



Investigations on the spin Hamiltonian parameters and defect structure for the interstitial Mo^{5+} centre in TiO_2



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ABSTRACT

The spin Hamiltonian parameters, g factors g_i ($i=x, y, z$) and the hyperfine structure constants A_i for the interstitial Mo^{5+} centre in rutile TiO_2 are quantitatively investigated from the perturbation formulas of these parameters for a $4d^1$ ion in rhombically compressed octahedra. From the studies, the local compression parameter τ' (≈ 0.024) and the rhombic distortion angle $\delta\phi'$ ($\approx 1.74^\circ$) around the impurity Mo^{5+} are smaller than the host values (≈ 0.091 and 3.5°). This means that the oxygen octahedron in the impurity centre has less rhombic distortion than that on the host interstitial site due to the Jahn–Teller effect and occupation of the impurity. The above local lattice distortion of the studied impurity centre is also discussed.

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1. Introduction

Rutile (TiO_2) has attracted interest of researchers due to its unique optical [1–3] and catalytic [4–6] properties when containing some transition-metal ions. Usually, these properties are sensitively dependent upon the local structures around the impurity ions, which may be studied by means of electron paramagnetic resonance (EPR) technique. Nevertheless, EPR studies are normally concentrated on the first group ($3d^n$) transition-metal ions, and investigations on the second group ($4d^n$) transition-metal ions are relatively scarce. Among them, $4d^1$ (Mo^{5+}) can be regarded as a useful model system with one ground state and a single excited state under ideal octahedral crystal-fields, suitable to act as a probe to investigate energy levels and local structures of host crystals. For example, EPR experiments for $\text{TiO}_2:\text{Mo}$ were performed and the spin Hamiltonian parameters g factors g_i ($i=x, y, z$) and the hyperfine structure constants A_i were also measured for a new interstitial Mo^{5+} centre after reducing treatments decades ago [7]. Up to now, however, the above EPR experimental results have not been theoretically interpreted, and information about local structure of this Mo^{5+} centre has not been acquired, either. Practically, Mo^{5+} in TiO_2 can exhibit unique paramagnetic relaxation [8] and photocatalytic behaviours [6]. Therefore, investigations on the EPR spectra and local structure for the interstitial Mo^{5+} centre in TiO_2 are of specific significance.

In this work, the high-order perturbation formulas of the spin Hamiltonian parameters for a $4d^1$ 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 Mo^{5+} centre in TiO_2 is originated from an interstitial Mo^{6+} (in MoO_2Cl_2) capturing an electron during reducing procedure [7]. The oxygen octahedron of the interstitial site is significantly compressed, with two parallel distances $R_{\parallel} \approx 1.67 \text{ \AA}$ and four perpendicular $R_{\perp} \approx 2.23 \text{ \AA}$ [9] from the six nearest oxygen ions. In addition, the planar bond angle $\phi \approx 48.5^\circ$ [9] is also larger than that ($=45^\circ$) for a regular octahedron, yielding some rhombic distortion. For a Mo^{5+} ($4d^1$) 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 [10,11]. Note that in the above notations $|xy\rangle$ and $|x^2 - y^2\rangle$ are interchanged, due to a rotation of the frame of axes in the XY plane.

Due to the high valence of Mo^{5+} , the studied $[\text{MoO}_6]^{7-}$ cluster may have strong covalency or admixture between impurity and ligand orbitals. Thus, the ligand orbital and spin-orbit coupling contributions, which were usually neglected in the previous studies [10,11], should be taken into account here. Then the one-electron

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wave functions of the ground and excited states for the octahedral $4d^1$ cluster can be written as:

$$\begin{aligned}\psi_t &= N_t^{1/2}(\varphi_t - \lambda_t \chi_{pt}), \\ \psi_e &= N_e^{1/2}(\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s),\end{aligned}\quad (1)$$

where φ_γ ($\gamma = e$ and t denote the irreducible representations E_g and T_{2g} of group O_h) are the d orbitals of the central metal ion. $\chi_{p\gamma}$ and χ_s stand for the p- and s-orbitals of the ligands. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital admixture coefficients. Utilizing the perturbation procedure similar to that in Refs. [10,11], the zero-order and perturbation Hamiltonians (including the ligand orbital and spin-orbit coupling contributions) for a $4d^1$ ion under external magnetic field and local crystal-fields with rhombic symmetry are expressed as follows:

$$\begin{aligned}H &= H_0 + H' \\ H_0 &= V_{CF}(Dq, Ds, Dt, D_\xi, D_\eta), \\ H' &= H_{ZM}(k, k') + H_{SO}(\zeta, \zeta') + H_{HF}(P),\end{aligned}\quad (2)$$

where V_{CF} denotes the crystal-field interaction, with the cubic field parameter Dq and the rhombic field parameters Ds , Dt , D_ξ and D_η . H_{ZM} and H_{SO} are, respectively, the Zeeman and spin-orbit coupling interactions, with the orbital reduction factors k , k' and the spin-orbit coupling coefficients ζ and ζ' denoting the anisotropic (axial and perpendicular) behaviours. H_{HF} is the hyperfine structure term, with the dipolar hyperfine structure parameter P for the $4d^1$ ion.

By applying the perturbation Hamiltonian in Eq. (2) to the ground and excited states in terms of the one-electron wave functions in Eq. (1), the high-order perturbation formulas of the spin Hamiltonian parameters for the $4d^1$ ion in rhombically compressed octahedra can be obtained on the basis of the cluster approach:

$$\begin{aligned}g_x &= g_s - \left(\frac{2k'\zeta'}{E_1}\right) + k\zeta^2 \left[\frac{1}{2E_1^2} - \frac{1}{2E_2^2}\right] + 2k'\zeta'\zeta \left[\frac{1}{E_2E_3} - \frac{1}{E_3^2}\right], \\ g_y &= g_s - \frac{2k'\zeta'}{E_2} - k\zeta^2 \left[\frac{1}{2E_1^2} - \frac{1}{2E_2^2}\right] + 2k'\zeta'\zeta \left[\frac{1}{E_1E_3} - \frac{1}{E_3^2}\right], \\ g_z &= g_s - \frac{8k'\zeta'}{E_3} - \left(\frac{1}{2}\right)k\zeta^2 \left(\frac{1}{E_1} + \frac{1}{E_2}\right)^2 + \frac{2k'\zeta'^2}{E_3^2}, \\ A_x &= P \left[-k + \frac{2N^2}{7} + \frac{11(g_x - g_s)}{14}\right], \\ A_y &= P \left[-k + \frac{2N^2}{7} + \frac{11(g_x - g_s)}{14}\right], \\ A_z &= P \left[-k - \frac{4N^2}{7} + (g_z - g_s) + \frac{3(g_x - g_s)}{14} + \frac{3(g_y - g_s)}{14}\right],\end{aligned}\quad (3)$$

where g_s ($=2.0023$) is the spin-only value. κ is the core polarization constants. 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 [10,11]. They can be expressed in terms of the cubic and rhombic field parameters: $E_1 = 5Dt - 3Ds + 3D_\xi - 4D_\eta$, $E_2 = 5Dt - 3Ds - 3D_\xi + 4D_\eta$ and $E_3 = 10Dq$.

Based on the cluster approach, the spin-orbit coupling coefficients ζ , ζ' and the orbital reduction factors k , k' can be expressed as follows:

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

where ζ_d and ζ_p are the spin-orbit coupling coefficients of the $4d^1$ and the ligand ions in free states, respectively. A denotes the integral $R \left\langle ns \left| \frac{\partial}{\partial y} \right| np_y \right\rangle$, where R is the reference impurity-ligand distance in the studied system. The normalization factors N_γ and the orbital admixture coefficients λ_γ (or λ_s) are usually determined from the normalization conditions

$$\begin{aligned}N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1,\end{aligned}\quad (5)$$

and the approximate relationships

$$\begin{aligned}N_2 &= N_t^2 [1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2 [1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}].\end{aligned}\quad (6)$$

Here N is the average covalency factor. S_{dpy} (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 $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ between the admixture coefficients and the related group overlap integrals within the same irreducible representation E_g .

From the superposition model [12–14] and the local geometrical relationship of the studied impurity centre, the rhombic field parameters are determined as follows:

$$\begin{aligned}Ds &= 4\bar{A}_2(R) \left[\frac{\left(\frac{R}{R_{\parallel}}\right)^{t^2} - \left(\frac{R}{R_{\perp}}\right)^{t^2}}{7} \right], \\ Dt &= 4\bar{A}_4(R) \left[\frac{\left(4\frac{R}{R_{\parallel}}\right)^{t^4} + (7\cos 4\phi + 3)\left(\frac{R}{R_{\perp}}\right)^{t^4}}{21} \right], \\ D_\xi &= 4\bar{A}_2(R) \left(\frac{R}{R_{\perp}}\right)^{t^2} \cos\left(\frac{2\phi}{7}\right), \\ D_\eta &= 20\bar{A}_4(R) \left(\frac{R}{R_{\perp}}\right)^{t^4} \cos\left(\frac{2\phi}{21}\right),\end{aligned}\quad (7)$$

where $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters (with the reference distance R). For transition-metal ions in octahedra, the relationships $\bar{A}_4(R) \approx (3/4)Dq$ and $\bar{A}_2(R) \approx 10.8\bar{A}_4(R)$ have been proved to be valid in many crystals [12–14]. In the calculations, the average distance $\bar{R} = (R_{\parallel} + 2R_{\perp})/3 \approx 2.043 \text{ \AA}$ [9] between the interstitial site and the nearest neighbour ligands in rutile can be taken as the reference distance R , i.e. $R = \bar{R}$.

Usually, occupation of the impurity Mo^{5+} 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 Mo^{5+} may suffer Jahn–Teller effect under octahedral environments [15–17], 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 [18]. Thus, the impurity-ligand bond lengths and angles can be conveniently determined from the average distance \bar{R} , the local compression parameter τ' and the rhombic distortion angle $\delta\phi'$ as: $R'_{\parallel} \approx \bar{R}(1 - 2\tau')$, $R'_{\perp} \approx \bar{R}(1 + \tau')$ and $\phi' \approx 45^\circ + \delta\phi'$. Thus, the immediate environment around the interstitial Mo^{5+} in TiO_2 can be described as the local structural parameters τ' and $\Delta\phi'$, and the host structural parameters R_{\parallel} , R_{\perp} and ϕ in Eq. (7) should be replaced by the local ones (R'_{\parallel} , R'_{\perp} and ϕ'). Moreover, the local structure of the studied system is also connected with the rhombic field parameters and hence

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