Theoretical Investigations of the Electron Paramagnetic Resonance *g* Factors for the Trivalent Cerium Ion in LiYF$_4$ Crystal

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The perturbation equations of the EPR parameters $g_{\parallel}$ and $g_{\perp}$ for the lowest Kramers doublet of a 4f^1 ion in tetragonal symmetry are established. In these equations, the contributions of the covalency effects, the admixture between $J = 7/2$ and $J = 5/2$ states and the second-order perturbation (which is not considered previously) are included. The crystal field parameters for the studied Ce^{3+} center are calculated from the superposition model. Based on the above perturbation equations and related parameters, the EPR *g* factors for the Ce^{3+} center in LiYF$_4$ crystals are reasonably explained. The results are discussed.

Key words: Crystal Field Theory; Electron Paramagnetic Resonance; Superposition Model; Ce^{3+}; LiYF$_4$.

1. Introduction

Yttrium fluoride single crystals, doped with trivalent cerium, have received much attention because of their potential application in sensors and optically pumped tunable solid-state lasers in the UV region [1 – 4]. Recently the *g* factors $g_{\parallel}$ and $g_{\perp}$ of Ce^{3+} in LiYF$_4$ crystals were measured by electron paramagnetic resonance (EPR) technique [5], which may be helpful to study the above properties of LiYF$_4$: Ce^{3+}. But until now no satisfactory theoretical explanation has been given for these EPR parameters. In order to explain these *g* values, in [5] the simple mixing eigenfunction of the ground state was applied by a linear combination within the $J = 5/2$ manifold [5], i. e.,

$$\begin{aligned}\Gamma\gamma(\text{or }\gamma') = {} & \cos\theta|5/2,\pm 5/2\rangle \\ & + \sin\theta|5/2,\mp 3/2\rangle,\end{aligned} \tag{1}$$

where cosθ (or sinθ) is an adjustable parameter. In their treatment, the EPR parameters of the 4f^1 ion are approximately calculated from the first-order perturbation equation, where the eigenfunction of the lowest Kramers doublet of the 4f^1 ion is obtained by considering only the interaction within the ground ^{2}F$_{5/2}$ multiplet [5]. The best fit of the $g_{\parallel}$ and $g_{\perp}$ values ($g_{\parallel} \approx 2.774$ and $g_{\perp} \approx 1.590$) was obtained from the value $\theta = 28^\circ$ for the tetragonal Ce^{3+} center in the LiYF$_4$ crystal by fitting the experimental results ($g_{\parallel} \approx 2.765$ and $g_{\perp} \approx 1.473$) [2, 5]. Obviously, these theoretical *g* factors do not agree with the observed ones. In order to explain more exactly these EPR parameters, in this paper we first establish the second-order perturbation equations of the EPR parameters for the 4f^1 ion in tetragonal symmetry. In these equations we consider the contributions to the EPR parameters due to the admixture between different states as well as the covalency reduction effect. From these equations, the EPR *g* factors for Ce^{3+} in LiYF$_4$ crystal are calculated by using Newman's superposition model parameters. The results are discussed.

2. Calculation Equations

For a Ce^{3+}(4f^1) ion in a tetragonal crystal fields, the ground ^{2}F$_{5/2}$ and excited ^{2}F$_{7/2}$ states of the free-ion splits into three and four Kramers doublets, respectively [2, 5]. The basis function of the lowest doublet

$\mathit{\Gamma}\gamma$ can be obtained by diagonalizing the 14×14 energy matrix in tetragonal symmetry, based on the J-mixing between the above $^2\mathrm{F}_{5/2}$ and $^2\mathrm{F}_{7/2}$ states via the crystal-field and the spin-orbit coupling interactions. In order to establish the above perturbation equations of a 4f^1 ion in tetragonal symmetry, we first obtain the basis functions of the $\mathit{\Gamma}\gamma$ doublet by diagonalizing the above 14×14 energy, i. e.,

$$\begin{aligned}
|\mathit{\Gamma}\gamma\rangle &= \sum_{M_{J1}} C(^2\mathrm{F}_{5/2};\mathit{\Gamma}\gamma M_{J1})|^2\mathrm{F}_{5/2}M_{J1}\rangle \\
&\quad + \sum_{M_{J2}} C(^2\mathrm{F}_{7/2};\mathit{\Gamma}\gamma M_{J2})|^2\mathrm{F}_{7/2}M_{J2}\rangle, \\
|\mathit{\Gamma}\gamma'\rangle &= \sum_{M_{J1}} C(^2\mathrm{F}_{5/2};\mathit{\Gamma}\gamma' M_{J1})|^2\mathrm{F}_{5/2}M_{J1}\rangle \\
&\quad + \sum_{M_{J2}} C(^2\mathrm{F}_{7/2};\mathit{\Gamma}\gamma' M_{J2})|^2\mathrm{F}_{7/2}M_{J2}\rangle,
\end{aligned} \tag{2}$$

where γ and γ' stand for the two components of irreducible $\mathit{\Gamma}$ representation. M_{J1} and M_{J2} are the half-integers in the ranges $-5/2 \sim 5/2$ and $-7/2 \sim 7/2$, respectively.

The perturbation Hamiltonian for a rare earth ion in the crystal under an external magnetic field can be written as [6]

$$\hat{H}' = \hat{H}_{\mathrm{so}} + \hat{H}_{\mathrm{CF}} + \hat{H}_{\mathrm{Z}}, \tag{3}$$

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

$$\hat{H}_{\mathrm{so}} = \zeta(L \cdot S), \tag{4}$$

where ζ is the spin-orbit coupling coefficient, and L and S are the orbital and spin momentum operators, respectively. The Zeeman interaction $\hat{H}_{\mathrm{Z}}$ can be written as $\hat{H}_{\mathrm{Z}} = g_J\mu_\beta \mathbf{H} \cdot \mathbf{J}$ with its original meaning [6].

Since the contributions to the EPR parameters come mainly from the first-order perturbation terms, only the first-order perturbation terms were considered by the previous authors [5–7]. However, the other $(7-1=6)$ irreducible representations $\mathit{\Gamma}$x may mix with the ground $\mathit{\Gamma}\gamma$ doublet via crystal field and orbital angular momentum interactions and lead to second-order perturbation contributions to the EPR parameters. It should be noted that the second-order perturbation terms for $g_\perp$ vanish because none of the $\mathit{\Gamma}$x has a nonzero matrix element with the lowest $\mathit{\Gamma}\gamma$ doublet for both $\hat{H}_{\mathrm{CF}}$ and the x or y component of the $\hat{J}$ operator. Thus, the second-order perturbation equations of the EPR parameters of the ground doublet $\mathit{\Gamma}\gamma$ for a 4f^1 ion in tetragonal symmetry can be derived as

$$\begin{aligned}
g_\parallel &= g_\parallel^{(1)} + g_\parallel^{(2)}, \\
g_\parallel^{(1)} &= 2g_J(^{2S+1}L_J)\langle\mathit{\Gamma}\gamma|\mathbf{J}_z|\mathit{\Gamma}\gamma\rangle] \\
&= 2\Big\{\sum_{M_{J1}} g_J(^2\mathrm{F}_{5/2})|C(^2\mathrm{F}_{5/2};\mathit{\Gamma}\gamma M_{J1})|^2 M_{J1} \\
&\quad + \sum_{M_{J2}} g_J(^2\mathrm{F}_{7/2})|C(^2\mathrm{F}_{7/2};\mathit{\Gamma}\gamma M_{J2})|^2 M_{J2}\Big\} \\
&\quad + 4\sum_{M_{J1}} g'_J(^2\mathrm{F}_{7/2},{}^2\mathrm{F}_{5/2})\Big[\Big(\frac{5}{2}+1\Big)^2 - M_{J1}^2\Big]^{1/2} \\
&\qquad \cdot C(^2\mathrm{F}_{5/2}\mathit{\Gamma}\gamma M_{J1})C(^2\mathrm{F}_{7/2};\mathit{\Gamma}\gamma M_{J1}), \\
g_\parallel^{(2)} &= 2\sum_X{}' \frac{\langle\mathit{\Gamma}\gamma|\hat{H}_{\mathrm{CF}}|\mathit{\Gamma}_X\gamma_X\rangle\langle\mathit{\Gamma}_X\gamma_X|\hat{J}_{\mathrm{Z}}|\mathit{\Gamma}\gamma\rangle}{E(\mathit{\Gamma}_{\mathrm{X}}) - E(\mathit{\Gamma}\gamma)}, \\
g_\perp &= g_\perp^{(1)} + g_\perp^{(2)} \\
g_\perp^{(1)} &= 2g_J(^{2S+1}L_J)\langle\mathit{\Gamma}\gamma|\mathbf{J}_x|\mathit{\Gamma}\gamma'\rangle \\
&= \sum_{M_{J1}}(-1)^{5/2-M_{J1}+1}\Big[\frac{5\cdot 7}{4} - (M_{J1}-1)M_{J1}\Big]^{1/2} \\
&\qquad \cdot g_J(^2\mathrm{F}_{5/2})C(^2\mathrm{F}_{5/2};\mathit{\Gamma}\gamma M_{J1}) \\
&\qquad \cdot C(^2\mathrm{F}_{5/2};\mathit{\Gamma}\gamma' M_{J1}-1) \\
&\quad + \sum_{M_{J2}}(-1)^{7/2-M_{J2}+1}\Big[\frac{7\cdot 9}{4} - (M_{J2}-1)M_{J2}\Big]^{1/2} \\
&\qquad \cdot g_J(^2\mathrm{F}_{7/2})C(^2\mathrm{F}_{7/2};\mathit{\Gamma}\gamma M_{J2}) \\
&\qquad \cdot C(^2\mathrm{F}_{7/2};\mathit{\Gamma}\gamma' M_{J2}-1) \\
&\quad + 2\sum_{M_{J1}}\Big[\Big(\frac{5}{2}+M_{J1}+1\Big)\Big(\frac{5}{2}+M_{J1}+2\Big)\Big]^{1/2} \\
&\qquad \cdot g'_J(^2\mathrm{F}_{7/2},{}^2\mathrm{F}_{5/2})C(^2\mathrm{F}_{5/2};\mathit{\Gamma}\gamma' M_{J1}) \\
&\qquad \cdot C(^2\mathrm{F}_{5/2};\mathit{\Gamma}\gamma' M_{J1}-1), \\
g_\perp^{(2)} &= 0,
\end{aligned} \tag{5}$$

where g_J and g'_J can be obtained in [6, 8].

3. Calculations for Ce^{3+} in LiYF$_4$ Crystal

The LiYF$_4$ crystal exhibits scheelite structure, belonging to the $I4_1$/a space group. The Y^{3+} ion is surrounded by eight nearest-neighbour F$^-$ ligands: four of them at a distance $R_1 \approx 2.246$ Å, and the other four at a slightly different distance ($R_2 \approx 2.293$ Å) [9, 10]. The local symmetry of the Y^{3+} site is S$_4$. Its structural data are given in Table 1. On the basis of the similar chemical properties and the ionic radii of Ce^{3+} and Y^{3+} ions, the doped Ce^{3+} ion substitutes the Y^{3+} ion, and there is no charge compensator [9, 10]. In fact, the D$_{2d}$ symmetry is proved to be a good approximation due to the rather small distortion from D$_{2d}$ to S$_4$ [10], so we take the D$_{2d}$ approximation here for simplicity. Thus, $\hat{H}_{CF}$ for the tetragonal Ce^{3+} center in this work can be expressed in terms of the irreducible tensor operators C_k^q [7]:

$$\begin{aligned}\hat{H}_{CF} = B_2^0C_2^0 + B_4^0C_4^0 + B_4^4(C_4^4 + C_4^{-4}) \\ + B_6^0C_6^0 + B_6^4(C_6^4 + C_6^{-4}),\end{aligned} \tag{6}$$

where B_k^q are crystal field parameters which can be calculated according to the superposition model of Newman [11], i. e.

$$B_k^q = \sum_{j=1}^{n} \bar{A}_k(R_0)(R_0/R_j)^{t_k} K_k^q(\theta_j, \phi_j). \tag{7}$$

Here $K_k^q(\theta_j, \phi_j)$ is the angular function which can be obtained from the local structural parameters of the studied system. t_k is the power law exponent, and $\bar{A}_k(R_0)$ is the intrinsic parameter related to ligands, with the reference distance R_0 (here we take $R_0 \approx 2.275$ Å [12]). R_j is the impurity-ligand distance. Generally $R_j \neq R_j^{\mathrm{H}}$ (where R_j^{H} is the cation-anion distance in the host crystal, see Table 1) because of the different ionic radii of Ce^{3+} and the replaced Y^{3+} ion. R_j can be reasonably estimated from the approximate formula [13]:

$$R_j = R_j^{\mathrm{H}} + (r_{\mathrm{i}} - r_{\mathrm{h}})/2, \tag{8}$$

where r_{i} and r_{h} are the ionic radii of the impurity and the host ions, respectively. For LiYF$_4$:Ce^{3+}: $r_{\mathrm{i}} \approx 1.034$ Å, $r_{\mathrm{h}} \approx 0.893$ Å [14].

Table 1. Structural data of the Y^{3+} site in LiYF$_4$ [9].

F$^-$ ligand	R	θ	ϕ
1	R_1^{H}	θ_1	ϕ_1
2	R_1^{H}	$\pi - \theta_1$	$\phi_1 + \pi/2$
3	R_1^{H}	θ_1	$\phi_1 + \pi$
4	R_1^{H}	$\pi - \theta_2$	$\phi_1 + 3\pi/2$
5	R_2^{H}	θ_2	ϕ_2
6	R_2^{H}	$\pi - \theta_2$	$\phi_2 + \pi/2$
7	R_2^{H}	θ_2	$\phi_2 + \pi$
8	R_2^{H}	$\pi - \theta_2$	$\phi_2 + 3\pi/2$

Here $R_1^{\mathrm{H}} \approx 2.246$ Å, $\theta_1 \approx 67°5'$, $\phi_1 \approx -33°$; $R_2^{\mathrm{H}} \approx 2.293$ Å, $\theta_2 \approx 142°3'$, $\phi_2 \approx -36°59'$.

Table 2. The EPR parameters $g_\parallel$ and $g_\perp$ of the tetragonal Ce^{3+} centers in LiYF$_4$ crystal.

	Cal.[a]	Cal.[b]	Cal.(tot)	Expt. [5]
$g_\parallel$	2.306	0.483	2.789	2.765(2)
$g_\perp$	1.472	0	1.472	1.473(2)

[a] Contributions due to the first-order perturbation terms. [b] Contributions due to the second-order perturbation terms.

For a (CeF$_8$)$^{5-}$ cluster, the exponents t_k and the intrinsic parameter $\bar{A}_k(R_0)$ are taken as those obtained for the similar crystal BaY$_2$F$_8$, i.e., $t_2 \approx 5$, $t_4 \approx 6$, $t_6 \approx 10$, $\bar{A}_4(R_0) \approx 22$ cm^{-1} and $\bar{A}_6(R_0) \approx 3.15$ cm^{-1} [12], with $\bar{A}_2(R_0)$ adjustable. The spin-orbital coupling coefficient is taken from [12], i.e., $\zeta \approx 650$ cm^{-1}. Considering the covalency of the Ce^{3+}-F$^-$ bonds, the orbital reduction factor k should be used, i. e., we take $k \approx 0.922$.

By fitting the calculated g factors to the observed values, we have $\bar{A}_2(R_0) \approx 5.0$ cm^{-1}. From these the above parameters and the complete energy matrix for a 4f^1 ion in tetragonal symmetry, the basis functions for the lowest $\Gamma\gamma$ and the other Kramers doublet Γ_X in terms of the linear combination of $|JM_{\mathrm{J}}\rangle$ can also be obtained. The comparisons between the calculated and experimental EPR g factors are shown in Table 2.

4. Discussion

From Table 2 it can be seen that the calculated results are consistent with the observed values. So, the perturbation formulae of the EPR g factors for a 4f^1 ion in tetragonal symmetry as well as the method used in this paper can be regarded as reasonable. The method can be applied to other similar systems.

Compared with the corresponding first-order perturbation contribution, the second-order contribution to the g factor ($g_\parallel$) is the same in sign and about 17% in magnitude. So, in order to explain the EPR g factors of a 4f^1 ion in crystals more exactly, the contribution of the second-order perturbation terms should be considered.

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