

Investigations on the local structure and g factors for the interstitial Ti^{3+} in TiO_2

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Abstract. The EPR g factors g_i ($i = x, y, z$) for the interstitial Ti^{3+} in rutile are theoretically studied from the perturbation formulas of these parameters for a $3d^1$ ion in rhombically compressed octahedra. The ligand octahedron in the impurity center is found to be less compressed than that on the host interstitial site due to the Jahn–Teller effect. The local compression parameter (≈ 0.026) and the rhombic distortion angle $\delta\phi'$ ($\approx 0.7^\circ$) around the impurity Ti^{3+} are smaller than the host values (≈ 0.091 and 3.5°). The theoretical g factors based on the above local structural parameters are in good agreement with the experimental data. In addition, the g factors for a tetragonal interstitial Ti^{3+} center are also reasonably interpreted.

Keywords. Electron paramagnetic resonance (EPR); crystal and ligand fields; Ti^{3+} ; rutile.

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1. Introduction

Rutile (TiO_2) has been extensively investigated because of its unique phase transition [1] and magnetic [2–4], optical [5–7] and catalytic [8,9] properties when it is doped with some transition metal ions. In general, these properties are sensitively dependent upon the local structures around the impurity ions, which may be studied using electron paramagnetic resonance (EPR) technique. Ti^{3+} ($3d^1$) can be regarded as a model system to study structure properties and conduction process of transition metal ions in this material. EPR experiments for $\text{TiO}_2:\text{Ti}$ were carried out, and the anisotropic g factors g_i ($i = x, y, z$) were also measured at 4.2 K [10]. The above EPR data (labeled as spectrum A) were attributed to the interstitial Ti^{3+} having rhombic symmetry. Additionally, the minor spectrum

C with axial g factors g_{\parallel} and g_{\perp} was ascribed to the tetragonal interstitial Ti^{3+} in the same host [10].

In order to interpret the rhombic Ti^{3+} center in TiO_2 , angular overlap model studies were performed by adjusting the radial integrals, spin-orbit coupling coefficient and the cubic field parameter [11]. Here, the contributions from the ligand orbitals and spin-orbit coupling interactions were ignored. Moreover, local lattice deformations around the Jahn–Teller ion Ti^{3+} were not taken into account. In fact, due to the Jahn–Teller effect and space effect arising from impurity Ti^{3+} on interstitial site in rutile, the impurity–ligand bond lengths and angles may differ from those in the host and then lead to local lattice distortion, as mentioned in various works [10,12–14]. Consequently, the calculations without taking into account the above contributions [11] yield ambiguous results (i.e., two solutions with different principal axis orientations were matched to the interstitial site).

Since information about local structure and electronic properties of Ti^{3+} in TiO_2 would be helpful to understand optical and magnetic properties of this material, investigations on the local structure and the g factors for the interstitial Ti^{3+} center to a better extent are of significance. In this work, the high-order perturbation formulas of the g factors for a $3d^1$ ion in rhombically compressed octahedra are applied, by taking into account reasonable local lattice distortion around the impurity ion due to the Jahn–Teller effect.

2. Calculations

The interstitial Ti^{3+} center in TiO_2 can arise from an interstitial Ti^{4+} capturing an electron at reduced atmosphere [10]. The oxygen octahedron around this site is significantly compressed, with two parallel distances $R_{\parallel} \approx 1.67 \text{ \AA}$ and four perpendicular $R_{\perp} \approx 2.23 \text{ \AA}$ [15] from the nearest six oxygen ions. Additionally, the planar bond angle $\phi \approx 48.5^\circ$ [15] is also larger than that for regular octahedra ($= 45^\circ$), yielding some rhombic distortion.

For a $\text{Ti}^{3+}(3d^1)$ ion in rhombically compressed octahedra, its higher orbital doublet 2E_g of original cubic case would split into two orbital singlets ${}^2A_{1g}(|z^2\rangle)$ and ${}^2A'_{1g}(|xy\rangle)$. Meanwhile, the original lower orbital triplet ${}^2T_{2g}$ would be separated into three orbital singlets ${}^2B_{2g}(|xz\rangle)$, ${}^2B_{3g}(|yz\rangle)$ and ${}^2B_{1g}(|x^2 - y^2\rangle)$, with the latter lying lowest [16,17]. Note that in the above notations $|xy\rangle$ and $|x^2 - y^2\rangle$ are interchanged due to a rotation of axes in the XY plane.

Including the contributions from ligand orbitals and applying similar perturbation procedure in refs [16,17], the high-order perturbation formulas of the g factors for the $3d^1$ ion in rhombically compressed octahedra can be obtained on the basis of the cluster approach:

$$\begin{aligned}
 g_x &= g_s - 2k'\zeta'/E_1 + k\zeta^2[1/(2E_1^2) - 1/(2E_2^2)] \\
 &\quad + 2k'\zeta'\zeta[1/(E_2E_3) - 1/E_3^2], \\
 g_y &= g_s - 2k'\zeta'/E_2 - k\zeta^2[1/(2E_1^2) - 1/(2E_2^2)] \\
 &\quad + 2k'\zeta'\zeta[1/(E_1E_3) - 1/E_3^2], \\
 g_z &= g_s - 8k'\zeta'/E_3 - (1/2)k\zeta^2(1/E_1 + 1/E_2)^2 + 2k'\zeta'^2/E_3^2,
 \end{aligned} \tag{1}$$

where g_s (=2.0023) is the spin-only value. The denominators E_i ($i = 1, 2, 3$) stand for the energy separations between the excited ${}^2B_{2g}$, ${}^2B_{3g}$ and ${}^2A_{1g}$ and the ground ${}^2B_{1g}$ states [16,17], which can be expressed in terms of the cubic field parameter Dq and the rhombic field parameters Ds , Dt , D_ξ and D_η . Thus, we have: $E_1 = 5Dt - 3Ds + 3D_\xi - 4D_\eta$, $E_2 = 5Dt - 3Ds - 3D_\xi + 4D_\eta$ and $E_3 = 10Dq$.

Based on the cluster approach, the spin-orbit coupling coefficients ζ , ζ' and the orbital reduction factors k, k' in eq. (1) can be correlated to the normalization factors N_γ and the orbital admixture coefficients λ_γ (or λ_s) for the O_h irreducible representations γ ($= e_g$ and t_{2g}). They are usually determined from the approximate relationships

$$\begin{aligned} N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}] \end{aligned} \quad (2)$$

and the normalization conditions

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1. \end{aligned} \quad (3)$$

Here N is the average covalency factor. $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the admixture coefficients increase with the increase of the group overlap integrals, and one can approximately adopt the proportional relationship between the admixture coefficients and the related group overlap integrals, i.e., $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ within the same irreducible representation e_g . Thus the spin-orbit coupling coefficients and the orbital reduction factors can be written as

$$\begin{aligned} \zeta &= N_t(\zeta_d + \lambda_t^2 \zeta_p/2), \quad \zeta' = (N_t N_e)^{1/2}(\zeta_d - \lambda_t \lambda_e \zeta_p/2), \\ k &= N_t(1 + \lambda_t^2/2), \quad k' = (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2], \end{aligned} \quad (4)$$

where ζ_d and ζ_p are the spin-orbit coupling coefficients of the $3d^1$ and the ligand ions in free states, respectively. A denotes the integral $R\langle ns | \frac{\partial}{\partial y} | n p_y \rangle$, where R is the impurity–ligand distance in the studied system.

From the point-charge model [18–20] and the local geometrical relationship of the studied impurity center, the cubic and rhombic field parameters can be determined as follows:

$$\begin{aligned} Dq &= -eq\langle r^4 \rangle / (6\bar{R}^5), \\ Ds &= 2eq\langle r^2 \rangle (1/R_{\parallel}^3 - 1/R_{\perp}^3) / 7, \\ Dt &= eq\langle r^4 \rangle [4/R_{\parallel}^5 + (7 \cos 4\phi + 3)/R_{\perp}^5] / 42, \\ D_\xi &= 2eq\langle r^2 \rangle \cos 2\phi / (7R_{\perp}^3), \\ D_\eta &= 5eq\langle r^4 \rangle \cos 2\phi / (42R_{\perp}^5), \end{aligned} \quad (5)$$

where q ($= -2e$) is the effective charge of the oxygen ligand. $\langle r^n \rangle$ ($n = 2, 4$) are the expectation values of the square and the quartic of the $3d^1$ radial wave function in crystals. From the free-ion expectation values [16] for Ti^{3+} and those for the iso-electronic V^{4+} in rutile [21], $\langle r^n \rangle$ can be expressed in terms of the average covalency factor due to the admixture between the metal and ligand orbitals [18–20]:

$$\langle r^2 \rangle \approx 4.0345N \text{ (a.u.)}, \quad \langle r^4 \rangle \approx 18.7184N \text{ (a.u.)}. \quad (6)$$

\bar{R} denotes the average distance between the interstitial site and the nearest-neighbour ligands in rutile, i.e., $\bar{R} = (R_{\parallel} + 2R_{\perp})/3 \approx 2.043 \text{ \AA}$ [15]. Usually, occupation of the impurity Ti^{3+} on the interstitial site can affect the impurity–ligand bond lengths R'_{\parallel} , R'_{\perp} and angle ϕ' , dissimilar to those (R_{\parallel} , R_{\perp} and ϕ) in the host. On the other hand, the Jahn–Teller ion Ti^{3+} may suffer Jahn–Teller effect under octahedral environments [12–14], which would also modify the immediate environment by stretching and contraction of the parallel and perpendicular impurity–ligand bonds. This point is supported by *ab initio* studies on some transition metal (e.g., Ti) impurities on the interstitial site in TiO_2 [22]. Thus, the impurity–ligand bond lengths can be conveniently determined from the average distance \bar{R} , the local compression parameter ρ' and the rhombic distortion angle $\delta\phi'$ as $R'_{\parallel} \approx \bar{R}(1 - 2\rho')$, $R'_{\perp} \approx \bar{R}(1 + \rho')$ and $\phi' \approx 45^\circ + \delta\phi'$. Thus the immediate environment around interstitial Ti^{3+} in TiO_2 can be described as the local structural parameters ρ' and $\delta\phi'$. Further, the local structure of the studied system is correlated to its EPR g factors, particularly to the anisotropy $(g_x + g_y)/2 - g_z$.

From the distance \bar{R} and the Slater-type SCF functions [23,24], the integrals $S_{dpt} \approx 0.0546$, $S_{dpe} \approx 0.1394$, $S_{ds} \approx 0.1122$ and $A \approx 1.3301$ are obtained. Since no optical spectra for Ti^{3+} in TiO_2 were reported, one can estimate the average covalency factor from the cubic field parameter Dq ($\approx 1910 \text{ cm}^{-1}$ [25]) of similar $[\text{TiO}_6]^{9-}$ cluster in Al_2O_3 (with the distance $\bar{R} \approx 1.912 \text{ \AA}$ [26]). According to the relationship $Dq \propto \bar{R}^{-5}$ [27,28], the value $Dq \approx 1371 \text{ cm}^{-1}$ can be obtained for the studied $\text{TiO}_2:\text{Ti}^{3+}$ here. Using eq. (1), the average covalency factor $N \approx 0.86$ can be determined. The molecular orbital coefficients $N_t \approx 0.881$, $N_e \approx 0.942$, $\lambda_t \approx 0.427$, $\lambda_e \approx 0.378$ and $\lambda_s \approx 0.304$ are calculated from eqs (2) and (3). Then the parameters $\zeta \approx 148 \text{ cm}^{-1}$, $\zeta' \approx 129 \text{ cm}^{-1}$, $k \approx 0.961$ and $k' \approx 0.758$ can be obtained from eq. (4) and the free-ion values $\zeta_d \approx 154 \text{ cm}^{-1}$ for Ti^{3+} [29] and $\zeta_p \approx 151 \text{ cm}^{-1}$ for O^{2-} [30].

Thus, in the formulas of the g factors, there are only two unknown local structural parameters ρ' and $\delta\phi'$. Substituting the related parameters into eq. (1) and matching the calculated g factors to the experimental data, we have

$$\rho' \approx 0.026, \quad \delta\phi' \approx 0.7^\circ. \quad (7)$$

The corresponding results (Cal.^c) are shown in table 1. For comparisons, the theoretical g factors (Cal.^a) based on neglecting the local lattice distortion (i.e., the host structural parameters $\rho \approx 0.091$ and $\delta\phi \approx 3.5^\circ$ of interstitial site are adopted) and those (Cal.^b) based on neglecting the ligand contributions (i.e., taking $\zeta = \zeta' = N\zeta_d$ and $k = k' = N$) are also given in table 1. In addition, calculations for the other tetragonal center (spectrum C) can be performed by merely taking the rhombic distortion angle as zero in eq. (7), i.e., $\delta\phi'' \approx 0$. The corresponding g factors g_{\parallel} ($= g_z$) and g_{\perp} ($= g_x = g_y$) are shown in table 1.

3. Discussion

Table 1 reveals that the theoretical g factors based on the perturbation formulas (eq. (1)) and the contributions from the local lattice distortion due to the Jahn–

Table 1. The EPR g factors for the two interstitial Ti^{3+} centers in rutile at 4.2 K.

Centers	Rhombic			Tetragonal	
	g_x	g_y	g_z	g_{\parallel}	g_{\perp}
Cal. ^a	1.995	1.996	1.943	1.943	1.995, 1.996
Cal. ^b	1.969	1.972	1.935	1.935	1.971
Cal. ^c	1.974	1.977	1.942	1.942	1.976
Expt. [10]	1.974	1.977	1.941	1.941	1.976

^aCalculations based on inclusion of the ligand contributions and neglecting the local lattice distortion (i.e., the host structural parameters ρ and $\delta\phi$ are adopted).

^bCalculations based on the local structural parameters ρ' and $\delta\phi'$ in eq. (7) and neglecting the ligand contributions (i.e., taking $\zeta = \zeta' = N\zeta_d$ and $k = k' = N$).

^cCalculations based on inclusion of both the local lattice distortion and the ligand contributions.

Teller effect and the ligand orbital and spin-orbit coupling contributions show better agreement with the experimental data than those in the absence of the above contributions. This means that the formulas and the local structural parameters in this work can be regarded as reasonable.

(1) The results (Cal.^a) based on the host structural parameters ($\rho = 0.091$ and $\delta\phi \approx 3.5^\circ$) are not as good as those based on the local structural parameters, particularly the values of g_x and g_y (and the anisotropy $(g_x + g_y)/2 - g_z$) are larger than the experimental data. This reveals that the axial distortion (D_s and D_t) based on the host compression parameter ρ would be overestimated and then the local structural parameters should be applied instead. The local compression parameter ρ' (≈ 0.026) and the rhombic distortion angle $\delta\phi'$ ($\approx 0.7^\circ$) obtained here are about twice and four times smaller than those in the host. This is originated from relaxation (by about 0.27 Å) and contraction (by about 0.13 Å) of the parallel and perpendicular bond lengths as well as reduction of the bond angle (by about 2.8°) via bending of the planar bonds, yielding a ligand octahedron with less compression and smaller non-axial distortion. The microscopic mechanism of the above transformation can be attributed to the Jahn–Teller effect, which tends to elongate the ligand octahedron, as for Cu^{2+} on the octahedral Al^{3+} site in $LaSrAlO_4$ [31]. Another reason may be the space effect arising from occupation of the impurity Ti^{3+} on the interstitial site, leading to further modification of the local impurity–ligand bond lengths and angles. Similar results $\rho' \approx 0.015$ (i.e., relaxation and contraction of the parallel and perpendicular distances by about 0.25 and 0.22 Å, respectively) and $\delta\phi' \approx 2.4^\circ$ and the results $\rho' \approx 0.017$ (i.e., relaxation and contraction of the parallel and perpendicular distances by about 0.30 and 0.15 Å) and $\delta\phi' \approx 0.1^\circ$ were also obtained for interstitial Ti impurity and Ni^{3+} in TiO_2 based on *ab initio* and EPR studies [22,32], respectively. Thus, the local lattice distortion around the interstitial Ti^{3+} in TiO_2 can be understood.

(2) The results (Cal.^c) based on the ligand contributions are better than those (Cal.^b) based on neglecting these contributions, particularly the calculated g factors are smaller than the experimental findings. Moreover, the above discrepancy is

difficult to remove by adjusting the local structural parameters ρ and $\Delta\phi'$. In fact, neglecting the ligand orbital contributions may lead to larger spin-orbit coupling coefficient and the orbital reduction factor (see eq. (4)) and hence to smaller g factors (see eq. (1)). In view of the trivalent state of Ti^{3+} , some covalency and admixture of the metal and ligand orbitals can be expected. This point may be described by the covalency factor N ($\approx 0.86 < 1$) and the moderate admixture coefficients (≈ 0.3 – 0.4) obtained in this work. Therefore, the formulas of the g factors including ligand contributions in the present work seem to be applicable for the investigations on the EPR spectra of $3d^1$ impurity ions with high valence state.

(3) The tetragonal center (spectrum C) has similar axial anisotropy $g_{\perp} - g_{\parallel}$ (≈ 0.035) to that (≈ 0.035) of the dominant rhombic one (spectrum A), suggesting that the local compression of ligand octahedron is almost the same for both centers. The only difference is that the rhombic distortion vanishes ($\delta\phi'' \approx 0$) in the tetragonal center. According to ref. [10], the a -axis resistivities for the tetragonal center are one order in magnitude smaller than that for the rhombic center. This may be tentatively attributed to increase in impurity mobility due to isotropy in the C_4 plane of the tetragonal center.

4. Summary

The local structure and the g factors for the interstitial Ti^{3+} center in TiO_2 are theoretically investigated in this work. The ligand octahedron is found to be less compressed in the impurity center than that on the host interstitial site due to the Jahn–Teller effect. The experimental g factors for the rhombic interstitial Ti^{3+} are unambiguously explained based on the local structural parameters ρ' and $\delta\phi'$.

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