

Theoretical Interpretation of the EPR Parameters for Dy³⁺ Ion in LuPO₄ Crystal

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Based on the superposition model, in this paper the EPR parameters g_{\parallel} and g_{\perp} of Dy³⁺, and the hyperfine structure constants A_{\parallel} and A_{\perp} of ¹⁶¹Dy³⁺ and ¹⁶³Dy³⁺ in LuPO₄ 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; LuPO₄; Dy³⁺.

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 Dy³⁺ and hyperfine structure constants A_{\parallel} of ¹⁶¹Dy³⁺ and ¹⁶³Dy³⁺ in LuPO₄ 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 Dy³⁺ are calculated approximately from the first-order perturbation formulas, where the eigenfunction of the lowest Kramers doublet of the 4f⁹ ion is obtained by considering only the interaction within the ground ⁶H_{15/2} multiplets [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 4f⁹ ion in tetragonal symmetry. In these formu-

las, the contributions to EPR parameters due to 1.) the J -mixing among the ground ⁶H_{15/2}, the first excited ⁶H_{13/2} and the second excited ⁶H_{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 $\Gamma\gamma$ and other 20 Kramers doublets Γx 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 Dy³⁺ in LuPO₄ crystal are calculated, based on the Newman's superposition model. The results are discussed.

2. Calculations

LuPO₄ crystal has the tetragonal zircon-type structure with space group $I4_1/amd(141)$ [10]. The impurity ion Dy³⁺ replaces the Lu³⁺ ion having non-centrosymmetrical D_{2d} point symmetry. Thus Dy³⁺ is surrounded by eight nearest-neighbour O²⁻ ions; four of these at a distance R_1 and the other four at a slightly different distance R_2 [11,12]. For the LuPO₄:Dy³⁺ 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 Γ_6 .

A Dy³⁺ ion with the 4f⁹ electronic configuration has the ground state ${}^6\text{H}_{15/2}$, the first excited state ${}^6\text{H}_{13/2}$ and the second excited state ${}^6\text{H}_{11/2}$. For a 4f⁹ ion in tetragonal symmetry, the states ${}^6\text{H}_{15/2}$, ${}^6\text{H}_{13/2}$ and ${}^6\text{H}_{11/2}$ 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 42×42 energy matrix related to the Hamilton

$$\hat{H} = \hat{H}_{\text{free}} + \hat{H}', \quad \hat{H}' = \hat{H}_{\text{cf}} + \hat{H}_{\text{Z}} + \hat{H}_{\text{hf}}, \quad (1)$$

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

$$\begin{aligned} \hat{H}_{\text{CF}} = & B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^4 (O_6^4 + O_6^{-4}) \\ & + B_6^0 O_6^0 + B_6^4 (O_6^4 + O_6^{-4}), \end{aligned} \quad (2)$$

where B_k^q are crystal field parameters. The Zeeman interaction \hat{H}_{Z} can be written as $\hat{H}_{\text{Z}} = g_J \mu_B \hat{H} \cdot \hat{J}$, with their original meanings [9, 13]. The hyperfine interaction \hat{H}_{hf} in tetragonal symmetry can be expressed by $\hat{H}_{\text{hf}} = A_{\parallel} \hat{S}_z \hat{I}_z + A_{\perp} (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+)$ in terms of hyperfine structure constants parallel and perpendicular to the tetragonal axis, and \hat{H}_{hf} can be also written as the equivalent operator \hat{N} of magnetic hyperfine structure, i. e., $\hat{H}_{\text{hf}} = P N_J \hat{N}$, where N_J is the diagonal matrix element for the $2S+1L_J$ 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_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} can be written as [14]

$$\begin{aligned} g_{\parallel} &= g_{\parallel}^{(1)} + g_{\parallel}^{(2)}, \\ g_{\parallel}^{(1)} &= 2g_J \langle \Gamma\gamma | \hat{J}_z | \Gamma\gamma \rangle, \\ g_{\parallel}^{(2)} &= 2 \sum_X' \frac{\langle \Gamma\gamma | \hat{H}_{\text{CF}} | \Gamma_X \gamma_X \rangle \langle \Gamma_X \gamma_X | \hat{J}_z | \Gamma\gamma \rangle}{E(\Gamma_X) - E(\Gamma)}, \\ g_{\perp} &= g_{\perp}^{(1)} + g_{\perp}^{(2)}, \\ g_{\perp}^{(1)} &= g_J \langle \Gamma\gamma | \hat{J}_+ | \Gamma\gamma' \rangle, \quad g_{\perp}^{(2)} = 0, \end{aligned} \quad (3)$$

$$A_{\parallel} = A_{\parallel}^{(1)} + A_{\parallel}^{(2)},$$

$$A_{\parallel}^{(1)} = 2PN_J \langle \Gamma\gamma | \hat{N}_z | \Gamma\gamma \rangle,$$

$$A_{\parallel}^{(2)} = 2P \sum_X' \frac{\langle \Gamma\gamma | \hat{H}_{\text{CF}} | \Gamma_X \gamma_X \rangle \langle \Gamma_X \gamma_X | \hat{N}_z | \Gamma\gamma \rangle}{E(\Gamma_X) - E(\Gamma)}, \quad (4)$$

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

$$A_{\perp}^{(1)} = PN_J \langle \Gamma\gamma | \hat{N}_+ | \Gamma\gamma' \rangle, \quad A_{\perp}^{(2)} = 0,$$

where $\Gamma_X \gamma_X$ denotes the excited doublets. The parameters g_J , g_J' , N_J and N_J' for various states can be obtained from [9] and [13].

Usually, only the contributions of the first-order perturbation terms to the EPR parameters are considered within the ground ${}^6\text{H}_{15/2}$ multiplets [9, 15]. In this paper we use the above second-order perturbation formulas of EPR parameters for a 4f⁹ 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 ${}^6\text{H}_{15/2}$, the first excited ${}^6\text{H}_{13/2}$ and the second excited ${}^6\text{H}_{11/2}$ states, the mixtures among the states with the same J -value (including ${}^6\text{H}_{15/2}$, ${}^6\text{I}_{15/2}$ and ${}^2\text{K}_{15/2}$, ${}^6\text{H}_{13/2}$, ${}^4\text{I}_{13/2}$ and ${}^4\text{H}_{13/2}$, and ${}^6\text{H}_{11/2}$, ${}^4\text{I}_{11/2}$ and ${}^4\text{G}_{11/2}$) via spin-orbit coupling interaction, the interactions between the lowest Kramers doublet $\Gamma\gamma$ and other 20 Kramers doublets Γx 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 γ' , where γ and γ' stand for the two components of Γ irreducible representation) can be expressed as

$$\begin{aligned} |\Gamma\gamma(\text{or } \gamma')\rangle = & \sum_{M_{J1}} C({}^6\text{H}_{15/2}; \Gamma\gamma(\text{or } \gamma') M_{J1}) \\ & \cdot N_{15/2} (|{}^6\text{H}_{15/2} M_{J1}\rangle + \lambda_1 |{}^4\text{I}_{15/2} M_{J1}\rangle + \lambda_1' |{}^4\text{I}_{15/2} M_{J1}\rangle) \\ & + \sum_{M_{J2}} C({}^6\text{H}_{13/2}; \Gamma\gamma(\text{or } \gamma') M_{J2}) N_{13/2} (|{}^6\text{H}_{13/2} M_{J2}\rangle \\ & + \lambda_1'' |{}^4\text{I}_{13/2} M_{J2}\rangle + \lambda_H' |{}^4\text{H}_{13/2} M_{J2}\rangle) \\ & + \sum_{M_{J3}} C({}^6\text{H}_{11/2}; \Gamma\gamma(\text{or } \gamma') M_{J3}) N_{11/2} (|{}^6\text{H}_{11/2} M_{J3}\rangle \\ & + \lambda_1''' |{}^4\text{I}_{11/2} M_{J3}\rangle + \lambda_F |{}^6\text{F}_{11/2} M_{J3}\rangle + \lambda_G |{}^4\text{G}_{11/2} M_{J3}\rangle), \end{aligned} \quad (5)$$

where M_{J1} , M_{J2} and M_{J3} are in the ranges $-15/2 \sim 15/2$, $-13/2 \sim 13/2$ and $-11/2 \sim 11/2$, respectively. N_i and λ_i 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^q in (2) can be expressed as

$$B_k^q = \sum_{j=1}^n \bar{A}_k(R_0)(R_0/R_j)^{t_k} K_k^q(\theta_j, \phi_j), \quad (6)$$

where the coordination factor $K_k^q(\theta_j, \phi_j)$ can be obtained from the local structural parameters of the studied system. t_k is the power law exponent and $\bar{A}_k(R_0)$ the intrinsic parameter with the reference distance R_0 . In LuPO₄ crystal, the host Lu³⁺ ion is coordinated by eight nearest-neighbour O²⁻ ions: four of these at a distance R_1^H and angle θ_1 , the other four at a slightly different distance R_2^H angle θ_2 , where θ_j is the angle between R_j^H and the fourfold crystal axis. For LuPO₄, $R_1^H \approx 2.264$ Å, $\theta_1 \approx 76^\circ 32'$; $R_2^H \approx 2.346$ Å, $\theta_2 \approx 30^\circ 57'$ [18]. Generally, considering the local lattice relaxation, when an impurity ion substitutes for a host ion, $R_j \neq R_j^H$ (where R_j^H is the cation-anion distance in the host crystal) because of the different ionic radii of Dy³⁺ and the replaced Lu³⁺ ion. R_j can be reasonably estimated from the approximate formula [19]

$$R_j = R_j^H + (r_i - r_h)/2, \quad (7)$$

where r_i and r_h are the ionic radii of the impurity and the host, respectively. For LuPO₄:Dy³⁺, $r_i \approx 0.908$ Å, $r_h \approx 0.85$ Å [10]. The free ion 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 (DyO₈)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 Er³⁺ and Yb³⁺ in zircon-type compounds, i. e., $t_2 \approx 7$, $t_4 \approx 12$ and $t_6 \approx 11$ [6, 7] and the intrinsic parameters and $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ with the reference distance $R_0 = 2.343$ are also taken from Yb³⁺ in the same host LuPO₄ crystal [7]. $\bar{A}_4(R_0)$ is taken as the adjustable parameter obtained by fitting the calculated EPR parameters (g_{\parallel} , g_{\perp} and A_{\parallel}) with the observed values.

Table 1. EPR parameters of Dy³⁺ in LuPO₄ crystal (A_i are in units of 10⁻⁴ cm⁻¹).

	¹⁶¹ Dy ³⁺		¹⁶³ Dy ³⁺			
	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	A_{\parallel}	A_{\perp}
Cal.	11.568	4.205	314.3(63)	115.2(22)	437.2(86)	160.3(31)
Expt. [4]	11.26(5)	4.2	312.9(30)	-	441.6(20)	-

Because of the covalency of the Dy³⁺-O²⁻ bonds, the orbital reduction factor k should be used in the calculations. So, the dipolar hyperfine structure constant for Dy³⁺ in LuPO₄ 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 ¹⁶¹Dy, and $P_0 \approx 71.5 \times 10^{-4}$ cm⁻¹ [8], the free ion value for the isotope ¹⁶³Dy, respectively [9]). From the above formulas and parameters, we reach good fits between calculated and experimental EPR parameters g factors g_{\parallel} , g_{\perp} of Dy³⁺ and hyperfine structure constants A_{\parallel} of ¹⁶¹Dy³⁺ and ¹⁶³Dy³⁺ isotopes in LuPO₄ crystal, these parameters are

$$\bar{A}_6(R_0) \approx 9.2 \text{ cm}^{-1}, \quad k \approx 0.981. \quad (8)$$

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

3. Discussions

In Table 1 it can be seen that the calculated EPR parameters g_{\parallel} , g_{\perp} of Dy³⁺, and the hyperfine structure constants A_{\parallel} of ¹⁶¹Dy³⁺ and ¹⁶³Dy³⁺ in LuPO₄ crystal agree with the experimental values. So EPR parameters for LuPO₄:Dy³⁺ 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.

Observed values of A_{\perp} of ¹⁶¹Dy³⁺ and ¹⁶³Dy³⁺ in LuPO₄ crystal are not reported. The theoretical values of A_{\perp} in Table 1 remain to be checked by future experimental studies.

Based on the superposition model, considering various admixtures and interactions and the local lattice relaxation, the EPR parameters of LuPO₄:Dy³⁺ are satisfactorily explained. These formulas, as well as the method of the study may be used in similar systems.

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