Theoretical Investigations of the Spin Hamiltonian Parameters of ZrSiO₄:Np⁴⁺

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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 ZrSiO₄:Np⁴⁺ are investigated on the basis of the perturbation formulas of these parameters for a 5f³ ion in tetragonal (D²d) 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 Zr⁴⁺ site occupied by the impurity Np⁴⁺. 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; Np⁴⁺; ZrSiO₄.

1. Introduction

Zircon (ZrSiO₄) 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 because 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 (Tb³⁺, Dy³⁺) ions in zircon was recently studied [8, 9]. However few studies on actinide (5fⁿ) ions in zircon have been performed. For example Poirot et. al. [10] have made optical and EPR investigations on tetravalent Np⁴⁺ (i.e., $^{237}$Np⁴⁺ 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 ZrSiO₄:Np⁴⁺ are investigated from the perturbation formulas of these parameters for a 5f³ ion in tetragonal (D²d) 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

ZrSiO₄ (and other isostructural zircon-type compounds) has tetragonal structure [11]. The tetravalent Np⁴⁺ impurity may substitute the host Zr⁴⁺ and then occupy magnetically equivalent sites of noncentrosymmetric D₂d point symmetry [11]. The tetragonally (D₂d) distorted dodecahedron [NpO₁₂]⁻ is formed, since no charge compensation is needed. Among the eight nearest O²⁻ ions of the host Zr⁴⁺ site, four are at the distance $R_H$ (≈ 2.268 Å) and an angle $\theta_1$ (≈ 32.43°), and the other four are at the distance $R_H$ (≈ 2.131 Å) and an angle $\theta_2$ (≈ 101.33°), where $\theta_i$ is the angle between $R_H$ and the four-fold axis [11].

For a $^{5f^3}$(Np⁴⁺) ion under tetragonal symmetry, its ground $^4I_{5/2}$ configuration will be separated into five Kramers doublets due to the spin-orbit coupling and tetragonal crystal-field interactions. From the average
value \( \bar{g} = (g|| + 2g) / 3 \approx 1.99(21) \) of the experimental \( g \) factors of \( \text{Np}^{4+} \) in \( \text{ZrSiO}_4 \) [10], one can ascribe the lowest doublet to \( \Gamma_0 \), whose \( \bar{g} \) would be about 2.67 for an \( n^6 \) 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 terms, which result from the admixtures between the lowest Kramers doublet with the other 10 irreducible representations \( \Gamma_i \) (i.e., five \( \Gamma_6 \) and five \( \Gamma_7 \)) due to the tetragonal splitting of the ground \( 4I_{9/2} \) and the first excited \( 4I_{11/2} \) via crystal-field \( H_{\text{CF}} \) and orbital angular momentum \( J \) (or hyperfine structure equivalent operator \( N \)) 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

\[
\begin{align*}
\bar{g} || &= g || (1) + g || (2), \\
g || (1) &= 2gJ(\Gamma \bar{g} | J \bar{g} | \gamma \bar{g}), \\
g || (2) &= 2 \sum_{\gamma} \frac{\langle \Gamma \bar{g} | H_{\text{CF}} | \Gamma_{\gamma \bar{g}} \rangle \langle \Gamma_{\gamma \bar{g}} | J \bar{g} | \gamma \bar{g} \rangle}{E(\Gamma) - E(\Gamma)}, \quad (1) \\
g \perp &= g \perp (1) + g \perp (2), \\
g \perp (1) &= 2gJ(\Gamma \bar{g} | J \bar{g} | \gamma \bar{g}), \\
g \perp (2) &= 0, \\
A_1 &= A_1 (1) + A_1 (2), \\
A_1 (1) &= 2PNJ(\Gamma \bar{g} | \bar{N}_J | \gamma \bar{g}), \\
A_1 (2) &= 2P \sum_{\gamma} \frac{\langle \Gamma g | H_{\text{CF}} | \Gamma_{\gamma \bar{g}} \rangle \langle \Gamma_{\gamma \bar{g}} | J \bar{g} | \gamma \bar{g} \rangle}{E(\Gamma) - E(\Gamma)}, \quad (2) \\
A_{\perp} &= A_{\perp} (1) + A_{\perp} (2), \\
A_{\perp} (1) &= 2PNJ(\Gamma \bar{g} | J \bar{g} | \gamma \bar{g}), \\
A_{\perp} (2) &= 0,
\end{align*}
\]

where the diagonal elements \( gJ \) (or \( N_J \)) of the operator \( J \) (or \( N \)) for various states can be obtained from [12, 13]. For example, \( gJ(4I_{9/2}) = 8/11 \), \( N_J(4I_{9/2}) = 476/363 \). The non-diagonal elements \( gJ' \) (or \( N_J' \)) may appear in the expansions of (1) and (2) for the interactions between different \( 2S_{1/2} \) configurations. Noted that the second-order perturbation term \( g \perp (2) \) (or \( A_{\perp} (2) \)) vanishes because none of the ten \( \Gamma_i \) has non-zero matrix element with the lowest \( \Gamma_0 \) doublet, for both \( H_{\text{CF}} \) and the \( \Gamma \) or \( \gamma \) component of \( J \) (or \( N \)) operators. \( P \) is the dipole hyperfine structure parameter for the \( 5f^3 \) ion in crystals.

As regards the lowest doublet \( \Gamma_0 \), the basic function \( \Gamma \gamma' \) (where \( \gamma \) and \( \gamma' \) 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 \( \Gamma \gamma' \) can be expressed as

\[
|\Gamma \gamma'\rangle = \sum_{M_J} C(|4I_{9/2} \gamma \langle J \bar{g} | \gamma \bar{g} \rangle M_J) N_{9/2} (|4I_{9/2} \gamma \bar{g} \rangle M_J) (3)
\]

\[
+ \lambda_{9/2} (|2H_{9/2} \gamma \rangle M_J) + \lambda_{9/2} (|4G_{9/2} \gamma \rangle M_J)
\]

\[
+ \sum_{M_{1/2}} C(4I_{11/2} \gamma \langle J \bar{g} | \gamma \bar{g} \rangle M_J) N_{11/2} (|4I_{11/2} \gamma \bar{g} \rangle M_J)
\]

\[
+ \lambda_{11/2} (|1H_{11/2} \gamma \rangle M_J) + \lambda_{11/2} (|1I_{11/2} \gamma \bar{g} \rangle M_J),
\]

where \( M_{1/2} \) and \( M_{3/2} \) are in the ranges of \( -9/2 \) to \( 9/2 \) and \( -11/2 \) to \( 11/2 \), respectively. The coefficients \( C(|4I_{9/2} \gamma \langle J \bar{g} | \gamma \bar{g} \rangle M_J) \) and \( C(|4I_{11/2} \gamma \langle J \bar{g} | \gamma \bar{g} \rangle M_J) \) are determined by diagonalizing the \( 22 \times 22 \) energy matrix containing \( 4I_{9/2} \) and \( 4I_{11/2} \) states. \( N_{9/2} \) and \( \lambda_{9/2} \) 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 \( 5f^3(\text{Np}^{4+}) \) ion in tetragonal (D\(_{2h}\)) symmetry, the crystal-field interaction \( \hat{H}_{\text{CF}} \) in the above formulas can be expressed in terms of the Stevens equivalent operators [12, 17, 18]:

\[
\hat{H}_{\text{CF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_8^0 O_8^0 + B_4^0 O_4^0.
\]

Here \( B_k^0 \) \( (k = 2, 4 \) and \( 6) \) 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

\[
B_k^0 = \sum_{j=1}^{2S+1} - \frac{1}{2} \frac{\hat{A}_k}{\hat{A}_k} K_j^2(\theta_j, \phi_j)(R_0 / R_j)^{A_k},
\]

where \( K_j^2(\theta_j, \phi_j) \) are the coordination factors [19, 20] obtained from the local geometrical relationship of the \( \text{Np}^{4+} \) center. The parameters \( t_k \) and \( \hat{A}_k \) are, respectively, the power-law exponents and the intrinsic parameters (with the reference distance or impurity-ligand distance \( R_0 \)). Since the ionic radius \( r_\text{Np} \approx 0.95 \text{ Å} \) [21] of the impurity \( \text{Np}^{4+} \) is larger than the radius \( r_{\text{Np}} \approx 0.79 \text{ Å} \)
Table 1. The crystal-field splittings (in cm\(^{-1}\)) of the \( ^{4}I_{9/2} \) and \( ^{4}I_{11/2} \) states for ZrSiO\(_{4}\): Np\(^{4+}\).

<table>
<thead>
<tr>
<th>Label</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
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<tr>
<td>( ^{4}I_{9/2} )</td>
<td>Cal.(^a)</td>
<td>–</td>
<td>0</td>
<td>340.4</td>
<td>520.5</td>
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</tr>
<tr>
<td>( ^{4}I_{11/2} )</td>
<td>Cal.(^b)</td>
<td>3512.4</td>
<td>5696.5</td>
<td>6012.6</td>
<td>6081.3</td>
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<tr>
<td>Expt. ([10])</td>
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<td>5723.0</td>
<td>6056.0</td>
<td>6072.0</td>
<td>6468.0</td>
</tr>
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</table>

\(^a\) Calculation based on the five crystal-field parameters \( R_{J} \) in \([10]\).

\(^b\) Calculation based on the superposition model parameters and the second-order perturbation formulas 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 \([14, 18]\)

\[ R_{J} \approx R_{J}^{H} + (r_{i} - r_{h})/2. \] (6)

The spectral parameters of the Coulomb repulsion (\( P_{3} \approx 47479 \) cm\(^{-1}\), \( P_{4} \approx 41455 \) cm\(^{-1}\) and \( P_{6} \approx 26528 \) 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 (\( \zeta_{\text{5f}} \approx 2088 \) cm\(^{-1}\)) were determined for Np\(^{4+}\) in ZrSiO\(_{4}\) \([10]\). In consideration of the admixture of 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 \( \zeta_{\text{5f}}^{0} \approx 2282 \) cm\(^{-1}\) for a free Np\(^{4+}\) ion \([22]\), we approximately have \( k \approx \zeta_{\text{5f}}^{0}/\zeta_{\text{5f}} \approx 0.91 \).

In general, the dipole hyperfine structure parameter \( P_{0} \) for a free 5f\(^{n}\) ion can be expressed as \( P_{0} \approx 2\beta g_{\|} g_{\perp} (r^{-3}) N_{\perp} \), where is the Bohr magneton, \( g_{\|} \) the nuclear \( g \) value, and \( g_{\perp} \) the nuclear magneton. \( (r^{-3}) \) is the average value of the inverse cube of the radial wavefunction for the 5f orbital in Np\(^{4+}\) \([12]\). From the values \( g_{\|} \approx 1.256 \) \([21]\) and \( (r^{-3}) \approx 8.57 \) 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 \( A_{1} \approx 2500(500) \) cm\(^{-1}\), \( A_{2} \approx 320(40) \) cm\(^{-1}\) and \( A_{3} \approx 250(50) \) 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 \( R(\approx 2.35) \) 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 \( A_{k} \) adjusted within the uncertainties. By fitting the crystal-field splitting spectra of the ground \( ^{4}I_{9/2} \) and the first excited \( ^{4}I_{11/2} \) states for ZrSiO\(_{4}\): Np\(^{4+}\) (note: the experimental optical spectra within \(^{4}I_{9/2} \) were not complete) \([10]\), we have \( A_{1} \approx 3000 \) cm\(^{-1}\), \( A_{2} \approx 360 \) cm\(^{-1}\) and \( A_{3} \approx 200 \) cm\(^{-1}\). Comparisons between the theoretical and experimental optical spectra within \(^{4}I_{9/2} \) and \(^{4}I_{11/2} \) states are given in Table 1. Substituting the basic functions of the lowest \( I_{6} \) doublet on the basis of the above parameters into (1) and (2), the SH parameters \( g_{\|}, g_{\perp}, A_{1} \) and \( A_{1} \) 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., \( B_{0} \approx -2537 \) cm\(^{-1}\), \( B_{2} \approx 2304 \) cm\(^{-1}\), \( B_{4} \approx -5281 \) cm\(^{-1}\), \( B_{6} \approx -5065 \) cm\(^{-1}\), \( B_{8} \approx 642 \) cm\(^{-1}\)) in \([10]\), as well as the theoretical SH parameters by using the \( B_{0}^{T} \) 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.

<table>
<thead>
<tr>
<th>Label</th>
<th>( g_{|} )</th>
<th>( g_{\perp} )</th>
<th>( A_{1} )</th>
<th>( A_{1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal.(^a)</td>
<td>–0.10</td>
<td>2.90</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cal.(^b)</td>
<td>0.32</td>
<td>3.21</td>
<td>193</td>
<td>1986</td>
</tr>
<tr>
<td>Cal.(^c)</td>
<td>1.43</td>
<td>2.62</td>
<td>899</td>
<td>1617</td>
</tr>
<tr>
<td>Expt. ([10])</td>
<td>0.8(6)</td>
<td>2.59(2)</td>
<td>–801(400)</td>
<td>1584(10)</td>
</tr>
</tbody>
</table>

\(^a\) Calculation based on the five crystal-field parameters \( R_{J} \) 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 \( g_{\|}, g_{\perp}, A_{1} \) and \( A_{1} \) (particularly \( g_{\|} \) and \( A_{1} \)) 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 \( B_{0}^{T} \) of \([10]\) with the observed values. In addition, the calculated crystal-field splittings for the \(^{4}I_{9/2} \) and \(^{4}I_{11/2} \) states in this work are also comparable with the experimental data (or those obtained from \( B_{0}^{T} \) 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 $B_k^j$ in [10]. Thus, the perturbation formulas and the related superposition model parameters adopted in this work can be regarded as reasonable.

(1) The calculated $\tilde{g}(\approx 2.22)$ based on the perturbation formulas in this work is smaller than the well known value ($\approx 2.67$ [12]) for the $t_{6g}$ lowest doublet of $n^3$ 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$^{4+}$ become stronger. Thus it is understandable that Np$^{4+}$ has by one-order of magnitude larger intrinsic para-
term contributions to $g_{\perp}$ than that of the lanthanides, e.g., $k$ is about 0.9818 for the similar Nd$^{3+}(4f^3)$ in CaF$_2$ [25]. (iii) 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 the crystal-field parameters $B_k^j$. If the host metal-ligand distances $R_j^H$ and the corresponding reference distance $R_0(\approx R^H)$ are applied, the theoretical SH parameters would change by not more than 3%. (iii) The errors of the superpo-
sition 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%.

(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 irre-
ducible representations $T_\lambda$ 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 the crystal-field parameters $B_k^j$. If the host metal-ligand distances $R_j^H$ and the corresponding reference distance $R_0(\approx R^H)$ are applied, the theoretical SH parameters would change by not more than 3%. (iii) The errors of the superpo-
sition 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 $\kappa$) are not considered, as treated for the lanthanides in the previous works [12 – 18]. For rare-earth (4fn) ions (except Eu$^{3+}$ 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.


