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Theoretical calculations of the EPR parameters for Yb^{3+} ions in YVO_4, $HfSiO_4$ and $ThSiO_4$

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Abstract

Based on the crystal-field theory, the EPR parameters g factors $g_\parallel$, $g_\perp$ of Yb^{3+} and hyperfine structure constants $A_\parallel$, $A_\perp$ of $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ isotopes in zircon-structure YVO_4, $HfSiO_4$ and $ThSiO_4$ crystals are calculated by the perturbation formulae. In the calculations, the contributions of various admixtures and interactions such as the *J*-mixing, two-order perturbation term, the covalency as well as the local lattice relaxation are all considered. The crystal field parameters used in the calculations are obtained from the superposition model. The calculated results are in reasonable agreement with the observed values.

Keywords: Electron paramagnetic resonance; Crystal-field theory; Yb^{3+}; Zircon

1. Introduction

The zircon-structure crystals doped with trivalent rare-earth ions have received much attention for their extensive applications as optical and electronic materials [1–4]. So many studies of optical and EPR spectra for rare-earth ions in zircon-type compounds have been reported. For instance, the EPR g factors $g_\parallel$, $g_\perp$, of Yb^{3+} and hyperfine structure constants $A_\parallel, A_\perp$ for isotopes $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ in zircon-structure YVO_4, $HfSiO_4$ and $ThSiO_4$ crystals were measured [5–6]. But up to now, no theoretical studies related to the structural data of Yb^{3+} centers have been made for these EPR parameters. The zircon-type compounds have tetragonal structure [7]. In this paper, we use the perturbation formulae of EPR parameters for $4f^{13}$ ion in tetragonal symmetry to study these experimental values. In these formulae, the contributions to EPR parameters from the *J*-mixing between the ground $^2F_{7/2}$ and excited $^2F_{5/2}$ states via crystal field interaction, the admixture among the other Kramers doublets Γ_x and the ground doublet via crystal-field and orbital angular momentum (or hyperfine structure) interactions and the covalency reduction effect are all considered. From these formulae, the EPR parameters for Yb^{3+} in above zircon-structure crystals are calculated. In the calculations, the tetragonal crystal-field parameters are estimated from the superposition model and the structural data of Yb^{3+} centers. The results including the local lattice relaxation and superposition model parameters are discussed.

2. Calculations

Yb^{3+} has a $4f^{13}$ electronic configuration with a $^2F_{7/2}$ free ion ground state and a $^2F_{5/2}$ excited state. The tetragonal crystal-field splits the $^2F_{7/2}$ and $^2F_{5/2}$ states into four and three Kramers doublets, respectively. The lowest doublet can be Γ_6 or Γ_7, corresponding to the average value $\bar{g}\,[= (g_\parallel + 2g_\perp)/3]$ of about 2.667 or 3.429, respectively

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[8–9]. According to the observed $\bar{g}$ for Yb^{3+} in YVO_4, $HfSiO_4$ and $ThSiO_4$ crystals [5,6,9], the lowest doublet is Γ_6.

In order to establish the perturbation formulas of the EPR parameters for a $4f^{13}$ ion in tetragonal symmetry, the zeroth-order Hamiltonian $\hat{H}_0$ and the perturbation Hamiltonian $\hat{H}'$ for the system under an external magnetic field $\hat{H}$ can be written as

$$\hat{H}_0 = \hat{H}_{\text{free}}, \qquad \hat{H}' = \hat{H}_{\text{CF}} + \hat{H}_{\text{Z}} + \hat{H}_{\text{hf}} \tag{1}$$

where the free-ion term $\hat{H}_{\text{free}}$ contains Coulombic repulsion and spin–orbit coupling interactions etc. $\hat{H}_{\text{CF}}$ denotes the crystal-field interaction. The Zeeman interaction $\hat{H}_{\text{Z}}$ can be expressed in terms of the Lande factor g_J and the orbital angular momentum operator $\hat{J}$ as $\hat{H}_{\text{Z}} = g_J \mu_\beta \hat{H}\hat{J}$ [9]. The hyperfine interaction term can be written as $\hat{H}_{\text{hf}} = PN_J\hat{N}$, where $\hat{N}$ is the hyperfine-structure equivalent operator (with the diagonal element N_J) and P is the dipolar hyperfine structure parameter.

Because of the J-mixing between $J = 7/2$ and $5/2$ states via crystal-field interaction, the basis function of ground doublet Γ_γ can be obtained by diagonalizing a 14×14 energy matrix for $4f^{13}$ ion in tetragonal symmetry. Thus, we have

$$\begin{aligned}
&|\Gamma_\gamma(\text{or}\,\gamma')\rangle \\
&\quad = \sum_{M_{J1}} C({}^2F_{7/2}; \Gamma\gamma(\text{or}\,\gamma')M_{J1})|{}^2F_{7/2}M_{J1}\rangle \\
&\qquad + \sum_{M_{J2}} C({}^2F_{5/2}; \Gamma\gamma(\text{or}\,\gamma')M_{J2})|{}^2F_{5/2}M_{J2}\rangle
\end{aligned} \tag{2}$$

where the subscript γ and γ' denotes the two components of Γ irreducible representation. M_{J1} and M_{J2} are half-integers in the ranges $-7/2$ to $7/2$ and $-5/2$ to $5/2$, respectively.

Considering that the other $(4 + 3 - 1 = 6)$ Kramers doublets Γ_x (which are obtained by diagonalizing the 14×14 energy matrix) may mix with the ground Γ_γ doublet via crystal-field interaction H_{CF} and orbital angular momentum $\hat{L}$ (or hyperfine structure equivalent operator $\hat{N}$) interaction and so they make the contributions to EPR parameters, the calculation formulae of EPR parameters for $4f^{13}$ ion in tetragonal symmetry should include the second-order contribution. The perturbation formulas of EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for $4f^{13}$ ion in tetragonal symmetry can be written as [10]

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

$$\begin{aligned}
&A_\parallel = A_\parallel^{(1)} + A_\parallel^{(2)}, \quad A_\parallel^{(1)} = 2PN_J\langle\Gamma_\gamma|\hat{N}_Z|\Gamma_{\gamma'}\rangle, \\
&A_\parallel^{(2)} = 2P\sum_X{}' \frac{\langle\Gamma_\gamma|\hat{H}_{\text{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_Z|\Gamma_\gamma\rangle}{E(\Gamma_X) - E(\Gamma)}, \\
&A_\perp = A_\perp^{(1)} + A_\perp^{(2)}, \quad A_\perp^{(1)} = 2PN_J\langle\Gamma_\gamma|\hat{N}_X|\Gamma_{\gamma'}\rangle, \\
&A_\perp^{(2)} = 0
\end{aligned} \tag{4}$$

where the parameters g_J, g'_J, N_J and N'_J [Noteworthily, the nondiagonal elements g'_J and N'_J may occur in the expansions of Eqs. (3) and (4) for the interactions between different ${}^{2S+1}L_J$ configurations] for various states can be obtained from Refs.[9,10]. P is the dipolar hyperfine structure constant. In the above formulae, the second-order terms $g_\perp^{(2)}$ and $A_\perp^{(2)}$ vanish because none of the six Γ_x nonzero matrix element with ground Γ_γ for both $\hat{H}_{\text{CF}}$ and x or y component of $\hat{L}$ and $\hat{N}$ operators.

In these zircon-type RXO_4 ($R = Y^{3+}$, Hf^{5+} or Th^{5+}; $X = V^{5+}$ or Si^{4+}, respectively) crystals, Yb^{3+} ions replace the R ions and they occupy the sites having noncentrosymmetrical D_{2d} point symmetry [11]. So, the Yb^{3+} ion is surrounded by a tetragonal dodecahedral array of eight neighbouring oxygens: four of these are at one distance R_1 and the other four at a slightly different distance R_2. The structural parameters R_i and θ_i (θ_i is the angle between R_i and C_4 axis) [11] of the studied zircon-type compounds RXO_4 are shown in Table 1. The crystal field Hamiltonian in the tetragonal symmetry can be expressed as [9]

$$\begin{aligned}
\hat{H}_{\text{CF}} = {}& B_2^0C_0^2 + B_4^0C_0^4 + B_6^0C_0^6 + B_4^4(C_4^4 + C_{-4}^4) \\
& + B_6^4(C_4^6 + C_{-4}^6)
\end{aligned} \tag{5}$$

where B_k^q are the crystal-field parameters.

Table 1
Structure data for Yb^{3+} in zircon-structure crystals

Compounds	R_1(Å)		R_1(Å)		θ_1	θ_2
	I[a]	II[b]	I[a]	II[b]		
YVO_4	2.291	2.274	2.433	2.416	101.90	32.84
$HfSiO_4$	2.10	2.139	2.260	2.299	101.37	32.33
$ThSiO_4$	2.460	2.289	2.500	2.329	104.48	28.60

[a] The values in pure crystals given in Ref. [11].

[b] Estimated by considering the local lattice relaxation.

Table 2
The orbital reduction factor k and intrinsic parameters $\bar{A}_K(R_0)$ for Yb^{3+} in zircon-structure crystals

	k	$\bar{A}_2$ (R0) (cm^{-1})	$\bar{A}_4$ (R0) (cm^{-1})	$\bar{A}_6$ (R0) (cm^{-1})
YVO_4	0.920	285	29.1	19.2
$HfSiO_4$	0.927	285	15.9	28.6
$ThSiO_4$	0.962	285	84.2	20

Table 3
EPR g factors and hyperfine structure constants (in 10^{-4} cm^{-1}) for Yb^{3+} in YVO_4, $HfSiO_4$ and $ThSiO_4$ crystals

	$g_\parallel$		$g_\perp$		$A_\parallel$		$A_\perp$		Isotope
	Calculated	Experimental [5,6]	Calculated	Experimental [5,6]	Calculated	Experimental [5,6]	Calculated	Experimental [5,6]	
YVO_4	6.128	6.08(1)	0.899	0.85(5)	1692.3	1607	236.2	225(12)	$^{171}Yb^{3+}$
					464.1	443(3)	64.8	63(5)	$^{173}Yb^{3+}$
$HfSiO_4$	6.996	6.998(6)	0.676	0.4(3)	5427.1	–	537.4	–	$^{171}Yb^{3+}$
					1488.3	–	147.4	–	$^{173}Yb^{3+}$
$ThSiO_4$	0.946	0.91(3)	3.520	3.519(2)	717.9	–	2746.0	–	$^{171}Yb^{3+}$
					196.8	–	753.1	–	$^{173}Yb^{3+}$

From the superposition model [12], the crystal-field parameters can be expressed as

$$B_k^q = \sum_{j=1}^{n} \bar{A}_k(R_0)\left(\frac{R_0}{R_j}\right)^{t_k} K_k^q(\theta_J, \phi_j) \tag{6}$$

where the coordination factor $K_k^q(\theta_j, \phi_j)$ can be obtained from the local structural data of the studied system. $\bar{A}_k(R_0)$ are the intrinsic parameters with the reference distance R_0, t_k are the power law exponents. For $(YbO_8)^{13-}$ cluster, the exponents $t_2 = 7$, $t_4 = 12$, $t_6 = 11$, and $\bar{A}_2 = 285$ cm^{-1} with $R_0 = 2.343$ Å, are taken as those obtained from Yb^{3+} ion in zircon-type orthophosphates [10]. $\bar{A}_4$ and $\bar{A}_6$ are the adjustable parameters obtained by fitting the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ to the observed values. In the calculations, the free-ion values of spin–orbit coupling coefficient ζ_{4f}^0 (≈ 2950 cm^{-1} [9]) and dipolar hyperfine structure constant P_0 ($\approx 388.4(7) \times 10^{-4}$ and $106.5(2) \times 10^{-4}$ cm^{-1} for isotopes $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$, respectively [9]) should be multiplied by the orbital reduction factor k because of the covalence effect for Yb^{3+} ion in crystals. Here we also take it as an adjustable parameter.

Generally, $R_j \neq R_H$(where is the cation–anion distance in the host crystal) because of the different ionic radii of Yb^{3+} and the replaced host ion. Considering the local lattice relaxation due to the size mismatch, we can assume reasonably the angles θ_i being unchanged. The R_j can be reasonably estimated from the approximate formula [10]

$$R_j = \frac{R_H + (r_i - r_h)}{2} \tag{7}$$

where R_H is the corresponding distance in the host crystal YVO_4, $HfSiO_4$ and $ThSiO_4$ crystals, r_i and r_h are the ionic radii of impurity and the host, respectively. According to Ref. [13], $r_i \approx 0.858$ Å, and $r_h \approx 0.893$ Å, 0.780 Å or 1.02 Å, for YVO_4, $HfSiO_4$ or $ThSiO_4$, respectively. Thus, we can estimate the Yb^{3+}–O^{2-} distances R_1 and R_2 for Yb^{3+} in various zircon-structure crystals. They are also shown in Table 1.

By using these local structural data to above formulae and fitting the calculated EPR parameters to the observed values, the intrinsic parameters $\bar{A}_K(R_0)$ for RXO_4:Yb^{3+} are obtained and collected in Table 2. The comparisons between the calculated and experimental EPR parameters are also shown in Table 3.

3. Discussions

From Table 3, it can be seen that the calculated EPR parameters for Yb^{3+} ions in YVO_4, $HfSiO_4$ and $ThSiO_4$ crystals, based on the perturbation formulae of the EPR parameters for $4f^{13}$ ions in tetragonal symmetry, are in good agreement with the observed values, indicating that the perturbation formulae and the related parameters adopted in this work are reasonable.

According to the calculations, we find that the contributions to $g_\parallel$ or $A_\parallel$ arising from the second-order perturbation terms are about 15% those from the first-order perturbation terms. This means that neglecting of the second-order perturbation terms in the previous works is not suitable. Therefore, in order to explain the EPR parameters for Yb^{3+} centers in crystals to a better extent, the second-order perturbation contributions should be taken into account.

The observed values of $A_\parallel$ and $A_\perp$ for Yb^{3+} ion in $HfSiO_4$ and $ThSiO_4$ crystals were not reported. The above-calculated results (see Table 3) remain to be checked by the further experimental studies.

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