Theoretical Studies of the Optical Spectra and EPR Parameters of CaWO₄: Sm³⁺ Crystal

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The optical spectra and EPR parameters (g factors \(g_\parallel\), \(g_\perp\) and hyperfine structure parameters \(A_\parallel\) and \(A_\perp\)) of Sm³⁺ in CaWO₄ crystal are calculated from the second-order perturbation formulas of EPR parameters for a 4f⁵ ion in tetragonal symmetry. In these formulas, the \(J\)-mixing among the \(6H_{5/2}\), \(7/2\) and \(9/2\) states via crystal-field interactions, the mixtures among the states with the same \(J\) value via spin-orbit coupling interaction and the interactions between the lowest Kramers doublet \(\Gamma\gamma\) and the same irreducible representations in the other 11 Kramers doublets \(\Gamma\chi\) via the crystal-field and orbital angular momentum (or hyperfine structure) are considered. The theoretical results agree reasonably with the observed values.

Key words: EPR; Crystal Field Theory; Sm³⁺; CaWO₄.

1. Introduction

Scheelite structure crystals (of CaWO₄ type) doped with rare-earth ions exhibit good fluorescence and are usually used as laser hosts for their high velocity of sound and large relaxation. Therefore many studies have been made to understand the properties of rare-earth ions in these materials [1 – 4]. For instance, the optical spectra and EPR parameters (g factors \(g_\parallel\), \(g_\perp\) and hyperfine structure parameters \(A_\parallel\) and \(A_\perp\)) of Sm³⁺ in CaWO₄ crystal are calculated from the second-order perturbation formulas of EPR parameters for a 4f⁵ ion in tetragonal symmetry. In these formulas, the \(J\)-mixing among the \(6H_{5/2}\), \(7/2\) and \(9/2\) states via crystal-field interactions, the mixtures among the states with the same \(J\) value via spin-orbit coupling interaction and the interactions between the lowest Kramers doublet \(\Gamma\gamma\) and the same irreducible representations in the other 11 Kramers doublets \(\Gamma\chi\) via the crystal-field and orbital angular momentum (or hyperfine structure) are considered. The theoretical results agree reasonably with the observed values.

Key words: EPR; Crystal Field Theory; Sm³⁺; CaWO₄.
crystal are studied in a unified way. The results are discussed.

2. Theory and Calculation

CaWO$_4$ crystal has the scheelite structure, which belongs to the $I4_1/a$ space group. Because of the similar radii of Sm$^{3+}$ and Ca$^{2+}$ ions ($r \approx 0.964$ Å for Sm$^{3+}$, $r \approx 0.99$ Å for Ca$^{2+}$ and $r \approx 0.70$ Å for W$^{4+}$ [9]), the doped Sm$^{3+}$ ion substitutes a Ca$^{2+}$ ion. The point symmetry at the site of Ca$^{2+}$ is $S_4$, but approximates $D_{2d}$ symmetry, so it is considered to be $D_{2d}$ by many authors [10–12]. For simplicity we also apply the $D_{2d}$ approximation.

Sm$^{3+}$ has a 4f$^5$ electronic configuration, the ground state $^6H_{5/2}$, the first excited one $^6H_{7/2}$ and second excited one $^6H_{9/2}$ [13, 14]. The tetragonal crystal-field splits the above states into 3, 4, and 5 Kramers doublets, respectively. Considering the crystal-field $J$-mixing among the $^6H_{5/2}, ^6H_{7/2}$, and $^6H_{9/2}$ states, thus the wave functions of the lowest Kramers doublet $\Gamma\gamma$ and other 11 Kramers doublets can be obtained by diagonalizing a 24·24 energy matrix of the 4f$^5$ ion in tetragonal symmetry. In addition, because of the admixtures among the states with the same $J$ values via spin-orbit coupling interaction, the wave function of the lowest doublet $\Gamma\gamma$ can be expressed as

$$\left| \Gamma\gamma(\text{or } \gamma') \right> = \sum_{M_J} C(M_J) \left| ^6H_{5/2}; \Gamma\gamma(\text{or } \gamma')M_J \right> N_{5/2}(M_J)$$

$$+ \lambda_{G1}(M_J) \left| ^6H_{7/2}; \Gamma\gamma(\text{or } \gamma')M_J \right> N_{7/2}(M_J)$$

$$+ \lambda'_{G1}(M_J) \left| ^6H_{9/2}; \Gamma\gamma(\text{or } \gamma')M_J \right> N_{9/2}(M_J)$$

$$+ \lambda''_{G1}(M_J) \left| ^6H_{9/2}; \Gamma\gamma(\text{or } \gamma')M_J \right> N_{9/2}(M_J)$$

where $\gamma$ and $\gamma'$ stand for the two components of the $\Gamma$ irreducible representation. $\lambda$, and $N_i$ are, respectively, the mixing coefficients and normalization factors. They can be obtained from the spin-orbit coupling matrix elements and perturbation method. $M_J$, $M_{J'}$, and $M_{J''}$ are the half-integers in the ranges $-5/2 \sim 5/2$, $-7/2 \sim 7/2$, and $-9/2 \sim 9/2$, respectively.

The perturbation Hamiltonian for a rare earth ion in the crystal under an external magnetic field can be written as [13]

$$H' = H_{so} + H_{CF} + H_Z,$$

where $H_{so}$ is the spin-orbit coupling interaction and $H_{CF}$ is the crystal field Hamiltonian. $H_{so}$ can be expressed as

$$H_{so} = \zeta (L \cdot S),$$

where $\zeta$ is the spin-orbit coupling coefficient. Here we take $\zeta \approx 1396$ cm$^{-1}$. $L$ and $S$ are the orbital and spin momentum operators, respectively. The crystal-field interaction $H_{CF}$ can be expressed in terms of the tensor operators $C^\gamma_{ij}$ [16]:

$$H_{CF} = B_{1}^2C_{2}^0 + B_{2}^2C_{4}^0 + B_{4}^2(C_{4}^2 + C_{4}^{-2})$$

$$+ B_{6}^2C_{6}^0 + B_{8}^2(C_{6}^4 + C_{6}^{-4}),$$

where $B_{ij}$ are the crystal field parameters. From the Zeeman interaction $H_Z = g_1\mu_B H \cdot J$, with their usual meanings [13, 14]) or the hyperfine interaction $H_{hf} = P N_J \hat{N}$ (where $P$ is the dipolar hyperfine structure constant and $N_J$ is the diagonal matrix element for $2S+1L_J$ state [13]) and in consideration of the contribution due to the interactions between the ground doublet $\Gamma\gamma$ and other 11 Kramers doublets $\Gamma_i$, the second-order perturbation formulas of the EPR parameters of the ground doublet $\Gamma\gamma$ for an 4f$^5$ ion in tetragonal symmetry can be obtained as

$$g_{||} = g_{(1)}^{(1)} + g_{(2)}^{(2)}, \quad g_{||}^{(1)} = 2g_{(1)}(\Gamma\gamma)\hat{J}_x|\Gamma\gamma>,$$

$$g_{||}^{(2)} = 2\sum_X \langle \Gamma\gamma|H_{CF}|\hat{J}_x|\gamma X \rangle \frac{X(\hat{J}_x \cdot \hat{J}_z)\gamma X|\Gamma\gamma>}{E(\hat{J}_x) - E(\Gamma)},$$

$$g_{\perp} = g_{(1)}^{(1)} + g_{(2)}^{(2)}, \quad g_{\perp}^{(1)} = 2g_{(1)}(\Gamma\gamma)\hat{J}_z|\Gamma\gamma>, \quad g_{\perp}^{(2)} = 0,$$

$$A_{||} = A_{(1)}^{(1)} + A_{(2)}^{(2)}, \quad A_{(1)}^{(1)} = 2P N_J (\Gamma\gamma)\hat{N}_x|\Gamma\gamma>,$$

$$A_{(2)}^{(2)} = 2P \sum_X \langle \Gamma\gamma|H_{CF}|\hat{J}_x|\gamma X \rangle \frac{(\hat{J}_z \cdot \hat{J}_z)\gamma X|\Gamma\gamma>}{E(\hat{J}_x) - E(\Gamma)},$$

$$A_{\perp} = A_{(1)}^{(1)} + A_{(2)}^{(2)}, \quad A_{(1)}^{(1)} = 2P N_J (\Gamma\gamma)\hat{N}_z|\Gamma\gamma>, \quad A_{(2)}^{(2)} = 0,$$

where the parameters $g_{(1)}, g_{(2)}, N_J$ and $N'_{(1)}$ (g$^{(1)}_{(1)}$ and N$^{(1)}_{J}$) occur in the expansions of the above formulas for various states can be obtained from [13] and [14].
Table 1. Free ion parameters of Sm$^{3+}$ (in units of cm$^{-1}$) [16].

<table>
<thead>
<tr>
<th>$F^1$</th>
<th>$F^2$</th>
<th>$F^3$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$r$</th>
<th>$P_r$</th>
<th>$P_{\alpha1}$</th>
<th>$P_{\beta1}$</th>
<th>$P_{\alpha1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>78749</td>
<td>57785</td>
<td>39557.6</td>
<td>20.16</td>
<td>566.9</td>
<td>1500</td>
<td>51.76</td>
<td>10$^{-3}$</td>
<td>41.8(6)</td>
<td>10$^{-3}$</td>
</tr>
</tbody>
</table>

Table 2. The energy levels of the tetragonal Sm$^{3+}$ center in CaWO$_4$ crystal (in units of cm$^{-1}$).

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| | Cal. | | | | | | | | | | | |
| | Expt. | | | | | | | | | | | |
| | | | | | | | | | | | | |

Table 3. EPR parameters of the tetragonal Sm$^{3+}$ center in CaWO$_4$ crystal.

<table>
<thead>
<tr>
<th>$g_{\parallel}$</th>
<th>$g_{\perp}$</th>
<th>$A_{\alpha1}^{(147)}$</th>
<th>$A_{\alpha1}^{(149)}$</th>
<th>$A_{\beta1}$</th>
<th>$A_{\beta2}$</th>
<th>$A_{\alpha1}^{(149)}$</th>
<th>$A_{\alpha1}^{(147)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Expt.</td>
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3. Discussion

From Table 2, it can be seen that the calculated results of calculated optical spectra are reasonable consistent with the observed values. So the parameters used in this paper can be regarded as reasonable.

From Table 3 one can see that the calculated EPR parameters ($g_{\parallel}$, $g_{\perp}$, and $A_{\alpha1}$, $A_{\beta1}$) of $^{147}$Sm and $^{149}$Sm of Sm$^{3+}$ in CaWO$_4$ crystal agree with the observed ones. Therefore the perturbation formulas of the EPR parameters for 4f$^5$ ions and the method used in this paper can be regarded as reasonable. The method is also effective in other similar systems.

From the above studies we find that, if considering only the interactions within the lowest $^6$H$_{5/2}$ state, the EPR parameters in agree poorly with the experimental values. For instance $g_{\parallel}$ $\approx$ 0.2552 and $g_{\perp}$ $\approx$ 0.7656 differ much from the observed values $g_{\parallel}$ $\approx$ 0.440 and $g_{\perp}$ $\approx$ 0.646 [7]. Since $g_{\parallel}/g_{\perp}$ and $A_{\alpha1}/A_{\beta1}$ differ considerably from unity, the method is not adequate for the theoretical calculation of EPR parameters within the ground $^6$H$_{5/2}$ multiplet. Otherwise, the contributions to EPR parameters due to the second-order term $g(2)_{\beta}$ (or $A(2)_{\beta}$) and the admixture among the states with the same $J$ values are very small ($\approx 2\%$). So, the dominant contribution to the EPR parameters for the tetragonal Sm$^{3+}$ ion is due to the crystal-field $J$-mixing among $^6$H$_J$ ($J = 5/2, 7/2$ and $9/2$) multiplets.