Theoretical Interpretation of the EPR Parameters for Dy$^{3+}$ Ion in LuPO$_4$ Crystal

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Based on the superposition model, in this paper the EPR parameters $g_{\parallel}$ and $g_{\perp}$ of Dy$^{3+}$, and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ of $^{161}$Dy$^{3+}$ and $^{163}$Dy$^{3+}$ in LuPO$_4$ crystal are calculated by perturbation formulas from the crystal-field theory. In the calculations, the contributions of various admixtures and interactions such as $J$-mixing, mixtures among states with the same $J$-value, two-order perturbation, covalency as well as local lattice relaxation are considered. The calculated results agree reasonably with the observed values.

Key words: Electron Paramagnetic Resonance; The Superposition Model; LuPO$_4$; Dy$^{3+}$.

1. Introduction

As a primary nuclear waste, the potentially important application of rare-earth orthophosphate has motivated a series of studies of the physical and chemical characteristics of mixed orthophosphate-impurity systems [1 – 4]. EPR is a powerful tool to determine the local symmetry of impurity centers. So, much experimental and theoretical work has been done to understand the physics of the rare-earth ion in orthophosphates [4 – 7]. For example, EPR $g$ factors $g_{\parallel}$, $g_{\perp}$ of Dy$^{3+}$ and hyperfine structure constants $A_{\parallel}$ of $^{161}$Dy$^{3+}$ and $^{163}$Dy$^{3+}$ in LuPO$_4$ crystal have been measured by Abraham et al. [4]. But until now there exists no theoretical explanation to these useful experimental data. Ordinarily, the EPR parameters of Dy$^{3+}$ are calculated approximately from the first-order perturbation formulas, where the eigenfunction of the lowest Kramers doublet of the 4f$^9$ ion is obtained by considering only the interaction within the ground $^6$H$_{15/2}$ multiplet [8, 9]. In order to calculate more exactly these EPR parameters, in this paper we use the second-order perturbation formulas of the EPR parameters for the 4f$^9$ ion in tetragonal symmetry. In these formulas, the contributions to EPR parameters due to 1.) the $J$-mixing among the ground $^6$H$_{15/2}$, the first excited $^6$H$_{13/2}$ and the second excited $^6$H$_{11/2}$ states, 2.) the mixtures among the states or levels with the same $J$-value via spin-orbit interaction, 3.) the interactions between the lowest Kramers doublet $^1\Gamma_\gamma$ and other 20 Kramers doublets $^1\Gamma_x$ via the crystal-field and orbital angular momentum (or hyperfine structure) as well as 4.) the covalency reduction effect due to the covalency of metal-ligand bonds are all considered. From these formulas, the EPR parameters $g$ and $A$ for Dy$^{3+}$ in LuPO$_4$ crystal are calculated, based on the Newman’s superposition model. The results are discussed.

2. Calculations

LuPO$_4$ crystal has the tetragonal zircon-type structure with space group $I4_1/amd$[141] [10]. The impurity ion Dy$^{3+}$ replaces the Lu$^{3+}$ ion having non-centrosymmetrical D$_{2d}$ point symmetry. Thus Dy$^{3+}$ is surrounded by eight nearest-neighbour O$^{2-}$ ions; four of these at a distance $R_1$ and the other four at a slightly different distance $R_2$ [11, 12]. For the LuPO$_4$:Dy$^{3+}$ crystal, the average values of $\bar{g} \approx (g_{\parallel} +$
2g_{\perp}/3 \approx 6.6 \ [9,13] suggest that the ground doublet \( \Gamma_{\gamma} \) is \( \Gamma_{6} \).

A Dy\(^{3+}\) ion with the \( 4f^9 \) electronic configuration has the ground state \( ^6H_{15/2} \), the first excited state \( ^6H_{13/2} \) and the second excited state \( ^6H_{11/2} \). For a \( 4f^9 \) ion in tetragonal symmetry, the states \( ^6H_{15/2}, ^6H_{13/2} \) and \( ^6H_{11/2} \) of the free-ion split into eight, seven and six Kramers doublets, respectively \([9,14]\). The wave functions of these doublets can be obtained by diagonalizing a \( 42 \times 42 \) energy matrix for the Hamiltonian

\[
\hat{H} = \hat{H}_{\text{free}} + \hat{H}' = \hat{H}_{\text{cf}} + \hat{H}_{Z} + \hat{H}_{\text{hf}},
\]

(1)

where the free-ion term \( \hat{H}_{\text{free}} \) contains Coulomb repulsion, spin-orbit coupling, two-body and three-body interactions etc., \( \hat{H}_{\text{free}} \) is the perturbation term, \( \hat{H}_{\text{cf}} \) is the crystal-field term and can be expressed in terms of Stevens equivalent operator under tetragonal symmetry \([9]\)

\[
\hat{H}_{\text{cf}} = B_0^gO_x^g + B_4^gO_x^g + B_4^0(O_x^g + O_c^4) + B_6^0O_x^g + B_6^gO_x^g + O_c^4),
\]

(2)

where \( B_0^g \) are crystal field parameters. The Zeeman interaction \( \hat{H}_Z \) can be expressed as \( \hat{H}_Z = g_f \mu_B \hat{H} \cdot \hat{J} \), with their original meanings \([9,13]\). The hyperfine interaction \( \hat{H}_{\text{hf}} \) in tetragonal symmetry can be expressed by \( \hat{H}_{\text{hf}} = A_{\perp} \hat{S}_- \hat{I}_+ + A_{\parallel} (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) \) in terms of hyperfine structure constants parallel and perpendicular to the tetragonal axis, and \( \hat{H}_{\text{hf}} \) can also be written as the equivalent operator \( \hat{N} \) of magnetic hyperfine structure, i.e., \( \hat{H}_{\text{hf}} = PN_{\gamma} \hat{N} \), where \( N_{\gamma} \) is the diagonal matrix element for the \( ^{2S+1}L_J \) state, and \( P \) is the dipolar hyperfine structure constant in the crystal \([9]\).

Thus, based on the perturbation method, the perturbation formulas of the EPR parameters \( g_{||}, g_{\perp}, A_{||}, \) and \( A_{\perp} \) can be written as \([14]\)

\[
g_{||} = g_{\parallel}^{(1)} + g_{\parallel}^{(2)}, \]

\[
g_{\parallel}^{(1)} = 2g_f \langle \Gamma_{\gamma} | \hat{J}_z | \Gamma_{\gamma} \rangle, \]

\[
g_{\parallel}^{(2)} = 2 \sum \frac{\langle \Gamma_{\gamma} | \hat{H}_{\text{cf}} | \Gamma_x \gamma \rangle \langle \Gamma_x \gamma | \hat{J}_z | \Gamma_{\gamma} \rangle}{E(\Gamma_{x}) - E(\Gamma)}, \]

(3)

\[
g_{\perp} = g_{\perp}^{(1)} + g_{\perp}^{(2)}, \]

\[
g_{\perp}^{(1)} = g_f \langle \Gamma_{\gamma} | \hat{J}_+ | \Gamma_{\gamma} \rangle, \quad g_{\perp}^{(2)} = 0,
\]

\[
A_{\parallel} = A_{||}^{(1)} + A_{||}^{(2)}, \]

\[
A_{||}^{(1)} = 2PN_{\gamma} \langle \Gamma_{\gamma} | \hat{N} | \Gamma_{\gamma} \rangle, \]

\[
A_{||}^{(2)} = 2 \sum \frac{(\langle \Gamma_{\gamma} | \hat{H}_{\text{cf}} | \Gamma_x \gamma \rangle \langle \Gamma_x \gamma | \hat{N} | \Gamma_{\gamma} \rangle)}{E(\Gamma_{x}) - E(\Gamma)} \]

(4)

\[
A_{\perp} = A_{\perp}^{(1)} + A_{\perp}^{(2)}, \]

\[
A_{\perp}^{(1)} = PN_{\gamma} \langle \Gamma_{\gamma} | \hat{N} | \Gamma_{\gamma} \rangle, \quad A_{\perp}^{(2)} = 0,
\]

where \( \langle \Gamma_{\gamma} | \hat{N} | \Gamma_{\gamma} \rangle \) denotes the excited doublets. The parameters \( g_{||}, g_{\perp}, N_{\gamma} \), and \( N'_{\gamma} \) for various states can be obtained \([9]\) and \([13]\).

Usually, only the contributions of the first-order perturbation terms to the EPR parameters are considered within the ground \( ^6H_{15/2} \) multiplets \([9,15]\). In this paper we use the above second-order perturbation formulas of EPR parameters for a \( 4f^9 \) ion in tetragonal symmetry, to study the EPR parameters \( g \) factors and \( A \) constants. Considering the various contributions to the EPR parameters, i.e., the \( J \)-mixing among the ground \( ^6H_{15/2} \), the first excited \( ^4H_{11/2} \) and the second excited \( ^6H_{11/2} \) states, the mixtures among the states with the same \( J \)-value (including \( ^6H_{15/2}, ^4H_{11/2} \) and \( ^2K_{15/2}, ^6H_{13/2}, ^4H_{13/2}, ^6H_{13/2}, ^4H_{11/2}, ^6H_{11/2}, ^4H_{11/2} \) and \( ^4G_{11/2} \)) via spin-orbit coupling interaction, the interactions between the lowest Kramers doublet \( \Gamma_{\gamma} \) and other 20 Kramers doublets \( \Gamma_x \) via crystal-field and orbital angular momentum (or hyperfine structure) as well as the covalency reduction effect due to the covalency of metal-ligand bonds, the lowest Kramers doublet \( \Gamma_{\gamma} \) (or \( \gamma' \), where \( \gamma \) and \( \gamma' \) stand for the two components of \( \Gamma \) irreducible representation) can be expressed as

\[
|\Gamma_{\gamma}(or \gamma')\rangle = \sum_{M_{J_{1}}} C^{(6)H_{15/2}; \Gamma_{\gamma}(or \gamma')M_{J_{1}}} \cdot N_{15/2}^{(6)H_{15/2}2M_{J_{1}}} + \lambda^{|4\text{I}_{15/2}2M_{J_{1}}} + \lambda^{|4\text{I}_{15/2}2M_{J_{1}}} + \lambda^{|4\text{I}_{13/2}2M_{J_{2}}}) \]

(5)

\[
+ \sum_{M_{J_{2}}} C^{(6)H_{13/2}; \Gamma_{\gamma}(or \gamma')M_{J_{2}}} N_{13/2}^{(6)H_{13/2}2M_{J_{2}}} \]

\[
+ \lambda^{|4\text{I}_{13/2}2M_{J_{2}}} + \lambda^{|4\text{I}_{13/2}2M_{J_{2}}} + \lambda^{|4\text{I}_{13/2}2M_{J_{2}}} > \]

\[
+ \sum_{M_{J_{3}}} C^{(6)H_{11/2}; \Gamma_{\gamma}(or \gamma')M_{J_{3}}} N_{11/2}^{(6)H_{11/2}2M_{J_{3}}} \]

\[
+ \lambda^{|4\text{I}_{11/2}2M_{J_{3}}} + \lambda^{|4\text{I}_{11/2}2M_{J_{3}}} + \lambda^{|4\text{I}_{11/2}2M_{J_{3}}} > \]

\[
+ \lambda^{|4\text{I}_{11/2}2M_{J_{3}}} + \lambda^{|4\text{I}_{11/2}2M_{J_{3}}} + \lambda^{|4\text{I}_{11/2}2M_{J_{3}}} \rangle.
\]

where \( M_{J_{1}}, M_{J_{2}} \) and \( M_{J_{3}} \) are in the ranges \( -15/2 \sim 15/2, -13/2 \sim 13/2 \) and \( -11/2 \sim 11/2 \), respectively. \( N_{\gamma} \) and \( \lambda_{\gamma} \) are the normalization factors and mixing coefficients. They can be calculated from the spin-orbit coupling matrix elements and perturbation method.
Based on Newman’s superposition model [16, 17], the crystal field parameters $B_k^i$ in (2) can be expressed as

$$B_k^i = \sum_{j=1}^{n} \tilde{A}_k(R_0)(R_0/R_j)^{t_k}K_k^i(\theta_j, \phi_j),$$  \hspace{1cm} (6)

where the coordination factor $K_k^i(\theta_j, \phi_j)$ can be obtained from the local structural parameters of the studied system. $t_k$ is the power law exponent and $\tilde{A}_k(R_0)$ the intrinsic parameter with the reference distance $R_0$. In LuPO$_4$ crystal, the host Lu$^{3+}$ ion is coordinated by eight nearest-neighbour O$^{2-}$ ions: four of these at a distance $R_0^1$ and angle $\theta_1$, the other four at a slightly different distance $R_0^2$ angle $\theta_2$, where $\theta_1$ is the angle between $R_0^1$ and the fourfold crystal axis. For LuPO$_4$, $R_0^1 \approx 2.264$ Å, $\theta_1 \approx 76^\circ32'; R_0^2 \approx 2.346$ Å, $\theta_2 \approx 30^\circ57'$ [18]. Generally, considering the local lattice relaxation, the EPR parameters of LuPO$_4$:Dy$^{3+}$ in LuPO$_4$ crystal are reasonably explained by the different ionic radii of Dy$^{3+}$ and the replaced Lu$^{3+}$ ion. $R_j$ can be reasonably estimated from the approximate formula [19]

$$R_j = R_0^j + (r_i - r_h)/2,$$  \hspace{1cm} (7)

where $r_i$ and $r_h$ are the ionic radii of the impurity and the host, respectively. For LuPO$_4$:Dy$^{3+}$, $r_i \approx 0.908$ Å, $r_h \approx 0.85$ Å [10]. The free ionic parameters of the Coulomb repulsion ($E^0 \approx 55395$ cm$^{-1}$, $E^1 \approx 6158$ cm$^{-1}$, $E^2 \approx 30.43$ cm$^{-1}$ and $E^3 \approx 622.75$ cm$^{-1}$), the two-body interaction parameters ($\alpha \approx 17.92$ cm$^{-1}$, $\beta \approx -612.15$ cm$^{-1}$ and $\gamma \approx 1679.85$ cm$^{-1}$) the spin-orbit coupling coefficient ($\zeta_{4f} \approx 1914$ cm$^{-1}$) in the energy matrix were obtained in [20].

For the (DyO$_{13}$) cluster, no superposition model parameters were reported. We estimate them as follows: the exponents $t_k$ are taken as those obtained for the similar trivalent rare-earth ions Er$^{3+}$ and Yb$^{3+}$ in zinc-type compounds, i.e., $t_2 \approx 7$, $t_4 \approx 12$ and $t_6 \approx 11$ [6, 7] and the intrinsic parameters $\tilde{A}_2(R_0)$ and $\tilde{A}_4(R_0)$ with the reference distance $R_0 = 2.343$ are also taken from Yb$^{3+}$ in the same host LuPO$_4$ crystal [7]. $\tilde{A}_2(R_0)$ is taken as the adjustable parameter obtained by fitting the calculated EPR parameters ($g_{||}$, $g_{\perp}$ and $A_{||}$) and the observed values.

### 3. Discussions

In Table 1 it can be seen that the calculated EPR parameters $g_{||}$, $g_{\perp}$ of Dy$^{3+}$, and the hyperfine structure constants $A_{||}$ of $^{161}$Dy$^{3+}$ and $^{163}$Dy$^{3+}$ in LuPO$_4$ crystal agree with the experimental values. So EPR parameters for LuPO$_4$:Dy$^{3+}$ crystal are reasonably explained by the above studies. This indicates that the perturbation formulas and the used parameters in this paper can be regarded as reasonable.

| Isotope | $g_{||}$ | $g_{\perp}$ | $A_{||}$ | $A_{\perp}$ |
|---------|---------|--------|--------|--------|
| $^{161}$Dy$^{3+}$ | 4.205 (11) | 314.3 | 312.9 | 441.6 |
| $^{163}$Dy$^{3+}$ | 4.205 (11) | 314.3 | 312.9 | 441.6 |

Table 1. EPR parameters of Dy$^{3+}$ in LuPO$_4$ crystal ($A_i$ are in units of $10^{-4}$ cm$^{-1}$).

Because of the covalency of the Dy$^{3+}$-O$^{2-}$ bonds, the orbital reduction factor $k$ should be used in the calculations. So, the dipolar hyperfine structure constant for Dy$^{3+}$ in LuPO$_4$ crystal can be written as $P = kP_0$ (where $P_0 \approx 51.4 \times 10^{-4}$ cm$^{-1}$, the free ion value for the isotope $^{161}$Dy, and $P_0 \approx 71.5 \times 10^{-4}$ cm$^{-1}$ [8], the free ion value for the isotope $^{163}$Dy, respectively [9]).

The above formulas and parameters, we reach good fits between calculated and experimental EPR parameters $g_{||}$, $g_{\perp}$ of Dy$^{3+}$ and hyperfine structure constants $A_{||}$ of $^{161}$Dy$^{3+}$ and $^{163}$Dy$^{3+}$ isotopes in LuPO$_4$ crystal, these parameters are

$$A_6(R_0) \approx 9.2 \text{ cm}^{-1}, \ k \approx 0.981.$$  \hspace{1cm} (8)

The comparisons between the calculated and experimental EPR parameters are shown in Table 1.