Theoretical Investigations of the Spin Hamiltonian Parameters of $ZrSiO_4$:Np^{4+}

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In this work, the spin Hamiltonian (SH) parameters $g_\parallel$ and $g_\perp$, and the hyperfine structure constants $A_\parallel$ and $A_\perp$ for $ZrSiO_4$:Np^{4+} are investigated on the basis of the perturbation formulas of these parameters for a $5f^3$ ion in tetragonal (D_{2d}) symmetry. In these formulas, the contributions to the SH parameters from the second-order perturbation terms, the admixtures of various energy levels and the covalency effect are taken into account. The related crystal-field parameters are calculated from the superposition model and the local structural data of the Zr^{4+} site occupied by the impurity Np^{4+}. The calculated SH parameters agree reasonably with the experimental data. The validity of the theoretical results is discussed.

Key words: Electron Paramagnetic Resonance (EPR); Crystal-fields and Spin Hamiltonian; Np^{4+}; $ZrSiO_4$.

1. Introduction

Zircon ($ZrSiO_4$) is widely investigated because of its application in geochronology (when containing rare-earth elements) [1 – 3], as porous material for refractory insulators [4], in irradiation researches [5, 6], and bcause of its important role as major source of zirconia, which is regarded as a high-technology material in industry due to its superior mechanical, thermal, electrical, chemical and optical properties [7]. Therefore the thermoluminescence (TL) and electron paramagnetic resonance (EPR) caused by some trivalent rare-earth (Tb^{3+}, Dy^{3+}) ions in zircon was recently studied [8, 9]. However few studies on actinide ($5f^n$) ions in zircon have been performed. For example Poirot et. al. [10] have made optical and EPR investigations on tetravalent Np^{4+} (i. e., $^{237}Np^{4+}$ with spin $I = 5/2$) in zircon, and the spin Hamiltonian (SH) g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$ and $A_\perp$ were also measured at 4.2 K. Until now, however, these SH parameters have not been theoretically interpreted. In these present paper, the SH parameters of $ZrSiO_4$:Np^{4+} are investigated from the perturbation formulas of these parameters for a $5f^3$ ion in tetragonal (D_{2d}) symmetry. In these formulas, the contributions to the SH parameters from the second-order perturbation terms, the admixtures of various energy levels and the covalency effect are taken into account. The validity of the results is analyzed.

2. Calculation

$ZrSiO_4$ (and other isostructural zircon-type compounds) has tetragonal structure [11]. The tetravalent Np^{4+} impurity may substitute the host Zr^{4+} and then occupy magnetically equivalent sites of noncentrosymmetric D_{2d} point symmetry [11]. The tetragonally (D_{2d}) distorted dodecahedron $[NpO_8]^{12-}$ is formed, since no charge compensation is needed. Among the eight nearest O^{2-} ions of the host Zr^{4+} site, four are at the distance $R_1{}^H$ (≈ 2.268 Å) and an angle θ_1 (≈ 32.43), and the other four are at the distance $R_2{}^H$ (≈ 2.131 Å) and an angle $\theta_2 (\approx 101.33)$, where θ_i is the angle between $R_i{}^H$ and the four-fold axis [11].

For a $5f^3(Np^{4+})$ ion under tetragonal symmetry, its ground $^4I_{9/2}$ configuration will be separated into five Kramers doublets due to the spin-orbit coupling and tetragonal crystal-field interactions. From the average

value $\bar{g}[= (g_\parallel + 2g)/3 \approx 1.99(21)]$ of the experimental g factors of Np^{4+} in $ZrSiO_4$ [10], one can ascribe the lowest doublet to Γ_6, whose $\bar{g}$ would be about 2.67 for an nf^3 ion [12, 13]. Unlike the treatments of the SH parameters in the previous works (where only the contributions due to the first-order perturbation terms were included) [12, 13], here we also take into account the contributions from the second-order perturbation terms, which result from the admixtures between the lowest Kramers doublet with 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 $^4I_{11/2}$ via crystal-field $\hat{H}_{CF}$ and orbital angular momentum $\hat{J}$ (or hyperfine structure equivalent operator $\hat{N}$) interactions, as mentioned in our recent works [14–16]. Therefore, the second-order perturbation formulas of the SH parameters for the $5f^3$ ion in tetragonal symmetry can be written as

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

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

where the diagonal elements g_J (or N_J) of the operator $\hat{J}$ (or $\hat{N}$) for various states can be obtained from [12, 13]. For example, $g_J(^4I_{9/2})$ = 8/11, $N_J(^4I_{9/2})$ = 476/363. The non-diagonal elements $g_J{}'$ (or $N_J{}'$) may appear in the expansions of (1) and (2) for the interactions between different $^{2S+1}L_J$ configurations. Noted that the second-order perturbation term $g_\perp{}^{(2)}$ (or $A_\perp{}^{(2)}$) vanishes because none of the ten Γ_x has nonzero matrix element with the lowest Γ_6 doublet, for both $\hat{H}_{CF}$ and the x or y component of $\hat{J}$ (or $\hat{N}$) operators. P is the dipole hyperfine structure parameter for the $5f^3$ ion in crystals.

As regards the lowest doublet Γ_6, the basic function $\Gamma\gamma^{(\gamma')}$ (where γ and γ' stand for the two components of the irreducible representation) includes the admixtures of various states, i. e., the admixture between the ground $^4I_{9/2}$ and the first excited $^4I_{11/2}$ states via crystal-field interactions, 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 interactions. So, the basic function $\Gamma\gamma^{(\gamma')}$ can be expressed as

$$\begin{aligned}
|\Gamma\gamma^{(\gamma')}\rangle = &\sum_{M_{J1}} C(^4I_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})N_{9/2}(|^4I_{9/2}M_{J1}\rangle\\
&+\lambda_H|^2H_{9/2}M_{J1}\rangle + \lambda_G|^4G_{9/2}M_{J1}\rangle)\\
&+\sum_{M_{J2}} C(^4I_{11/2};\Gamma\gamma^{(\gamma')}M_{J2})N_{11/2}(|^4I_{11/2}M_{J2}\rangle\\
&+\lambda_H{}'|^2H_{11/2}M_{J2}\rangle + \lambda_I|^2I_{11/2}M_{J2}\rangle),
\end{aligned} \tag{3}$$

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 $C(^4I_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})$ and $C(^4I_{11/2};\Gamma\gamma^{(\gamma')}M_{J2})$ are determined by diagonalizing the 22×22 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 calculated from spin-orbit coupling matrix elements and the perturbation method.

For the $5f^3(Np^{4+})$ ion in tetragonal (D_{2d}) symmetry, the crystal-field interaction $\hat{H}_{CF}$ in the above formulas can be expressed in terms of the Stevens equivalent operators [12, 17, 18]:

$$\hat{H}_{CF} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4. \tag{4}$$

Here B_k^q (k = 2, 4 and 6; $|q| \le k$) are the crystal-field parameters, which can be determined by the superposition model [19] and the local structural data of the studied impurity center. Thus we have

$$B_k^q = \sum_{j=1}^{2} \bar{A}_k K_k^q(\theta_j,\phi_j)(R_0/R_j)^{t_k}, \tag{5}$$

where $K_k^q(\theta_j,\phi_j)$ are the coordination factors [19, 20] obtained from the local geometrical relationship of the Np^{4+} center. The parameters t_k and $\bar{A}_k$ are, respectively, the power-law exponents and the intrinsic parameters (with the reference distance or impurity-ligand distance R_0). Since the ionic radius r_i(≈ 0.95 Å [21]) of the impurity Np^{4+} is larger than the radius r_h(≈ 0.79 Å

Table 1. The crystal-field splittings (in cm^{-1}) of the $^4I_{9/2}$ and $^4I_{11/2}$ states for $ZrSiO_4$: Np^{4+}.

	Label	1	2	3	4	5	
$^4I_{9/2}$	Cal.[a]	0	340.4	520.5	795.6	1327.7	
	Cal.[b]	0	363.8	557.8	831.1	1374.5	
	Expt. [10]	0	350.0	–	–	–	
	Label	6	7	8	9	10	11
$^4I_{11/2}$	Cal.[a]	5512.4	5696.5	6012.6	6081.3	6422.2	6452.8
	Cal.[b]	5500.1	5704.3	6066.9	6067.7	6466.5	6496.3
	Expt. [10]	5514.0	5723.0	6056.0	6072.0	6468.0	6496.0

[a] Calculation based on the five crystal-field parameters B_k^q in [10]. [b] Calculation based on the superposition model parameters in this work.

[21]) of the host Zr^{4+}, one can reasonably estimate the impurity-ligand distances R_j of the Np^{4+} center from the host bonding length ${R_j}^H$ and the empirical relationship [14, 18]

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

The spectral parameters of the Coulomb repulsion ($F^2 \approx 47479$ cm^{-1}, $F^4 \approx 41455$ cm^{-1} and $F^6 \approx 26528$ cm^{-1}) and the two-body interaction parameters ($\alpha \approx 392$ cm^{-1}, $\beta \approx -611$ cm^{-1} and $\gamma \approx 1200$ cm^{-1}) as well as the spin-orbit coupling coefficient ($\zeta_{5f} \approx 2088$ cm^{-1}) were determined for Np^{4+} in $ZrSiO_4$ [10]. In consideration of the admixture (orcovalency effect) between the 5f orbitals of Np^{4+} and the 2p orbitals of O^{2-} ions for the Np^{4+}-O^{2-} bond in the studied system, the orbital reduction factor k may be introduced. From the expectation value ${\zeta_{5f}}^0$ (≈ 2282 cm^{-1}) for a free Np^{4+} ion [22], we approximately have $k \approx \zeta_{5f}/{\zeta_{5f}}^0 \approx 0.91$.

In general, the dipole hyperfine structure parameter P_0 for a free $5f^n$ ion can be expressed as $P_0 \approx 2\beta g_n \beta_n \langle r^{-3}\rangle N_J$, where is the Bohr magneton, g_n the nuclear g value, and β_n the nuclear magneton. $\langle r^{-3}\rangle$ is the average value of the inverse cube of the radial wavefunction for the 5f orbital in Np^{4+} [12]. From the values $g_n \approx 1.256$ [21] and $\langle r^3\rangle \approx 8.57$ a.u. [23] for ^{237}Np, one can obtain $P_0 \approx 400 \cdot 10^{-4}$ cm^{-1}. Similarly, the dipole hyperfine structure parameter of the studied Np^{4+} in zircon can be written as $P \approx kP_0$.

According to the studies of the crystal-field superposition model analyses for tetravalent actinides [24], the intrinsic parameters $\bar{A}_2 \approx 2500(500)$ cm^{-1}, $\bar{A}_4 \approx 320(40)$ cm^{-1} and $\bar{A}_6 \approx 250(50)$ cm^{-1} were obtained for the Np^{4+}-O^{2-} clusters (with $R_0 \approx 2.3$ Å, which is close to the average impurity-ligand distance $\bar{R}(\approx 2.35$ Å) in the studied system). In addition, the power-law exponents $t_2 \approx 7$, $t_4 \approx 11$ and $t_6 \approx 8$ were also estimated for the Np^{4+} with Cl^- ligands. For the sake of reducing the number of adjustable parameters, the above parameters are approximately adopted for Np^{4+} in $ZrSiO_4$ of this work, with only the intrinsic parameters $\bar{A}_k$ adjusted within the uncertainties. By fitting the crystal-field splitting spectra of the ground $^4I_{9/2}$ and the first excited $^4I_{11/2}$ states for $ZrSiO_4$:Np^{4+} (note: the experimental optical spectra within $^4I_{9/2}$ were not complete) [10], we have $\bar{A}_2 \approx 3000$ cm^{-1}, $\bar{A}_4 \approx 360$ cm^{-1} and $\bar{A}_6 \approx 200$ cm^{-1}. Comparisons between the theoretical and experimental optical spectra within $^4I_{9/2}$ and $^4I_{11/2}$ states are given in Table 1. Substituting the basic functions of the lowest Γ_6 doublet on the basis of the above parameters into (1) and (2), the SH parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for Np^{4+} in $ZrSiO_4$ are calculated and shown in Table 2. For comparison we also collect the theoretical optical spectra and the SH parameters based on the related eigenvectors due to the five freely adjustable crystal-field parameters (i.e., $B_2^0 \approx -2537$ cm^{-1}, $B_4^0 \approx 2304$ cm^{-1}, $B_4^4 \approx -5281$ cm^{-1}, $B_6^0 \approx -5065$ cm^{-1}, $B_6^4 \approx 642$ cm^{-1}) in [10], as well as the theoretical SH parameters by using the B_k^q in [10] and the second-order perturbation formulas in this work (see Tables 1 and 2).

Table 2. The g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) for $ZrSiO_4$: Np^{4+} at 4.2 K.

	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$
Cal.[a]	−0.10	2.90	–	–
Cal.[b]	0.32	3.21	193	1986
Cal.[c]	1.43	2.62	899	1617
Expt. [10]	0.8 (6)	2.59 (2)	−801 (400)	1584 (10)

[a] Calculation based on the five crystal-field parameters B_k^q in [10]. [b] Calculation based on the crystal-field parameters in [10] and the second-order perturbation formulas in this work. [c] Calculation based on the superposition model parameters and the second-order perturbation formulas in this work.

3. Discussions

From Table 2 one can find that the calculated values of $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ (particularly $g_\perp$ and $A_\perp$) based on the perturbation formulas of the SH parameters for a $5f^3$ ion in tetragonal symmetry and the related superposition model parameters in the present work agree better than those based on the B_k^q of [10] with the observed values. In addition, the calculated crystal-field splittings for the $^4I_{9/2}$ and $^4I_{11/2}$ states in this work are also comparable with the experimental data (or those obtained from B_k^q in [10]). Interestingly, by using the same second-order perturbation formulas of the SH parameters, the theoretical results based on

the superposition model parameters in the present work are still better than those based on the B_k^q in [10]. Thus, the perturbation formulas and the related superposition model parameters adopted in this work can be regarded as reasonable.

(1) The calculated $\bar{g}(\approx 2.22)$ based on the perturbation formulas in this work is smaller than the well known value (≈ 2.67 [12]) for the Γ_6 lowest doublet of nf^3 ions in crystals. This may be due to the following reasons. (i) The covalency effect ($k \approx 0.91$) for Np^{4+} (or other actinides) is found to be more significant than that of the lanthanides, e.g., k is about 0.9818 for the similar $Nd^{3+}(4f^3)$ in CaF_2 [25]. (ii) Due to the size mismatching substitution of the smaller Zr^{4+} by the larger Np^{4+} in the impurity center, local tenseness around the impurity can be expected and the crystal-field acting on Np^{4+} may become stronger. Thus it is understandable that Np^{4+} has by one-order of magnitude larger intrinsic parameters than rare-earth ions in crystals (e.g., the intrinsic parameters are $\bar{A}_2 \approx 522\ cm^{-1}$, $\bar{A}_4 \approx 66.3\ cm^{-1}$ and $\bar{A}_6 \approx 4.1\ cm^{-1}$ for the similar tetragonal $[NdO_8]^{13-}$ cluster in $CaWO_4$ [26]). As a result, the very strong crystal-fields would also lower the average g value to some extent. Besides, in spite of the large experimental errors of $g_\parallel$ and $A_\parallel$, the approximate relationship $|g_\parallel/A_\parallel| \approx |g_\perp/A_\perp|$, valid for many Kramers $4f^n$ ions in crystals [12, 15, 17, 18], is also held for the theoretical SH parameters of $ZrSiO_4$:Np^{4+} in this work (see Table 2). Therefore, our calculations 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 are about $10 \sim 11\%$ those due to the first-order perturbation terms. Therefore, in order to get better SH parameters for Np^{4+} in crystals, the second-order perturbation contributions should be taken into account. From the above studies, the importance of contributions from second-order perturbation terms is related to the tetragonal crystal-fields. According to (1) and (2), both the numerators and the denominators increase with increasing strength of the crystal-fields. On the other hand, the contributions arising from irreducible representations Γ_x are very small or cancel one another. As for the contributions to the SH parameters from the admixtures of various states, they amount to about 5%, and are thus smaller than those from the second-order perturbation terms. It can be expected that the higher excited states (e.g., $^2H_{9/2}$, $^2I_{11/2}$ etc.) contribute even less.

(3) There are some errors in our calculations due to the following: (i) The approximation of the theoretical model can lead to some errors. (ii) The errors of the impurity-ligand distances R_j obtained from the empirical formula (6) can affect slightly the crystal-field parameters B_k^q. If the host metal-ligand distances R_j^H and the corresponding reference distance $R_0(\approx \bar{R}^H)$ are applied, the theoretical SH parameters would change by not more than 3%. (iii) The errors of the superposition model parameters can also affect the calculated SH parameters. Based on the studies, the errors of the theoretical SH parameters are estimated to be less than 4% if the parameters t_k change by 10%.

(iv) The contributions to the hyperfine structure parameter P (and hence the A factors) from the core polarization effect (characterized by the constant κ) are not considered, as treated for the lanthanides in the previous works [12 – 18]. For rare-earth ($4f^n$) ions (except Eu^{2+} or Gd^{3+}), the core polarization contributions to the A factors are usually regarded as small compared to those from the coupling between the electronic orbital moment and the nuclear moment [12]. However, this may not always be true for the actinide series. Therefore this point remains to be further investigated.

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