Investigation of the EPR Parameters of a Trigonal Dy^{3+} Center in $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ Crystal

Hui-Ning Dong[a,b], Shao-Yi Wu[c], and David J. Keeble[b]

[a] Institute of Applied Physics and College of Electronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, P. R. China
[b] Division of Electronic Engineering and Physics, University of Dundee, Dundee DD1 4HN, UK
[c] Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

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

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The electron paramagnetic resonance parameters $g_\parallel$ and $g_\perp$ of Dy^{3+}, and the hyperfine structure parameters $A_\parallel$ and $A_\perp$ of $^{161}Dy^{3+}$ and $^{163}Dy^{3+}$ in a $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ crystal are calculated by the perturbation formulas of the EPR parameters for a $4f^9$ ion in trigonal symmetry. In these formulas, the J-mixing among the ^6H_J ($J = 15/2$, 13/2 and 11/2) states via crystal-field interactions, the mixtures of 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 20 Kramers doublets Γ_X via the crystal-field and orbital angular momentum (or hyperfine structure) are all considered. The crystal-field parameters for the studied Dy^{3+} center are obtained with the superposition model. The calculated results are in good agreement with the observed values.

Key words: Crystal-Field Theory; Electron Paramagnetic Resonance; Dy^{3+}; $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$.

1. Introduction

Lanthanum magnesium double nitrate (LMN) crystals have been used as magnetic thermometers, material for adiabatic demagnetization as well as a proton spin-polarized target in physics and polarized neutron diffraction [1]. The hydrated double nitrates $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ belong to an interesting isomorphous series of LMNs with the general formula $3[X(H_2O)_6]2[Y(NO_3)_6] \cdot 6H_2O$, where X is a divalent cation and Y a trivalent one. Generally, the divalent transition metal ions occupy the X sites and the trivalent rare-earth ions occupy the Y sites. These are one trivalent cation (A) site with C_{3i} local symmetry and two different divalent cation (B) sites (site I and site II) with D_{3d} local symmetry for site I and C_{3i} for site II. As the EPR experiment is a powerful tool to determine the local symmetry of impurity centers, many experimental and theoretical studies, including EPR technology, have been made for rare-earth ions and transition metal impurities in these crystals [2 – 9]. In previous works, these theoretical studies are usually related to transition metal impurities, and those of rare-earth ions are comparatively rare. For instance, the EPR parameters $g_\parallel$ and $g_\perp$, and the hyperfine structure constants $A_\parallel$ and $A_\perp$ for a Dy^{3+} center in $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ were measured [10]. Until now, however, the above EPR experimental results have not been theoretically investigated. In order to calculate these EPR parameters, in this paper we first of all establish the second-order perturbation formulas of the EPR parameters g_i and A_i for the $4f^9$ ion in trigonal symmetry. In these formulas, the contributions to EPR parameters due to (i) the mixtures among the states or levels with the same J-value via spin-orbit interaction, (ii) the J-mixing among the ground $^6H_{15/2}$, the first excited $^6H_{13/2}$ and the second excited $^6H_{11/2}$ states via crystal-field (CF) interactions (i. e., a 42×42 energy matrix is used), and (iii) the interactions between the lowest Kramers doublet $\Gamma\gamma$ and other 20 Kramers doublets (or irreducible representations) Γ_X via crystal-field and orbital angular momentum (or hyperfine structure) are considered. From these formulas, the EPR parameters g_i and A_i for Dy^{3+} in $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ crystals are calculated based on Newman's superposition model. The results are discussed.

2. Calculations

In the host $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ crystal, the La^{3+} ion is coordinated by six nearest neighbours $NO_3{}^-$: three of these at the distance R_1^H and angle θ_1, the other three at a slightly different distance R_2^H and the angle θ_2, where θ_j is the angle between the R_j^H and three-fold crystal axis. The doped impurity Dy^{3+} replaces a La^{3+} site and occupies the site having C_{3i} point symmetry [11, 12]. For the $La_2Mg_3(NO_3)_{12} \cdot 24H_2O{:}Dy^{3+}$ crystal, the average values of $\bar{g} \approx (g_\parallel + 2g_\perp)/3 \approx 7.38$ [9, 12] suggest that the ground doublet $\Gamma\gamma$ is Γ_7.

The Dy^{3+} ion has a $4f^9$ electronic configuration with 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 a trigonal symmetry crystal-field, the above states ${}^6H_{15/2}$, ${}^6H_{13/2}$ and ${}^6H_{11/2}$ of the free-ion splits into eight, seven and six Kramers doublets, respectively [10, 13]. Usually, only the contributions of the first-order perturbation terms to the EPR parameters are considered within the ground ${}^6H_{15/2}$ multiplets [13 – 15].

In this work, the base function $\Gamma\gamma$ (or γ', where γ and γ' stand for the two components of the irreducible representation) of the lowest doublet includes the admixture of different states, i. e., the admixture among the ground ${}^6H_{15/2}$, the first excited ${}^6H_{13/2}$ and second excited ${}^6H_{11/2}$ states via crystal-field interaction, and the admixture among the states with the same J-values (including ${}^6H_{15/2}$, ${}^6I_{15/2}$ and ${}^2K_{15/2}$; ${}^6H_{13/2}$, ${}^4I_{13/2}$ and ${}^4H_{13/2}$; and ${}^6H_{11/2}$, ${}^4I_{11/2}$ and ${}^4G_{11/2}$) via spin-orbit coupling interaction. Thus, the formula of $\Gamma\gamma$ can be expressed as [16]

$$\begin{aligned}
&|\Gamma\gamma(\text{or } \gamma')\rangle = \\
&\sum_{M_{J1}} C({}^6H_{15/2};\Gamma\gamma(\text{or } \gamma')M_{J1})N_{15/2}(|{}^6H_{15/2}M_{J1}\rangle \\
&\qquad + \lambda_I|{}^4I_{15/2}M_{J1}\rangle + \lambda_I'|{}^4I_{15/2}M_{J1}\rangle) \\
&+ \sum_{M_{J2}} C({}^6H_{13/2};\Gamma\gamma(\text{or } \gamma')M_{J2})N_{13/2}(|{}^6H_{13/2}M_{J2}\rangle \\
&\qquad + \lambda_I''|{}^4I_{13/2}M_{J2}\rangle + \lambda_H|{}^4H_{13/2}M_{J2}\rangle) \\
&+ \sum_{M_{J3}} C({}^6H_{11/2};\Gamma\gamma(\text{or } \gamma')M_{J3})N_{11/2}(|{}^6H_{11/2}M_{J3}\rangle \\
&\qquad + \lambda_I'''|{}^4I_{11/2}M_{J3}\rangle + \lambda_F|{}^4F_{11/2}M_{J3}\rangle \\
&\qquad + \lambda_G|{}^4G_{11/2}M_{J3}\rangle),
\end{aligned} \tag{1}$$

where λ_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 range $-15/2 \sim 15/2$, $-13/2 \sim 13/2$ and $-11/2 \sim 11/2$, respectively.

The wave functions of these doublets can be obtained by diagonalizing the 42×42 energy matrix related to the Hamiltonian

$$\hat{H} = \hat{H}_{\text{free}} + \hat{H}', \tag{2}$$

where the free ion term $\hat{H}_{\text{free}}$ includes Coulomb repulsion, spin-orbital coupling, two-body and three-body interactions etc. The perturbation Hamiltonian $\hat{H}'$ for a rare-earth ion in the crystal under an external magnetic field can be expressed as [13]

$$\hat{H}' = \hat{H}_{\text{cf}} + \hat{H}_Z + \hat{H}_{\text{hf}}, \tag{3}$$

where $\hat{H}_{\text{cf}}$ is the crystal-field term and can be written in terms of Stevens equivalent operator under trigonal symmetry [13]

$$\hat{H}_{\text{cf}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^3 O_4^3 + B_6^3 O_6^3 + B_6^6 O_6^6, \tag{4}$$

where B_k^q are crystal-field parameters. The Zeeman interaction $\hat{H}_Z$ can be expressed as $\hat{H}_Z = g_J \mu_\beta \hat{H} \cdot \hat{J}$, with their original meanings [13]. The hyperfine interaction $\hat{H}_{\text{hf}}$ in trigonal symmetry can be written as $\hat{H}_{\text{hf}}$ in terms of hyperfine structure constants parallel and perpendicular to the tetragonal axis. $\hat{H}_{\text{hf}}$ can be also expressed as the equivalent operator $\hat{N}$ of magnetic hyperfine structure, i. e., $\hat{H}_{\text{hf}} = PN_J\hat{N}$, where N_J is the diagonal matrix element for the ${}^{2S+1}L_J$ state, and P is the dipolar hyperfine structure constant (where $P \approx -51.4 \cdot 10^{-4}$ cm^{-1} is the free ion value for the isotope ${}^{161}Dy$, and $P \approx 71.5 \cdot 10^{-4}$ cm^{-1} is the free ion value for the isotope ${}^{163}Dy$, respectively [10]).

Based on the perturbation method, furthermore, in consideration of the contribution due to the interactions between the ground doublet $\Gamma\gamma$ and other 20 Kramers doublets Γ_X within ${}^6H_J$ (J = 15/2, 13/2, 11/2) states via crystal-field and orbital angular momentum interactions, the perturbation formulas of the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for an $4f^9$ ion in trigonal symmetry can be obtained:

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

Parameter	ζ_{4f}	E^0	E^1	E^2	E^3	α	β	γ
Value (cm^{-1})	1914	55395	6158	30.43	622.75	17.92	−612.15	1679.85

Table 1. Free ion parameters of Dy^{3+}; values taken from [22].

			$^{161}Dy^{3+}$ (10^{-4} cm^{-1})		$^{163}Dy^{3+}$ (10^{-4} cm^{-1})	
	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$
Cal.	4.240	8.826	113.7	247.4	154.7	344.3
Expt. [10]	4.281(6)	8.923(16)	116.1(7)	246.3(15)	162.2(7)	341.5(15)

Table 2. EPR parameters of Dy^{3+} in $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ crystal.

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

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

where $\Gamma_X\gamma_X$ denotes the excited doublets, the parameters g_J, g'_J, N_J and N'_J [note: g'_J and N'_J occur in the expansions of (5) and (6)] for various states can be obtained from [10] and [11]. In (5) and (6), the second-order terms $g_\perp{}^{(2)}$ and $A_\perp{}^{(2)}$ vanish because none of the twenty Γ_X has a non-zero matrix element with the lowest $\Gamma\gamma$ doublet for both $\hat{H}_{cf}$ and the x or y component of $\hat{L}$ operators.

According to Newman's superposition model [17, 18], the crystal-field parameters B_k^q in (4) can be written as

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

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 (which is often taken as the average bond distance in compounds of paramagnetic ions). For the $[Dy(NO_3)_6]^{3-}$ cluster, no superposition model parameters were reported. We estimate them as follows: The exponents t_k are taken as those obtained in a similar trivalent rare-earth ion in some oxides, i. e., $t_2 \approx 7$, $t_4 \approx 12$ and $t_6 \approx 11$ [19, 20], and the intrinsic parameter $\bar{A}_k(R_0)$ are the adjustable parameters obtained by fitting the calculated EPR parameters ($g_\parallel, g_\perp, A_\parallel$ and $A_\perp$) with the observed values.

The structural data for an La^{3+} ion in a host hydrated LMN crystal are $R_1^H \approx 3.093(5)$ Å, $\theta_1 \approx 55.45(14)°$; $R_2^H \approx 3.073(5)$ Å, $\theta_2 \approx 57.54(14)°$ [11]. 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^{3+} and the replaced La^{3+} ion. The R_j can be reasonably estimated from the approximate formula [19]

$$R_j = R_j^H + (r_i - r_h)/2, \tag{8}$$

where r_i and r_h are the ionic radii of the impurity and the host, respectively. For $La_2Mg_3(NO_3)_{12} \cdot 24H_2O{:}Dy^{3+}$, $r_i \approx 0.908$ Å, $r_h \approx 1.061$ Å [21]. The free-ion parameters of 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 [22]. They are all collected in Table 1.

Thus, from the above formulas and parameters we find that to reach good fits between calculated and experimental EPR parameters $g_\parallel$ and $g_\perp$ of Dy^{3+} and hyperfine structure constants $A_\parallel$ and $A_\perp$ of $^{161}Dy^{3+}$ and $^{163}Dy^{3+}$ isotopes in $La_2Mg_3(NO_3)_{12}$ crystal, these parameters are

$$\begin{aligned} &\bar{A}_2 \approx 674.2\ cm^{-1}, \quad \bar{A}_4 \approx 160.4\ cm^{-1}, \\ &\bar{A}_6 \approx 113.2\ cm^{-1}. \end{aligned} \tag{9}$$

The comparisons between the calculated and experimental EPR parameters are shown in Table 2.

3. Discussion

In Table 2 one can find that the calculated EPR parameters $g_\parallel$ and $g_\perp$ of Dy^{3+} and hyperfine structure constants $A_\parallel$ and $A_\perp$ of $^{161}Dy^{3+}$ and $^{163}Dy^{3+}$ isotopes in $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ crystal agree well with those of experimental values. Therefore, the perturbation formulas and the used parameters in this paper can be regard as reasonable. Thus the EPR parameters for the Dy^{3+} center in the $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ crystal are reasonably explained by the above studies.

Based on the calculations, we find that the contributions to the EPR parameters come mainly from the ground Kramers doublet. If not considering the first-order perturbation, those from the excited $^6H_{13/2}$ and $^6H_{11/2}$ states via the CF J-mixing interaction are about 3%. Obviously, the higher excited states $^6I_{15/2}$, $^2K_{15/2}$, $^4I_{13/2}$, $^4H_{13/2}$, $^6H_{11/2}$, $^4I_{11/2}$, $^4G_{11/2}$ etc., would have even smaller influence. On the other hand, the contributions to $g_\parallel$ and $A_\parallel$ from the second-order perturbation terms are about $9-10\%$. So, in order to explain the EPR parameters for Dy^{3+} centers in crystals to a better extent, the second-order perturbation contributions should be taken into account. Obviously, a significant improvement of the calculated EPR parameters can hardly be achieved by merely expanding the size of the energy matrix within the limit of the first-order perturbation treatments.

Based on the superposition model, considering various admixtures and interactions as mentioned above, EPR parameters of $La_2Mg_3(NO_3)_{12} \cdot 24H_2O{:}Dy^{3+}$ are satisfactorily explained. These formulas as well as the method of this study may be also effective in other similar systems.

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