Theoretical Studies of the Local Structure and the EPR Parameters for Substitutional Mo^{5+} in TiO_2

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The electron paramagnetic resonance(EPR) parameters g-factors g_i(i=x,y,z) and the hyperfine structure constants A_i for the substitutional Mo^{5+} in rutile are theoretically studied from the perturbation formulas of these parameters for a d^1 ion in a rhombically compressed octahedron. On the basis of the studies, The oxygen octahedron around Mo^{5+} is found to transform from the original elongation on the host Ti^{4+} site to compression in the impurity center due to the Jahn-Teller effect. The calculated EPR parameters based on the above local structure in this work are in good agreement with the experimental data.

1. INTRODUCTION

Rutile (TiO_2) doped with transition-metal ions has attracted interest extensively because of its unique phase transition [1] and magnetic [2-4], optical [5,6] and catalytic [7-9] properties. In general, these properties are sensitively dependent upon the local structures around the impurity ions in the host, It is well known that electron paramagnetic resonance (EPR) is a useful technique to study the electronic and local structure properties of paramagnetic impurities in crystals. For example, EPR investigations were performed decades ago, and one rhombic center was observed for the substitutional Mo^{5+} in rutile by means of EPR technique, and the EPR parameters anisotropic g factors g_i(i=x,y,z) and the hyperfine structure constants A_i were also measured at 77°K [10].

Till date, however, the above experimental results have not been satisfactorily interpreted. In the treatments of the g factors based on angular overlap model and the simple perturbation formulas in Refs [11]., the contributions from the ligand orbitals and spin-orbit coupling interactions were ignored. In fact, the covalency effect and hence the admixtures between the orbitals of the metal and the ligand ions may become significant, due to the high valence state of the impurity Mo^{5+}. Meanwhile, the energy denominators in the formulas of g factors were not correlated with the local structure around the impurity center. Actually, the local structure properties around Jahn-Teller ions(such as Ni^{3+}, Ti^{3+},V^{4+}) in crystals may be dissimilar to those of the hosts due to the local modification of bond-lengths and angles arising from the Jahn-Teller effect [12-14], In view that the studies on the Jahn-Teller behaviours of Mo^{5+} in rutile would be useful to understand the properties of this material with dopants. In addition, the hyperfine structure constants were not interpreted.

In order to make further investigations on the EPR parameters for the substitutional Mo^{5+} center in rutile, the EPR parameters are quantitatively analyzed from the second-order perturbation formulas of these parameters for a d^1 ion in rhombic symmetry, by considering reasonable local lattice (angular) distortion around the impurity ion. In these formulas, the contributions from the rhombic distortion as well as the spin-orbit coupling and the orbitals of the ligands are taken into account based on the cluster approach.

2. CALCULATIONS

In rutile, there are one substitutional and one interstitial octahedral site which can be occupied by the doping transition-metal ions. The oxygen octahedra in both sites exhit significant low symmetrical distortions. For the substitutional site, the ligand octahedron is slightly elongated with two longer bond-lengths $R_{||}(\approx 1.99\,\mathring{A})$ parallel with the [110] axis and four coplanar shorter bond-lengths $R_{\perp}(\approx 1.94\,\mathring{A})$ perpendicular to the axis, with the planar bonding angle θ of about 81° [15].The above low symmetrical distortions can be characterized by the axial distortion angle $\Delta\alpha = \alpha - \alpha_0$, with $\alpha \approx \tan^{-1}(R_{\perp}/R_{//})$ and $\alpha_0 \approx 45°$ of the cubic symmetry. Thus, we have $\Delta\alpha \approx -0.73°$ for the host substitutional site [15]. Additionally, the ligand octahedron for this site also suffers large perpendicular (or rhombic) distortion characterized by the deviation Δθ of the plannar bonding angle θ related to the cubic value θ_0 (=90°), i.e., $\Delta\theta = \theta - \theta_0$ = −9° [15]. Thus, the ligand octahedron has large rhombic distortion for the host substitutional site . When Mo^{5+} is doped into the lattice of TiO_2, it may occupy the substitutional site [10]. and the local structure around the ion Mo^{5+} may exhibit deformation because of the Jahn-Teller effect, the impurity-ligand bonding lengths and angles may be unlike those in the host and lead to local lattice (angular) distortion.

For a d^1(Mo^{5+}) ion in rhombically-distorted octahedra, its higher orbital doublet ^2E_g of the original cubic case would split into two orbital singlets $^2A_{1g}$ ($|z^2>$) and $^2A'_{1g}(|xy>)$, while the original lower orbital triplet $^2T_{2g}$ would be separated into three orbital singlets $^2B_{2g}$ ($|xz>$), $^2B_{3g}$ $|yz>$) and $^2B_{1g}$ ($|x^2-y^2>$), with the latter lying lowest [11]. Note that in the above notations $|xy>$ and $|x^2-y^2>$ are interchanged due to a rotation of the frame of axes in the XY plane.

According to Refs [11], the perturbation formulas of the g factors for a d^1 ion in rhombic symmetry were established based on the conventional crystal-field theory. The experimental g factors were investigated from the above formulas by adjusting various parameters (i.e.,the energy separations between the ground and the excited states). Nevertheless,

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the contributions from the ligand orbitals and spin-orbit coupling interactions were ignored in these treatments. By including the above contributions and the similar perturbation procedure in Refs. [16], the perturbation formulas of the g factors and the hyperfine structure constants for the d^1 ion in rhombically-distorted octahedra can be obtained on the basis of the cluster approach:

$$g_x = g_s - 2k'\zeta'/E_1$$
$$g_y = g_s - 2k'\zeta'/E_2$$
$$g_z = g_s - 8k'\zeta'/E_3$$
$$A_x = P_0[-\kappa + 2N^2/7 - 3(g_y - g_s)/14 + (g_x - g_s)]$$
$$A_y = P_0[-\kappa + 2N^2/7 - 3(g_x - g_s)/14 + (g_y - g_s)]$$
$$A_z = P_0[-\kappa - 4N^2/7 + (g_z - g_s) + 3(g_x - g_s)/14$$
$$+ 3(g_y - g_s)/14] \qquad (1)$$

where g_s (=2.0023) is the spin-only value. P_0 is the dipolar hyperfine structure parameter of the free d^1 ion. κ is the isotropic core polarization constant. N is the average covalency factor, characteristic of the covalency effect of the studied system. The energy denominators E_1, E_2 and E_3 stand for the energy separations between the excited $^2B_{2g}$, $^2B_{3g}$ and $^2A'_{1g}$ and the ground $^2B_{1g}$ states and can be obtained from the strong cubic field approach:

$$E_1 = 3D_s - 5D_t + 3D_\xi - 4D_\eta$$
$$E_2 = 3D_s - 5D_t - 3D_\xi + 4D_\eta \ ,$$
$$E_3 = 10D_q \ . \qquad (2)$$

Here D_q is the cubic field parameter, and D_s, D_t, D_ξ and D_η the rhombic ones.

Based on the cluster approach, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k' in equation (1) may be written as

$$\zeta = N_t(\zeta_d + \lambda_t^2 \zeta_p/2), \quad \zeta' = (N_t N_e)^{1/2}(\zeta_d - \lambda_t \lambda_e \zeta_p/2),$$
$$k = N_t(1 + \lambda_t^2/2), \quad k' = (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2],$$
$$(3)$$

where ζ_d and ζ_p are the spin-orbit coupling coefficients of the d^1 and the ligand ions in free states, respectively. A denotes the integral $R\langle ns|\frac{\partial}{\partial y}|np_y\rangle$, where R is the impurity-ligand distance in the studied system. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital mixing coefficients for the cubic (O_h) irreducible representations $\gamma(= e_g$ and $t_{2g})$. They are usually determined from the normalization conditions

$$N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) = 1$$
$$N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1 \qquad (4)$$

and the approximate relationships

$$N^2 = N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}]$$
$$N^2 = N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}] \qquad (5)$$

Here N is the average covalency factor. $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the mixing coefficients increase with increasing the group overlap integrals,

and one can approximately adopt the proportional relationship between the mixing coefficients and the related group overlap integrals, i.e., $\lambda_e/S_{dpe} \approx \lambda_s/S_s$ within the same irreducible representation e_g.

From the superposition model [17] and the geometrical relationship of the studied impurity center, and rhombic field parameters can be determined as follows:

$$D_s = \frac{4}{7}\bar{A}_2(R_0)[(R_0/R'_{||})^{t2} - (R_0/R'_\perp)^{t2}]$$
$$D_t = \frac{4}{21}\bar{A}_4(R_0)[(7\cos 2\theta' + 3)(R_0/R'_\perp)^{t4} + 4(R_0/R'_{||})^{t4}]$$
$$D_\xi = \frac{4}{7}\bar{A}_2(R_0)(R_0/R'_\perp)^{t2}\cos\theta'$$
$$D_\eta = \frac{20}{21}\bar{A}_4(R_0)(R_0/R'_\perp)^{t4}\cos\theta' \qquad (6)$$

Here $\theta'(=\theta_0 + \Delta\theta')$ denotes the planar bonding angle for the substitutional site in rutile, . $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters (with the reference bonding length R_0), while t_2 (≈ 3)and $t_4(\approx 5)$ are the power-law exponents [18]. The relationships $\bar{A}_4(R_0) = \frac{3}{4}D_q$ and $\bar{A}_2(R_0) = 9\sim 12\bar{A}_4(R_0)$ can be obtained from Refs. [18] and we take $\bar{A}_2(R_0) = 12\bar{A}_4(R_0)$ here. The reference bonding length R_0 can be reasonably estimated from the empirical relationship $R_0 \approx \bar{R} + (r_i - r_h)/2$, $\bar{R} = (R_{//} + 2R_\perp)/3 \approx 1.957$ Å (the average metal-ligand bonding length), r_i (≈ 0.66 Å)and r_h (≈ 0.68 Å) denote the ionic radius for the impurity Mo^{5+} and the host Ti^{4+} [19]. From the distance R_0 (≈ 1.947 Å) and the Slater-type SCF functions [20,21] the integrals $S_{dpt} \approx 0.047$, $S_{dpe} \approx 0.1168$, $S_{ds} \approx 0.0935$ and $A \approx 1.2673$ are obtained. As mentioned before, because of the Jahn -Teller effect, the impurity-ligand bonding lengths $R'_{//}$ and $R'_\perp$, and hence the angle $\alpha' \approx \tan^{-1}(R'_\perp/R'_{//})$ may be different from those $(R_{//}, R_\perp$ and $\alpha)$ in the host. The impurity-ligand bonding lengths can be written in terms of the local distortion angle $\Delta\alpha'(= \alpha' - \alpha_0)$, the average distance $\bar{R}$ as:

$$R'_{//} \approx \frac{3\bar{R}}{1 + 2\tan(45° + \Delta\alpha')} \quad R'_\perp \approx \frac{3\bar{R}}{2 + \cot(45° + \Delta\alpha')} \qquad (7)$$

For $TiO_2:Mo^{5+}$, to our knowledge, no optical spectra data were reported. However, the value $D_q \approx 2500 cm^{-1}$ was obtained for the $[MoO_4]^{3-}$ cluster in $CaWO_4:Mo^{5+}$ [22] .thus, the value $D_q \approx 3750 cm^{-1}$ can be approximately estimated for the studied octahedral $[MoO_6]^{7-}$ cluster here.

Thus, by using the formulas of the g factors (Eq. (1)), and fitting the calculated g factors to the experimental data, we have

$$N \approx 0.733, \quad \Delta d' \approx 0.995° \quad \Delta\theta' \approx -0.305° \ . \qquad (8)$$

The values $N_t \approx 0.7550$, $N_e \approx 0.8124$, $\lambda_t \approx 0.6187$, $\lambda_e \approx 0.5098$ and $\lambda_s \approx 0.4081$ are calculated from equations (4) and (5). Then the parameters $\zeta \approx 799 cm^{-1}$, $\zeta' \approx 788 cm^{-1}$, $k \approx 0.899$ and $k' \approx 0.534$ can be determined from equation (3) and the free-ion values $\zeta_d \approx 1030 cm^{-1}$ for Mo^{5+} [22] and $\zeta \approx 151 cm^{-1}$ for O^{2-} [23].

In the formulas of the hyperfine structure constants, the free-ion value P_0 is about -68.2×10^{-4} cm^{-1} for Mo^{5+} [24]. By fitting the calculated hyperfine structure constants to

the observed values, the core polarization constant is determined: $\kappa \approx 0.42$.

The corresponding EPR parameters are shown in table 1. For comparisons, the calculated results based on the formulas of the g factors within the scheme of the conventional crystal-field theory and various fitted parameters in Refs. [11] are also collected in Table 1.

Table 1. The EPR parameters for the substitutional Mo^{5+} center in rutile.

	g_x	g_y	g_z	A_x $(10^{-4}\,cm^{-1})$	A_y $(10^{-4}\,cm^{-1})$	A_z $(10^{-4}\,cm^{-1})$
Cal. [a]	1.8155	1.7923	1.9167	--	--	--
Cal. [b]	1.8116	1.7883	1.9125	28	30	62
Expt. [10]	1.8117	1.7883	1.9125	24.74	30.50	65.85

[a] Calculations by using the simple perturbation formulas and adjusting various parameters in the previous work [11].
[b] Calculations by using equation (1) and including both the local distortion and the ligand orbital contributions in this work.

3. DISCUSSION

From table 1, one can find that the calculated EPR parameters based on the perturbation formulas in Eq. (1) by considering the local lattice deformation as well as 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 related parameters adopted in this work can be regarded as suitable.

The local axial and rhombic distortion angles $\Delta\alpha'$ and $\Delta\theta'$ for the impurity center are different from those in the host sites. The ligand octahedron in the substitutional center is found to be slightly ($\Delta\alpha' \approx 0.995°$) compressed while elongated ($\Delta\alpha \approx -0.73°$) in the host Ti^{4+} site, and the perpendicular distortion ($\Delta\theta' \approx -0.305°$) are much smaller than that ($\Delta\theta \approx -9.0°$) in the replaced cation site. The above distortions can be described as the contraction (by about 0.08Å) and relaxation (by about 0.04Å) of the parallel and perpendicular bond lengths, and the angle θ' is much closer to that ($\approx 90°$) of cubic case. As a result, the ligand octahedron is slightly compressed. The reason may be due to the Jahn-Teller effect which may lend to compress the ligand octahedron, as Ni^{3+} on the octahedral Al^{3+} site in $LaSrAlO_4$ [12]. Interestingly, similar local lattice modifications around impurity ions in crystals are also found for substitutional V^{4+} centres in rutile-type crystals [13]. Thus, the local structure properties around Mo^{5+} ion in rutile obtained in this work can be regarded as reasonable and the anisotropy of the experimental g factors can be understood, by considering the local axial and rhombic distortion angles $\Delta\alpha'$ and $\Delta\theta'$.

Seen from Table 1 one can find that the agreement between the theoretical g factors and the experimental data in present work is better than that in Refs. [11]. Based on the formulas of the g factors within the scheme of the conventional crystal-field theory in Refs. [11] , the observed g factors were explained by various fitted parameters and the energy separations were not determined from the local structure of the impurity center. In addition, the contributions from the SO coupling coefficient and the orbitals of the ligands were not taken into account. In view of the high valence state of Mo^{5+}, the distinct covalency and hence, significant admixture of the metal and ligand orbitals can be expected. This point may be illustrated by the small covalency factor N ($\approx 0.733 < 1$) in equation (5) and the obvious mixing coefficients ($\lambda_t \approx 0.6187$, $\lambda_e \approx 0.5098$ and $\lambda_s \approx 0.4081$) obtained in this work. Based on the studies, inclusion of the contributions from the SO coupling coefficient and the orbitals of the ligands leads to the variations of about 0.04, 0.05 and 0.016 for the calculated g_x, g_y and g_z, respectively. Obviously, for the impurity ion Mo^{5+} with high valence state in the octahedral cluster, the above contributions could not to be ignored.

There may be some errors in the above calculations. First, the approximation of the perturbation formulas and the cluster approach adopted here can induce some errors. Second, the cubic field parameter Dq extrapolated from the $[MoO_4]^{3-}$ cluster in $CaWO_4$ would lead to some errors. Finally, the impurity-ligand distance is obtained from the empeirical relationship related to the difference between the ionic radius for impurity and host ions, which may bring forward some errors in the average distance $\bar{R}$ for present system. It means that the actual average distance can be slightly different from $\bar{R}$. This would bring small errors to the group overlap integrals in the calculations. In fact, the errors in the final g factors and distortion angles in Eqs. (1) and (7) due to the above variation in the average distance $\bar{R}$ turn out to be no more than 0.4%, since $\bar{R}$ is mainly related to the magnitude of the g factors.

4. CONCLUSIONS

The electron paramagnetic resonance(EPR) parameters g-factors g_i(i=x,y,z) and the hyperfine structure constants A_i for the substitutional Mo^{5+} in rutile are theoretically investigated in this work. Based on the studies, The oxygen octahedron around Mo^{5+} is found to transform from the original elongation on the host Ti^{4+} site to compression in the impurity center due to the Jahn-Teller effect. The theoretical EPR parameters based on the above local structure in this work are in good agreement with the experimental data.

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