# Theoretical Studies of the Optical Spectra and EPR Parameters of CaWO$_4$: Sm$^{3+}$ Crystal

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The optical spectra and EPR parameters ($g$ factors $g_\parallel$, $g_\perp$ and hyperfine structure parameters $A_\parallel$, $A_\perp$ of $^{147}$Sm and $^{149}$Sm) of Sm$^{3+}$ in CaWO$_4$ crystal are calculated from the second-order perturbation formulas of EPR parameters for a 4f$^5$ ion in tetragonal symmetry. In these formulas, the $J$-mixing among the $^6$H$_J$($J = 5/2$, 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 $\Gamma_x$ 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; Sm$^{3+}$; CaWO$_4$.

## 1. Introduction

Scheelite structure crystals (of CaWO$_4$ 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 $A_\parallel$, $A_\perp$ of $^{147}$Sm$^{3+}$ and $^{149}$Sm$^{3+}$) of Sm$^{3+}$ in CaWO$_4$ crystal were measured decades ago [5 – 7], but until now no theoretical explanation has been made for these experimental results. The $g$ factors of Sm$^{3+}$ in crystals were often studied roughly by using first-order perturbation formulas and considering only the interactions in the lowest $^6$H$_{5/2}$ state. Since $A_\parallel g_\perp / A_\perp g_\parallel$ differs considerably from unity, this is not adequate for the theoretical calculation of $g$ factors within the ground $^6$H$_{5/2}$ multiplet [6, 8]. In this paper we consider the contributions to EPR parameters due to 1) the J-mixing among the ground $^6$H$_{5/2}$, the first excited $^6$H$_{7/2}$ and the second excited $^6$H$_{9/2}$ states via crystal-field interactions (thus a $24 \cdot 24$ energy matrix should be used), 2) the admixtures among the states with the same $J$ values (i.e., $^6$H$_{5/2}$,$^4$G1$_{5/2}$ and $^4$G4$_{5/2}$; $^6$H$_{7/2}$,$^4$G1$_{7/2}$ and $^4$G4$_{7/2}$; $^6$H$_{9/2}$,$^4$G1$_{9/2}$ and $^4$G4$_{9/2}$) via spin-orbit coupling interactions, 3) the contribution due to the admixtures between the lowest Kramers doublet $\Gamma\gamma$ and the other Kramers doublets (or irreducible representations) $\Gamma_X$ via crystal-field and orbital angular momentum interactions (which results in second-order perturbation terms) and 4) the covalence reduction effects.

By diagonalizing the $24 \cdot 24$ energy matrix, the crystal-field energy levels, the ground doublet wave functions $\Gamma\gamma$ and other 11 Kramers doublets $\Gamma_X$ can be obtained. In this paper we establish the perturbation formulas of the EPR parameters for a 4f$^5$ ion in tetragonal symmetry by considering all the above interactions. With these formulas the EPR $g$ factors and hyperfine structure parameters A of $^{147}$Sm$^{3+}$ and $^{149}$Sm$^{3+}$ for a tetragonal Sm$^{3+}$ center in a CaWO$_4$ crystal are studied. Thus, the EPR $g$ factors and the optical spectra of a tetragonal Sm$^{3+}$ center in CaWO$_4$

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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 $24 \cdot 24$ 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

$$\begin{aligned} |\Gamma\gamma(\text{or }\gamma')\rangle = {} & \\ & \sum_{M_J1} C({}^6H_{5/2};\Gamma\gamma(\text{or }\gamma')M_{J1})N_{5/2}\Big(|{}^6H_{5/2}M_{J1}\rangle \\ & \quad + \lambda_{G1}|{}^4G1_{5/2}M_{J1}\rangle + \lambda_{G4}|{}^4G4_{5/2}M_{J1}\rangle\Big) \\ & + \sum_{M_J2} C({}^6H_{7/2};\Gamma\gamma(\text{or }\gamma')M_{J2})N_{7/2}\Big(|{}^6H_{7/2}M_{J2}\rangle \\ & \quad + \lambda'_{G1}|{}^4G1_{7/2}M_{J2}\rangle + \lambda'_{G4}|{}^4G4_{7/2}M_{J2}\rangle\Big) \\ & + \sum_{M_J3} C({}^6H_{9/2};\Gamma\gamma(\text{or }\gamma')M_{J3})N_{9/2}\Big(|{}^6H_{9/2}M_{J3}\rangle \\ & \quad + \lambda''_{G1}|{}^4G1_{9/2}M_{J3}\rangle + \lambda''_{G4}|{}^4G4_{9/2}M_{J3}\rangle) \end{aligned} \tag{1}$$

where $\gamma$ and $\gamma'$ stand for the two components of the $\Gamma$ irreducible representation. $\lambda_i$ 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. $M_{J1}$, $M_{J2}$, and $M_{J3}$ 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]

$$\hat{H}' = \hat{H}_{\text{so}} + \hat{H}_{\text{CF}} + \hat{H}_{\text{Z}}, \tag{2}$$

where $\hat{H}_{\text{so}}$ is the spin-orbit coupling interaction and $\hat{H}_{\text{CF}}$ is the crystal field Hamiltonian. $\hat{H}_{\text{so}}$ can be expressed as

$$\hat{H}_{\text{so}} = \zeta(L \cdot S), \tag{3}$$

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

$$\begin{aligned} \hat{H}_{\text{CF}} = {} & B_2^0 C_2^0 + B_4^0 C_4^0 + B_4^4(C_4^4 + C_4^{-4}) \\ & + B_6^0 C_6^0 + B_6^4(C_6^4 + C_6^{-4}), \end{aligned} \tag{4}$$

where $B_k^q$ are the crystal field parameters. From the Zeeman interaction $\hat{H}_{\text{Z}}$ ($= g_J\mu_B \mathbf{H}\cdot\mathbf{J}$, with their usual meanings [13, 14]) or the hyperfine interaction $\hat{H}_{\text{hf}}$ ($=PN_J\hat{N}$, where P is the dipolar hyperfine structure constant and $N_J$ is the diagonal matrix element for ${}^{2S+1}L_J$ state [13]) and in consideration of the contribution due to the interactions between the ground doublet $\Gamma\gamma$ and other 11 Kramers doublets $\Gamma_x$, 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

$$\begin{aligned} & g_\parallel = g_\parallel^{(1)} + g_\parallel^{(2)}, \quad g_\parallel^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_z|\Gamma\gamma\rangle, \\ & \quad g_\parallel^{(2)} = 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\text{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{J}_Z|\Gamma\gamma\rangle}{E(\Gamma_X) - E(\Gamma)}, \\ & g_\perp = g_\perp^{(1)} + g_\perp^{(2)}, \\ & \quad g_\perp^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_x|\Gamma\gamma'\rangle, \quad g_\perp^{(2)} = 0, \end{aligned} \tag{5}$$

$$\begin{aligned} & A_\parallel = A_\parallel^{(1)} + A_\parallel^{(2)}, \quad A_\parallel^{(1)} = 2PN_J\langle\Gamma\gamma|\hat{N}_z|\Gamma\gamma'\rangle, \\ & \quad A_\parallel^{(2)} = 2P\sum_X{}' \frac{\langle\Gamma\gamma|H_{\text{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_Z|\Gamma\gamma\rangle}{E(\Gamma_X) - E(\Gamma)}, \\ & A_\perp = A_\perp^{(1)} + A_\perp^{(2)}, \\ & \quad A_\perp^{(1)} = 2PN_J\langle\Gamma\gamma|\hat{N}_x|\Gamma\gamma'\rangle, \quad A_\perp^{(2)} = 0, \end{aligned} \tag{6}$$

where the parameters $g_J$, $g'_J$, $N_J$ and $NJ'$ ($g'_J$ and $NJ'$ 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].

| $F^2$ | $F^4$ | $F^6$ | $\alpha$ | $\beta$ | $r$ | $P_0$ ($^{147}$Sm) [13] | $P_0$ ($^{149}$Sm) [13] |
|---|---|---|---|---|---|---|---|
| 78749 | 57785 | 39557.6 | 20.16 | −566.9 | 1500 | $-51.7(6)\cdot 10^{-4}$ | $-41.8(6)\cdot 10^{-4}$ |

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. | 0 | 89 | 264 | 1028 | 1095 | 1106 | 1227 | 2297 | 2336 | 2373 | 2386 | 2494 |
| Exp.[5] | 0 | 67 | 222 | 1061 | 1091 | 1219 | 1288 | 2265 | 2275 | 2319 | 2403 | 2494 |

Table 3. EPR parameters of the tetragonal $Sm^{3+}$ center in $CaWO_4$ crystal.

| | $g_\parallel$ | $g_\perp$ | $A_\parallel$ ($^{147}$Sm) | $A_\perp$ ($^{147}$Sm) | $A_\parallel$ ($^{149}$Sm) | $A_\perp$ ($^{149}$Sm) |
|---|---|---|---|---|---|---|
| Cal. | 0.4441 | 0.6414 | 66.1(8) | 240.1(29) | 53.6(8) | 194.7(28) |
| Expt. [6] | 0.4396(5) | 0.6416(1) | 65.1(4) | 245.3(6) | 53.7(4) | 200.3(7) |
| Expt. [7] | 0.440(5) | 0.646(5) | 66(1) | 244(2) | 54(1) | 202(2) |

The free ion values (Coulomb repulsion $F^K$, two-body interaction parameters $\alpha$, $\beta$, $r$ [16] and the dipolar hyperfine structure constant $P_0$ [13]) for $Sm^{3+}$ are collected in Table 1. Because of the covalence of the $Sm^{3+}$-$O^{2-}$ bonds, the orbital reduction factor $k$ should be used. Here we take $k \approx 0.983$.

Applying all these parameters to the $42\cdot 42$ energy matrix and hence to (5) and (6), and fitting the optical spectra and calculated EPR parameters to those of the observed values, the best fitting results of the crystal parameters for the $CaWO_4$:$Sm^{3+}$ crystal are obtained:

$$B_2^0 \approx 567\ \mathrm{cm}^{-1}, B_4^0 \approx -755\ \mathrm{cm}^{-1}, B_4^4 \approx -808\ \mathrm{cm}^{-1},$$
$$B_6^0 \approx 293\ \mathrm{cm}^{-1}, B_6^4 \approx -158\ \mathrm{cm}^{-1}. \tag{7}$$

The results of the optical spectra and EPR parameters are compared with those of the observed values in Tables 2 and 3, respectively.

## 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 $A_\parallel$, $A_\perp$ 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 $^6H_{5/2}$ 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 $A_\parallel/A_\perp$ differ considerably from unity, the method is not adequate for the theoretical calculation of EPR parameters within the ground $^6H_{5/2}$ multiplet. Otherwise, the contributions to EPR parameters due to the second-order term $g_\parallel^{(2)}$ (or $A_\parallel^{(2)}$) 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 $^6H_J$ ($J = 5/2$, 7/2 and 9/2) multiplets.

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