Theoretical evaluation of the electron paramagnetic resonance spin Hamiltonian parameters for the impurity displacements for Fe^{3+} and Ru^{3+} in corundum

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Abstract. The impurity displacements for Fe^{3+} and Ru^{3+} in corundum (Al_2O_3) are theoretically studied using the perturbation formulas of the spin Hamiltonian parameters (zero-field splitting and anisotropic g factors) for a $3d^5$ (with high spin $S = 5/2$) and a $4d^5$ (with low spin $S = 1/2$) ion in trigonal symmetry, respectively. According to the investigations, the nd^5 ($n = 3$ and 4) impurity ions may not locate at the ideal Al^{3+} site but undergo axial displacements by about 0.132 Å and 0.170 Å for Fe^{3+} and Ru^{3+}, respectively, away from the center of the ligand octahedron along the C_3 axis. The calculated spin Hamiltonian parameters based on the above axial displacements show good agreement with the observed values. The validity of the results is discussed.

Keywords. Defect structures; electron paramagnetic resonance (EPR); crystal fields and spin Hamiltonians; Fe^{3+}; Ru^{3+}; corundum.

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1. Introduction

Corundum is a useful laser material when doped with transition-metal ($3d^n$) ions [1–5]. In addition, it is also regarded as a model material to study crystal fields and local structures (e.g., impurity displacements) for transition-metal dopants by means of optical (crystal-field theory) and electron paramagnetic resonance (EPR) techniques [6–11]. Among them, investigations on the spin Hamiltonian parameters zero-field splitting D and the axial displacements of the $3d^5$ ions (e.g., Fe^{3+}) in corundum have attracted interest of the workers for the ground orbital singlet $^6A_{1g}$ state due to quenching of the orbital angular momentum ($L = 0$) [12–15]. The

zero-field splittings of the Fe^{3+} impurity in corundum (and also Mn^{2+} in some fluorides) were elaborately investigated by complete diagonalization procedure [12,13]. In addition, the axial displacement ΔZ (≈ 0.04 Å) away from the center of the oxygen octahedron along the C_3 axis was obtained from the simple fourth-order perturbation formula based on the weak crystal-field scheme [14]. Nevertheless, studies on the spin Hamiltonian parameters and local structures for the second transition-metal series ($4d^n$) are relatively fewer. For example, the EPR experiments for Ru^{3+} ($4d^5$) were carried out, and the anisotropic g factors $g_\parallel$ and $g_\perp$ were also measured [16]. They have significant discrepancies from those of Fe^{3+}, which are very close to the spin-only value g_s (=2.0023) for the case of high spin ($S = 5/2$) under weak crystal fields [12]. Unlike Fe^{3+}, Ru^{3+} has strong crystal fields with low-spin $S = 1/2$ [16,17]. Based on the estimation of the spin-orbit coupling coefficient for Ru^{3+} from that for Ru^{2+}, the authors [17] gave some explanations to the above experimental findings [16]. Up to now, however, local structure of the trigonal Ru^{3+} center in corundum has not been determined.

In order to study the spin Hamiltonian parameters and the local structures for both d^5 ions in corundum, which may be helpful to understand properties of the materials, in this work, the impurity displacement of Fe^{3+} is theoretically studied using the fourth-order perturbation formulas of the zero-field splitting D and the g factors for a $3d^5$ (with high-spin $S = 5/2$) in trigonal symmetry. Meanwhile, the axial displacement for Ru^{3+} is also obtained by analyzing the g factors for a $4d^5$ (with low-spin $S = 1/2$) in trigonal crystal fields. The validity of the results and the differences in the axial displacement and the g factors for the two ions are discussed.

2. Calculations

Corundum consists of trigonally distorted oxygen octahedra sharing faces along the C_3 axis. The centers of the octahedra are cations in the sequence of Al^{3+}, Al^{3+} and vacancy octahedron. The electrostatic repulsions between the neighbouring Al^{3+} may displace them from the centers of their octahedra. As a result, the cations in corundum are eccentric and close to the respective neighbouring vacancies. When the impurity Fe^{3+} and Ru^{3+} are doped into the lattice of corundum, they prefer to replace the host Al^{3+} ion, since no charge compensation is needed. If the host Al^{3+} ion is replaced by an impurity with larger size (e.g., Fe^{3+} and Ru^{3+}), the repulsive forces acting upon the impurity would increase and then push it further away from the center of the octahedron by an amount ΔZ along the C_3 axis [14,18]. Therefore, the local structures around Fe^{3+} and Ru^{3+} may be different from that of the host Al^{3+} in corundum due to the axial displacements of the impurities. In the following, the impurity displacements for the Fe^{3+} and Ru^{3+} centers are studied by analyzing their experimental EPR data.

2.1 *Studies for the Fe^{3+} center*

For the $^6A_{1g}$ ground state of Fe^{3+} ($3d^5$) ion in trigonal symmetry, the perturbation formulas of the spin Hamiltonian parameters D, $g_\parallel$ and $g_\perp$ based on the

dominant spin-orbit coupling mechanism can be similarly derived as those in tetragonal symmetry [19]. By introducing the contributions from the spin-orbit coupling interaction, trigonal parts of the crystal fields, off-diagonal parts of the Columbic repulsion interactions for zero-field splitting and the additional orbital and spinal angular momentum interactions for the g factors, the fourth-order perturbation formulas of the spin Hamiltonian parameters are obtained as follows:

$$
\begin{aligned}
D =\ & (1/10)V\zeta^2(1/E_1^2 - 1/E_3^2) + (3\sqrt{2}/10)\zeta^2(1/E_1E_2 - 1/E_2E_3)V' \\
& + V\{\zeta'^2 C(1/E_1 - 1/E_3)/(5E_1E_3) - \zeta^2 B(1/E_1^2 - 1/E_3^2)/(5E_2) \\
& + \zeta^3[-(1/E_1^2 + 1/E_3^2)/(20E_2) + 3/(20E_1E_2E_4) - 1/(10E_1E_2E_5) \\
& + 2/(5E_1E_2E_7) + 2/(5E_2E_3E_7) - 1/(10E_1E_2E_5) - 1/(10E_2^2E_5) \\
& - 1/(5E_2^2E_7)]\} + \sqrt{2}V'\{\zeta^3[3/(20E_1E_2E_3) + 3(1/E_1^2 - 1/E_3^2)/(20E_5) \\
& - (3/E_1E_3 + 1/E_1^2 + 1/E_3^2)/(10E_8) - 3/(40E_2^2E_3) + 3/(20E_1E_2E_5) \\
& + 3(1/E_2E_4 + 1/E_2E_6)/(40E_2) - 3/(20E_2E_3E_5)] \\
& - 9\zeta^2 B(1/E_1 + 1/E_3)/(5E_1) - 3\zeta^2(C/E_1 - 3B/E_2)/(10E_2E_3) \\
& - V^2\zeta^2\{[4/(15E_7) + 1/(30E_5)]/E_2^2 + 1/20[1/(E_1^2E_4) + 1/(E_3^2E_6)]\} \\
& + V'^2\zeta^2\{[(1/E_4 + 1/E_6)/(40E_2^2) + [(1/E_1^2 + 2/E_1E_3 + 1/E_3^2)/(10E_8) \\
& + 3(1/E_1^2 - 1/E_1/E_3 + 1/E_3^2)/(20E_5) + (2/E_1/E_3 + 1/E_1^2 + 1/E_3^2)/(5E_9)] \\
& + \sqrt{2}VV'\zeta^2(1/E_1/E_4 - 2/E_1E_5 + 2/E_3E_5 + 1/E_3E_6)/(10E_2) \\
g_\parallel =\ & g_s - 5\zeta^2(1/E_1^2 + 1/E_3^2)/6 - \zeta^2/E_2^2 + 4\zeta^2(1/E_1 + 1/E_3)/(5E_2) \\
& + V\{2\zeta^2 k(1/E_1^3 - 1/E_3^3)/15 - 2\zeta^2 g_s(1/E_1^3 - 1/E_3^3)/5 \\
& - 2k\zeta^2[(1/E_1^2 + 1/E_3^2)/(15E_2) - (3/E_1 - 2/E_5)/(15E_1E_2) \\
& + (2/E_5 - 3/E_6)/(15E_3E_2) - 4k(1/E_1 + 1/E_3)/(15E_7E_2)\} \\
& - \sqrt{2}V'\{2k\zeta^2(1/E_1 - 1/E_3)/(5E_1E_2) + k\zeta^2(1/E_2 + 1/E_3)/(5E_3E_2) \\
& + 2k\zeta^2(1/E_1^2 - 2/E_1/E_3 + 1/E_3^2)/(5E_5) + k\zeta^2(1/E_4 - 1/E_6)/(5E_2^2) \\
& - k\zeta^2/(5E_2E_3E_5) - 4k\zeta^2(1/E_1 + 1/E_3)[1/(5E_1E_8) + 1/(5E_3E_8)] \\
& + 3\zeta^2 g_s(1/E_1^2 - 1/E_3E_2)/(5E_2)\} \\
g_\perp =\ & g_\parallel - V\{14\zeta^2 k(1/E_1^3 - 1/E_3^3)/75 - 14\zeta^2 g_s(1/E_1^3 - 1/E_3^3)/25 \\
& - 14\zeta^2[k(1/E_1^2 + 1/E_3^2)/(75E_2) - 7k(3/E_1 - 2/E_5)/(75E_1E_2) \\
& + k(2/E_5 - 3/E_6)/(15E_3E_2) - 28k(1/E_1 + 1/E_3)/(75E_7E_2)\} \\
& + \sqrt{2}V'\{14k\zeta^2(1/E_1 - 1/E_3)/(25E_1E_2) + 7k\zeta^2(1/E_2 + 1/E_3)/(25E_3E_2) \\
& - 14k\zeta^2(1/E_1^2 - 2/E_1/E_3 + 1/E_3^2)/(25E_5) + 7k\zeta^2(1/E_4 - 1/E_6)/(25E_2^2) \\
& - 7k\zeta^2/(25E_2E_3E_5) - 28k\zeta^2(1/E_1 + 1/E_3)[1/(25E_1E_8) \\
& + 1/(25E_3E_8)] + 21\zeta^2 g_s(1/E_1^2 - 1/E_3E_2)/(25E_2).
\end{aligned}
\tag{1}
$$

Here V and V' are the trigonal field parameters, characteristic of the trigonal distortion of the crystal fields. ζ is the spin-orbit coupling coefficient for the $3d^5$ ion in crystals. k is the orbital reduction factor for the orbital angular momentum due to admixture (or covalency) between the impurity and the ligand orbitals. g_s (=2.0023) is the g value for pure spin. The energy denominators E_i ($i = 1$–9) denote the zero-order energy separations between the ground $^6A_{1g}$ and

the excited $^4T_{1g}[t_2^4(^3T_1)e]$, $^4T_{1g}[t_2^3(^2T_2)e^2(^3A_2)]$, $^4T_{1g}[t_2^2(^3T_1)e^3]$, $^4T_{2g}[t_2^4(^3T_1)e]$, $^4T_{2g}[t_2^3(^2T_1)e^2(^3A_2)]$, $^4T_{2g}[t_2^2(^3T_1)e^3]$, $^4E_g[t_2^3(^2E)e^2(^3A_2)]$, $^4E_g[t_2^3(^4A_2)e^2(^1E)]$ and $^4A_{2g}[t_2^3(^4A_2)e^2(^1A_1)]$ states, respectively. Based on the energy matrices for $3d^5$ ions under strong field scheme [20], these energy differences can be obtained in terms of the cubic field parameter Dq and the Racah parameters B and C for the $3d^5$ ion in crystals:

$$
\begin{aligned}
&E_1 = 10B + 6C - 10Dq, \quad E_2 = 19B + 7C, \\
&E_3 = 10B + 6C + 10Dq, \quad E_4 = 18B + 6C - 10Dq, \\
&E_5 = 13B + 5C, \quad E_6 = 18B + 6C + 10Dq, \\
&E_7 = 13B + 5C, \quad E_8 = 14B + 5C, \quad E_9 = 22B + 7C.
\end{aligned} \tag{2}
$$

From the local geometrical relationship of the impurity centers and the generalized crystal-field model [10,13,21–23], the crystal-field parameters Dq, V and V' can be determined:

$$
Dq = \sum_{j=1}^{2} -\frac{3}{8\sqrt{2}} \sin^3 \beta_j \cos \beta_j eq\langle r^4\rangle / R_j^5,
$$

$$
\begin{aligned}
V = \sum_{j=1}^{2} [&9(3\cos^2 \beta_j - 1)eq\langle r^2\rangle/(14R_j^3) \\
&+5(35\cos^4 \beta_j - 30\cos^2 \beta_j + 3)eq\langle r^4\rangle/(42R_j^5) \\
&+5\sqrt{2}\sin^3 \beta_j \cos \beta_j eq\langle r^4\rangle/(6R_j^5)],
\end{aligned}
$$

$$
\begin{aligned}
V' = \sum_{j=1}^{2} [&-3\sqrt{2}(3\cos^2 \beta_j - 1)eq\langle r^2\rangle/(14R_j^3) \\
&+5\sqrt{2}(35\cos^4 \beta_j - 30\cos^2 \beta_j + 3)eq\langle r^4\rangle/(168R_j^5) \\
&+5\sin^3 \beta_j \cos \beta_j eq\langle r^4\rangle/(12R_j^5)],
\end{aligned} \tag{3}
$$

where $q(= -2e)$ is the effective charge of the oxygen ligand. R_i and β_j are the impurity–ligand bonding lengths and their angles between the C_3 axis. For the host Al^{3+} site in corundum, the cation–anion bonding lengths and angles are $R_1^0 \approx 1.966$ Å, $\beta_1^0 \approx 46.7°$, $R_2^0 \approx 1.857$ Å and $\beta_2^0 \approx 62.7°$ [24,25]. From the above formulas, it can be found that the trigonal distortions (or local structures) of the impurity centers are correlated with their spin Hamiltonian parameters, especially the zero-field splitting D. In view of the overlap between the central ion and the ligand orbitals [21–23], the spin-orbit coupling coefficient ζ and the expectation values $\langle r^n\rangle$ of the radial wave function for the $3d^5$ ion in crystals can be reasonably expressed in terms of the average covalency factor $N(\approx k^{1/2})$ and the corresponding free-ion values [13,22]:

$$
\begin{aligned}
&B \approx 1030.22N^4 \text{ cm}^{-1}, \quad C \approx 4111.45N^4 \text{ cm}^{-1}, \quad \zeta \approx 588.946N^2 \text{ cm}^{-1}, \\
&\langle r^2\rangle \approx 1.89039N^2 \text{ a.u.}, \quad \langle r^4\rangle \approx 11.46485N^2 \text{ a.u.}
\end{aligned} \tag{4}
$$

As mentioned before, the impurity Fe^{3+} may not locate at the regular Al^{3+} site in corundum but undergo an axial displacement ΔZ_{Fe} away from the center of the

ligand octahedron. Thus, the impurity–ligand distance and angles in eq. (3) can be determined from the host values (R_j^0 and β_j^0) and the displacement ΔZ_{Fe}.

In the above formulas, only the covalency factor N and the displacement ΔZ_{Fe} are unknown. Substituting the related parameters into eqs (1)–(3) and fitting the calculated spin Hamiltonian parameters to the observed values, we have

$$N \approx 0.835, \quad \Delta Z_{\mathrm{Fe}} \approx 0.132 \text{ Å}. \tag{5}$$

Note that displacement direction away from the center of the ligand octahedron is defined as positive. The corresponding calculation results are shown in table 1. For comparisons, the theoretical values using the host structural parameters of the Al^{3+} site (i.e., $\Delta Z_{\mathrm{Fe}} = 0$) are also given in table 1.

2.2 Studies for the Ru^{3+} center

Unlike Fe^{3+} ($3d^5$) ion, Ru^{3+} ($4d^5$) in octahedra belongs to the case of strong crystal fields. The five 4d electrons occupy the t_{2g} orbitals (corresponding to one t_{2g} hole), associated with the ground state $^2T_{2g}$ of low spin ($S = 1/2$) [15,17,26]. When the ligand octahedron is trigonally distorted (e.g., at the Al^{3+} site in corundum), the $^2T_{2g}$ state may split into one orbital singlet $^2A_{1g}$ and one doublet ^2E_g, the latter lying lowest. The energy separation between $^2A_{1g}$ and ^2E_g is often defined as the trigonal field parameter V [15,17,26]. In addition, inclusion of the spin-orbit coupling interactions may result in splitting of the above states into three Kramers doublets.

By considering the contributions to the EPR g factors from the orbital reduction (or covalency effect) and spin-orbit coupling interactions, the perturbation formulas of the anisotropic g factors can be written as [17,26]

$$g_\parallel = 2|(1+k)\cos^2\alpha - \sin^2\alpha|,$$
$$g_\perp = 2|k\sin 2\alpha/\sqrt{2} + \sin^2\alpha|, \tag{6}$$

with

$$\alpha = \frac{1}{2}\tan^{-1}\frac{\sqrt{2}\zeta}{\frac{1}{2}\zeta - V}, \tag{7}$$

where k is the orbital reduction factor, as mentioned in eq. (1). The trigonal field parameter V can be similarly obtained from the local structure (the axial displacement ΔZ_{Ru} of Ru^{3+}) for the impurity center as eq. (3). The spin-orbit coupling coefficient ζ and the expectation values $\langle r^n \rangle$ can also be expressed in terms of the average covalency factor N ($\approx k^{1/2}$) and the corresponding free-ion values for Ru^{3+} [15]:

$$\zeta \approx 1180N^2 \text{ cm}^{-1}, \quad \langle r^2 \rangle \approx 2.31N^2 \text{ a.u.}, \quad \langle r^4 \rangle \approx 9.17N^2 \text{ a.u.} \tag{8}$$

Substituting these parameters into eqs (6) and (7) and fitting the calculated g factors to the observed values, we have the average covalency factor and the displacement of the impurity Ru^{3+}:

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$$N \approx 0.920, \quad \Delta Z_{Ru} \approx 0.170 \text{ Å}. \tag{9}$$

The corresponding calculation results are shown in table 1. For comparisons, the theoretical values using the host structural parameters of the Al^{3+} site (i.e., $\Delta Z_{Ru} = 0$) are also given in table 1.

3. Discussion

From table 1, the calculated spin Hamiltonian parameters for Fe^{3+} and Ru^{3+} in corundum based on ΔZ_{Fe} and ΔZ_{Ru} in eqs (5) and (9) show better agreement with the experimental data than those in the absence of the above displacements. This means that the perturbation formulas of the spin Hamiltonian parameters for both ions and the related parameters adopted here can be regarded as reasonable.

(1) The positive signs of the impurity displacements for Fe^{3+} and Ru^{3+} obtained here by analyzing their spin Hamiltonian parameters are consistent with the displacement mechanism for impurity ions in corundum-type trigonally distorted octahedral environments [14,18]. Since both impurities Fe^{3+} and Ru^{3+} have larger ionic radii (≈ 0.785 Å and 0.82 Å for high-spin Fe^{3+} and low-spin Ru^{3+} respectively [27] than that for the host Al^{3+} ion (≈ 0.67 Å [27]), the repulsive interactions acting upon the impurity ions would increase and then push them further away from the center of the octahedron by an amount along the C_3 axis. The displacement ΔZ_{Fe} (≈ 0.132 Å) for Fe^{3+} based on eq. (1) in this work has the same sign (displacement direction) and qualitatively close magnitude to that (≈ 0.04 Å) based on the simple fourth-order perturbation formula and that ($\approx 0.05 \pm 0.03$ Å) based on the superposition model studies for D factor in the previous work [14]. The discrepancy in the impurity displacement for various cases may be due to the different formulas and the related parameters adopted in the theoretical calculations. Interestingly, the larger displacement ΔZ_{Ru} (≈ 0.170 Å) for Ru^{3+} than that for Fe^{3+} ($\Delta Z_{Fe} \approx 0.132$ Å) obtained in this work is also in agreement with the greater radius and hence with the more significant local size mismatch around the impurity in the former. If the

Table 1. The spin Hamiltonian parameters for Fe^{3+} and Ru^{3+} in corundum.

		D (10^{-4} cm^{-1})	$g_\parallel$	$g_\perp$
Fe^{3+}	Cal.[a]	1393	1.998	1.999
	Cal.[b]	1675	2.001	2.000
	Expt. [12]	1679	2.003(1)	2.003(1)
Ru^{3+}	Cal.[a]	–	0.642	0.5025
	Cal.[b]	–	0.045	2.4301
	Expt. [16]	–	<0.060	2.4300

[a]Calculations based on the host structural parameters in the absence of the impurity displacements (i.e., $\Delta Z_{Fe} = \Delta Z_{Ru} = 0$) in this work.
[b]Calculations based on the local structural parameters due to the impurity displacements of eqs (5) and (9) in this work.

above impurity displacements are neglected in the calculations of the spin Hamiltonian parameters, the theoretical zero-field splitting for Fe^{3+} and the anisotropy Δg ($= g_\perp - g_\parallel$) for Ru^{3+} would be smaller in magnitude than the observed values. This means that the trigonal distortions for both ions based on the host structural parameters of the ideal Al^{3+} site are somewhat underestimated. Meanwhile, the above disagreement is difficult to remove by adjusting the covalency factor, e.g., the optimal results are $g_\parallel \approx 0.970$ and $g_\perp \approx 1.330$ for the Ru^{3+} center with $N \approx 0.40$. Obviously, this fitted value of N in the absence of the impurity displacement is too low to be regarded as reasonable. Thus the impurity ions are expected to undergo an outward displacement away from the center of the octahedron along the C_3 axis so as to result in larger trigonal distortions and hence in better spin Hamiltonian parameters. In addition, if one changes the signs of the impurity displacements into negative ones (i.e., inward displacements towards the center of the octahedra), good agreement between theory and experiment cannot be acquired, regardless of the values of ΔZ_{Fe} (or ΔZ_{Ru}) and N. Therefore, the displacement direction of the impurity ions in corundum may be further illustrated qualitatively.

(2) The differences in magnitude for the spin Hamiltonian parameters of Fe^{3+} and Ru^{3+} can be described by their perturbation formulas due to distinct spin states ($S = 5/2$ or $1/2$). For the Fe^{3+} center, the zero-field splitting D arises mainly from the combination effect (i.e., third- and fourth-order perturbation terms) of the spin-orbit coupling and the low symmetrical (trigonal) crystal-field interactions (see eq. (1)). Thus, the large zero-field splitting D of the Fe^{3+} center can be ascribed to the outward displacement of the impurity ion along the C_3 axis. In addition, for the $3d^5$ ion with $^6A_{1g}$ ground orbital singlet of high spin ($S = 5/2$) due to the quenching of the orbital angular momentum, the g factors and their anisotropy arise mainly from, respectively, the third- and fourth-order perturbation contributions via the combination of trigonal fields, spin-orbit coupling and orbital angular momentum interactions (see eq. (1)). Thus, the experimental g factors close to g_s and the negligible anisotropy Δg for the Fe^{3+} center can be understood. For Ru^{3+} with ground orbital doublet ^2E_g of low spin ($S = 1/2$), however, the g factors and their anisotropy originate mainly from the first-order perturbation contributions (see eq. (6)) via the trigonal fields, spin-orbit coupling and orbital angular momentum interactions. Therefore, significant deviations of the g factors from g_s and large anisotropy (~ 2.4) are expected for this center.

(3) The studied impurity centers have some covalency, characterized by the average covalency factor N (≈ 0.835 and 0.920 for Fe^{3+} and Ru^{3+}, respectively). This may be due to the high valence state of the impurity ions and the small impurity–ligand distances (the average bonding length is about 1.9 Å), which can lead to moderate admixture of the d orbitals of the central d^5 ion and the 2p orbitals of the oxygen ligands. Further, the value of N (≈ 0.835) for Fe^{3+} obtained by analyzing its spin Hamiltonian parameters in this work is also comparable with the value (≈ 0.864) obtained by studying the optical absorption spectra of the same system [13] and the value (≈ 0.85) for the similar trigonal $[FeO_6]^{9-}$ octahedra in the garnets based on the crystal-field analyses [28] and can be regarded as reasonable. For the same ligands, the optical electronegativity for Ru^{3+} (≈ 2.0–2.1 [29]) is smaller than that for Fe^{3+} (≈ 2.5 [29]), suggesting that weaker covalency effect and hence higher average covalency factor of the former can be expected here.

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