

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

Hui-Ning Dong<sup>a,b</sup>, Hui-Ping Du<sup>a</sup>, Shao-Yi Wu<sup>b,c</sup>, and Peng Li<sup>d</sup>

<sup>a</sup> Institute of Applied Physics & College of Electronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, P. R. China

<sup>b</sup> International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

<sup>c</sup> Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

<sup>d</sup> Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

Reprint requests to Dr. H.-N.D.; E-mail: donghn@163.com

Z. Naturforsch. **59a**, 765 – 768 (2004); received December 19, 2003

Based on the superposition model, in this paper the EPR parameters  $g_{\parallel}$  and  $g_{\perp}$  of  $\text{Dy}^{3+}$ , and the hyperfine structure constants  $A_{\parallel}$  and  $A_{\perp}$  of  $^{161}\text{Dy}^{3+}$  and  $^{163}\text{Dy}^{3+}$  in  $\text{LuPO}_4$  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;  $\text{LuPO}_4$ ;  $\text{Dy}^{3+}$ .

## 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  $\text{Dy}^{3+}$  and hyperfine structure constants  $A_{\parallel}$  of  $^{161}\text{Dy}^{3+}$  and  $^{163}\text{Dy}^{3+}$  in  $\text{LuPO}_4$  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  $\text{Dy}^{3+}$  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  $^6\text{H}_{15/2}$  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  $4f^9$  ion in tetragonal symmetry. In these formu-

las, the contributions to EPR parameters due to 1.) 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, 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  $\Gamma_7$  and other 20 Kramers doublets  $\Gamma_8$  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  $\text{Dy}^{3+}$  in  $\text{LuPO}_4$  crystal are calculated, based on the Newman's superposition model. The results are discussed.

## 2. Calculations

$\text{LuPO}_4$  crystal has the tetragonal zircon-type structure with space group  $I4_1/amd(141)$  [10]. The impurity ion  $\text{Dy}^{3+}$  replaces the  $\text{Lu}^{3+}$  ion having non-centrosymmetrical  $\text{D}_{2d}$  point symmetry. Thus  $\text{Dy}^{3+}$  is surrounded by eight nearest-neighbour  $\text{O}^{2-}$  ions; four of these at a distance  $R_1$  and the other four at a slightly different distance  $R_2$  [11,12]. For the  $\text{LuPO}_4:\text{Dy}^{3+}$  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<sup>3+</sup> ion with the 4f<sup>9</sup> 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 4f<sup>9</sup> 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  $42 \times 42$  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  $\hat{H}_{\text{free}}$  includes Coulomb repulsion, spin-orbital 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]

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

where  $B_k^q$  are crystal field parameters. The Zeeman interaction  $\hat{H}_{\text{Z}}$  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  $\hat{H}_{\text{hf}}$  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  $\hat{H}_{\text{hf}}$  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 4f<sup>9</sup> 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  $\Gamma x$  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

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

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  $\lambda_i$  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 LuPO<sub>4</sub> crystal, the host Lu<sup>3+</sup> ion is coordinated by eight nearest-neighbour O<sup>2-</sup> ions: four of these at a distance  $R_1^H$  and angle  $\theta_1$ , the other four at a slightly different distance  $R_2^H$  angle  $\theta_2$ , where  $\theta_j$  is the angle between  $R_j^H$  and the fourfold crystal axis. For LuPO<sub>4</sub>,  $R_1^H \approx 2.264$  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 Dy<sup>3+</sup> and the replaced Lu<sup>3+</sup> 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 LuPO<sub>4</sub>:Dy<sup>3+</sup>,  $r_i \approx 0.908$  Å,  $r_h \approx 0.85$  Å [10]. The free ion parameters of the Coulomb repulsion ( $E^0 \approx 55395$  cm<sup>-1</sup>,  $E^1 \approx 6158$  cm<sup>-1</sup>,  $E^2 \approx 30.43$  cm<sup>-1</sup> and  $E^3 \approx 622.75$  cm<sup>-1</sup>), the two-body interaction parameters ( $\alpha \approx 17.92$  cm<sup>-1</sup>,  $\beta \approx -612.15$  cm<sup>-1</sup> and  $\gamma \approx 1679.85$  cm<sup>-1</sup>) the spin-orbit coupling coefficient ( $\zeta_{4f} \approx 1914$  cm<sup>-1</sup>) in the energy matrix were obtained in [20].

For the (DyO<sub>8</sub>)<sup>13-</sup> 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<sup>3+</sup> and Yb<sup>3+</sup> 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 Yb<sup>3+</sup> in the same host LuPO<sub>4</sub> 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 Dy<sup>3+</sup> in LuPO<sub>4</sub> crystal ( $A_i$  are in units of  $10^{-4}$  cm<sup>-1</sup>).

	<sup>161</sup> Dy <sup>3+</sup>			<sup>163</sup> Dy <sup>3+</sup>		
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	$A_{\parallel}$	$A_{\perp}$
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 Dy<sup>3+</sup>-O<sup>2-</sup> bonds, the orbital reduction factor  $k$  should be used in the calculations. So, the dipolar hyperfine structure constant for Dy<sup>3+</sup> in LuPO<sub>4</sub> crystal can be written as  $P = kP_0$  (where  $P_0 \approx 51.4 \times 10^{-4}$  cm<sup>-1</sup>, the free ion value for the isotope <sup>161</sup>Dy, and  $P_0 \approx 71.5 \times 10^{-4}$  cm<sup>-1</sup> [8], the free ion value for the isotope <sup>163</sup>Dy, 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 Dy<sup>3+</sup> and hyperfine structure constants  $A_{\parallel}$  of <sup>161</sup>Dy<sup>3+</sup> and <sup>163</sup>Dy<sup>3+</sup> isotopes in LuPO<sub>4</sub> 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 Dy<sup>3+</sup>, and the hyperfine structure constants  $A_{\parallel}$  of <sup>161</sup>Dy<sup>3+</sup> and <sup>163</sup>Dy<sup>3+</sup> in LuPO<sub>4</sub> crystal agree with the experimental values. So EPR parameters for LuPO<sub>4</sub>:Dy<sup>3+</sup> 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 <sup>161</sup>Dy<sup>3+</sup> and <sup>163</sup>Dy<sup>3+</sup> in LuPO<sub>4</sub> 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 LuPO<sub>4</sub>:Dy<sup>3+</sup> are satisfactorily explained. These formulas, as well as the method of the study may be used in similar systems.

- [1] M. M. Abraham, L. A. Boatner, and M. Rappaz, *Phys. Rev. Lett.* **45**, 893 (1980).
- [2] L. A. Boatner, G. W. Beall, M. M. Abraham, C. B. Finch, P. G. Huray, and M. Rappaz, *Scientific Basis for Nuclear Waste Management*, Plenum, New York 1980, p. 289.
- [3] G. W. Beall, L. A. Boatner, D. F. Mullica, and W. O. Milligan, *J. Norg. Nucl. Chem.* **43**, 101 (1981).
- [4] M. M. Abraham, L. A. Boatner, J. O. Ramey, and M. Rappaz, *J. Chem. Phys.* **78**, 1 (1983).
- [5] S. K. Misra, S. Isber, J. A. Capobianco, and E. Cavalli, *Chemical Physics* **240**, 313 (1999).
- [6] Vishwamittar and S. P. Puri, *Phys. Rev. B* **9**, 4673 (1974).
- [7] H. N. Dong, W. C. Zheng, S. Y. Wu, and S. Tang, *Z. Naturforsch.* **58a**, 434 (2003).
- [8] D. Bravo, A. A. Kaminskii, and F. J. Lopez, *J. Phys.: Condens. Matter* **10**, 3261 (1998).
- [9] A. Abragam and B. Bleaney, *Electron paramagnetic resonance of Transition-Ions*, Oxford University press, London 1970.
- [10] R. C. Weast, *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton 1989, F187.
- [11] D. J. Newman and W. Urban, *J. Phys. C5*, 3101 (1972).
- [12] O. Muller and R. Roy, *Crystal Chemistry of Non-Metallic Materials*, University Park, PA, 1974.
- [13] I. A. Sorin and M. V. Vlasova, *Electron spin resonance of paramagnetic crystals*, Translated from Russian by P. Gluck, Plenum Press, New York 1973.
- [14] H. N. Dong, W. C. Zheng, S. Y. Wu, and S. Tang, *J. Phys. Chem. Solids* **64**, 1213 (2003).
- [15] D. Bravo, A. A. Kaminskii, and F. J. Lopez, *J. Phys.: Condens. Matter* **10**, 3261 (1998).
- [16] D. J. Newman and B. Ng, *Rep. Prog. Phys.* **52**, 699 (1989).
- [17] D. J. Newman and B. Ng, *Crystal Handbook*, Cambridge University Press, Cambridge 2000.
- [18] D. J. Newman and W. Urban, *J. Phys. Chem.* **5**, 3101 (1972).
- [19] H. N. Dong and S. Y. Wu, *Z. Naturforsch.* **58a**, 507 (2003).
- [20] M. Yin, J. C. Krupa, E. Antic-Fidancev and A. Lorriaux-Rubbens, *Phys. Rev. B* **61**, 8073 (2000).