Theoretical Studies of the EPR Parameters of Nd^{3+} in $LiYF_4$

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Z. Naturforsch. **59a,** 235 – 238 (2004); received November 6, 2003

The perturbation formulas of the electron paramagnetic resonance (EPR) parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for a $4f^3(Nd^{3+})$ ion in tetragonal symmetry are established in this work. In these formulas, the contributions to the EPR parameters arising from the second-order perturbation terms and the admixtures of different states are included. Then the above formulas are applied to a tetragonal Nd^{3+} center in $LiYF_4$, where the related crystal-field parameters are calculated from the superposition model and the local structural parameters of the Y^{3+} site occupied by the impurity Nd^{3+}. The EPR parameters and the optical spectra within the $^4I_{9/2}$ and $^4I_{11/2}$ states obtained in this work agree reasonably with the observed values.

Key words: EPR; Crystal-fields and Spin Hamiltonian; Nd^{3+}; $LiYF_4$.

1. Introduction

$LiYF_4$: Nd^{3+} crystal has attracted interest due to its application as laser host [1 – 4] and its magneto-optical properties [5]. These properties are closely related to the electronic states and the local structure of the impurity Nd^{3+}. Since EPR is a useful tool to analyse electronic states and local structures of paramagnetic ions in crystals, EPR experiments were carried out on this interesting system and the g factors $g_\parallel$, $g_\perp$, and hyperfine structure constants $A_\parallel$ and $A_\perp$ were measured recently [6]. Up to now, however, these experimental results have not been theoretically studied. In order to explane these EPR parameters, which may be helpful to understand the optical properties of $LiYF_4$: Nd^{3+}, in this paper the perturbation formulas of $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for a $4f^3$ ion in tetragonal symmetry are established and applied to the above system. In these formulas, the contributions to the EPR parameters arising from the second-order perturbation terms and the admixtures of different states are considered.

2. Calculation

In the scheelite-structured crystal $LiYF_4$, the impurity Nd^{3+} replaces the host Y^{3+} and forms a tetragonally distorted $[NdF_8]^{5-}$ cluster [5, 6]. For an $Nd^{3+}(4f^3)$ ion under tetragonal symmetry, its ground $^4I_{9/2}$ configuration may be split into five Kramers doublets because of the spin-orbit coupling and tetragonal crystal-field interactions. According to the $\bar{g}[= (g_\parallel + 2g_\perp)/3 \approx 2.34]$ of the experimental g factors of Nd^{3+} in $LiYF_4$ [6], it can be attributed to the lowest doublet Γ_6, whose average value $\bar{g}$ would be about 2.67 for a $4f^3$ ion [7, 8]. In [7, 8] only the contributions to the EPR parameters from the first-order perturbation terms were included. However, besides the lowest Γ_6, the other 10 irreducible representations Γ_x (i.e., five Γ_6 and five Γ_7) due to the tetragonal splitting of the ground $^4I_{9/2}$ and the first excited $^4I_{11/2}$ levels would mix with the lowest Γ_6 via crystal-field $\hat{H}_{CF}$ and orbital angular momentum $\hat{J}$ (or hyperfine structure equivalent operator $\hat{N}$) interactions and lead to the second-order perturbation contributions to g factors (or hyperfine structure constants), as pointed out in [9, 10]. Thus, the second-order perturbation formulas of the EPR parameters for an $Nd^{3+}(4f^3)$ ion in tetragonal symmetry can be derived as

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

$$g_\parallel^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_Z|\Gamma\gamma\rangle,$$

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$$g_{\parallel}^{(2)} = 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{L}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)},$$

$$g_{\perp} = g_{\perp}^{(1)} + g_{\perp}^{(2)},\ g_{\parallel}^{(1)} = 2g_J\langle\Gamma\gamma|\hat{J}_X|\Gamma\gamma\rangle,\ g_{\perp}^{(2)} = 0, \quad (1)$$

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

$$A_{\parallel}^{(2)} = 2P\sum_X{}' \frac{\langle\Gamma\gamma|H_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)},$$

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

where the diagonal elements g_J (or N_J) of the operator $\hat{J}$ (or $\hat{N}$) for various states can be obtained from [7, 8]. The nondiagonal elements g'_J (or N'_J) may occur in the expansions of (1) and (2) for the interactions between different ^{2S+1}L configurations. Note that the second-order perturbation term $g_{\perp}^{(2)}$ (or $A_{\perp}^{(2)}$) vanishes because none of the ten Γ_x has a non-zero matrix element with the lowest Γ_6 doublet for both $\hat{H}_{\mathrm{CF}}$, and the x or y component of $\hat{J}$ (or $\hat{N}$) operators. P is the dipole hyperfine structure parameter for the $Nd^{3+}(4f^3)$ ion in crystals. For the lowest doublet Γ_6, the basis function $\Gamma\gamma^{(\gamma')}$ (where γ and γ' denote the two components of the irreducible representation) contains admixtures of different states, i.e., the admixture between the ground $^4I_{9/2}$ and the first excited $^4I_{11/2}$ states via crystal-field interaction, the admixture among $^2H_{9/2}$, $^4G_{9/2}$ and $^4I_{9/2}$ and that among $^2I_{11/2}$, $^2H_{11/2}$ and $^4I_{11/2}$ via spin-orbit coupling interaction. Thus, the basis $\Gamma\gamma^{(\gamma')}$ may be expressed as

$$|\Gamma\gamma^{(\gamma')}\rangle = \sum_{M_{J1}} C(^4\mathrm{I}_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})N_{9/2}(|^4\mathrm{I}_{9/2}M_{J1}\rangle + \lambda_H|^2H_{9/2}M_{J1}\rangle + \lambda_G|^4G_{9/2}M_{J1}\rangle) + \sum_{M_{J2}} C(^4\mathrm{I}_{11/2};\Gamma\gamma^{(\gamma')}M_{J1})N_{11/2}(|^4\mathrm{I}_{11/2}M_{J2}\rangle + \lambda'_H|^2H_{11/2}M_{J2}\rangle + \lambda_I|^2I_{11/2}M_{J2}\rangle), \quad (3)$$

where M_{J1} and M_{J2} are in the ranges of $-9/2$ to $9/2$ and $-11/2$ to $11/2$, respectively. The coefficients $C(^4\mathrm{I}_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})$ and $C(^4\mathrm{I}_{11/2};\Gamma\gamma^{(\gamma')}M_{J1})$ can be obtained by diagonalizing the $22\cdot 22$ energy matrix containing $^4I_{9/2}$ and $^4I_{11/2}$ states. N_i and λ_i are, respectively, the normalization factors and the mixing coefficients, which can be determined by using spin-orbit coupling matrix elements and the perturbation method.

In $LiYF_4$, the Y^{3+} ion is coordinated to eight nearest F^- ions which form the edges of a slightly distorted dodecahedron with S_4 local symmetry [5]. Because of the rather small distortion from D_{2d} to S_4 [11 – 14], the imaginary parts of the rank-4 and rank-6 crystal-field parameters are very small, as pointed out in [13, 15], and so their contributions to the coefficient $C(^4\mathrm{I}_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})$ or $C(^4\mathrm{I}_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})$ in the basis $\Gamma\gamma^{(\gamma')}$, and hence to the EPR parameters may be regarded as insignificant. Thus the D_{2d} symmetry turns out to be a good approach, and we still take D_{2d} approximation here for simplicity. For the $Nd^{3+}(4f^3)$ ion in D_{2d} symmetry, the crystal-field interaction $\hat{H}_{\mathrm{CF}}$ in the above formulas can be written in terms of the Stevens operator equivalents as [8, 10]

$$\hat{H}_{\mathrm{CF}} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4, \quad (4)$$

where B_k^q ($k = 2$, 4 and 6; $|q| \le k$) are the crystal-field parameters. By using the superposition model (SPM) [16], they can be expressed as

$$B_k^q = \sum_{j=1}^{N} \bar{A}_k(R_0)(R_0/R_j)^{t_k}K_k^q(\theta_j,\phi_j), \quad (5)$$

where $K_k^q(\theta_j,\phi_j)$ are the coordination factors [16, 17] obtained from the local structural data of the studied Nd^{3+} center. t_k and $\bar{A}_k(R_0)$ are, respectively, the power-law exponents and the intrinsic parameters (with the reference distance or impurity-ligand distance R_0). Among the eight nearest F^- ions of the Y^{3+} site, four of them are at the distance $R_1{}^{\mathrm{H}}$ (≈ 2.2481 Å) and the angle θ_1 ($\approx 67.14°$), and the other four are at the distance $R_2{}^{\mathrm{H}}$ (≈ 2.2996 Å) and the angle θ_2 ($\approx 37.86°$), where θ_i is the angle between $R_i{}^{\mathrm{H}}$ and the four-fold axis [5]. Since the ionic radius r_i (≈ 0.995 Å [18]) of the impurity Nd^{3+} is larger than the radius r_h (≈ 0.893 Å [18]) of the host Y^{3+} ion, we can reasonably estimate the impurity-ligand distances R_j of the impurity center from the host values $R_j{}^{\mathrm{H}}$ and the empirical relationship [19]

$$R_j \approx R_j{}^{\mathrm{H}} + (r_i - r_h)/2. \quad (6)$$

Thus, the average impurity-ligand distance $\bar{R}$ (≈ 2.325 Å) is taken as the reference distance of the studied system, i.e., $R_0 \approx \bar{R}$.

In view of the admixture (or covalency) between the 4f orbitals of Nd^{3+} and the 2p orbitals of F^- ions

Table 1. The optical spectra (in cm^{-1}) of the $^4I_{9/2}$ and $^4I_{11/2}$ states of $LiYF_4$: Nd^{3+}.

	No.	1	2	3	4			σ^c
$^4I_{9/2}$	Cal.^{a}	139	180	244	533			
	Cal.^{b}	150	193	264	552			
	Expt. [15]	136	179	244	524			
	No.	5	6	7	8	9	10	
$^4I_{11/2}$	Cal.^{a}	1982	2020	2027	2057	2220	2255	10.1
	Cal.^{b}	2001	2042	2050	2080	2232	2270	11.2
	Expt. [15]	1997	2040	2042	2077	2227	2262	

^{a} Calculation based on the five crystal-field parameters B_k^q in [13]. ^{b} Calculation based on the SPM parameters in this work. ^{c} The root-mean-square deviation for the optical spectra is defined as $\sigma = [\Sigma_i^n (E_i^c - E_i^e)^2/n]^{1/2}$, where E_i^c and E_i^e denote the calculated and experimental optical spectral data. n is the number of spectral bands.

for the Nd^{3+}-F^- bond in $LiYF_4$:Nd^{3+}, the orbital reduction factor k (≈ 0.9818 [20]) for the similar tetragonal CaF_2:Nd^{3+} system can also be applied here. The dipole hyperfine structure parameter can be written as $P \approx kP_0$ (where P_0 is the corresponding free-ion value). For a free Nd^{3+} ion [7], the values for P_0 are about $54.2 \cdot 10^{-4}$ cm^{-1} and $33.7 \cdot 10^{-4}$ cm^{-1} for the isotopes ^{143}Nd and ^{145}Nd, respectively. The free-ion parameters of the Coulomb repulsion ($E^1 \approx 4821.7$ cm^{-1}, $E^2 \approx 23.72$ cm^{-1} and $E^3 \approx 485.37$ cm^{-1}) and the two-body interaction parameters ($\alpha \approx 21.79$ cm^{-1}, $\beta \approx -604$ cm^{-1} and $\gamma \approx 1513$ cm^{-1}) as well as the spin-orbit coupling coefficient ($\zeta_{4f} \approx 874.5$ cm^{-1}) in the energy matrix were obtained for $LiYF_4$:Nd^{3+} in [13].

According to [21, 22], the power-law exponents $t_4 \approx 6.3$, $t_6 \approx 10.1$ and the intrinsic parameters $\bar{A}_4(R_0) \approx 75$ cm^{-1} and $\bar{A}_6(R_0) \approx 34$ cm^{-1} were acquired from the similar tetragonal CaF_2:Nd^{3+} system, where the reference distance R_0 (≈ 2.356 Å [21]) is close to that (≈ 2.325 Å) of the studied system. For the sake of reducing the number of adjustable parameters, the above superposition model (SPM) parameters are also adopted for Nd^{3+} in $LiYF_4$ of this work, with only the rank-2 SPM parameters t_2 and $\bar{A}_2(R_0)$ adjustable. By fitting the optical spectra of $LiYF_4$:Nd^{3+} within the ground $^4I_{9/2}$ and the first excited $^4I_{11/2}$ states, we have $t_2 \approx 3.8$ and $\bar{A}_2(R_0) \approx 460$ cm^{-1}. The comparisons between the theoretical and experimental optical spectra within $^4I_{9/2}$ and $^4I_{11/2}$ states are shown in Table 1. Substituting the basis functions based on the above parameters into (1) and (2), the EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for Nd^{3+} in $LiYF_4$ are calculated and collected in Table 2. For comparisons, the theoretical optical spectra and EPR parameters based on the five adjustable crystal-field parameters (i.e., $B_2^0 \approx 421$ cm^{-1}, $B_4^0 \approx -985$ cm^{-1}, $B_4^4 \approx -1146$ cm^{-1}, $B_6^0 \approx 7$ cm^{-1}, $B_6^4 \approx -1074$ cm^{-1}) in [13] are also given in Table 1 and 2, respectively.

Table 2. The g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) for Nd^{3+} in $LiYF_4$.

	$g_\parallel$	$g_\perp$	$A_\parallel$ (^{143}Nd)	$A_\perp$ (^{143}Nd)	$A_\parallel$ (^{143}Nd)	$A_\perp$ (^{143}Nd)
Cal.^{a}	1.990	2.574	207.3	269.4	127.1	162.2
Cal.^{b}	1.972	2.568	201.6	260.5	125.7	160.8
Expt. [6]	1.955(2)	2.530(3)	196.5 (2)	254.2 (2)	121.4 (2)	157.1 (2)

^{a} Calculation based on the five crystal-field parameters B_k^q in [13].
^{b} Calculation based on the SPM parameters in this work.

3. Discussion

From Table 1 and 2 several points may be discussed here.

1) The calculated $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$, based on the perturbation formulas of the EPR parameters for a $4f^3$ ion in tetragonal symmetry and the SPM parameters of this work, agree better than those based on the B_k^q of [13] with the observed values, suggesting that the above perturbation formulas of the EPR parameters are suitable. Meanwhile, the SPM parameters $t_2 \approx 3.8$ and $\bar{A}_2(R_0) \approx 460$ cm^{-1} for the $(NdF_8)^{5-}$ cluster obtained in this work are also comparable with, but smaller, than those ($t_2 \approx 5.0(5)$ and $\bar{A}_2(R_0) \approx 630(20)$ cm^{-1} [23]) for the similar $(NdF_8)^{5-}$ cluster in BaY_2F_8. Since the reference distance R_0 (≈ 2.325 Å) for $LiYF_4$:Nd^{3+} is larger than that (≈ 2.275 Å [23]) for BaY_2F_8:Nd^{3+}, the weaker crystal fields and hence the smaller rank-2 SPM parameters in this work can be regarded as suitable.

2) Based on the calculations, we find that the contributions to $g_\parallel$ or $A_\parallel$ due to the second-order perturbation terms amount to about $9 \sim 10\%$ of those due to the first-order perturbation terms. Obviously, in order to obtain a better interpretation of the EPR parameters of Nd^{3+} in crystals, the second-order perturbation contributions should be considered.

3) The calculated optical spectra of the $^4I_{9/2}$ and $^4I_{11/2}$ states in this work are also consistent with the experimental data, whereas the corresponding root-mean-square deviation σ is slightly larger than that of the previous work [13]. Even so, the theoretical EPR parameters based on the B_k^q in [13] agree poorly with the observed values. This means that the crystal-field parameters good for optical calculations are not necessarily good for studies of the EPR parameters of Nd^{3+} in $LiYF_4$, as mentioned for Er^{3+} in zircon-type compounds by Vishwamittar et. al. [24]. In view of this, the

whole theoretical results in this paper can be regarded as more reasonable.

4) There may be some errors in our calculations. For simplicity, the D_{2d} approximation instead of the S_4 symmetry is adopted to describe the crystal-field interaction by (4) in this work. In fact, even though one takes exactly the S_4 symmetry, the magnitudes of the imaginary parts of the rank-4 and rank-6 crystal-field parameters are rather small, as stated in [13–15]. As a result, their contributions to the coefficient $C(^4\mathrm{I}_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})$ or $C(^4\mathrm{I}_{11/2};\Gamma\gamma^{(\gamma')}M_{J1})$ in $\Gamma\gamma^{(\gamma')}$ and hence to the final EPR parameters are expected to be smaller than 5%.

In summary, the perturbation formulas of the EPR parameters for a $4f^3(Nd^{3+})$ ion in tetragonal symmetry are established for the first time. Based on these formulas, the EPR parameters for Nd^{3+} in $LiYF_4$ are theoretically interpreted. Obviously, these formulas can also be applied to Nd^{3+} in other tetragonal ABO_4-type compounds.

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