that of the above estimation (see Table 2).

In order to overcome the above difficulties, in the present paper we apply the irreducible tensor technique to establish the complete energy matrix including both $^2F_{5/2}$ and $^2F_{7/2}$ states and the covalency reduction effect for the $4f^1$ (Ce^{3+}) ion in tetragonal symmetry. By diagonalizing the complete energy matrix, the crystal-field energy levels and the ground doublet wave functions can be obtained. Thus, the EPR g factors and the optical spectra of the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 crystals were studied in a unified way. The results (including the new estimated values of the $\Gamma = 5/2$ manifold) are discussed.

2. Calculation

The electronic configuration of the free Ce^{3+} ($4f^1$) ion has a $^2F_{5/2}$ ground state and a $^2F_{7/2}$ excited state. The tetragonal (C_{4V}) crystal field splits the $^2F_{5/2}$ and $^2F_{7/2}$ states into three and four Kramers doublets, respectively. The lowest lying doublet is Γ_7 [14].

The total Hamiltonian for a rare earth ion in a crystal has the form [14]:

$$\hat{H} = \hat{H}_{\text{free}} + \hat{H}_{\text{so}} + \hat{H}_{\text{cf}}, \tag{4}$$

where $\hat{H}_{\text{free}}$ is the free ion Hamiltonian (not including spin-orbit coupling), $\hat{H}_{\text{so}}$ is the spin-orbit coupling interaction and $\hat{H}_{\text{cf}}$ is the crystal field Hamiltonian. $\hat{H}_{\text{so}}$ can be represented as

$$\hat{H}_{\text{so}} = \xi(S \cdot L), \tag{5}$$

where S and L are the spin and orbital momentum operators, ξ is the spin-orbit coupling coefficient in crystal. Considering the covalency reduction effect, we have $\xi = k_0 \xi_0$, where ξ_0 is the spin-orbit coefficient of free ion and k_0 is the orbital reduction factor. For Ce^{3+} in CaF_2 and SrF_2 crystals, $\xi_0 \approx 640$ cm^{-1} [14], $k_0 \approx 0.9840$ [15].

The matrix elements of H_{so} may with the irreducible tensor operator technique be written as

$$\langle 4f^n\alpha SLJM|H_{\mathrm{SO}}|4f^n\alpha' S'L'J'M'\rangle = \delta(MM')$$

$$\cdot\,\delta(JJ')\zeta_{4\mathrm{f}}(-1)^{J+L+S'}[l(l+1)(2l+1)]^{1/2}\left\{\begin{matrix} L\,L'\,1 \\ S'\,S\,J\end{matrix}\right\}$$

$$\cdot\,\langle 4f^n\alpha SL||V^{(11)}||4f^n\alpha' S'L'\rangle. \qquad (6)$$

H_{cf} is expressed in terms of the tensor operators C_k^q and the crystal field parameters B_k^q [16]:

$$H_{\mathrm{cf}} = B_0^2C_0^2 + B_0^4C_0^4 + B_4^4(C_4^4 + C_{-4}^4) \qquad (7)$$

$$+ B_0^6C_0^6 + B_4^6(C_4^6 + C_{-4}^6).$$

The matrix elements of H_{cf} may be written as

$$\langle 4f^1\alpha SLJM_J|H_{CF}|4f^1\alpha' S'L'J'M'_J\rangle$$

$$= \sum_{k,q}(-1)^{2J-M_J+S+L'+k}\left\{\begin{matrix} J & k & J' \\ -M_J & q & M'_J\end{matrix}\right\}\left\{\begin{matrix} J' & k & J \\ L & S & L'\end{matrix}\right\}$$

$$\cdot\ [(2J+1)(2J'+1)]^{1/2} \qquad (8)$$

$$\cdot\ \langle f||c^{(k)}||f\rangle\langle 4f^1\alpha SL||U^{(k)}||4f^1\alpha' S'L'\rangle B_{kq}\delta_{S,S'},$$

where k = 2, 4, 6; q = 0, ±4 and $\leq k$; $\left\{\begin{matrix} J & k & J' \\ -M_J & q & M'_J\end{matrix}\right\}$ and $\left\{\begin{matrix} J' & k & J \\ L & S & L'\end{matrix}\right\}$ are the $3j$ and the $6j$ symbols, respectively. The corresponding reducible matrix elements $\langle f||c^{(k)}||f\rangle$ and $\langle 4f^1\alpha SL||U^{(k)}||4f^1\alpha' S'L'\rangle$ can be obtained in the tables of Nielson-Koster [17].

From the above expressions, the complete energy matrix (14×14) including both $^2\mathrm{F}_{5/2}$ and $^2\mathrm{F}_{7/2}$ states can be established. In the energy matrix, five crystal-field parameters B_k^q are used as adjustable parameters. By diagonalizing the complete energy matrix, the seven energy levels (which are related to the absorption bands of optical spectra) and the basis functions for Γ_7 in terms of a linear combination of $|JM_J\rangle$ doublet can be obtained. By using these energy levels, the ground doublet wave functions $\Gamma_7(\pm)$ can be obtained. Based on these functions $\Gamma_7(\pm)$, the g factors $g_{\|}$ and $g_{\perp}$ for the tetragonal Ce^{3+} centers in CaF_2 and SrF_2 crystals can be calculated from the following expressions [16]:

$$g_{\|} = 2g_J\langle +|\hat{J}_z|+\rangle,\ \ g_{\perp} = g_J\langle +|\hat{J}_+ + \hat{J}_-|-\rangle. \qquad (9)$$

Thus, by fitting the calculated optical and EPR spectral data to the observed values, the crystal-field parameters B_k^q can be obtained. They are $B_2^0 \approx$ 333cm^{-1}, $B_4^0 \approx$ –2176 cm^{-1}, $B_6^0 \approx$ 725 cm^{-1}, $B_4^4 \approx$ –1573 cm^{-1}, $B_6^4 \approx$ –2872 cm^{-1} for CaF_2:Ce^{3+} and B_2^0 ≈333 cm^{-1}, $B_4^0 \approx$ –2349 cm^{-1}, $B_6^0 \approx$ 925 cm^{-1}, B_4^4 ≈ –1996 cm^{-1}, $B_6^4 \approx$ –619 cm^{-1} for SrF_2:Ce^{3+}. The comparisons between the calculated and observed g factors and those between calculated and experimental optical spectra are shown in Table 1 and 2, respectively. In the calculations, the ground doublet wave functions are

$$\Gamma_7(\pm) \approx \pm 0.9026|5/2,\pm 5/2\rangle \pm 0.4158|5/2,\mp 3/2\rangle$$

$$+\ 0.0595|7/2,\pm 5/2\rangle + 0.0938|7/2,\mp 3/2\rangle \qquad (10)$$

for CaF_2:Ce^{3+} crystals, and

$$\Gamma_7(\pm) \approx \pm 0.8931|5/2,\pm 5/2\rangle \pm 0.4359|5/2,\mp 3/2\rangle$$

$$+\ 0.0385|7/2,\pm 5/2\rangle + 0.0907|7/2,\mp 3/2\rangle \qquad (11)$$

for SrF_2:Ce^{3+} crystals. In these wave functions, the four adjustable parameters in (2) are obtained from the above calculations related to the optical spectra and EPR data. The small mixing coefficients of $|7/2,\pm 5/2\rangle$ and $|7/2,\mp 3/2\rangle$ of the first excited state $^2\mathrm{F}_{7/2}$ are reasonable.

3. Discussion

From the above studies it can be seen that for the tetragonal Ce^{3+} centres in CaF_2 and SrF_2, the EPR g factors $g_{\|}$ and $g_{\perp}$ calculated in this paper show excellent agreement with the observed values (see Table 1), suggesting that, to explain the g factors for Ce^{3+} centers in crystals to a better extent, the admixture between $J = 5/2$ and $J = 7/2$ manifolds should be taken into account. The present calculated energy levels of the above Ce^{3+} centers are in better agreement than those in the previous paper [4] with the observed values (see Table 2, not including the estimated experimental energy levels). According to the calculations, the present estimated value of level $\Gamma_6(\mathrm{F}_{5/2},\Gamma_8)$ for CaF_2:Ce^{3+} is 207 cm^{-1}. Although it is larger than that estimated in [2] (see Table 2), it is close to the value

($\approx$200 cm^{-1}) calculated by using the crystal-field parameters given in [2]. For SrF_2:Ce^{3+}, the present estimated energy level $\Gamma_7(F_{5/2},\Gamma_7)$ is close to the previous estimation, but the energy level $\Gamma_6(F_{5/2},\Gamma_8)$ estimated here is much larger than the previous estimated value from the magnetic-susceptibility measurements (see Table 2). Since (i) the magnetic-susceptibility measurements may not be the best way to locate the energy levels [2] and (ii) the estimated values in the paper are obtained by calculating the optical spectra and EPR parameters in a unified way, the present estimated values may be more reasonable. This point remains to be checked by other methods.

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