Investigations on the Spin Hamiltonian Parameters and the Local Structures for Various Rh^{2+} Centers in NaCl

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The spin Hamiltonian parameters (the g factors, the hyperfine structure constants, and the superhyperfine parameters) and the local structures for various Rh^{2+} centers OI, OII, and RTAX in NaCl are theoretically investigated from the perturbation formulas of these parameters for a $4d^7$ ion in tetragonally and orthorhombically elongated octahedra. The related molecular orbital coefficients and the ligand unpaired spin densities are determined quantitatively from the cluster approach in a uniform way. The centers OI, OII (orthorhombic) or RTAX (tetragonal) are attributed to the substitutional Rh^{2+} on Na^+ site, associated with two, one or none next nearest neighbour cation vacancies V_{Na} along [100] (or [010]) axis, respectively. The ligand octahedra in the orthorhombic centers OI and OII are found to suffer the relative elongations $\Delta Z \approx 0.071$ and 0.068 Å along the [001] axis due to the Jahn-Teller effect, and the intervening ligand(s) in the V_{Na} and the Rh^{2+} may undergo the inward displacements $\Delta X \approx 0.001$ and 0.011 Å towards Rh^{2+}, respectively. As for the tetragonal center RTAX, the uncompensated $[RhCl_6]^{4-}$ cluster is found to experience the relative elongation $\Delta Z \approx 0.067$ Å along the [001] axis of the Jahn-Teller nature. The calculated spin Hamiltonian parameters based on the above local structures show good agreement with the observed values for all the centers.

Key words: Crystal-Fields and Spin Hamiltonians; Electron Paramagnetic Resonance (EPR); Rh^{2+}; NaCl.

1. Introduction

Rhodium doped NaCl can act as useful catalyst [1] and models materials for crystal-field calculations [2] and electron nuclear double resonance studies [3] of the electronic states and defect structures for Rh^{2+} (and other transition-metal) impurities. Particularly, NaCl containing impurity ions of high valence state may induce various means of charge compensation (i. e., cation vacancy V_{Na}) and produce some sorts of defect centers of special scientific significance. Usually, the defect structures of transition-metal ions in crystals can be conveniently investigated by means of the electron paramagnetic resonance (EPR) technique. For example, EPR studies on Rh^{2+} doped NaCl were performed, and the spin Hamiltonian parameters (the g factors g_x, g_y, g_z, the hyperfine structure constants A_x, A_y, A_z, and the superhyperfine parameters A' and B') were also measured for various centers, i. e., orthorhombic centers OI and OII and the tetragonal center RTAX [4 – 6]. These centers were attributed to the substitutional Rh^{2+} on Na^+ site, associated with two, one or none next nearest neighbour cation vacancies V_{Na} along the [100] (or [010]) axis, respectively. Until now, however, uniform and systematic studies of the spin Hamiltonian parameters have not been carried out, except that the vanishing of the hyperfine structure constants for center RTAX were theoretically analyzed from the Rh 4d-5s orbital admixture due to the axial lattice elongation (by about 3 %) based on the experimental g factors [7, 8]. Moreover, further information about the defect structures of these centers has not been obtained yet.

In general, such information and the microscopic mechanisms of the spin Hamiltonian parameters for transition-metal ions in NaCl would be useful to understand properties of this material (and other NaCl type crystals) with dopants. Furthermore, $Rh^{2+}(4d^7)$ belongs to the strong crystal-field case of low spin ($S = 1/2$), which is quite different from the intermediate crystal-field case of high spin ($S = 3/2$) for conventional $3d^7$ (e. g., Fe^+, Co^{2+}) ions in NaCl (or similar alkali halides) [9 – 11]. Therefore, further investigations of the spin Hamiltonian parameters and the local structures for these Rh^{2+} centers are of fundamental and practical significance. In this work, the improved formulas of the spin Hamiltonian parameters are established for a $4d^7$ ion in tetragonally and orthorhombically elongated octahedra and thus applied to NaCl:Rh^{2+}. The calculations include the ligand orbital and spin-orbit coupling contributions and the influence of suitable lattice distortions, i. e., the axial elongations of the ligand octahedra due to the Jahn-Teller effect and the displacement(s) of the intervening ligand(s) due to the charge compensation. The related molecular orbital coefficients and the ligand unpaired spin densities are determined quantitatively from the cluster approach in a uniform way.

2. Theory and Formulas

The studied Rh^{2+} centers originate from the doped Rh^{3+} (in $RhCl_3$) capturing one electron during the process of X-ray irradiation [4 – 6]. Since the substitutional Rh^{2+} has extra charge as compared with the replaced Na^+, some means of charge compensation may happen. For example, two V_{Na} in the next nearest neighbour site of Rh^{2+} along the [100] (or X) and the [010] (or Y) axes forms the orthorhombic center OI. Similarly, one next nearest neighbour V_{Na} along the [100] or the [010] direction produces the orthorhombic center OII. If the charge compensation occurs far from the impurity, the uncompensated center (with axial symmetry at room temperature) RTAX is also generated. Belonging to the Jahn-Teller ion, Rh^{2+} can suffer the Jahn-Teller effect via stretching two Rh^{2+}-Cl^- bonds along the [001] (or Z) axis and then lead to a relative elongation ΔZ of the ligand octahedron in each center. This point is supported by the similar tetragonally elongated $[RhCl_6]^{4-}$ cluster (R6 center) in AgCl [12] and the isoelectronic $[PdX_6]^{3-}$ (X= Cl, Br) clusters in AgCl and AgBr [13, 14] due to the Jahn-Teller effect. On the other hand, the ligand(s) Cl^- intervening in the V_{Na} and the Rh^{2+} may experience an inward displacement towards the Rh^{2+} by an amount ΔX due to the electrostatic repulsion of the effectively negative V_{Na} in centers OI and OII. Thus, the local structures can be characterized by the relative elongation ΔZ for the tetragonal center RTAX, and the elongation ΔZ and the ligand displacement ΔX for the orthorhombic centers OI and OII.

Unlike conventional $3d^7$ ions in chlorides, Rh^{2+} exhibits strong crystal-fields and the ground orbital doublet $^2E_g(t_{2g}{}^6e_g)$ of low spin (S = 1/2), with an unpaired electron in e_g state [15, 16]. As the ligand octahedron is elongated, the ground ^2E_g state would be split into two orbital singlets $^2B_{1g}$ and $^2A_{1g}$, with the latter lying lowest. When the ligand octahedron is further distorted with orthorhombic (D_2) components, the $^2B_{1g}$ and $^2A_{1g}$ representations of tetragonal symmetry should be rewritten as $^2A_{1g}$ and $^2A_{1g}{}'$. The related excited $^4T_1[t_2{}^5e^2(^3A_2)]$, $^2T_1[t_2{}^5e^2(^3A_2)]$, $^2T_1[t_2{}^5e^2(^1E)]$, $^2T_2[t_2{}^5e^2(^1E)]$, and $^2T_2[t_2{}^5e^2(^1A_1)]$ states would also be separated into three orbital singlets A_{1g} (or A_{2g}), B_{1g}, and B_{2g}.

For a tetragonally elongated d^7 cluster, the third-order perturbation formulas of the g factors were obtained from the perturbation procedure based on the conventional crystal-field model [15, 16]. As opposed to $3d^n$ ions, where covalence has little influence on the g and self hyperfine interactions, it can no longer be neglected for Rh^{2+} in chlorides. Meanwhile, the reduction effect (characterized by the reduction factor H) due to the Rh^{2+} 4d-5s orbital admixtures may also bring forward the anisotropic contributions to the hyperfine structure constants [8]. As for the previous studies on the superhyperfine parameters for Rh^{2+} in crystals [17], the ligand unpaired spin densities were usually obtained by fitting the two experimental superhyperfine parameters, whereas the influences of covalency, ligand pσ orbitals, and the dipole-dipole interactions on the superhyperfine parameters were only insufficiently treated. Therefore, by including the above contributions as well as the orthorhombic distortion (characterized by the related crystal-field parameters), the previous tetragonal formulas of the spin Hamiltonian parameters should be improved and extended to the orthorhombic ones as follows:

$$\begin{aligned}
g_x &= g_s + 2k'\zeta'^2/E_{1x}{}^2 + 3k\zeta/E_x \\
&\quad - k'\zeta'(1/E_{2x} - 1/E_{5x}), \\
g_y &= g_s + 2k'\zeta'^2/E_{1y}{}^2 + 3k\zeta/E_y \\
&\quad - k'\zeta'(1/E_{2y} - 1/E_{5y}), \\
g_z &= g_s + 2k'\zeta'^2/E_{1z}{}^2 - 4k\zeta(1/E_{2z} - 1/E_{5z}), \\
A_x &= P[-\kappa - (2/7)H + (15/14)(g_x - g_s)], \\
A_y &= P[-\kappa - (2/7)H + (15/14)(g_y - g_s)], \\
A_z &= P[-\kappa + (4/7)H - (1/14)(g_x + g_y - 2g_s)], \\
A' &= A_s + 2A_\sigma + 2(1 - \lambda_e{}^2)[1 + 12\langle r^2\rangle/(7R^2) \\
&\qquad + 30\langle r^4\rangle/(7R^4)]A_D,
\end{aligned}$$

$$B' = A_\mathrm{s} - A_\sigma - (1-\lambda_\mathrm{e}{}^2)[1 + 12\langle r^2\rangle/(7R^2) + 30\langle r^4\rangle/(7R^4)]A_\mathrm{D} \tag{1}$$

with

$$\begin{aligned} 1/E_x &= 1/E_{3x} + 1/E_{4x} + 0.38(1/E_{3x} - 1/E_{4x}),\\ 1/E_y &= 1/E_{3y} + 1/E_{4y} + 0.38(1/E_{3y} - 1/E_{4y}). \end{aligned} \tag{2}$$

Here g_s ($= 2.0023$) is the spin-only value. ζ (and ζ') and k (and k') are the spin-orbit coupling coefficients and the orbital reduction factors, denoting the diagonal (and off-diagonal) matrix elements for the spin-orbit coupling and orbital angular momentum operators within the irreducible representations t_{2g} and e_g. They are determined from the cluster approach [18]:

$$\begin{aligned} \zeta &= N_\mathrm{t}(\zeta_\mathrm{d}{}^0 + \lambda_\mathrm{t}{}^2\zeta_\mathrm{p}{}^0/2),\\ \zeta' &= (N_\mathrm{t}N_\mathrm{e})^{1/2}(\zeta_\mathrm{d}{}^0 - \lambda_\mathrm{t}\lambda_\mathrm{e}\zeta_\mathrm{p}{}^0/2),\\ k &= N_\mathrm{t}(1 + \lambda_\mathrm{t}{}^2/2),\\ k' &= (N_\mathrm{t}N_\mathrm{e})^{1/2}[1 - \lambda_\mathrm{t}(\lambda_\mathrm{e} + \lambda_\mathrm{s}A)/2], \end{aligned} \tag{3}$$

where $\zeta_\mathrm{d}{}^0$ and $\zeta_\mathrm{p}{}^0$ are the spin-orbit coupling coefficients of the free $4d^7$ and the ligand ions, respectively. N_γ ($\gamma = t$ and e) and λ_γ (or λ_s) denote the normalization factors and the orbital admixture coefficients. A is the integral $R\left\langle ns\left|\frac{\partial}{\partial y}\right|np_y\right\rangle$, with the impurity-ligand (or reference) distance R of the studied systems.

In (1), P and κ are the dipolar hyperfine structure parameter and the core polarization constant, respectively. E_i ($i = 1-5$) are the energy separations between the excited ${}^4T_1[t_2{}^5e^2({}^3A_2)]$, ${}^2T_1[t_2{}^5e^2({}^3A_2)]$, ${}^2T_2[t_2{}^5e^2({}^1E)]$, ${}^2T_2[t_2{}^5e^2({}^1A_1)]$, and ${}^2T_1[t_2{}^5e^2({}^1E)]$ and the ground ${}^2E[t_2{}^6e]$ states under orthorhombic crystal-fields. The subscripts α ($= x$, y, and z) denote the various components of the orthorhombic splittings for these energy separations. They are usually obtained from the energy matrices for a $4d^7$ ion in orthorhombic symmetry:

$$\begin{aligned} E_{1z} &= 10Dq - 4B - 4C,\\ E_{1x} &= 10Dq - 4B - 4C - 3Ds + 5Dt - 3D_\xi + 4D_\eta,\\ E_{1y} &= 10Dq - 4B - 4C - 3Ds + 5Dt + 3D_\xi - 4D_\eta,\\ E_{2z} &= 10Dq + 2B - C,\\ E_{2x} &= 10Dq + 2B - C + 3Ds - 5Dt - 3D_\xi + 4D_\eta,\\ E_{2y} &= 10Dq + 2B - C + 3Ds - 5Dt + 3D_\xi - 4D_\eta,\\ E_{3x} &= 10Dq + 6B - C - 3Ds + 5Dt - 3D_\xi + 4D_\eta,\\ E_{3y} &= 10Dq + 6B - C - 3Ds + 5Dt + 3D_\xi - 4D_\eta,\\ E_{4x} &= 10Dq + 14B + C - 3Ds + 5Dt - 3D_\xi + 4D_\eta,\\ E_{4y} &= 10Dq + 14B + C - 3Ds + 5Dt + 3D_\xi - 4D_\eta,\\ E_{5z} &= 10Dq + 6B - C,\\ E_{5x} &= 10Dq + 6B - C + 3Ds - 5Dt - 3D_\xi + 4D_\eta,\\ E_{5y} &= 10Dq + 6B - C + 3Ds - 5Dt + 3D_\xi - 4D_\eta, \end{aligned} \tag{4}$$

where Dq is the cubic field parameter, and Ds, Dt, D_ξ, and D_η are the orthorhombic ones. B and C are the Racah parameters for the $4d^7$ ion in crystals. When neglecting the ligand orbital and spin-orbit coupling contributions (i. e., taking $k = k'$ and $\zeta = \zeta' = k\zeta_\mathrm{d}{}^0$), the formulas are reduced to those based on the conventional crystal-field model (similar to those in the previous works [15, 16]). As the perpendicular components of the orthorhombic distortions (related to D_ξ and D_η) and the differences between x and y-components of the energy denominators in (2) and (4) vanish, (1) can be simplified to the formulas for the tetragonal symmetry.

In the formulas of the superhyperfine parameters, A_s stands for the isotropic contributions from the ligand 3s orbitals. A_σ and A_D reflect the anisotropic contributions due to the admixtures between the metal 4d and ligand 3p orbitals and the dipole-dipole interactions between the metal electron and ligand nucleus, respectively. $\langle r^n\rangle$ ($n = 2, 4$) are the expectation values of the square and the quartic of Rh^{2+} $4d^7$ radial wave function. The isotropic and anisotropic parts of the superhyperfine parameters can be expanded as follows [19]:

$$A_\mathrm{s} = f_\mathrm{s}A_\mathrm{s}{}^0, \quad A_\sigma = f_\sigma A_\mathrm{p}{}^0, \quad A_\mathrm{D} = g\beta g_\mathrm{n}\beta_\mathrm{n}/R^3. \tag{5}$$

In these expressions, f_s and f_σ are the ligand unpaired spin densities. $A_\mathrm{s}{}^0 = g_\mathrm{s}\beta g_\mathrm{n}\beta_\mathrm{n}|\phi(0)|^2$ and $A_\mathrm{p}{}^0 = g_\mathrm{s}\beta g_\mathrm{n}\beta_\mathrm{n}\langle r^{-3}\rangle_{3p}$ are the related nuclear parameters for the ligand Cl^-. Here g_n is the nuclear g value. β and β_n are the electron Bohr magneton and nuclear magneton. $\phi(0)$ is the wave function of the chlorine 3s orbital at the nucleus. $\langle r^{-3}\rangle_{3p}$ is the expectation value of the inverse cube of the Cl^- 3p radial wave function. For the dipole-dipole interaction term, the g factor is usually taken as the average $[= (g_x + g_y + g_z)/3]$ of those in (1), in view of the small anisotropy.

Applying the cluster approach [18], the molecular orbital coefficients N_γ and λ_γ can be obtained from the approximate relationships

$$\begin{aligned} N^2 &= N_\mathrm{t}{}^2[1 + \lambda_\mathrm{t}{}^2 S_\mathrm{dpt}{}^2 - 2\lambda_\mathrm{t}S_\mathrm{dpt}],\\ N^2 &= N_\mathrm{e}{}^2[1 + \lambda_\mathrm{e}{}^2 S_\mathrm{dpe}{}^2 + \lambda_\mathrm{s}{}^2 S_\mathrm{ds}{}^2 - 2\lambda_\mathrm{e}S_\mathrm{dpe} - 2\lambda_\mathrm{s}S_\mathrm{ds}], \end{aligned} \tag{6}$$

and the normalization conditions

$$\begin{aligned} &N_\mathrm{t}(1-2\lambda_\mathrm{t}S_\mathrm{dpt}+\lambda_\mathrm{t}^2)=1,\\ &N_\mathrm{e}(1-2\lambda_\mathrm{e}S_\mathrm{dpe}-2\lambda_\mathrm{s}S_\mathrm{ds}+\lambda_\mathrm{e}^2+\lambda_\mathrm{s}^2)=1. \end{aligned} \tag{7}$$

Here $S_{\mathrm{dp}\gamma}$ (and S_ds) are the group overlap integrals. N is the average covalency factor, characteristic of the covalency for the impurity ion in crystals. In general, the orbital admixture coefficients increase with increasing the group overlap integrals, and one can reasonably adopt the proportional relationship $\tau\lambda_\mathrm{e}/S_\mathrm{dpe} \approx \lambda_\mathrm{s}/S_\mathrm{ds}$ for the same irreducible representation $\mathrm{e_g}$, with the proportionality factor τ. In the previous treatments of the superhyperfine parameters [17], the ligand unpaired spin densities were not quantitatively determined but taken as adjustable parameters by fitting the experimental data. Unlikely, they are theoretically calculated from the relevant molecular orbital coefficients based on the cluster approach in this work: $f_\mathrm{s} \approx N_\mathrm{e}\lambda_\mathrm{s}^2/3$ and $f_\sigma \approx N_\mathrm{e}\lambda_\mathrm{e}^2/3$.

3. Applications to NaCl:Rh^{2+}

Now the above formulas of the spin Hamiltonian parameters are applied to the studies of the EPR spectra and the local structures for the tetragonal center RTAX and the orthorhombic centers OI and OII in NaCl:Rh^{2+}.

3.1. Orthorhombic Center OI

For the orthorhombic center OI, both the next nearest neighbour sites along the [100] and [010] axes are occupied by one V_Na. Utilizing the superposition model [20], the orthorhombic field parameters of this center can be determined from the relative elongation ΔZ and the ligand displacement ΔX:

$$\begin{aligned} Ds &\approx (2/7)\bar{A}_2\{2[R/(R-\Delta Z)]^{t_2}\\ &\quad -[R/(R+2\Delta Z)]^{t_2}-[R/(R-\Delta Z-\Delta X)]^{t_2}\},\\ Dt &\approx (4/21)\bar{A}_4\{2[R/(R-\Delta Z)]^{t_4}\\ &\quad -[R/(R+2\Delta Z)]^{t_4}-[R/(R-\Delta Z-\Delta X)]^{t_4}\},\\ D_\xi &\approx (2/7)\bar{A}_2\{[R/(R-\Delta Z-\Delta X)]^{t_2}\\ &\quad -[R/(R-\Delta Z)]^{t_2}\},\\ D_\eta &\approx (5/21)\bar{A}_4\{[R/(R-\Delta Z-\Delta X)]^{t_4}\\ &\quad -[R/(R-\Delta Z)]^{t_4}\}. \end{aligned} \tag{8}$$

Here $\bar{A}_2$ and $\bar{A}_4$ are the intrinsic parameters. For transition-metal ions in octahedra, $\bar{A}_4 \approx (3/4)Dq$ and $\bar{A}_2 \approx 10.8\bar{A}_4$ [21–24] are proved valid in many crystals and reasonably adopted here. t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents [20]. Thus, the spin Hamiltonian parameters (particularly the axial anisotropy $\Delta g = (g_x+g_y)/2-g_z$ and the perpendicular anisotropy $\delta g = g_x - g_y$) are connected with the orthorhombic field parameters and hence with the local structures of the impurity centers.

In general, the effective impurity-ligand (reference) distance R may be dissimilar to the host cation-anion distance in a pure crystal due to the difference between the ionic radius for the impurity and host ions. Fortunately, powerful density function theory (DFT) calculations for NaCl:Rh^{2+} reveal that the impurity-ligand distance is 2.53 Å, about 10% smaller than that ($\approx$ 2.82 Å) of the host Na^+-Cl^- bond length in pure NaCl [7]. From the optical spectral studies for Rh^{2+} in NaCl, $Dq \approx 1640\ \mathrm{cm^{-1}}$ and $N \approx 0.738$ can be obtained [25]. Using the distance R and the Slater-type self-consistent field (SCF) functions [26, 27], the group overlap integrals $S_\mathrm{dpt} \approx 0.0151$, $S_\mathrm{dpe} \approx 0.0481$, $S_\mathrm{ds} \approx 0.0354$, and the integral $A \approx 1.2781$ are calculated. The related molecular orbital coefficients can be determined from (6) and (7), if the proportionality factor τ is known. Then the spin-orbit coupling coefficients and the orbital reduction factors can be obtained from (3) utilizing the free-ion values $\zeta_\mathrm{d}^0 \approx 1299\ \mathrm{cm^{-1}}$ [28] for Rh^{2+} and $\zeta_\mathrm{p}^0 \approx 587\ \mathrm{cm^{-1}}$ [29] for Cl^-. Based on the relationships $B \approx N^2 B_0$ and $C \approx N^2 C_0$ [30] and the values $B_0 \approx 918\ \mathrm{cm^{-1}}$ and $C_0 \approx 3669\ \mathrm{cm^{-1}}$ [28] for a free Rh^{2+} ion, the Racah parameters in (4) are calculated. In the formulas of the hyperfine structure constants, the dipolar hyperfine structure parameter is $P \approx -36.36 \times 10^{-4}\ \mathrm{cm^{-1}}$ for Rh^{2+} [8]. The reduction factor $H \approx 0.65$ [8] were acquired for NaCl:Rh^{2+} due to the Rh^{2+} 4d-5s orbital admixtures. The effective core polarization constant is estimated to be about 0.3 [8] for center RTAX in NaCl:Rh^{2+}, in consideration of the Rh 4d-4s (or 4d-5s) orbital admixtures. In view of the differences in the local structure and the hyperfine structure constants among the three centers, one can approximately take $\kappa \approx 0.20$, 0.23, and 0.30 for centers OI, OII, and RTAX, respectively. In the formulas of the superhyperfine parameters, the ligand nuclei parameters are $A_\mathrm{s}^0 \approx 1570 \times 10^{-4}$ and $A_\mathrm{p}^0 \approx 46.75 \times 10^{-4}\ \mathrm{cm^{-1}}$ for ^{35}Cl [31].

Thus, only the proportionality factor τ, the relative axial elongation ΔZ and the ligand displacement ΔX are unknown in the formulas of the spin Hamiltonian parameters. Substituting these values into (1) and

Table 1. g factors, hyperfine structure constants (in 10^{-4} cm^{-1}), and superhyperfine parameters (in 10^{-4} cm^{-1}) for various Rh^{2+} centers in NaCl.

Centers		g_x	g_y	g_z	A_x	A_y	A_z	A'	B'
O(I)	Cal. [a]	2.6424	2.6383	2.0243	11.06	11.22	3.07	–	–
	Cal. [b]	2.4741	2.4712	2.0178	4.55	4.66	3.94	24.2	11.9
	Expt. [4 – 6]	2.4797(4)	2.4712(4)	2.0118(8)	4.77(30)	4.77(30)	3.72(30)	24.3(7)	11.3(3)
O(II)	Cal. [a]	2.6391	2.6023	2.0242	8.40	9.84	2.08	–	–
	Cal. [b]	2.4718	2.4451	2.0177	2.28	3.32	2.92	24.2	11.9
	Expt. [4 – 6]	2.4779(4)	2.4301(6)	2.0154(8)	2.67(30)	3.25(30)	2.73(3)	24.4(7)	11.7(3)
RTAX	Cal. [a]	2.6124	2.6124	2.0242	6.34	6.34	0.49	–	–
	Cal. [b]	2.4524	2.4524	2.0177	0.11	0.11	0.34	24.2	11.9
	Expt. [4 – 6]	2.4510(1)	2.4510(1)	2.0190(1)	~ 0	~ 0	~ 0	25.2(7)	11.3(3)

[a] Calculations of the g and A factors based on the conventional crystal-field model (similar to those in [15, 16]) by neglecting the ligand contributions (i. e., $k = k' = N$ and $\zeta = \zeta' = N\zeta_d{}^0$). [b] Calculations based on the improved formulas (1) by considering the ligand contributions from the cluster approach.

fitting the calculated results to the experimental data, one can obtain

$$\tau \approx 0.55, \quad \Delta Z \approx 0.071 \text{ Å}, \quad \Delta X \approx 0.001 \text{ Å}. \quad (9)$$

The molecular orbital coefficients ($N_t \approx 0.745$, $N_e \approx 0.766$, $\lambda_t \approx 0.601$, $\lambda_e \approx 0.496$, and $\lambda_s \approx 0.201$), the spin-orbit coupling coefficients ($\zeta \approx 1046$ cm^{-1} and $\zeta' \approx 915$ cm^{-1}) and the orbital reduction factors ($k \approx 0.879$ and $k' \approx 0.585$) as well as the unpaired spin densities ($f_s \approx 0.010$ and $f_\sigma \approx 0.063$) are obtained from (3), (6), and (7). The corresponding spin Hamiltonian parameters are shown in Table 1. In order to clarify the importance of the covalency, the theoretical g and A factors (Cal. [a]) based on the conventional crystal-field model (similar to those in [15, 16]) by neglecting the ligand orbital and spin-orbit coupling contributions (i. e., taking $k = k' = N$ and $\zeta = \zeta' = N\zeta_d{}^0$) are also collected in Table 1.

3.2. Orthorhombic Center OII

In the orthorhombic center OII, only one V_{Na} occurs on the next nearest neighbour site along the [100] axis. The orthorhombic field parameters are similarly determined from the relative elongation ΔZ and the ligand displacement ΔX based on the superposition model [20]:

$$\begin{aligned} Ds &\approx (2/7)\bar{A}_2\{3[R/(R-\Delta Z)]^{t_2} \\ &\quad -2[R/(R+2\Delta Z)]^{t_2} - [R/(R-\Delta Z-\Delta X)]^{t_2}\}, \\ Dt &\approx (4/21)\bar{A}_4\{3[R/(R-\Delta Z)]^{t_4} \\ &\quad -2[R/(R+2\Delta Z)]^{t_4} - [R/(R-\Delta Z-\Delta X)]^{t_4}\}, \\ D\xi &\approx (1/7)\bar{A}_2\{[R/(R-\Delta Z-\Delta X)]^{t_2} \\ &\quad -[R/(R-\Delta Z)]^{t_2}\}, \\ D\eta &\approx (5/21)\bar{A}_4\{[R/(R-\Delta Z-\Delta X)]^{t_4} \\ &\quad -[R/(R-\Delta Z)]^{t_4}\}. \end{aligned} \quad (10)$$

Here the reference distance, the intrinsic parameters and the power-law exponents have the same definitions and values as those in (9). In view of the similarity in the superhyperfine parameters for all the centers, the proportionality factor τ in (10) is adopted here for center OII (and also the following tetragonal center RTAX). Substituting the related values into (1) and matching the theoretical results to the observed data, we have

$$\Delta Z \approx 0.068 \text{ Å}, \quad \Delta X \approx 0.011 \text{ Å}. \quad (11)$$

The corresponding spin Hamiltonian parameters are shown in Table 1. For comparison, the theoretical results of the g and A factors (Cal. [a]) based on the conventional crystal-field model by neglecting the ligand contributions are also listed in Table 1.

3.3. Tetragonal Center RTAX

For this center, the tetragonal field parameters are determined from the superposition model [20] and the relative axial elongation ΔZ:

$$\begin{aligned} Ds &\approx (4/7)\bar{A}_2(R)\{[R/(R-\Delta Z)]^{t_2} \\ &\quad -[R/(R+2\Delta Z)]^{t_2}\}, \\ Dt &\approx (16/21)\bar{A}_4(R)\{[R/(R-\Delta Z)]^{t_4} \\ &\quad -[R/(R+2\Delta Z)]^{t_4}\}. \end{aligned} \quad (12)$$

Substituting the relevant values into (1) and fitting the calculated results to the experimental data for this center, we obtain

$$\Delta Z \approx 0.067 \text{ Å}. \quad (13)$$

The corresponding results are given in Table 1. Similarly, the theoretical g and A factors (Cal. ^{a}) based on omission of the ligand contributions are shown in Table 1.

4. Discussion

Table 1 indicates that the calculated spin Hamiltonian parameters (Cal. ^{b}) for all the centers in NaCl:Rh^{2+} are in good agreement with the experimental data by considering the suitable lattice distortions (i. e., the relative axial elongation ΔZ and the ligand displacement ΔX). Thus, the observed EPR spectra [4 – 6] for the tetragonal and orthorhombic Rh^{2+} centers in NaCl are satisfactorily explained in a uniform way, and the information about the defect structures are also obtained.

1) The relative elongation ΔZ (≈ 0.067 Å) obtained here for the tetragonal center RTAX based on the analysis of the EPR spectra is comparable with but slightly smaller than that (≈ 0.09 Å [7, 8]) based on the DFT calculations. In addition, the oxygen octahedron around the Jahn-Teller impurity Ir^{4+} (with the same low spin $S = 1/2$) on the Ti^{4+} site in $SrTiO_3$ is also found to exhibit the relative elongation of about 0.05 Å based on the EPR calculations [32]. So, the axial elongations acquired in this work for center RTAX (and also OI and OII) may be regarded as valid in physics. Similar tetragonal elongations of the ligand octahedra around a $4d^7$ impurity were reported for the uncompensated Rh^{2+} center in AgCl [12] and the isoelectronic Pd^{3+} centers in AgCl and AgBr [13, 14] due to the Jahn-Teller effect. Thus, it can be understood that Rh^{2+} tends to experience tetragonal elongation of the Jahn-Teller nature under octahedral environments.

2) The EPR spectra of these centers can be characterized by the anisotropies Δg and δg, arising from the axial (related to Ds and Dt) and perpendicular (related to D_ξ and D_η) orthorhombic distortions, respectively (see (1), (2) and (4)). Consequently, Δg and δg depend largely upon the relative elongation ΔZ and the ligand displacement ΔX in these impurity centers (see (9), (11) and (13)). The fitted ΔZ (≈ 0.067, 0.068, and 0.071 Å) for centers RTAX, OII, and OI are in reasonable agreement with the observed Δg (≈ 0.432, 0.439, and 0.464 [4 – 6]). The slightly larger ΔZ for the orthorhombic centers can be attributed to the inward ligand displacement(s) ΔX towards the center of the ligand octahedra, which somewhat enhances the Jahn-Teller elongation. Moreover, the more (two) V_{Na} in center OI may suitably account for the further planar shrinkage (or further axial elongation) and, hence, for the larger ΔZ of this center. On the other hand, the much larger ΔX (≈ 0.011 Å) in center OII than that (≈ 0.001 Å) in center OI are consistent with the higher δg (≈ 0.048) in the former than that (≈ 0.009) in the latter. It appears that useful information about local structures for impurity ions in crystals can be obtained by analyzing the spin Hamiltonian parameters.

3) The calculated hyperfine structure constants (Cal. ^{b}) for center RTAX in this work are very small (even within the experimental errors for centers OI and OII) and in accordance with not only the calculation results of the previous work [8] but also the observed values [4 – 6]. Meanwhile, the theoretical A factors (Cal. ^{b}) for the orthorhombic centers OI and OII show good agreement with the experimental data. Thus, the observed hyperfine structure constants for all the centers are satisfactorily and uniformly explained in this work. The reduction factor H (≈ 0.65 [8]) adopted here arises mainly from the Rh^{2+} 4d-5s orbital admixture in NaCl, which can make it decline from the ideal value of unit in the absence of the above admixture. In addition, the smaller κ ($\approx 0.2 - 0.3$) for NaCl:Rh^{2+} than those ($\approx 0.36 - 0.55$ [33]) for Rh^{2+} in MgO and CaO may be ascribed to the much larger impurity-ligand distance R and, hence, weaker Rh^{2+} 4d-4s (or 4d-5s) orbital admixture in the former.

4) Despite of typical ionicity of the host NaCl, the studied $[RhCl_6]^{4-}$ clusters exhibit significant covalency and impurity-ligand orbital admixtures, characteristic of the low covalency factor N ($\approx 0.738 \ll 1$) and the moderate orbital admixture coefficients ($\approx 0.2 \sim 0.6$). When the contributions from the ligand orbital and spin-orbit coupling interactions are neglected, the theoretical g factors (Cal. ^{a}) are larger than the experimental data and yield the higher Δg and average $\bar{g}$ [$= (2g_\perp + g_\parallel)/3$]. Further, the above deviations can hardly be removed by modifying the relative elongation ΔZ (or the ligand displacement ΔX). In fact, these local structure parameters influence merely the orthorhombic distortion (characterized by Ds, Dt, D_ξ, and D_η) and cannot depress the increase of $\bar{g}$ based on omission of the ligand contributions. From the cluster approach calculations, the obvious relative deviations (anisotropies) of 50% and 14% are obtained for the orbital reduction factors and the spin-orbit coupling coefficients in NaCl:Rh^{2+}. As for the hyperfine structure constants, the theoretical results (Cal. ^{a}) based on omission of the ligand contributions are larger than

the experimental data. From (1), the isotropic contributions to the hyperfine structure constants are actually unimportant due to the low κ. As a result, the dominant contributions to the A factors originate from the anisotropic parts dependent on H and the g-shifts $(= g_i - g_s, i = x, y, \text{and } z)$, which are relevant to the defect structures and the ligand contributions. Thus, the significant errors in the theoretical g factors (Cal. [a]) based on omission of the ligand contributions may consequently impact the hyperfine structure constants. Therefore, the ligand contributions should be taken into account in the studies of the spin Hamiltonian parameters for the Rh^{2+} centers in chlorides.

5) Although the g factors and the hyperfine structure constants show some differences for various centers in NaCl:Rh^{2+}, the observed superhyperfine parameters A' and B' are almost the same within the experimental uncertainties. This can be explained by the similarity in the local structures of these centers (i. e., the dominant relative elongation $\Delta Z \sim 0.07$ Å for each $[RhCl_6]^{4-}$ cluster). The tiny deviations of the superhyperfine parameters of these centers are attributed to the slight modifications of the planar environments due to the small displacement(s) ΔX of the intervening ligand(s) in centers OI and OII. From the present cluster approach treatments, the fitted proportionality factor τ (≈ 0.55) for all the centers are much lower than unit, suggesting that the ratio λ_s/S_s is about 45% smaller than λ_e/S_e. This may be ascribed to the less admixture of the Rh^{2+} 4d orbital with the Cl^- 3s orbital than that with the chlorine 3p orbital, since the 3s orbital is usually more compact than the 3p one for the same ligand. Interestingly, the unpaired spin densities $(f_s \approx 0.010$ and $f_\sigma \approx 0.063)$ for NaCl:Rh^{2+} obtained quantitatively from the cluster approach in this work are comparable with those $(\approx 0.011$ and 0.086 [34]) for similar AgCl:Rh^{2+} obtained by fitting the experimental superhyperfine parameters and can be regarded as suitable. The slightly higher values in the latter (corresponding to the larger superhyperfine parameters $A' \approx 25.5 \times 10^{-4}$ cm^{-1} and $B' \approx 13.4 \times 10^{-4}$ cm^{-1} [34]) are understandable in view of the shorter bond length and, hence, stronger impurity-ligand spin transfer (or covalency) for AgCl:Rh^{2+}.

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