Theoretical Studies of the EPR $g$ Factors and Optical Spectra for Tetragonal Ce$^{3+}$ Centers in CaF$_2$ and SrF$_2$ Crystals

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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 Ce$^{3+}$ (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.,

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

where $\Gamma_7(\pm)$ denotes the two components of $\Gamma_7$ 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, $\mp 5/2$] and [7/2, $\pm 3/2$] of the first excited state $2F_{7/2}$. Thus, the ground doublet wave functions can be rewritten as [11, 12]:

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

with the normalization relationship

$$ p^2 + q^2 + r^2 + t^2 = 1, $$ (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 $g_1$ and $g_\perp$ of the tetragonal Ce$^{3+}$ centers in CaF$_2$ and SrF$_2$ crystals.

<table>
<thead>
<tr>
<th></th>
<th>CaF$_2$</th>
<th>SrF$_2$</th>
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<tbody>
<tr>
<td>$g_1$</td>
<td>[3]</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td>3.13</td>
<td>3.036</td>
</tr>
<tr>
<td>$g_\perp$</td>
<td>1.43</td>
<td>1.394</td>
</tr>
</tbody>
</table>

Table 2. Energy levels for the tetragonal Ce$^{3+}$ centers in CaF$_2$ and SrF$_2$ crystals (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Energy levels</th>
<th>CaF$_2$</th>
<th>SrF$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_7(F_{5/2}, \Gamma_8)$</td>
<td>3395</td>
<td>3689</td>
</tr>
<tr>
<td>$\Gamma_6(F_{5/2}, \Gamma_7)$</td>
<td>3258</td>
<td>2476</td>
</tr>
<tr>
<td>$\Gamma_5(F_{5/2}, \Gamma_5)$</td>
<td>2770</td>
<td>2287</td>
</tr>
<tr>
<td>$\Gamma_4(F_{5/2}, \Gamma_4)$</td>
<td>2182</td>
<td>2186</td>
</tr>
<tr>
<td>$\Gamma_3(F_{5/2}, \Gamma_3)$</td>
<td>759</td>
<td>403</td>
</tr>
<tr>
<td>$\Gamma_2(F_{5/2}, \Gamma_2)$</td>
<td>984</td>
<td>207</td>
</tr>
<tr>
<td>$\Gamma_1(F_{5/2}, \Gamma_1)$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
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<tr>
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<tbody>
<tr>
<td></td>
<td>3.13</td>
<td>3.458</td>
<td>3.380</td>
<td>3.380</td>
</tr>
<tr>
<td></td>
<td>3.090</td>
<td>2585</td>
<td>2.933</td>
<td>2.933</td>
</tr>
<tr>
<td></td>
<td>2.495</td>
<td>2406</td>
<td>2.840</td>
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<tr>
<td></td>
<td>2.190</td>
<td>2177</td>
<td>2.215</td>
<td>2.215</td>
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<tr>
<td></td>
<td>1.984</td>
<td>780</td>
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</tr>
<tr>
<td></td>
<td>632</td>
<td>231</td>
<td>39/2</td>
<td>39/2</td>
</tr>
</tbody>
</table>

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 $\Gamma_6(F_{5/2}, \Gamma_6)$ 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 $\Gamma_7(F_{5/2}, \Gamma_8) \approx 110 \text{ cm}^{-1}$ for CaF$_2$:Ce$^{3+}$ from the crystal-field parameters $B_0^\parallel$ given by him and the additional information of the measured $g$ values [13]. However no details were reported, and the value of the level $\Gamma_7(F_{5/2}, \Gamma_8)$ calculated using these $B_0^\parallel$ is about $200 \text{ cm}^{-1}$. For SrF$_2$:Ce$^{3+}$, Walker and Mires [5] estimated the energy levels $\Gamma_7(F_{5/2}, \Gamma_8) = 1085\pm250 \text{ cm}^{-1}$ and $\Gamma_7(F_{5/2}, \Gamma_7) = 39\pm2 \text{ cm}^{-1}$ 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$\text{\textsubscript{4v}}$) crystal field splits the $2F_{5/2}$ and $2F_{7/2}$ states into three and four Kramers doublets, respectively. The lowest lying doublet is $\Gamma_7$ [14].

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

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

(4)

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

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

(5)

where $S$ and $L$ are the spin and orbital momentum operators, $\xi$ is the spin-orbit coupling coefficient in crystal. Considering the covalency reduction effect, we have $\xi = k_0 \xi_0$, where $\xi_0$ 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, $\xi_0 \approx 640 \text{ cm}^{-1}$ [14], $k_0 \approx 0.9840$ [15].

The matrix elements of $\hat{H}_{so}$ may with the irreducible tensor operator technique be written as
\( \langle 4 f^m a S L J M | H_{so} | 4 f^m a' S' L' J' M' \rangle = \delta (M M') \)

\[
\cdot \langle J | \langle J' | \sum_{k=1}^{4} (1 + J + L + S') (1 + (J + 1)(2J + 1))^{1/2} \left\{ \begin{array}{c} L \ L' \ \ \ J \ k \ k' \ \ \ J' \ q \ M_j \ M' \end{array} \right\} \left\{ \begin{array}{c} S \ S' \ \ \ J \ k \ J' \ q \ M'_j \ M' \end{array} \right\} \right\} \end{equation}

\[
\cdot \langle J | \langle J' | \sum_{k=1}^{4} (1 + J + L + S') (1 + (J + 1)(2J + 1))^{1/2} \left\{ \begin{array}{c} L \ L' \ \ \ J \ k \ J' \ q \ M_j \ M' \end{array} \right\} \left\{ \begin{array}{c} S \ S' \ \ \ J \ k \ J' \ q \ M'_j \ M' \end{array} \right\} \right\} \end{equation}

\( H_{cf} \) is expressed in terms of the tensor operators \( C_{ik}^q \) and the crystal field parameters \( B_i \) [16]:

\[
H_{cf} = B_0^S C_{ik}^S + B_0^L C_{ik}^L + B_1^S (C_4^k + C_4^L) + B_2^S (C_6^k + C_6^L) + B_3^S (C_8^k + C_8^L).
\]

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

\[
\langle 4 f^1 a S L J M_j | H_{CF} | 4 f^1 a' S' L' J' M'_j \rangle = \sum_{k=1}^{4} (1 + J + L + S') (1 + (J + 1)(2J + 1))^{1/2} \left\{ \begin{array}{c} L \ L' \ \ \ J \ k \ J' \ q \ M_j \ M' \end{array} \right\} \left\{ \begin{array}{c} S \ S' \ \ \ J \ k \ J' \ q \ M'_j \ M' \end{array} \right\} \right\} \end{equation}

\[
\cdot (2J + 1)(2J' + 1) \end{equation}

where \( k = 2, 4, 6; q = 0, \pm 4 \) and \( k \leq k_j \). The corresponding reducible matrix elements \( \langle f | c^{k+1} | f \rangle \) and \( \langle 4 f^1 a S L | U^{(k')}| 4 f^1 a' S' L' \rangle \) can be obtained in the tables of Nielsen-Koster [17].

From the above expressions, the complete energy matrix \( (14 \times 14) \) including both \( 2 F_{j=1/2} \) and \( 2 F_{j=3/2} \) states can be established. In the energy matrix, five crystal-field parameters \( B_i \) 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 \( \Gamma_j \) in terms of a linear combination of \( | J M_j \rangle \) doublet can be obtained. By using these energy levels, the ground doublet wave functions \( \Gamma_j(\pm) \) can be obtained. Based on these functions \( \Gamma_j(\pm) \), the \( g \) factors \( g_\parallel \) and \( g_\perp \) for the tetragonal \( \text{Ce}^{3+} \) centers in \( \text{CaF}_2 \) and \( \text{SrF}_2 \) crystals can be calculated from the following expressions [16]:

\[
g_\parallel = 2 g_j (\pm \hat{J}_z \pm), \quad g_\perp = g_j (\pm \hat{J}_z \pm \hat{J}_z \pm) \end{equation}

Thus, by fitting the calculated optical and EPR spectral data to the observed values, the crystal-field parameters \( B_i \) can be obtained. They are \( B_0^S \approx 333 \text{ cm}^{-1}, B_0^L \approx -2176 \text{ cm}^{-1}, B_1^S \approx 725 \text{ cm}^{-1}, B_1^L \approx -1573 \text{ cm}^{-1}, B_2^S \approx -2872 \text{ cm}^{-1} \) for \( \text{CaF}_2: \text{Ce}^{3+} \) and \( B_2^L \approx 333 \text{ cm}^{-1}, B_0^S \approx -2349 \text{ cm}^{-1}, B_0^L \approx 925 \text{ cm}^{-1}, B_2^S \approx -1996 \text{ cm}^{-1}, B_2^L \approx -619 \text{ cm}^{-1} \) for \( \text{SrF}_2: \text{Ce}^{3+} \).

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 for \( \text{CaF}_2: \text{Ce}^{3+} \) crystals and \( \text{SrF}_2: \text{Ce}^{3+} \) crystals. In these wave functions, the admixture between \( J = 5/2 \) and \( J = 7/2 \) manifolds should be taken into account. The present calculated energy levels of the above \( \text{Ce}^{3+} \) centers are in better agreement than those in the previous paper [4] with the observed values (see Table 1), suggesting that, to explain the \( g \) factors for \( \text{Ce}^{3+} \) 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 \( \text{Ce}^{3+} \) 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 \( \Gamma_7(\pm) \) for \( \text{CaF}_2: \text{Ce}^{3+} \) is 207 cm\(^{-1}\). Although it is larger than that estimated in [2] (see Table 2), it is close to the value
(≈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.