Investigation of the Spin Hamiltonian Parameters and the Local Structure of Two Ni^{3+} Centers in $KTaO_3$

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The spin Hamiltonian anisotropic g factors $g_\parallel$ and $g_\perp$ and the local structures of the Ni^{3+} centers I and II in $K\,Ta\,O_3$ are theoretically investigated by using the perturbation formulas of the spin Hamiltonian parameters for $3d^7$ ions in tetragonally distorted octahedrons and dodecahedrons. By analyzing the electron paramagnetic resonance data of the studied systems, the centers I and II can be attributed to Ni^{3+} ions occupying octahedral Ta^{5+} (associated with a nearest-neighbour oxygen vacancy V_O along the C_4 axis) and the dodecahedral K^+ (associated with a nearest-neighbour interstitial oxygen O_I along the C_4 axis) sites, respectively. Based on these studies, it is found that at the center I the impurity Ni^{3+} is displaced away from V_O by $\Delta Z_I \approx -0.31(2)$ Å along the C_4 axis. At the center II a large off-center displacement, $\Delta Z_{II} \approx 1.12(2)$ Å, towards the O_I along the C_4 axis is obtained, due to Ni^{3+}-O_I covalent bonding.

Key words: Electron Paramagnetic Resonance; Defect Structures; Crystal- and Ligand-field Theory; Ni^{3+}; $K\,Ta\,O_3$.

1. Introduction

Studies on $K\,Ta\,O_3$ have attracted interest due to its unusual properties such as second harmonic generation and hyper-Rayleigh scattering [1 – 3]. These properties are regarded as due to internal electric and elastic fields produced by impurities [4]. As an incipient ferroelectric which remains cubic to zero temperature, $K\,Ta\,O_3$ is a useful host to study transition-metal defects [5]. For example, the spin Hamiltonian parameters $g_\parallel$ and $g_\perp$ of the Ni^{3+} centers I and II in $K\,Ta\,O_3$ crystal were measured by means of electron paramagnetic resonance [6]. The authors suggested that the centers I and II correspond to the impurity Ni^{3+} substituting octahedral Ta^{5+} and dodecahedral K^+ sites, respectively, and that the local symmetries for both Ni^{3+} centers are tetragonal (C_{4V}) due to charge compensation [6]. Up to now, however, the above spin Hamiltonian parameters have not been explained and information about the local structure of these centers has not been obtained either. In general, $K\,Ta\,O_3$ may serve as model material to investigate charge states and defect structures of impurity centers similar to other important perovskite-type ferroelectrics such as $KNbO_3$ and $BaTiO_3$ [7, 8].

In this paper we investigate the local structure of the Ni^{3+} centers I and II in $K\,Ta\,O_3$ by analyzing their g factors $g_\parallel$ and $g_\perp$ via perturbation formulas of the spin Hamiltonian parameters for a $3d^7$ ion in tetragonally distorted octahedron and dodecahedron, based on a cluster approach. In these formulas, contributions to g factors from admixture of different states, covalency effect and low symmetry (tetragonal) distortion are included. Based on the studies, the local structures are determined and the spin Hamiltonian parameters $g_\parallel$ and $g_\perp$ are satisfactorily explained for both centers. The validity of the results is discussed.

2. Calculation

For a $3d^7$ ion in a cubic field, the ground state ^4F of sevenfold orbital degeneracy is split into a singlet $^4A_2$ and two triplets $^4T_1$ and $^4T_2$. According to crystal-field theory, the ground $^4T_1$ and $^4A_2$ states correspond

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to, respectively, the $3d^7$ ion in octahedral and dodecahedral (or tetrahedral) environments, associated with negative and positive cubic field parameter D_q [9]. As regards the anisotropic g factors $g_\parallel \approx 2.219(1)$ and $g_\perp \approx 4.430(2)$ of the center I, and $g_\parallel \approx 2.236(2)$ and $g_\perp \approx 2.116(2)$ of the center II [6], the average values $\bar{g}[= (g_\parallel + 2g_\perp)/3]$ are 3.693 for center I and 2.234 for center II. They are close to 4 and 2 for $3d^7$ ions in octahedron and dodecahedron (or tetrahedron), respectively [9]. It is noted that the value $\bar{g}$ of center I close to 4 reveals the ground $^4T_1$ state of high spin ($S = 3/2$), rather than the ^2E ground state of low spin ($S = 1/2$) with $\bar{g} \sim 2$ [9]. So the centers I and II can be reasonably attributed to Ni^{3+} ions occupying the octahedral Ta^{5+} and the dodecahedral K^+ site [6], respectively. Since the charge of the impurity Ni^{3+} is different from that of the host Ta^{5+}, a nearest-neighbour oxygen vacancy V_O along the tetragonal (C_4) axis is introduced at center I for charge compensation and so the $[NiO_5]^{7-}$ cluster is formed. On the other hand, a nearest-neighbour interstitial oxygen O_I occurs along the C_4 axis for compensating the two positive charges of Ni^{3+} substituting for K^+ in center II (i.e., $[NiO_{13}]^{23-}$ cluster), as does trivalent Fe^{3+} replacing K^+ in $KTaO_3$ [5]. In view of the positive (or negative) effective charge of the compensator V_O (or O_I), the impurity Ni^{3+} would be shifted away from (or towards) the compensator by an amount ΔZ_I (or ΔZ_{II}) along the C_4 axis for center I (or II) due to the electrostatic repulsion (or attraction). Thus, the local symmetry of both centers is tetragonal (C_{4V}). In the following, the local structures and g factors for both centers will be studied by using the perturbation formulas of the spin Hamiltonian parameters for $3d^7$ ions in tetragonally distorted octahedron and dodecahedron.

2.1. Center I

For a Ni^{3+} ($3d^7$) ion in a tetragonally distorted octahedron, the ground $^4T_1$ orbital triplet would split into six Kramers doublets due to the tetragonal field and spin-orbit coupling interactions, with the doublet $\Gamma_6(J' = 1/2)$ lying lowest. The second-order perturbation formulas of the spin Hamiltonian parameters $g_\parallel$ and $g_\perp$ can be written as [10]:

$$g_\parallel = 2 + \frac{4(k\alpha+2)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right] + 2\left[\frac{9}{x^2} - \frac{4}{(x+2)^2}\right]\nu_1 - 2\left(\frac{\alpha}{\alpha'}\right)\left[\frac{3}{x} - \frac{4}{x+2}\right]\nu_3}{\left[\left(\frac{\alpha}{\alpha'}{}^{2}\right) + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right]},$$

$$g_\perp = \frac{4\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{2k\alpha}{x+2} + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha'}\right)^2\nu_4 + \frac{8}{(x+2)^2}\nu_5 + \frac{12}{x(x+2)}\nu_6 - \left(\frac{\alpha}{\alpha'}\right)\frac{4}{(x+2)}\nu_7}{\left[\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right]}. \qquad (1)$$

The parameter x can be determined from the energy splitting $\Delta[= E(^4A_2) - E(^4E)]$ of the ground state $^4T_1$ in the tetragonal crystal field by the expression $\Delta = \frac{\zeta\alpha'^2}{3\alpha}[\frac{3}{x} + \frac{4}{x+2}] - \frac{\zeta\alpha}{6}(x+3)$ [10]. The splitting Δ can be obtained from the d-d transition energy matrices for the $3d^7$ ion in tetragonally distorted octahedra [10].

For an octahedral Ni^{3+} cluster, the orbital reduction factors k and k' and the spin-orbit coupling coefficients ζ and ζ' can be determined from a cluster approach [10, 11]:

$$k = N_t(1 + \lambda_t^2/2),$$

$$k' = (N_t N_e)^{1/2}(1 - \lambda_t\lambda_e/2),$$

$$\zeta = N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),$$

$$\zeta' = (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \qquad (2)$$

where ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficient of d electrons of a free $3d^7$ ion and that of p electrons of a free ligand ion. N_γ and $\lambda_\gamma(\gamma = e_g$ or $t_{2g})$ are, respectively, the normalization factor and the orbital mixing coefficient, which can be obtained from the normalization conditions [10, 11]

$$N_\gamma(1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2) = 1 \qquad (3)$$

and the approximate relations [10, 11]

$$f_\gamma \approx B/B_0 \approx C/C_0 \approx N_\gamma^2[1 + \lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_\gamma S_{dp}(\gamma)], \qquad (4)$$

where $S_{\mathrm{dp}}(\gamma)$ is the group overlap integral. B and C are the Racah parameters for a 3d^7 ion in a crystal and B_0 and C_0 are those in a free ion.

The parameters α, α' and ν_{i} in (1) are relevant to the admixture of the ground and excited states via crystal-field and the Coulombic interactions. Their expressions are given in [10]. The tetragonal field parameters D_{s} and D_{t} occur in these expressions and the d-d transition energy matrices, so the anisotropy $\Delta g (= g_{\parallel} - g_{\perp})$ is related to the tetragonal field parameters and hence to the off-center displacement ΔZ_{I} of the impurity ion.

For center I, since the ionic radius $r_{\mathrm{i}}(\approx 0.63$ Å [12]) of the impurity Ni^{3+} ion is smaller than the radius $r_{\mathrm{h}}(\approx 0.68$ Å [13]) of the host Ta^{5+}, the reference bonding length (or the effective impurity-ligand distance) R_0 may be estimated from the empirical formula [14, 15] $R_0 \approx R_{\mathrm{H}} + (r_{\mathrm{i}} - r_{\mathrm{h}})/2$, where $R_{\mathrm{H}}(= a/2 \approx$ 1.9943 Å, with the lattice constant $a \approx 3.9885$ Å [16]) is the host Ta^{5+}-O^{2-} distance in pure $\mathrm{KTaO_3}$ crystal. Thus, we have $R_0 \approx 1.969$ Å for center I. By using the distance R_0 and the Slater-type SCF functions [17, 18], the group overlap integrals $S_{\mathrm{dp}}(\mathrm{e_g}) \approx 0.041$ and $S_{\mathrm{dp}}(\mathrm{t_{2g}}) \approx 0.013$ can be calculated.

For center I in $\mathrm{KTaO_3}$:Ni^{3+} crystal, to our knowledge, no optical spectral data were reported. Fortunately, for isoelectronic Co^{2+} in $\mathrm{KTaO_3}$ crystal (where the impurity Co^{2+} also substitutes for Ta^{5+}), the spectral parameters $D_{\mathrm{q}} \approx -1214$ cm^{-1}, $B \approx$ 785 cm^{-1} and $f_\gamma \approx 0.801$ were obtained [19]. So, we can estimate the spectral parameters of the studied center I in $\mathrm{KTaO_3}$:Ni^{3+} from the empirical formulas [20]

$$10D_{\mathrm{q}} \approx -f(\mathrm{L})\,g(\mathrm{M}), \quad 1 - f_\gamma \approx h(\mathrm{L})\,k(\mathrm{M}), \tag{5}$$

where the parameter $f(\mathrm{L})$ or $h(\mathrm{L})$ is the characteristic of the ligand, and $g(\mathrm{M})$ or $k(\mathrm{M})$ that of the central metal ions (note: the minus sign of D_{q} is due to the three holes of the 3d^7 configuration). For the same ligand O^{2-} ion, D_{q} and $(1 - f_\gamma)$ are approximately proportional to the parameters $g(\mathrm{M})$ and $k(\mathrm{M})$, respectively. According to the values $g(\mathrm{Co}^{2+}) \approx$ 9000 cm^{-1}, $g(\mathrm{Ni}^{3+}) \approx 18000$ cm^{-1}, $k(\mathrm{Co}^{2+}) \approx 0.24$ and $k(\mathrm{Ni}^{3+}) \approx 0.49$, and the free-ion parameters $B_0 \approx$ 1115 cm^{-1} and $C_0 \approx 5450$ cm^{-1} for Ni^{3+} [20], we obtain for center I

$$\begin{aligned} &D_{\mathrm{q}} \approx -2428\ \mathrm{cm}^{-1}, \quad f_\gamma \approx 0.594, \\ &B \approx 662\ \mathrm{cm}^{-1}, \quad C \approx 3237\ \mathrm{cm}^{-1}. \end{aligned} \tag{6}$$

By using (3) and (4), we have $N_{\mathrm{t}} \approx 0.776$, $N_{\mathrm{e}} \approx 0.789$, $\lambda_{\mathrm{t}} \approx 0.550$ and $\lambda_{\mathrm{e}} \approx 0.560$. From (2) and the free-ion values $\zeta_{\mathrm{d}}^0(\mathrm{Ni}^{3+}) \approx 816$ cm^{-1} [9] and $\zeta_{\mathrm{p}}^0(\mathrm{O}^{2-}) \approx$ 151 cm^{-1} [21], the parameters $k \approx 0.894$, $k' \approx 0.662$, $\zeta \approx 651$ cm^{-1} and $\zeta' \approx 620$ cm^{-1} can be obtained for center I.

Table 1. Spin Hamiltonian parameters for the Ni^{3+} centers I and II in $\mathrm{KTaO_3}$:Ni^{3+} crystals.

		D (cm^{-1})	$g_{\parallel}$	$g_{\perp}$
Center I	Cal.	–	2.187	4.452
	Expt. [6]	–	2.219 (1)	4.430 (2)
Center II	Cal.	−14.5	2.241	2.123
	Expt. [6]	(−12.2)$^{\mathrm{a}}$	2.236 (2)	2.116 (2)

$^{\mathrm{a}}$ The value estimated from the approximate relationship $D \approx \zeta'(g_{\perp} - g_{\parallel})/6$ [25].

As mentioned before, the nearest-neighbour V_{O} at the C_4 axis in center I may push away the impurity Ni^{3+} along the C_4 axis by an amount ΔZ_{I}. From the superposition model [22] and the local geometrical relationship of center I, the tetragonal field parameters can be written as

$$\begin{aligned} D_{\mathrm{s}} &= \frac{4}{7}\bar{A}_2(R_0)\left[(3\cos^2\theta - 1)(R_0/R_2)^{\mathrm{t}_2} + \frac{1}{2}(R_0/R_1)^{\mathrm{t}_2}\right], \\ D_{\mathrm{t}} &= \frac{8}{21}\bar{A}_4(R_0)\left[\frac{1}{2}(35\cos^4\theta - 30\cos^2\theta + 3\right. \\ &\qquad \left. - 7\sin^4\theta)(R_0/R_2)^{\mathrm{t}_4} + (R_0/R_1)^{\mathrm{t}_4}\right], \end{aligned} \tag{7}$$

with

$$R_1 \approx R_0 + \Delta Z_{\mathrm{I}}, \quad R_2 \approx (R_0^2 + \Delta Z_{\mathrm{I}}^2)^{1/2}, \tag{8}$$

where θ is the angle between R_2 and the C_4 axis. t_2 and t_4 are the power-law exponents, and we take $t_2 \approx 3$ and $t_4 \approx 5$ for octahedral complexes [22]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference bonding length R_0. For 3d^n ions in octahedra, $\bar{A}_4(R_0) \approx (3/4)D_{\mathrm{q}}$ and $\bar{A}_2(R_0) \approx (9 \sim 12)\bar{A}_4(R_0)$ are valid for many crystals [23, 24]. Thus, we take $\bar{A}_2(R_0) \approx (10.5 \pm 1.5)\bar{A}_4(R_0)$ within the uncertainty. Substituting the above parameters into (1), and fitting the calculated g factors to the observed values, we obtain that the displacement (note: the displacement direction towards the charge compensator is defined as positive) of Ni^{3+} along the C_4 axis is

$$\Delta Z_{\mathrm{I}} \approx -0.31(2)\ \text{Å} \tag{9}$$

for center I. The corresponding theoretical values of $g_{\parallel}$ and $g_{\perp}$ are shown in Table 1.

2.2. Center II

For a Ni^{3+} ion in a tetragonally distorted dodecahedron (or tetrahedron), the fourth-order perturbation formulas of the spin Hamiltonian parameters zero-field splitting D, and g factors $g_\parallel$ and $g_\perp$ for the ground state $^4A_2$ can be written as [25]

$$D = \frac{35}{9} D_t \zeta'^2 [1/E_1^2 - 1/E_3^2] - 35 B D_t \zeta\zeta'/(E_2 E_3^2),$$

$$\begin{aligned} g_\parallel = {} & g_s + 8k'\zeta'/(3E_1) - 2\zeta'(2k'\zeta - k\zeta' + 2g_s k)/(9E_1^2) \\ & + 4\zeta'^2(k - 2g_s)/(9E_3^2) - 2\zeta^2(k + g_s)/(3E_2^2) \\ & + k'\zeta\zeta'[4/(9E_1E_3) - 4/(3E_1E_2) + 4/(3E_2E_3)] \\ & - 140k'\zeta' D_t/(9E_1^2), \end{aligned} \qquad (10)$$

$$g_\perp = g_\parallel + 210k'\zeta' D_t/(9E_1^2),$$

where $g_s (= 2.0023)$ is the spin-only value. The denominators $E_i (i = 1 \sim 3)$ are the energy separations between the excited states $^4T_2$, $^2T_{2a}$ and $^2T_{2b}$ and the ground state $^4A_2$. The orbital reduction factors k and k', and the spin-orbit coupling coefficients ζ and ζ' can be obtained from the cluster approach for a tetrahedral complex [25]:

$$\begin{aligned} \zeta &= N_t^2[\zeta_d^0 + (\sqrt{2}\lambda_\pi\lambda_\sigma - \lambda_\pi^2/2)\zeta_p^0], \\ \zeta\text{‘} &= N_t N_e[\zeta_d^0 + (\lambda_\pi\lambda_\sigma/\sqrt{2} + \lambda_\pi^2/2)\zeta_p^0], \\ k &= N_t^2(1 - \lambda_\pi^2/2 + \sqrt{2}\lambda_\pi\lambda_\sigma + 2\lambda_\sigma S_{dp}(\sigma) \\ & \quad + 2\lambda_\pi S_{dp}(\pi)), \\ k' &= N_t N_e[1 + \lambda_\pi^2/2 + \lambda_\pi\lambda_\sigma/\sqrt{2} + 4\lambda_\pi S_{dp}(\pi) \\ & \quad + \lambda_\sigma S_{dp}(\sigma)], \end{aligned} \qquad (11)$$

where N_γ ($\gamma =$ e and t, which stand for the irreducible representations of the T_d group) are the normalization factors, and $\lambda_j (j = \sigma$ and $\pi)$ are the orbital mixing coefficients. They satisfy the normalization conditions

$$\begin{aligned} N_t &= [1 + \lambda_\sigma^2 + \lambda_\pi^2 + 2\lambda_\sigma S_{dp}(\sigma) + 2\lambda_\pi S_{dp}(\pi)]^{-1/2}, \\ N_e &= [1 + 3\lambda_\pi^2 + 6\lambda_\pi S_{dp}(\pi)]^{-1/2}. \end{aligned} \qquad (12)$$

Since no optical spectra of the dodecahedral (or tetrahedral) Ni^{3+}-O^{2-} cluster are reported, we can approximately estimate the parameters N_t, N_e and the cubic field parameter D_q from (i) the empirical formulas [i. e., for the same central Ni^{3+} ion, D_q and $(1 - f_\gamma)$ are approximately proportional to the parameters $f(L)$ and $h(L)$, respectively] (5) and the optical spectral parameters ($D_q \approx 845$ cm^{-1}, $f_\gamma \approx 0.4$ [26]) of the tetrahedral Ni^{3+}-N^{3-} cluster in GaN, and (ii) the approximate relationship $N_t \approx N_e \approx f_\gamma^{1/4}$, in consideration of reducing the number of adjustable parameters and of the small difference between N_t and N_e. From the values $f(O^{2-}) \approx h(O^{2-}) \approx 1.0$, $f(N^{3-}) \approx 1.25$ and $h(N^{3-}) \approx 1.4$ [20] we have for center II

$$\begin{aligned} & D_q \approx 676 \text{ cm}^{-1}, \quad f_\gamma \approx 0.571, \\ & B \approx 637 \text{ cm}^{-1}, \quad C \approx 3112 \text{ cm}^{-1}. \end{aligned} \qquad (13)$$

Since the ionic radius $r_i (\approx 0.63$ Å [12]) of the impurity Ni^{3+} ion is much smaller than that ($r_h' \approx 1.33$ Å [13]) of the host K^+, the impurity-ligand distance $R_0' \approx 2.4703$ Å for center II can be approximately obtained from the empirical formula $R_0' \approx R_H' + (r_i - r_h')/2$ [14, 15], where $R_H' (= a/\sqrt{2} \approx 2.8203$ Å [16]) is the K^+-O^{2-} distance in pure $KTaO_3$. Thus, the considerable reduction (≈ 0.35 Å) of the metal-ligand distance on K^+ site from the host to Ni^{3+}-doped crystals can be understood, considering the extra positive charge and small size of the impurity Ni^{3+} compared to the replaced K^+. By using the distance R_0' and the Slater-type SCF functions [17, 18], the group overlap integrals $S_{dp}(\pi) \approx 0.001$ and $S_{dp}(\sigma) \approx -0.006$ for center II can be calculated. Thus, the parameters $k \approx 0.575$, $k' \approx 0.722$, $\zeta \approx 589$ cm^{-1} and $\zeta' \approx 611$ cm^{-1} are obtained from (11) and (12).

For center II, the interstitial oxygen O_I and the central impurity Ni^{3+} may approach each other along the C_4 axis due to the electrostatic attraction and then form a considerably covalent bond. This point is supported by the studies on similar trivalent Fe^{3+} substituting for K^+ in $KTaO_3$ [5, 16], where the covalent bonding length R_{CO} between Fe^{3+} and O_I is found to be in the range of $1.69 \sim 1.85$ Å [5, 16]. This means that the bonding length for Fe^{3+}-O_I is by about $0.11 \sim 0.27$ Å smaller than the sum of the radii $r_{Fe^{3+}} (\approx 0.64$ Å [13]) and $r_{O}^{2-} (\approx 1.32$ Å [13]). Considering that Ni^{3+} in this work has similar electronegativity and the same charge as Fe^{3+}, the length R_{CO} for Ni^{3+}-O_I may be approximately taken as $(r_{Ni^{3+}} + r_{O^{2-}}) - 0.19\ (8)$ Å $\approx 1.76\ (8)$ Å, i. e., an average reduction (≈ 0.19 Å) with an uncertainty of 0.08 Å for the Fe^{3+}-O_I bond in $KTaO_3$ is adopted here. As mentioned above, the impurity Ni^{3+} may undergo an off-center (away from the ideal K^+ site) displacement towards the O_I by an amount ΔZ_{II}. Thus, from the superposition model [22] and the geometrical relationship of center II, the tetragonal field parameter D_t in (10) can be written as

$$D_t = -\frac{4}{21}\bar{A}_4(R'_0)\left[\sum_{i=1}^{3}(35\cos^4\theta_i - 30\cos^2\theta_i + 3 - 14\sin^4\theta_i/3)(R'_0/R_i)^{t4} + 2(R'_0/R_{CO})^{t4}\right] \quad (14)$$

with

$$\begin{aligned} R_1 &= \left[\frac{a^2}{4} + \left(\frac{a}{2} - \Delta Z_{II}\right)^2\right]^{1/2}, \\ R_2 &= ({R'_0}^2 + \Delta Z_{II}^2)^{1/2}, \\ R_3 &= \left[\frac{a^2}{4} + \left(\frac{a}{2} + \Delta Z_{II}\right)^2\right]^{1/2}, \\ \theta_1 &= tg^{-1}\left(\frac{a}{a - 2\Delta Z_{II}}\right), \\ \theta_2 &= \frac{\pi}{2} + tg^{-1}\left(\frac{\Delta Z_{II}}{R_0}\right), \\ \theta_3 &= \frac{\pi}{2} + tg^{-1}\left(\frac{a}{a + 2\Delta Z_{II}}\right), \end{aligned} \quad (15)$$

where the intrinsic parameter $\bar{A}_4(R'_0) \approx (27/16)D_q$ (with the reference bonding length R_0') and the power-law exponent $t_4 \approx 5$ for a tetrahedral cluster [22].

Substituting the above parameters into (10) and fitting the calculated g factors to the observed values, one obtains the displacement of the impurity Ni^{3+} towards the O_I along the C_4 axis for center II, i. e.,

$$\Delta Z_{II} \approx 1.12(22)\ \text{Å}. \quad (16)$$

The corresponding values of the theoretical D, $g_\parallel$ and $g_\perp$ are also shown in Table 1.

3. Discussion

From Table 1, one can find that the calculated g factors for the centers I and II agree with the observed values, by considering the displacements of the impurity Ni^{3+} ions. Therefore, the assignments of both centers in $KTaO_3$:Ni^{3+} by the experimentalists [6] are theoretically verified.

1. The sign of the displacement $\Delta Z_I < 0$ (or $\Delta Z_{II} > 0$) for Ni^{3+} in center I (or II) is consistent with the expectation based on the electrostatic interaction between Ni^{3+} and the compensator V_O (or O_I). So, the displacement directions for centers I and II can be regarded as reasonable. Interestingly, if one exchanges the signs of ΔZ_I and ΔZ_{II}, i. e., taking $\Delta Z_I > 0$ and $\Delta Z_{II} < 0$, agreement between theory and experiment cannot be achieved for the spin Hamiltonian parameters in both centers, regardless of the magnitudes of the displacements ΔZ_I and ΔZ_{II}.

2. The displacement $\Delta Z_I(\approx -0.31$ Å) for center I obtained in this work is consistent in sign and comparable in magnitude with that (≈ -0.29 Å) for the isoelectronic Co^{2+} on a Ta^{5+} site in $KTaO_3$ obtained from the theoretical analysis of its spin Hamiltonian parameters [19], and that (≈ -0.25 Å) for similar trivalent Fe^{3+} on an Nb^{5+} site in $KNbO_3$ obtained from both the shell-model simulations and the embedded-cluster calculations [27]. Thus, the displacement pattern (i. e., moving away from V_O) of impurity ions on the B site in ABO_3 perovskites suggested by Donnerberg [27] is also supported by the studies on Ni^{3+} center I of $KTaO_3$ in this work. It is noted that the small value of the calculated $\bar{g}(\approx 3.697)$ compared with the usual value ~ 4 [9] for $^4T_1$ ground state of $3d^7$ ions in octahedral fields may be attributed to the large cubic spectral parameter $D_q(\approx -2428\ \text{cm}^{-1})$ and strong covalency effect $(f_\gamma \approx 0.594 \ll 1)$ of the Ni^{3+}-O^{2-} cluster in center I.

3. The large off-center displacement ΔZ_{II} (≈ 1.12 Å) for center II estimated in this work is qualitatively consistent with that (~ 1 Å) obtained for some other transition-metal ions (e. g., Mn^{2+}, Co^{2+}, Cu^{2+} and Fe^{3+}) on a K^+ site in $KTaO_3$ due to metal-oxygen covalent bonding [5, 16]. From (10), (14), and (15), the magnitude of the anisotropy $\Delta g(= g_\parallel - g_\perp)$ and zero-field splitting D are mainly proportional to the values of the tetragonal field parameter D_t, which results from the interstitial O_I and the displacement ΔZ_{II} of the impurity Ni^{3+}. Based on the calculations, it is found that a large ΔZ_{II} leads to a small D_t (or tetragonal distortion), and hence small values of Δg and D. In addition, the value of D_t depends also the distance R_{CO} between the interstitial O_I and Ni^{3+}. As for the magnitude (or average) of the g factors, the large theoretical g factors compared with the observed values (see Table 1) are mainly due to the approximation of the adopted parameters (e. g., D_q and f_γ) for center II. In fact, presence of the O_I may increase the crystal field (i. e., larger D_q) and the covalency (i. e., smaller f_γ) of center II, and then

better or smaller calculated $g_{\parallel}$ and $g_{\perp}$ can be expected according to (10) and (11).

It is noted that there may be some errors in the theoretical spin Hamiltonian parameters as well as the displacements ΔZ_{I} and ΔZ_{II} for both centers. This is because by (i) the approximation of the theoretical models and the related parameters in the calculations and (ii) the neglection of displacements of the oxygen ligands in the Ni^{3+} centers. In general, the displacements of the ligands O^{2-} in both centers should be much smaller than those of the central Ni^{3+} ions, due to the larger distances between the ligands and the compensators. So, the influence of the above factors on our theoretical results can be regarded as unimportant.

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